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Synthesis, Structure and Spectroscopy of Heteropentadienyl-Cobalt Complexes

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Department of Chemistry

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SYNTHESIS, STRUCTURE AND SPECTROSCOPY OF HETEROPENTADIENYL-COBALT COMPLEXES

by

Bryn Lucille Lutes

A dissertation presented to the
Graduate School of Arts and Sciences
of Washington University in
partial fulfillment of the
requirements for the degree
of Doctor of Philosophy

August 2010

Saint Louis, Missouri

ABSTRACT OF THE DISSERTATION

Synthesis, Structure and Spectroscopy of Heteropentadienyl-Cobalt Complexes

by

Bryn Lucille Lutes

Doctor of Philosophy in Chemistry

Washington University in St. Louis, 2010

Professor John R. Bleeke, Chair

A heteropentadienyl ligand is a molecule in which the terminal carbon of a pentadienyl ligand has been replaced with a heteroatom (O, PR, NR, S, SiR_2). The study of heteropentadienyl-transition metal complexes has been an active area of research in the last decade, and has recently received significant attention in the chemical literature. These molecules can now be synthesized by generalized methods, allowing their unique reactivity to be the focus of current research. These molecules have shown the ability to adopt and shift between a variety of bonding modes, opening coordination sites at the metal center and showing promise for use as homogeneous catalysts.

This work has focused on the synthesis and spectroscopy of a new class of heteropentadienyl-transition metal-phosphine complexes. Specifically, thiapentadienyl-cobalt- and oxapentadienyl-cobalt-phosphine complexes were synthesized for comparison to the existing heteropentadienyl-iridium and –rhodium systems. Though some similarities in initial bonding modes were seen, the thiapentadienyl system showed distinctive dimeric and trimeric ground state bonding modes as a result of the small size of the cobalt metal center relative to other metals in the same group. Treatment of $ClCo(PMe_3)_3$ with potassium thiapentadienide produced the dimer $[Co(PMe_3)_2(thiapentadienyl)]_2$. This dimer was reactive toward the small two-electron donor ligand, CO, forming the products (5-η^1-*cis*-5-thiapentadienyl)$Co(PMe_3)_2(CO)_2$ and (5-η^1-*trans*-5-thiapentadienyl)$Co(PMe_3)_2(CO)_2$. Treatment of $ClCo(PMe_3)_3$ with lithium 2,3-dimethyl-5-thiapentadienide yielded the trimer $[Co(PMe_3)_2$(η^4-2,3-dimethylthiapentadienyl)$]_2[\mu$-Co(2,3-dimethylthiapentadienyl)$_2]$. This trimer was also reactive toward the two-electron donor, CO, forming (5-η^1-*trans*-2,3-dimethyl-5-thiapentadienyl)$Co(PMe_3)_2(CO)_2$, upon reaction. Some similarities to previously reported systems were seen in the initial bonding modes, though one new bonding mode was seen: μ_2-η^4,η^1-bonding mode where one cobalt center bonds to the butadiene moiety in an η^4-fashion while a second cobalt coordinates the anionic sulfur atom.

When $ClCo(PMe_3)_3$ was treated with potassium oxapentadienide, the monomeric product, (1,2,3-η-oxapentadienyl)$Co(PMe_3)_3$ was formed. The oxapentadienyl-cobalt-phosphine system showed a remarkable stability of the all carbon η^3 bonding mode, losing a phosphine ligand to form (1,2,3-η-oxapentadienyl)$Co(PMe_3)_2(CO)$ upon exposure to carbon monoxide. The addition of methyl groups to the *oxa*pentadienyl ligand resulted in

no change to the initial reactivity. Treatment of $ClCo(PMe_3)_3$ with potassium 2,4-dimethyloxapentadienide again afforded the monomeric, η^3 product: (1,2,3-η-2,4-dimethyloxapentadienyl)$Co(PMe_3)_3$. However, the additional steric bulk of the methyl groups, along with their electron donating properties, did affect the reaction of (1,2,3-η-2,4-dimethyloxapentadienyl)$Co(PMe_3)_3$ with CO. In this case, two phosphine ligands were lost to form (1,2,3-η-2,4-dimethyloxapentadienyl)$Co(PMe_3)(CO)_2$. The compounds (1,2,3-η-oxapentadienyl)$Co(PMe_3)_3$ and (1,2,3-η-oxapentadienyl)$Co(PMe_3)_2(CO)$ were reactive toward small electrophiles, H^+ and Me^+, at the ligand oxygen forming stable η^4-butadienol-cobalt or η^4-butadienyl methyl ether-cobalt complexes. The compounds (1,2,3-η-2,4-dimethyl oxapentadienyl)$Co(PMe_3)_3$ and (1,2,3-η-2,4-dimethyl oxapentadienyl)$Co(PMe_3)(CO)_2$ were also reactive exclusively at the ligand oxygen; however, the initially formed products were not stable, resulting in the formation of $Co(PMe_3)_4{}^+O_3SCF_3{}^-$ *in situ* which was then converted to $Co(PMe_3)_3(CO)_2{}^+O_3SCF_3{}^-$ by exposure to CO.

Acknowledgments

I would like to thank my research advisor, Dr. John Bleeke for all of his guidance and mentorship throughout my graduate career. Dr. Bleeke has always had the perfect combination of being available when I needed help, letting me figure out problems on my own, giving a little push when I needed it, and being supportive of the development of my teaching career at Washington University. I would also like to thank Dr. Bill Buhro and Dr. Sophia Hayes for serving on my committee. They are excellent teachers and mentors, and I am very grateful for their advice and support. I would also like to thank Dr. Liviu Mirica, Dr. Nigam Rath, and Dr. Jay Turner for reviewing my dissertation and serving on my oral defense committee.

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Rhiannon, you get a whole line to yourself, thank you for everything.

There are a number of people in the department that I would like to thank. Ed Hiss, Andre D'Avignon, Norma Taylor, Jessica Owens, Phyllis Noelken, and Angie Stevens are amazing people that have provided invaluable amounts of help throughout my graduate career.

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To the distractions that kept me sane and forced me to develop the ability to work absolutely everywhere.

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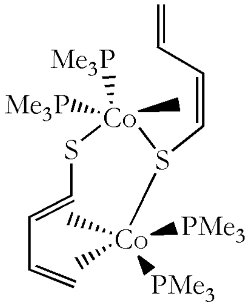
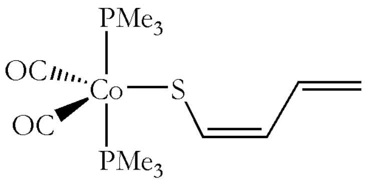
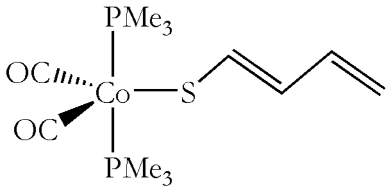
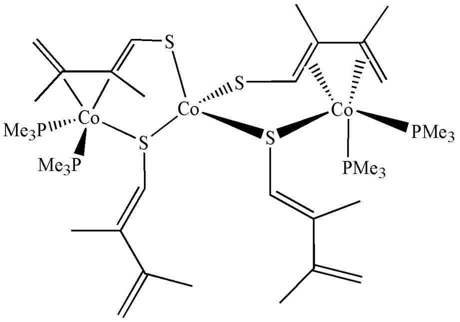
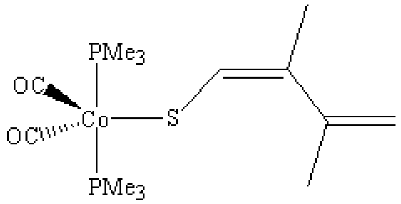
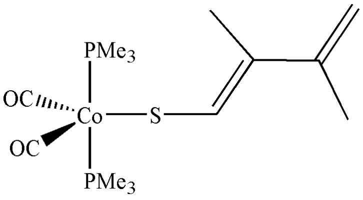
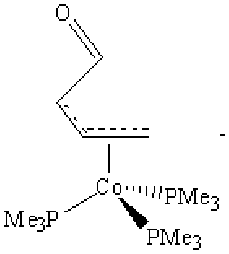
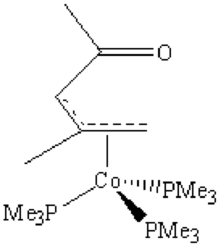
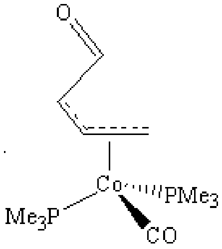
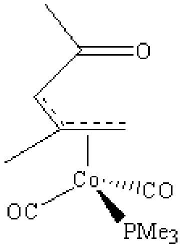
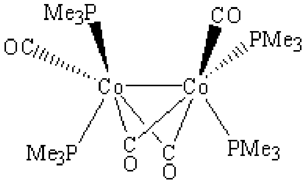
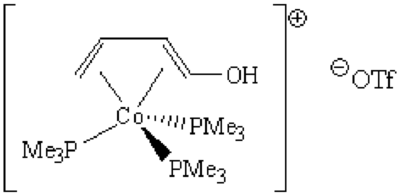
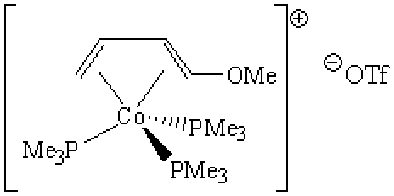
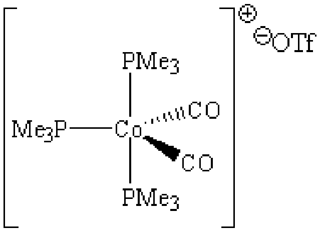
[Co(PMe$_3$)$_2$(thiapentadienyl)]$_2$	**1**		28
(5-η^1-*cis*-5-thiapentadienyl)Co(PMe$_3$)$_2$(CO)$_2$	**cis-2**		33
(5-η^1-*trans*-5-thiapentadienyl)Co(PMe$_3$)$_2$(CO)$_2$	**trans-2**		33
[Co(PMe$_3$)$_2$(η^4-2,3-dimethylthiapentadienyl)][μ-Co(2,3-dimethylthiapentadienyl)$_2$]	**3**		35

(5-η^1-*cis*-2,3-dimethyl-5-thiapentadienyl)Co(PMe$_3$)$_2$(CO)$_2$	**cis-4**		42
(5-η^1-*trans*-2,3-dimethyl-5-thiapentadienyl)Co(PMe$_3$)$_2$(CO)$_2$	**trans-4**		39
(1,2,3-η-oxapentadienyl)Co(PMe$_3$)$_3$	**5**		60
(1,2,3-η-2,4-dimethyl oxapentadienyl)Co(PMe$_3$)$_3$	**6**		62
(1,2,3-η-oxapentadienyl)Co(PMe$_3$)$_2$CO	**7**		65

(1,2,3-η-2,4-dimethyl oxapentadienyl)Co(PMe$_3$)(CO)$_2$	**8**		68
[(PMe$_3$)$_2$(CO)Co]$_2$(μ_2-CO)$_2$	**9**		72
(η^4-butadienol)Co(PMe$_3$)$_3$$^+O_3SCF_3$$^-$	**10**		75
(η^4-butadienyl-methyl-ether)Co(PMe$_3$)$_3$$^+O_3SCF_3$$^-$	**11**		78
Co(PMe$_3$)$_3$(CO)$_2$$^+O_3SCF_3$$^-$	**12**		81

CHAPTER ONE

INTRODUCTION

Introduction

1.1. Cyclopentadienyl- and Allyl-Metal Complexes.

Prior to the research popularity of open pentadienyl-transition metal complexes in the 1980's, there were major developments in two closely related areas of organometallic chemistry: closed pentadienyl- and allyl-transition metal complexes. The closed pentadienyl ligand, abbreviated Cp, is known as a stabilizing ligand and is found in the quintessential organometallic compounds, metallocenes or bis(cyclopentadienyl)metal "sandwich" complexes[1]. The structure of ferrocene is shown in Figure 1.1 below. A number of other stable Cp-metal complexes have been synthesized, including zirconocene dichloride (Figure 1.1), an important polymerization catalyst. The synthesis and utility of allyl-transition metal complexes have also been greatly explored, though these compounds are not as stable as their Cp analogs. However, the ability of the allyl ligand (Figure 1.2) to shift between bonding modes leads to enhanced reactivity and has also imparted the allyl-transition metal complexes with versatility as catalysts[2-8].

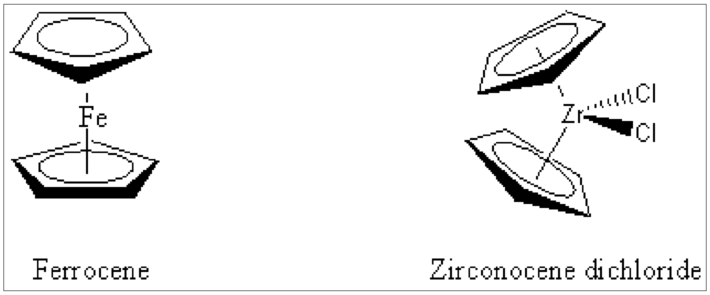


Figure 1.1. Prominent examples of Cp complexes. Ferrocene was the first Cp complex to be discovered, and zirconocene dichloride is a polymerization catalyst.

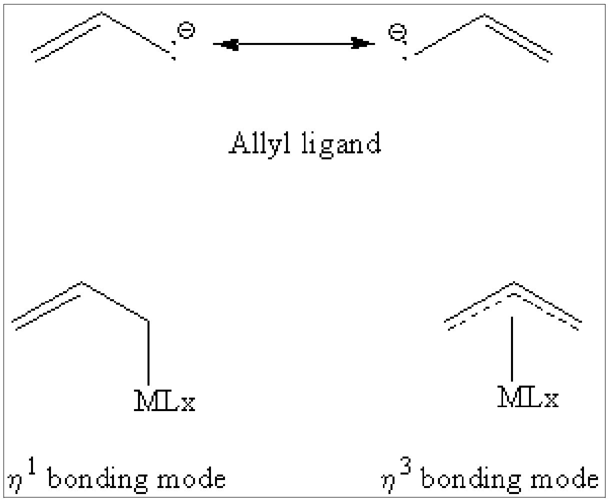


Figure 1.2. An allyl ligand and the ways in which it can bind to a metal.

1.2. Pentadienyl-Metal Complexes.

Although the first open pentadienyl-metal complex was synthesized in 1962[9], research in open pentadienyl- and heteropentadienyl-transition metal chemistry has blossomed in the last 30 years. Interest in pentadienyl-transition metal complexes stems from their potential use as catalysts because the ligand can form stable bonds to the metal center, like Cp, while maintaining the ability to shift bonding modes, like an allyl ligand. In fact, a large family of compounds containing both a stabilizing Cp ligand and a pentadienyl ligand exists; these are called half-open metallocenes (Figure 1.3).

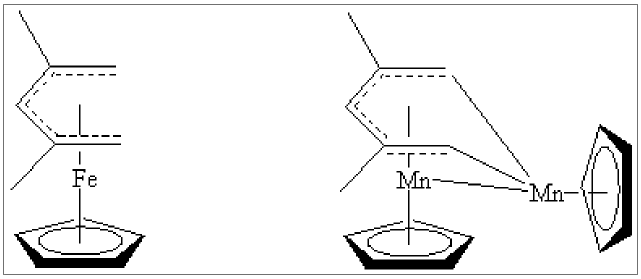


Figure 1.3. Examples of half-open metallocenes. On the left, a half open ferrocene[10] . On the right, a bimetallic half open manganese metallocene[11] .

A large family of compounds also exists containing only one pentadienyl ligand plus 2-5 ancillary ligands, including CO, halide, phosphines, phosphites, olefins and solvent molecules[10]. These mono-pentadienyl complexes exhibit pentadienyl bonding modes of η^1, η^3 and η^5, and have shown the ability to shift easily between these modes (Figure 1.4).

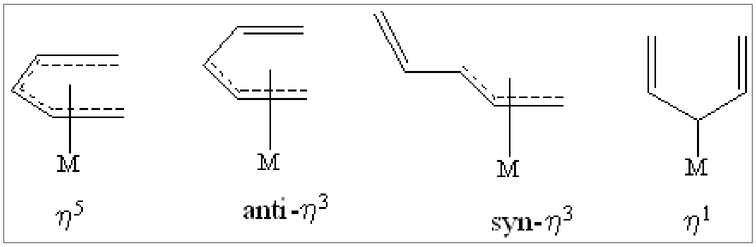


Figure 1.4. Pentadienyl bonding modes.

1.3. Mono-Pentadienyl-Cobalt Complexes.

Pentadienyl complexes of cobalt were synthesized in the Bleeke group from $ClCo(PMe_3)_3$[12,13] or from $CoCl_2$ directly[13] for the PEt_3 compound. A one pot reaction of

$CoCl_2$, PEt_3, 2,4-dimethylpentadienide, and a reducing agent (either Zn dust or additional 2,4-dimethylpentadienide) produced (η^5-2,4-dimethylpentadienyl)Co(PEt_3)$_2$ (A, Figure 1.5), which exhibited structural properties common to U-shaped η^5 pentadienyl complexes. The pentadienyl carbons were all essentially coplanar, though the outer carbons (C1 and C5) were slightly farther from Co than the internal carbons (C2, C3, C4) with the difference not exceeding 0.039 Å. The methyl carbons (C6 and C7) were displaced from the pentadienyl plane toward Co due to the p_z orbitals on C2 and C4 bending toward Co to achieve better overlap with the metal orbitals[13]. This complex was also reactive toward a number of reagents, undergoing ligand substitution reactions that demonstrate the ease of pentadienyl ligand isomerizations ($\eta^5 \rightarrow \eta^3 \rightarrow \eta^5$ and $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$), and oxidations producing Co(II) pentadienyl complexes[14].

The Bleeke group also demonstrated that an η^5 pentadienyl complex can been synthesized with the ancillary chelating ligand "pinacop"[15] (B, Figure 1.5), where the reaction of $CoCl_2$, two equivalents of 2,4-dimethylpentadienide and pinacop produced (η^5-2,4-dimethylpentadienyl)Co(pinacop).

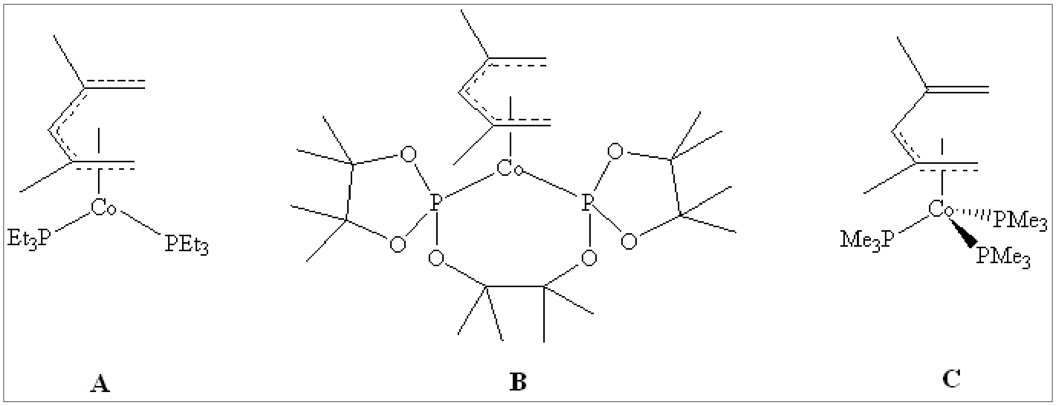
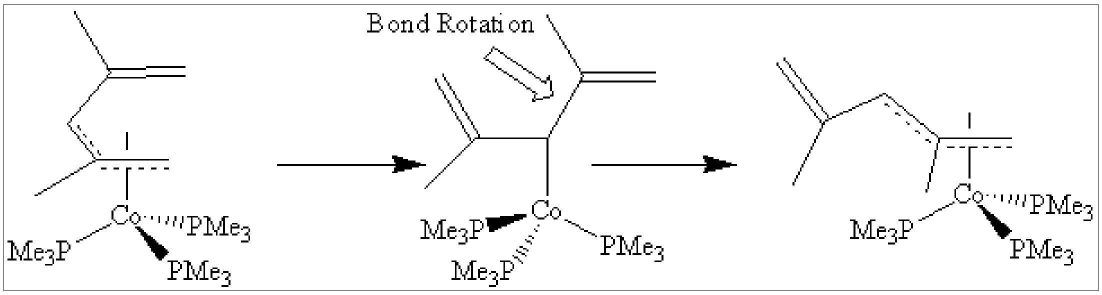


Figure 1.5. Drawing of (η^5-2,4-dimethylpentadienyl)Co(PEt$_3$)$_2$, A, (η^5-2,4-dimethylpentadienyl)Co(pinacop), B, and (*anti*-η^3-2,4-dimethylpentadienyl)Co(PMe$_3$)$_3$, C.

Reaction of ClCo(PMe$_3$)$_3$ with potassium 2,4-dimethylpentadienide produced (*anti*-η^3-2,4-dimethylpentadienyl)Co(PMe$_3$)$_3$ (C, Figure 1.5) exclusively. The production of an η^3-bound pentadienyl-complex is likely due to the size of the phosphine ligands. A PMe$_3$ ligand is small enough that the Co metal center can accommodate three phosphines to produce an 18 e$^-$ product, while a PEt$_3$ ligand is too large for the metal center to accommodate three ligands. Thus the product in the PEt$_3$ system contained two phosphine ligands and the pentadienyl ligand was bound η^5 to give an 18 e$^-$ product. The 2,4-dimethylpentadienyl ligand in (*anti*-η^3-2,4-dimethylpentadienyl)Co(PMe$_3$)$_3$ was U-shaped, but not planar, with C4-C5-C7 sitting above the basal plane. In solution (*anti*-η^3-2,4-dimethylpentadienyl)Co(PMe$_3$)$_3$ converted to (*syn*-η^3-2,4-dimethylpentadienyl)Co(PMe$_3$)$_3$ in a 70:30 anti:syn equilibrium mixture. The anti and syn complexes and the mechanism of their conversion are shown in Scheme 1.1.



Scheme 1.1. Mechanism for conversion of (anti-η^3-2,4-dimethylpentadienyl)Co(PMe$_3$)$_3$ (left) to (syn-η^3-2,4-dimethylpentadienyl)Co(PMe$_3$)$_3$ (right).

In the absence of phosphine, the reaction of $CoCl_2$ with two equivalents of 2,4-dimethylpentadienide produced a dimer (Figure 1.6) where each cobalt was coordinated to one η^5-2,4-dimethylpentadienyl ligand and in an η^4-fashion to one of the butadiene portions of 2,4,7,9-tetramethyl-2,4,6,8-decatetraene, which was formed from the intermolecular coupling of two 2,4-dimethylpentadienyl ligands[16].

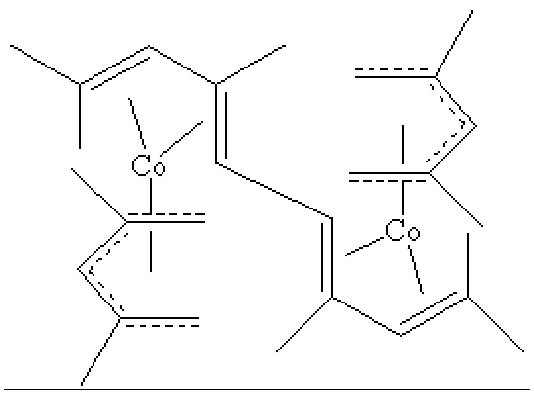
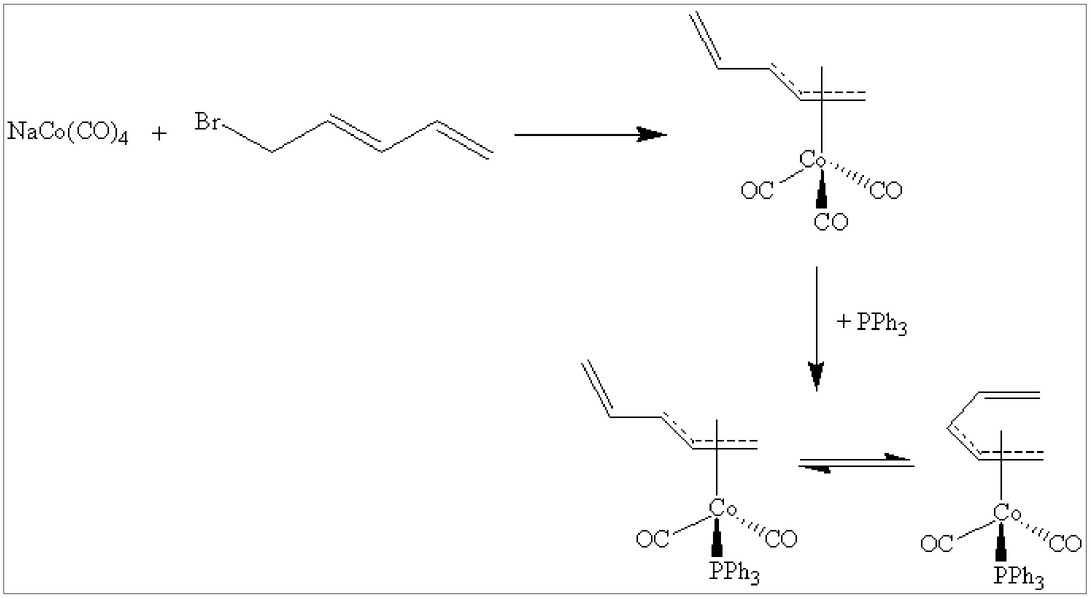


Figure 1.6. Drawing of dimer that resulted from the coupling of two 2,4-dimethylpentadienyl ligands.

Another method for synthesizing pentadienyl-cobalt complexes was demonstrated by Lee and coworkers who reacted $NaCo(CO)_4$ with *trans*-1-bromopenta-2,4-diene[17] producing (*syn*-η^3-pentadienyl)$Co(CO)_3$. This complex was also capable of ligand substitution reactions, reacting with triphenylphosphine to give (*syn*-η^3-pentadienyl)$Co(CO)_2(PPh_3)$. While the all-carbonyl complex was stable with respect to pentadienyl ligand isomerization, the PPh_3-substituted complex converted from (*syn*-η^3-pentadienyl)$Co(CO)_2(PPh_3)$ to (*anti*-η^3-pentadienyl)$Co(CO)_2(PPh_3)$ in solution at room temperature (Scheme 1.2).



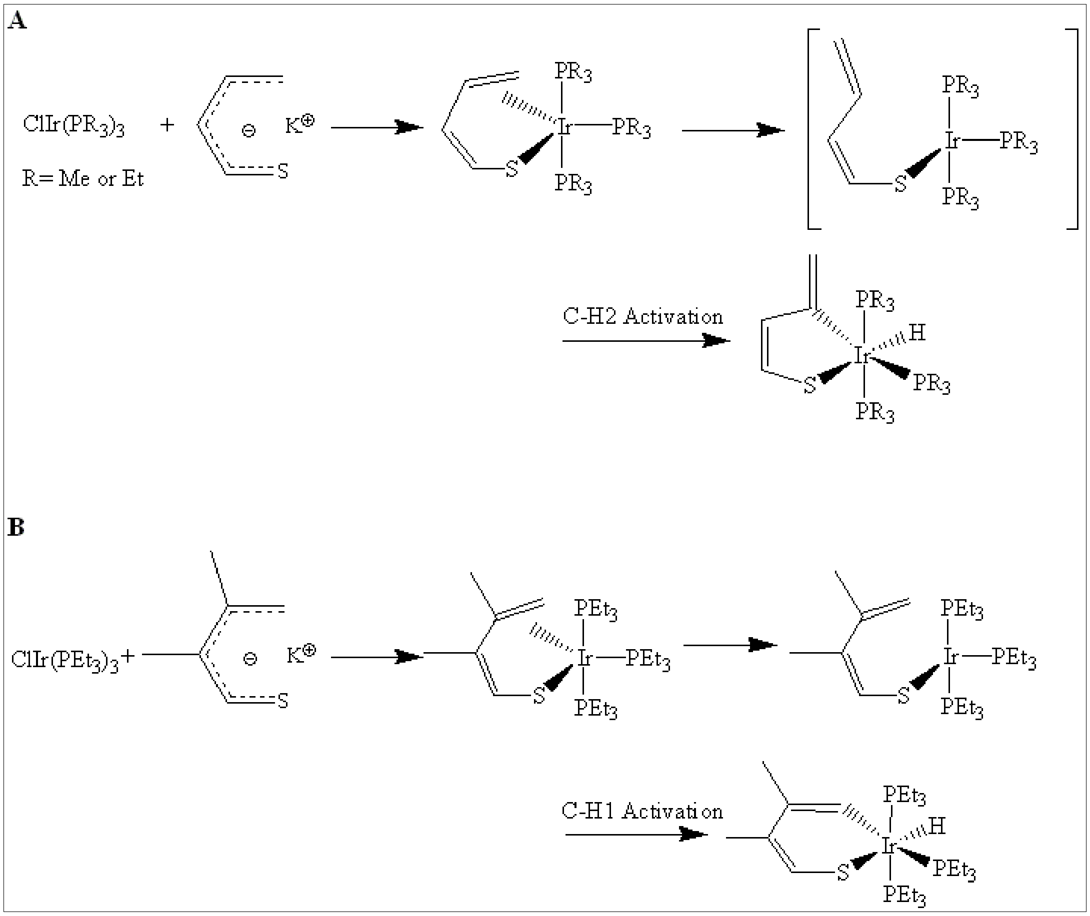
Scheme 1.2. Synthesis of (syn-η^3-2,4-pentadienyl)$Co(CO)_3$ and its reaction with PPh_3.

As with the allyl-transition metal complexes mentioned above, one goal for the synthesis of all-carbon pentadienyl-transition metal complexes was the creation of a versatile catalyst. In terms of basic reactivity, pentadienyl-transition metal complexes have shown the ability to catalyze the same reactions that allyl-transition metal complexes can, such as $Ti(C_5H_5)(2,4\text{-}C_7H_{11})(PEt_3)$ catalyzing coupling reactions[18]. Examples have also been seen of open and half-open metallocenes acting as polymerization catalysts, but only after immobilization on silica or aluminophosphate[19].

1.4. Heteropentadienyl-Metal Complexes.

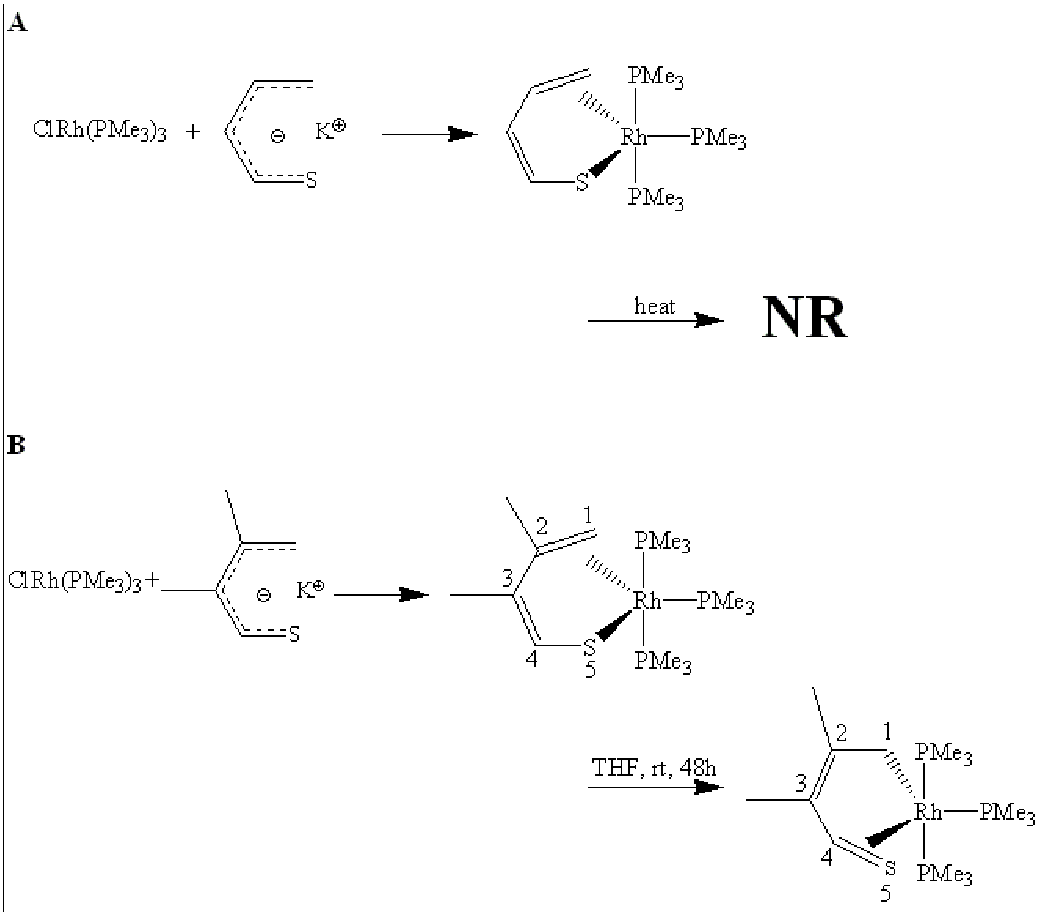
Growing out of the research on pentadienyl-transition metal complexes was the synthesis and study of heteropentadienyl-transition metal complexes, where a heteropentadienyl ligand possesses a heteroatom in place of one carbon (typically a terminal carbon). The beginning of research in the area of heteropentadienyl-transition metal chemistry was concurrent with pentadienyl-transition metal chemistry with the first heteropentadienyl complexes reported in 1959 for oxapentadienyl[20] complexes and 1987 for thiapentadienyl[21] complexes. The last 30 years have seen the development of an extensive library of heteropentadienyl-metal complexes including oxa[22-24]-, phospha[25,26]-, aza[27,28]-, thia[29-33]- and silapentadienyl[34-36] (O, PR, NR_2, S, SiR_2) complexes of a variety of transition metals. These compounds show a marked potential for catalysis because they retain the reactivity of the parent pentadienyl ligands, displaying bonding modes of η^1, η^3 and η^5 with the ability to shift easily between bonding modes, but with an altered and potentially tunable reactivity from the presence of a heteroatom.

Thiapentadienyl-transition metal chemistry began in the Bleeke group with the reaction of $ClIr(PR_3)_3$ (R = Me, Et) with potassium thiapentadienide[29], which produced ((1,2,5-η)-5-thiapentadienyl)$Ir(PMe_3)_3$ and ((1,2,5-η)-5-thiapentadienyl)$Ir(PEt_3)_3$ (see A, Scheme 1.3). These underwent C-H bond activation in solution at room temperature (PEt_3 complex) or in refluxing toluene (PMe_3 complex) to produce the iridathiacyclopentenes shown in A, Scheme 1.3. Though the 5-membered metallacycle was quite stable, a 6-membered metallacycle was obtained as the final product when the site of C-H bond activation was blocked. Hence, the reaction of $ClIr(PEt_3)_3$ with lithium 2,3-dimethyl-5-thiapentadienide produced the iridathiacyclohexene shown in B, Scheme 1.3 from C-H bond activation in the intermediate (5-η^1-2,3-dimethyl-5-thiapentadienyl)$Ir(PEt_3)_3$.



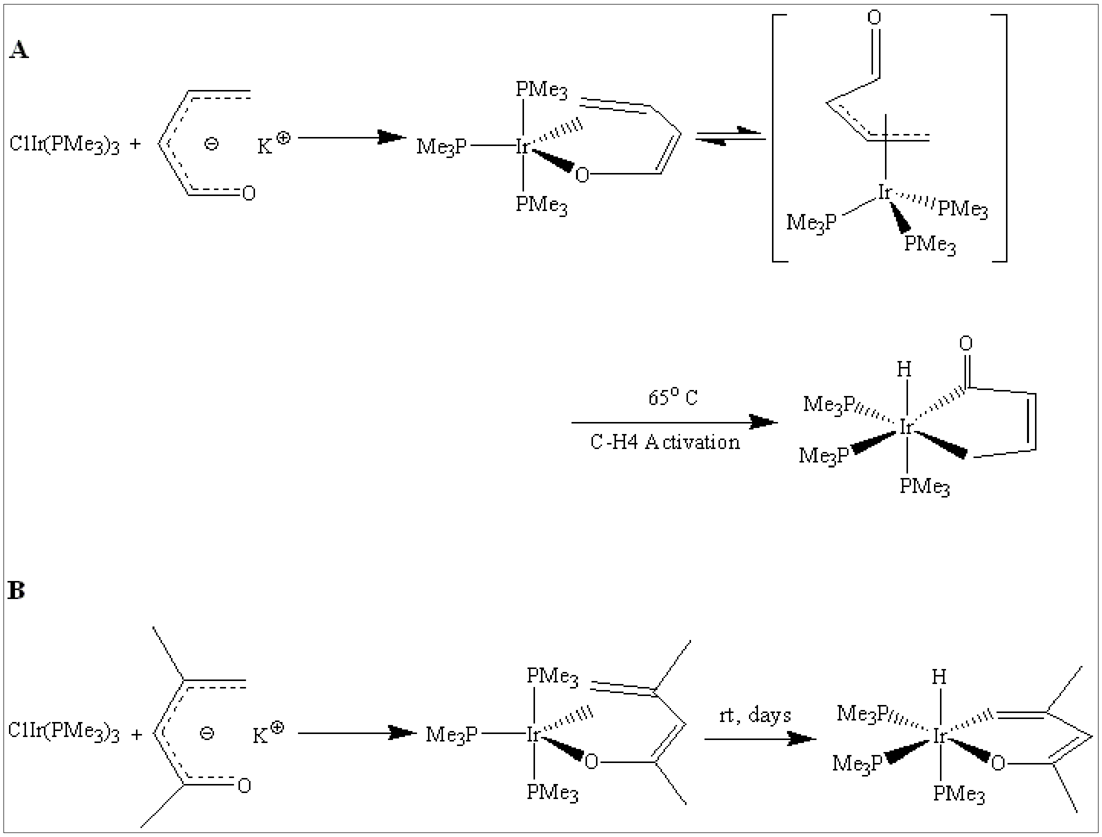
Scheme 1.3. Thiapentadienyl-iridium chemistry in the Bleeke group.

Thiapentadienyl-rhodium chemistry was also investigated in the Bleeke group, and although the initially formed bonding modes were analogous to those seen in the iridium compounds, C-H bond activation was not observed. The reaction of $ClRh(PMe_3)_3$ with potassium thiapentadienide yielded ((1,2,5-η)-5-thiapentadienyl)$Rh(PMe_3)_3$ which was stable in solution, even when heated. Treatment of $ClRh(PMe_3)_3$ with the methylated thiapentadienyl ligand (from lithium 2,3-dimethylthiapentadienide) initially gave the analogous product, ((1,2,5-η)-2,3-dimethyl-5-thiapentadienyl)$Rh(PMe_3)_3$, but this isomerized at room temperature to. ((1,4,5-η)-2,3-dimethyl-5-thiapentadienyl)Rh(PMe_3)$_3$[31,32] (B, Scheme 1.4).



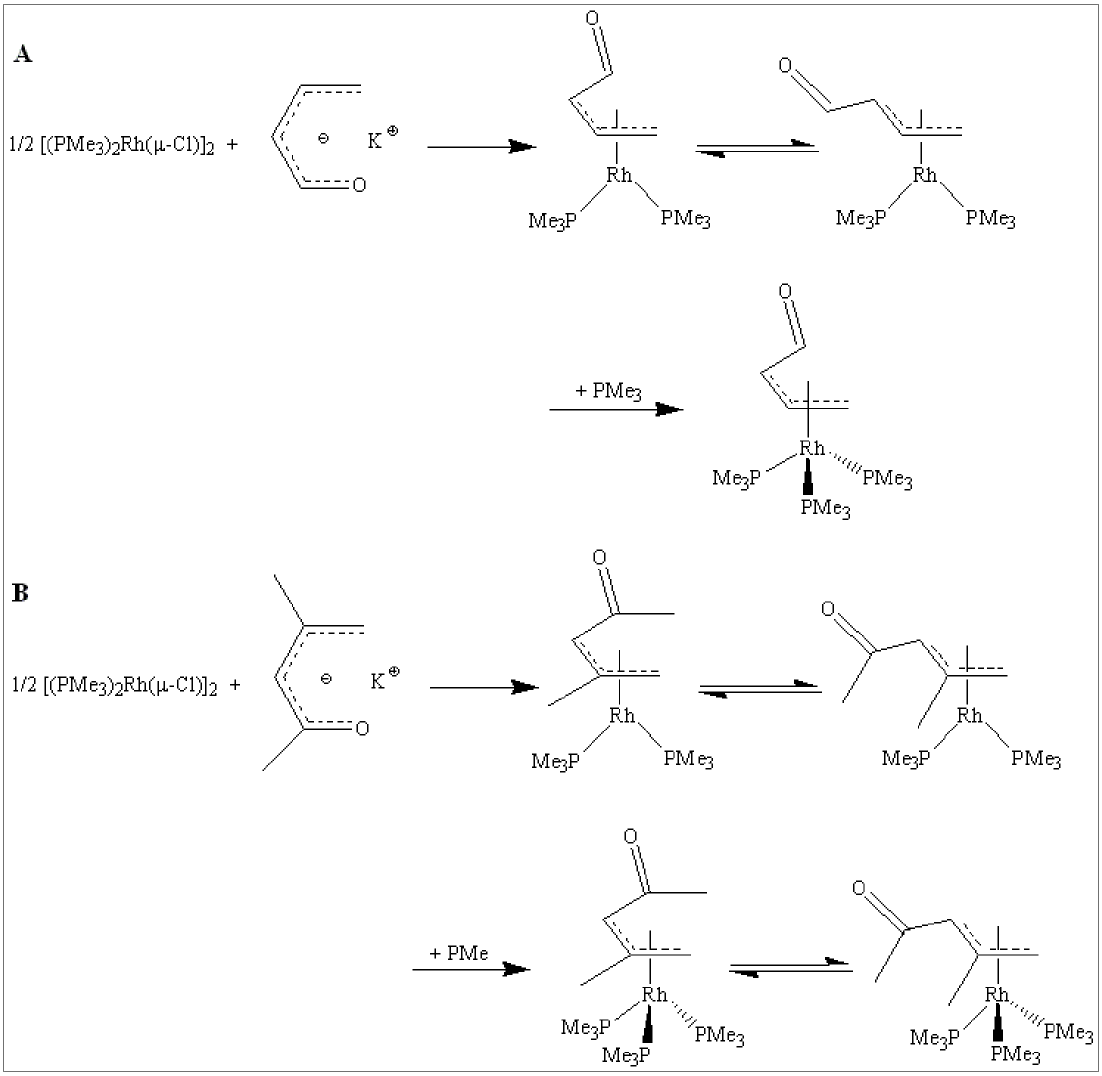
Scheme 1.4. Thiapentadienyl-rhodium chemistry in the Bleeke group.

The first example of an oxapentadienyl-transition metal complex in the Bleeke group was produced from the reaction of ClIr(PMe_3)$_3$ with potassium oxapentadienide. The heteropentadienyl ligand exhibited the same initial bonding mode seen in the thiapentadienyl-iridium system, ((1,2,5-η)-5-oxapentadienyl)Ir(PMe_3)$_3$. However, unlike the thiapentadienyl system, this compound did not undergo C-H bond activation from this state. Through an η^5 intermediate, the oxapentadienyl ligand isomerized at room temperature, giving ((1,2,3-η)-5-oxapentadienyl)Ir(PMe_3)$_3$ which then underwent C-H bond activation at 65 °C to produce the iridacyclopentenone[37] shown in A, Scheme 1.5. A strategically methylated ligand reagent, potassium 2,4-dimethyl-5-oxapentadienide, was also employed for reaction with ClIr(PMe_3)$_3$, producing ((1,2,5-η)-2,4-dimethyl-5-oxapentadienyl)Ir(PMe_3)$_3$, which yielded iridaoxacyclohexadiene[22] upon C-H bond activation (B, Scheme 1.5).



Scheme 1.5. Oxapentadienyl-iridium chemistry in the Bleeke group.

Synthesis of oxapentadienyl-rhodium complexes used the dimer $[(PMe_3)_2Rh(\mu\text{-}Cl)]_2$ as the transition metal-containing starting material. Reaction of this dimer with potassium oxapentadienide produced a mixture of the anti and syn isomers of the 16 e^- species ((1,2,3-η)-5-oxapentadienyl)Rh(PMe_3)$_2$, which was converted to the 18 e^- ((1,2,3-η)-5-oxapentadienyl)Rh(PMe_3)$_3$ upon addition of phosphine[24], and trapped only the anti isomer (A, Scheme 1.6). The reaction of $[(PMe_3)_2Rh(\mu\text{-}Cl)]_2$ with potassium 2,4-dimethyl-5-oxapentadienide was also explored, and the initially formed product showed an identical bonding arrangement to the unmethylated system, producing ((1,2,3-η)-2,4-dimethyl-5-oxapentadienyl)Rh(PMe_3)$_2$ as a mixture of anti and syn isomers. Production of the 18 e^- species, ((1,2,3-η)-2,4-dimethyl-5-oxapentadienyl)Rh(PMe_3)$_3$, was accomplished by addition of phosphine, but this species remained as a mixture of anti and syn isomers[24] (B, Scheme 1.6).



Scheme 1.6. Oxapentadienyl-rhodium chemistry in the Bleeke group.

While a number of heteropentadienyl-transition metal complexes have been prepared with first row transition metals (Mn[38-40,27,41,42], Fe[43]), the work reported in this dissertation presents the first examples of heteropentadienyl-cobalt complexes and the first examples of thiapentadienyl complexes of first row transition metals. The development of heteropentadienyl-cobalt complexes is of interest due to the low cost and known catalytic activity[44-50] of organometallic cobalt compounds. The strategy employed in the synthesis of these compounds parallels the work previously reported in the Bleeke group on analogous rhodium and iridium systems which involves synthesis from anionic heteropentadienides and halo-metal-phosphine precursors.

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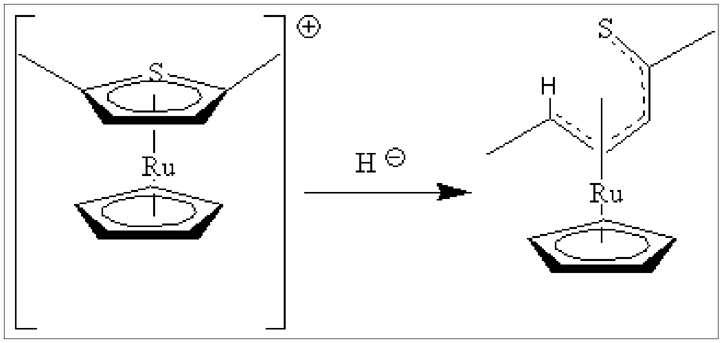
CHAPTER TWO

THIAPENTADIENYL-COBALT CHEMISTRY

Thiapentadienyl-Cobalt Chemistry

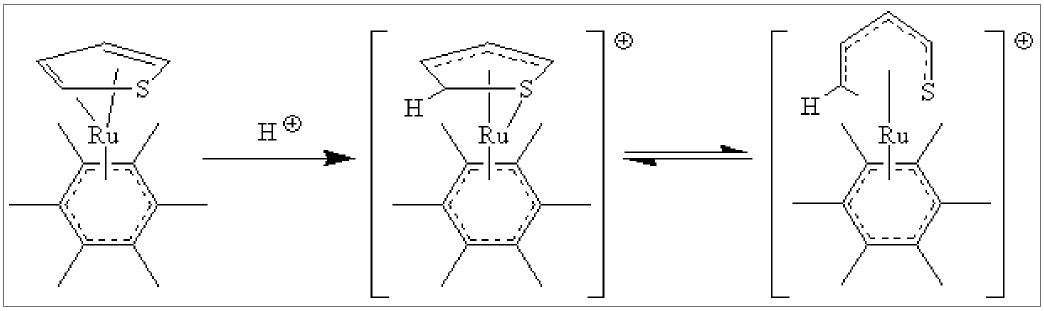
2.1 Introduction

Research in the area of thiapentadienyl chemistry has led to several approaches to the synthesis of thiapentadienyl-metal complexes, including nucleophilic addition to thiophene ligands, electrophilic addition to thiophene ligands, reaction of anionic thiapentadienide reagents with metal halides, and from thiophene-based metallacycles. The first example of a thiapentadienyl-metal complex was reported in the Angelici group in 1987[1]. The complex, (η^5-1,4-dimethyl-5-thiapentadienyl)Ru(Cp), was synthesized by an on-metal ring opening of the 2,5-dimethylthiophene ligand in [(η^5-2,5-dimethylthiophene)Ru(Cp)]$^+$ (Scheme 2.1). The reaction proceeded through nucleophilic attack by hydride at the carbon adjacent to sulfur and cleavage of the carbon-sulfur bond. Nucleophilic ring-opening of thiophene-metal complexes has yielded a number of thiapentadienyl-metal complexes.



Scheme 2.1. Synthesis of (η^5-1,4-dimethyl-5-thiapentadienyl)Ru(Cp). (Ref 1)

Though nucleophilic attack did not always occur in the same place, this approach worked for several nucleophiles (H^-, $(CO_2Me)_2HC^-$, EtS^-, MeO^-) and thiophenes with varied methylation patterns[2,3]. Electrophilic addition of H^+ to (η^4-thiophene)Ru(η^6-C_6Me_6) resulted in protonation at the metal center, followed by hydride migration, leading to on-metal ring opening of thiophene to give the thiapentadienyl-ruthenium complex[4,5] shown in Scheme 2.2.



Scheme 2.2. Protonation of (η^4-thiophene)Ru(η^6-C_6Me_6). (Refs 4,5)

The Bleeke group has also reported on the synthesis and reactivity of thiapentadienyl-rhodium-phosphine[6,7] and thiapentadienyl-iridium-phosphine[8-12] complexes. These compounds have, in general, been produced by reacting halo-metal-phosphine precursors such as $ClRh(PR_3)_3$ or $ClIr(PR_3)_3$ (R = Me or Et) with anionic thiapentadienide reagents. Some of this work has been summarized in Chapter 1, but Figure 2.1 shows all of the different thiapentadienyl bonding modes that have been observed. Please note that the thiapentadienyl ligand is numbered starting from the end opposite sulfur.

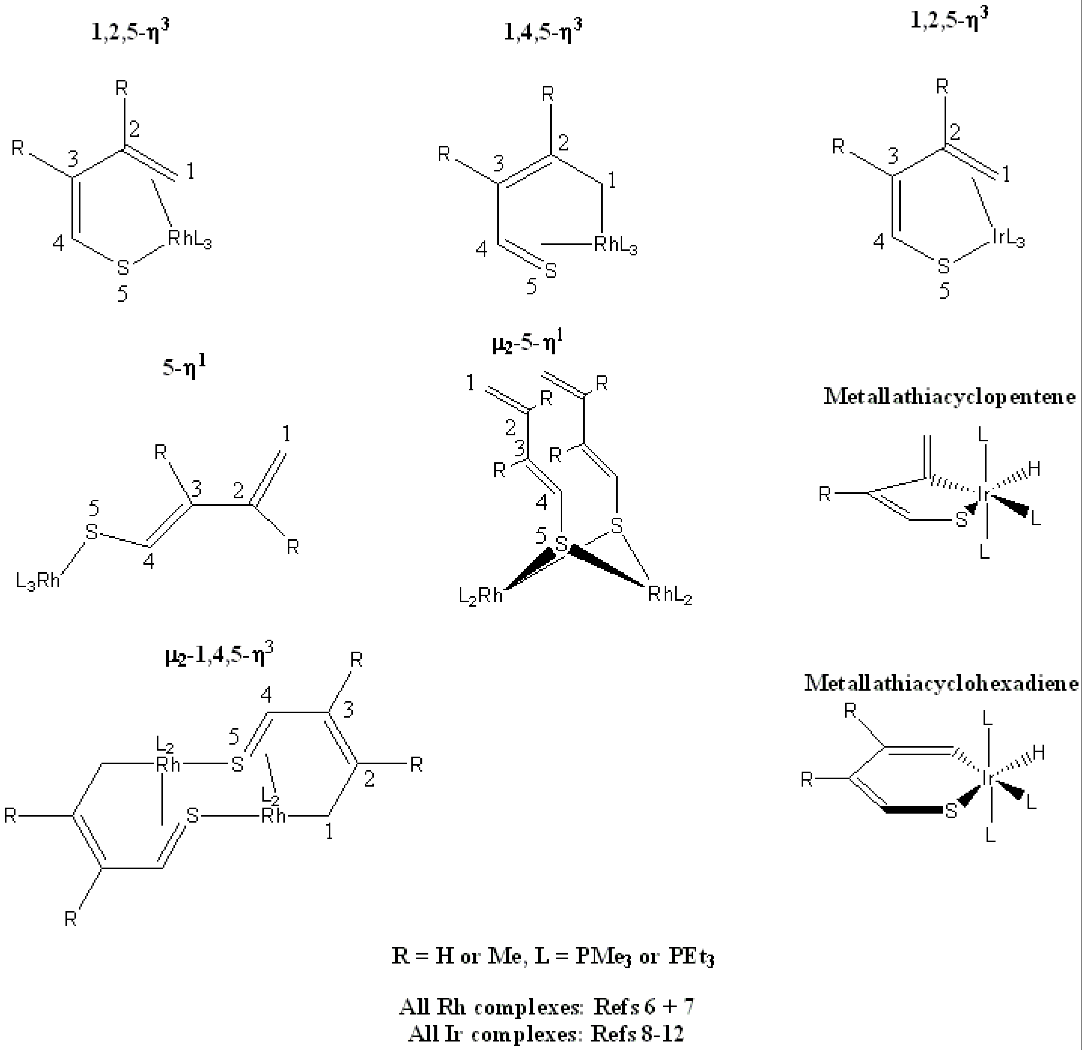


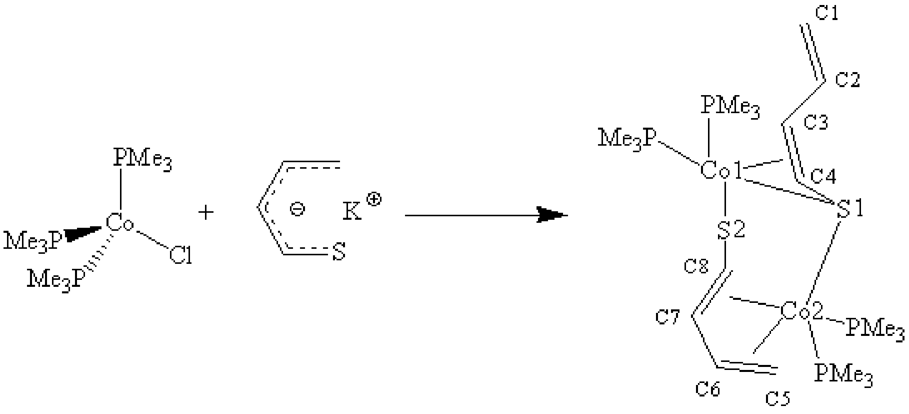
Figure 2.1. A representation of thiapentadienyl bonding modes as previously reported in the Bleeke group.

This chapter reports on the synthesis and reactivity of thiapentadienyl-cobalt-phosphine complexes using an analogous approach. The small size of the first-row transition metal leads to the formation of dimeric and trimeric products, held together by bridging thiapentadienyl ligands in new bonding modes.

2.2 Results and Discussion

2.2.1 Reaction of $ClCo(PMe_3)_3$ with Potassium Thiapentadienide.

Treatment of $ClCo(PMe_3)_3$[13] with potassium thiapentadienide in THF produces the dimeric product, **1**, shown in Scheme 2.3 in 56% yield. The X-ray crystal structure of **1** has been obtained and is shown in Figure 2.2.



Scheme 2.3. Synthesis of compound 1.

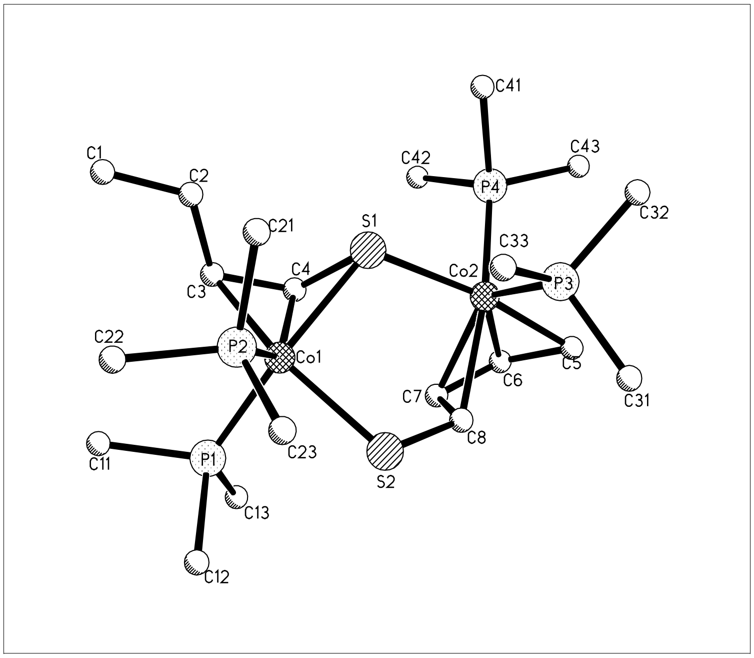


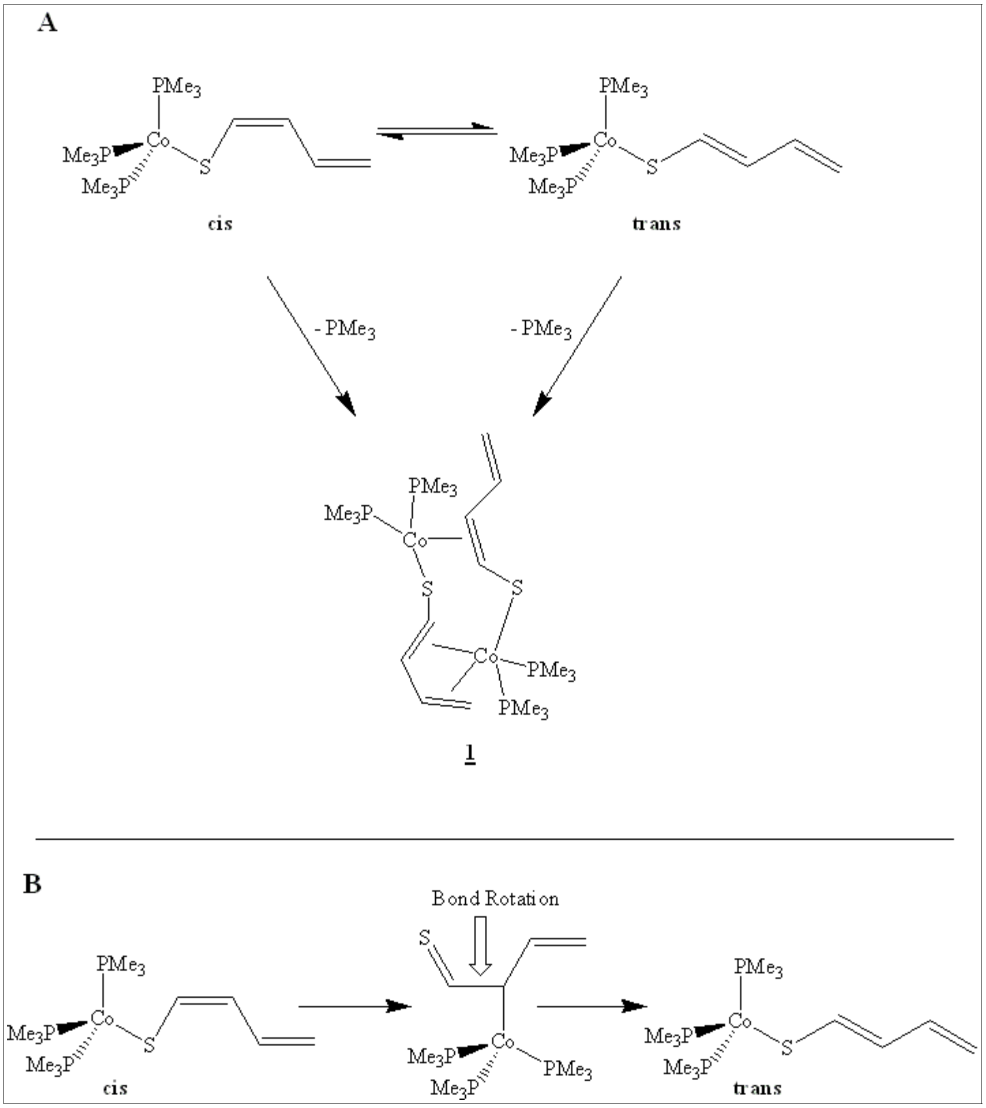
Figure 2.2. X-ray crystal structure of 1, using thermal ellipsoids at the 50% level. PMe_3 methyl and ligand H's are not shown.

The crystal structure of **1** contains two cobalt atoms, both formally Co(I) and $18e^-$, two thiapentadienyl ligands, and four PMe_3's and is held together only by the two thiapentadienyl ligands. Select bond distances are listed in Table 2.1. In the first thiapentadienyl ligand (C1/C2/C3/C4/S1), S1 exhibits a μ_2-bonding mode and the internal double bond (C3-C4) is coordinated to Co1, while the terminal double bond (C1-C2) remains uncoordinated. This bonding mode is similar to one reported in a ruthenium dimer[14], though in the ruthenium complex, the terminal double bond is coordinated to a second metal center. In the second thiapentadienyl ligand (C5/C6/C7/C8/S2), S2 is bound only to Co1, while the butadiene portion of the ligand coordinates to Co2 in an η^4-bonding mode.

Table 2.1. Select bond distances from the crystal strucutre of 1.

Bond	Distance (Å)	Bond	Distance (Å)
Co1-P1	2.1486(10)	Co2-P3	2.1803(10)
Co1-P2	2.2117(9)	Co2-P4	2.2029(9)
Co1-S1	2.2906(9)	Co2-S1	2.2665(9)
Co1-S2	2.2947(9)	Co2-C5	2.049(3)
Co1-C3	2.079(3)	Co2-C6	2.010(3)
Co1-C4	1.927(3)	Co2-C7	2.020(3)
C1-C2	1.337(5)	Co2-C8	2.112(3)
C2-C3	1.441(5)	C5-C6	1.426(5)
C3-C4	1.437(4)	C6-C7	1.413(5)
C4-S1	1.750(3)	C7-C8	1.417(5)
		C8-S2	1.749(3)

An interesting feature of the crystal structure is the internal double bond geometries in the thiapentadienyl ligands. The first thiapentadienyl ligand has a *cis* internal double bond (C3-C4), while the second ligand contains a *trans* internal double bond (C7-C8). The potassium thiapentadienide starting material used in the synthesis of **1** shows strong evidence of containing only a *cis* internal double bond (see Section 2.2.2, independent synthesis of ***cis*-2**), indicating that rearrangement of the ligand before formation of the dimer, **1**, must occur. The rearrangement likely occurs in the 16e$^-$ intermediate, (5-η^1-5-thiapentadienyl)Co(PMe_3)$_3$, through cobalt migration to C3 of the thiapentadienyl ligand, rotation about C3-C4, and migration of cobalt back to sulfur or through an 18e$^-$ 3,4,5-η^3-5-thiapentadienyl intermediate (B, Scheme 2.4).

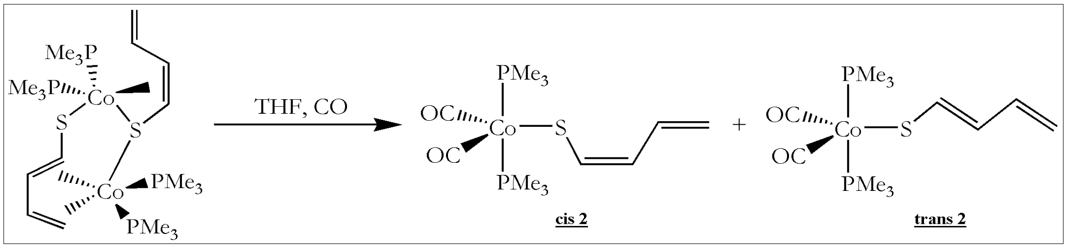


Scheme 2.4. Mechanism for formation of dimer, 1. A shows dimer formation occurring through the combination of *cis* and *trans* isomers. B shows a potential mechanism for bond isomerization.

In the ^{1}H NMR spectrum of **1**, the most downfield signal is for H2 on the uncoordinated double bond of the first thiapentadienyl ligand (at δ 5.26). The two H1's also resonate downfield at δ 4.58 and 4.30. H3 and H4 of the coordinated double bond resonate at δ 2.42 and 5.14, respectively. The shifts for the protons in the second thiapentadienyl ligand are typical of those for a bound butadienyl moiety with the internal H's, H6 and H7, appearing relatively downfield at δ 4.96 and 5.04, respectively, and the terminal H's, H8 and both H5's, appearing upfield at δ 2.14, 0.45, and -0.95. The $^{31}P\{^{1}H\}$ NMR spectrum at room temperature is quite broad, probably due to phosphine exchange, but sharpens to four well-separated peaks at low temperature (-70 C).

2.2.2 Reaction of Compound 1 with Carbon Monoxide.

When compound **1** is exposed to carbon monoxide gas, its deep brown color quickly changes to bright orange. Analysis by NMR spectroscopy shows quantitative conversion to (5-η^{1}-5-thiapentadienyl)Co$(PMe_3)_2(CO)_2$ as a mixture of *cis* and *trans* isomers (Scheme 2.5). In the ^{1}H NMR spectrum, all of the thiapentadienyl protons resonate downfield, as expected for the η^{1} bonding mode. In the *cis* isomer, H2 appears farthest downfield at δ 7.15, followed by H3 (δ 6.02), H4 (δ 5.90), and the H1's (δ 4.99 and 4.85). In the *trans* isomer, H4 is farthest downfield at δ 6.38, followed by H2 (δ 6.31), H3 (δ 6.14), and the H1's (δ 4.71 and 4.50). The two isomers are easily distinguished by the coupling between H3 and H4. In the *cis* isomer, J_{H3-H4} is 9.6 Hz, while in the *trans* isomer the same coupling increases to 13.5 Hz. In both isomers, the phosphine ligands give rise to a singlet in the $^{31}P\{^1H\}$ NMR spectrum and a virtual triplet in the ^1H NMR spectrum, implying a *trans*-diaxial arrangement.



Scheme 2.5. Reaction of 1 with carbon monoxide.

The *cis* isomer, ***cis*-2**, can be produced independently by reaction $ClCo(PMe_3)_2(CO)_2$[13] with potassium thiapentadienide. The ^1H NMR spectrum shows evidence of only the *cis* isomer, providing strong evidence that the potassium thiapentadienide reagent contains a *cis* internal double bond. This is expected because potassium thiapentadiendide is synthesized from cyclic dihydrothiophene. The X-ray crystal structure of ***cis*-2** is shown in Figure 2.3; select bond distances are listed in Table 2.2. The coordination geometry about cobalt is trigonal bipyramidal, with the bulky PMe_3 ligands occupying the axial sites. The η^1-thiapentadienyl ligand is planar (mean deviation = 0.0043 Å) and sickle-shaped with a *cis* internal double bond.

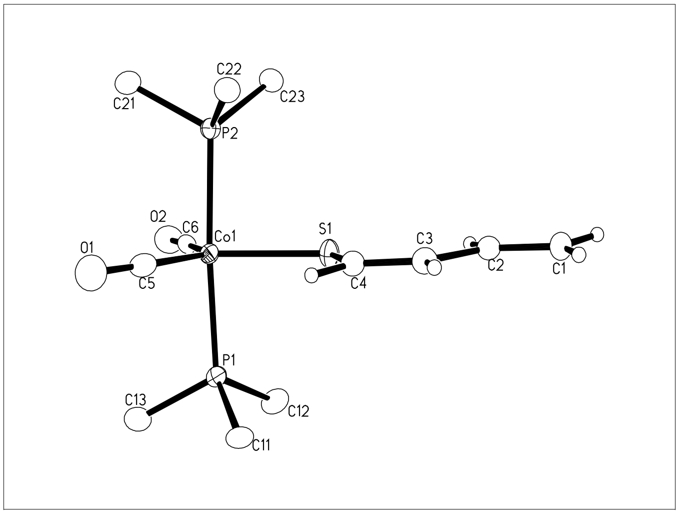


Figure 2.3. X-ray crystal structure of *cis*-2, using thermal ellipsoids at the 50% level. PMe_3 methyl H's are not shown.

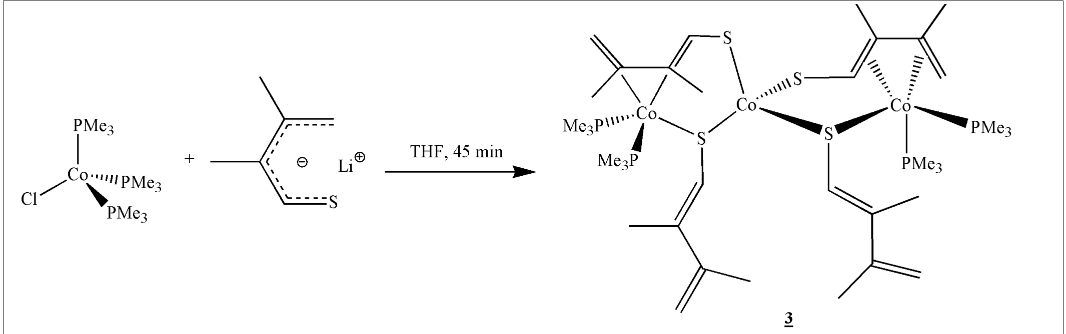
Table2.2. Select bond distances from the crystal structure of *cis*-2.

Bond	Distance (Å)
Co1-P1	2.1815(8)
Co1-P2	2.1836(8)
Co1-S1	2.3132(8)
Co1-C5	1.740(3)
Co1-C6	1.743(3)
C1-C2	1.318(4)
C2-C3	1.446(4)
C3-C4	1.346(4)
C4-S1	1.734(3)

When pure ***cis*-2** is dissolved in acetone-d_6 and heated in a sealed tube at 100 C, it slowly isomerizes to the thermodynamically favored *trans* isomer. After 141 h, the *cis*:*trans* ratio was approximately 1:2, as measured by NMR. This isomerization probably proceeds through a 16e$^-$ intermediate, which, in turn, requires a reversible dissociation of PMe_3, a slow step.

2.2.3 Reaction of $ClCo(PMe_3)_3$ with Lithium 2,3-Dimethyl-5-thiapentadienide.

As shown in Scheme 2.6, treatment of $ClCo(PMe_3)_3$ with lithium 2,3-dimethyl-5-thiapentadienide[12] produces the trimer **3** in 91% yield.



Scheme 2.6. Synthesis of compound 3.

The X-ray crystal structure of **3** was obtained and is shown in Figure 2.4. The crystal structure of **3** contains three cobalt atoms, two formally Co(I) and 18e$^-$ and one formally Co(II) and 15e$^-$, four dimethylthiapentadienyl ligands, and four PMe_3's and is held together only by the four bridging thiapentadienyl ligands, all of which contain *trans* internal double bonds.

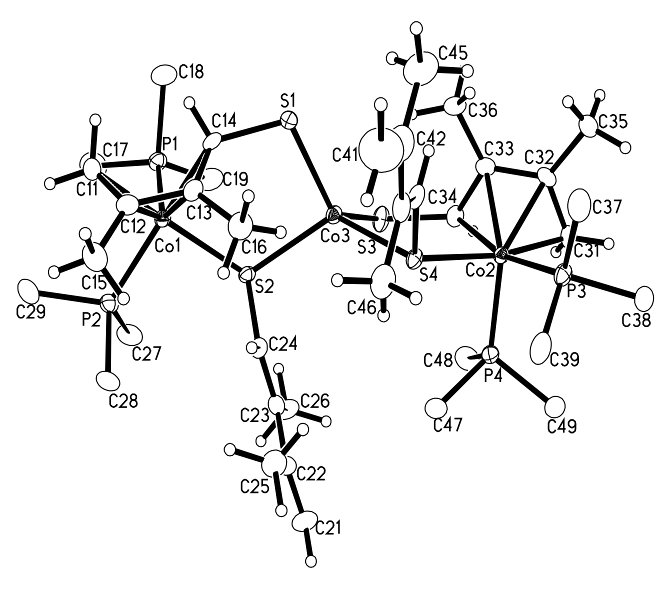


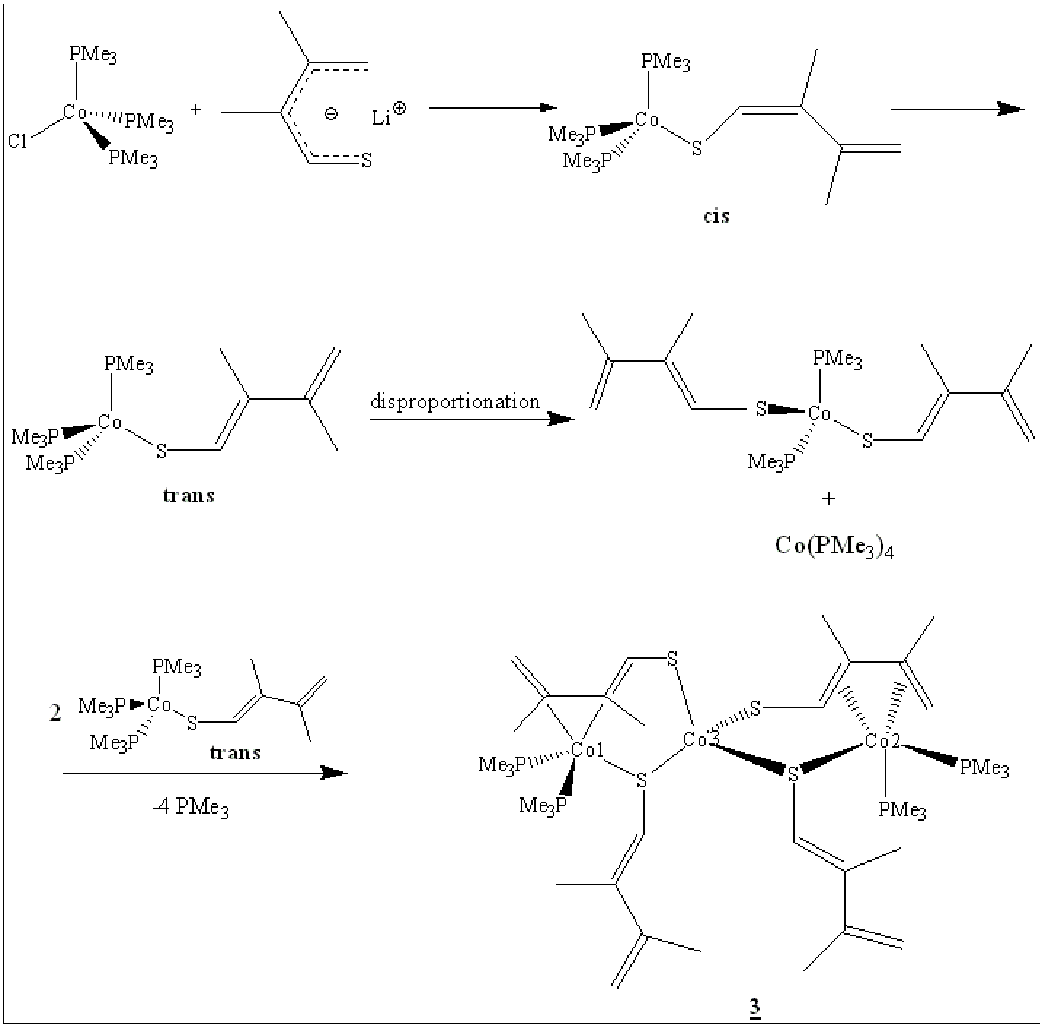
Figure 2.4. X-ray crystal structure of compound 3, using thermal ellipsoids at the 40% level. Hydrogen atoms and the OEt_2 solvate are not shown.

Select bond distances are listed in Table 2.3. In dimethylpentadienyl ligands (C11/C12/C13/C14/S1) and (C31/C32/C33/C34/S3), the butadiene moieties are coordinated in an η^4-fashion to Co1 and Co2, respectively, while sulfurs S1 and S3 are bonded to the central cobalt, Co3. The remaining dimethylthiapentadienyl ligands, (C21/C22/C23/C24/S2) and (C41/C42/C43/C44/S4), are coordinated in a μ_2,η^1-fashion to a terminal cobalt (Co1 and Co2, respectively) and the central cobalt, Co3. As mentioned earlier, the central cobalt is formally Co(II) and 15e$^-$ which renders the compound paramagentic and prevents characterization by NMR spectroscopy due to extreme signal broadening.

Table 2.3. Select bond distances from the crystal structure of Compound 3.

Bond	Distance (Å)	Bond	Distance (Å)
Co1-P1	2.1916(10)	Co2-S4	2.3082(10)
Co1-P2	2.2078(10)	Co2-C31	2.016(4)
Co1-S2	2.3008(9)	Co2-C32	2.038(3)
Co1-C11	2.015(4)	Co2-C33	2.070(3)
Co1-C12	2.014(3)	Co2-C34	2.105(4)
Co1-C13	2.075(3)	C31-C32	1.437(5)
Co1-C14	2.087(3)	C32-C33	1.409(5)
C11-C12	1.437(5)	C33-C34	1.430(5)
C12-C13	1.409(5)	C34-S3	1.767(4)
C13-C14	1.435(5)	C41-C42	1.334(5)
C14-S1	1.774(4)	C42-C43	1.468(5)
C21-C22	1.323(5)	C43-C44	1.334(5)
C22-C23	1.481(5)	C44-S4	1.766(3)
C23-C24	1.350(5)	Co3-S1	2.2649(9)
C24-S2	1.760(3)	Co3-S2	2.3560(10)
Co2-P3	2.2281(10)	Co3-S3	2.2415(10)
Co2-P4	2.1979(10)	Co3-S4	2.3626(10)

The proposed mechanism for formation of **3** is shown in Scheme 2.7. Like potassium thiapentadienide, lithium 2,3-dimethyl-5-thiapentadienide is prepared from a cyclic starting material and possesses a *cis* internal double bond, which could lead to the initial formation of the *cis* isomer of the 16e$^-$ (5-η^1-2,3-dimethyl-5-thiapentadienyl)Co(PMe_3)$_3$ intermediate. As discussed in Section 2.2.1, this 16e$^-$ species could rapidly isomerize to the favored *trans* isomer. Partial disproportionation of this Co(I) species would then lead to the formation of (5-η^1-*trans*-2,3-dimethyl-5-thiapentadienyl)$_2$Co(PMe$_3$)$_2$ (a Co(II) species) and Co(PMe$_3$)$_4$ (a Co(0) species). Disproportionation reactions involving 16e$^-$ Co(I) species are common, and species containing bulky ligands are more reactive than those with smaller ligands[15]. Further reaction of the Co(II) species with two additional equivalents of (5-η^1-*trans*-2,3-dimethyl-5-thiapentadienyl)Co(PMe$_3$)$_3$ would generate the observed trimetallic product, **3**.

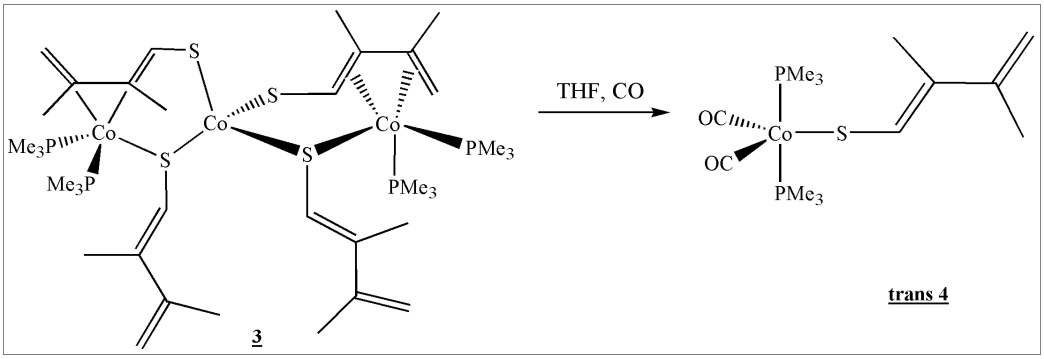


Scheme 2.7. Proposed mechanism for the formation of compound 3.

2.2.4 Reaction of Compound 3 with Carbon Monoxide

When compound **3** is exposed to carbon monoxide gas, the color immediately changes from brown to orange due to the formation of (5-η^1-*trans*-2,3-dimethyl-5-thiapentadienyl)Co(PMe$_3$)$_2$(CO)$_2$, ***trans*-4** (Scheme 2.8). This complex is produced from the terminal Co(I) centers in trimer **3**, and the fate of the Co(II) center is unknown. In the

^{1}H NMR spectrum of ***trans*-4**, H4 appears farthest downfield at δ 6.14, while the H1's resonate at δ 4.66 and 4.58. The methyl groups give rise to singlets at δ 1.98 and 1.84, and the PMe_3 ligands appear as a virtual triplet, confirming their *trans*-diaxial orientation. The $^{31}P\{^1H\}$ NMR spectrum consists of a sharp singlet.



Scheme 2.8. Reaction of 3 with carbon monoxide to form *trans*-4.

The X-ray crystal structure is shown in Figure 2.5; select bond distances are listed in Table 2.4. The coordination geometry about cobalt is trigonal bipyramidal with the PMe_3 ligands occupying the axial sites. The dimethylthiapentadienyl ligand is planar (mean deviation = 0.036 Å) and W-shaped with a *trans* internal double bond.

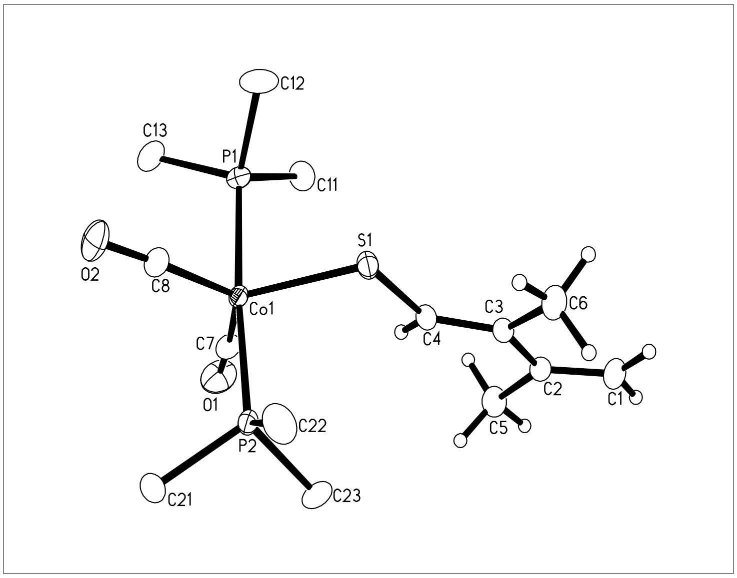


Figure 2.5. X-ray crystal structure of *trans*-4, using thermal ellipsoids at the 50% level. PMe_3 methyl H's are not shown.

Table 2.4. Select bond distanced from the crystal structure of *trans*-4.

Bond	Distance (Å)
Co1-P1	2.1821(3)
Co1-P2	2.1784(3)
Co1-S1	2.3138(3)
Co1-C7	1.7436(8)
Co1-C8	1.7460(8)
C1-C2	1.3426(11)
C2-C3	1.4670(10)
C2-C5	1.5043(11)
C3-C4	1.3544(10)
C3-C6	1.5018(10)
C4-S1	1.7399(8)

The *cis* isomer, ***cis*-4**, can be produced independently by reaction $ClCo(PMe_3)_2(CO)_2$[13] with lithium 2,3-dimethyl-5-thiapentadienide. The ^1H NMR spectrum shows evidence of only the *cis* isomer, providing strong evidence that the lithium 2,3-dimethyl-5-thiapentadienide reagent contains a *cis* internal double bond. This is expected because lithium 2,3-dimethyl-5-thiapentadienide is synthesized from a cyclic precursor. The X-ray crystal structure of ***cis*-4** is shown in Figure 2.6. When pure ***cis*-4** is dissolved in acetone-d_6 and heated in a sealed tube at 100 C, it isomerizes to the thermodynamically preferred *trans* isomer. This isomerization proceeds significantly faster than the analogous isomerization of ***cis*-2** (see Section 2.2.2), suggesting that the required $16e^-$ intermediate is more accessible via PMe_3 dissociation. A *cis*:*trans* ratio of 1:2, as measured by NMR, was achieved after only 3 h of heating.

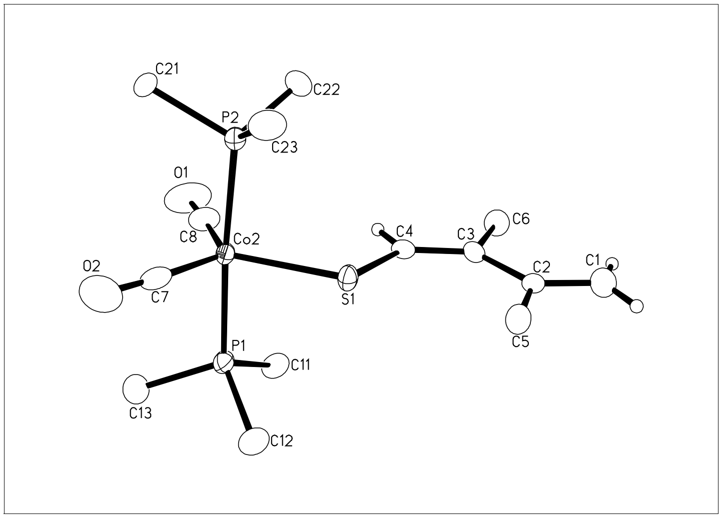


Figure 2.6. X-ray crystal structure of *cis*-4, using thermal ellipsoids at the 50% level. PMe_3 methyl H's are not shown.

2.3 Conclusions

This chapter reported the synthesis, structure and spectroscopy of the first thiapentadienyl-cobalt complexes. The thiapentadienyl system showed distinctive dimeric and trimeric ground state bonding modes as a result of the small size of the cobalt metal center relative to other metals in the same group. Treatment of $ClCo(PMe_3)_3$ with potassium thiapentadienide produced the dimer **1**. This dimer was reactive toward the small two-electron donor ligand, CO, forming the products ***cis*-2** and ***trans*-2**. Treatment of $ClCo(PMe_3)_3$ with lithium 2,3-dimethylthiapentadienide yielded the trimer **3**. This trimer was also reactive toward the two-electron donor, CO, forming $Co(PMe_3)_2(CO)_2(\eta^1$-*trans*-thiapentadienyl) upon reaction. Some similarities to previously reported systems were seen in the initial bonding modes, though one new bonding mode was seen: μ_2-η^4,η^1-bonding mode where one cobalt center bonds to the butadiene moiety in an η^4-fashion while a second cobalt coordinates the anionic sulfur atom.

2.4 Experimental

General Comments on Experimental Techniques.

All manipulations were carried out under a nitrogen atmosphere, using either glovebox or double-manifold Schlenk techniques. Solvents were stored under nitrogen after being distilled from the appropriate drying agents. Deuterated NMR solvents were obtained in sealed vials and used as received. $(Cl)Co(PMe_3)_3$ and $(Cl)Co(PMe_3)_2(CO)_2$ were prepared by the procedure of Klein and Karsch[13]. Potassium thiapentadienide was prepared by a Birch reduction of thiophene[16] followed by ring-opening of dihydrothiophene with potassium amide. Lithium 2,3-dimethyl-5-thiapentadienide was synthesized using our previously published procedure[12]. High purity carbon monoxide gas was obtained from Praxair and used as received.

NMR experiments were performed on a Varian Unity Plus- 300 spectrometer (^{1}H, 300 MHz; ^{13}C, 75 MHz; ^{31}P, 121 MHz), a Varian Mercury-300 spectrometer (^{1}H, 300 MHz; ^{13}C, 75 MHz; ^{31}P, 121 MHz), a Varian Unity Plus-500 spectrometer (^{1}H, 500 MHz; ^{13}C, 125 MHz; ^{31}P, 202 MHz), or a Varian Unity-600 spectrometer (^{1}H, 600 MHz; ^{13}C, 150 MHz; ^{31}P, 242 MHz).

^{1}H and ^{13}C spectra were referenced to tetramethylsilane, while ^{31}P spectra were referenced to external H_3PO_4. HMQC (^{1}Hdetected multiple quantum coherence), HMBC (heteronuclear multiple-bond correlation), and COSY (correlation spectroscopy) experiments aided in assigning some of the ^{1}H and ^{13}C peaks.

Synthesis of Compound 1. Potassium thiapentadienide (0.17 g, 1.40 mmol) and $(Cl)Co(PMe_3)_3$ (0.40 g, 1.24 mmol) were weighed into a 50 mL Erlenmeyer flask with 20 mL of THF. The resulting brown solution was stirred at room temperature for 45 min. Solvent was removed under vacuum, and the product was extracted with pentane and filtered. Pentane was removed under vacuum, and the brown residue was dissolved in a mixture of pentane and ether. Cooling the solution to -30 C produced brown crystals of **1** over several days. Yield: 0.20 g (56%). Anal. Calcd for $C_{20}H_{46}Co_2P_4S_2$: C, 40.54; H, 7.84. Found: C, 39.93; H, 7.73.

^{1}H NMR (acetone-d_6, -20 C): δ5.26 (ddd, $J_{H2\text{-}H1a}$ = 16.5 Hz, $J_{H2\text{-}H3}$ = 10.2 Hz, $J_{H2\text{-}H1s}$ = 9.9 Hz, 1, H2), 5.14 (br m, 1, H4), 5.04 (br m, 1, H7), 4.96 (br m, 1, H6), 4.58 (d, $J_{H1a\text{-}H2}$ = 16.5 Hz, 1, H1a), 4.30 (d, $J_{H1s\text{-}H2}$ = 9.9 Hz, 1, H1s), 2.42 (m, 1, H3), 2.14 (m, 1, H8), 1.45 (d, $J_{H\text{-}P}$= 7.8 Hz, 9,PMe_3), 1.34-1.31 (m, 18,PMe_3's), 1.19 (d, $J_{H\text{-}P}$=8.4Hz, 9, PMe_3), 0.45 (m, 1, H5s), -0.95 (m, 1, H5a).

^{13}C{^{1}H} NMR (acetone-d_6, -20 C): δ 146.5 (s, C2), 97.8 (s, C1), 95.4 (s, C8), 95.1 (s, C7), 81.6 (s, C6), 74.3 (m, C4), 43.4 (m, C3), 22.2 (s, C5), 19.0-17.2 (complex m, PMe_3's).

^{31}P{^{1}H} NMR (acetone-d_6, -70 C): δ14.6 (d, $J_{P\text{-}P}$=31.2 Hz, 1, PMe_3), 9.2 (s, 1, PMe_3), 6.6 (s, 1, PMe_3), -6.1 (d, $J_{P\text{-}P}$=31.2 Hz, 1, PMe_3).

Reaction of Compound 1 with CO. Synthesis of a Mixture of Compounds *cis*-2 and *trans*-2. Under nitrogen, compound **1** was dissolved in 1.0 mLof acetone-d6 in an NMR tube capped with a septum. The tube was connected to a CO Schlenk line, and the N_2 atmosphere was replaced with CO. The brown solution quickly turned orange after 5 min of CO exposure and shaking the tube. Analysis of the product by NMR revealed quantitative conversion to compound **2**, as a mixture of *cis* and *trans* isomers.

NMR Data for Compound *cis*-2. ^{1}H NMR(acetone-d_6, 22 C): δ 7.15 (ddd, $J_{H2\text{-}H1a}$ = 17.1 Hz, $J_{H2\text{-}H1s}$ = 9.9 Hz, $J_{H2\text{-}H3}$ = 9.9 Hz, 1, H2), 6.02 (dd, $J_{H3\text{-}H2}$=9.9 Hz, $J_{H3\text{-}H4}$=9.6 Hz, 1, H3), 5.90 (d, $J_{H4\text{-}H3}$=9.6 Hz, 1, H4), 4.99 ($J_{H1a\text{-}H2}$=17.1 Hz, $J_{H1a\text{-}H1s}$=2.7 Hz, 1, H1a), 4.85 (dd, $J_{H1s\text{-}H2}$=9.9 Hz, $J_{H1s\text{-}H1a}$ = 2.7 Hz, 1, H1s), 1.60 (virtual t, $J_{H\text{-}P}$ = 9.0 Hz, 18, PMe_3's).

$^{13}C\{^1H\}$ NMR (acetone-d_6, 22 C): δ ~200 (br, CO's), 147.0 (s, C4), 134.5 (s, C2), 127.5 (s, C3), 111.5 (s, C1), 17.3 (virtual t, $J_{C\text{-}P}$ = 35.1 Hz, PMe_3's).

$^{31}P\{^1H\}$ NMR (acetone-d_6, 22 C): δ 27.6 (s, PMe_3's).

NMR Data for Compound *trans*-2. ^1H NMR (acetone-d_6, 22 C): δ 6.38 (d, $J_{H4\text{-}H3}$=13.5 Hz, 1, H4), 6.31 (ddd, $J_{H2\text{-}H1a}$=16.0 Hz, $J_{H2\text{-}H3}$=10.5 Hz, $J_{H2\text{-}H1s}$=10.0 Hz, 1, H2), 6.14 (dd, $J_{H3\text{-}H4}$ = 13.5 Hz, $J_{H3\text{-}H2}$ = 10.5 Hz, 1, H3), 4.71 (d, $J_{H1a\text{-}H2}$=16.0 Hz, 1, H1a), 4.50 (d, $J_{H1s\text{-}H2}$=10.0 Hz, 1, H1s), 1.61 (virtual t, 18, PMe_3's).

$^{13}C\{^1H\}$ NMR(acetone-d_6, 22 C): δ ~200 (br, CO's), 145.3 (s, C4), 138.3 (s, C2), 128.6 (s, C3), 106.2 (s, C1), 17.5 (virtual t, $J_{C\text{-}P}$=34.6 Hz, PMe_3's).

$^{31}P\{^1H\}$ NMR (acetone-d_6, 22 C): δ 27.9 (br s, PMe_3's).

Independent Synthesis of Compound *cis*-2. To a cold solution of potassium thiapentadienide (0.25 g, 2.01 mmol) in 10 mL of THF was added a cold solution of $(Cl)Co(PMe_3)_2(CO)_2$ (0.40 g, 1.33 mmol) in 10 mL of THF. The resulting orange solution was stirred at room temperature for 45 min. Solvent was removed under vacuum, and the orange solid was dissolved in acetone. Cooling the acetone solution to -30 C yielded bright orange crystals of ***cis*-2** overnight. Yield: 0.29 g (62%). Anal. Calcd for $C_{12}H_{23}CoO_2P_2S$: C, 40.92; H, 6.60. Found: C, 41.18; H, 6.78. The NMR spectra for *cis*-2 matched those reported above.

Partial Conversion of Compound *cis*-2 to Compound *trans*-2 upon Heating in Acetone. In an NMR tube compound -was dissolved in 1.0 mL of acetone-6, and the tube was sealed. The tube was then heated in an oil bath at 100 C for a total of 141 h, and the reaction was monitored by ^{1}H NMR. Slowly, -converted to -. After 141 h, the ratio of *cis* to *trans* isomers was approximately 1:2.

Synthesis of Compound 3. Lithium 2,3-dimethyl-5-thiapentadienide (0.11 g, 0.92 mmol) and (Cl)Co(PMe_3)$_3$ (0.30 g, 0.93 mmol) were weighed into a 50 mL Erlenmeyer flask with 20 mL of THF. The resulting brown solution was stirred at room temperature for 45 min. Solvent was removed under vacuum, and the product was extracted with pentane and filtered. Pentane was removed under vacuum, and the brown residue was dissolved in a mixture of pentane and ether. Cooling the solution to -30 C produced brown crystals of as the etherate over several days. Yield: 0.21 g (91%). The sample was dried under vacuum to remove diethyl ether prior to analysis. Anal. Calcd for $C_{36}H_{72}Co_3P_4S_4$: C, 46.29; H, 7.79. Found: C, 46.67; H, 7.41. NMR spectra of compound **3** could not be obtained, due to its paramagnetism.

Reaction of Compound 3 with CO. Synthesis of Compound *trans*-4. Under nitrogen, compound 3 (0.23 g, 0.23 mmol) was dissolved in THF in an Erlenmeyer flask capped with a septum. The flask was connected to a CO Schlenk line and the N_2 atmosphere replaced with CO. The sample was exposed to CO for 1 h. Solvent was then removed under vacuum, and the product was extracted with pentane. After filtration, pentane was removed under vacuum. The sample was dissolved in acetone and cooled to 0 C. Bright orange crystals of *trans*-**4** formed over the course of a week. Yield: 0.17 g (95%). Anal. Calcd for $C_{14}H_{27}CoO_2P_2S$: C, 44.21; H, 7.17. Found: C, 44.67; H, 7.21.

^{1}H NMR (acetone-d_6, 22 C): δ 6.14 (s, 1, H4), 4.66 (d, $J_{H1a\text{-}H1s}$=2.1 Hz, 1, H1a), 4.58 (d, $J_{H1s\text{-}H1a}$=2.1 Hz, 1, H1s), 1.98 (s, 3, H6's), 1.84 (s, 3, H5's), 1.59 (virtual t, 9.0 Hz, 18, PMe_3's).

$^{13}C\{^1H\}$ NMR (acetone-d_6, 22 C): δ ~200 (br, CO's), 144.6 (s, C2), 144.2 (s, C4), 133.0 (s, C3), 106.0 (s, C1), 21.1 (s, C5), 18.0 (virtual t, $J_{C\text{-}P}$ = 35.2 Hz, PMe_3's), 14.8 (s, C6).

$^{31}P\{^1H\}$ NMR (acetone-d_6, 22 C): δ 27.5 (s, PMe_3's).

Synthesis of Compound *cis*-4. To a cold solution of lithium 2,3- dimethyl-5-thiapentadienide (0.06 g, 0.50 mmol) in 5 mL of THF was added a cold solution of $(Cl)Co(PMe_3)_2(CO)_2$ (0.09 g, 0.30 mmol) in 5 mL of THF. The resulting orange solution was stirred at room temperature for 45 min. Solvent was removed under vacuum, and the product was extracted with pentane and filtered. Pentane was removed under vacuum, and the orange solid was dissolved in acetone. Cooling the acetone solution to -30 C produced orange crystals of *cis*-**4** overnight. Yield: 0.068 g (60%). Anal. Calcd for $C_{14}H_{27}CoO_2P_2S$: C, 44.21; H, 7.17. Found: C, 44.67; H, 7.21.

^{1}H NMR (acetone-d_6, 22 C): δ 5.77 (s, 1, H4), 5.11 (s, 1, H1a), 4.81 (s, 1, H1s), 2.15 (s, 3, H5's), 1.77 (s, 3, H6's), 1.60 (virtual t, $J_{H\text{-}P}$=8.7 Hz, 18, PMe_3's).

$^{13}C\{^1H\}$ NMR(acetone-d_6, 22 C): δ~200 (br, CO's), 146.0 (s, C2), 141.4 (s, C4), 132.0 (s, C3), 111.7 (s, C1), 25.1 (s, C6), 24.3 (s, C5), 18.0 (virtual t, $J_{C\text{-}P}$=35.2 Hz, PMe_3's).

^{31}P{^{1}H}NMR(acetone-d$_6$, 22 C): δ 27.3 (s, PMe$_3$'s).

Partial Conversion of *cis*-4 to *trans*-4 upon Heating in Acetone. In an NMR tube compound was dissolved in 1.0 mL of acetone-d6, and the tube was sealed. The tube was heated in an oil bath at 100 C for a total of 3 h, and the reaction monitored by ^{1}H NMR. After 3 h, NMR analysis showed the ratio of to isomers to be approximately 1:2.

X-ray Diffraction Studies. Crystals of X-ray diffraction quality were obtained for compounds **1**, ***cis*-2**, **3** and ***trans*-4**. In all cases crystals of appropriate dimensions were mounted on MiTeGen loops in random orientations. Preliminary examination and data collection were performed using a Bruker Kappa Apex II charge-coupled device (CCD) detector system single-crystal X-ray diffractometer equipped with an Oxford Cryostream LT device. All data were collected using graphite-monochromated Mo K radiation (= 0.71013 Å) from a fine-focus sealed tube X-ray source. Preliminary unit cell constants were determined with a set of 36 narrow frame scans. Typical data sets consisted of combinations of w and f scan frames with typical scan width of 0.5 and counting time of 15-30 s/frame at a crystal to detector distance of 4.0 cm. The collected frames were integrated using an orientation matrix determined from the narrow frame scans. Apex II and SAINT software packages[17] were used for data collection and data integration. Analysis of the integrated data did not show any decay. Final cell constants were determined by global refinement of reflections from the complete data set. Collected data were corrected for systematic errors using SADABS[18] based on the Laue symmetry using equivalent reflections.

All crystal data for this chapter may be found in Appendix A.

Structure solution and refinement were carried out using the SHELXTL-PLUS software package[19]. The structures were solved by direct methods and refined with full matrix least-squares refinement by minimizing $w(F^2_o - F^2_c)^2$. All non-hydrogen atoms were refined anisotropically to convergence. Specific experimental details for individual structures are given below.

Compound **1** was a twinned crystal, and data reduction was carried out using two domains. Twin refinement resulted in a ratio of 62:38% for the two domains (BASF/HKLF 5 refinement in SHELXTL). The two H atoms for C5 were located, and their coordinates were refined using geometrical restraint (SADI). All other H atoms were added in the calculated position and were refined using appropriate riding models (AFIX m3). For compound ***cis*-2**, all H atoms were located and were refined freely except for the Me H's, which were refined using geometrical restraint (SADI). The H atoms for compound **3** were treated with a combination of independent and restrained refinements. The H's on C11 and C31 were located and were refined using geometrical restraint (SADI). Other ligand H's were refined freely. All other H atoms were added in the calculated positions and were refined using appropriate riding models (AFIX m3).

Similarly, the H atoms for compound ***trans*-4** were treated with a combination of independent and restrained refinements. The H's on the ligand carbon C1 were located and refined using distance restraints (SADI). Other ligand H's were refined freely. All other H atoms were added in the calculated positions and were refined using appropriate riding models (AFIX m3).

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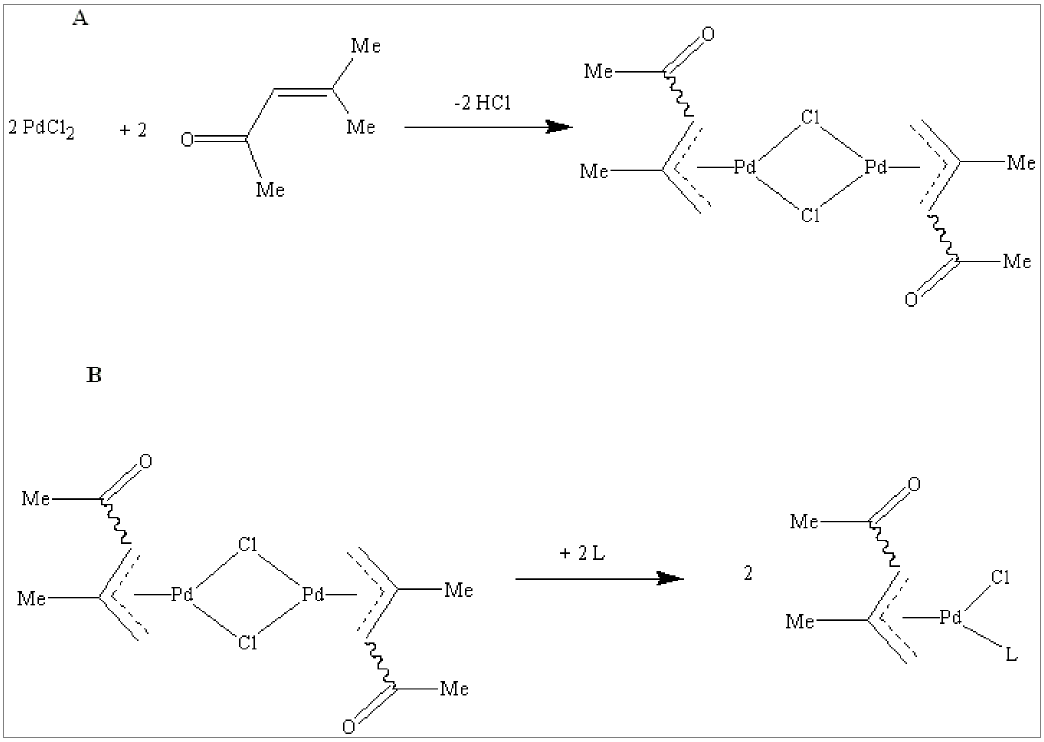
CHAPTER THREE

OXAPENTADIENYL-COBALT CHEMISTRY

Oxapentadienyl-Cobalt Chemistry

3.1 Introduction

Research in the area of oxapentadienyl chemistry began even earlier than the work on their thiapentadienyl counterparts, with the first oxapentadienyl-metal complex, [((1,2,3-η)-2,4-dimethyl-5-oxapentadienyl)PdCl]$_2$, being synthesized in 1959[1] (Scheme 3.1A) and characterized in 1962[2]. The dimeric product was reactive toward 2e$^-$ donor ligands, such as PPh$_3$ and 2-methylpyridine, falling apart to give a mixture of the *syn*-η^3 and *anti*-η^3 isomers of (1,2,3-η-2,4-dimethyl-5-oxapentadienyl)Pd(L)(Cl) (Scheme 3.1B).



Scheme 3.1. Synthesis of the first oxapentadienyl-metal complex

Subsequent inadvertent discoveries of oxapentadienyl-metal complexes produced the compounds shown in Figure 3.1. These compounds were produced through a variety of pathways, including: butadiene reacting with a carbonyl ligand[3,4], transition metal-induced aldol condensations[5,6], and on-metal furan ring opening[7].

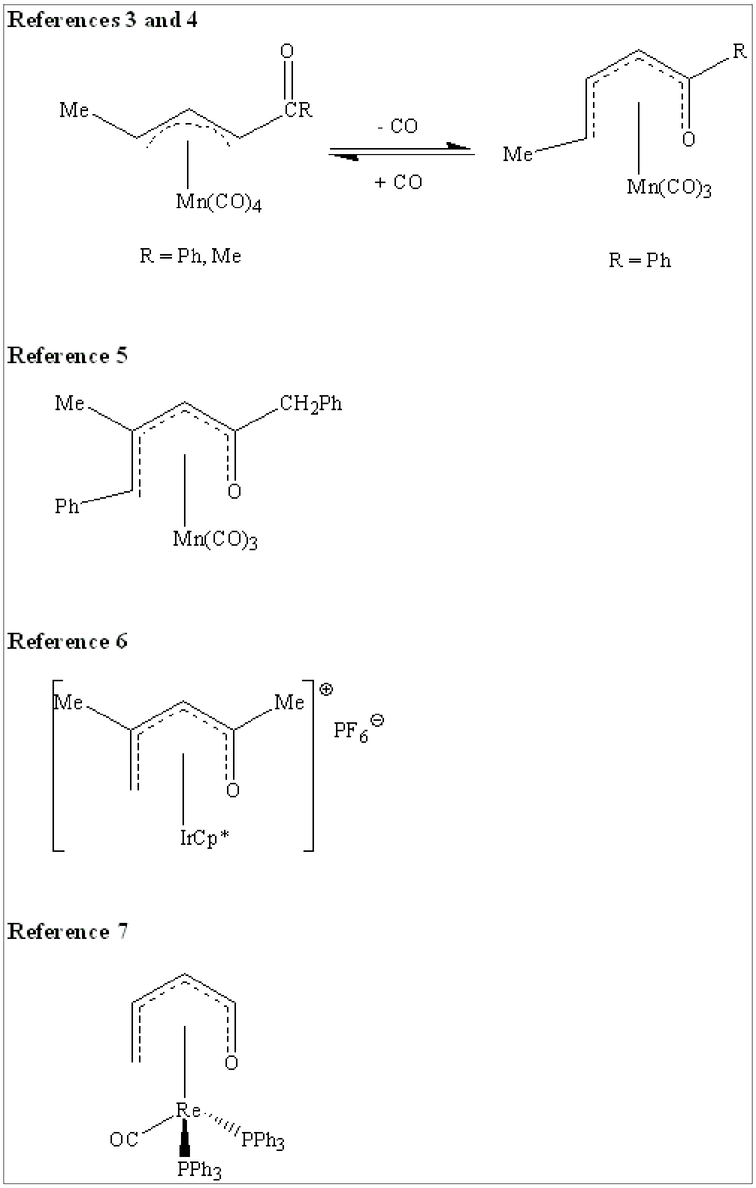
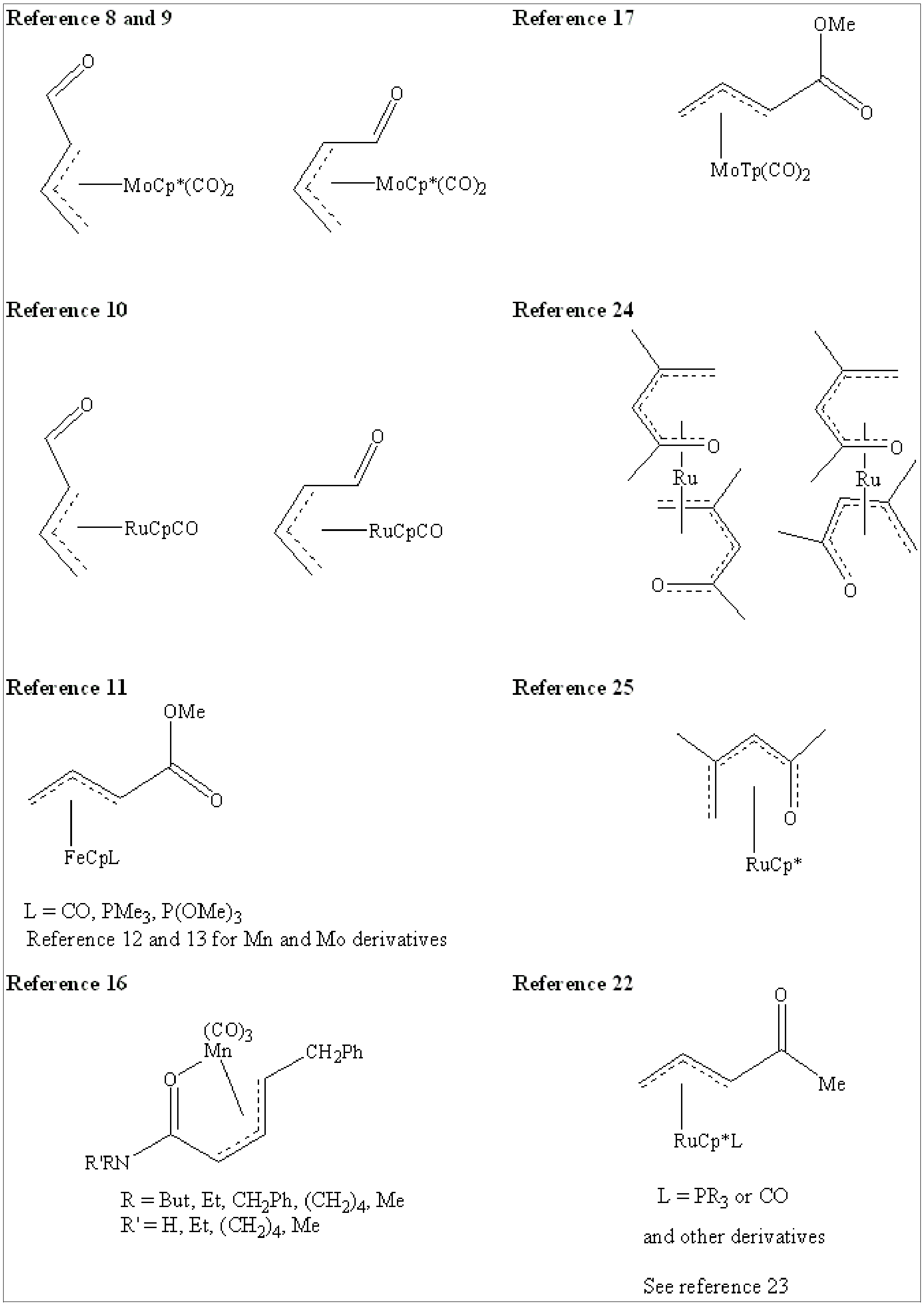


Figure 3.1. Examples of early oxapentadienyl-metal complexes

Beginning in 1989, strategic synthetic methods toward oxapentadienyl-metal complexes began to appear (Scheme 3.2). These synthetic methods utilized a variety of starting materials, including cationic[8-10] and anionic metal complexes with halogenated esters and ketones[11-17], anionic oxapentadienide reagents[18-23], enones and enals[24-26]. These varied methods have also allowed the synthesis of oxapentadienyl-metals complexes containing a wide range of metals (first, second and third row transition): Pd, Mn, Ir, Rh, Re, Mo, Ru, Fe.

The use of anionic oxapentadienide reagents and metal halides has been the focus of research in the Bleeke group. Utilizing this method has led to the production of a number of oxapentadienyl complexes containing rhodium and iridium, and this work has been summarized in Chapter 1. This chapter reports on the synthesis and reactivity of oxapentadienyl-cobalt-phosphine complexes using an analogous approach.

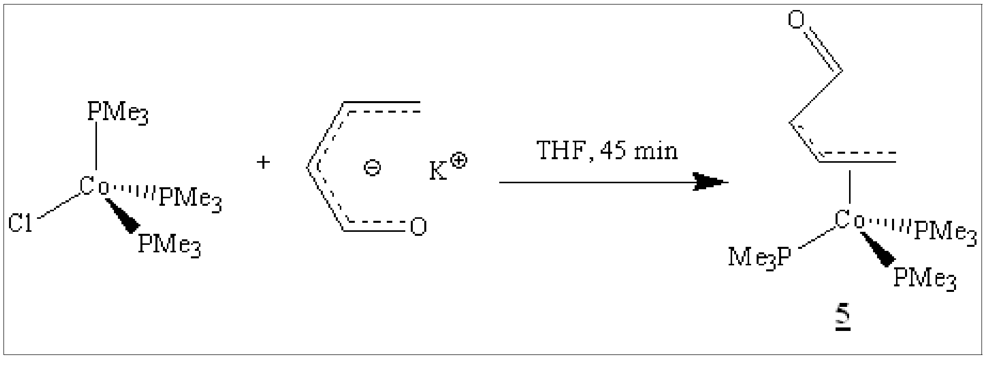


Scheme 3.2. Examples of more recent oxapentadienyl-metal complexes

3.2 Results and Discussion

3.2.1. Synthesis of (1,2,3-η-5-Oxapentadienyl)Co(PMe$_3$)$_3$ (5).

When ClCo(PMe$_3$)$_3$[27] is treated with potassium oxapentadienide[28], (1,2,3-η-oxapentadienyl)Co(PMe$_3$)$_3$ (**5**) is formed in 94% yield (Scheme 3.3). In the ^{1}H NMR the protons on the coordinated allyl portion of the ligand appear at δ4.54 (H2), 3.41 (H3), 0.72 (H1), and 0.12 (H1) with the proton on the uncoordinated C4 appearing farther downfield at δ6.53. The ^{13}C{^{1}H} NMR shows a similar pattern with the uncoordinated C4 appearing downfield at δ170.2, while the coordinated carbons appear upfield at δ69.0 (C3), 67.0 (C2) and ~30.0 (C1). At room temperature the ^{31}P{^{1}H} NMR spectrum shows a single peak at δ2.8 due to the rotation of the oxapentadienyl ligand about the Co-allyl axis which exchanges the positions of the three PMe$_3$ ligands. Upon cooling to -70 C in acetone-d$_6$, the ^{31}P{^{1}H} NMR signal broadens, but does not fully split into three peaks. The oxapentadienyl C=O stretch appears at 1574.0 cm^{-1} in the infrared spectrum.



Scheme 3.3. Synthesis of compound 5.

The X-ray crystal structure of **5** is shown in Figure 3.2 and selected bond distances are presented in Table 3.1. The oxapentadienyl ligand is *cis* (*anti*) with respect to the C2-C3 bond and is sickle-shaped. The C2-C3-C4-O1 torsional angle is 179.6(3)°, approaching the torsional angle of 180° for an idealized sickle shape. The formyl group is rotated out of the allyl plane, resulting in a C1-C2-C3-C4 torsional angle of 20.2(4)°. This rotation causes C4 to lie 0.396 Å out of the plane. The *cis* geometry of the oxapentadienyl ligand may be stabilized by the contribution of a second resonance structure (Figure 3.3), featuring an η^4-oxapentadienyl ligand. Consistent with this bonding picture is the relatively short bond length of C3-C4 (1.389(5) Å).

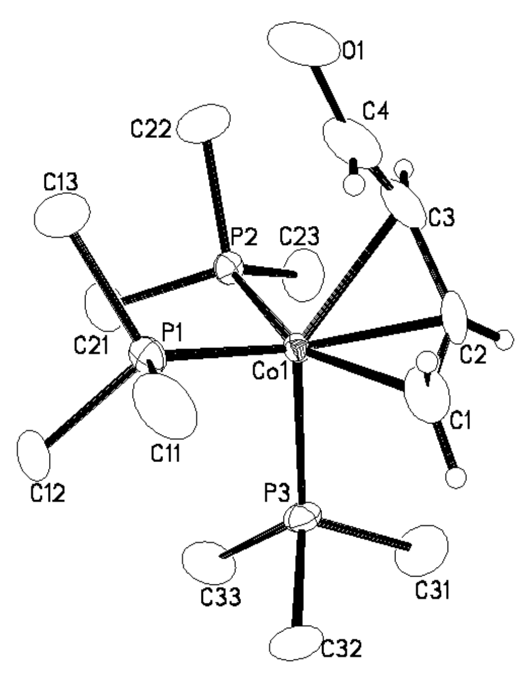


Figure 3.2. X-ray crystal structure of compound 5, using thermal ellipsoids at the 40% level. PMe_3 methyl H's are not shown.

Table 3.1. Select bond distances from the crystal structure of 5.

Bond	Distance (Å)
Co1-P1	2.1873(8)
Co1-P2	2.1744(8)
Co1-P3	2.1644(6)
Co1-C1	2.044(3)
Co1-C2	1.946(3)
Co1-C3	2.112(3)
C1-C2	1.368(6)
C2-C3	1.443(5)
C3-C4	1.389(5)
C4-O1	1.223(4)

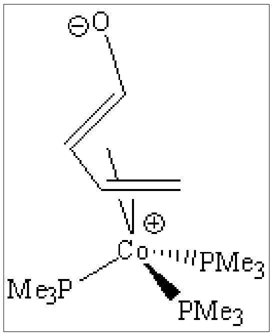
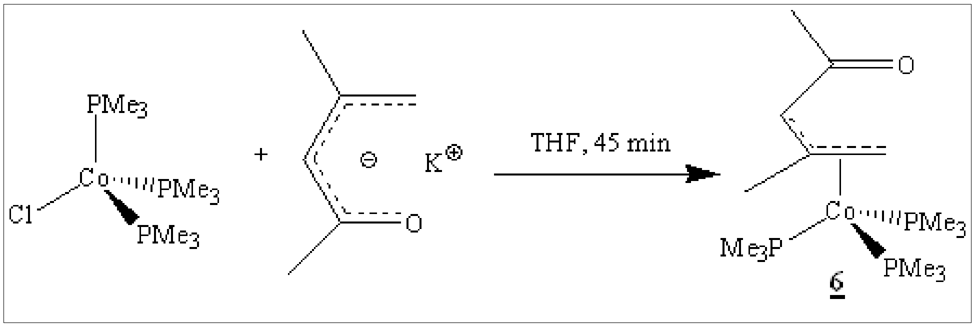


Figure 3.3. η⁴-Resonance structure contributing in compound 5.

3.2.2. Synthesis of (1,2,3-η-2,4-Dimethyl-5-oxapentadienyl)Co(PMe$_3$)$_3$ (6).

When ClCo(PMe$_3$)$_3$[3] is treated with potassium 2,4-dimethyloxapentadienide[18], (1,2,3-η-2,4-dimethyl-5-oxapentadienyl)Co(PMe$_3$)$_3$ (**6**) is formed in 89% yield (Scheme 3.4). In the ^{1}H NMR spectrum of **6**, the allylic H signals appear at δ2.93 (H1), 2.62 (H3), and

1.48 (H1). In the $^{13}C\{^1H\}$ NMR the allyl carbon signals appear at δ84.0 (C2), 56.7 (C3), and 39.0 (C1), while the uncoordinated C4 signal appears at δ204.0, even farther downfield that the corresponding signal for C4 in compound **5** (δ170.2). Compound **6** gives rise to one peak in the $^{31}P\{^1H\}$ NMR spectrum at room temperature due the rapid rotation of the dimethyoxapentadienyl ligand which exchanges the positions of the three PMe_3 ligands. Upon cooling to -70 C in acetone-d_6, the $^{31}P\{^1H\}$ NMR signal splits into three separate peaks showing that the rotation has been stopped.



Scheme 3.4. Synthesis of compound 6.

The X-ray crystal structure of **6** is shown in Figure 3.4 and selected bond distances are presented in Table 3.2. The dimethyloxapentadienyl ligand is *cis* with respect to the C2-C3 bond and is U-shaped. Torsional angle C2-C3-C4-O1 is 7.4(3)° (an idealized U-shape would have a torsional angle of 0°), while the C1-C2-C3-C4 torsional angle is 38.1(3)°, indicating a substantial rotation of the acetyl group out of the allyl plane. As a result of this rotation, atom C4 is displaced 0.713 Å out of the C1-C2-C3 plane, as compared to

0.396 Å for **5**. This enhanced displacement, together with the relatively long C3-C4 bond distance (1.459(3) Å), suggests that the η^4-diene resonance structure (Figure 3.5) may be less important in this compound. Spectroscopic evidence is also consistent with this view, particularly the downfield shifting of C4 in the ^{13}C NMR and the higher energy of the C=O stretch in the IR.

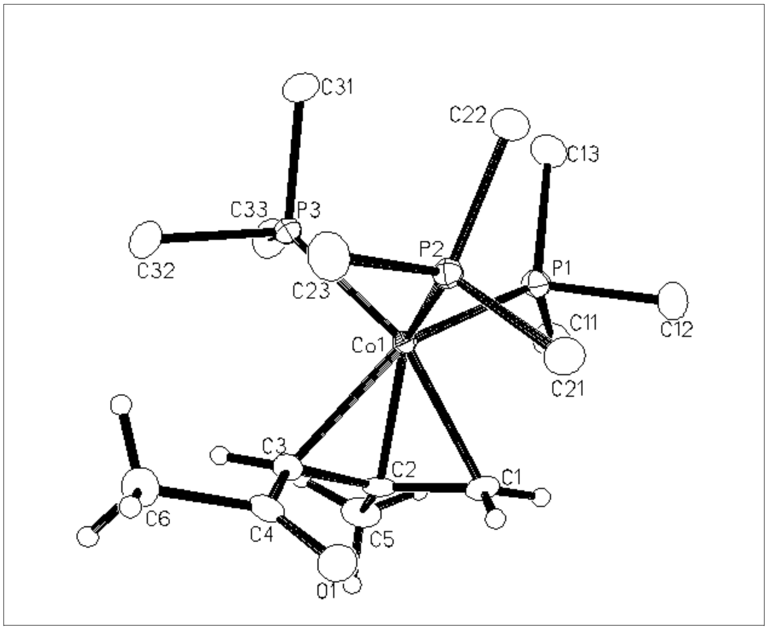


Figure 3.4. X-ray crystal structure of 6, using thermal ellipsoids at the 50% level. PMe_3 methyl H's are not shown.

Table 3.2. Select bond distances from the crystal structure of 6.

Bond	Distance (Å)	Bond	Distance (Å)
Co1-P1	2.1655(5)	C1-C2	1.422(3)
Co1-P2	2.2123(5)	C2-C3	1.431(2)
Co1-P3	2.1790(5)	C2-C5	1.509(2)
Co1-C1	2.0521(18)	C3-C4	1.459(3)
Co1-C2	1.9733(17)	C4-C6	1.523(3)
Co1-C3	2.1088(18)	C4-O1	1.234(2)

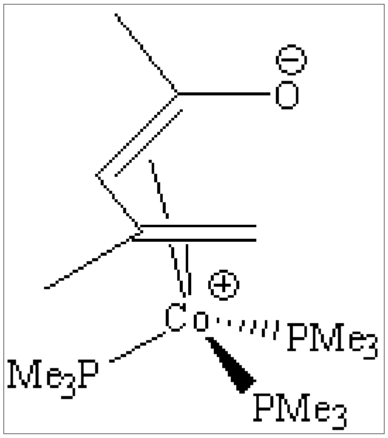
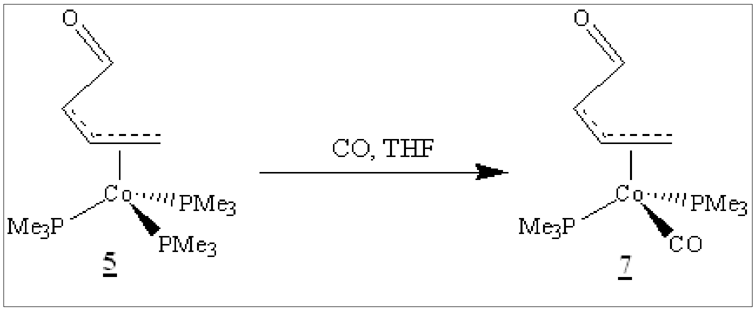


Figure 3.5. η^4-Resonance structure of compound 6.

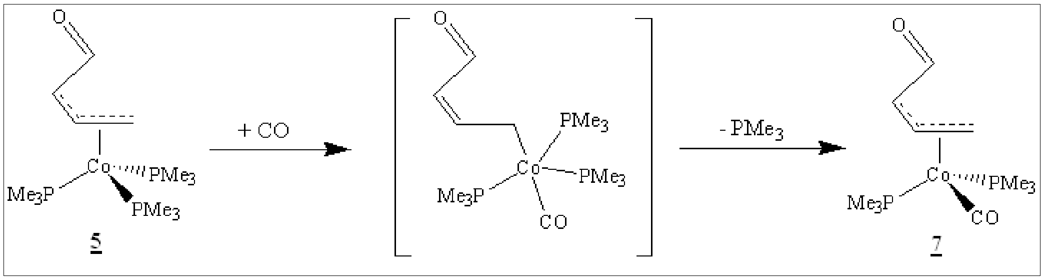
3.2.3. Reactions of Compounds 5 and 6 with Carbon Monoxide.

In an attempt to cause a shift in the oxapentadienyl ligand bonding mode, compounds **5** and **6** were exposed to carbon monoxide in THF. Exposure of compound **5** to carbon monoxide leads to the formation of (1,2,3-η-5-oxapentadienyl)Co(PMe_3)$_2$(CO) (**7**) in 71% yield (Scheme 3.5). A proposed mechanism is shown in Scheme 3.6. The ^{1}H and

$^{13}C\{^1H\}$ NMR spectra of **7** are very similar to those of **5** with all signals shifted slightly downfield. The $^{31}P\{^1H\}$ NMR, however, shows two distinct peaks, even at room temperature, indicating that the ligand is no longer rotating about the Co-allyl axis. The oxapentadienyl C=O stretch appears at 1612.3 cm^{-1} in the infrared spectrum, and the C≡O stretch appears at 1935.0 cm^{-1}.



Scheme 3.5. Synthesis of compound 7.



Scheme 3.6. Proposed mechanism for the formation of compound 7.

The X-ray crystal structure of **7** is presented in Figure 3.6 with selected bond distances listed in Table 3.3. As in **5**, the oxapentadienyl ligand is *cis* and sickle-shaped. Torsional angle C2-C3-C4-O1 is 178.94(12)°, while torsional angle C1-C2-C3-C4 is 21.66(18)°.

This rotation of the formyl group results in atom C4 being displaced 0.441 Å out of the allyl plane. An interesting aspect of the structure is the orientation of the phosphine and carbonyl ligands. One of the large PMe_3 ligands (P2) resides in the site under the open "mouth" of the allyl moiety (a site traditionally noted for accommodating large ligands), while the other PMe_3 ligand (P1) lies under allyl "edge" C2-C3 and the carbonyl ligand resides under allyl "edge" C1-C2. In this way, the oxapentadienyl's formyl moiety is "tucked in " between the two bulky PMe_3's.

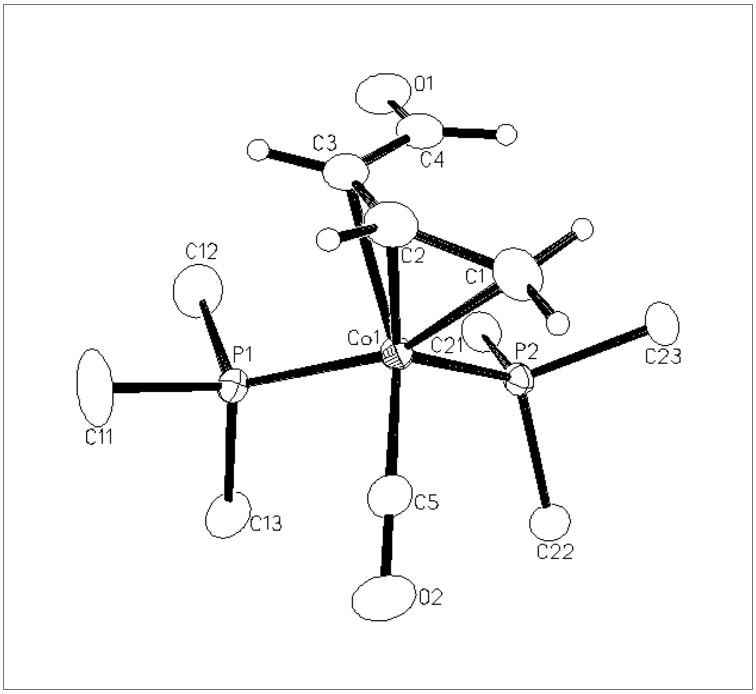
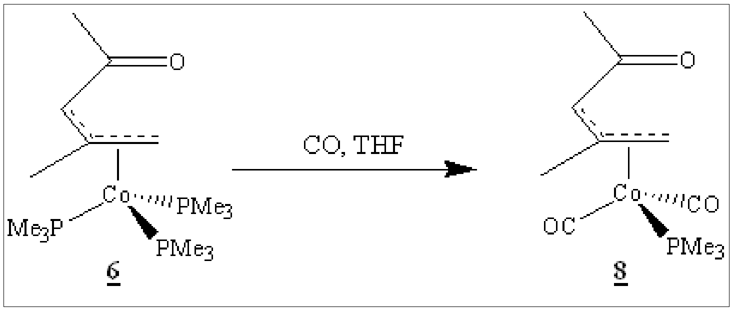


Figure 3.6. X-ray crystal structure of compound 7, using thermal ellipsoids at the 50% level. PMe_3 methyl H's are not shown.

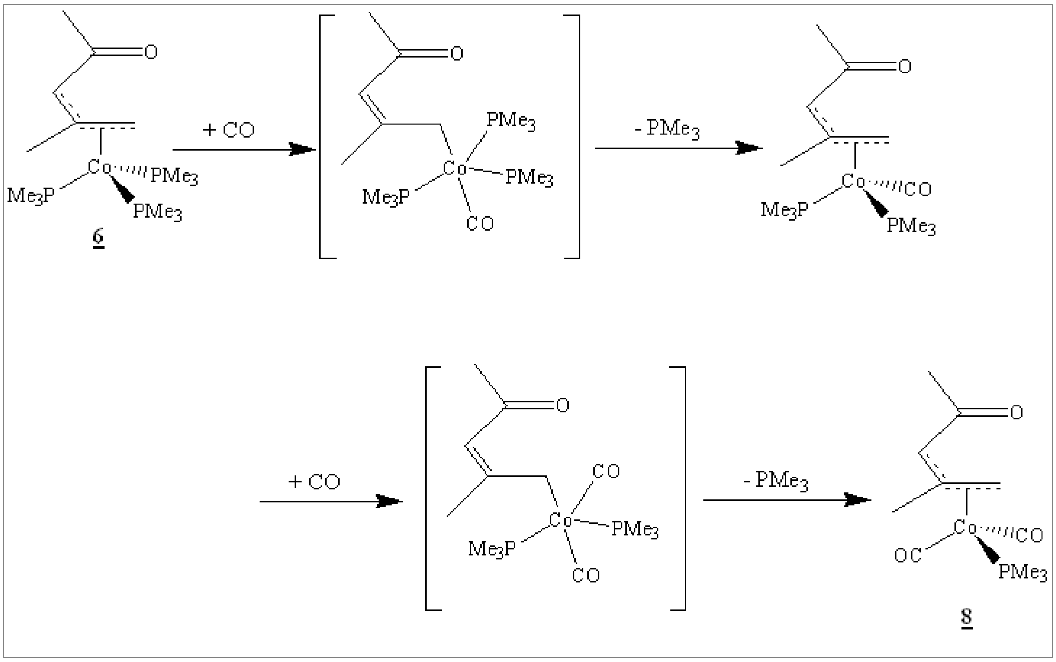
Table 3.3. Select bond distances in compound 7.

Bond	Distance (Å)
Co1-P1	2.1750(3)
Co1-P2	2.2167(3)
Co1-C5	1.7387(12)
Co1-C1	2.0569(12)
Co1-C2	1.9734(12)
Co1-C3	2.1134(12)
C1-C2	1.425(2)
C2-C3	1.4183(19)
C3-C4	1.4385(18)
C4-O1	1.2541(18)

Exposure of compound **6** to carbon monoxide leads to the formation of (1,2,3-η-2,3-dimethyl-5-oxapentadienyl)Co(PMe_3)$(CO)_2$ (**8**) in 84% yield (Scheme 3.7). A proposed mechanism is shown in Scheme 3.8. The ^{1}H and ^{13}C{^{1}H} NMR spectra of **8** are very similar to those of **6**. In the IR spectrum, the dimethyloxapentadienyl C=O stretch appears at 1668.2 cm^{-1}, while the carbonyl ligands give rise to C≡O stretches at 1992.5 cm^{-1} and 1939.3 cm^{-1}.



Scheme 3.7. Synthesis of compound 8.



Scheme 3.8. Proposed mechanism for the formation of compound 8.

The X-ray crystal structure of **8** is presented in Figure 3.7 with selected bond distances listed in Table 3.4. As in **6**, the oxapentadienyl ligand is *cis* about C2-C3 and U-shaped. Torsional angle C2-C3-C4-O1 is 0.8(5)°, while torsional angle C1-C2-C3-C4 is 37.6(5)°. This rotation of the formyl group results in atom C4 being displaced 0.719 Å out of the allyl plane. The orientation of the ligands in **8** is exactly opposite that in **7**; the carbon monoxide ligands reside under the "mouth" and the C2-C3 "edge" of the allyl moiety, while the largest ligand, PMe_3, sits under the C1-C2 "edge".

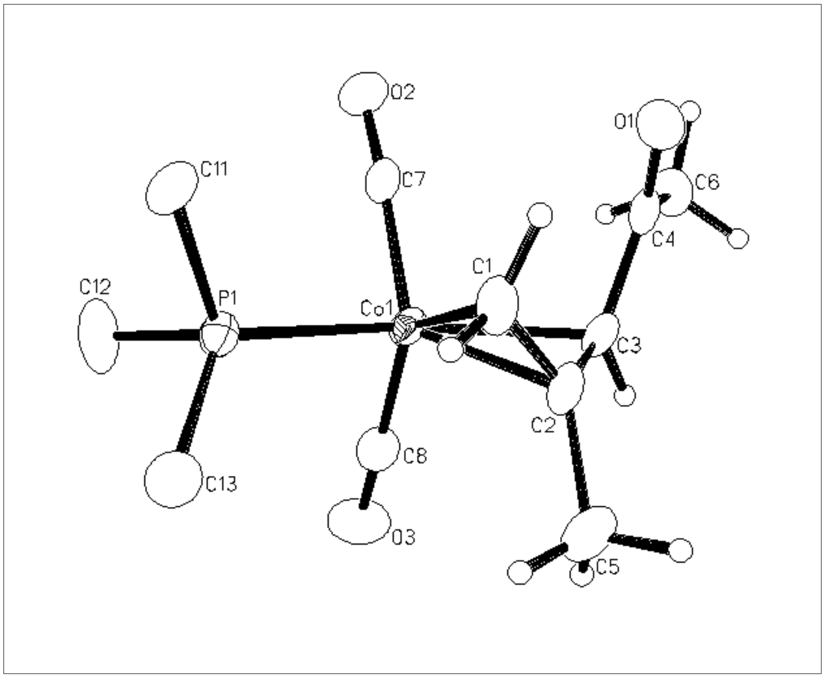


Figure 3.7. X-ray crystal structure of compound 8, using thermal ellipsoids at the 50% level. PMe_3 methyl H's are not shown.

Table 3.4. Select bond distances from compound 8.

Bond	Distance (Å)	Bond	Distance (Å)
Co1-P1	2.1673(10)	C1-C2	1.396(4)
Co1-C7	1.784(4)	C2-C3	1.430(5)
Co1-C8	1.766(3)	C2-C5	1.510(5)
Co1-C1	2.120(3)	C3-C4	1.468(4)
Co1-C2	2.039(3)	C4-C6	1.512(5)
Co1-C3	2.087(3)	C4-O1	1.228(4)

An overlay of the crystal structures for compounds **7** and **8** is shown in Figure 3.8.. In this view, the allyl moieties of **7** (C1-C2-C3) and **8** (C1'-C2'-C3') are overlaid to allow a comparison of the positions of the phosphine and carbon monoxide ligands. In **7** the PMe_3 ligands (P1 and P2) are situated so the formyl portion of the oxapentadienyl ligand (C4-O1) can tuck in between them. Carbon monoxide (C5-O2) lies opposite the formyl. However, in **8** the bulky acetyl portion of the dimethyloxapentadienyl (C6'-C4'-O1') is flanked by small carbon monoxide ligands (C7'-O2' and C8'-O3') while the bulky PMe_3 (P1') lies opposite. From the overlay view, it is clear that if a PMe_3 ligand were situated under the allyl "mouth" in **8**, it would encounter unfavorable steric interactions with the acetyl group.

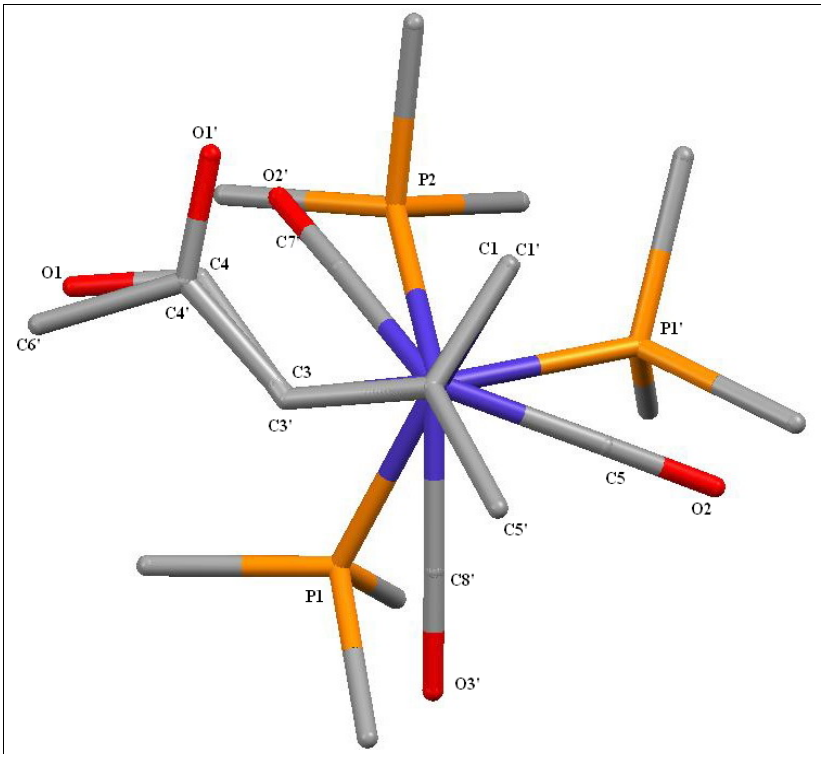
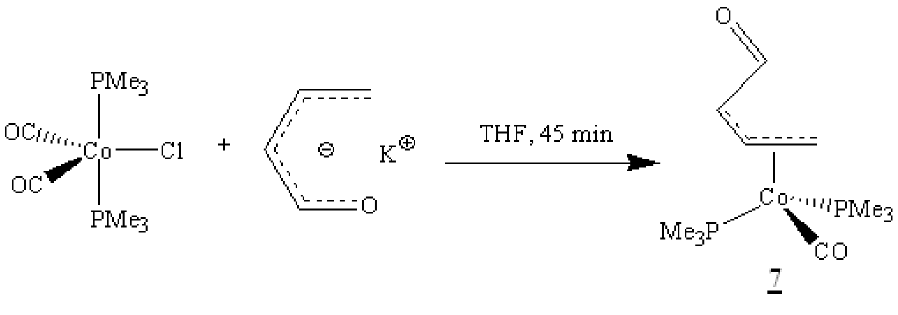


Figure 3.8. Overlay of compounds 7 and 8.

The formation of the dicarbonyl substitution product, **8**, is probably driven by electronic and steric factors. Due to the inductive effect of the methyl groups, the dimethyloxapentadienyl ligand is a better electron donor than oxapentadienyl, putting more electron density on cobalt and driving the need for electron-withdrawing ligand such as carbon monoxide.

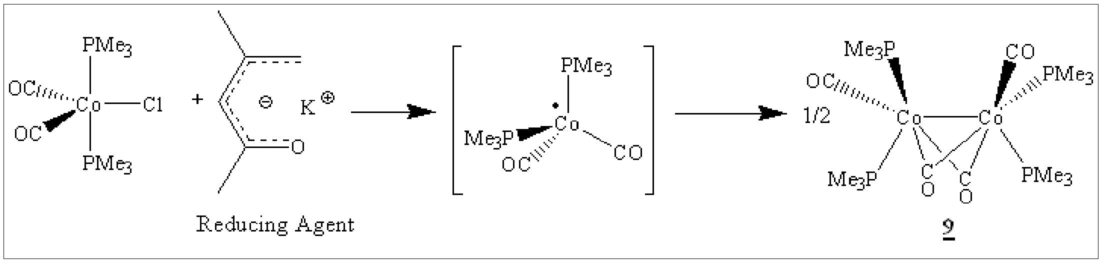
3.2.4. Alternative Synthetic Approach to Compounds 7 and 8.

Similar to the work conducted on thiapentadienyl-cobalt complexes, alternate synthetic routes toward compounds **7** and **8** from $ClCo(PMe_3)_2(CO)_2$[27] were explored. Treatment of this cobalt starting material with potassium oxapentadienide in THF generates compound **7** in 59% yield, along with one equivalent of CO (Scheme 3.9).



Scheme 3.9. Alternate synthesis of compound 7.

However, treatment of $ClCo(PMe_3)_2(CO)_2$ with potassium 2,4-dimethyloxapentadienide produces the dimer, $(CO)(PMe_3)_2Co(\mu_2\text{-}CO)_2Co(PMe_3)_2(CO)$ (**9**), in 43% yield. The formation of this dimer likely proceeds with the dimethyloxapentadienyl ligand, which has a greater electron donating capability when compared to the unmethylated oxapentadienyl ligand, acting as a reducing agent to produce the 17 e$^-$ Co(0) radical (Scheme 3.10) which then dimerizes to form **9**.



Scheme 3.10. Synthesis of compound 9.

Compound **9** has been previously observed[29], and its identity has been confirmed by ^{1}H NMR and IR spectroscopy and X-ray diffraction (Figure 3.9, Table 3.5). The molecule possesses a two-fold rotation axis which renders the ligands on Co1 chemically equivalent to those on Co2, i.e., P1 equivalent to P4, P2 equivalent to P3, and C1O1 equivalent to C4O4. The two bridging CO's lie on the same side of the Co-Co bond and are also equivalent to each other via the rotation axis.

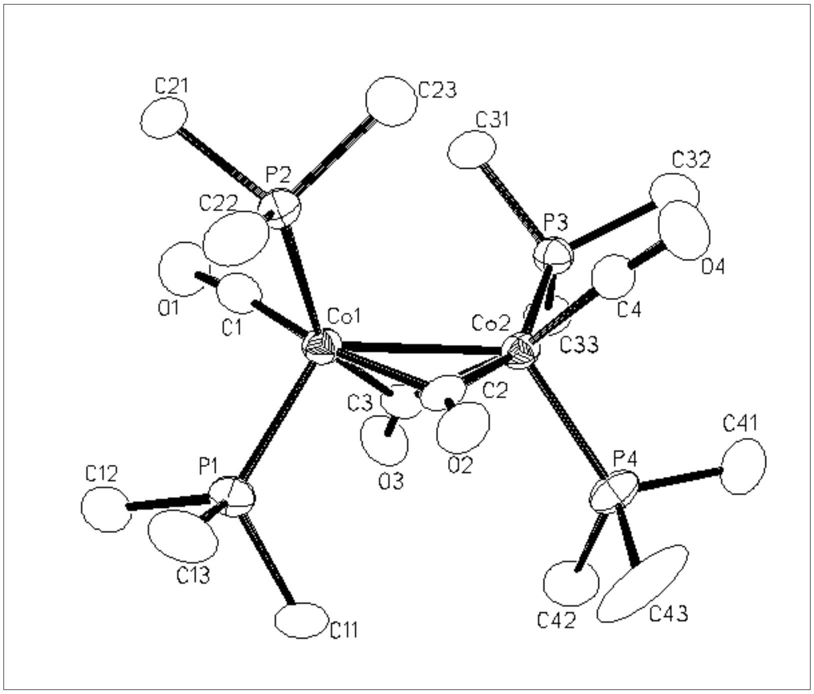
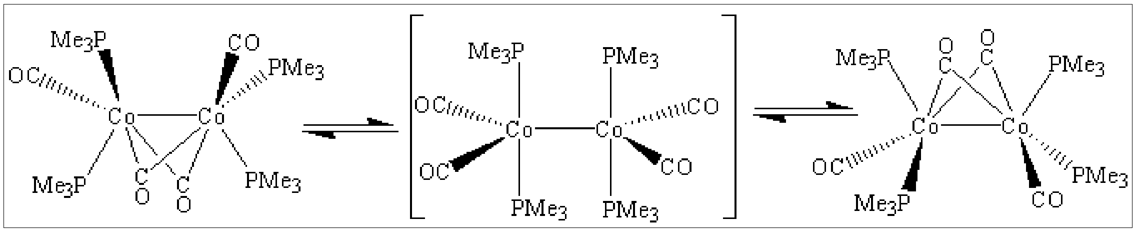


Figure 3.9. X-ray crystal structure of compound 9, using thermal ellipsoids at the 50% level. PMe_3 methyl H's are not shown.

Table 3.5. Select bond distances from compound 9.

Bond	Distance (Å)	Bond	Distance (Å)
Co1-Co2	2.5209(8)	Co1-C2	1.920(4)
Co1-P1	2.1800(13)	Co1-C3	1.897(4)
Co1-P2	2.2136(13)	Co2-C2	1.914(4)
Co2-P3	2.2199(13)	Co2-C3	1.916(4)
Co2-P4	2.1742(13)	Co2-C4	1.753(5)
Co1-C1	1.761(5)		

At room temperature, the $^{31}P\{^1H\}$ NMR spectrum of **9** consists of one peak due to a fluxional process that causes all of the phosphine ligands to appear equivalent. Upon cooling to -70 C, the signal splits into two peaks, one for the PMe_3's that lie above the Co-Co bond axis (P2 and P3) and one signal for the PMe_3's that lie below the Co-Co bond axis (P1 and P4). A proposed mechanism for the fluxional process is shown in Scheme 3.11.

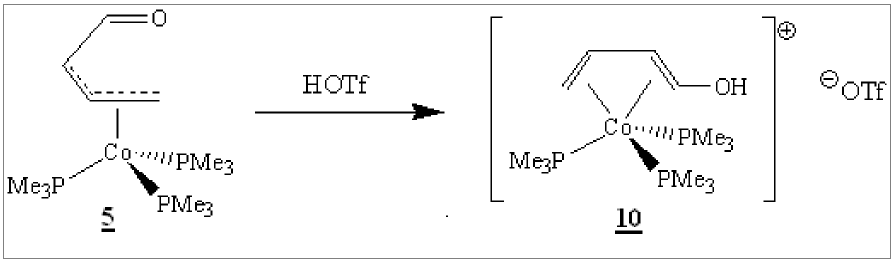


Scheme 3.11. Fluxional process in compound 9.

3.2.5. Reactions of Compound 5 with Triflic Acid and Methyl Triflate.

A second method for probing the reactivity of compounds **5** and **6** was accomplished by treatment with simple electrophiles, H^+ and Me^+. These compounds possess two potential sites for electrophile addition, the oxapentadienyl oxygen and the cobalt (I) center. When compound **5** is treated with triflic acid (a source of H^+) in diethyl ether, (η^4-butadienol)$Co(PMe_3)_3{}^+O_3SCF_3{}^-$, compound **10**, precipitates immediately in 65% yield (Scheme 3.12). The ^1H NMR spectrum of **10** shows a downfield peak at δ7.18, due to the

OH group. The peak due to H4 is now shifted substantially upfield to δ3.59 (from d6.53 in **5**) indicating that C4 is now coordinated to cobalt. The remaining η^4-diene protons resonate at δ5.21 (H2), 5.05 (H3), 1.29 (H1) and -0,70 (H1). In the $^{13}C\{^1H\}$ NMR, the now coordinated C4 shifts upfield to δ96.9 (from δ170.2 in **5**), while the remaining diene carbons appear at δ80.4 (C2), 79.3 (C3), and 35.7 (C1). The $^{31}P\{^1H\}$ NMR spectrum of **10** is a broad singlet at room temperature due to the rotation of the diene ligand about the Co-diene axis. The rotation is slowed upon cooling to -70 C but not completely halted. The IR spectrum presents one peak at 3306.9 cm^{-1} for the new O-H stretch and no peaks in the carbonyl region (1500-2000 cm^{-1}).



Scheme 3.12. Synthesis of compound 10.

The X-ray crystal structure of **10** has been obtained and is presented in Figure 3.10; select bond distances are listed in Table 3.6. The η^4-butadienol ligand in **10** retains the sickle-shape of the η^3-oxapentadienyl ligand in precursor **5**, as reflected in the C2-C3-C4-O1 torsional angle of 175.7(2)°. The torsional angle for C1-C2-C3-C4 is 1.9(3)°, and the four dienol carbons (C1-C4) are nearly coplanar with a mean deviation of 0.0066 Å.

Atom O1 lies 0.11 Å out of this plane. The dienol carbon-carbon bond lengths are essentially equivalent (see Table 3.6), while C4-O1 lengthens to 1.380(3) Å from its value of 1.223(4) Å in **5**. The cobalt-carbon bonds exhibit substantial variation in length. Carbons C1 through C3 are bound tightly, with Co-C distances in the range of 2.026(1) Å to 2.066(2) Å , while Co-C4 is much longer at 2.173(2) Å. The hydrogen atom on the OH group was located and refined; it resides *cis* to the hydrogen atom on C4 (H4).

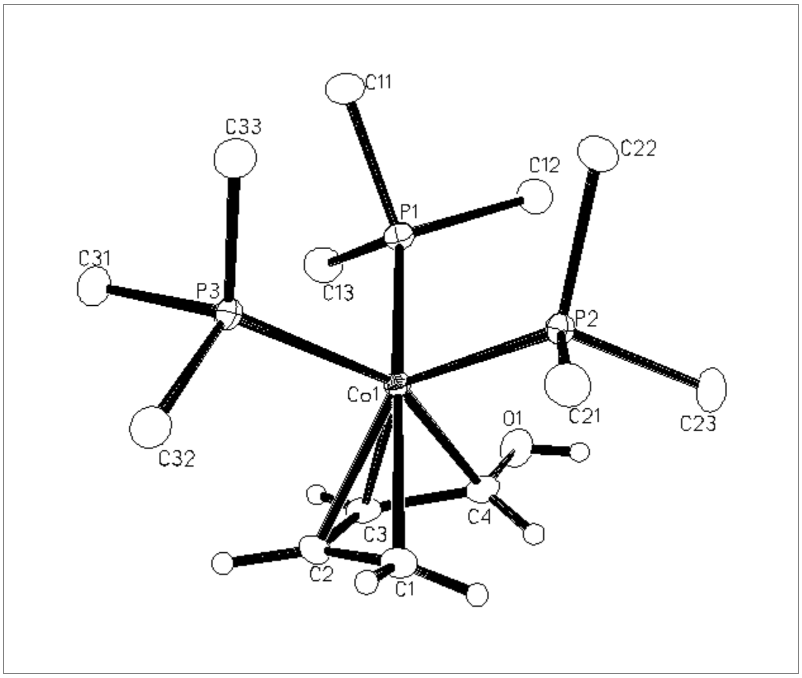
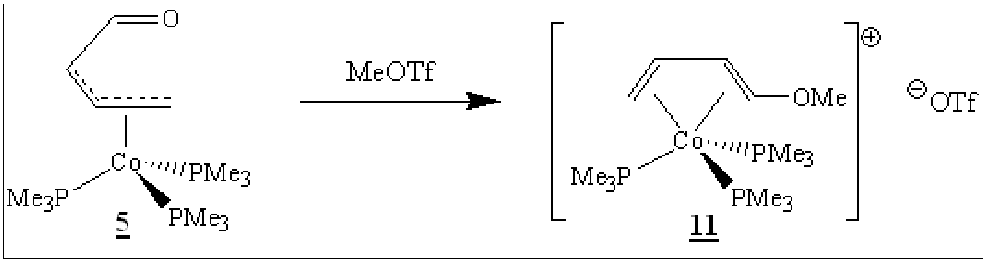


Figure 3.10. X-ray crystal structure of compound 10, using thermal ellipsoids at the 50% level. PMe_3 methyl H's are not shown.

Table 3.6. Select bond distances in compound 10.

Bond	Distance (Å)	Bond	Distance (Å)
Co1-P1	2.2108(7)	Co1-C4	2.173(2)
Co1-P2	2.1898(6)	C1-C2	1.423(3)
Co1-P3	2.2371(6)	C2-C3	1.404(3)
Co1-C1	2.065(2)	C3-C4	1.408(3)
Co1-C2	2.026(2)	C4-O1	1.380(3)
Co1-C3	2.066(2)		

Treatment of **5** with methyl triflate (a source of Me^+) in diethyl ether, (η^4-butadienyl methyl ether)$Co(PMe_3)_3{}^+O_3SCF_3{}^-$, compound **11**, precipitates immediately in 83% yield (Scheme 3.13). The ^1H NMR spectrum of **11** shows a sharp singlet at δ3.55 for the ether methyl group, which resonates in the $^{13}C\{^1H\}$ NMR at δ60.6. The peaks due to the η^4-butadiene portion of the ligand are very similar to those observed for **10**. As with **10**, the $^{31}P\{^1H\}$ NMR spectrum of **11** is a broad singlet at room temperature due to the rotation of the diene ligand about the Co-diene axis. The rotation is slowed upon cooling to -70 C but not completely halted.



Scheme 3.13. Synthesis of compound 11.

The X-ray crystal structure of **11** is presented in Figure 3.11; select bond distances are listed in Table 3.7. The butadienyl methyl ether ligand in **11** retains the sickle-shape of the η^3-oxapentadienyl ligand in precursor **5**, as reflected in the C2-C3-C4-O1 torsional angle of 177.30(9)°. The torsional angle for C1-C2-C3-C4 is 0.87(15)°, and the four dienol carbons (C1-C4) are nearly coplanar with a mean deviation of 0.0030 Å. Atom O1 lies 0.065 Å out of this plane. Methyl carbon C5 resides *cis* to the hydrogen on C4 (H4), but is rotated out of the ligand plane toward cobalt. This results in a C3-C4-O1-C5 torsional angle of 165.60(10)° and a displacement of 0.27 Å for C5 out of the C1-C2-C3-C4 plane. The carbon-carbon bond lengths within the diene portion of the ligand are all essentially equivalent, but as in **10** the cobalt-carbon distances show variation. Carbons C1-C3 are tightly bound (2.019(1) to 2.070(1) Å), while Co-C4 is longer at 2.169(1) Å.

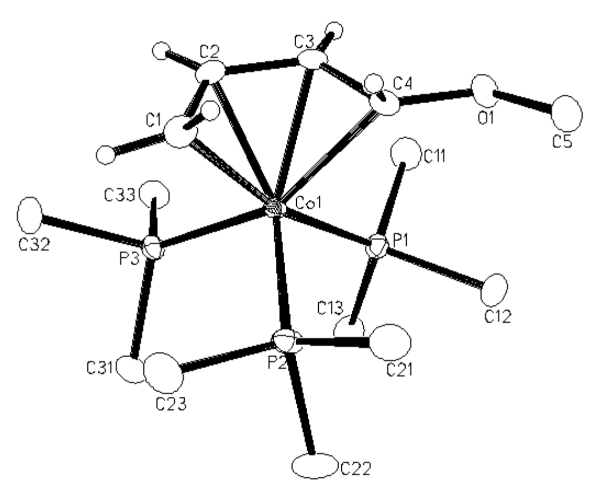


Figure 3.11. X-ray crystal structure of compound 11, using thermal ellipsoids at the 50% level. PMe_3 methyl H's are not shown.

Table 3.7. Select bond distances from compound 11.

Bond	Distance (Å)	Bond	Distance (Å)
Co1-P1	2.2070(3)	Co1-C4	2.1693(11)
Co1-P2	2.2026(3)	C1-C2	1.4231(16)
Co1-P3	2.2307(3)	C2-C3	1.4008(16)
Co1-C1	2.0702(11)	C3-C4	1.4177(15)
Co1-C2	2.0188(11)	C4-O1	1.3849(14)
Co1-C3	2.0629(11)	O1-C5	1.4283(15)

3.2.6. Reactions of Compound 6 with Triflic Acid and Methyl Triflate.

Treatment of (1,2,3-η-2,4-dimethyl-5-oxapentadienyl)Co(PMe_3)$_3$ (**6**) with triflic acid leads to a dramatically different product from those described in Section 3.2.5. Instead of a yellow-orange product, a deep green product is formed. The green compound is paramagnetic, preventing characterization by NMR. Its infrared spectrum shows no peaks in the CO or OH stretching regions, indicating that the dimethyloxapentadienyl ligand or its protonated derivative is no longer coordinated to the metal. The first potential candidate for the green compound was the 16 e^- tetrahedral $Co(PMe_3)_3(O_3SCF_3)$. However, this neutral compound would be expected to have some solubility in non-polar solvents such as pentane or ether, similar to the solubility of $Co(PMe_3)_3(O_2CCH_3)$[27], and the obtained product is only soluble in polar solvents such as THF and methylene chloride. The solubility suggests that the green compound is a salt, likely the triflate derviative of $Co(PMe_3)_4{}^+BPh_4{}^-$, a green salt reported by Klein[27]. Klein's synthesis was repeated and the colors of $Co(PMe_3)_4{}^+O_3SCF_3{}^-$ and $Co(PMe_3)_4{}^+BPh_4{}^-$ were found to match by UV-visible spectroscopy (Figure 3.12). The reactivity of $Co(PMe_3)_4^+O_3SCF_3^-$ and $Co(PMe_3)_4^+BPh_4^-$ toward excess carbon monoxide was also compared. In each case a rapid color change from green to orange was observed indicating production of $Co(PMe_3)_3(CO)_2^+O_3SCF_3^-$ (**12**) or $Co(PMe_3)_3(CO)_2^+BPh_4$.

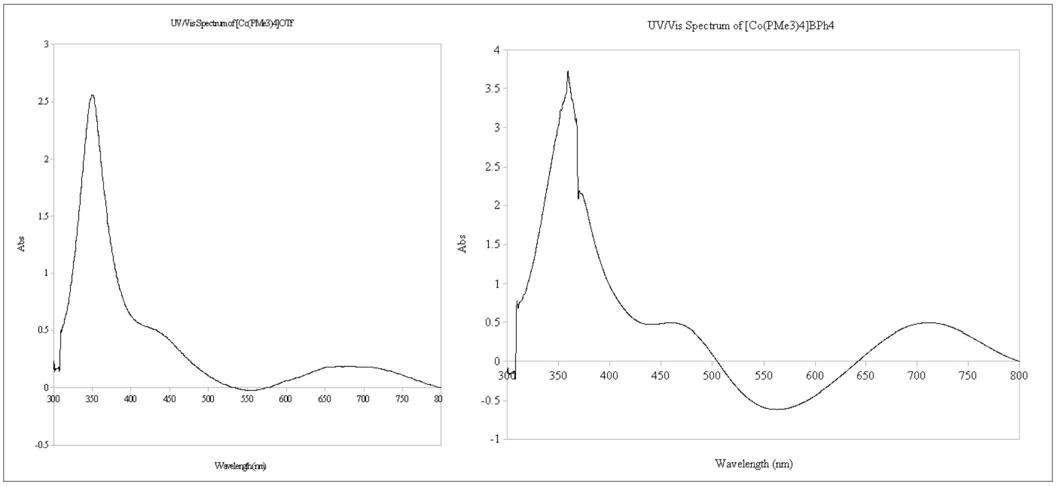


Figure 3.12. UV-visible spectra of $Co(PMe_3)_4^+O_3SCF_3^-$ and $Co(PMe_3)_4^+BPh_4^-$.

The synthesis of $Co(PMe_3)_3(CO)_2^+BPh_4$ has been reported in the literature[30], but the crystal structure has not. The crystal structure of $Co(PMe_3)_3(CO)_2^+O_3SCF_3^-$ (**12**) is shown in Figure 3.13; select bond lengths are presented in Table 3.8. The coordination geometry about cobalt is trigonal bipyramidal with two of the large PMe_3 (P2 and P3) ligands occupying the axial sites. However, these ligands are tipped toward the smaller CO ligands (and away from the equitorial phosphine P1) such that the P2-Co1-P3 angle is 165.94(1)°, much smaller than the idealized 180°. The ^1H NMR spectrum of **12** at room temperature shows one doublet at δ1.77 ($J_{H\text{-}P}$ = 8.7 Hz), indicating that the phosphines are exchanging. The $^{31}P\{^{1}H\}$ NMR shows one singlet at δ8.68 at room temperature. None of the signals split upon cooling to -70 C. The carbonyl ligand stretching frequencies in the IR are 1988.5 cm^{-1} and 1929.1 cm^{-1}.

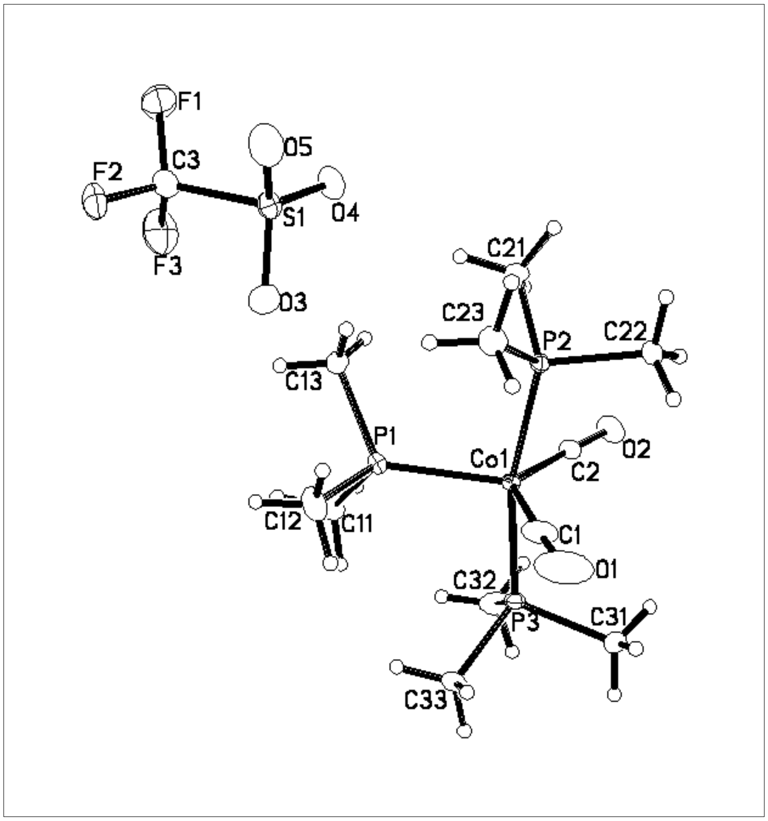


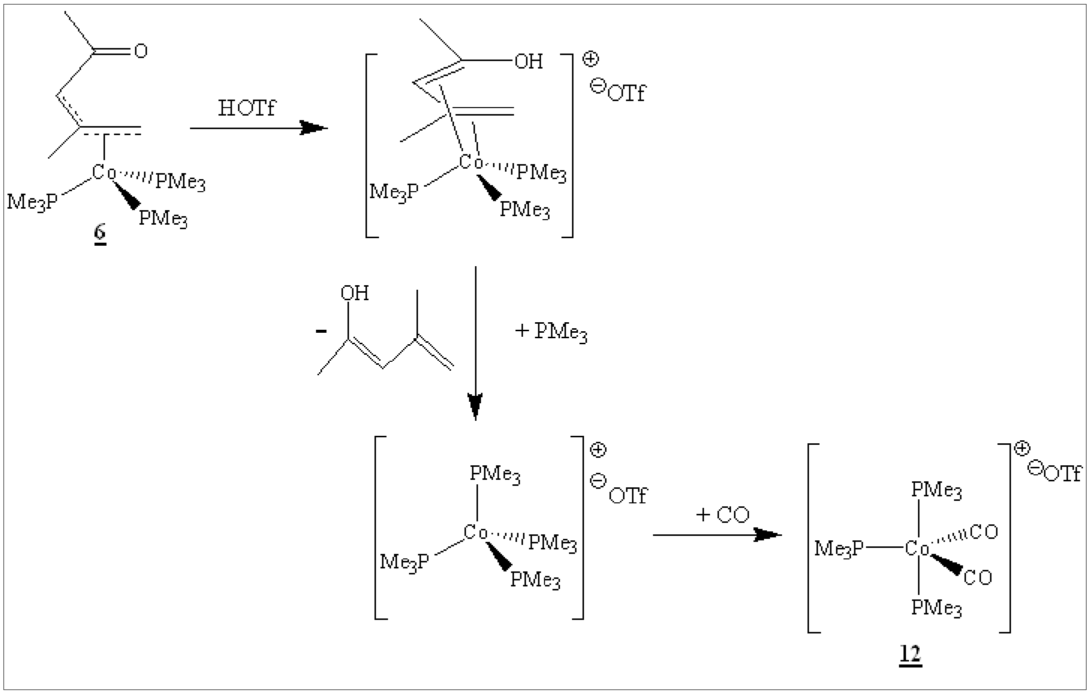
Figure 3.13. X-ray crystal structure of compound 12, using thermal ellipsoids at the 50% level. PMe_3 methyl H's are not shown.

Table 3.8. Select bond distances in compound 12.

Bond	Distance (Å)
Co1-P1	2.2489(3)
Co1-P2	2.1996(3)
Co1-P3	2.2029(3)
Co1-C1	1.7470(10)
Co1-C2	1.7519(9)

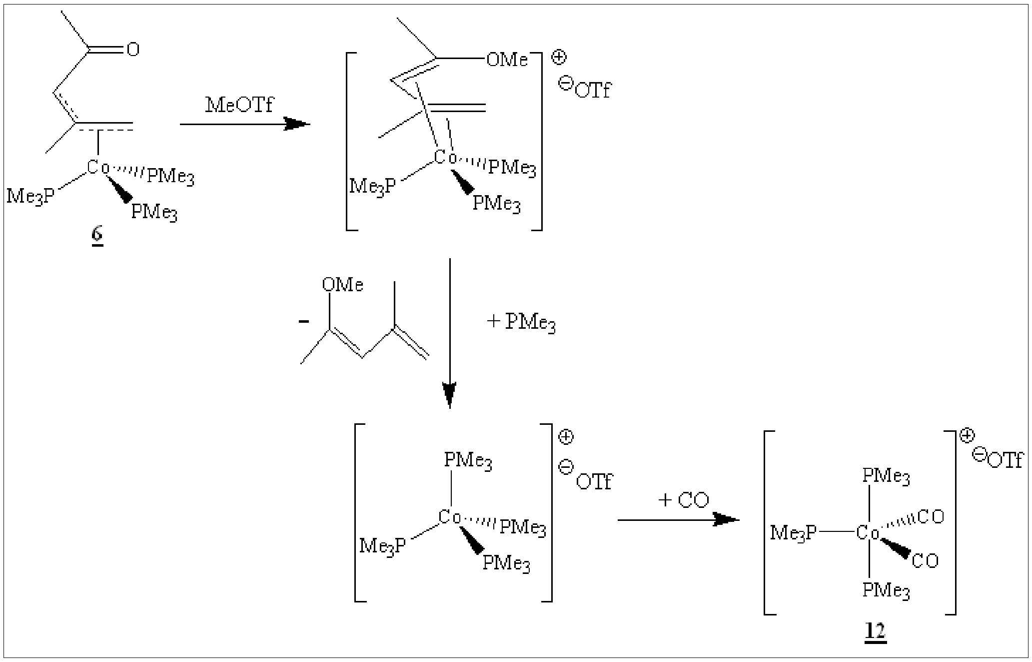
The proposed mechanism for the reaction of triflic acid with **6** is shown in Scheme 3.14. The formation of the green compound, $Co(PMe_3)_4{}^+O_3SCF_3{}^-$, likely occurs with initial protonation of the dimethyloxapentadienyl ligand at oxygen. Based on the features of the crystal structure of compound **6**, the $(\eta^4$-2,4-dimethyl-5-butadienol$)Co(PMe_3)_3{}^+O_3SCF_3{}^-$ complex would be quite unstable. As mentioned in Section 3.2.2, in compound **6**, the carbon atom C4 is displaced much further out of the allyl (C1-C2-C3) plane than the corresponding displacement in compound **5** (see Section 3.2.1). This displacement most likely results from unfavorable steric interactions involving the acetyl moiety in **6** (C6-C4-O1) and the phosphine ligands, and results in a very weak interaction between C4 and Co upon formation of the η^4-bonding mode. Ligand loss would lead to the formation of $Co(PMe_3)_3{}^+O_3SCF_3{}^-$ which would form $Co(PMe_3)_4{}^+O_3SCF_3{}^-$ after scavenging one equivalent of phosphine. Phosphine scavenging by Co(I) complexes was seen in Chapter 2 in the formation of dimeric and trimeric products **1** and **3**, and the synthesis of

$Co(PMe_3)_4^+BPh_4^-$ has been reported[31] from the reaction of $BrCo(PMe_3)_3$ with $Na^+BPh_4^-$ in the absence of added PMe_3.



Scheme 3.14. Proposed mechanism for the formation of compound 12 with HOTf.

When compound **6** is treated with methyl triflate, the dark green compound is again obtained. As shown in Scheme 3.15, the proposed mechanism parallels the mechanism predicted for the triflic acid reaction. Treatment of the green solution with carbon monoxide produces **12** in high yield.



Scheme 3.15. Proposed mechanism for the formation of compound 12 with MeOTf.

3.3 Conclusions

This chapter reported on the synthesis, structure, spectroscopy and reactivity of the first oxapentadienyl-cobalt complexes. When $ClCo(PMe_3)_3$ was treated with potassium oxapentadienide, (1,2,3-η-oxapentadienyl)$Co(PMe_3)_3$ was formed. The oxapentadienyl-cobalt-phosphine system showed a remarkable stability of the 1,2,3-η-5-oxapentadienyl bonding mode, losing a phosphine ligand to form (1,2,3-η-oxapentadienyl)$Co(PMe_3)_2(CO)$ upon exposure to carbon monoxide. The addition of methyl groups to the oxapentadienyl ligand resulted in no change to the initial reactivity.

Treatment of $ClCo(PMe_3)_3$ with potassium 2,4-dimethyl oxapentadienide again afforded the monomeric, η^3 product: (1,2,3-η-2,4-dimethyl oxapentadienyl)$Co(PMe_3)_3$. However, the additional steric bulk of the methyl groups, along with their electron donating properties affected the reaction of (1,2,3-η-2,4-dimethyl oxapentadienyl)$Co(PMe_3)_3$ with CO, leading to loss of two phosphine ligands to form (1,2,3-η-2,4-dimethyl oxapentadienyl)$Co(PMe_3)(CO)_2$.

The tris-phosphine complexes containing the unmethylated oxapentadienyl ligand were reactive toward small electrophiles, H^+ and Me^+, at the ligand oxygen, forming stable η^4-butadienol-cobalt or η^4-butadienyl methyl ether-cobalt complexes. Tris-phosphine complexes containing the 2,4-dimethyloxapentadienyl ligand were also reactive exclusively at the ligand oxygen; however, the initially formed products were not stable, forming $Co(PMe_3)_4^+O_3SCF_3^-$ *in situ* which was then converted to $Co(PMe_3)_3(CO)_2^+O_3SCF_3^-$ by exposure to CO.

3.4 Experimental

General Comments on Experimental Techniques.

All manipulations were carried out under a nitrogen atmosphere, using either glovebox or double-manifold Schlenk techniques. Solvents were stored under nitrogen after being distilled from the appropriate drying agents. Deuterated NMR solvents were obtained in sealed vials and used as received. $(Cl)Co(PMe_3)_3$ and $(Cl)Co(PMe_3)_2(CO)_2$ were prepared by the procedure of Klein and Karsch.

Potassium oxapentadienide and potassium 2,4-dimethyloxapentadienide were prepared by literature procedures. High purity carbon monoxide gas was obtained from Praxair and used as received. Triflic acid (trifluoromethanesulfonic acid) and methyl triflate (methyl trifluoromethanesulfonate) were obtained from Aldrich and used as received.

NMR experiments were performed on a Varian Unity Plus- 300 spectrometer (^1H, 300 MHz; ^{13}C, 75 MHz; ^{31}P, 121 MHz), a Varian Mercury-300 spectrometer (^1H, 300 MHz; ^{13}C, 75 MHz; ^{31}P, 121 MHz), a Varian Unity Plus-500 spectrometer (^1H, 500 MHz; ^{13}C, 125 MHz; ^{31}P, 202 MHz), or a Varian Unity-600 spectrometer (^1H, 600 MHz; ^{13}C, 150 MHz; ^{31}P, 242 MHz).

^1H and ^{13}C spectra were referenced to tetramethylsilane, while ^{31}P spectra were referenced to external H_3PO_4. HMQC (^1H-detected multiple quantum coherence), HMBC (heteronuclear multiple-bond correlation), and COSY (correlation spectroscopy) experiments aided in assigning some of the ^{1}H and ^{13}C peaks.

Note: Carbonyl Ligands always gave rise to very weak ^{13}C NMR signals and could not be reliably assigned.

Synthesis of (1,2,3-η-5-Oxapentadienyl)Co(PMe$_3$)$_3$ (5). Potassium oxapentadienide (0.65 g, 6.01 mmol) and ClCo(PMe$_3$)$_3$ (1.00 g, 3.10 mmol) were weighed into a 125 mL Erlemeyer flask, and 70 mL of tetrahydrofuran (THF) was added. The resulting solution was stirred at room temperature for 45 min. After removal of the solvent under vacuum, the product was extracted with 100 mL diethyl ether and filtered through Celite. The ether was then removed under vacuum. The resulting powder was dissolved in a minimal quantity of diethyl ether and cooled to -30 C, producing red-orange crystals of **5** overnight. Yield: 1.035 g (94%). Anal. Calcd for $C_{13}H_{32}CoOP_3$: C, 43.82; H, 9.07. Found: C, 44.09; H, 8.81.

^{1}H NMR (acetone-d$_6$, 22 C): δ6.53 (d, $J_{H\text{-}H}$ = 8.4 Hz, 1, H4), 4.54 (br s, 1, H2), 3.41 (br s, 1, H3), 1.28 (s, 27, Pme$_3$'s), 0.77 (br s, 1, H1), 0.12 (br s, 1, H1).

^{13}C{^{1}H} NMR (acetone-d$_6$, 22 C): δ170.2 (s, C4), 69.0 (d, $J_{C\text{-}P}$ = 12.8 Hz, C3), 67.0 (d, $J_{C\text{-}P}$ = 9.6 Hz, C2), ~30.0 (obscured by solvent, C1), 21.3 (complex m, PMe$_3$'s).

^{31}P{^{1}H} NMR (acetone-d$_6$, 22 C): δ2.8 (br s, PMe$_3$'s).

Note: Upon cooling to -70 C, the ^{31}P NMR signal broadened but did not split.

IR (Nujol mull): 1574.0 cm^{-1} (C=O).

Synthesis of (1,2,3-η-2,4-Dimethyl-5-oxapentadienyl)Co(PMe$_3$)$_3$ (6).

Potassium 2,4-dimethyloxapentadienide (0.40 g, 2.94 mmol) and ClCo(PMe$_3$)$_3$ (0.47 g, 1.47 mmol) were weighed into a 125 mL Erlenmeyer flask, and 70 mL of THF was added. The resulting solution was stirred at room temperature for 45 min. After removal of the solvent under vacuum, the product was extracted with 100 mL of diethyl ether and filtered through Celite. The ether was then removed under vacuum. The resulting powder was dissolved in a minimal quantity of diethyl ether and cooled to -30 C, producing dark red crystals of **6** overnight. Yield" 0.50 g (89%). Anal. Calcd for $C_{15}H_{36}CoOP_3$: C, 46.87; H, 9.46. Found: C, 46.38; H, 9.34.

^{1}H NMR (benzene-d$_6$, 22 C): δ2.93 (br s, 1, H1), 2.62 (br s, 1, H3), 2.13 (br s, 3, H5's), 1.98 (br s, 3, H6's), 1.48 (br s, 1, H1), 1.01 (br s, 27, PMe$_3$'s).

Note: Upon cooling to -70 C in toluene-d$_8$, the signal at δ1.01 split into the following three peaks: δ1.13 (br s, 9, PMe$_3$), 0.76 (br s, 9, PMe$_3$), 0.62 (br s, 9, PMe$_3$).

^{13}C{^{1}H} NMR (benzene-d$_6$, 22 C): δ204.0 (s, C4), 84.0 (s, C2), 56.7 (s, C3), 39.0 (s, C1), 32.9 (s, C6), 27.5 (s, C5), 22.4 (br s, PMe$_3$'s).

^{31}P{^{1}H} NMR (benzene-d$_6$, 22 C): δ0.5 (br s, PMe$_3$'s).

Note: Upon cooling to -70 C in toluene-d$_8$, the ^{31}P NMR signal split into the following three peaks: δ16.3 (br s, 1, PMe$_3$), 2.3 (br s, 1, PMe$_3$), -9.5 (br s, 1, PMe$_3$).

IR (Nujol mull): 1606.6 cm^{-1} (C=O).

Synthesis of (1,2,3-η-5-oxapentadienyl)Co(PMe_3)$_2$CO (7).

Compound **5** (0.39 g, 1.10 mmol) was dissolved in 30 mL of THF in a 50 mL Erlenmeyer flask and capped with a rubber septum. Carbon monoxide gas was then bubbled through the solution for one hour, using a needle that penetrated the septum. During this exposure, the color of the solution changed from red to red-orange. After filtration through Celite, the solvent was removed under vacuum. The resulting powder was dissolved in a minimal quantity of diethyl ether and cooled to -30 C, causing oranged crystals of **7** to form overnight. Yield: 0.24 g (71%). Anal. Calcd for $C_{11}H_{23}CoOP_2$: C, 42.86; H, 7.54. Found: C, 42.39; H, 7.49.

^{1}H NMR (acetone-d_6, 22 C): δ7.10 (d, $J_{H\text{-}H}$ = 8.4 Hz, 1, H4), 5.09 (m, 1, H2), 3.78 (m, 1, H3), 1.88 (m, 1, H1), 1.44-1.40 (m, 18, PMe_3's), 1.17 (dd, J = 16.2 Hz, 9.6 Hz, 1, H1).

^{13}C{^{1}H} NMR (acetone-d_6, 22 C): δ177.0 (s, C4), 74.2 (s, C2), 71.2 (s, C3), 36.2 (s, C1), 19.8 (dd, $J_{C\text{-}P}$ = 22.6 Hz, 2.4 Hz, PMe_3), -3.7 (s, 1, PMe_3).

IR (Nujol mull): 1935.0 cm^{-1} (C≡O), 1612.3 cm^{-1} (C=O).

Alternative Synthesis of (1,2,3-η-5-oxapentadienyl)Co(PMe_3)$_2$CO (7).

Potassium oxapentadienide (0.072 g, 0.67 mmol) and $ClCo(PMe_3)_2(CO)_2$ (0.16 g, 0.53 mmol) were weighed into a 50 mL Erlenmeyer flask, and 20 mL of THF was added. The resulting solution was stirred at room temperature for 45 min. After removal of the solvent under vacuum, the product was extracted with pentane and filtered through Celite. The pentane was then removed under vacuum. The resulting powder was dissolved in a minimal quantity of pentane and cooled to -30 C, producing orange crystals of **7** after several days. Yiled: 0.097 g (59%).

Synthesis of (1,2,3-η-2,4-dimethyl-5-oxapentadienyl)Co(PMe_3)$(CO)_2$ (8).

Compound **6** (0.54 g, 1.40 mmol) was dissolved in 30 mL of THF in a 50 mL Erlenmeyer flask and capped with a rubber septum. Carbon monoxide gas was then bubbled through the solution for one hour, using a needle that penetrated the septum. During this exposure, the color of the solution changed from dark red to red-orange. After filtration through Celite, the solvent was removed under vacuum. The resulting powder was dissolved in a minimal quantity of diethyl ether and cooled to -30 C, causing red-orange crystals of **8** to form overnight. Yield: 0.34 g (84%). Anal. Calcd for $C_{11}H_{18}CoO_3P$: C, 45.84; H, 6.31. Found: C, 45.81; H, 6.10.

^{1}H NMR (benzene-d_6, 25 C): δ3.77, 3.75 (overlapping s's, 2, H1 and H3), 2.71 (d, J = 7.5 Hz, 1, H1), 2.06 (s, 3, H6's), 1.70 (s, 3, H5's), 0.76 (d, J_{H-P} = 8.5 Hz, 9, PMe_3).

^{13}C{^{1}H} NMR (benzene-d_6, 25 C): δ200.5 (s, C4), 100.2 (s, C2), 63.1 (s, C3), 56.7 (s, C1), 29.5 (s, C5), 19.5 (d, J_{C-P} = 29.9 Hz, PMe_3).

^{31}P{^{1}H} NMR (benzene-d_6, 25 C): δ22.1 (s, PMe_3).

IR (Nujol mull): 1992.5 cm^{-1} (C≡O), 1939.3 cm^{-1} (C≡O), 1668.2 cm^{-1} (C=O).

Reaction of Potassium 2,4,-Dimethyloxapentadienide with $ClCo(PMe_3)_2(CO)_2$. Synthesis of $(CO)(PMe_3)_2Co(\mu_2\text{-}CO)_2Co(PMe_3)_2(CO)$ (9).

Potassium 2,4-dimethyloxapentadienide (0.75 g, 5.50 mmol) and $ClCo(PMe_3)_2(CO)_2$ (1.66 g, 5.48 mmol) were weighed into a 50 mL Erlenmeyer flask, and 25 mL of THF was added. The resulting solution was stirred at room temperature for 45 min. After removal of the solvent under vacuum, the product was extracted with pentane and filtered through Celite. The pentane was then removed under vacuum. The resulting powder was dissolved in a minimal quantity of pentane and cooled to -30 C, producing orange crystals of **9** overnight. Yield: 0.63 g, (43%). Anal. Calcd for $C_{16}H_{36}Co_2O_4P_4$: C, 35.97; H, 6.81. Found: C, 35.99; H, 6.46.

^1H NMR (acetone-d_6, 22 C): δ1.30 (virtual t, $J_{H\text{-}P}$ = 6.9 Hz, Pme_3's).

Note: At -70 C, the ^1H NMR signal split into the following two peaks: δ1.33 (br s, 9, PMe_3), 1.14 (br s, 9, Pme_3).

$^{13}C\{^1H\}$ NMR (acetone-d_6, 22 C): δ18.7 (virtual t, $J_{C\text{-}P}$ = 25.6 Hz, Pme_3's).

$^{31}P\{^1H\}$ NMR (acetone-d_6, 22 C): δ0.7 (br s, Pme_3's).

Note: At -70 C, the ^{31}P NMR signal split into the following two peaks: δ-2.6 (br s, 1, PMe_3), -3.5 (br s, 1, Pme_3).

IR (Nujol mull): 1918.1 cm^{-1} (C≡O), 1718.1 cm^{-1} (μ_2-CO).

Synthesis of $(\eta^4\text{-butadienol})Co(PMe_3)_3^+\ O_3SCF_3^-$ (10).

Compound **5** (0.12 g, 0.35 mmol) was dissolved in 8 mL of diethyl ether and cooled to

-30 C. The resulting red solution was treated with a 1.66 M solution of triflic acid in diethyl ether (0.18 mL, 0.30 mmol), causing a yellow-orange precipitate to form immediately. The precipitate was allowed to settle, and the supernatant was decanted. The remaining solid was washed twice with diethyl ether and twice with pentane. It was then dissolved in a minimal quantity of acetone and cooled to -30 C, causing yellow crystals of **10** to form overnight. Yield: 0.098 g (65%). Anal. Calcd for $C_{14}H_{33}CoF_3O_4P_3S$: C, 33.20; H, 6.58. Found: C, 33.34; H, 6.46.

^{1}H NMR (acetone-d_6, 25 C): δ7.18 (s, 1, OH), 5.21 (s, 1, H2), 5.05 (br s, 1, H3), 3.59 (s, 1, H4), 1.52 (br s, 27, PMe_3's), 1.29 (s, 1, H1), -0.70 (s, 1, H1).

Note: At -70 C, the PMe_3 signal split into the following two peaks: δ1.60 (br s, 9, PMe_3), 1.40 (br s, 18, PMe_3's).

$^{13}C\{^1H\}$ NMR (acetone-d_6, 25 C): δ96.9 (d, C4), 80.4 (d, J_{C-P} = 26.6 Hz, C2), 79.3 (d, J_{C-P} = 28.9 Hz, C3), 35.7 (s, C1), 19.9 (br s, Pme_3's).

$^{31}P\{^1H\}$ NMR (acetone-d_6, 25 C): δ4.7 (br s, PMe_3's).

Note: At -70 C, the 31P NMR signal split into the following two peaks: δ7.2 (br s, 2, PMe_3's), 6.2 (s, 1, Pme_3).

IR (Nujol mull): 3306.9 cm^{-1} (O-H). There were no significant peaks in the carbonyl region (1500-2000 cm^{-1}).

Synthesis of (η^4-butadienyl methyl ether)Co(PMe_3)$_3$$^+$ $O_3SCF_3^-$ (11).

Compound **5** (0.46 g, 1.29 mmol) was dissolved in 15 mL of diethyl ether and cooled to

-30 C. The resulting red solution was treated with a 1.45 M solution of methyl triflate in diethyl ether (0.89 mL, 1.29 mmol), causing a yellow-orange precipitate to form immediately. The reaction mixture was stirred at room temperature for 5 min and then cooled to -30 C for 10 min before collecting the precipitate by filtration. After washing with pentane, the precipitate was dissolved in acetone and filtered. The acetone was removed under vacuum, and the resulting powder was dissolved in a minimal quantity of acetone. Addition of a small quantity of pentane, followed by cooling to -30 C, caused orange crystals of **11** to form overnight. Yield: 0.56 g (83%). Anal. Calcd for $C_{15}H_{35}CoF_3O_4P_3S$: C, 34.62; H, 6.79. Found: C, 34.70; H, 6.56.

^{1}H NMR (acetone-d_6, 22 C): δ5.20 (s, 1, H3 or H2), 5.10 (s, 1, H2 or H3), 3.55 (s, 3, Me), 2.90 (s, 1, H4), 1.79 (br s, 9, PMe_3), 1.44 (br s, 18, PMe_3's), 1.32 (s, 1, H1), -0.56 (s, 1, H1).

$^{13}C\{^1H\}$ NMR (acetone-d_6, 22 C): δ101.0 (s, C4), 81.2 (d, J_{C-P} = 30.2 Hz, C2 or C3), 79.6 (d, J_{C-P} = 25.2 Hz, C3 or C2), 60.6 (d, J_{C-P} = 18.3 Hz, Me), 36.5 (s, C1), 21.7 (br s, PMe_3), 20.0 (br s, PMe_3), 19.1 (br s, PMe_3).

$^{31}P\{^1H\}$ NMR (acetone-d_6, 22 C): δ4.4 (br s, PMe_3's).

Note: At -70 C, the ^{31}P NMR signal split into the following two peaks: δ7.1 (br s, 1, PMe_3), 6.4 (br s, 2, PMe_3's).

IR (Nujol mull): There were no significant peaks in the carbonyl region (1500-2000 cm^{-1}).

Reaction of Compound 6 with Triflic Acid.

Synthesis of $Co(PMe_3)_3(CO)_2^+ O_3SCF_3^-$ (12).

Compound **6** (0.54 g, 1.40 mmol) was dissolved in 70 mL of THF and cooled to -30 C. Upon addition of a 1.66 M solution of triflic acid in diethyl ether (0.84 mL, 1.40 mmol), the color of the solution changed immediately from re-orange to dark green. Carbon monoxide was then bubbled through the solution for one hour, causing the color to change from green to orange. After filtration through Celite, the solvent was removed under vacuum. The resulting powder was dissolved in a minimal quantity of THF/ether and cooled to -30 C, causing yellow crystals of **12** to form overnight. Yield: 0.56 g (81%). Anal. Calcd for $C_{12}H_{27}CoF_3O_5P_3S$: C, 29.28; H, 5.54. Found: C, 29.01; H, 5.32.

^1H NMR (acetone-d_6, 22 C): δ1.77 (d, $J_{H\text{-}P}$ = 8.7 Hz, PMe_3's).

$^{13}C\{^1H\}$ NMR (acetone-d_6, 22 C): δ19.9-20.6 (complex m, PMe_3's).

$^{31}P\{^1H\}$ NMR (acetone-d_6, 22 C): δ8.7 (s, PMe_3's).

IR (Nujol mull): 1988.5 cm^{-1} (C≡O), 1929.1 cm^{-1} (C≡O).

Notes: 1) Upon cooling to -70 C, the ^1H and ^{31}P NMR signals did not split. 2) Reaction of **6** with methyl triflate, followed by treatment with CO, also produced **12** in quantitative yield.

X-ray Diffraction Studies. Crystals of X-ray diffraction quality were obtained for compounds **5-12**. In all cases crystals of appropriate dimensions were mounted on MiTeGen loops in random orientations. Preliminary examination and data collection were performed using a Bruker Kappa Apex II charge-coupled device (CCD) detector system single-crystal X-ray diffractometer equipped with an Oxford Cryostream LT device. All data were collected using graphite-monochromated Mo K radiation (= 0.71013 Å) from a fine-focus sealed tube X-ray source. Preliminary unit cell constants were determined with a set of 36 narrow frame scans. Typical data sets consisted of combinations of w and f scan frames with typical scan width of 0.5 and counting time of 15-30 s/frame at a crystal to detector distance of 4.0 cm. The collected frames were integrated using an orientation matrix determined from the narrow frame scans. Apex II and SAINT software packages[32] were used for data collection and data integration. Analysis of the integrated data did not show any decay. Final cell constants were determined by global refinement of reflections from the complete data set. Collected data were corrected for systematic errors using SADABS or TWINABS[32].

All crystal data for this chapter may be found in Appendix B.

Structure solution and refinement were carried out using the SHELXTL-PLUS software package[33]. The structures were solved by direct methods and refined with full matrix least-squares refinement by minimizing $\Sigma w(F^2_o - F^2_c)^2$. All non-hydrogen atoms were refined anisotropically to convergence. Specific experimental details for individual structures are given below.

For compounds **5**, **8**, **9**, **11** and **12**, all H atoms were added in the calculated positions and were refined using appropriate riding models (AFIX m3). For **6**, the H atoms on C1 (H1A, H1B) and C3 (H3) were located and refined using geometric constraints (SADI). All other H atoms were added in the calculated positions and were refined using appropriate riding modes. For **7**, the H's on the oxapentadienyl ligand (H1A, H1B, H2, H3, and H4) were located and refined freely. All other H atoms were added in the calculated positions using appropriate riding models. For **10**, the H atoms of the dienol ligand (H1, H1A, H1B, H2, H3, and H4) were located and their positions were refined with thermal parameters riding on the parent non-H atoms. All other H's were added in the calculated positions and were refined using appropriate riding models. Compound **10** was a twinned crystal and data reduction was carried out using two domains. Refinements were performed using merged HKLF 5 data. Twin refinement resulted in a ratio of 53:47% for the two domains (BASF/HKLF 5 refinement in SHELXTL). Significant improvement in structure quality (R_1, wR_2, goodness of fit, and residual densities) was observed when using merged HKLF 5 data, as compared to HKLF 4 or unresolved (non-twin) data.

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CHAPTER FOUR

CONCLUSIONS

Conclusions

Research exploring heteropentadienyl-transition metal chemistry has been an active area in the last decade. In the Bleeke group alone, oxa-, phospha-, aza-, thia- and silapentadienyl complexes of a variety of transition metals have been synthesized and their reactivity studied. The work reported in this dissertation focused on both the synthesis and reactivity of thiapentadienyl-cobalt and oxapentadienyl-cobalt complexes as a continuation of the work conducted on thiapentadienyl-rhodium and -iridium, and oxapentadienyl-rhodium and -iridium complexes.

4.1. Summary of Research

Chapter 2 reported the work on thiapentadienyl-cobalt complexes. The thiapentadienyl system showed distinctive dimeric and trimeric ground state bonding modes as a result of the small size of the cobalt metal center relative to other metals in the same group. The reaction of $ClCo(PMe_3)_3$ with potassium thiapentadienide produced the dimer $[Co(PMe_3)_2(\text{thiapentadienyl})]_2$. This dimer, which contained one thiapentadienyl ligand with a *cis* internal double bond and one thiapentadienyl ligand with a *trans* internal double bond, was reactive toward the small two-electron donor ligand, CO, forming the products (5-η^1-*cis*-5-thiapentadienyl)$Co(PMe_3)_2(CO)_2$ and (5-η^1-*trans*-5-thiapentadienyl)$Co(PMe_3)_2(CO)_2$. The reaction of $ClCo(PMe_3)_3$ with lithium 2,3-dimethyl-5-thiapentadienide yielded the trimer $[Co(PMe_3)_2(\eta^4\text{-2,3-dimethylthiapentadienyl})]_2[\mu\text{-Co(2,3-dimethylthiapentadienyl)}_2]$. This trimer, which contained dimethylthiapentadienyl ligands exhibiting only *trans* double bonds, was also reactive toward the two-electron donor, CO, forming (5-η^1-*trans*-2,3-dimethyl-5-thiapentadienyl)$Co(PMe_3)_2(CO)_2$. Some similarities to previously reported systems were seen in the initial bonding modes, though one new bonding mode was seen: the μ_2-η^4,η^1-bonding mode where one cobalt center bonded to the butadiene moiety in an η^4-fashion while a second cobalt coordinated the anionic sulfur atom.

Chapter 3 reported the work on oxapentadienyl-cobalt complexes. Treatment of $ClCo(PMe_3)_3$ with potassium oxapentadienide gave the monomeric product, (1,2,3-η-oxapentadienyl)$Co(PMe_3)_3$. Treatment of this compound with CO resulted in loss of a phosphine ligand and formation of (1,2,3-η-oxapentadienyl)$Co(PMe_3)_2CO$, illustrating the remarkable stability of the carbon-based η^3 bonding mode. The addition of methyl groups to the oxapentadienyl ligand resulted in no change to the initial reactivity. Hence, the reaction of $ClCo(PMe_3)_3$ with potassium 2,4-dimethyl oxapentadienide afforded the η^3 product: (1,2,3-η-2,4-dimethyl oxapentadienyl)$Co(PMe_3)_3$. However, the additional steric bulk of the methyl groups, along with their electron donating properties affected the reaction of (1,2,3-η-2,4-dimethyl oxapentadienyl)$Co(PMe_3)_3$ with CO, resulting in the loss of two phosphine ligands to form (1,2,3-η-2,4-dimethyl oxapentadienyl)$Co(PMe_3)(CO)_2$. The compound, (1,2,3-η-oxapentadienyl)$Co(PMe_3)_3$, was reactive toward small electrophiles, H^+ and Me^+, at the ligand oxygen forming stable η^4-butadienol-cobalt or η^4-

butadienyl methyl ether-cobalt complexes. The compound, (1,2,3-η-2,4-dimethyl oxapentadienyl)Co(PMe_3)$_3$ was also reactive exclusively at the ligand oxygen, but immediately lost the protonated or methylated ligand to form $Co(PMe_3)_4{}^+O_3SCF_3{}^-$ which was converted to $Co(PMe_3)_3(CO)_2{}^+O_3SCF_3{}^-$ by exposure to CO.

4.2. Comparisons to Related Compounds

Overall, the reactions of oxa- and thiapentadienyl ligand reagents with cobalt-phosphine starting materials produced heteropentadienyl-cobalt-phosphine complexes that presented bonding modes similar to those seen in the related rhodium and iridium systems. However, the small size of the cobalt metal center led to the formation of a new μ_2-η^4,η^1-bonding mode in the thiapentadienyl system. The size of cobalt was also an influence on the reactivity of the oxapentadienyl complexes with electrophiles, directing all electrophiles to react with the ligand oxygen regardless of the electron density pushed on to cobalt by the ancillary ligands.

The oxapentadienyl-cobalt system showed strong similarities to the initial bonding modes seen in the oxapentadienyl-rhodium and -iridium-trimethylphosphine systems and the dimethylpentadienyl-cobalt-trimethylphosphine system discussed in Chapter 1. All systems presented an initial all-carbon η^3 bonding mode of the ligand, and the oxapentadienyl-rhodium-tris(trimethylphosphine) complex existed as only the anti isomer. Beyond this point, differences were observed: oxapentadienyl—iridium-tris(trimethylphosphine) underwent C-H bond activation, dimethyloxapentadienyl-rhodium-tris(trimethylphosphine) existed as an equilibrium mixture of anti and syn isomers, and the anti isomer of dimethylpentadienyl-cobalt-tris(trimethylphosphine) converted to syn (70:30 anti:syn) in solution.

Similarities between the thiapentadienyl-cobalt, -rhodium, and -iridium systems are only seen in the overwhelming preference for sulfur to be bound to the metal center. Thiapentadienyl-iridium complexes underwent C-H bond activation, and thiapentadienyl-rhodium complexes completed the need for 18 e^- stability by coordinating the available ligand double bond or dimerizing after ligand isomerization. However, for the rhodium dimer, each rhodium center was still able to accommodate η^1,η^2 coordination of one ligand. The small size of the cobalt center led to the formation of dimeric and trimeric products where the cobalt center achieved an 18 e^- configuration by bonding to two different thiapentadienyl ligands.

4.3. Future direction

The next step in the study of oxapentadienyl-cobalt-phosphine complexes involves using larger phosphine ligands to push the system toward an η^5 ligand bonding mode. Work in the Bleeke group on the related pentadienyl-cobalt system has already shown that an η^5 bonding mode can be achieved through the use of PEt_3 in a one-pot preparation or with the chelating phosphine, pinacop. If an η^5 oxapentadienyl-cobalt complex can be synthesized, the weak interaction between the metal center and the carbonyl group should make the highly reactive 16 e^- η^3-oxapentadienyl-cobalt complex easily accessible, further demonstrating the potential for catalytic activity.

APPENDIX A:

THIAPENTADIENYL-COBALT CHEMISTRY

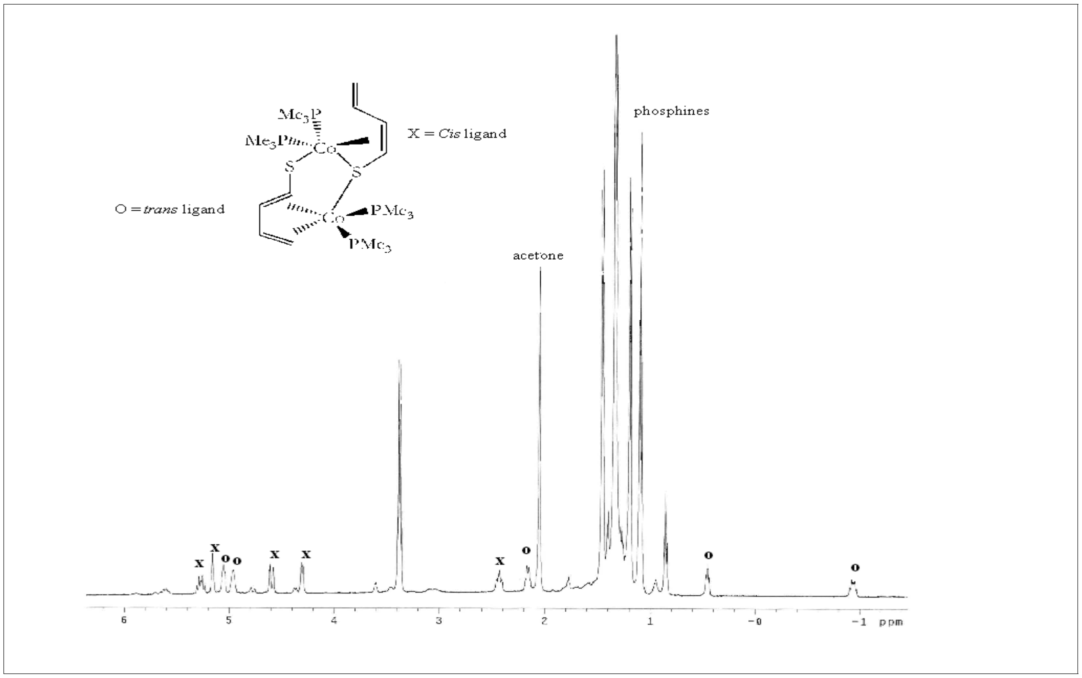

Figure A-1. ^{1}H NMR Spectrum of 1

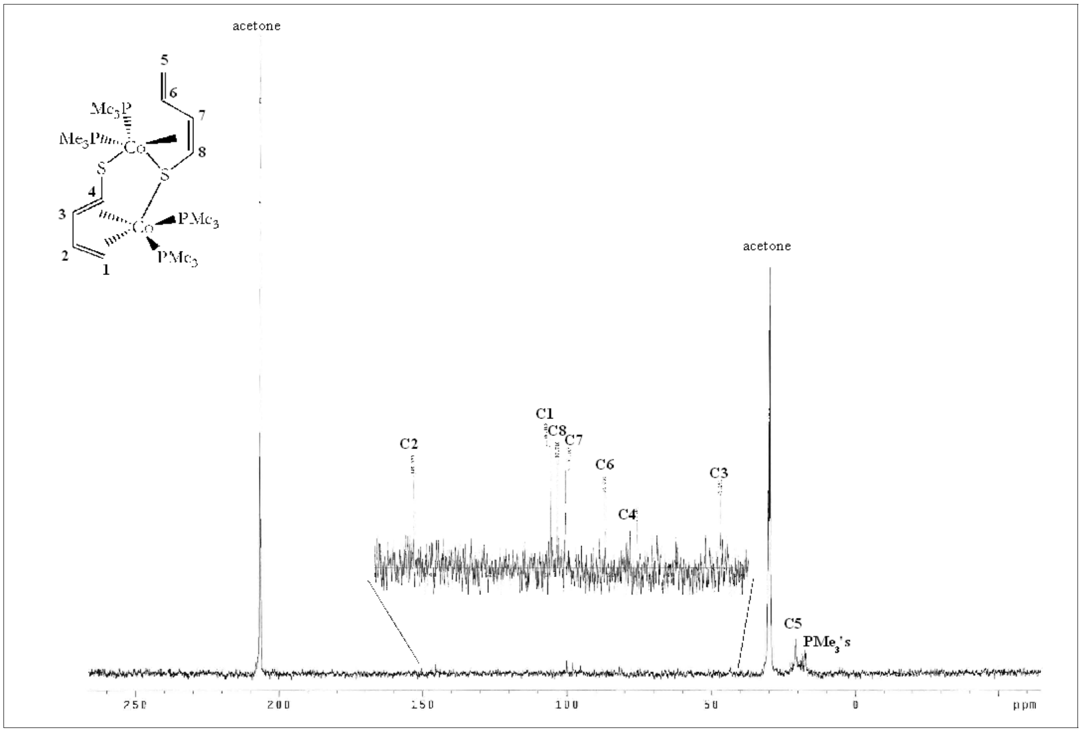

Figure A-2. ^{13}C NMR Spectrum of 1 at -20 C

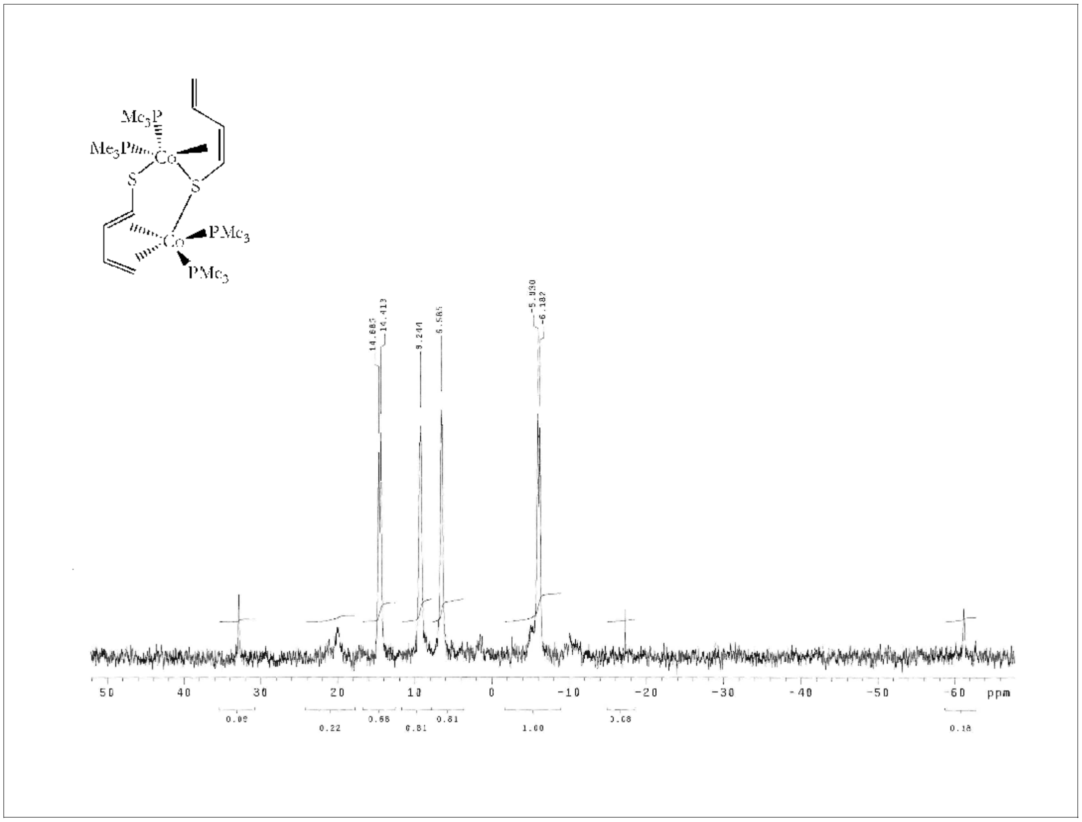

Figure A-3. ^{31}P NMR Spectrum of 1 at -70 C

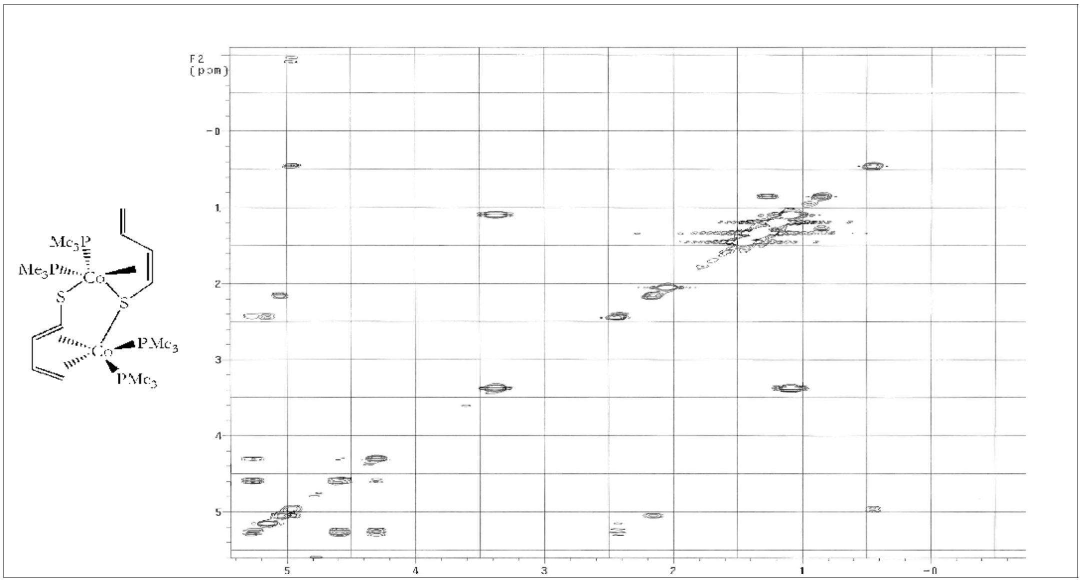

Figure A-4. COSY Spectrum of 1

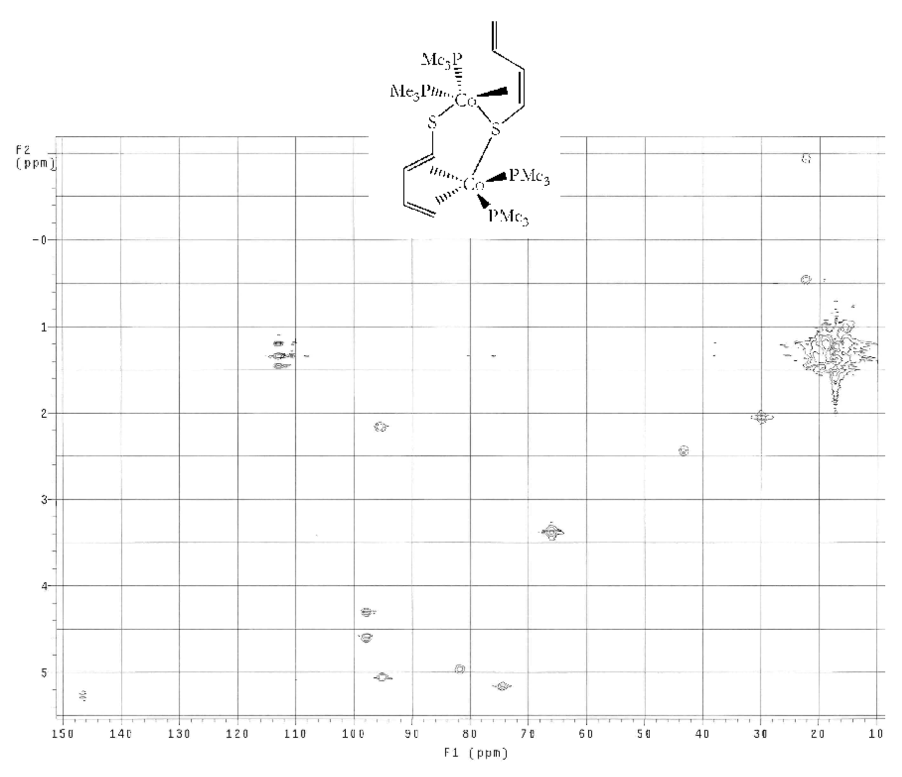

Figure A-5. HMQC Spectrum of 1

Table A-1.1. Crystal Data and Structure Refinement for Compound 1

Empirical formula	$C_{20} H_{46} Co_2 P_4 S_2$	
Formula weight	592.43	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 17.2050(19) Å	α= 90°.
	b = 14.5502(16) Å	β= 105.104(4)°.
	c = 11.8771(11) Å	γ = 90°.
Volume	2870.6(5) $Å^3$	
Z	4	
Density (calculated)	1.371 Mg/m^3	
Absorption coefficient	1.530 mm^{-1}	
F(000)	1248	
Crystal size	0.27 x 0.21 x 0.10 mm^3	
Theta range for data collection	2.80 to 27.67°.	
Index ranges	$-22 \le h \le 21$, $0 \le k \le 18$, $0 \le l \le 15$	
Reflections collected	6679	
Independent reflections	6692 [R(int) = 0.0]	
Completeness to theta = 27.67°	98.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8583 and 0.6836	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6692 / 1 / 260	
Goodness-of-fit on F^2	1.030	
Final R indices [I>2sigma(I)]	R1 = 0.0410, wR2 = 0.0699	
R indices (all data)	R1 = 0.0564, wR2 = 0.0748	
Largest diff. peak and hole	0.453 and -0.481 e.$Å^{-3}$	

Table A-1.2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for Compound 1. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Co(1)	12897(1)	4756(1)	-3498(1)	13(1)
Co(2)	11278(1)	5316(1)	-1941(1)	13(1)
S(1)	12278(1)	5866(1)	-2673(1)	15(1)
S(2)	12499(1)	3618(1)	-2431(1)	17(1)
P(1)	12876(1)	3746(1)	-4826(1)	16(1)
P(2)	14193(1)	4762(1)	-2582(1)	18(1)
P(3)	11990(1)	5243(1)	-132(1)	17(1)
P(4)	10760(1)	6710(1)	-2184(1)	14(1)
C(1)	13755(2)	6915(3)	-4986(4)	38(1)
C(2)	13285(2)	6591(3)	-4340(3)	27(1)
C(3)	12723(2)	5843(2)	-4673(3)	21(1)
C(4)	12070(2)	5637(2)	-4169(3)	17(1)
C(5)	10274(2)	4713(3)	-1642(4)	24(1)
C(6)	10259(2)	4706(2)	-2848(3)	21(1)
C(7)	10930(2)	4319(2)	-3150(3)	18(1)
C(8)	11559(2)	3942(2)	-2252(3)	17(1)
C(11)	13283(2)	4015(3)	-6067(3)	29(1)
C(12)	13391(2)	2666(2)	-4382(3)	22(1)
C(13)	11867(2)	3371(2)	-5594(3)	27(1)
C(21)	14581(2)	5769(3)	-1695(3)	31(1)
C(22)	14914(2)	4727(3)	-3466(3)	29(1)
C(23)	14585(2)	3832(3)	-1554(3)	29(1)
C(31)	11888(2)	4188(3)	650(3)	32(1)
C(32)	11831(2)	6080(3)	925(3)	32(1)
C(33)	13076(2)	5308(3)	112(3)	35(1)
C(41)	11386(2)	7688(2)	-1594(3)	22(1)
C(42)	10400(2)	7044(2)	-3711(3)	19(1)
C(43)	9873(2)	6932(2)	-1655(3)	20(1)

Table A-1.3. Bond lengths [Å] for Compound 1

Co(1)-C(4)	1.927(3)
Co(1)-C(3)	2.079(3)
Co(1)-P(1)	2.1486(10)
Co(1)-P(2)	2.2117(9)
Co(1)-S(1)	2.2906(9)
Co(1)-S(2)	2.2947(9)
Co(2)-C(6)	2.010(3)
Co(2)-C(7)	2.020(3)
Co(2)-C(5)	2.049(3)
Co(2)-C(8)	2.112(3)
Co(2)-P(3)	2.1803(10)
Co(2)-P(4)	2.2029(9)
Co(2)-S(1)	2.2665(9)
S(1)-C(4)	1.750(3)
S(2)-C(8)	1.749(3)
P(1)-C(12)	1.815(4)
P(1)-C(13)	1.821(3)
P(1)-C(11)	1.832(4)
P(2)-C(22)	1.823(3)
P(2)-C(21)	1.827(4)
P(2)-C(23)	1.830(4)
P(3)-C(33)	1.817(3)
P(3)-C(32)	1.822(4)
P(3)-C(31)	1.826(4)
P(4)-C(41)	1.812(3)
P(4)-C(42)	1.824(3)
P(4)-C(43)	1.825(3)
C(1)-C(2)	1.337(5)
C(1)-H(1A)	0.9500
C(1)-H(1B)	0.9500
C(2)-C(3)	1.441(5)
C(2)-H(2)	0.9500
C(3)-C(4)	1.437(4)
C(3)-H(3)	0.9500
C(4)-H(4)	1.0000
C(5)-C(6)	1.426(5)
C(5)-H(5A)	0.95(3)
C(5)-H(5B)	0.94(3)
C(6)-C(7)	1.413(5)
C(6)-H(6A)	1.0000
C(7)-C(8)	1.417(5)
C(7)-H(7)	0.9500
C(8)-H(8)	1.0000
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800
C(31)-H(31A)	0.9800
C(31)-H(31B)	0.9800
C(31)-H(31C)	0.9800
C(32)-H(32A)	0.9800
C(32)-H(32B)	0.9800
C(32)-H(32C)	0.9800
C(33)-H(33A)	0.9800
C(33)-H(33B)	0.9800
C(33)-H(33C)	0.9800
C(41)-H(41A)	0.9800
C(41)-H(41B)	0.9800
C(41)-H(41C)	0.9800
C(42)-H(42A)	0.9800
C(42)-H(42B)	0.9800
C(42)-H(42C)	0.9800
C(43)-H(43A)	0.9800
C(43)-H(43B)	0.9800

C(43)-H(43C)	0.9800

Table A-1.4. Bond angles [°] for Compound 1

C(4)-Co(1)-C(3)	41.81(13)
C(4)-Co(1)-P(1)	106.39(10)
C(3)-Co(1)-P(1)	93.19(10)
C(4)-Co(1)-P(2)	137.88(11)
C(3)-Co(1)-P(2)	106.09(10)
P(1)-Co(1)-P(2)	100.74(4)
C(4)-Co(1)-S(1)	48.09(10)
C(3)-Co(1)-S(1)	75.47(10)
P(1)-Co(1)-S(1)	151.07(4)
P(2)-Co(1)-S(1)	107.93(4)
C(4)-Co(1)-S(2)	114.45(10)
C(3)-Co(1)-S(2)	155.25(10)
P(1)-Co(1)-S(2)	87.80(4)
P(2)-Co(1)-S(2)	97.99(4)
S(1)-Co(1)-S(2)	91.92(3)
C(6)-Co(2)-C(7)	41.04(13)
C(6)-Co(2)-C(5)	41.10(15)
C(7)-Co(2)-C(5)	73.06(15)
C(6)-Co(2)-C(8)	72.29(13)
C(7)-Co(2)-C(8)	40.04(13)
C(5)-Co(2)-C(8)	82.38(14)
C(6)-Co(2)-P(3)	133.95(11)
C(7)-Co(2)-P(3)	130.66(10)
C(5)-Co(2)-P(3)	95.23(12)
C(8)-Co(2)-P(3)	91.74(10)
C(6)-Co(2)-P(4)	94.02(10)
C(7)-Co(2)-P(4)	122.22(10)
C(5)-Co(2)-P(4)	94.96(11)
C(8)-Co(2)-P(4)	162.07(10)
P(3)-Co(2)-P(4)	106.18(4)
C(6)-Co(2)-S(1)	126.43(11)
C(7)-Co(2)-S(1)	95.42(10)
C(5)-Co(2)-S(1)	167.44(12)
C(8)-Co(2)-S(1)	92.00(9)
P(3)-Co(2)-S(1)	96.16(4)
P(4)-Co(2)-S(1)	86.93(3)
C(4)-S(1)-Co(2)	110.31(12)
C(4)-S(1)-Co(1)	55.03(11)
Co(2)-S(1)-Co(1)	113.54(4)
C(8)-S(2)-Co(1)	106.89(11)
C(12)-P(1)-C(13)	102.47(16)
C(12)-P(1)-C(11)	99.12(17)
C(13)-P(1)-C(11)	100.08(18)
C(12)-P(1)-Co(1)	117.73(12)
C(13)-P(1)-Co(1)	113.89(13)
C(11)-P(1)-Co(1)	120.49(13)
C(22)-P(2)-C(21)	98.78(18)
C(22)-P(2)-C(23)	100.15(18)
C(21)-P(2)-C(23)	101.09(19)
C(22)-P(2)-Co(1)	117.83(12)
C(21)-P(2)-Co(1)	117.23(13)
C(23)-P(2)-Co(1)	118.30(12)
C(33)-P(3)-C(32)	100.86(19)
C(33)-P(3)-C(31)	101.17(19)
C(32)-P(3)-C(31)	99.18(19)
C(33)-P(3)-Co(2)	116.44(13)
C(32)-P(3)-Co(2)	119.96(13)
C(31)-P(3)-Co(2)	116.03(14)
C(41)-P(4)-C(42)	100.88(16)
C(41)-P(4)-C(43)	101.18(16)
C(42)-P(4)-C(43)	101.36(16)
C(41)-P(4)-Co(2)	119.54(11)
C(42)-P(4)-Co(2)	113.39(11)
C(43)-P(4)-Co(2)	117.64(12)
C(2)-C(1)-H(1A)	120.0
C(2)-C(1)-H(1B)	120.0
H(1A)-C(1)-H(1B)	120.0
C(1)-C(2)-C(3)	124.8(4)
C(1)-C(2)-H(2)	117.6
C(3)-C(2)-H(2)	117.6
C(4)-C(3)-C(2)	125.8(3)
C(4)-C(3)-Co(1)	63.43(18)

C(2)-C(3)-Co(1)	114.9(2)
C(4)-C(3)-H(3)	117.1
C(2)-C(3)-H(3)	117.1
Co(1)-C(3)-H(3)	91.6
C(3)-C(4)-S(1)	114.1(2)
C(3)-C(4)-Co(1)	74.75(19)
S(1)-C(4)-Co(1)	76.88(13)
C(3)-C(4)-H(4)	122.8
S(1)-C(4)-H(4)	122.8
Co(1)-C(4)-H(4)	122.8
C(6)-C(5)-Co(2)	68.0(2)
C(6)-C(5)-H(5A)	116(2)
Co(2)-C(5)-H(5A)	124(2)
C(6)-C(5)-H(5B)	119(2)
Co(2)-C(5)-H(5B)	104(2)
H(5A)-C(5)-H(5B)	116(3)
C(7)-C(6)-C(5)	117.2(3)
C(7)-C(6)-Co(2)	69.85(18)
C(5)-C(6)-Co(2)	70.9(2)
C(7)-C(6)-H(6A)	121.0
C(5)-C(6)-H(6A)	121.0
Co(2)-C(6)-H(6A)	121.0
C(6)-C(7)-C(8)	118.5(3)
C(6)-C(7)-Co(2)	69.10(19)
C(8)-C(7)-Co(2)	73.5(2)
C(6)-C(7)-H(7)	120.7
C(8)-C(7)-H(7)	120.7
Co(2)-C(7)-H(7)	128.8
C(7)-C(8)-S(2)	124.2(3)
C(7)-C(8)-Co(2)	66.48(18)
S(2)-C(8)-Co(2)	122.54(17)
C(7)-C(8)-H(8)	112.1
S(2)-C(8)-H(8)	112.1
Co(2)-C(8)-H(8)	112.1
P(1)-C(11)-H(11A)	109.5
P(1)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
P(1)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
P(1)-C(12)-H(12A)	109.5
P(1)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
P(1)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
P(1)-C(13)-H(13A)	109.5
P(1)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
P(1)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
P(2)-C(21)-H(21A)	109.5
P(2)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
P(2)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
P(2)-C(22)-H(22A)	109.5
P(2)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
P(2)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
P(2)-C(23)-H(23A)	109.5
P(2)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
P(2)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
P(3)-C(31)-H(31A)	109.5
P(3)-C(31)-H(31B)	109.5
H(31A)-C(31)-H(31B)	109.5
P(3)-C(31)-H(31C)	109.5
H(31A)-C(31)-H(31C)	109.5
H(31B)-C(31)-H(31C)	109.5
P(3)-C(32)-H(32A)	109.5
P(3)-C(32)-H(32B)	109.5
H(32A)-C(32)-H(32B)	109.5
P(3)-C(32)-H(32C)	109.5
H(32A)-C(32)-H(32C)	109.5
H(32B)-C(32)-H(32C)	109.5
P(3)-C(33)-H(33A)	109.5
P(3)-C(33)-H(33B)	109.5
H(33A)-C(33)-H(33B)	109.5
P(3)-C(33)-H(33C)	109.5

H(33A)-C(33)-H(33C)	109.5
H(33B)-C(33)-H(33C)	109.5
P(4)-C(41)-H(41A)	109.5
P(4)-C(41)-H(41B)	109.5
H(41A)-C(41)-H(41B)	109.5
P(4)-C(41)-H(41C)	109.5
H(41A)-C(41)-H(41C)	109.5
H(41B)-C(41)-H(41C)	109.5
P(4)-C(42)-H(42A)	109.5
P(4)-C(42)-H(42B)	109.5
H(42A)-C(42)-H(42B)	109.5
P(4)-C(42)-H(42C)	109.5
H(42A)-C(42)-H(42C)	109.5
H(42B)-C(42)-H(42C)	109.5
P(4)-C(43)-H(43A)	109.5
P(4)-C(43)-H(43B)	109.5
H(43A)-C(43)-H(43B)	109.5
P(4)-C(43)-H(43C)	109.5
H(43A)-C(43)-H(43C)	109.5
H(43B)-C(43)-H(43C)	109.5

Table A-1.5. Anisotropic displacement parameters (Å^{2}x 10^3) for Compound 1. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\, h^2\, a^{*2}U^{11} + \ldots + 2\, h\, k\, a^*\, b^*\, U^{12}\,]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Co(1)	13(1)	13(1)	12(1)	-1(1)	2(1)	-1(1)
Co(2)	12(1)	11(1)	17(1)	0(1)	4(1)	-1(1)
S(1)	16(1)	12(1)	18(1)	-1(1)	5(1)	-2(1)
S(2)	18(1)	14(1)	20(1)	4(1)	7(1)	4(1)
P(1)	17(1)	16(1)	14(1)	-2(1)	2(1)	0(1)
P(2)	14(1)	26(1)	14(1)	-2(1)	3(1)	-2(1)
P(3)	17(1)	19(1)	16(1)	2(1)	6(1)	4(1)
P(4)	16(1)	12(1)	15(1)	0(1)	2(1)	1(1)
C(1)	38(2)	28(2)	53(3)	8(2)	22(2)	-4(2)
C(2)	29(2)	24(2)	29(2)	3(2)	9(2)	2(2)
C(3)	28(2)	17(2)	20(2)	5(2)	12(2)	6(2)
C(4)	20(2)	14(2)	16(2)	1(1)	2(1)	1(1)
C(5)	17(2)	17(2)	41(2)	1(2)	13(2)	-2(2)
C(6)	13(2)	10(2)	36(2)	-1(2)	2(1)	-5(1)
C(7)	18(2)	10(2)	25(2)	-5(2)	4(2)	-4(1)
C(8)	14(2)	10(2)	27(2)	2(1)	5(1)	-3(1)

C(11)	40(2)	28(2)	20(2)	-4(2)	9(2)	-5(2)
C(12)	24(2)	20(2)	23(2)	-6(2)	6(2)	5(2)
C(13)	21(2)	23(2)	32(2)	-11(2)	-3(2)	-1(2)
C(21)	21(2)	41(2)	27(2)	-11(2)	1(2)	-7(2)
C(22)	19(2)	46(2)	26(2)	-2(2)	10(2)	-3(2)
C(23)	20(2)	39(2)	26(2)	6(2)	1(2)	1(2)
C(31)	41(2)	26(2)	31(2)	8(2)	10(2)	2(2)
C(32)	42(2)	34(2)	18(2)	-3(2)	3(2)	14(2)
C(33)	17(2)	65(3)	21(2)	0(2)	0(2)	-1(2)
C(41)	25(2)	18(2)	21(2)	-2(1)	4(2)	-1(1)
C(42)	24(2)	15(2)	17(2)	1(1)	4(1)	3(1)
C(43)	20(2)	19(2)	23(2)	0(2)	8(2)	5(1)

Table A-1.6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10 ^{3}) for Compound 1.

	x	y	z	U(eq)
H(1A)	13732	6648	-5725	45
H(1B)	14112	7411	-4707	45
H(2)	13325	6875	-3606	32
H(3)	12791	5451	-5280	25
H(4)	11523	5454	-4647	21
H(5A)	9855(19)	5050(20)	-1440(30)	29
H(5B)	10470(20)	4190(20)	-1180(30)	29
H(6A)	9841	5057	-3432	25
H(7)	10959	4311	-3938	22
H(8)	11355	3498	-1755	21
H(11A)	13223	3480	-6583	44

H(11B)	13854	4172	-5784	44
H(11C)	12989	4537	-6499	44
H(12A)	13335	2269	-5065	33
H(12B)	13155	2360	-3814	33
H(12C)	13963	2784	-4025	33
H(13A)	11903	2913	-6184	41
H(13B)	11554	3900	-5975	41
H(13C)	11602	3097	-5038	41
H(21A)	15159	5690	-1336	46
H(21B)	14298	5840	-1084	46
H(21C)	14497	6319	-2190	46
H(22A)	15463	4732	-2955	44
H(22B)	14836	5265	-3979	44
H(22C)	14831	4166	-3938	44
H(23A)	15163	3922	-1216	44
H(23B)	14494	3242	-1964	44
H(23C)	14307	3836	-930	44
H(31A)	12231	4225	1450	48
H(31B)	12053	3661	252	48
H(31C)	11326	4111	668	48
H(32A)	12197	5950	1690	48
H(32B)	11273	6042	979	48
H(32C)	11936	6699	676	48
H(33A)	13334	5269	950	53
H(33B)	13219	5892	-192	53
H(33C)	13261	4797	-291	53
H(41A)	11069	8253	-1775	33
H(41B)	11844	7718	-1941	33
H(41C)	11585	7622	-746	33
H(42A)	10177	7667	-3761	28
H(42B)	9981	6615	-4115	28
H(42C)	10849	7030	-4078	28
H(43A)	9704	7572	-1816	31

H(43B)	10003	6821	-813	31
H(43C)	9435	6522	-2052	31

Table A-1.7. Torsion angles [°] for Compound 1

C(6)-Co(2)-S(1)-C(4)	-2.87(18)
C(7)-Co(2)-S(1)-C(4)	26.49(15)
C(5)-Co(2)-S(1)-C(4)	3.4(5)
C(8)-Co(2)-S(1)-C(4)	66.48(15)
P(3)-Co(2)-S(1)-C(4)	158.45(12)
P(4)-Co(2)-S(1)-C(4)	-95.60(12)
C(6)-Co(2)-S(1)-Co(1)	-62.52(13)
C(7)-Co(2)-S(1)-Co(1)	-33.16(10)
C(5)-Co(2)-S(1)-Co(1)	-56.2(5)
C(8)-Co(2)-S(1)-Co(1)	6.83(10)
P(3)-Co(2)-S(1)-Co(1)	98.80(4)
P(4)-Co(2)-S(1)-Co(1)	-155.25(4)
C(3)-Co(1)-S(1)-C(4)	36.68(17)
P(1)-Co(1)-S(1)-C(4)	-32.82(16)
P(2)-Co(1)-S(1)-C(4)	139.22(14)
S(2)-Co(1)-S(1)-C(4)	-121.75(14)
C(4)-Co(1)-S(1)-Co(2)	99.05(14)
C(3)-Co(1)-S(1)-Co(2)	135.73(10)
P(1)-Co(1)-S(1)-Co(2)	66.23(9)
P(2)-Co(1)-S(1)-Co(2)	-121.73(4)
S(2)-Co(1)-S(1)-Co(2)	-22.70(4)
C(4)-Co(1)-S(2)-C(8)	-10.72(17)
C(3)-Co(1)-S(2)-C(8)	-24.9(3)
P(1)-Co(1)-S(2)-C(8)	-117.74(12)
P(2)-Co(1)-S(2)-C(8)	141.72(12)
S(1)-Co(1)-S(2)-C(8)	33.31(12)
C(4)-Co(1)-P(1)-C(12)	-164.42(17)
C(3)-Co(1)-P(1)-C(12)	155.20(16)
P(2)-Co(1)-P(1)-C(12)	48.16(14)
S(1)-Co(1)-P(1)-C(12)	-139.55(14)
S(2)-Co(1)-P(1)-C(12)	-49.56(13)
C(4)-Co(1)-P(1)-C(13)	-44.44(18)
C(3)-Co(1)-P(1)-C(13)	-84.82(18)
P(2)-Co(1)-P(1)-C(13)	168.13(15)
S(1)-Co(1)-P(1)-C(13)	-19.57(18)
S(2)-Co(1)-P(1)-C(13)	70.42(15)
C(4)-Co(1)-P(1)-C(11)	74.43(18)
C(3)-Co(1)-P(1)-C(11)	34.05(18)
P(2)-Co(1)-P(1)-C(11)	-73.00(15)
S(1)-Co(1)-P(1)-C(11)	99.30(16)
S(2)-Co(1)-P(1)-C(11)	-170.71(15)
C(4)-Co(1)-P(2)-C(22)	-87.5(2)
C(3)-Co(1)-P(2)-C(22)	-54.42(19)
P(1)-Co(1)-P(2)-C(22)	42.11(16)
S(1)-Co(1)-P(2)-C(22)	-133.98(16)
S(2)-Co(1)-P(2)-C(22)	131.38(16)
C(4)-Co(1)-P(2)-C(21)	30.2(2)
C(3)-Co(1)-P(2)-C(21)	63.35(19)
P(1)-Co(1)-P(2)-C(21)	159.88(16)
S(1)-Co(1)-P(2)-C(21)	-16.21(16)
S(2)-Co(1)-P(2)-C(21)	-110.86(16)
C(4)-Co(1)-P(2)-C(23)	151.8(2)
C(3)-Co(1)-P(2)-C(23)	-175.13(18)
P(1)-Co(1)-P(2)-C(23)	-78.60(16)

S(1)-Co(1)-P(2)-C(23)	105.31(15)	C(7)-Co(2)-P(4)-C(43)	90.40(18)
S(2)-Co(1)-P(2)-C(23)	10.67(16)	C(5)-Co(2)-P(4)-C(43)	17.32(17)
C(6)-Co(2)-P(3)-C(33)	143.3(2)	C(8)-Co(2)-P(4)-C(43)	97.9(3)
C(7)-Co(2)-P(3)-C(33)	86.9(2)	P(3)-Co(2)-P(4)-C(43)	-79.60(13)
C(5)-Co(2)-P(3)-C(33)	159.0(2)	S(1)-Co(2)-P(4)-C(43)	-175.13(13)
C(8)-Co(2)-P(3)-C(33)	76.47(19)	C(1)-C(2)-C(3)-C(4)	-162.4(4)
P(4)-Co(2)-P(3)-C(33)	-104.31(17)	C(1)-C(2)-C(3)-Co(1)	123.5(4)
S(1)-Co(2)-P(3)-C(33)	-15.73(17)	P(1)-Co(1)-C(3)-C(4)	111.19(19)
C(6)-Co(2)-P(3)-C(32)	-94.7(2)	P(2)-Co(1)-C(3)-C(4)	-146.67(18)
C(7)-Co(2)-P(3)-C(32)	-151.2(2)	S(1)-Co(1)-C(3)-C(4)	-41.83(18)
C(5)-Co(2)-P(3)-C(32)	-79.0(2)	S(2)-Co(1)-C(3)-C(4)	19.5(4)
C(8)-Co(2)-P(3)-C(32)	-161.56(19)	C(4)-Co(1)-C(3)-C(2)	119.3(3)
P(4)-Co(2)-P(3)-C(32)	17.67(17)	P(1)-Co(1)-C(3)-C(2)	-129.5(2)
S(1)-Co(2)-P(3)-C(32)	106.25(17)	P(2)-Co(1)-C(3)-C(2)	-27.4(3)
C(6)-Co(2)-P(3)-C(31)	24.4(2)	S(1)-Co(1)-C(3)-C(2)	77.4(2)
C(7)-Co(2)-P(3)-C(31)	-32.07(19)	S(2)-Co(1)-C(3)-C(2)	138.8(2)
C(5)-Co(2)-P(3)-C(31)	40.05(19)	C(2)-C(3)-C(4)-S(1)	-35.0(4)
C(8)-Co(2)-P(3)-C(31)	-42.46(17)	Co(1)-C(3)-C(4)-S(1)	67.70(19)
P(4)-Co(2)-P(3)-C(31)	136.77(15)	C(2)-C(3)-C(4)-Co(1)	-102.7(3)
S(1)-Co(2)-P(3)-C(31)	-134.65(15)	Co(2)-S(1)-C(4)-C(3)	-171.6(2)
C(6)-Co(2)-P(4)-C(41)	-178.20(17)	Co(1)-S(1)-C(4)-C(3)	-66.4(2)
C(7)-Co(2)-P(4)-C(41)	-146.35(17)	Co(2)-S(1)-C(4)-Co(1)	-105.12(9)
C(5)-Co(2)-P(4)-C(41)	140.58(18)	P(1)-Co(1)-C(4)-C(3)	-76.0(2)
C(8)-Co(2)-P(4)-C(41)	-138.9(3)	P(2)-Co(1)-C(4)-C(3)	51.9(2)
P(3)-Co(2)-P(4)-C(41)	43.66(14)	S(1)-Co(1)-C(4)-C(3)	119.8(2)
S(1)-Co(2)-P(4)-C(41)	-51.87(14)	S(2)-Co(1)-C(4)-C(3)	-171.16(17)
C(6)-Co(2)-P(4)-C(42)	-59.40(16)	C(3)-Co(1)-C(4)-S(1)	-119.8(2)
C(7)-Co(2)-P(4)-C(42)	-27.55(17)	P(1)-Co(1)-C(4)-S(1)	164.14(7)
C(5)-Co(2)-P(4)-C(42)	-100.63(17)	P(2)-Co(1)-C(4)-S(1)	-67.92(17)
C(8)-Co(2)-P(4)-C(42)	-20.1(3)	S(2)-Co(1)-C(4)-S(1)	68.99(12)
P(3)-Co(2)-P(4)-C(42)	162.45(12)	C(7)-Co(2)-C(5)-C(6)	-31.8(2)
S(1)-Co(2)-P(4)-C(42)	66.92(12)	C(8)-Co(2)-C(5)-C(6)	-71.7(2)
C(6)-Co(2)-P(4)-C(43)	58.55(17)	P(3)-Co(2)-C(5)-C(6)	-162.8(2)

P(4)-Co(2)-C(5)-C(6)	90.4(2)
S(1)-Co(2)-C(5)-C(6)	-7.7(7)
Co(2)-C(5)-C(6)-C(7)	54.0(3)
C(5)-Co(2)-C(6)-C(7)	-129.9(3)
C(8)-Co(2)-C(6)-C(7)	-31.0(2)
P(3)-Co(2)-C(6)-C(7)	-105.7(2)
P(4)-Co(2)-C(6)-C(7)	137.2(2)
S(1)-Co(2)-C(6)-C(7)	48.0(2)
C(7)-Co(2)-C(6)-C(5)	129.9(3)
C(8)-Co(2)-C(6)-C(5)	98.9(2)
P(3)-Co(2)-C(6)-C(5)	24.2(3)
P(4)-Co(2)-C(6)-C(5)	-92.9(2)
S(1)-Co(2)-C(6)-C(5)	177.92(18)
C(5)-C(6)-C(7)-C(8)	1.8(5)
Co(2)-C(6)-C(7)-C(8)	56.4(3)
C(5)-C(6)-C(7)-Co(2)	-54.6(3)
C(5)-Co(2)-C(7)-C(6)	31.8(2)
C(8)-Co(2)-C(7)-C(6)	130.3(3)
P(3)-Co(2)-C(7)-C(6)	114.0(2)
P(4)-Co(2)-C(7)-C(6)	-53.3(2)
S(1)-Co(2)-C(7)-C(6)	-143.1(2)
C(6)-Co(2)-C(7)-C(8)	-130.3(3)
C(5)-Co(2)-C(7)-C(8)	-98.5(2)
P(3)-Co(2)-C(7)-C(8)	-16.3(2)
P(4)-Co(2)-C(7)-C(8)	176.43(15)
S(1)-Co(2)-C(7)-C(8)	86.65(18)
C(6)-C(7)-C(8)-S(2)	-168.7(3)
Co(2)-C(7)-C(8)-S(2)	-114.4(3)
C(6)-C(7)-C(8)-Co(2)	-54.2(3)
Co(1)-S(2)-C(8)-C(7)	43.1(3)
Co(1)-S(2)-C(8)-Co(2)	-39.0(2)
C(6)-Co(2)-C(8)-C(7)	31.7(2)
C(5)-Co(2)-C(8)-C(7)	72.7(2)
P(3)-Co(2)-C(8)-C(7)	167.72(18)
P(4)-Co(2)-C(8)-C(7)	-9.8(4)
S(1)-Co(2)-C(8)-C(7)	-96.05(18)
C(6)-Co(2)-C(8)-S(2)	148.4(2)
C(7)-Co(2)-C(8)-S(2)	116.7(3)
C(5)-Co(2)-C(8)-S(2)	-170.6(2)
P(3)-Co(2)-C(8)-S(2)	-75.6(2)
P(4)-Co(2)-C(8)-S(2)	106.8(3)
S(1)-Co(2)-C(8)-S(2)	20.6(2)

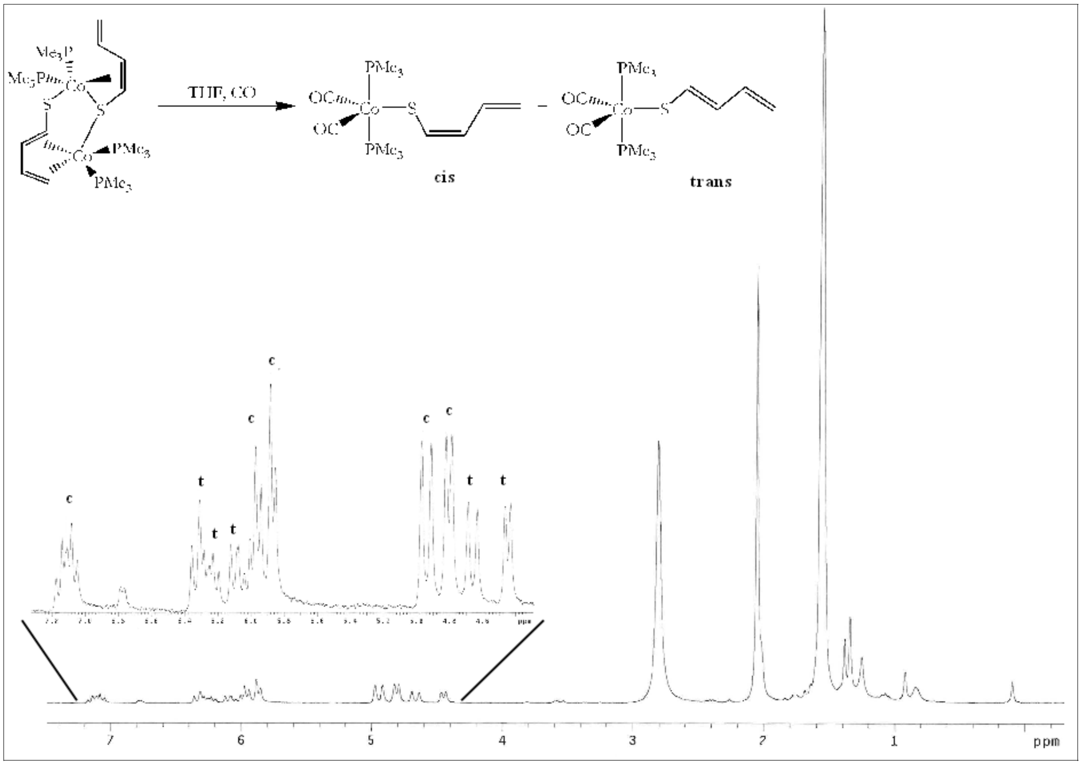

Figure A-6. Reaction of Compound 1 with CO

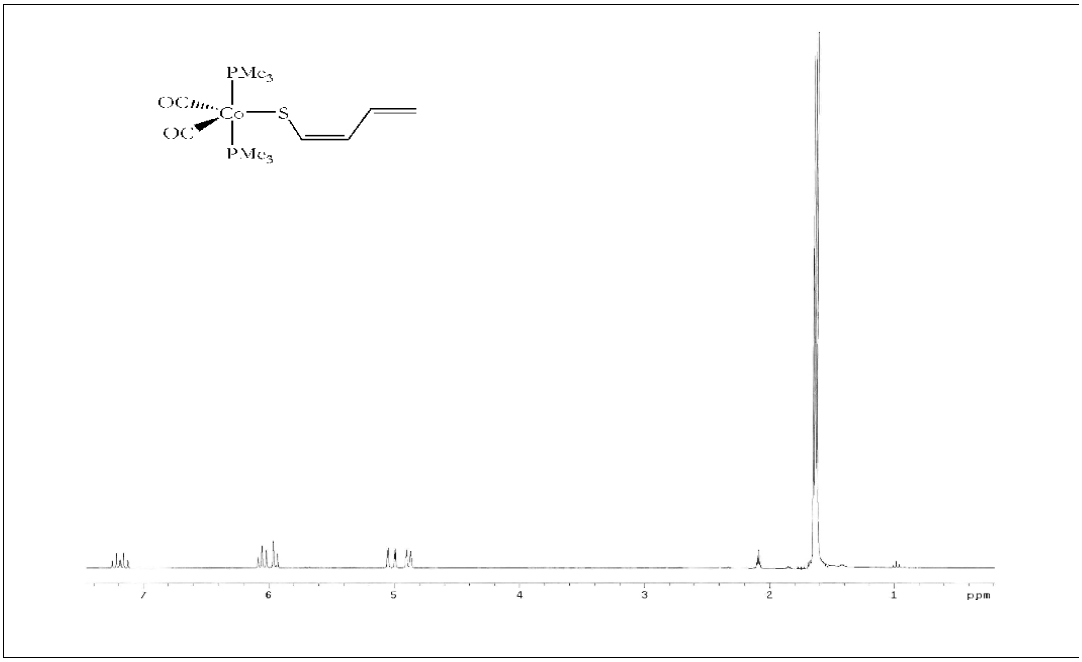

Figure A-7. ^{1}H NMR Spectrum of *cis*-2

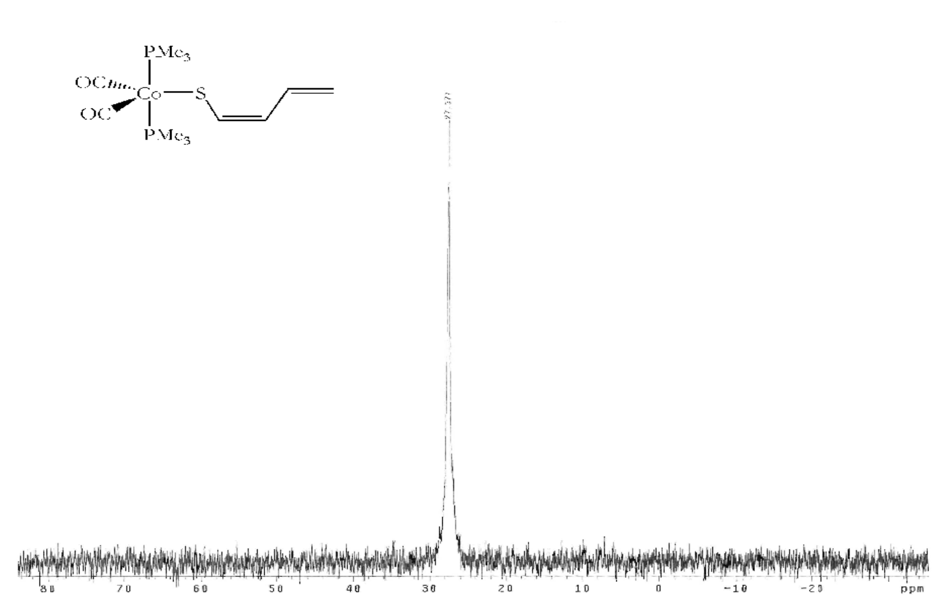

Figure A-8. ^{31}P NMR Spectrum of *cis*-2

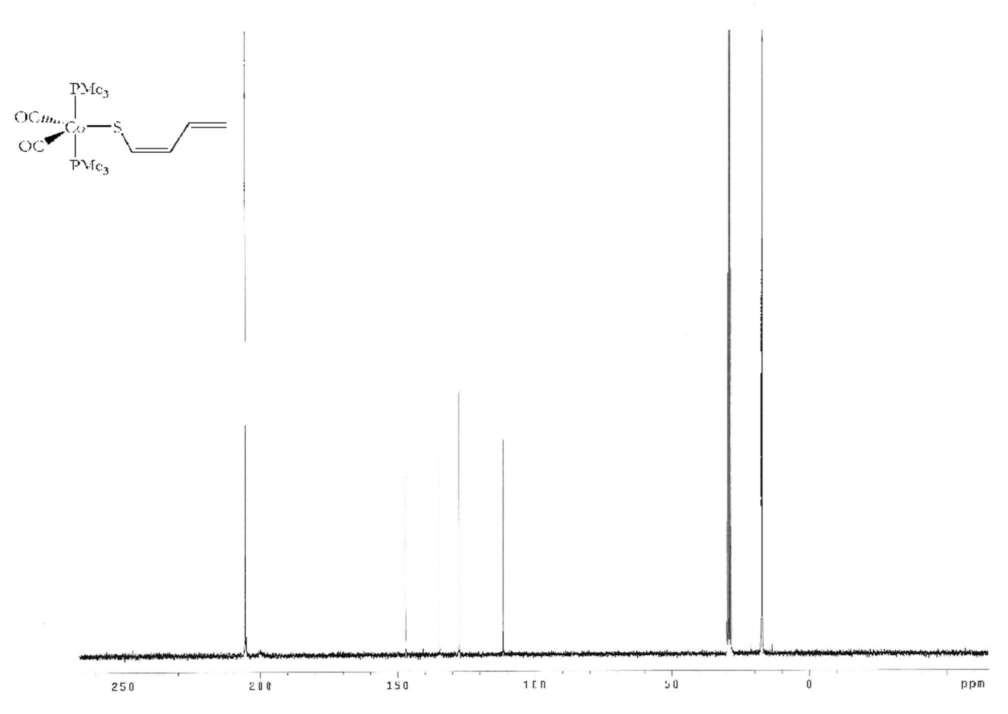

Figure A-9. ^{13}C NMR Spectrum of *cis*-2

Table A-2.1. Crystal data and structure refinement for Compound *cis*-2

Empirical formula	$C_{12} H_{23} Co O_2 P_2 S$	
Formula weight	352.23	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.7220(5) Å	α= 89.688(5)°.
	b = 9.4726(7) Å	β= 78.641(4)°.
	c = 10.5396(8) Å	γ = 86.959(4)°.
Volume	852.51(10) $Å^3$	
Z	2	
Density (calculated)	1.372 Mg/m^3	
Absorption coefficient	1.309 mm^{-1}	
F(000)	368	
Crystal size	0.19 x 0.16 x 0.15 mm^3	
Theta range for data collection	1.97 to 26.85°.	
Index ranges	$-11\le h\le 11$, $-12\le k\le 11$, $-12\le l\le 13$	
Reflections collected	14720	
Independent reflections	3619 [R(int) = 0.066]	
Completeness to theta = 26.85°	99.3 %	
Absorption correction	Numerical	
Max. and min. transmission	0.8841 and 0.8369	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3619 / 18 / 255	
Goodness-of-fit on F^2	1.048	
Final R indices [I>2sigma(I)]	R1 = 0.0393, wR2 = 0.0715	
R indices (all data)	R1 = 0.0634, wR2 = 0.0807	
Largest diff. peak and hole	0.473 and -0.375 e.$Å^{-3}$	

Table A-2.2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for Compound *cis*-2. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Co(1)	1367(1)	2975(1)	2595(1)	13(1)
P(1)	2997(1)	4655(1)	2538(1)	17(1)
P(2)	-188(1)	1276(1)	2451(1)	14(1)
S(1)	3087(1)	1960(1)	845(1)	19(1)
O(1)	-1146(2)	5043(2)	2446(2)	35(1)
O(2)	1812(2)	2149(2)	5156(2)	29(1)
C(1)	5213(4)	702(4)	-3285(3)	23(1)
C(2)	4532(3)	1101(3)	-2104(3)	19(1)
C(3)	3274(3)	2174(3)	-1777(3)	18(1)
C(4)	2588(3)	2600(3)	-573(3)	18(1)
C(5)	-126(3)	4220(3)	2444(3)	21(1)
C(6)	1682(3)	2433(3)	4109(3)	18(1)
C(11)	3193(4)	5760(4)	1121(3)	23(1)
C(12)	4980(4)	4061(4)	2640(4)	29(1)
C(13)	2472(4)	5913(4)	3854(3)	29(1)
C(21)	-1864(4)	1256(4)	3763(3)	22(1)
C(22)	-1087(4)	1367(3)	1042(3)	19(1)
C(23)	660(4)	-504(3)	2436(3)	20(1)

Table A-2.3. Bond lengths [Å] for Compound *cis*-2.

Co(1)-C(5)	1.740(3)	Co(1)-S(1)	2.3132(8)
Co(1)-C(6)	1.743(3)	P(1)-C(11)	1.804(3)
Co(1)-P(1)	2.1815(8)	P(1)-C(13)	1.807(4)
Co(1)-P(2)	2.1836(8)	P(1)-C(12)	1.813(3)

P(2)-C(23)	1.804(3)
P(2)-C(21)	1.805(3)
P(2)-C(22)	1.810(3)
S(1)-C(4)	1.734(3)
O(1)-C(5)	1.151(3)
O(2)-C(6)	1.159(3)
C(1)-C(2)	1.318(4)
C(1)-H(1A)	0.94(3)
C(1)-H(1B)	0.96(3)
C(2)-C(3)	1.446(4)
C(2)-H(2)	0.99(3)
C(3)-C(4)	1.346(4)
C(3)-H(3)	0.91(3)
C(4)-H(4)	0.94(3)
C(11)-H(11A)	0.967(19)
C(11)-H(11B)	0.975(18)
C(11)-H(11C)	0.978(18)
C(12)-H(12A)	0.957(18)
C(12)-H(12B)	0.944(18)
C(12)-H(12C)	0.952(18)
C(13)-H(13A)	0.964(18)
C(13)-H(13B)	0.960(19)
C(13)-H(13C)	0.967(19)
C(21)-H(21A)	0.941(18)
C(21)-H(21B)	0.930(17)
C(21)-H(21C)	0.941(18)
C(22)-H(22A)	0.936(17)
C(22)-H(22B)	0.940(17)
C(22)-H(22C)	0.946(17)
C(23)-H(23A)	0.964(18)
C(23)-H(23B)	0.961(17)
C(23)-H(23C)	0.960(17)

Table A-2.4. Bond angles [°] for Compound *cis*-2

C(5)-Co(1)-C(6)	121.22(13)
C(5)-Co(1)-P(1)	90.28(10)
C(6)-Co(1)-P(1)	91.22(10)
C(5)-Co(1)-P(2)	89.98(10)
C(6)-Co(1)-P(2)	93.34(10)
P(1)-Co(1)-P(2)	174.51(4)
C(5)-Co(1)-S(1)	123.45(10)
C(6)-Co(1)-S(1)	115.32(9)
P(1)-Co(1)-S(1)	87.55(3)
P(2)-Co(1)-S(1)	87.73(3)
C(11)-P(1)-C(13)	103.08(17)
C(11)-P(1)-C(12)	105.28(16)
C(13)-P(1)-C(12)	102.85(17)
C(11)-P(1)-Co(1)	114.91(11)
C(13)-P(1)-Co(1)	114.25(12)
C(12)-P(1)-Co(1)	115.00(13)
C(23)-P(2)-C(21)	103.27(16)
C(23)-P(2)-C(22)	104.72(15)
C(21)-P(2)-C(22)	102.34(15)
C(23)-P(2)-Co(1)	116.46(11)
C(21)-P(2)-Co(1)	113.83(11)
C(22)-P(2)-Co(1)	114.57(11)
C(4)-S(1)-Co(1)	109.04(10)
C(2)-C(1)-H(1A)	120.4(17)

C(2)-C(1)-H(1B)	121.1(18)	P(1)-C(13)-H(13A)	109.2(19)
H(1A)-C(1)-H(1B)	118(2)	P(1)-C(13)-H(13B)	111(2)
C(1)-C(2)-C(3)	125.6(3)	H(13A)-C(13)-H(13B)	112(3)
C(1)-C(2)-H(2)	125.7(16)	P(1)-C(13)-H(13C)	108(2)
C(3)-C(2)-H(2)	108.6(16)	H(13A)-C(13)-H(13C)	108(3)
C(4)-C(3)-C(2)	125.9(3)	H(13B)-C(13)-H(13C)	108(3)
C(4)-C(3)-H(3)	117.6(18)	P(2)-C(21)-H(21A)	107.3(19)
C(2)-C(3)-H(3)	116.6(18)	P(2)-C(21)-H(21B)	109.0(18)
C(3)-C(4)-S(1)	125.4(2)	H(21A)-C(21)-H(21B)	115(2)
C(3)-C(4)-H(4)	119.7(17)	P(2)-C(21)-H(21C)	113.0(18)
S(1)-C(4)-H(4)	114.8(17)	H(21A)-C(21)-H(21C)	105(3)
O(1)-C(5)-Co(1)	174.7(3)	H(21B)-C(21)-H(21C)	108(2)
O(2)-C(6)-Co(1)	175.0(3)	P(2)-C(22)-H(22A)	109.8(17)
P(1)-C(11)-H(11A)	112(2)	P(2)-C(22)-H(22B)	108.8(17)
P(1)-C(11)-H(11B)	110.6(19)	H(22A)-C(22)-H(22B)	114(2)
H(11A)-C(11)-H(11B)	106(3)	P(2)-C(22)-H(22C)	109.1(16)
P(1)-C(11)-H(11C)	107.6(18)	H(22A)-C(22)-H(22C)	109(2)
H(11A)-C(11)-H(11C)	114(3)	H(22B)-C(22)-H(22C)	106(2)
H(11B)-C(11)-H(11C)	107(2)	P(2)-C(23)-H(23A)	112.6(18)
P(1)-C(12)-H(12A)	110.4(17)	P(2)-C(23)-H(23B)	108.8(17)
P(1)-C(12)-H(12B)	110.0(18)	H(23A)-C(23)-H(23B)	110(2)
H(12A)-C(12)-H(12B)	106(3)	P(2)-C(23)-H(23C)	106.8(16)
P(1)-C(12)-H(12C)	109.8(17)	H(23A)-C(23)-H(23C)	112(2)
H(12A)-C(12)-H(12C)	107(2)	H(23B)-C(23)-H(23C)	106(2)
H(12B)-C(12)-H(12C)	113(3)		

Table A-2.5. Anisotropic displacement parameters ($Å^2$x 10^3) for Compound *cis*-2. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Co(1)	14(1)	14(1)	12(1)	1(1)	-2(1)	-1(1)
P(1)	16(1)	17(1)	17(1)	0(1)	-1(1)	-4(1)
P(2)	16(1)	15(1)	11(1)	0(1)	-3(1)	-2(1)
S(1)	20(1)	21(1)	14(1)	1(1)	-1(1)	3(1)
O(1)	25(1)	28(1)	52(2)	5(1)	-11(1)	6(1)
O(2)	39(1)	32(1)	19(1)	4(1)	-11(1)	-7(1)
C(1)	20(2)	27(2)	22(2)	-6(2)	0(1)	-4(2)
C(2)	17(2)	20(2)	20(2)	-2(1)	-3(1)	-4(1)
C(3)	21(2)	19(2)	16(2)	2(1)	-5(1)	-2(1)
C(4)	17(2)	15(2)	21(2)	3(1)	-4(1)	1(1)
C(5)	21(2)	23(2)	19(2)	1(1)	-6(1)	-8(1)
C(6)	17(2)	13(2)	22(2)	-3(1)	-1(1)	-2(1)
C(11)	28(2)	18(2)	23(2)	5(2)	-1(2)	-8(2)
C(12)	19(2)	32(2)	36(2)	3(2)	-6(2)	-7(2)
C(13)	33(2)	26(2)	26(2)	-6(2)	-2(2)	-11(2)
C(21)	23(2)	25(2)	18(2)	1(2)	-4(1)	-8(2)
C(22)	22(2)	19(2)	17(2)	2(1)	-5(1)	-4(1)
C(23)	25(2)	17(2)	18(2)	3(1)	-5(1)	-4(1)

Table A-2.6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10 ^{3}) for Compound *cis*-2.

	x	y	z	U(eq)
H(1A)	4900(30)	1130(30)	-4010(30)	19(8)
H(1B)	6000(30)	-60(30)	-3430(30)	25(8)
H(2)	4830(30)	750(30)	-1300(30)	18(8)
H(3)	2910(30)	2590(30)	-2450(30)	20(8)
H(4)	1810(30)	3340(30)	-460(30)	17(8)
H(11A)	3520(30)	5220(30)	330(20)	42(10)
H(11B)	4000(30)	6430(30)	1120(30)	38(10)
H(11C)	2200(20)	6310(30)	1170(30)	32(9)
H(12A)	5640(30)	4850(20)	2560(30)	31(9)
H(12B)	5000(30)	3660(30)	3460(20)	31(9)
H(12C)	5400(30)	3420(30)	1950(20)	27(9)
H(13A)	3190(30)	6660(30)	3720(30)	38(10)
H(13B)	2440(30)	5450(30)	4670(20)	40(10)
H(13C)	1440(30)	6320(30)	3830(30)	43(10)
H(21A)	-2410(30)	2140(20)	3780(30)	36(10)
H(21B)	-2450(30)	490(20)	3650(30)	21(8)
H(21C)	-1590(30)	1170(30)	4580(20)	29(9)
H(22A)	-1640(30)	560(20)	1000(30)	17(8)
H(22B)	-1700(30)	2220(20)	1080(30)	20(8)
H(22C)	-300(30)	1420(30)	290(20)	21(8)
H(23A)	-80(30)	-1210(30)	2360(30)	34(9)
H(23B)	1050(30)	-660(30)	3220(20)	23(8)
H(23C)	1560(20)	-560(30)	1740(20)	17(8)

Table A-2.7. Torsion angles [°] for Compound *cis*-2.

C(5)-Co(1)-P(1)-C(11)	-56.76(16)
C(6)-Co(1)-P(1)-C(11)	-177.99(15)
P(2)-Co(1)-P(1)-C(11)	35.9(4)
S(1)-Co(1)-P(1)-C(11)	66.71(13)
C(5)-Co(1)-P(1)-C(13)	62.10(17)
C(6)-Co(1)-P(1)-C(13)	-59.13(16)
P(2)-Co(1)-P(1)-C(13)	154.8(3)
S(1)-Co(1)-P(1)-C(13)	-174.42(14)
C(5)-Co(1)-P(1)-C(12)	-179.26(17)
C(6)-Co(1)-P(1)-C(12)	59.51(17)
P(2)-Co(1)-P(1)-C(12)	-86.6(4)
S(1)-Co(1)-P(1)-C(12)	-55.79(14)
C(5)-Co(1)-P(2)-C(23)	176.27(16)
C(6)-Co(1)-P(2)-C(23)	-62.46(15)
P(1)-Co(1)-P(2)-C(23)	83.6(4)
S(1)-Co(1)-P(2)-C(23)	52.78(12)
C(5)-Co(1)-P(2)-C(21)	-63.72(15)
C(6)-Co(1)-P(2)-C(21)	57.56(15)
P(1)-Co(1)-P(2)-C(21)	-156.4(3)
S(1)-Co(1)-P(2)-C(21)	172.80(12)
C(5)-Co(1)-P(2)-C(22)	53.60(15)
C(6)-Co(1)-P(2)-C(22)	174.87(15)
P(1)-Co(1)-P(2)-C(22)	-39.1(4)
S(1)-Co(1)-P(2)-C(22)	-69.88(12)
C(5)-Co(1)-S(1)-C(4)	-1.82(16)
C(6)-Co(1)-S(1)-C(4)	179.28(15)
P(1)-Co(1)-S(1)-C(4)	-90.54(11)
P(2)-Co(1)-S(1)-C(4)	86.65(11)
C(1)-C(2)-C(3)-C(4)	-179.1(3)
C(2)-C(3)-C(4)-S(1)	0.7(5)
Co(1)-S(1)-C(4)-C(3)	-175.7(2)
C(6)-Co(1)-C(5)-O(1)	-3(3)
P(1)-Co(1)-C(5)-O(1)	-94(3)
P(2)-Co(1)-C(5)-O(1)	91(3)
S(1)-Co(1)-C(5)-O(1)	179(100)
C(5)-Co(1)-C(6)-O(2)	-8(3)
P(1)-Co(1)-C(6)-O(2)	83(3)
P(2)-Co(1)-C(6)-O(2)	-100(3)
S(1)-Co(1)-C(6)-O(2)	171(3)

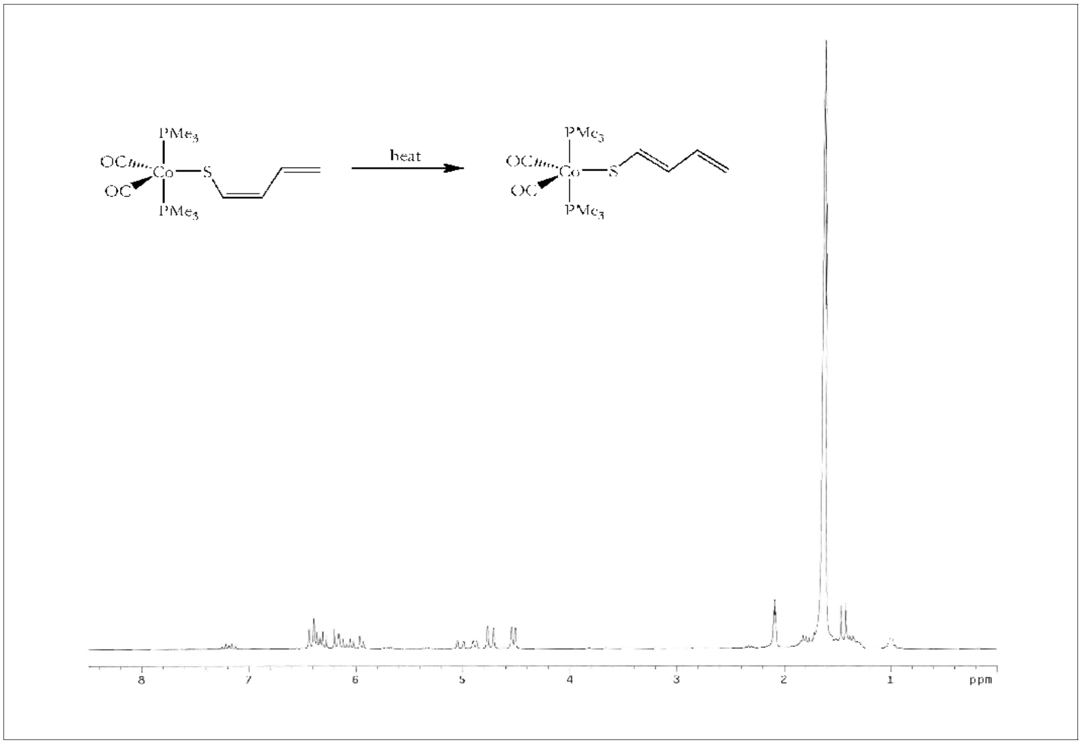

Figure A-10. ^{1}H NMR Spectrum. Partial Conversion of *cis*-2 to trans-2 by Heating.

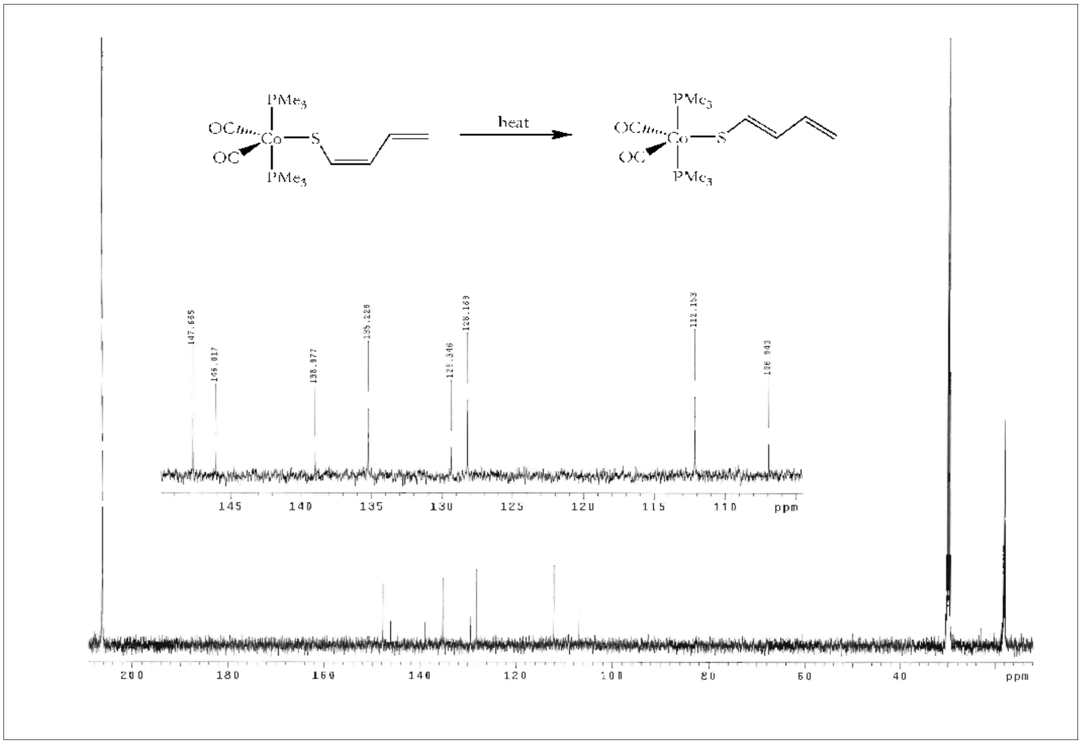

Figure A-11. ^{13}C NMR Spectrum. Partial Conversion of *cis*-2 to trans-2 by Heating.

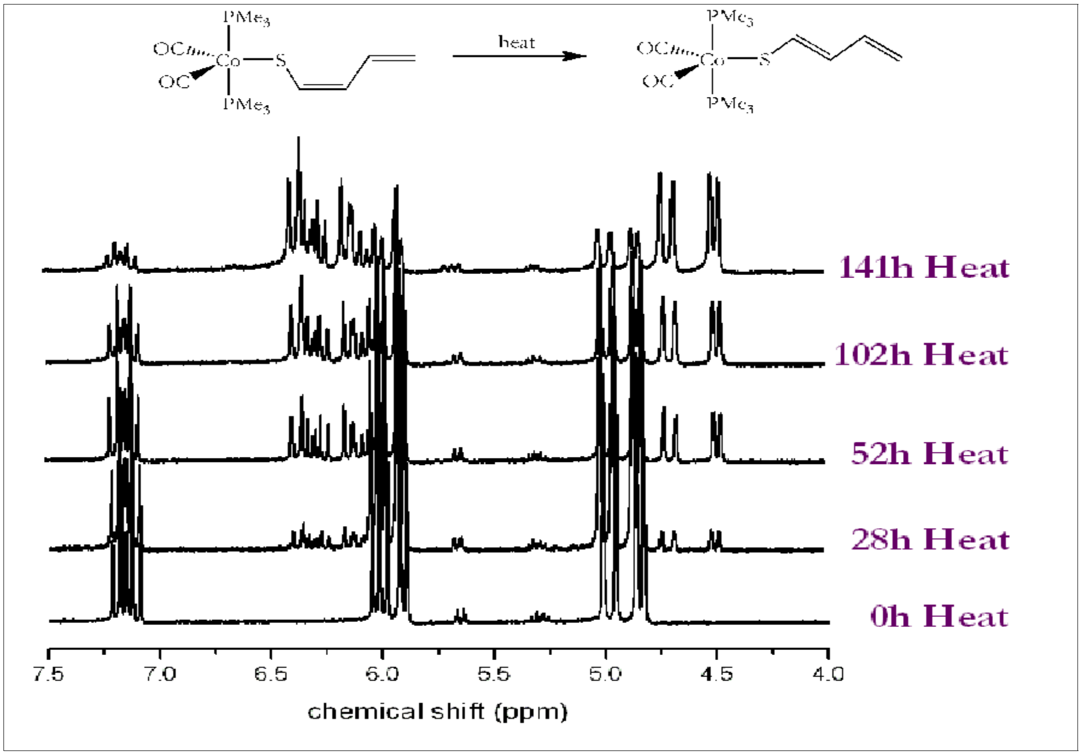

Figure A-12. ^{1}H NMR Series of Partial Conversion of *cis*-2 to trans-2 by Heating.

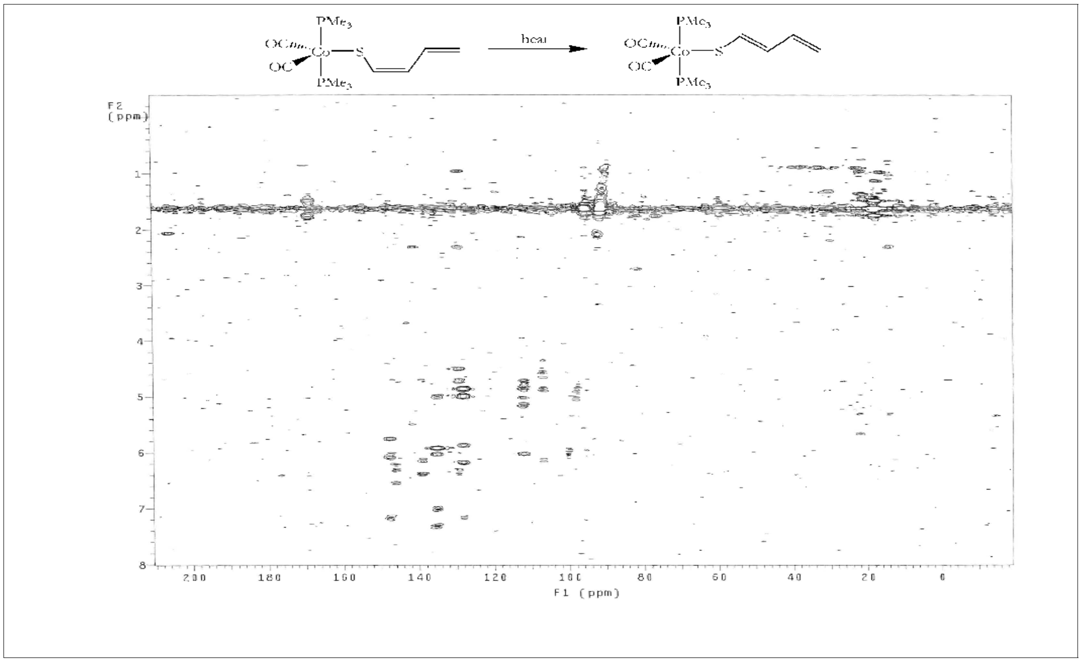

Figure A-13. HMBC Spectrum of Partial Conversion of *cis*-2 to trans-2 by Heating.

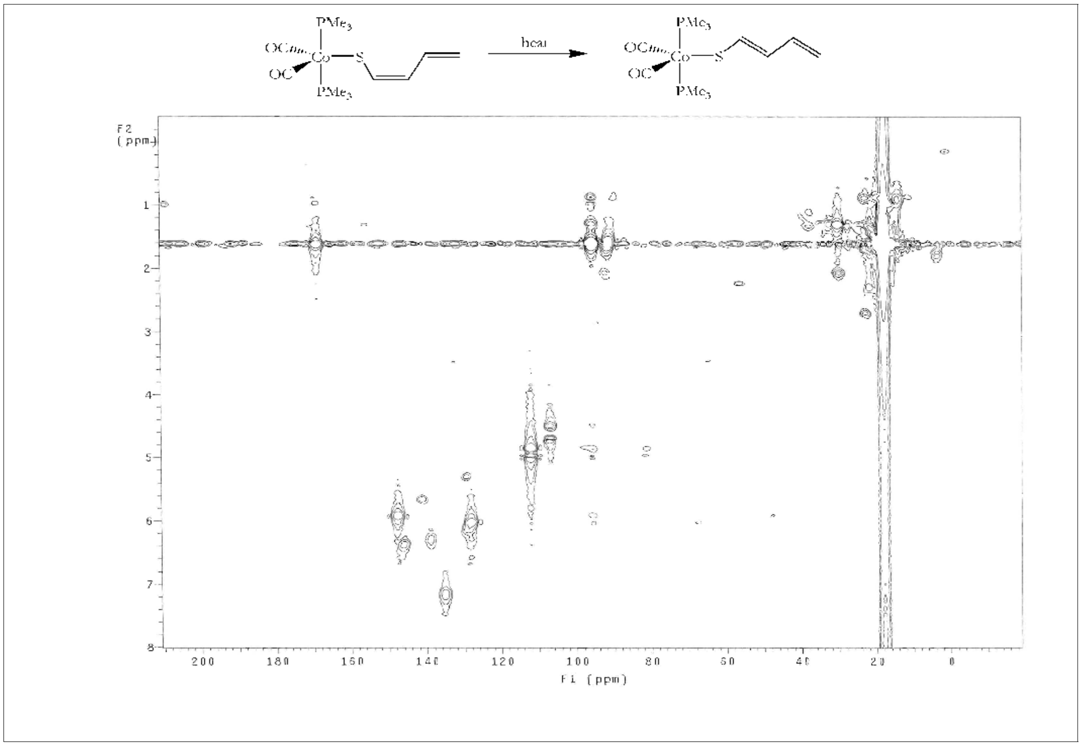

Figure A-14. HMQC Spectrum of Partial Conversion of *cis*-2 to trans-2 by Heating.

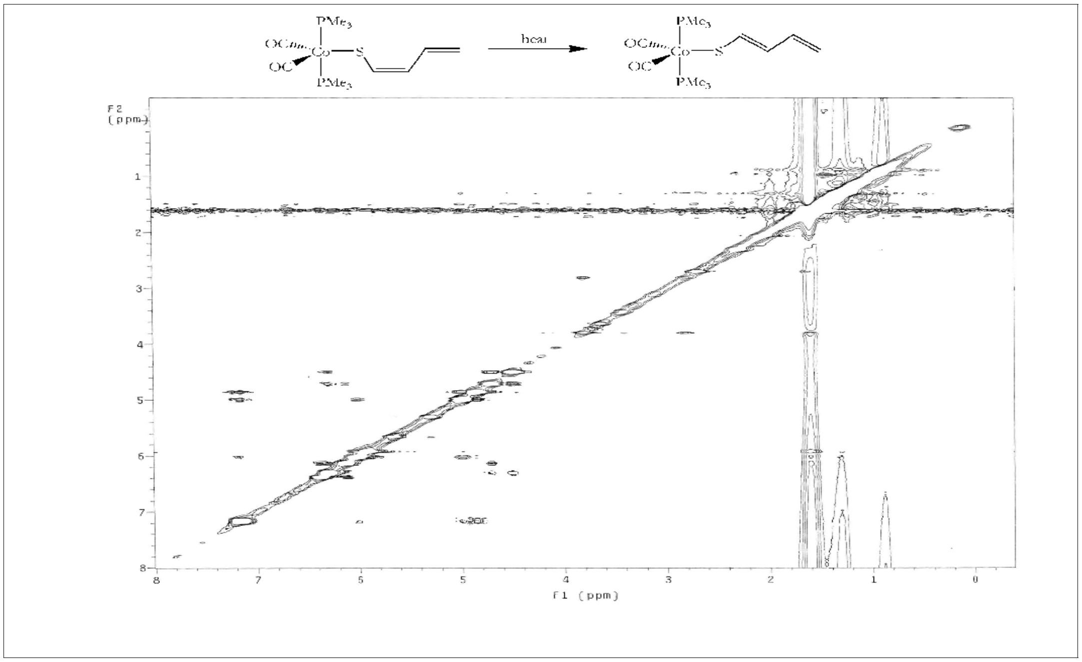

Figure A-15. NOESY Spectrum of Partial Conversion of *cis*-2 to trans-2 by Heating.

Table A-3.1. Crystal data and structure refinement for Compound 3.

Empirical formula	$C_{40} H_{82} Co_3 O P_4 S_4$	
Formula weight	1007.97	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 14.5966(6) Å	α= 90°.
	b = 21.6485(7) Å	β= 104.590(2)°.
	c = 16.5808(6) Å	γ = 90°.
Volume	5070.5(3) $Å^3$	
Z	4	
Density (calculated)	1.320 Mg/m^3	
Absorption coefficient	1.289 mm^{-1}	
F(000)	2140	
Crystal size	0.16 x 0.10 x 0.06 mm^3	
Theta range for data collection	1.58 to 25.50°.	
Index ranges	$-17 \le h \le 17$, $-26 \le k \le 26$, $-19 \le l \le 19$	
Reflections collected	52298	
Independent reflections	9360 [R(int) = 0.0899]	
Completeness to theta = 25.00°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9220 and 0.8242	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9360 / 2 / 532	
Goodness-of-fit on F^2	0.997	
Final R indices [I>2sigma(I)]	R1 = 0.0410, wR2 = 0.0697	
R indices (all data)	R1 = 0.0819, wR2 = 0.0824	
Largest diff. peak and hole	0.437 and -0.426 $e.Å^{-3}$	

Table A-3.2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for Compound 3. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Co(1)	7484(1)	946(1)	4494(1)	14(1)
Co(2)	6980(1)	2053(1)	8706(1)	13(1)
Co(3)	6945(1)	1341(1)	6580(1)	14(1)
P(1)	6041(1)	607(1)	3977(1)	18(1)
P(2)	7580(1)	1635(1)	3538(1)	19(1)
P(3)	8250(1)	2092(1)	9783(1)	18(1)
P(4)	6921(1)	3021(1)	8298(1)	18(1)
S(1)	7155(1)	331(1)	6321(1)	18(1)
S(2)	7071(1)	1723(1)	5281(1)	14(1)
S(3)	5573(1)	1720(1)	6740(1)	21(1)
S(4)	7904(1)	1737(1)	7839(1)	15(1)
C(11)	8096(3)	258(2)	3998(3)	23(1)
C(12)	8786(2)	548(2)	4663(2)	19(1)
C(13)	8557(2)	576(2)	5439(2)	18(1)
C(14)	7668(3)	303(2)	5459(2)	18(1)
C(15)	9695(2)	798(2)	4516(2)	27(1)
C(16)	9184(2)	881(2)	6188(2)	23(1)
C(17)	5583(3)	578(2)	2846(2)	40(1)
C(18)	5785(3)	-179(2)	4234(3)	29(1)
C(19)	5104(2)	1033(2)	4258(3)	31(1)
C(21)	8618(3)	3904(2)	5936(2)	38(1)
C(22)	8701(3)	3298(2)	5890(2)	25(1)
C(23)	7865(2)	2892(2)	5603(2)	19(1)
C(24)	7978(2)	2274(2)	5584(2)	17(1)
C(25)	9664(3)	3003(2)	6133(3)	36(1)
C(26)	6906(3)	3187(2)	5341(2)	27(1)
C(27)	6595(3)	2180(2)	3248(2)	27(1)

C(28)	8565(3)	2179(2)	3737(2)	25(1)
C(29)	7655(3)	1346(2)	2516(2)	34(1)
C(31)	6047(3)	2193(2)	9401(2)	19(1)
C(32)	6149(2)	1543(2)	9274(2)	21(1)
C(33)	5994(2)	1347(2)	8440(2)	18(1)
C(34)	5719(2)	1818(2)	7823(2)	17(1)
C(35)	6386(3)	1099(2)	9994(2)	29(1)
C(36)	6119(3)	679(2)	8212(2)	25(1)
C(37)	8810(3)	1384(2)	10260(2)	31(1)
C(38)	8128(3)	2492(2)	10719(2)	23(1)
C(39)	9269(2)	2499(2)	9606(2)	28(1)
C(41)	10781(3)	234(2)	8617(3)	55(1)
C(42)	9872(3)	354(2)	8567(3)	33(1)
C(43)	9461(3)	961(2)	8298(2)	22(1)
C(44)	8539(2)	1058(2)	8213(2)	19(1)
C(45)	9246(3)	-142(2)	8780(3)	45(1)
C(46)	10102(2)	1451(2)	8109(2)	28(1)
C(47)	7716(3)	3262(2)	7675(2)	27(1)
C(48)	5795(3)	3282(2)	7636(2)	30(1)
C(49)	7121(3)	3625(2)	9093(2)	29(1)
O(1)	7683(5)	3695(3)	3069(4)	36(2)
C(51)	8507(8)	3869(5)	3713(6)	37(3)
O(1')	7687(7)	4035(4)	2747(6)	67(3)
C(51')	8581(8)	4091(5)	3296(8)	52(3)
C(52)	8603(3)	4569(2)	3940(3)	53(1)
C(53)	7704(4)	3691(3)	2166(4)	74(2)
C(54)	6782(4)	3616(2)	1572(3)	57(2)

Table A-3.3. Bond lengths [Å] for Compound 3.

Co(1)-C(11)	2.015(4)	S(2)-C(24)	1.760(3)
Co(1)-C(12)	2.041(3)	S(3)-C(34)	1.767(4)
Co(1)-C(13)	2.075(3)	S(4)-C(44)	1.766(3)
Co(1)-C(14)	2.087(3)	C(11)-C(12)	1.437(5)
Co(1)-P(1)	2.1916(10)	C(11)-H(11A)	0.97(2)
Co(1)-P(2)	2.2078(10)	C(11)-H(11B)	0.96(2)
Co(1)-S(2)	2.3008(9)	C(12)-C(13)	1.409(5)
Co(2)-C(31)	2.016(4)	C(12)-C(15)	1.509(5)
Co(2)-C(32)	2.038(3)	C(13)-C(14)	1.435(5)
Co(2)-C(33)	2.070(3)	C(13)-C(16)	1.498(5)
Co(2)-C(34)	2.105(4)	C(14)-H(14)	0.91(3)
Co(2)-P(4)	2.1979(10)	C(15)-H(15A)	0.9800
Co(2)-P(3)	2.2281(10)	C(15)-H(15B)	0.9800
Co(2)-S(4)	2.3082(10)	C(15)-H(15C)	0.9800
Co(3)-S(3)	2.2415(10)	C(16)-H(16A)	0.9800
Co(3)-S(1)	2.2649(9)	C(16)-H(16B)	0.9800
Co(3)-S(2)	2.3560(10)	C(16)-H(16C)	0.9800
Co(3)-S(4)	2.3626(10)	C(17)-H(17A)	0.9800
P(1)-C(19)	1.805(4)	C(17)-H(17B)	0.9800
P(1)-C(18)	1.815(3)	C(17)-H(17C)	0.9800
P(1)-C(17)	1.827(4)	C(18)-H(18A)	0.9800
P(2)-C(28)	1.823(3)	C(18)-H(18B)	0.9800
P(2)-C(27)	1.828(3)	C(18)-H(18C)	0.9800
P(2)-C(29)	1.835(4)	C(19)-H(19A)	0.9800
P(3)-C(39)	1.815(4)	C(19)-H(19B)	0.9800
P(3)-C(37)	1.823(3)	C(19)-H(19C)	0.9800
P(3)-C(38)	1.825(4)	C(21)-C(22)	1.323(5)
P(4)-C(47)	1.813(4)	C(21)-H(21A)	0.9500
P(4)-C(48)	1.821(4)	C(21)-H(21B)	0.9500
P(4)-C(49)	1.826(4)	C(22)-C(23)	1.481(5)
S(1)-C(14)	1.774(4)	C(22)-C(25)	1.503(5)

C(23)-C(24)	1.350(5)
C(23)-C(26)	1.500(5)
C(24)-H(24A)	0.9500
C(25)-H(25A)	0.9800
C(25)-H(25B)	0.9800
C(25)-H(25C)	0.9800
C(26)-H(26A)	0.9800
C(26)-H(26B)	0.9800
C(26)-H(26C)	0.9800
C(27)-H(27A)	0.9800
C(27)-H(27B)	0.9800
C(27)-H(27C)	0.9800
C(28)-H(28A)	0.9800
C(28)-H(28B)	0.9800
C(28)-H(28C)	0.9800
C(29)-H(29A)	0.9800
C(29)-H(29B)	0.9800
C(29)-H(29C)	0.9800
C(31)-C(32)	1.437(5)
C(31)-H(31A)	0.93(2)
C(31)-H(31B)	0.94(2)
C(32)-C(33)	1.409(5)
C(32)-C(35)	1.502(5)
C(33)-C(34)	1.430(5)
C(33)-C(36)	1.517(5)
C(34)-H(34)	0.89(3)
C(35)-H(35A)	0.9800
C(35)-H(35B)	0.9800
C(35)-H(35C)	0.9800
C(36)-H(36A)	0.9800
C(36)-H(36B)	0.9800
C(36)-H(36C)	0.9800
C(37)-H(37A)	0.9800
C(37)-H(37B)	0.9800
C(37)-H(37C)	0.9800
C(38)-H(38A)	0.9800
C(38)-H(38B)	0.9800
C(38)-H(38C)	0.9800
C(39)-H(39A)	0.9800
C(39)-H(39B)	0.9800
C(39)-H(39C)	0.9800
C(41)-C(42)	1.334(5)
C(41)-H(41A)	0.9500
C(41)-H(41B)	0.9500
C(42)-C(43)	1.468(5)
C(42)-C(45)	1.507(6)
C(43)-C(44)	1.334(5)
C(43)-C(46)	1.497(5)
C(44)-H(44A)	0.9500
C(45)-H(45A)	0.9800
C(45)-H(45B)	0.9800
C(45)-H(45C)	0.9800
C(46)-H(46A)	0.9800
C(46)-H(46B)	0.9800
C(46)-H(46C)	0.9800
C(47)-H(47A)	0.9800
C(47)-H(47B)	0.9800
C(47)-H(47C)	0.9800
C(48)-H(48A)	0.9800
C(48)-H(48B)	0.9800
C(48)-H(48C)	0.9800
C(49)-H(49A)	0.9800
C(49)-H(49B)	0.9800
C(49)-H(49C)	0.9800
O(1)-C(51)	1.443(13)
O(1)-C(53)	1.504(9)

C(51)-C(52)	1.558(12)	C(52)-H(52B)	0.9800
C(51)-H(51A)	0.9900	C(52)-H(52C)	0.9800
C(51)-H(51B)	0.9900	C(53)-C(54)	1.463(7)
O(1')-C(53)	1.223(9)	C(53)-H(53A)	0.9900
O(1')-C(51')	1.396(14)	C(53)-H(53B)	0.9900
C(51')-C(52)	1.482(13)	C(54)-H(54A)	0.9800
C(51')-H(51C)	0.9900	C(54)-H(54B)	0.9800
C(51')-H(51D)	0.9900	C(54)-H(54C)	0.9800
C(52)-H(52A)	0.9800		

Table A-3.4. Bond angles [°] for Compound 3.

C(11)-Co(1)-C(12)	41.48(14)	C(31)-Co(2)-C(32)	41.52(14)
C(11)-Co(1)-C(13)	72.31(15)	C(31)-Co(2)-C(33)	72.52(14)
C(12)-Co(1)-C(13)	40.04(14)	C(32)-Co(2)-C(33)	40.12(14)
C(11)-Co(1)-C(14)	80.57(15)	C(31)-Co(2)-C(34)	80.56(15)
C(12)-Co(1)-C(14)	71.20(14)	C(32)-Co(2)-C(34)	70.92(14)
C(13)-Co(1)-C(14)	40.33(13)	C(33)-Co(2)-C(34)	40.05(13)
C(11)-Co(1)-P(1)	94.26(12)	C(31)-Co(2)-P(4)	93.04(11)
C(12)-Co(1)-P(1)	133.03(10)	C(32)-Co(2)-P(4)	132.68(11)
C(13)-Co(1)-P(1)	129.36(10)	C(33)-Co(2)-P(4)	131.94(10)
C(14)-Co(1)-P(1)	90.08(11)	C(34)-Co(2)-P(4)	93.26(10)
C(11)-Co(1)-P(2)	95.25(12)	C(31)-Co(2)-P(3)	94.68(12)
C(12)-Co(1)-P(2)	99.17(10)	C(32)-Co(2)-P(3)	97.00(11)
C(13)-Co(1)-P(2)	129.08(10)	C(33)-Co(2)-P(3)	126.32(10)
C(14)-Co(1)-P(2)	169.36(11)	C(34)-Co(2)-P(3)	166.35(10)
P(1)-Co(1)-P(2)	100.03(4)	P(4)-Co(2)-P(3)	99.80(4)
C(11)-Co(1)-S(2)	168.02(12)	C(31)-Co(2)-S(4)	170.12(11)
C(12)-Co(1)-S(2)	126.81(11)	C(32)-Co(2)-S(4)	129.52(11)
C(13)-Co(1)-S(2)	96.27(10)	C(33)-Co(2)-S(4)	97.62(10)
C(14)-Co(1)-S(2)	93.09(10)	C(34)-Co(2)-S(4)	92.36(10)
P(1)-Co(1)-S(2)	95.92(4)	P(4)-Co(2)-S(4)	94.25(4)
P(2)-Co(1)-S(2)	89.20(4)	P(3)-Co(2)-S(4)	90.65(4)

S(3)-Co(3)-S(1)	122.92(4)
S(3)-Co(3)-S(2)	104.95(4)
S(1)-Co(3)-S(2)	96.90(3)
S(3)-Co(3)-S(4)	96.32(4)
S(1)-Co(3)-S(4)	116.08(4)
S(2)-Co(3)-S(4)	121.03(3)
C(19)-P(1)-C(18)	101.79(18)
C(19)-P(1)-C(17)	100.2(2)
C(18)-P(1)-C(17)	99.54(19)
C(19)-P(1)-Co(1)	116.34(13)
C(18)-P(1)-Co(1)	117.16(13)
C(17)-P(1)-Co(1)	118.69(14)
C(28)-P(2)-C(27)	99.40(17)
C(28)-P(2)-C(29)	99.24(18)
C(27)-P(2)-C(29)	101.71(19)
C(28)-P(2)-Co(1)	119.74(13)
C(27)-P(2)-Co(1)	115.94(13)
C(29)-P(2)-Co(1)	117.47(13)
C(39)-P(3)-C(37)	100.48(18)
C(39)-P(3)-C(38)	99.61(17)
C(37)-P(3)-C(38)	99.09(17)
C(39)-P(3)-Co(2)	116.08(13)
C(37)-P(3)-Co(2)	120.52(13)
C(38)-P(3)-Co(2)	117.43(12)
C(47)-P(4)-C(48)	100.27(18)
C(47)-P(4)-C(49)	101.37(17)
C(48)-P(4)-C(49)	99.72(18)
C(47)-P(4)-Co(2)	117.97(12)
C(48)-P(4)-Co(2)	116.09(13)
C(49)-P(4)-Co(2)	118.22(13)
C(14)-S(1)-Co(3)	106.88(12)
C(24)-S(2)-Co(1)	111.84(12)
C(24)-S(2)-Co(3)	101.72(12)
Co(1)-S(2)-Co(3)	110.75(4)
C(34)-S(3)-Co(3)	106.39(13)
C(44)-S(4)-Co(2)	111.47(12)
C(44)-S(4)-Co(3)	98.63(12)
Co(2)-S(4)-Co(3)	110.42(4)
C(12)-C(11)-Co(1)	70.2(2)
C(12)-C(11)-H(11A)	120(2)
Co(1)-C(11)-H(11A)	112.9(19)
C(12)-C(11)-H(11B)	117(2)
Co(1)-C(11)-H(11B)	121(2)
H(11A)-C(11)-H(11B)	111(3)
C(13)-C(12)-C(11)	116.0(3)
C(13)-C(12)-C(15)	123.5(3)
C(11)-C(12)-C(15)	120.5(3)
C(13)-C(12)-Co(1)	71.3(2)
C(11)-C(12)-Co(1)	68.3(2)
C(15)-C(12)-Co(1)	130.7(2)
C(12)-C(13)-C(14)	115.3(3)
C(12)-C(13)-C(16)	122.7(3)
C(14)-C(13)-C(16)	122.0(3)
C(12)-C(13)-Co(1)	68.7(2)
C(14)-C(13)-Co(1)	70.3(2)
C(16)-C(13)-Co(1)	130.1(2)
C(13)-C(14)-S(1)	125.0(3)
C(13)-C(14)-Co(1)	69.40(19)
S(1)-C(14)-Co(1)	126.61(18)
C(13)-C(14)-H(14)	117(2)
S(1)-C(14)-H(14)	107(2)
Co(1)-C(14)-H(14)	107(2)
C(12)-C(15)-H(15A)	109.5
C(12)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(12)-C(15)-H(15C)	109.5

H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(13)-C(16)-H(16A)	109.5
C(13)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(13)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
P(1)-C(17)-H(17A)	109.5
P(1)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
P(1)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
P(1)-C(18)-H(18A)	109.5
P(1)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
P(1)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
P(1)-C(19)-H(19A)	109.5
P(1)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
P(1)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
C(22)-C(21)-H(21A)	120.0
C(22)-C(21)-H(21B)	120.0
H(21A)-C(21)-H(21B)	120.0
C(21)-C(22)-C(23)	121.8(4)
C(21)-C(22)-C(25)	120.0(4)
C(23)-C(22)-C(25)	118.2(3)
C(24)-C(23)-C(22)	120.0(3)
C(24)-C(23)-C(26)	121.7(3)
C(22)-C(23)-C(26)	118.3(3)
C(23)-C(24)-S(2)	126.3(3)
C(23)-C(24)-H(24A)	116.9
S(2)-C(24)-H(24A)	116.9
C(22)-C(25)-H(25A)	109.5
C(22)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5
C(22)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5
C(23)-C(26)-H(26A)	109.5
C(23)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26B)	109.5
C(23)-C(26)-H(26C)	109.5
H(26A)-C(26)-H(26C)	109.5
H(26B)-C(26)-H(26C)	109.5
P(2)-C(27)-H(27A)	109.5
P(2)-C(27)-H(27B)	109.5
H(27A)-C(27)-H(27B)	109.5
P(2)-C(27)-H(27C)	109.5
H(27A)-C(27)-H(27C)	109.5
H(27B)-C(27)-H(27C)	109.5
P(2)-C(28)-H(28A)	109.5
P(2)-C(28)-H(28B)	109.5
H(28A)-C(28)-H(28B)	109.5
P(2)-C(28)-H(28C)	109.5
H(28A)-C(28)-H(28C)	109.5
H(28B)-C(28)-H(28C)	109.5
P(2)-C(29)-H(29A)	109.5
P(2)-C(29)-H(29B)	109.5
H(29A)-C(29)-H(29B)	109.5
P(2)-C(29)-H(29C)	109.5

H(29A)-C(29)-H(29C)	109.5
H(29B)-C(29)-H(29C)	109.5
C(32)-C(31)-Co(2)	70.1(2)
C(32)-C(31)-H(31A)	122(2)
Co(2)-C(31)-H(31A)	107(2)
C(32)-C(31)-H(31B)	113(2)
Co(2)-C(31)-H(31B)	124(2)
H(31A)-C(31)-H(31B)	115(3)
C(33)-C(32)-C(31)	116.2(3)
C(33)-C(32)-C(35)	122.3(3)
C(31)-C(32)-C(35)	121.5(3)
C(33)-C(32)-Co(2)	71.1(2)
C(31)-C(32)-Co(2)	68.4(2)
C(35)-C(32)-Co(2)	132.0(3)
C(32)-C(33)-C(34)	115.7(3)
C(32)-C(33)-C(36)	122.2(3)
C(34)-C(33)-C(36)	122.1(3)
C(32)-C(33)-Co(2)	68.73(19)
C(34)-C(33)-Co(2)	71.31(19)
C(36)-C(33)-Co(2)	129.5(2)
C(33)-C(34)-S(3)	125.6(3)
C(33)-C(34)-Co(2)	68.6(2)
S(3)-C(34)-Co(2)	126.59(19)
C(33)-C(34)-H(34)	116(2)
S(3)-C(34)-H(34)	109(2)
Co(2)-C(34)-H(34)	105(2)
C(32)-C(35)-H(35A)	109.5
C(32)-C(35)-H(35B)	109.5
H(35A)-C(35)-H(35B)	109.5
C(32)-C(35)-H(35C)	109.5
H(35A)-C(35)-H(35C)	109.5
H(35B)-C(35)-H(35C)	109.5
C(33)-C(36)-H(36A)	109.5
C(33)-C(36)-H(36B)	109.5
H(36A)-C(36)-H(36B)	109.5
C(33)-C(36)-H(36C)	109.5
H(36A)-C(36)-H(36C)	109.5
H(36B)-C(36)-H(36C)	109.5
P(3)-C(37)-H(37A)	109.5
P(3)-C(37)-H(37B)	109.5
H(37A)-C(37)-H(37B)	109.5
P(3)-C(37)-H(37C)	109.5
H(37A)-C(37)-H(37C)	109.5
H(37B)-C(37)-H(37C)	109.5
P(3)-C(38)-H(38A)	109.5
P(3)-C(38)-H(38B)	109.5
H(38A)-C(38)-H(38B)	109.5
P(3)-C(38)-H(38C)	109.5
H(38A)-C(38)-H(38C)	109.5
H(38B)-C(38)-H(38C)	109.5
P(3)-C(39)-H(39A)	109.5
P(3)-C(39)-H(39B)	109.5
H(39A)-C(39)-H(39B)	109.5
P(3)-C(39)-H(39C)	109.5
H(39A)-C(39)-H(39C)	109.5
H(39B)-C(39)-H(39C)	109.5
C(42)-C(41)-H(41A)	120.0
C(42)-C(41)-H(41B)	120.0
H(41A)-C(41)-H(41B)	120.0
C(41)-C(42)-C(43)	121.1(4)
C(41)-C(42)-C(45)	120.0(4)
C(43)-C(42)-C(45)	118.9(3)
C(44)-C(43)-C(42)	119.7(4)
C(44)-C(43)-C(46)	122.3(3)
C(42)-C(43)-C(46)	118.0(3)
C(43)-C(44)-S(4)	126.5(3)

C(43)-C(44)-H(44A)	116.8
S(4)-C(44)-H(44A)	116.8
C(42)-C(45)-H(45A)	109.5
C(42)-C(45)-H(45B)	109.5
H(45A)-C(45)-H(45B)	109.5
C(42)-C(45)-H(45C)	109.5
H(45A)-C(45)-H(45C)	109.5
H(45B)-C(45)-H(45C)	109.5
C(43)-C(46)-H(46A)	109.5
C(43)-C(46)-H(46B)	109.5
H(46A)-C(46)-H(46B)	109.5
C(43)-C(46)-H(46C)	109.5
H(46A)-C(46)-H(46C)	109.5
H(46B)-C(46)-H(46C)	109.5
P(4)-C(47)-H(47A)	109.5
P(4)-C(47)-H(47B)	109.5
H(47A)-C(47)-H(47B)	109.5
P(4)-C(47)-H(47C)	109.5
H(47A)-C(47)-H(47C)	109.5
H(47B)-C(47)-H(47C)	109.5
P(4)-C(48)-H(48A)	109.5
P(4)-C(48)-H(48B)	109.5
H(48A)-C(48)-H(48B)	109.5
P(4)-C(48)-H(48C)	109.5
H(48A)-C(48)-H(48C)	109.5
H(48B)-C(48)-H(48C)	109.5
P(4)-C(49)-H(49A)	109.5
P(4)-C(49)-H(49B)	109.5
H(49A)-C(49)-H(49B)	109.5
P(4)-C(49)-H(49C)	109.5
H(49A)-C(49)-H(49C)	109.5
H(49B)-C(49)-H(49C)	109.5
C(51)-O(1)-C(53)	121.1(7)
O(1)-C(51)-C(52)	116.1(8)
O(1)-C(51)-H(51A)	108.3
C(52)-C(51)-H(51A)	108.3
O(1)-C(51)-H(51B)	108.3
C(52)-C(51)-H(51B)	108.3
H(51A)-C(51)-H(51B)	107.4
C(53)-O(1')-C(51')	111.4(9)
O(1')-C(51')-C(52)	112.2(9)
O(1')-C(51')-H(51C)	109.2
C(52)-C(51')-H(51C)	109.2
O(1')-C(51')-H(51D)	109.2
C(52)-C(51')-H(51D)	109.2
H(51C)-C(51')-H(51D)	107.9
C(51')-C(52)-C(51)	33.1(5)
C(51')-C(52)-H(52A)	119.6
C(51)-C(52)-H(52A)	109.5
C(51')-C(52)-H(52B)	125.2
C(51)-C(52)-H(52B)	109.5
H(52A)-C(52)-H(52B)	109.5
C(51')-C(52)-H(52C)	76.5
C(51)-C(52)-H(52C)	109.5
H(52A)-C(52)-H(52C)	109.5
H(52B)-C(52)-H(52C)	109.5
O(1')-C(53)-C(54)	113.6(6)
O(1')-C(53)-O(1)	37.2(5)
C(54)-C(53)-O(1)	115.2(5)
O(1')-C(53)-H(53A)	74.6
C(54)-C(53)-H(53A)	108.5
O(1)-C(53)-H(53A)	108.5
O(1')-C(53)-H(53B)	134.7
C(54)-C(53)-H(53B)	108.5
O(1)-C(53)-H(53B)	108.5
H(53A)-C(53)-H(53B)	107.5

C(53)-C(54)-H(54A)	109.5
C(53)-C(54)-H(54B)	109.5
H(54A)-C(54)-H(54B)	109.5
C(53)-C(54)-H(54C)	109.5
H(54A)-C(54)-H(54C)	109.5
H(54B)-C(54)-H(54C)	109.5

Table A-3.5. Anisotropic displacement parameters ($Å^2$x 10^3) for jb11109. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Co(1)	16(1)	13(1)	11(1)	0(1)	1(1)	-1(1)
Co(2)	13(1)	13(1)	12(1)	-1(1)	1(1)	-1(1)
Co(3)	15(1)	14(1)	12(1)	-1(1)	1(1)	0(1)
P(1)	20(1)	17(1)	16(1)	-2(1)	1(1)	-4(1)
P(2)	22(1)	18(1)	14(1)	2(1)	2(1)	-4(1)
P(3)	18(1)	20(1)	14(1)	-2(1)	-1(1)	0(1)
P(4)	24(1)	13(1)	17(1)	0(1)	6(1)	1(1)
S(1)	26(1)	14(1)	15(1)	1(1)	6(1)	-1(1)
S(2)	15(1)	12(1)	13(1)	-1(1)	1(1)	-2(1)
S(3)	17(1)	30(1)	14(1)	-4(1)	-2(1)	3(1)
S(4)	14(1)	16(1)	12(1)	-2(1)	0(1)	2(1)
C(11)	33(2)	19(2)	19(2)	0(2)	12(2)	1(2)
C(12)	19(2)	14(2)	21(2)	4(2)	2(2)	4(2)
C(13)	20(2)	15(2)	16(2)	0(2)	0(2)	4(2)
C(14)	28(2)	9(2)	16(2)	-2(2)	2(2)	1(2)
C(15)	22(2)	32(2)	29(3)	6(2)	8(2)	5(2)
C(16)	17(2)	27(2)	21(2)	2(2)	-4(2)	5(2)
C(17)	48(3)	46(3)	17(3)	0(2)	-10(2)	-19(2)
C(18)	28(2)	22(2)	36(3)	-3(2)	5(2)	-10(2)
C(19)	20(2)	25(2)	46(3)	-3(2)	5(2)	-4(2)
C(21)	57(3)	27(2)	23(3)	-3(2)	0(2)	-21(2)
C(22)	36(3)	25(2)	12(2)	0(2)	-1(2)	-16(2)
C(23)	25(2)	20(2)	12(2)	2(2)	4(2)	-3(2)
C(24)	16(2)	22(2)	13(2)	-4(2)	1(2)	-6(2)
C(25)	33(3)	44(3)	28(3)	-10(2)	6(2)	-21(2)
C(26)	34(2)	16(2)	25(2)	3(2)	-7(2)	-1(2)

C(27)	27(2)	23(2)	25(2)	12(2)	-2(2)	1(2)
C(28)	30(2)	20(2)	28(3)	6(2)	11(2)	-4(2)
C(29)	52(3)	34(2)	16(2)	4(2)	11(2)	-11(2)
C(31)	18(2)	27(2)	13(2)	-2(2)	6(2)	-1(2)
C(32)	22(2)	24(2)	17(2)	3(2)	6(2)	-9(2)
C(33)	14(2)	19(2)	21(2)	0(2)	4(2)	-5(2)
C(34)	12(2)	20(2)	18(2)	-2(2)	4(2)	2(2)
C(35)	41(3)	27(2)	19(2)	0(2)	10(2)	-11(2)
C(36)	28(2)	19(2)	27(2)	-2(2)	6(2)	-11(2)
C(37)	35(2)	32(2)	20(2)	2(2)	-2(2)	14(2)
C(38)	25(2)	25(2)	16(2)	-1(2)	2(2)	0(2)
C(39)	20(2)	40(2)	22(2)	-10(2)	2(2)	-3(2)
C(41)	39(3)	51(3)	68(4)	15(3)	3(3)	28(2)
C(42)	33(3)	36(3)	26(3)	1(2)	2(2)	16(2)
C(43)	24(2)	28(2)	10(2)	-1(2)	-2(2)	8(2)
C(44)	22(2)	20(2)	11(2)	-4(2)	-1(2)	3(2)
C(45)	55(3)	27(2)	46(3)	5(2)	2(2)	22(2)
C(46)	17(2)	40(2)	25(2)	-5(2)	0(2)	4(2)
C(47)	37(2)	18(2)	27(3)	1(2)	11(2)	-3(2)
C(48)	33(2)	24(2)	32(3)	9(2)	8(2)	9(2)
C(49)	46(3)	17(2)	27(2)	-2(2)	15(2)	-1(2)
O(1)	34(4)	48(5)	26(5)	5(3)	7(3)	2(4)
C(51)	33(6)	50(8)	21(7)	0(5)	-6(5)	9(5)
O(1')	69(6)	89(7)	41(6)	-11(5)	8(5)	35(6)
C(51')	38(7)	32(7)	77(11)	-2(6)	-2(8)	-1(5)
C(52)	62(4)	60(3)	38(3)	7(3)	15(3)	17(3)
C(53)	62(4)	84(4)	84(5)	43(4)	34(4)	53(3)
C(54)	84(4)	58(3)	37(3)	14(3)	32(3)	36(3)

Table A-3.6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for Compound 3.

	x	y	z	U(eq)
H(15A)	9857	1187	4820	41
H(15B)	9614	871	3919	41
H(15C)	10205	498	4714	41
H(16A)	9594	570	6529	35
H(16B)	8794	1078	6517	35
H(16C)	9576	1194	6008	35
H(17A)	4926	434	2708	61
H(17B)	5968	293	2610	61
H(17C)	5610	991	2613	61
H(18A)	5897	-220	4840	44
H(18B)	6198	-466	4034	44
H(18C)	5122	-277	3968	44
H(19A)	4494	838	4003	47
H(19B)	5101	1459	4059	47
H(19C)	5209	1032	4866	47
H(21A)	8010	4091	5783	45
H(21B)	9167	4153	6122	45
H(24A)	8608	2122	5751	21
H(25A)	10149	3324	6290	53
H(25B)	9770	2767	5660	53
H(25C)	9700	2725	6606	53
H(26A)	6423	2866	5166	41
H(26B)	6887	3470	4876	41
H(26C)	6781	3418	5811	41
H(27A)	6555	2422	3737	40
H(27B)	6003	1952	3037	40
H(27C)	6698	2458	2813	40

H(28A)	8536	2425	3235	38
H(28B)	9164	1952	3887	38
H(28C)	8524	2454	4197	38
H(29A)	7615	1694	2130	51
H(29B)	7131	1060	2299	51
H(29C)	8258	1130	2574	51
H(35A)	5801	921	10080	43
H(35B)	6722	1319	10499	43
H(35C)	6789	769	9872	43
H(36A)	6685	508	8596	37
H(36B)	6190	658	7641	37
H(36C)	5562	439	8253	37
H(37A)	9042	1147	9849	46
H(37B)	8348	1136	10457	46
H(37C)	9342	1487	10733	46
H(38A)	8745	2508	11126	34
H(38B)	7677	2269	10961	34
H(38C)	7898	2913	10575	34
H(39A)	9103	2932	9474	42
H(39B)	9462	2308	9139	42
H(39C)	9792	2477	10109	42
H(41A)	11174	544	8476	66
H(41B)	11035	-162	8793	66
H(44A)	8190	728	8370	22
H(45A)	9610	-524	8923	67
H(45B)	8709	-216	8299	67
H(45C)	9012	-8	9256	67
H(46A)	9733	1824	7911	42
H(46B)	10399	1301	7678	42
H(46C)	10594	1547	8616	42
H(47A)	7594	3015	7164	40
H(47B)	8372	3202	7994	40
H(47C)	7610	3700	7530	40

H(48A)	5848	3715	7484	44
H(48B)	5301	3242	7939	44
H(48C)	5628	3028	7131	44
H(49A)	7766	3590	9448	43
H(49B)	6666	3577	9434	43
H(49C)	7038	4031	8823	43
H(51A)	9078	3741	3535	44
H(51B)	8502	3634	4223	44
H(51C)	9048	4198	2977	63
H(51D)	8768	3688	3572	63
H(52A)	9187	4637	4376	79
H(52B)	8058	4700	4143	79
H(52C)	8625	4809	3444	79
H(53A)	7987	4083	2041	89
H(53B)	8123	3351	2080	89
H(54A)	6478	3239	1704	85
H(54B)	6869	3585	1006	85
H(54C)	6381	3973	1607	85
H(11A)	7850(20)	-146(12)	4080(20)	21(10)
H(11B)	8200(20)	293(15)	3449(17)	28(11)
H(14)	7530(20)	-75(14)	5220(19)	11(9)
H(31A)	5540(20)	2419(15)	9080(20)	36(12)
H(31B)	6220(20)	2304(14)	9969(16)	23(10)
H(34)	5290(20)	2084(14)	7910(20)	15(10)

Table A-3.7. Torsion angles [°] for Compound 3.

C(11)-Co(1)-P(1)-C(19)	177.05(19)	C(12)-Co(1)-P(2)-C(29)	65.68(19)
C(12)-Co(1)-P(1)-C(19)	160.4(2)	C(13)-Co(1)-P(2)-C(29)	95.5(2)
C(13)-Co(1)-P(1)-C(19)	106.5(2)	C(14)-Co(1)-P(2)-C(29)	90.3(6)
C(14)-Co(1)-P(1)-C(19)	96.50(18)	P(1)-Co(1)-P(2)-C(29)	-71.24(16)
P(2)-Co(1)-P(1)-C(19)	-86.85(16)	S(2)-Co(1)-P(2)-C(29)	-167.11(16)
S(2)-Co(1)-P(1)-C(19)	3.38(15)	C(31)-Co(2)-P(3)-C(39)	-139.66(17)
C(11)-Co(1)-P(1)-C(18)	56.37(19)	C(32)-Co(2)-P(3)-C(39)	178.65(17)
C(12)-Co(1)-P(1)-C(18)	39.7(2)	C(33)-Co(2)-P(3)-C(39)	148.64(18)
C(13)-Co(1)-P(1)-C(18)	-14.2(2)	C(34)-Co(2)-P(3)-C(39)	151.5(5)
C(14)-Co(1)-P(1)-C(18)	-24.18(18)	P(4)-Co(2)-P(3)-C(39)	-45.76(14)
P(2)-Co(1)-P(1)-C(18)	152.47(15)	S(4)-Co(2)-P(3)-C(39)	48.67(14)
S(2)-Co(1)-P(1)-C(18)	-117.30(15)	C(31)-Co(2)-P(3)-C(37)	98.77(19)
C(11)-Co(1)-P(1)-C(17)	-63.2(2)	C(32)-Co(2)-P(3)-C(37)	57.08(19)
C(12)-Co(1)-P(1)-C(17)	-79.8(2)	C(33)-Co(2)-P(3)-C(37)	27.1(2)
C(13)-Co(1)-P(1)-C(17)	-133.7(2)	C(34)-Co(2)-P(3)-C(37)	29.9(5)
C(14)-Co(1)-P(1)-C(17)	-143.71(19)	P(4)-Co(2)-P(3)-C(37)	-167.33(16)
P(2)-Co(1)-P(1)-C(17)	32.94(17)	S(4)-Co(2)-P(3)-C(37)	-72.90(16)
S(2)-Co(1)-P(1)-C(17)	123.17(17)	C(31)-Co(2)-P(3)-C(38)	-22.06(17)
C(11)-Co(1)-P(2)-C(28)	-96.33(18)	C(32)-Co(2)-P(3)-C(38)	-63.75(17)
C(12)-Co(1)-P(2)-C(28)	-54.68(17)	C(33)-Co(2)-P(3)-C(38)	-93.76(18)
C(13)-Co(1)-P(2)-C(28)	-24.9(2)	C(34)-Co(2)-P(3)-C(38)	-90.9(5)
C(14)-Co(1)-P(2)-C(28)	-30.1(6)	P(4)-Co(2)-P(3)-C(38)	71.84(14)
P(1)-Co(1)-P(2)-C(28)	168.39(14)	S(4)-Co(2)-P(3)-C(38)	166.27(13)
S(2)-Co(1)-P(2)-C(28)	72.53(14)	C(31)-Co(2)-P(4)-C(47)	174.89(19)
C(11)-Co(1)-P(2)-C(27)	144.52(18)	C(32)-Co(2)-P(4)-C(47)	-171.3(2)
C(12)-Co(1)-P(2)-C(27)	-173.83(17)	C(33)-Co(2)-P(4)-C(47)	-116.0(2)
C(13)-Co(1)-P(2)-C(27)	-144.06(18)	C(34)-Co(2)-P(4)-C(47)	-104.41(18)
C(14)-Co(1)-P(2)-C(27)	-149.2(6)	P(3)-Co(2)-P(4)-C(47)	79.61(15)
P(1)-Co(1)-P(2)-C(27)	49.24(15)	S(4)-Co(2)-P(4)-C(47)	-11.79(15)
S(2)-Co(1)-P(2)-C(27)	-46.63(14)	C(31)-Co(2)-P(4)-C(48)	-66.11(19)
C(11)-Co(1)-P(2)-C(29)	24.03(19)	C(32)-Co(2)-P(4)-C(48)	-52.3(2)

C(33)-Co(2)-P(4)-C(48)	3.0(2)
C(34)-Co(2)-P(4)-C(48)	14.59(18)
P(3)-Co(2)-P(4)-C(48)	-161.39(15)
S(4)-Co(2)-P(4)-C(48)	107.21(15)
C(31)-Co(2)-P(4)-C(49)	52.33(19)
C(32)-Co(2)-P(4)-C(49)	66.2(2)
C(33)-Co(2)-P(4)-C(49)	121.4(2)
C(34)-Co(2)-P(4)-C(49)	133.03(18)
P(3)-Co(2)-P(4)-C(49)	-42.95(15)
S(4)-Co(2)-P(4)-C(49)	-134.35(15)
S(3)-Co(3)-S(1)-C(14)	130.50(13)
S(2)-Co(3)-S(1)-C(14)	17.68(13)
S(4)-Co(3)-S(1)-C(14)	-111.92(13)
C(11)-Co(1)-S(2)-C(24)	49.4(6)
C(12)-Co(1)-S(2)-C(24)	38.31(18)
C(13)-Co(1)-S(2)-C(24)	66.70(16)
C(14)-Co(1)-S(2)-C(24)	107.05(16)
P(1)-Co(1)-S(2)-C(24)	-162.55(13)
P(2)-Co(1)-S(2)-C(24)	-62.56(13)
C(11)-Co(1)-S(2)-Co(3)	-63.2(6)
C(12)-Co(1)-S(2)-Co(3)	-74.38(13)
C(13)-Co(1)-S(2)-Co(3)	-46.00(10)
C(14)-Co(1)-S(2)-Co(3)	-5.64(11)
P(1)-Co(1)-S(2)-Co(3)	84.75(4)
P(2)-Co(1)-S(2)-Co(3)	-175.25(4)
S(3)-Co(3)-S(2)-C(24)	108.23(12)
S(1)-Co(3)-S(2)-C(24)	-124.98(12)
S(4)-Co(3)-S(2)-C(24)	1.15(13)
S(3)-Co(3)-S(2)-Co(1)	-132.77(4)
S(1)-Co(3)-S(2)-Co(1)	-5.98(5)
S(4)-Co(3)-S(2)-Co(1)	120.15(4)
S(1)-Co(3)-S(3)-C(34)	102.03(13)
S(2)-Co(3)-S(3)-C(34)	-149.25(13)
S(4)-Co(3)-S(3)-C(34)	-24.75(13)
C(31)-Co(2)-S(4)-C(44)	-66.1(7)
C(32)-Co(2)-S(4)-C(44)	-42.97(19)
C(33)-Co(2)-S(4)-C(44)	-70.13(16)
C(34)-Co(2)-S(4)-C(44)	-110.01(16)
P(4)-Co(2)-S(4)-C(44)	156.55(13)
P(3)-Co(2)-S(4)-C(44)	56.67(13)
C(31)-Co(2)-S(4)-Co(3)	42.5(7)
C(32)-Co(2)-S(4)-Co(3)	65.60(14)
C(33)-Co(2)-S(4)-Co(3)	38.44(11)
C(34)-Co(2)-S(4)-Co(3)	-1.44(10)
P(4)-Co(2)-S(4)-Co(3)	-94.88(4)
P(3)-Co(2)-S(4)-Co(3)	165.24(4)
S(3)-Co(3)-S(4)-C(44)	131.64(13)
S(1)-Co(3)-S(4)-C(44)	0.11(13)
S(2)-Co(3)-S(4)-C(44)	-116.67(13)
S(3)-Co(3)-S(4)-Co(2)	14.80(5)
S(1)-Co(3)-S(4)-Co(2)	-116.73(4)
S(2)-Co(3)-S(4)-Co(2)	126.49(4)
C(13)-Co(1)-C(11)-C(12)	-31.5(2)
C(14)-Co(1)-C(11)-C(12)	-72.2(2)
P(1)-Co(1)-C(11)-C(12)	-161.59(19)
P(2)-Co(1)-C(11)-C(12)	97.9(2)
S(2)-Co(1)-C(11)-C(12)	-13.5(7)
Co(1)-C(11)-C(12)-C(13)	54.7(3)
Co(1)-C(11)-C(12)-C(15)	-125.5(3)
C(11)-Co(1)-C(12)-C(13)	-129.3(3)
C(14)-Co(1)-C(12)-C(13)	-32.1(2)
P(1)-Co(1)-C(12)-C(13)	-103.7(2)
P(2)-Co(1)-C(12)-C(13)	143.19(18)
S(2)-Co(1)-C(12)-C(13)	47.3(2)
C(13)-Co(1)-C(12)-C(11)	129.3(3)
C(14)-Co(1)-C(12)-C(11)	97.1(2)

P(1)-Co(1)-C(12)-C(11)	25.5(3)
P(2)-Co(1)-C(12)-C(11)	-87.6(2)
S(2)-Co(1)-C(12)-C(11)	176.53(18)
C(11)-Co(1)-C(12)-C(15)	112.2(4)
C(13)-Co(1)-C(12)-C(15)	-118.5(4)
C(14)-Co(1)-C(12)-C(15)	-150.7(4)
P(1)-Co(1)-C(12)-C(15)	137.7(3)
P(2)-Co(1)-C(12)-C(15)	24.6(4)
S(2)-Co(1)-C(12)-C(15)	-71.3(4)
C(11)-C(12)-C(13)-C(14)	1.0(5)
C(15)-C(12)-C(13)-C(14)	-178.9(3)
Co(1)-C(12)-C(13)-C(14)	54.1(3)
C(11)-C(12)-C(13)-C(16)	-178.0(3)
C(15)-C(12)-C(13)-C(16)	2.2(5)
Co(1)-C(12)-C(13)-C(16)	-124.8(3)
C(11)-C(12)-C(13)-Co(1)	-53.2(3)
C(15)-C(12)-C(13)-Co(1)	127.0(3)
C(11)-Co(1)-C(13)-C(12)	32.6(2)
C(14)-Co(1)-C(13)-C(12)	128.9(3)
P(1)-Co(1)-C(13)-C(12)	113.32(19)
P(2)-Co(1)-C(13)-C(12)	-49.6(2)
S(2)-Co(1)-C(13)-C(12)	-143.72(18)
C(11)-Co(1)-C(13)-C(14)	-96.3(2)
C(12)-Co(1)-C(13)-C(14)	-128.9(3)
P(1)-Co(1)-C(13)-C(14)	-15.6(2)
P(2)-Co(1)-C(13)-C(14)	-178.53(16)
S(2)-Co(1)-C(13)-C(14)	87.39(19)
C(11)-Co(1)-C(13)-C(16)	148.0(4)
C(12)-Co(1)-C(13)-C(16)	115.4(4)
C(14)-Co(1)-C(13)-C(16)	-115.7(4)
P(1)-Co(1)-C(13)-C(16)	-131.3(3)
P(2)-Co(1)-C(13)-C(16)	65.7(4)
S(2)-Co(1)-C(13)-C(16)	-28.3(3)
C(12)-C(13)-C(14)-S(1)	-174.3(3)
C(16)-C(13)-C(14)-S(1)	4.7(5)
Co(1)-C(13)-C(14)-S(1)	-121.0(3)
C(12)-C(13)-C(14)-Co(1)	-53.3(3)
C(16)-C(13)-C(14)-Co(1)	125.6(3)
Co(3)-S(1)-C(14)-C(13)	59.8(3)
Co(3)-S(1)-C(14)-Co(1)	-29.3(3)
C(11)-Co(1)-C(14)-C(13)	73.7(2)
C(12)-Co(1)-C(14)-C(13)	31.9(2)
P(1)-Co(1)-C(14)-C(13)	168.02(19)
P(2)-Co(1)-C(14)-C(13)	6.2(7)
S(2)-Co(1)-C(14)-C(13)	-96.05(19)
C(11)-Co(1)-C(14)-S(1)	-167.4(3)
C(12)-Co(1)-C(14)-S(1)	150.8(3)
C(13)-Co(1)-C(14)-S(1)	118.9(3)
P(1)-Co(1)-C(14)-S(1)	-73.1(2)
P(2)-Co(1)-C(14)-S(1)	125.1(5)
S(2)-Co(1)-C(14)-S(1)	22.8(2)
C(21)-C(22)-C(23)-C(24)	-178.4(4)
C(25)-C(22)-C(23)-C(24)	1.6(5)
C(21)-C(22)-C(23)-C(26)	1.5(5)
C(25)-C(22)-C(23)-C(26)	-178.6(3)
C(22)-C(23)-C(24)-S(2)	178.8(3)
C(26)-C(23)-C(24)-S(2)	-1.0(5)
Co(1)-S(2)-C(24)-C(23)	139.5(3)
Co(3)-S(2)-C(24)-C(23)	-102.3(3)
C(33)-Co(2)-C(31)-C(32)	31.4(2)
C(34)-Co(2)-C(31)-C(32)	71.8(2)
P(4)-Co(2)-C(31)-C(32)	164.6(2)
P(3)-Co(2)-C(31)-C(32)	-95.3(2)
S(4)-Co(2)-C(31)-C(32)	27.2(8)
Co(2)-C(31)-C(32)-C(33)	-54.4(3)
Co(2)-C(31)-C(32)-C(35)	127.0(3)

C(31)-Co(2)-C(32)-C(33)	129.6(3)
C(34)-Co(2)-C(32)-C(33)	32.2(2)
P(4)-Co(2)-C(32)-C(33)	108.4(2)
P(3)-Co(2)-C(32)-C(33)	-141.28(19)
S(4)-Co(2)-C(32)-C(33)	-44.6(2)
C(33)-Co(2)-C(32)-C(31)	-129.6(3)
C(34)-Co(2)-C(32)-C(31)	-97.4(2)
P(4)-Co(2)-C(32)-C(31)	-21.1(3)
P(3)-Co(2)-C(32)-C(31)	89.2(2)
S(4)-Co(2)-C(32)-C(31)	-174.17(18)
C(31)-Co(2)-C(32)-C(35)	-113.5(4)
C(33)-Co(2)-C(32)-C(35)	116.9(4)
C(34)-Co(2)-C(32)-C(35)	149.1(4)
P(4)-Co(2)-C(32)-C(35)	-134.6(3)
P(3)-Co(2)-C(32)-C(35)	-24.4(4)
S(4)-Co(2)-C(32)-C(35)	72.3(4)
C(31)-C(32)-C(33)-C(34)	-2.3(5)
C(35)-C(32)-C(33)-C(34)	176.3(3)
Co(2)-C(32)-C(33)-C(34)	-55.3(3)
C(31)-C(32)-C(33)-C(36)	177.2(3)
C(35)-C(32)-C(33)-C(36)	-4.2(5)
Co(2)-C(32)-C(33)-C(36)	124.2(3)
C(31)-C(32)-C(33)-Co(2)	53.0(3)
C(35)-C(32)-C(33)-Co(2)	-128.4(3)
C(31)-Co(2)-C(33)-C(32)	-32.4(2)
C(34)-Co(2)-C(33)-C(32)	-128.6(3)
P(4)-Co(2)-C(33)-C(32)	-110.4(2)
P(3)-Co(2)-C(33)-C(32)	50.4(2)
S(4)-Co(2)-C(33)-C(32)	146.87(19)
C(31)-Co(2)-C(33)-C(34)	96.2(2)
C(32)-Co(2)-C(33)-C(34)	128.6(3)
P(4)-Co(2)-C(33)-C(34)	18.2(3)
P(3)-Co(2)-C(33)-C(34)	178.96(17)
S(4)-Co(2)-C(33)-C(34)	-84.6(2)
C(31)-Co(2)-C(33)-C(36)	-147.2(4)
C(32)-Co(2)-C(33)-C(36)	-114.8(4)
C(34)-Co(2)-C(33)-C(36)	116.7(4)
P(4)-Co(2)-C(33)-C(36)	134.8(3)
P(3)-Co(2)-C(33)-C(36)	-64.4(4)
S(4)-Co(2)-C(33)-C(36)	32.1(3)
C(32)-C(33)-C(34)-S(3)	174.5(3)
C(36)-C(33)-C(34)-S(3)	-5.0(5)
Co(2)-C(33)-C(34)-S(3)	120.5(3)
C(32)-C(33)-C(34)-Co(2)	54.0(3)
C(36)-C(33)-C(34)-Co(2)	-125.5(3)
Co(3)-S(3)-C(34)-C(33)	-55.8(3)
Co(3)-S(3)-C(34)-Co(2)	32.7(2)
C(31)-Co(2)-C(34)-C(33)	-74.0(2)
C(32)-Co(2)-C(34)-C(33)	-32.2(2)
P(4)-Co(2)-C(34)-C(33)	-166.55(19)
P(3)-Co(2)-C(34)-C(33)	-3.5(6)
S(4)-Co(2)-C(34)-C(33)	99.05(19)
C(31)-Co(2)-C(34)-S(3)	166.8(3)
C(32)-Co(2)-C(34)-S(3)	-151.4(3)
C(33)-Co(2)-C(34)-S(3)	-119.2(3)
P(4)-Co(2)-C(34)-S(3)	74.2(2)
P(3)-Co(2)-C(34)-S(3)	-122.7(4)
S(4)-Co(2)-C(34)-S(3)	-20.1(2)
C(41)-C(42)-C(43)-C(44)	176.6(4)
C(45)-C(42)-C(43)-C(44)	-2.7(6)
C(41)-C(42)-C(43)-C(46)	-2.2(6)
C(45)-C(42)-C(43)-C(46)	178.6(4)
C(42)-C(43)-C(44)-S(4)	-176.0(3)
C(46)-C(43)-C(44)-S(4)	2.7(5)
Co(2)-S(4)-C(44)-C(43)	-131.5(3)
Co(3)-S(4)-C(44)-C(43)	112.5(3)

C(53)-O(1)-C(51)-C(52)	89.7(10)	C(51')-O(1')-C(53)-C(54)	179.9(8)
C(53)-O(1')-C(51')-C(52)	172.4(8)	C(51')-O(1')-C(53)-O(1)	78.8(10)
O(1')-C(51')-C(52)-C(51)	97.1(16)	C(51)-O(1)-C(53)-O(1')	-72.9(11)
O(1)-C(51)-C(52)-C(51')	-64.7(12)	C(51)-O(1)-C(53)-C(54)	-169.4(7)

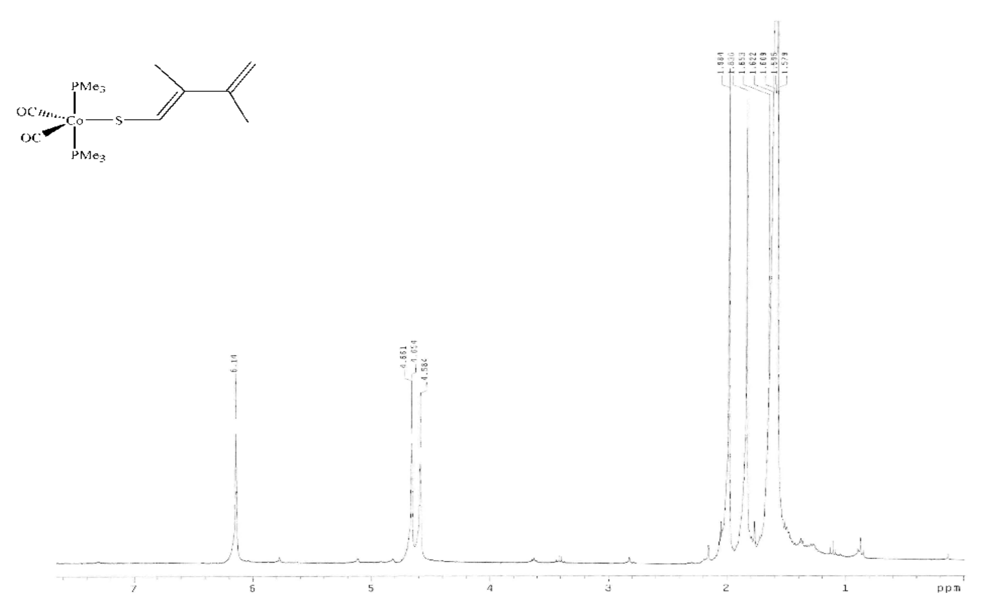

Figure A-16. ^{1}H NMR Spectrum of Compound *trans*-4.

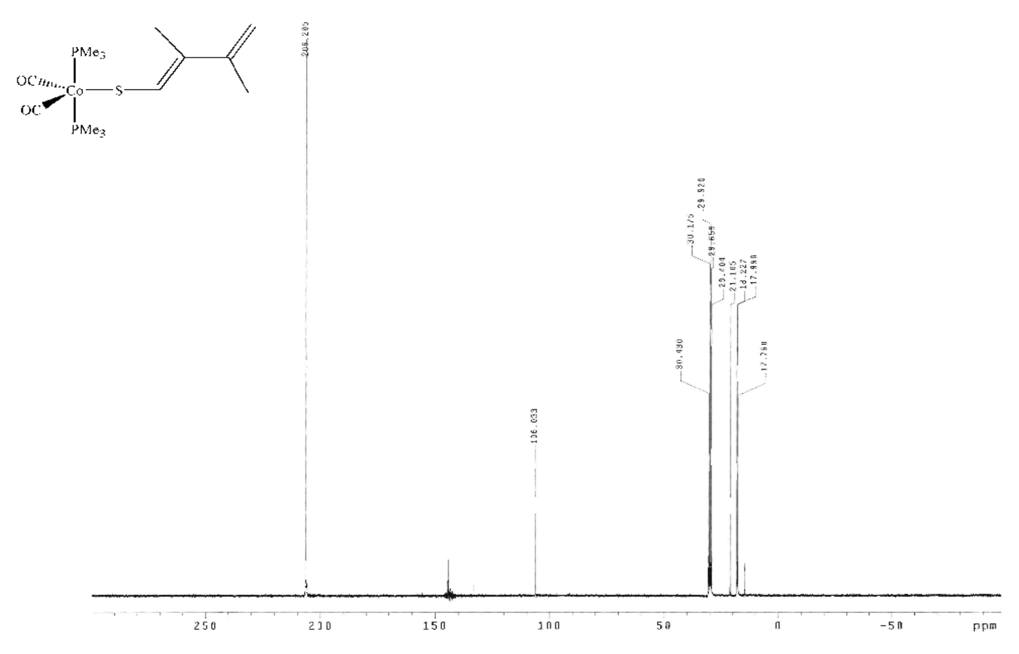

Figure A-17. ^{13}C NMR Spectrum of Compound *trans*-4.

Table A-4.1. Crystal data and structure refinement for Compound *trans*-4.

Empirical formula	$C_{14} H_{27} Co O_2 P_2 S$	
Formula weight	380.29	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 13.6591(11) Å	α= 90°.
	b = 11.6484(9) Å	β= 115.651(3)°.
	c = 13.3723(10) Å	γ = 90°.
Volume	1917.9(3) $Å^3$	
Z	4	
Density (calculated)	1.317 Mg/m^3	
Absorption coefficient	1.169 mm^{-1}	
F(000)	800	
Crystal size	0.32 x 0.31 x 0.24 mm^3	
Theta range for data collection	1.65 to 38.03°.	
Index ranges	$-23\leq h\leq 23$, $-20\leq k\leq 14$, $-23\leq l\leq 23$	
Reflections collected	48979	
Independent reflections	10361 [R(int) = 0.025]	
Completeness to theta = 25.00°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7667 and 0.7082	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10361 / 1 / 201	
Goodness-of-fit on F^2	1.024	
Final R indices [I>2sigma(I)]	R1 = 0.0240, wR2 = 0.0579	
R indices (all data)	R1 = 0.0350, wR2 = 0.0629	
Largest diff. peak and hole	0.598 and -0.327 $e.Å^{-3}$	

Table A-4.2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for Compound *trans*-4. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Co(1)	7197(1)	1187(1)	7505(1)	13(1)
S(1)	6739(1)	-592(1)	6659(1)	17(1)
P(1)	5721(1)	1102(1)	7753(1)	16(1)
P(2)	8632(1)	1140(1)	7188(1)	16(1)
O(1)	8514(1)	1308(1)	9878(1)	36(1)
O(2)	6427(1)	3245(1)	6175(1)	29(1)
C(1)	8265(1)	-4670(1)	8114(1)	23(1)
C(2)	8223(1)	-3543(1)	8303(1)	17(1)
C(3)	7612(1)	-2736(1)	7407(1)	16(1)
C(4)	7474(1)	-1629(1)	7631(1)	16(1)
C(5)	8821(1)	-3092(1)	9466(1)	24(1)
C(6)	7143(1)	-3174(1)	6236(1)	24(1)
C(7)	7993(1)	1228(1)	8935(1)	20(1)
C(8)	6713(1)	2401(1)	6668(1)	19(1)
C(11)	5716(1)	-9(1)	8697(1)	24(1)
C(12)	4478(1)	891(1)	6508(1)	30(1)
C(13)	5469(1)	2397(1)	8354(1)	26(1)
C(21)	9409(1)	2459(1)	7513(1)	22(1)
C(22)	8401(1)	878(1)	5771(1)	31(1)
C(23)	9638(1)	91(1)	7988(1)	34(1)

Table A-4.3. Bond lengths [Å] for Compound *trans*-4.

Co(1)-C(7)	1.7436(8)	C(5)-H(5B)	0.9800
Co(1)-C(8)	1.7460(8)	C(5)-H(5C)	0.9800
Co(1)-P(2)	2.1784(3)	C(6)-H(6A)	0.9800
Co(1)-P(1)	2.1821(3)	C(6)-H(6B)	0.9800
Co(1)-S(1)	2.3138(3)	C(6)-H(6C)	0.9800
S(1)-C(4)	1.7399(8)	C(11)-H(11A)	0.9800
P(1)-C(12)	1.8068(9)	C(11)-H(11B)	0.9800
P(1)-C(11)	1.8107(8)	C(11)-H(11C)	0.9800
P(1)-C(13)	1.8109(9)	C(12)-H(12A)	0.9800
P(2)-C(23)	1.8038(9)	C(12)-H(12B)	0.9800
P(2)-C(22)	1.8067(9)	C(12)-H(12C)	0.9800
P(2)-C(21)	1.8097(8)	C(13)-H(13A)	0.9800
O(1)-C(7)	1.1521(10)	C(13)-H(13B)	0.9800
O(2)-C(8)	1.1537(9)	C(13)-H(13C)	0.9800
C(1)-C(2)	1.3426(11)	C(21)-H(21A)	0.9800
C(1)-H(1A)	0.957(11)	C(21)-H(21B)	0.9800
C(1)-H(1B)	0.959(11)	C(21)-H(21C)	0.9800
C(2)-C(3)	1.4670(10)	C(22)-H(22A)	0.9800
C(2)-C(5)	1.5043(11)	C(22)-H(22B)	0.9800
C(3)-C(4)	1.3544(10)	C(22)-H(22C)	0.9800
C(3)-C(6)	1.5018(10)	C(23)-H(23A)	0.9800
C(4)-H(4)	0.911(10)	C(23)-H(23B)	0.9800
C(5)-H(5A)	0.9800	C(23)-H(23C)	0.9800

Table A-4.4. Bond angles [°] for Compound *trans*-4

C(7)-Co(1)-C(8)	124.34(4)	P(2)-Co(1)-P(1)	175.384(9)
C(7)-Co(1)-P(2)	91.61(3)	C(7)-Co(1)-S(1)	117.98(3)
C(8)-Co(1)-P(2)	91.03(3)	C(8)-Co(1)-S(1)	117.68(3)
C(7)-Co(1)-P(1)	90.77(3)	P(2)-Co(1)-S(1)	87.594(8)
C(8)-Co(1)-P(1)	90.90(3)	P(1)-Co(1)-S(1)	87.797(8)

C(4)-S(1)-Co(1)	108.06(3)
C(12)-P(1)-C(11)	105.04(5)
C(12)-P(1)-C(13)	103.84(5)
C(11)-P(1)-C(13)	103.12(4)
C(12)-P(1)-Co(1)	115.32(3)
C(11)-P(1)-Co(1)	114.88(3)
C(13)-P(1)-Co(1)	113.27(3)
C(23)-P(2)-C(22)	104.48(5)
C(23)-P(2)-C(21)	102.42(4)
C(22)-P(2)-C(21)	102.33(4)
C(23)-P(2)-Co(1)	114.83(3)
C(22)-P(2)-Co(1)	116.45(3)
C(21)-P(2)-Co(1)	114.55(3)
C(2)-C(1)-H(1A)	120.5(8)
C(2)-C(1)-H(1B)	122.2(7)
H(1A)-C(1)-H(1B)	117.3(11)
C(1)-C(2)-C(3)	121.93(7)
C(1)-C(2)-C(5)	119.24(7)
C(3)-C(2)-C(5)	118.83(6)
C(4)-C(3)-C(2)	120.94(7)
C(4)-C(3)-C(6)	121.12(7)
C(2)-C(3)-C(6)	117.93(6)
C(3)-C(4)-S(1)	125.86(6)
C(3)-C(4)-H(4)	119.7(6)
S(1)-C(4)-H(4)	114.4(6)
C(2)-C(5)-H(5A)	109.5
C(2)-C(5)-H(5B)	109.5
H(5A)-C(5)-H(5B)	109.5
C(2)-C(5)-H(5C)	109.5
H(5A)-C(5)-H(5C)	109.5
H(5B)-C(5)-H(5C)	109.5
C(3)-C(6)-H(6A)	109.5
C(3)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5
C(3)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
O(1)-C(7)-Co(1)	176.93(8)
O(2)-C(8)-Co(1)	175.63(8)
P(1)-C(11)-H(11A)	109.5
P(1)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
P(1)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
P(1)-C(12)-H(12A)	109.5
P(1)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
P(1)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
P(1)-C(13)-H(13A)	109.5
P(1)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
P(1)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
P(2)-C(21)-H(21A)	109.5
P(2)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
P(2)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
P(2)-C(22)-H(22A)	109.5
P(2)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5

P(2)-C(22)-H(22C)	109.5	H(23A)-C(23)-H(23B)	109.5
H(22A)-C(22)-H(22C)	109.5	P(2)-C(23)-H(23C)	109.5
H(22B)-C(22)-H(22C)	109.5	H(23A)-C(23)-H(23C)	109.5
P(2)-C(23)-H(23A)	109.5	H(23B)-C(23)-H(23C)	109.5
P(2)-C(23)-H(23B)	109.5		

Table A-4.5. Anisotropic displacement parameters ($Å^2$x 10^3) for Compound *trans*-4. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Co(1)	13(1)	11(1)	14(1)	1(1)	6(1)	2(1)
S(1)	19(1)	13(1)	18(1)	-1(1)	6(1)	-1(1)
P(1)	13(1)	19(1)	16(1)	3(1)	7(1)	2(1)
P(2)	17(1)	11(1)	23(1)	0(1)	12(1)	1(1)
O(1)	30(1)	48(1)	20(1)	-5(1)	2(1)	7(1)
O(2)	38(1)	20(1)	30(1)	10(1)	17(1)	10(1)
C(1)	29(1)	16(1)	30(1)	1(1)	17(1)	2(1)
C(2)	18(1)	15(1)	21(1)	1(1)	11(1)	0(1)
C(3)	16(1)	15(1)	18(1)	-2(1)	9(1)	-1(1)
C(4)	17(1)	14(1)	17(1)	-1(1)	7(1)	-2(1)
C(5)	28(1)	21(1)	20(1)	2(1)	8(1)	1(1)
C(6)	29(1)	22(1)	20(1)	-5(1)	9(1)	3(1)
C(7)	18(1)	21(1)	20(1)	-1(1)	7(1)	3(1)
C(8)	20(1)	17(1)	20(1)	2(1)	11(1)	3(1)
C(11)	27(1)	23(1)	25(1)	4(1)	15(1)	-2(1)
C(12)	15(1)	46(1)	24(1)	2(1)	4(1)	2(1)
C(13)	27(1)	25(1)	32(1)	3(1)	19(1)	9(1)
C(21)	21(1)	18(1)	28(1)	-2(1)	12(1)	-4(1)
C(22)	38(1)	32(1)	34(1)	-14(1)	26(1)	-11(1)
C(23)	24(1)	22(1)	63(1)	16(1)	26(1)	10(1)

Table A-4.6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for Compound *trans*-4.

	x	y	z	U(eq)
H(5A)	9233	-3716	9960	36
H(5B)	8298	-2782	9717	36
H(5C)	9321	-2482	9478	36
H(6A)	6557	-3717	6121	36
H(6B)	7713	-3561	6102	36
H(6C)	6855	-2529	5720	36
H(11A)	6254	174	9451	36
H(11B)	5897	-748	8469	36
H(11C)	4994	-56	8683	36
H(12A)	3864	857	6701	45
H(12B)	4523	171	6152	45
H(12C)	4375	1532	5997	45
H(13A)	5469	3061	7904	39
H(13B)	6041	2492	9111	39
H(13C)	4762	2339	8375	39
H(21A)	9625	2659	8292	33
H(21B)	8964	3077	7036	33
H(21C)	10059	2353	7388	33
H(22A)	9099	858	5728	46
H(22B)	7950	1494	5294	46
H(22C)	8029	141	5522	46
H(23A)	9318	-678	7818	51
H(23B)	9887	249	8780	51
H(23C)	10255	133	7800	51
H(1A)	7885(9)	-4975(11)	7381(9)	30(3)
H(1B)	8661(10)	-5201(10)	8698(9)	28(3)
H(4)	7744(8)	-1388(9)	8349(9)	12(2)

Table A-4.7. Torsion angles [°] for Compound *trans*-4.

C(7)-Co(1)-S(1)-C(4)	-8.79(4)
C(8)-Co(1)-S(1)-C(4)	171.66(4)
P(2)-Co(1)-S(1)-C(4)	81.76(3)
P(1)-Co(1)-S(1)-C(4)	-98.49(3)
C(7)-Co(1)-P(1)-C(12)	-174.13(5)
C(8)-Co(1)-P(1)-C(12)	61.51(5)
P(2)-Co(1)-P(1)-C(12)	-53.15(12)
S(1)-Co(1)-P(1)-C(12)	-56.15(4)
C(7)-Co(1)-P(1)-C(11)	-51.72(4)
C(8)-Co(1)-P(1)-C(11)	-176.08(4)
P(2)-Co(1)-P(1)-C(11)	69.26(11)
S(1)-Co(1)-P(1)-C(11)	66.25(3)
C(7)-Co(1)-P(1)-C(13)	66.43(4)
C(8)-Co(1)-P(1)-C(13)	-57.93(4)
P(2)-Co(1)-P(1)-C(13)	-172.59(11)
S(1)-Co(1)-P(1)-C(13)	-175.59(3)
C(7)-Co(1)-P(2)-C(23)	48.85(5)
C(8)-Co(1)-P(2)-C(23)	173.25(5)
P(1)-Co(1)-P(2)-C(23)	-72.10(12)
S(1)-Co(1)-P(2)-C(23)	-69.09(5)
C(7)-Co(1)-P(2)-C(22)	171.38(5)
C(8)-Co(1)-P(2)-C(22)	-64.22(5)
P(1)-Co(1)-P(2)-C(22)	50.43(12)
S(1)-Co(1)-P(2)-C(22)	53.44(4)
C(7)-Co(1)-P(2)-C(21)	-69.31(4)
C(8)-Co(1)-P(2)-C(21)	55.08(4)
P(1)-Co(1)-P(2)-C(21)	169.74(10)
S(1)-Co(1)-P(2)-C(21)	172.75(3)
C(1)-C(2)-C(3)-C(4)	172.22(7)
C(5)-C(2)-C(3)-C(4)	-7.87(10)
C(1)-C(2)-C(3)-C(6)	-7.77(11)
C(5)-C(2)-C(3)-C(6)	172.13(7)
C(2)-C(3)-C(4)-S(1)	-178.02(5)
C(6)-C(3)-C(4)-S(1)	1.98(11)
Co(1)-S(1)-C(4)-C(3)	-165.16(6)
C(8)-Co(1)-C(7)-O(1)	3.8(15)
P(2)-Co(1)-C(7)-O(1)	96.2(14)
P(1)-Co(1)-C(7)-O(1)	-87.8(14)
S(1)-Co(1)-C(7)-O(1)	-176(92)
C(7)-Co(1)-C(8)-O(2)	0.5(9)
P(2)-Co(1)-C(8)-O(2)	-92.2(9)
P(1)-Co(1)-C(8)-O(2)	92.0(9)
S(1)-Co(1)-C(8)-O(2)	-180(100)

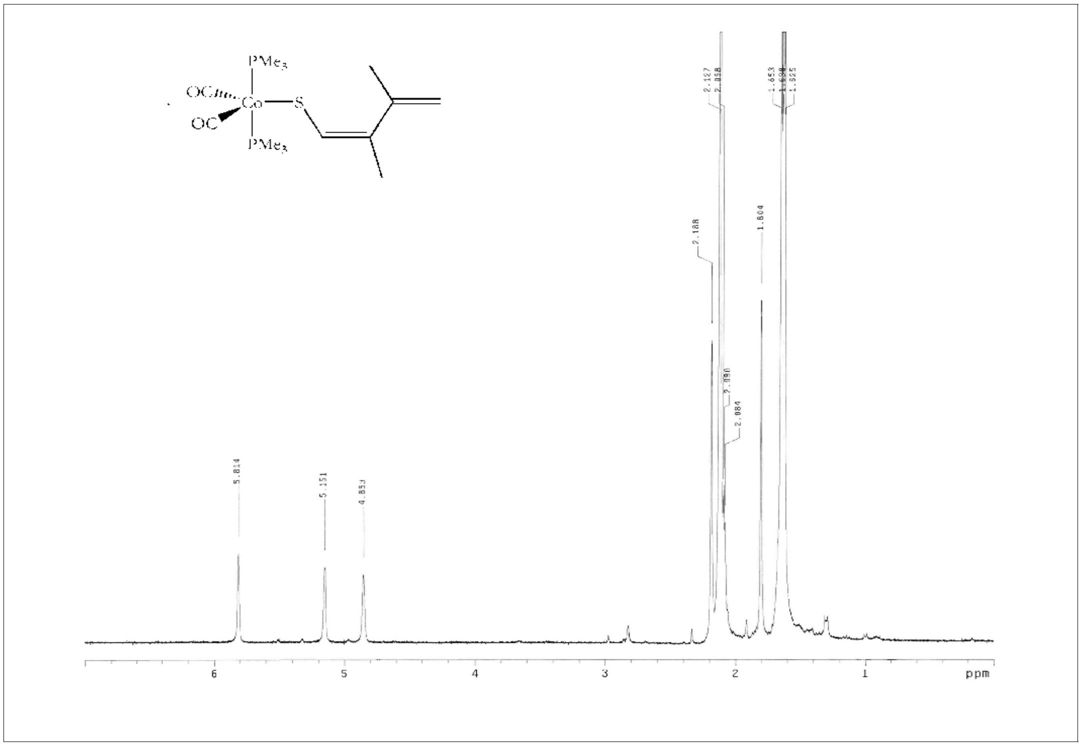

Figure A-18. ^{1}H NMR Spectrum of Compound *cis*-4.

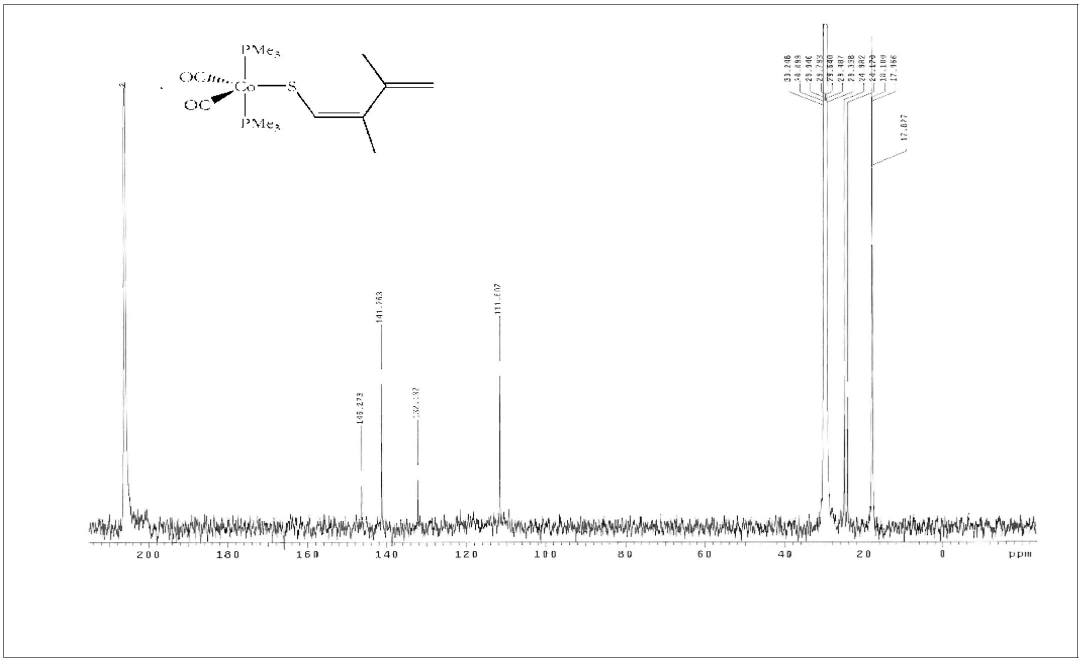

Figure A-19. ^{13}C NMR Spectrum of Compound *cis*-4.

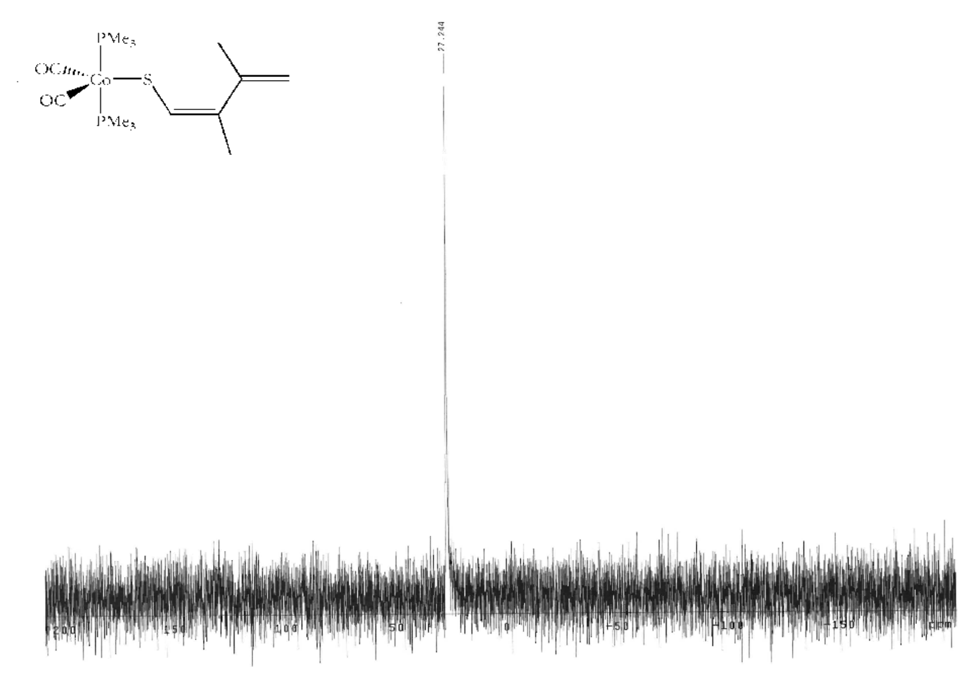

Figure A-20. ^{31}**P NMR Spectrum of Compound** ***cis*****-4.**

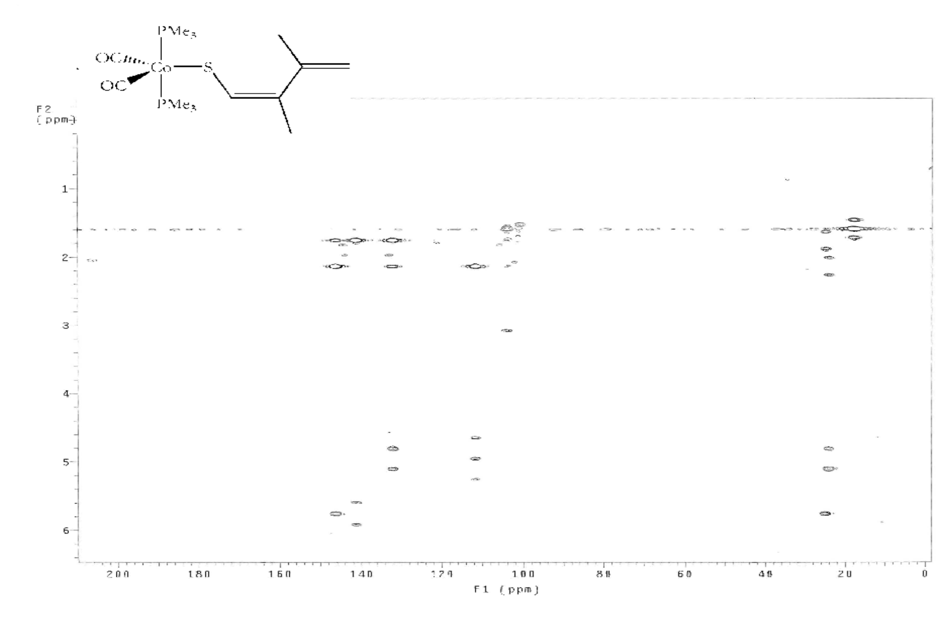

Figure A-21. HMBC Spectrum of Compound ***cis*****-4.**

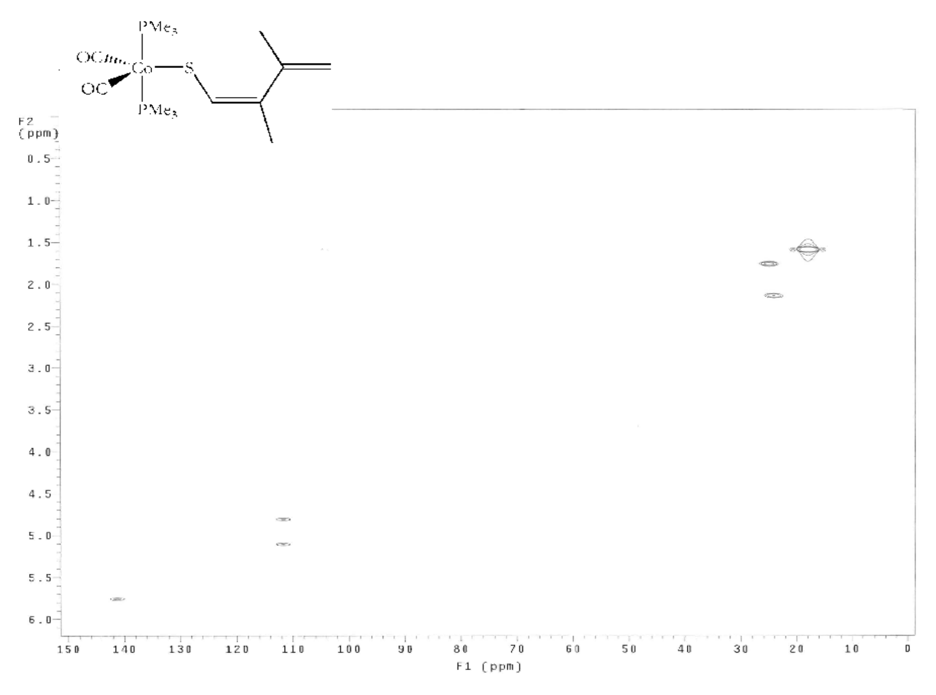

Figure A-22. HMQC Spectrum of Compound *cis*-4.

Table A-5.1. Crystal data and structure refinement for Compound *cis*-4.

Empirical formula	$C_{14} H_{27} Co O_2 P_2 S$	
Formula weight	380.29	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 8.947(4) Å	α= 90°.
	b = 12.078(4) Å	β= 97.440(17)°.
	c = 17.630(7) Å	γ = 90°.
Volume	1889.0(12) $Å^3$	
Z	4	
Density (calculated)	1.337 Mg/m^3	
Absorption coefficient	1.187 mm^{-1}	
F(000)	800	
Crystal size	0.21 x 0.15 x 0.09 mm^3	
Theta range for data collection	2.85 to 26.00°.	
Index ranges	$-11 \le h \le 11, -11 \le k \le 14, -21 \le l \le 21$	
Reflections collected	57317	
Independent reflections	3707 [R(int) = 0.065]	
Completeness to theta = 26.00°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9007 and 0.7887	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3707 / 6 / 232	
Goodness-of-fit on F^2	1.063	
Final R indices [I>2sigma(I)]	R1 = 0.0512, wR2 = 0.1265	
R indices (all data)	R1 = 0.0702, wR2 = 0.1378	
Largest diff. peak and hole	1.877 and -0.806 $e.Å^{-3}$	

Table A-5.2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for Compound *cis*-4. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Co(2)	9946(1)	2676(1)	1108(1)	19(1)
P(1)	11497(1)	2658(1)	250(1)	22(1)
P(2)	8273(1)	2683(1)	1902(1)	22(1)
O(1)	10907(4)	496(3)	1621(2)	53(1)
O(2)	11381(4)	4638(2)	1848(2)	46(1)
C(1)	4051(5)	2272(4)	-1860(2)	36(1)
C(7)	10765(4)	3887(3)	1529(2)	28(1)
C(8)	10490(5)	1355(3)	1397(2)	31(1)
C(11)	11291(4)	1452(3)	-370(2)	30(1)
C(12)	11409(4)	3823(3)	-401(2)	31(1)
C(13)	13467(4)	2635(4)	663(2)	36(1)
C(21)	9093(4)	2584(3)	2894(2)	24(1)
C(22)	6938(4)	1557(4)	1788(2)	33(1)
C(23)	7110(4)	3926(4)	1880(2)	37(1)
S(1)	8012(1)	3113(1)	131(1)	18(1)
C(2)	5182(14)	2529(6)	-1312(6)	22(2)
C(4)	7164(5)	1891(3)	-239(2)	16(1)
C(3)	6026(5)	1705(4)	-809(3)	20(1)
C(5)	5531(5)	3743(5)	-1211(3)	25(1)
C(6)	5558(5)	515(5)	-962(3)	27(1)
S(1')	8094(6)	1888(5)	143(3)	25(2)
C(2')	5120(80)	2340(30)	-1260(40)	22(2)
C(3')	6011(19)	3194(17)	-820(10)	20(1)
C(4')	7170(20)	3072(16)	-261(11)	26(5)
C(5')	5580(30)	1160(30)	-1125(16)	33(7)
C(6')	5480(30)	4350(20)	-987(15)	25(5)

Table A-5.3. Bond lengths [Å] for Compound *cis*-4.

Co(2)-C(8)	1.726(4)	C(22)-H(22A)	0.9800
Co(2)-C(7)	1.757(4)	C(22)-H(22B)	0.9800
Co(2)-P(2)	2.1779(12)	C(22)-H(22C)	0.9800
Co(2)-P(1)	2.1808(12)	C(23)-H(23A)	0.9800
Co(2)-S(1)	2.3379(14)	C(23)-H(23B)	0.9800
Co(2)-S(1')	2.410(6)	C(23)-H(23C)	0.9800
P(1)-C(12)	1.812(4)	S(1)-C(4)	1.745(4)
P(1)-C(11)	1.815(4)	C(2)-C(3)	1.475(8)
P(1)-C(13)	1.818(4)	C(2)-C(5)	1.504(9)
P(2)-C(22)	1.804(4)	C(4)-C(3)	1.354(7)
P(2)-C(21)	1.811(4)	C(4)-H(4A)	0.9500
P(2)-C(23)	1.824(4)	C(3)-C(6)	1.512(7)
O(1)-C(8)	1.155(5)	C(5)-H(5A)	0.9800
O(2)-C(7)	1.167(5)	C(5)-H(5B)	0.9800
C(1)-C(2')	1.333(17)	C(5)-H(5C)	0.9800
C(1)-C(2)	1.342(6)	C(6)-H(6A)	0.9800
C(1)-H(1A)	0.92(3)	C(6)-H(6B)	0.9800
C(1)-H(1B)	0.93(4)	C(6)-H(6C)	0.9800
C(11)-H(11A)	0.9800	S(1')-C(4')	1.756(16)
C(11)-H(11B)	0.9800	C(2')-C(3')	1.46(2)
C(11)-H(11C)	0.9800	C(2')-C(5')	1.50(2)
C(12)-H(12A)	0.9800	C(3')-C(4')	1.343(18)
C(12)-H(12B)	0.9800	C(3')-C(6')	1.49(3)
C(12)-H(12C)	0.9800	C(4')-H(4'A)	0.9500
C(13)-H(13A)	0.9800	C(5')-H(5'A)	0.9800
C(13)-H(13B)	0.9800	C(5')-H(5'B)	0.9800
C(13)-H(13C)	0.9800	C(5')-H(5'C)	0.9800
C(21)-H(21A)	0.9800	C(6')-H(6'A)	0.9800
C(21)-H(21B)	0.9800	C(6')-H(6'B)	0.9800
C(21)-H(21C)	0.9800	C(6')-H(6'C)	0.9800

Table A-5.4. Bond angles [°] for Compound *cis*-4.

C(8)-Co(2)-C(7)	123.95(19)
C(8)-Co(2)-P(2)	90.29(12)
C(7)-Co(2)-P(2)	90.53(12)
C(8)-Co(2)-P(1)	90.86(12)
C(7)-Co(2)-P(1)	91.88(12)
P(2)-Co(2)-P(1)	176.16(4)
C(8)-Co(2)-S(1)	125.45(14)
C(7)-Co(2)-S(1)	110.60(13)
P(2)-Co(2)-S(1)	88.17(5)
P(1)-Co(2)-S(1)	88.17(5)
C(8)-Co(2)-S(1')	89.17(19)
C(7)-Co(2)-S(1')	146.89(18)
P(2)-Co(2)-S(1')	89.34(14)
P(1)-Co(2)-S(1')	87.01(14)
S(1)-Co(2)-S(1')	36.31(14)
C(12)-P(1)-C(11)	104.40(19)
C(12)-P(1)-C(13)	103.07(19)
C(11)-P(1)-C(13)	104.28(19)
C(12)-P(1)-Co(2)	116.89(13)
C(11)-P(1)-Co(2)	113.66(13)
C(13)-P(1)-Co(2)	113.16(14)
C(22)-P(2)-C(21)	103.73(18)
C(22)-P(2)-C(23)	104.5(2)
C(21)-P(2)-C(23)	103.51(18)
C(22)-P(2)-Co(2)	115.15(13)
C(21)-P(2)-Co(2)	113.22(13)
C(23)-P(2)-Co(2)	115.31(13)
C(2')-C(1)-C(2)	11(3)
C(2')-C(1)-H(1A)	123(3)
C(2)-C(1)-H(1A)	112(3)
C(2')-C(1)-H(1B)	109(4)
C(2)-C(1)-H(1B)	119(4)
H(1A)-C(1)-H(1B)	128(5)
O(2)-C(7)-Co(2)	174.6(4)
O(1)-C(8)-Co(2)	176.4(4)
P(1)-C(11)-H(11A)	109.5
P(1)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
P(1)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
P(1)-C(12)-H(12A)	109.5
P(1)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
P(1)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
P(1)-C(13)-H(13A)	109.5
P(1)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
P(1)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
P(2)-C(21)-H(21A)	109.5
P(2)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
P(2)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
P(2)-C(22)-H(22A)	109.5
P(2)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5

P(2)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
P(2)-C(23)-H(23A)	109.5
P(2)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
P(2)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
C(4)-S(1)-Co(2)	109.19(16)
C(1)-C(2)-C(3)	123.8(6)
C(1)-C(2)-C(5)	115.9(5)
C(3)-C(2)-C(5)	120.3(4)
C(3)-C(4)-S(1)	131.8(4)
C(3)-C(4)-H(4A)	114.1
S(1)-C(4)-H(4A)	114.1
C(4)-C(3)-C(2)	127.7(5)
C(4)-C(3)-C(6)	117.1(4)
C(2)-C(3)-C(6)	115.2(5)
C(2)-C(5)-H(5A)	109.5
C(2)-C(5)-H(5B)	109.5
H(5A)-C(5)-H(5B)	109.5
C(2)-C(5)-H(5C)	109.5
H(5A)-C(5)-H(5C)	109.5
H(5B)-C(5)-H(5C)	109.5
C(3)-C(6)-H(6A)	109.5
C(3)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5
C(3)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
C(4')-S(1')-Co(2)	102.1(7)
C(1)-C(2')-C(3')	139(3)
C(1)-C(2')-C(5')	102.8(19)
C(3')-C(2')-C(5')	118(2)
C(4')-C(3')-C(2')	129(2)
C(4')-C(3')-C(6')	116.3(17)
C(2')-C(3')-C(6')	115(2)
C(3')-C(4')-S(1')	131.8(18)
C(3')-C(4')-H(4'A)	114.1
S(1')-C(4')-H(4'A)	114.1
C(2')-C(5')-H(5'A)	109.5
C(2')-C(5')-H(5'B)	109.5
H(5'A)-C(5')-H(5'B)	109.5
C(2')-C(5')-H(5'C)	109.5
H(5'A)-C(5')-H(5'C)	109.5
H(5'B)-C(5')-H(5'C)	109.5
C(3')-C(6')-H(6'A)	109.5
C(3')-C(6')-H(6'B)	109.5
H(6'A)-C(6')-H(6'B)	109.5
C(3')-C(6')-H(6'C)	109.5
H(6'A)-C(6')-H(6'C)	109.5
H(6'B)-C(6')-H(6'C)	109.5

Table A-5.5. Anisotropic displacement parameters (Å^{2}x 10^3) for Compound *cis*-4. The anisotropic displacement factor exponent takes the form: $-2\pi^2$[h^2 $a^{*2}U^{11}$ + ... + 2 h k a* b* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Co(2)	14(1)	32(1)	13(1)	-1(1)	1(1)	-1(1)
P(1)	16(1)	34(1)	15(1)	0(1)	2(1)	1(1)
P(2)	15(1)	35(1)	15(1)	-1(1)	1(1)	-2(1)
O(1)	77(2)	33(2)	56(2)	12(2)	32(2)	16(2)
O(2)	56(2)	34(2)	52(2)	-9(2)	18(2)	-14(2)
C(1)	25(2)	56(3)	26(2)	1(2)	3(2)	1(2)
C(7)	29(2)	39(2)	18(2)	5(2)	10(2)	3(2)
C(8)	37(2)	33(3)	26(2)	-5(2)	14(2)	-4(2)
C(11)	36(2)	32(2)	21(2)	-1(2)	6(2)	0(2)
C(12)	34(2)	38(2)	23(2)	2(2)	7(2)	1(2)
C(13)	19(2)	60(3)	29(2)	-1(2)	4(2)	2(2)
C(21)	24(2)	36(2)	13(2)	0(1)	2(1)	-4(2)
C(22)	22(2)	49(3)	28(2)	-6(2)	6(2)	-12(2)
C(23)	29(2)	52(3)	33(2)	9(2)	12(2)	12(2)
S(1)	19(1)	16(1)	18(1)	2(1)	-4(1)	-1(1)
C(2)	16(2)	37(3)	15(3)	2(3)	6(2)	-1(3)
C(4)	18(2)	14(2)	18(2)	0(2)	6(2)	-1(2)
C(3)	15(2)	27(3)	18(2)	-3(2)	4(2)	-3(2)
C(5)	22(2)	27(3)	27(3)	5(2)	0(2)	6(2)
C(6)	29(3)	28(3)	22(3)	-7(2)	2(2)	-7(2)
S(1')	20(3)	33(3)	19(3)	-5(2)	-9(2)	2(2)
C(2')	16(2)	37(3)	15(3)	2(3)	6(2)	-1(3)
C(3')	15(2)	27(3)	18(2)	-3(2)	4(2)	-3(2)
C(4')	13(11)	32(14)	36(14)	-16(10)	11(11)	-4(9)
C(5')	20(13)	40(20)	33(16)	26(15)	4(11)	-1(13)
C(6')	25(12)	12(14)	37(15)	6(10)	-4(10)	0(10)

Table A-5.6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for Compound *cis*-4.

	x	y	z	U(eq)
H(11A)	12018	1496	-739	44
H(11B)	10265	1431	-643	44
H(11C)	11478	780	-61	44
H(12A)	12151	3723	-758	47
H(12B)	11630	4507	-110	47
H(12C)	10397	3869	-689	47
H(13A)	14107	2626	253	54
H(13B)	13663	1971	980	54
H(13C)	13692	3295	980	54
H(21A)	8289	2591	3222	36
H(21B)	9767	3215	3023	36
H(21C)	9666	1893	2973	36
H(22A)	6234	1627	2167	49
H(22B)	7478	851	1863	49
H(22C)	6379	1580	1272	49
H(23A)	6395	3854	2254	56
H(23B)	6555	4019	1367	56
H(23C)	7756	4572	2008	56
H(4A)	7578	1238	4	19
H(5A)	4836	4171	-1574	38
H(5B)	6569	3882	-1307	38
H(5C)	5414	3965	-688	38
H(6A)	6203	27	-617	40
H(6B)	5664	327	-1494	40
H(6C)	4505	419	-877	40
H(4'A)	7562	3749	-45	32

H(5'A)	5128	704	-1555	49
H(5'B)	5241	895	-651	49
H(5'C)	6683	1104	-1082	49
H(6'A)	5899	4839	-568	38
H(6'B)	4378	4374	-1037	38
H(6'C)	5821	4602	-1465	38
H(1A)	3660(50)	2890(30)	-2130(20)	37(12)
H(1B)	3810(60)	1530(30)	-1950(30)	75(18)

Table A-5.7. Torsion angles [°] for Compound *cis*-4.

C(8)-Co(2)-P(1)-C(12)	173.6(2)
C(7)-Co(2)-P(1)-C(12)	-62.44(19)
P(2)-Co(2)-P(1)-C(12)	66.2(7)
S(1)-Co(2)-P(1)-C(12)	48.11(15)
S(1')-Co(2)-P(1)-C(12)	84.4(2)
C(8)-Co(2)-P(1)-C(11)	51.8(2)
C(7)-Co(2)-P(1)-C(11)	175.79(19)
P(2)-Co(2)-P(1)-C(11)	-55.6(7)
S(1)-Co(2)-P(1)-C(11)	-73.66(15)
S(1')-Co(2)-P(1)-C(11)	-37.3(2)
C(8)-Co(2)-P(1)-C(13)	-66.9(2)
C(7)-Co(2)-P(1)-C(13)	57.1(2)
P(2)-Co(2)-P(1)-C(13)	-174.3(6)
S(1)-Co(2)-P(1)-C(13)	167.63(16)
S(1')-Co(2)-P(1)-C(13)	-156.0(2)
C(8)-Co(2)-P(2)-C(22)	-55.8(2)
C(7)-Co(2)-P(2)-C(22)	-179.7(2)
P(1)-Co(2)-P(2)-C(22)	51.6(7)
S(1)-Co(2)-P(2)-C(22)	69.67(16)
S(1')-Co(2)-P(2)-C(22)	33.4(2)
C(8)-Co(2)-P(2)-C(21)	63.34(19)
C(7)-Co(2)-P(2)-C(21)	-60.61(18)
P(1)-Co(2)-P(2)-C(21)	170.7(6)
S(1)-Co(2)-P(2)-C(21)	-171.20(14)
S(1')-Co(2)-P(2)-C(21)	152.51(19)
C(8)-Co(2)-P(2)-C(23)	-177.7(2)
C(7)-Co(2)-P(2)-C(23)	58.3(2)
P(1)-Co(2)-P(2)-C(23)	-70.3(7)
S(1)-Co(2)-P(2)-C(23)	-52.25(17)
S(1')-Co(2)-P(2)-C(23)	-88.5(2)
C(8)-Co(2)-C(7)-O(2)	-2(4)
P(2)-Co(2)-C(7)-O(2)	89(4)
P(1)-Co(2)-C(7)-O(2)	-94(4)
S(1)-Co(2)-C(7)-O(2)	177(3)
S(1')-Co(2)-C(7)-O(2)	178(100)
C(7)-Co(2)-C(8)-O(1)	3(6)
P(2)-Co(2)-C(8)-O(1)	-87(6)
P(1)-Co(2)-C(8)-O(1)	96(6)
S(1)-Co(2)-C(8)-O(1)	-175(6)
S(1')-Co(2)-C(8)-O(1)	-177(100)
C(8)-Co(2)-S(1)-C(4)	1.9(2)
C(7)-Co(2)-S(1)-C(4)	-176.99(18)
P(2)-Co(2)-S(1)-C(4)	-87.12(14)
P(1)-Co(2)-S(1)-C(4)	91.69(14)

S(1')-Co(2)-S(1)-C(4)	4.3(3)	P(2)-Co(2)-S(1')-C(4')	86.1(7)
C(2')-C(1)-C(2)-C(3)	21(23)	P(1)-Co(2)-S(1')-C(4')	-92.7(7)
C(2')-C(1)-C(2)-C(5)	-157(25)	S(1)-Co(2)-S(1')-C(4')	-1.7(7)
Co(2)-S(1)-C(4)-C(3)	-179.0(4)	C(2)-C(1)-C(2')-C(3')	21(14)
S(1)-C(4)-C(3)-C(2)	2.2(11)	C(2)-C(1)-C(2')-C(5')	-147(29)
S(1)-C(4)-C(3)-C(6)	-178.7(3)	C(1)-C(2')-C(3')-C(4')	-172(8)
C(1)-C(2)-C(3)-C(4)	-179.2(9)	C(5')-C(2')-C(3')-C(4')	-5(10)
C(5)-C(2)-C(3)-C(4)	-1.5(17)	C(1)-C(2')-C(3')-C(6')	12(13)
C(1)-C(2)-C(3)-C(6)	1.6(17)	C(5')-C(2')-C(3')-C(6')	180(5)
C(5)-C(2)-C(3)-C(6)	179.4(9)	C(2')-C(3')-C(4')-S(1')	2(6)
C(8)-Co(2)-S(1')-C(4')	176.4(7)	C(6')-C(3')-C(4')-S(1')	177.3(17)
C(7)-Co(2)-S(1')-C(4')	-3.9(8)	Co(2)-S(1')-C(4')-C(3')	-178.8(19)

APPENDIX B:

OXAPENTADIENYL-COBALT CHEMISTRY

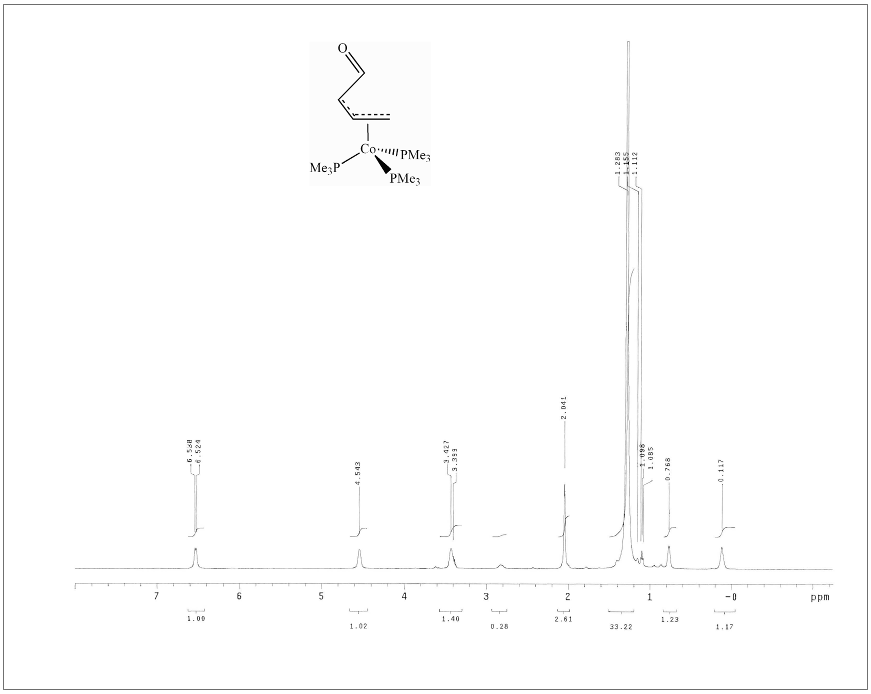

Figure B-1. ^{1}H NMR of Compound 5.

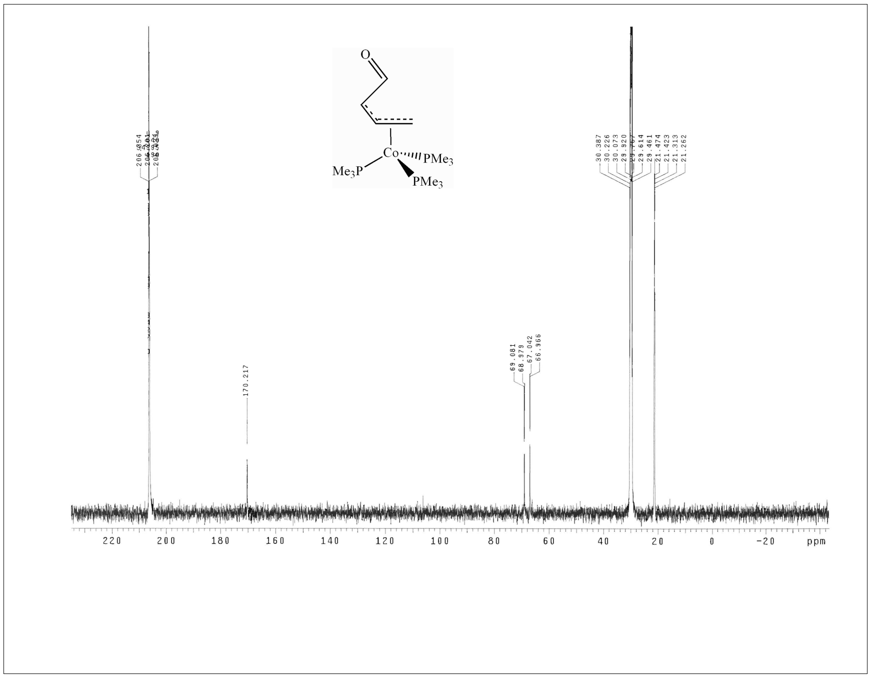

Figure B-2. ^{13}C NMR of Compound 5.

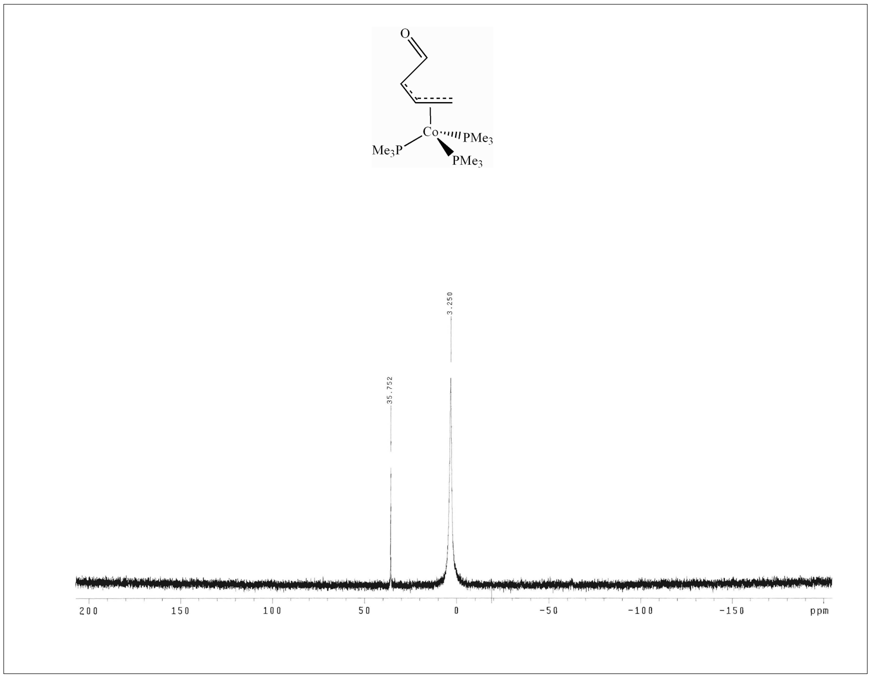

Figure B-3. ^{31}P NMR of Compound 5.

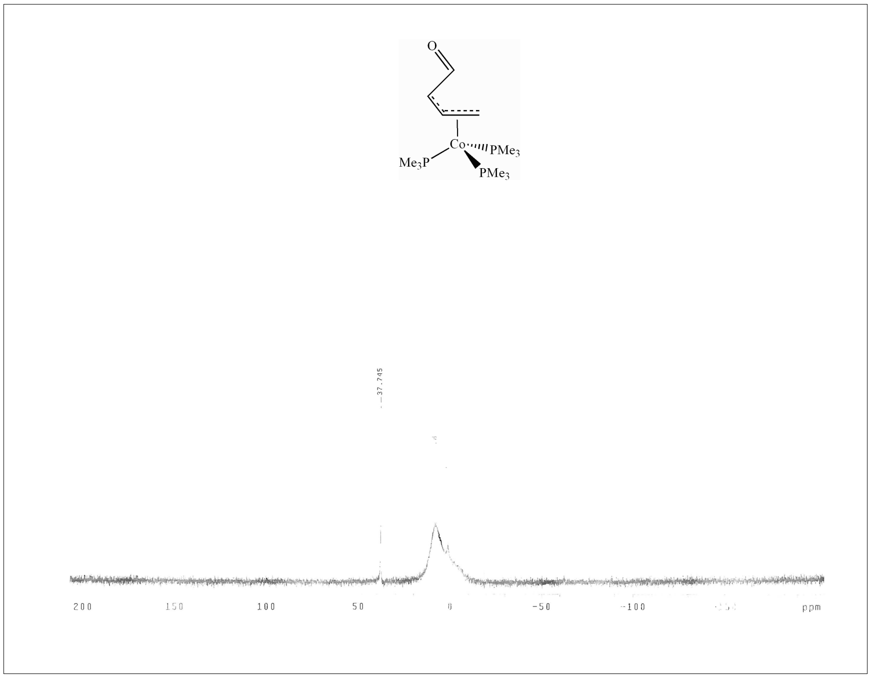

Figure B-4. ^{31}P NMR of Compound 5 at -70 C.

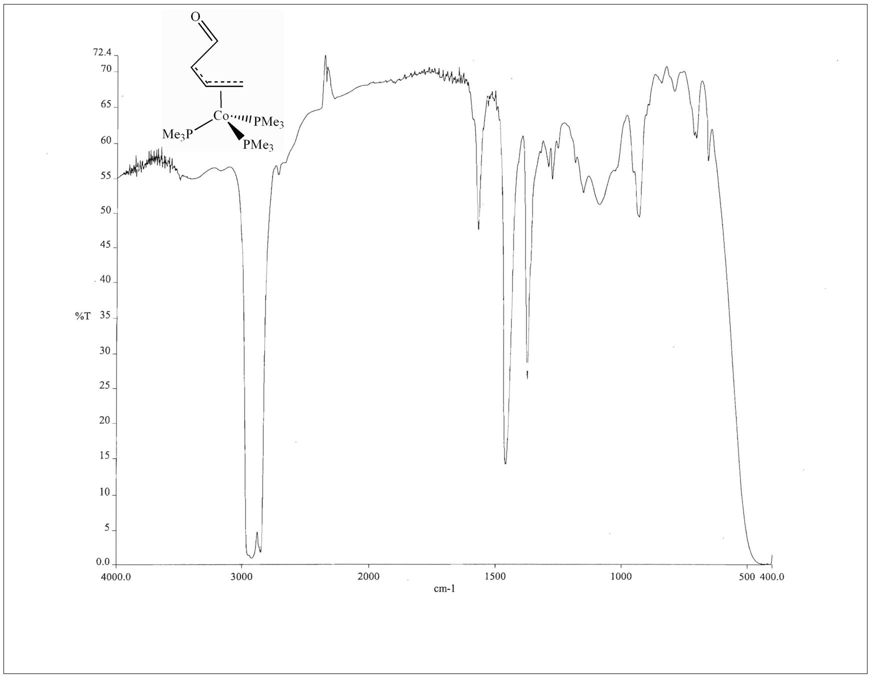

Figure B-5. IR Spectrum of Compound 5.

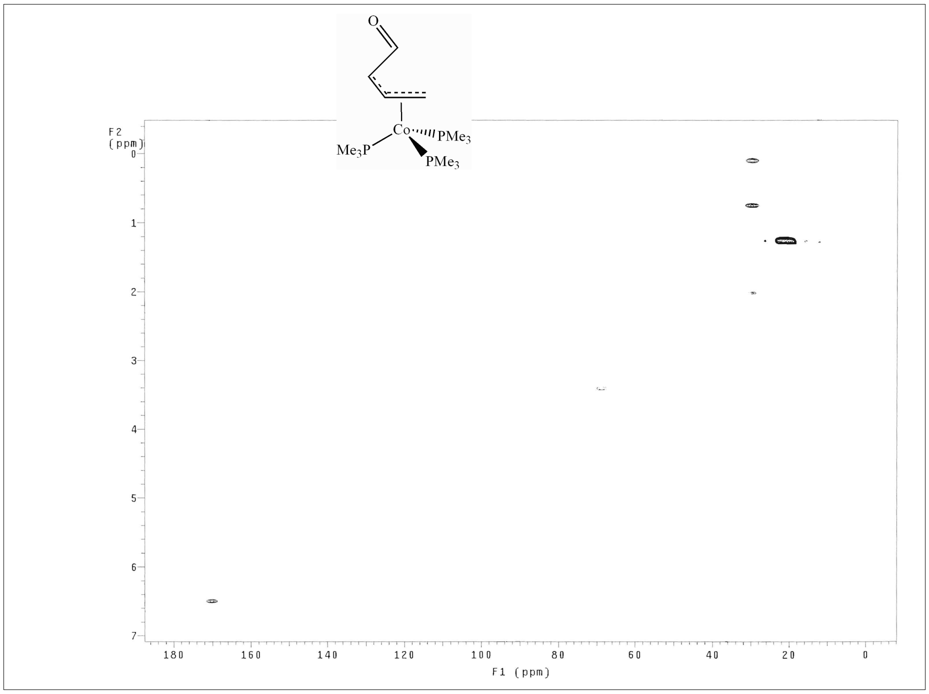

Figure B-6. HMQC Spectrum of Compound 5.

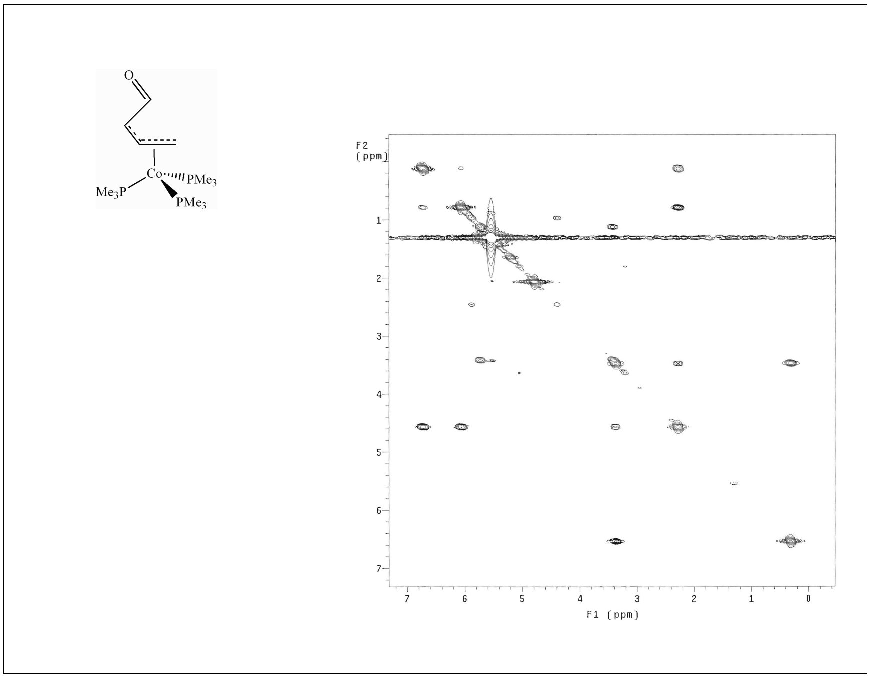

Figure B-7. COSY Spectrum of Compound 5.

Table B-1.1. Crystal data and structure refinement for Compound 5.

Empirical formula	$C_{13} H_{32} Co O P_3$	
Formula weight	356.23	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$Pna2_1$	
Unit cell dimensions	a = 18.8012(14) Å	α= 90°.
	b = 7.9575(6) Å	β= 90°.
	c = 12.0680(10) Å	γ = 90°.
Volume	1805.5(2) $Å^3$	
Z	4	
Density (calculated)	1.311 Mg/m^3	
Absorption coefficient	1.206 mm^{-1}	
F(000)	760	
Crystal size	0.41 x 0.37 x 0.19 mm^3	
Theta range for data collection	2.75 to 30.78°.	
Index ranges	$-26\leq h\leq 27$, $-11\leq k\leq 11$, $-17\leq l\leq 17$	
Reflections collected	53265	
Independent reflections	5610 [R(int) = 0.038]	
Completeness to theta = 30.78°	99.9 %	
Absorption correction	Numerical	
Max. and min. transmission	0.7998 and 0.6403	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5610 / 1 / 173	
Goodness-of-fit on F^2	1.060	
Final R indices [I>2sigma(I)]	R1 = 0.0350, wR2 = 0.0871	
R indices (all data)	R1 = 0.0413, wR2 = 0.0901	
Absolute structure parameter	0.548(15)	
Largest diff. peak and hole	0.826 and -0.527 $e.Å^{-3}$	

Table B-1.2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for Compound 5. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Co(1)	1042(1)	1741(1)	6789(1)	13(1)
P(1)	1522(1)	3156(1)	8151(1)	19(1)
P(2)	1467(1)	3097(1)	5372(1)	16(1)
P(3)	-33(1)	2712(1)	6792(1)	24(1)
O(1)	2805(1)	-159(3)	6886(4)	59(1)
C(1)	665(2)	-309(4)	7625(3)	44(1)
C(2)	868(2)	-645(3)	6560(4)	50(2)
C(3)	1603(2)	-410(3)	6254(3)	34(1)
C(4)	2164(2)	-353(4)	7002(3)	45(1)
C(11)	1445(2)	2271(5)	9553(2)	41(1)
C(12)	1206(2)	5288(4)	8411(3)	30(1)
C(13)	2485(2)	3568(5)	8098(3)	42(1)
C(21)	1494(2)	5403(4)	5350(3)	36(1)
C(22)	2394(2)	2746(5)	5046(3)	38(1)
C(23)	1050(2)	2660(5)	4047(2)	35(1)
C(31)	-679(2)	1503(6)	6002(4)	56(1)
C(32)	-494(2)	2762(5)	8136(3)	45(1)
C(33)	-261(2)	4825(5)	6313(3)	41(1)

Table B-1.3. Bond lengths [Å] for Compound 5.

Co(1)-C(2)	1.946(3)
Co(1)-C(1)	2.044(3)
Co(1)-C(3)	2.112(3)
Co(1)-P(3)	2.1644(6)
Co(1)-P(2)	2.1744(8)
Co(1)-P(1)	2.1873(8)
P(1)-C(12)	1.824(3)
P(1)-C(11)	1.838(3)
P(1)-C(13)	1.840(3)
P(2)-C(22)	1.810(3)
P(2)-C(23)	1.815(3)
P(2)-C(21)	1.836(3)
P(3)-C(31)	1.818(3)
P(3)-C(33)	1.828(4)
P(3)-C(32)	1.839(3)
O(1)-C(4)	1.223(4)
C(1)-C(2)	1.368(6)
C(1)-H(1A)	0.9900
C(1)-H(1B)	0.9900
C(2)-C(3)	1.443(5)
C(2)-H(2)	0.9500
C(3)-C(4)	1.389(5)
C(3)-H(3)	0.9500
C(4)-H(4)	0.9500
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800
C(31)-H(31A)	0.9800
C(31)-H(31B)	0.9800
C(31)-H(31C)	0.9800
C(32)-H(32A)	0.9800
C(32)-H(32B)	0.9800
C(32)-H(32C)	0.9800
C(33)-H(33A)	0.9800
C(33)-H(33B)	0.9800
C(33)-H(33C)	0.9800

Table B-1.4. Bond angles [°] for Compound 5.

C(2)-Co(1)-C(1)	39.99(17)
C(2)-Co(1)-C(3)	41.39(14)
C(1)-Co(1)-C(3)	71.20(13)
C(2)-Co(1)-P(3)	101.07(11)
C(1)-Co(1)-P(3)	87.75(12)
C(3)-Co(1)-P(3)	139.17(10)
C(2)-Co(1)-P(2)	115.72(15)
C(1)-Co(1)-P(2)	155.70(11)
C(3)-Co(1)-P(2)	88.72(9)
P(3)-Co(1)-P(2)	99.62(4)
C(2)-Co(1)-P(1)	132.72(15)
C(1)-Co(1)-P(1)	100.54(12)
C(3)-Co(1)-P(1)	116.18(10)
P(3)-Co(1)-P(1)	101.56(4)
P(2)-Co(1)-P(1)	100.59(2)
C(12)-P(1)-C(11)	99.95(16)
C(12)-P(1)-C(13)	99.23(16)
C(11)-P(1)-C(13)	100.21(19)
C(12)-P(1)-Co(1)	118.28(11)
C(11)-P(1)-Co(1)	117.51(13)
C(13)-P(1)-Co(1)	118.10(12)
C(22)-P(2)-C(23)	101.23(17)
C(22)-P(2)-C(21)	97.14(17)
C(23)-P(2)-C(21)	101.01(18)
C(22)-P(2)-Co(1)	116.65(12)
C(23)-P(2)-Co(1)	116.06(11)
C(21)-P(2)-Co(1)	121.18(12)
C(31)-P(3)-C(33)	99.50(19)
C(31)-P(3)-C(32)	99.19(17)
C(33)-P(3)-C(32)	98.59(18)
C(31)-P(3)-Co(1)	115.68(14)
C(33)-P(3)-Co(1)	123.10(11)
C(32)-P(3)-Co(1)	116.65(13)
C(2)-C(1)-Co(1)	66.15(18)
C(2)-C(1)-H(1A)	117.1
Co(1)-C(1)-H(1A)	117.1
C(2)-C(1)-H(1B)	117.1
Co(1)-C(1)-H(1B)	117.1
H(1A)-C(1)-H(1B)	114.1
C(1)-C(2)-C(3)	118.9(4)
C(1)-C(2)-Co(1)	73.9(2)
C(3)-C(2)-Co(1)	75.48(16)
C(1)-C(2)-H(2)	120.6
C(3)-C(2)-H(2)	120.6
Co(1)-C(2)-H(2)	121.3
C(4)-C(3)-C(2)	124.4(3)
C(4)-C(3)-Co(1)	98.9(2)
C(2)-C(3)-Co(1)	63.13(15)
C(4)-C(3)-H(3)	117.8
C(2)-C(3)-H(3)	117.8
Co(1)-C(3)-H(3)	108.6
O(1)-C(4)-C(3)	132.6(4)
O(1)-C(4)-H(4)	113.7
C(3)-C(4)-H(4)	113.7
P(1)-C(11)-H(11A)	109.5
P(1)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
P(1)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
P(1)-C(12)-H(12A)	109.5
P(1)-C(12)-H(12B)	109.5

H(12A)-C(12)-H(12B)	109.5	P(2)-C(23)-H(23B)	109.5
P(1)-C(12)-H(12C)	109.5	H(23A)-C(23)-H(23B)	109.5
H(12A)-C(12)-H(12C)	109.5	P(2)-C(23)-H(23C)	109.5
H(12B)-C(12)-H(12C)	109.5	H(23A)-C(23)-H(23C)	109.5
P(1)-C(13)-H(13A)	109.5	H(23B)-C(23)-H(23C)	109.5
P(1)-C(13)-H(13B)	109.5	P(3)-C(31)-H(31A)	109.5
H(13A)-C(13)-H(13B)	109.5	P(3)-C(31)-H(31B)	109.5
P(1)-C(13)-H(13C)	109.5	H(31A)-C(31)-H(31B)	109.5
H(13A)-C(13)-H(13C)	109.5	P(3)-C(31)-H(31C)	109.5
H(13B)-C(13)-H(13C)	109.5	H(31A)-C(31)-H(31C)	109.5
P(2)-C(21)-H(21A)	109.5	H(31B)-C(31)-H(31C)	109.5
P(2)-C(21)-H(21B)	109.5	P(3)-C(32)-H(32A)	109.5
H(21A)-C(21)-H(21B)	109.5	P(3)-C(32)-H(32B)	109.5
P(2)-C(21)-H(21C)	109.5	H(32A)-C(32)-H(32B)	109.5
H(21A)-C(21)-H(21C)	109.5	P(3)-C(32)-H(32C)	109.5
H(21B)-C(21)-H(21C)	109.5	H(32A)-C(32)-H(32C)	109.5
P(2)-C(22)-H(22A)	109.5	H(32B)-C(32)-H(32C)	109.5
P(2)-C(22)-H(22B)	109.5	P(3)-C(33)-H(33A)	109.5
H(22A)-C(22)-H(22B)	109.5	P(3)-C(33)-H(33B)	109.5
P(2)-C(22)-H(22C)	109.5	H(33A)-C(33)-H(33B)	109.5
H(22A)-C(22)-H(22C)	109.5	P(3)-C(33)-H(33C)	109.5
H(22B)-C(22)-H(22C)	109.5	H(33A)-C(33)-H(33C)	109.5
P(2)-C(23)-H(23A)	109.5	H(33B)-C(33)-H(33C)	109.5

Table B-1.5. Anisotropic displacement parameters ($Å^2$x 10^3) for Compound 5. The anisotropic displacement factor exponent takes the form: -$2\pi^2$[h^2 $a^{*2}U^{11}$ + ... + 2 h k a* b* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Co(1)	15(1)	10(1)	15(1)	0(1)	2(1)	0(1)
P(1)	21(1)	20(1)	16(1)	-3(1)	-3(1)	3(1)
P(2)	18(1)	15(1)	16(1)	2(1)	0(1)	0(1)
P(3)	12(1)	31(1)	28(1)	-10(1)	0(1)	-1(1)
O(1)	39(1)	55(1)	81(2)	0(2)	1(2)	28(1)
C(1)	58(2)	21(1)	53(2)	6(1)	19(2)	-1(2)
C(2)	44(2)	8(1)	99(5)	-7(2)	13(2)	-6(1)
C(3)	54(2)	17(1)	32(2)	0(1)	16(1)	10(1)
C(4)	46(2)	26(1)	62(3)	8(2)	0(2)	23(1)
C(11)	62(2)	42(2)	18(1)	-2(1)	-4(1)	14(2)
C(12)	30(1)	23(1)	37(2)	-13(1)	-10(1)	1(1)
C(13)	20(1)	64(2)	42(2)	-21(2)	-8(1)	3(1)
C(21)	50(2)	16(1)	44(2)	8(1)	13(2)	-2(1)
C(22)	23(1)	44(2)	47(2)	14(2)	13(1)	0(1)
C(23)	48(2)	40(2)	19(1)	-2(1)	-4(1)	-9(2)
C(31)	26(2)	79(3)	62(2)	-36(2)	-10(2)	-14(2)
C(32)	23(1)	66(2)	45(2)	-25(2)	16(1)	-11(2)
C(33)	28(1)	48(2)	49(2)	-7(2)	-9(1)	18(1)

Table B-1.6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3)for Compound 5.

	x	y	z	U(eq)
H(1A)	968	-766	8226	53
H(1B)	149	-337	7788	53
H(2)	531	-1027	6031	60
H(3)	1711	-285	5489	41
H(4)	2022	-493	7752	54
H(11A)	1685	3013	10083	61
H(11B)	1668	1158	9571	61
H(11C)	942	2170	9753	61
H(12A)	698	5260	8588	45
H(12B)	1283	5978	7749	45
H(12C)	1469	5771	9036	45
H(13A)	2588	4333	7483	63
H(13B)	2740	2508	7986	63
H(13C)	2638	4082	8796	63
H(21A)	1733	5813	6020	55
H(21B)	1008	5845	5326	55
H(21C)	1756	5782	4694	55
H(22A)	2491	1536	5038	57
H(22B)	2693	3288	5608	57
H(22C)	2501	3223	4316	57
H(23A)	1313	3234	3457	53
H(23B)	558	3063	4058	53
H(23C)	1055	1446	3910	53
H(31A)	-658	323	6231	84
H(31B)	-568	1589	5210	84
H(31C)	-1157	1947	6139	84
H(32A)	-996	3040	8021	67

H(32B)	-274	3614	8612	67
H(32C)	-457	1658	8491	67
H(33A)	-126	4946	5533	62
H(33B)	-4	5658	6758	62
H(33C)	-774	5005	6392	62

Table B-1.7. Torsion angles [°] for Compound 5.

C(2)-Co(1)-P(1)-C(12)	-149.2(2)	P(3)-Co(1)-P(2)-C(23)	-62.65(14)
C(1)-Co(1)-P(1)-C(12)	-121.93(17)	P(1)-Co(1)-P(2)-C(23)	-166.44(14)
C(3)-Co(1)-P(1)-C(12)	163.96(16)	C(2)-Co(1)-P(2)-C(21)	167.7(2)
P(3)-Co(1)-P(1)-C(12)	-32.08(13)	C(1)-Co(1)-P(2)-C(21)	166.5(3)
P(2)-Co(1)-P(1)-C(12)	70.14(13)	C(3)-Co(1)-P(2)-C(21)	-159.86(18)
C(2)-Co(1)-P(1)-C(11)	-29.1(2)	P(3)-Co(1)-P(2)-C(21)	60.34(16)
C(1)-Co(1)-P(1)-C(11)	-1.82(18)	P(1)-Co(1)-P(2)-C(21)	-43.46(15)
C(3)-Co(1)-P(1)-C(11)	-75.93(17)	C(2)-Co(1)-P(3)-C(31)	-27.3(2)
P(3)-Co(1)-P(1)-C(11)	88.03(14)	C(1)-Co(1)-P(3)-C(31)	-65.2(2)
P(2)-Co(1)-P(1)-C(11)	-169.75(14)	C(3)-Co(1)-P(3)-C(31)	-7.8(2)
C(2)-Co(1)-P(1)-C(13)	91.2(2)	P(2)-Co(1)-P(3)-C(31)	91.49(18)
C(1)-Co(1)-P(1)-C(13)	118.5(2)	P(1)-Co(1)-P(3)-C(31)	-165.51(18)
C(3)-Co(1)-P(1)-C(13)	44.38(19)	C(2)-Co(1)-P(3)-C(33)	-149.5(2)
P(3)-Co(1)-P(1)-C(13)	-151.66(17)	C(1)-Co(1)-P(3)-C(33)	172.63(18)
P(2)-Co(1)-P(1)-C(13)	-49.44(16)	C(3)-Co(1)-P(3)-C(33)	-129.95(19)
C(2)-Co(1)-P(2)-C(22)	-74.5(2)	P(2)-Co(1)-P(3)-C(33)	-30.66(15)
C(1)-Co(1)-P(2)-C(22)	-75.7(3)	P(1)-Co(1)-P(3)-C(33)	72.34(15)
C(3)-Co(1)-P(2)-C(22)	-42.06(18)	C(2)-Co(1)-P(3)-C(32)	88.8(2)
P(3)-Co(1)-P(2)-C(22)	178.14(15)	C(1)-Co(1)-P(3)-C(32)	50.86(18)
P(1)-Co(1)-P(2)-C(22)	74.34(15)	C(3)-Co(1)-P(3)-C(32)	108.27(19)
C(2)-Co(1)-P(2)-C(23)	44.67(19)	P(2)-Co(1)-P(3)-C(32)	-152.43(14)
C(1)-Co(1)-P(2)-C(23)	43.5(3)	P(1)-Co(1)-P(3)-C(32)	-49.44(14)
C(3)-Co(1)-P(2)-C(23)	77.15(17)	C(3)-Co(1)-C(1)-C(2)	-34.2(2)

P(3)-Co(1)-C(1)-C(2)	110.2(2)	Co(1)-C(2)-C(3)-C(4)	82.1(3)
P(2)-Co(1)-C(1)-C(2)	1.6(5)	C(1)-C(2)-C(3)-Co(1)	-61.9(3)
P(1)-Co(1)-C(1)-C(2)	-148.4(2)	C(2)-Co(1)-C(3)-C(4)	-124.2(3)
Co(1)-C(1)-C(2)-C(3)	62.8(2)	C(1)-Co(1)-C(3)-C(4)	-91.1(2)
C(3)-Co(1)-C(2)-C(1)	126.5(4)	P(3)-Co(1)-C(3)-C(4)	-153.87(18)
P(3)-Co(1)-C(2)-C(1)	-72.8(2)	P(2)-Co(1)-C(3)-C(4)	102.9(2)
P(2)-Co(1)-C(2)-C(1)	-179.3(2)	P(1)-Co(1)-C(3)-C(4)	1.7(2)
P(1)-Co(1)-C(2)-C(1)	44.5(3)	C(1)-Co(1)-C(3)-C(2)	33.1(3)
C(1)-Co(1)-C(2)-C(3)	-126.5(4)	P(3)-Co(1)-C(3)-C(2)	-29.7(3)
P(3)-Co(1)-C(2)-C(3)	160.7(2)	P(2)-Co(1)-C(3)-C(2)	-133.0(3)
P(2)-Co(1)-C(2)-C(3)	54.3(3)	P(1)-Co(1)-C(3)-C(2)	125.8(2)
P(1)-Co(1)-C(2)-C(3)	-82.0(3)	C(2)-C(3)-C(4)-O(1)	-179.6(3)
C(1)-C(2)-C(3)-C(4)	20.2(4)	Co(1)-C(3)-C(4)-O(1)	-116.2(4)

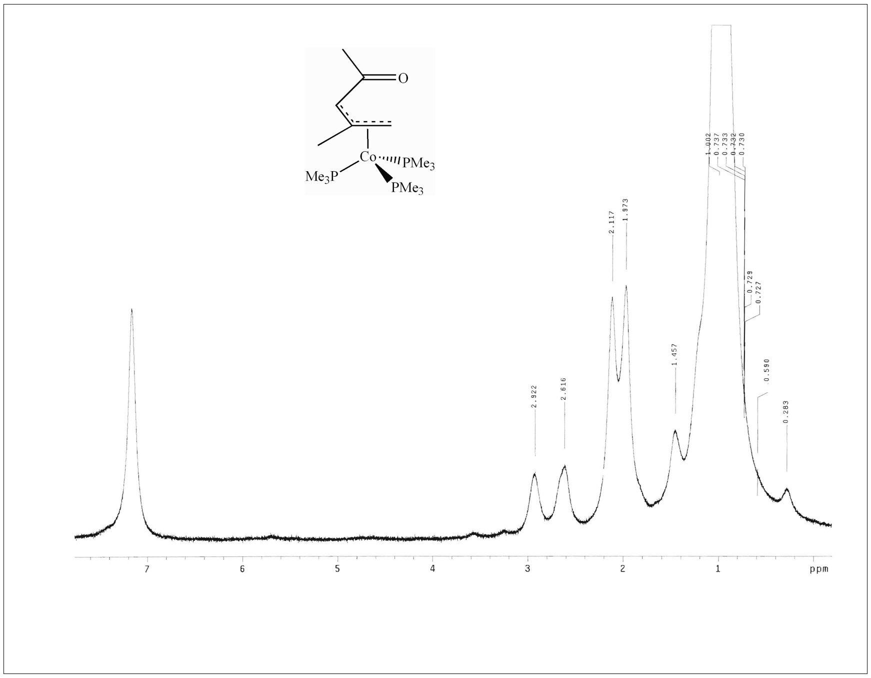

Figure B-8. **^{1}H NMR Spectrum of Compound 6.**

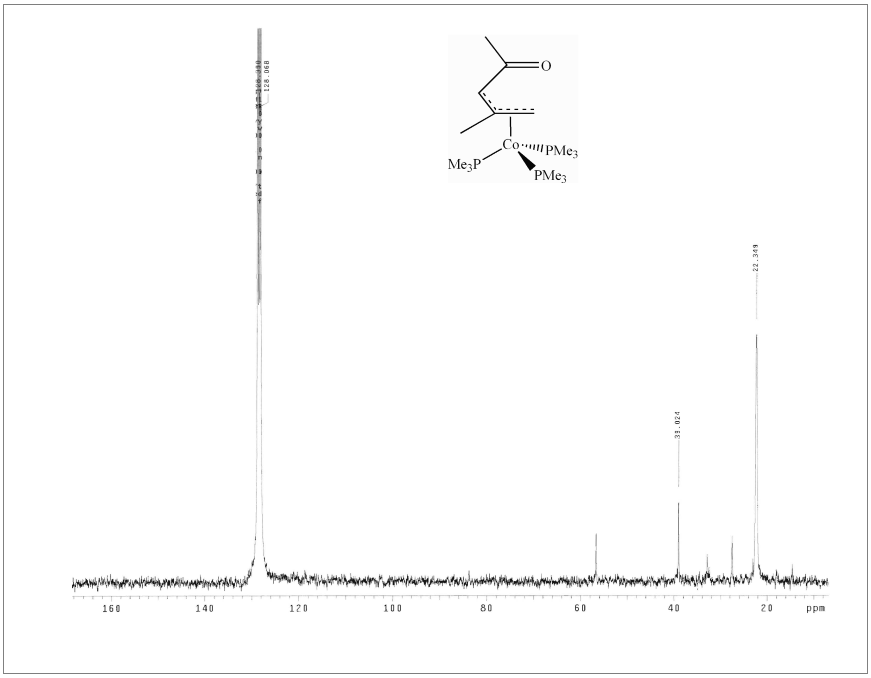

Figure B-9. **^{13}C NMR Spectrum of Compound 6.**

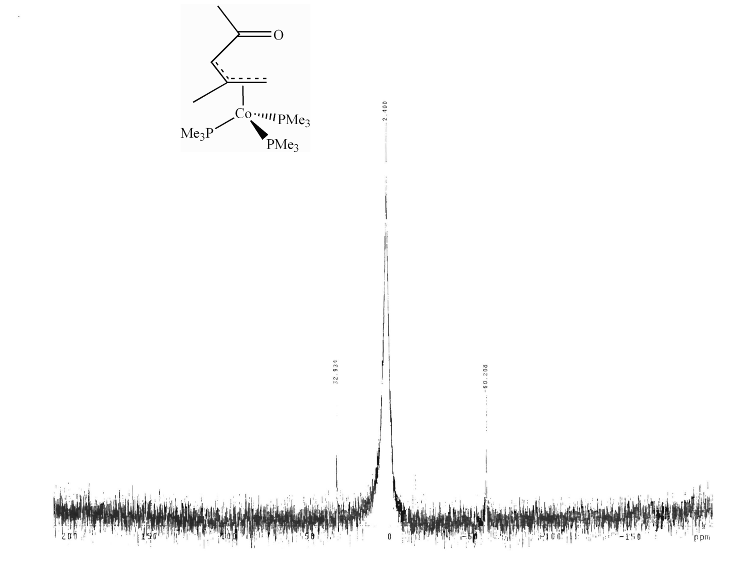

Figure B-10. ^{31}P NMR Spectrum of Compound 6.

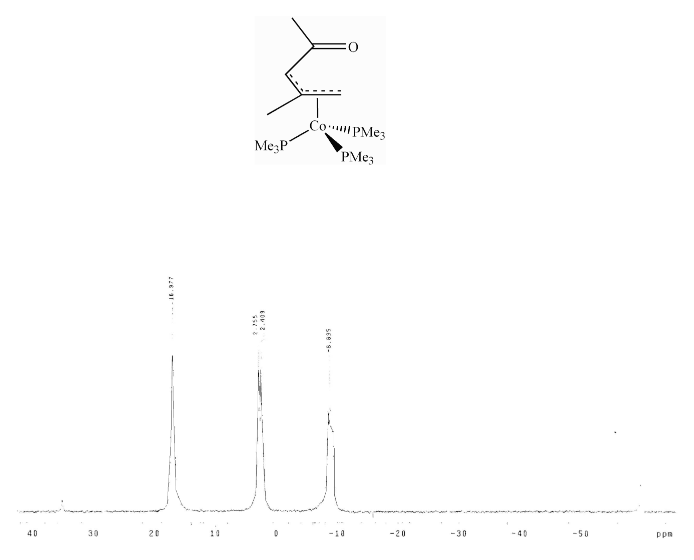

Figure B-11. ^{31}P NMR Spectrum of Compound 6 at -70 C.

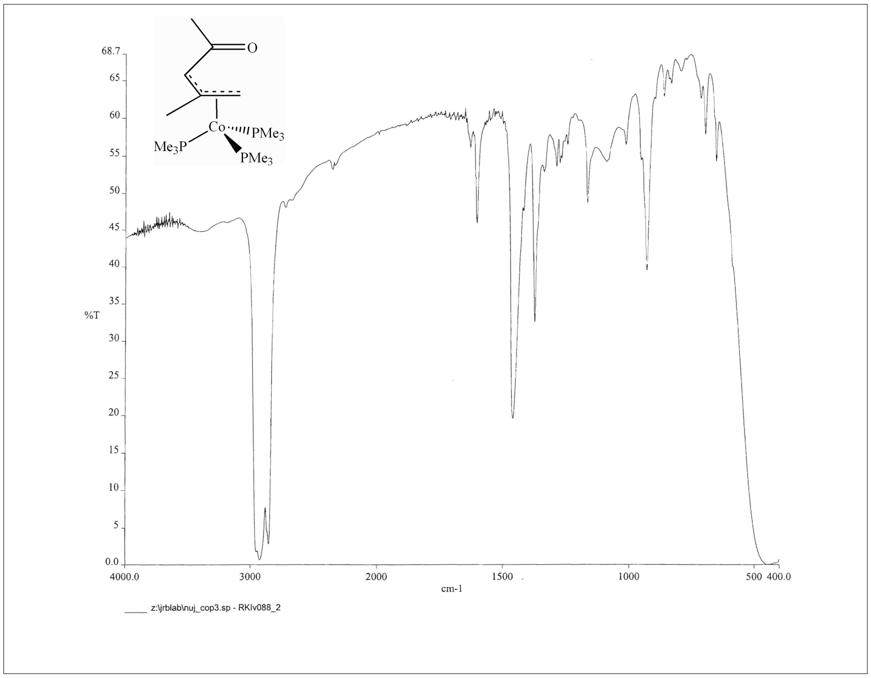

Figure B-12. IR Spectrum of Compound 6.

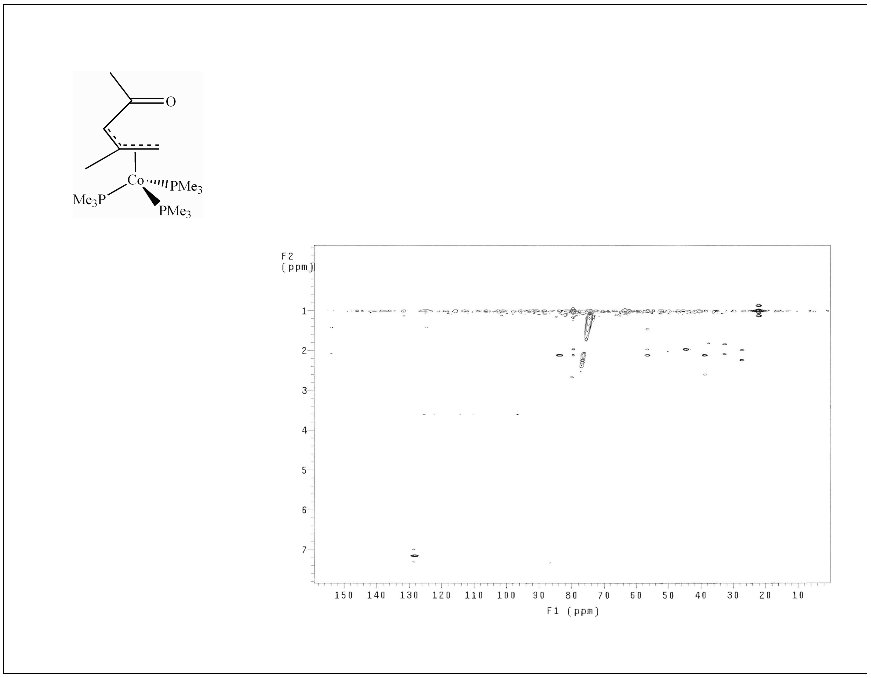

Figure B-13. HMBC Spectrum of Compound 6.

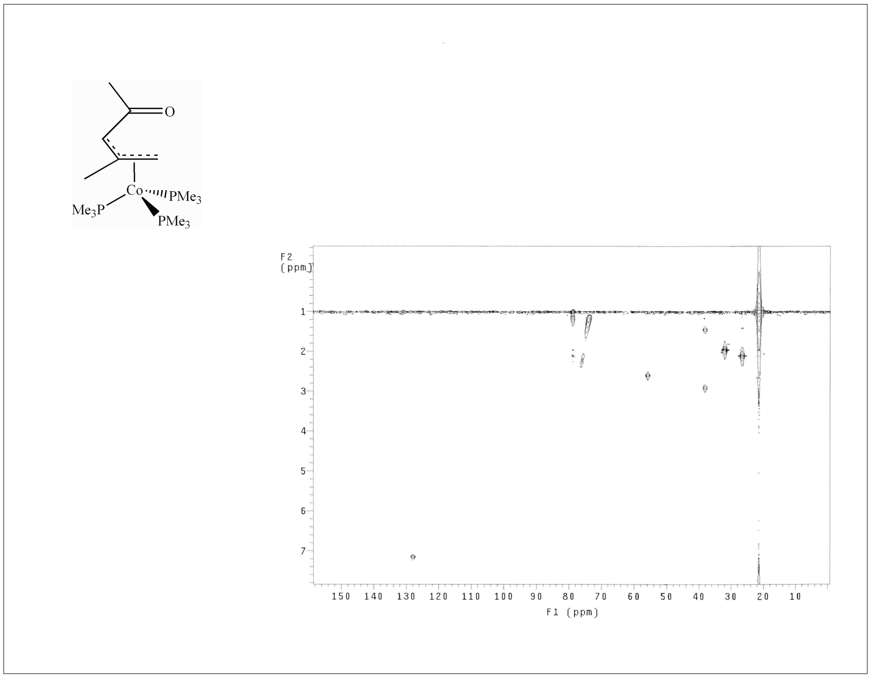

Figure B-14. HMQC Spectrum of Compound 6.

Table B-2.1. Crystal data and structure refinement for Compound 6.

Empirical formula	$C_{15} H_{36} Co O P_3$	
Formula weight	384.28	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 8.7078(5) Å	α= 90°.
	b = 16.0967(8) Å	β= 93.930(2)°.
	c = 14.2582(8) Å	γ = 90°.
Volume	1993.83(19) $Å^3$	
Z	4	
Density (calculated)	1.280 Mg/m^3	
Absorption coefficient	1.097 mm^{-1}	
F(000)	824	
Crystal size	0.38 x 0.29 x 0.09 mm^3	
Theta range for data collection	2.66 to 27.54°.	
Index ranges	$-11\leq h\leq 11$, $-20\leq k\leq 18$, $-18\leq l\leq 18$	
Reflections collected	38063	
Independent reflections	4585 [R(int) = 0.0565]	
Completeness to theta = 27.54°	99.8 %	
Absorption correction	Numerical	
Max. and min. transmission	0.9058 and 0.6838	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4585 / 1 / 204	
Goodness-of-fit on F^2	1.023	
Final R indices [I>2sigma(I)]	R1 = 0.0301, wR2 = 0.0605	
R indices (all data)	R1 = 0.0461, wR2 = 0.0660	
Largest diff. peak and hole	0.350 and -0.368 e.$Å^{-3}$	

Table B-2.2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for Compound 6. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Co(1)	4953(1)	1893(1)	2128(1)	10(1)
P(1)	4867(1)	755(1)	2931(1)	14(1)
P(2)	4640(1)	2814(1)	3251(1)	13(1)
P(3)	7432(1)	1917(1)	1999(1)	13(1)
O(1)	2487(1)	3455(1)	1195(1)	19(1)
C(1)	2731(2)	1636(1)	1643(1)	14(1)
C(2)	3770(2)	1694(1)	919(1)	13(1)
C(3)	4475(2)	2490(1)	824(1)	14(1)
C(4)	3774(2)	3306(1)	923(1)	16(1)
C(5)	4026(2)	1013(1)	219(1)	20(1)
C(6)	4753(2)	4030(1)	623(1)	21(1)
C(11)	4566(2)	-217(1)	2276(1)	23(1)
C(12)	3300(2)	671(1)	3721(1)	21(1)
C(13)	6442(2)	399(1)	3758(1)	22(1)
C(21)	2666(2)	2978(1)	3572(1)	19(1)
C(22)	5604(2)	2641(1)	4417(1)	19(1)
C(23)	5203(2)	3903(1)	3098(1)	24(1)
C(31)	8782(2)	1980(1)	3041(1)	27(1)
C(32)	8237(2)	2789(1)	1364(1)	20(1)
C(33)	8263(2)	1045(1)	1381(2)	23(1)

Table B-2.3. Bond lengths [Å] for Compound 6.

Co(1)-C(2)	1.9733(17)
Co(1)-C(1)	2.0521(18)
Co(1)-C(3)	2.1088(18)
Co(1)-P(1)	2.1655(5)
Co(1)-P(3)	2.1790(5)
Co(1)-P(2)	2.2123(5)
P(1)-C(11)	1.8317(19)
P(1)-C(12)	1.8327(19)
P(1)-C(13)	1.8379(18)
P(2)-C(21)	1.8279(19)
P(2)-C(22)	1.8317(18)
P(2)-C(23)	1.8377(19)
P(3)-C(33)	1.8325(19)
P(3)-C(31)	1.8326(19)
P(3)-C(32)	1.8352(19)
O(1)-C(4)	1.234(2)
C(1)-C(2)	1.422(3)
C(1)-H(1A)	0.957(15)
C(1)-H(1B)	0.948(15)
C(2)-C(3)	1.431(2)
C(2)-C(5)	1.509(2)
C(3)-C(4)	1.459(3)
C(3)-H(3)	0.983(18)
C(4)-C(6)	1.523(3)
C(5)-H(5A)	0.9800
C(5)-H(5B)	0.9800
C(5)-H(5C)	0.9800
C(6)-H(6A)	0.9800
C(6)-H(6B)	0.9800
C(6)-H(6C)	0.9800
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800
C(31)-H(31A)	0.9800
C(31)-H(31B)	0.9800
C(31)-H(31D)	0.9800
C(32)-H(32A)	0.9800
C(32)-H(32D)	0.9800
C(32)-H(32B)	0.9800
C(33)-H(33D)	0.9800
C(33)-H(33A)	0.9800
C(33)-H(33B)	0.9800

Table B-2.4. Bond angles [°] for Compound 6.

C(2)-Co(1)-C(1)	41.32(7)	C(31)-P(3)-Co(1)	121.11(7)
C(2)-Co(1)-C(3)	40.88(7)	C(32)-P(3)-Co(1)	117.95(6)
C(1)-Co(1)-C(3)	70.75(7)	C(2)-C(1)-Co(1)	66.37(10)
C(2)-Co(1)-P(1)	106.84(5)	C(2)-C(1)-H(1A)	116.7(12)
C(1)-Co(1)-P(1)	86.62(5)	Co(1)-C(1)-H(1A)	121.2(11)
C(3)-Co(1)-P(1)	147.15(5)	C(2)-C(1)-H(1B)	120.6(12)
C(2)-Co(1)-P(3)	112.96(6)	Co(1)-C(1)-H(1B)	109.5(11)
C(1)-Co(1)-P(3)	153.10(6)	H(1A)-C(1)-H(1B)	114.2(16)
C(3)-Co(1)-P(3)	93.15(5)	C(1)-C(2)-C(3)	115.20(16)
P(1)-Co(1)-P(3)	97.452(19)	C(1)-C(2)-C(5)	124.22(16)
C(2)-Co(1)-P(2)	131.17(5)	C(3)-C(2)-C(5)	120.30(16)
C(1)-Co(1)-P(2)	102.63(6)	C(1)-C(2)-Co(1)	72.31(10)
C(3)-Co(1)-P(2)	107.84(5)	C(3)-C(2)-Co(1)	74.65(10)
P(1)-Co(1)-P(2)	99.99(2)	C(5)-C(2)-Co(1)	127.12(12)
P(3)-Co(1)-P(2)	102.801(19)	C(2)-C(3)-C(4)	127.71(17)
C(11)-P(1)-C(12)	99.43(9)	C(2)-C(3)-Co(1)	64.47(10)
C(11)-P(1)-C(13)	97.79(9)	C(4)-C(3)-Co(1)	112.51(13)
C(12)-P(1)-C(13)	97.89(9)	C(2)-C(3)-H(3)	115.9(10)
C(11)-P(1)-Co(1)	117.53(7)	C(4)-C(3)-H(3)	110.9(10)
C(12)-P(1)-Co(1)	116.21(6)	Co(1)-C(3)-H(3)	117.1(10)
C(13)-P(1)-Co(1)	123.47(7)	O(1)-C(4)-C(3)	126.92(17)
C(21)-P(2)-C(22)	100.07(9)	O(1)-C(4)-C(6)	118.52(16)
C(21)-P(2)-C(23)	98.91(9)	C(3)-C(4)-C(6)	114.53(16)
C(22)-P(2)-C(23)	98.22(9)	C(2)-C(5)-H(5A)	109.5
C(21)-P(2)-Co(1)	116.30(6)	C(2)-C(5)-H(5B)	109.5
C(22)-P(2)-Co(1)	118.91(6)	H(5A)-C(5)-H(5B)	109.5
C(23)-P(2)-Co(1)	120.42(7)	C(2)-C(5)-H(5C)	109.5
C(33)-P(3)-C(31)	100.33(10)	H(5A)-C(5)-H(5C)	109.5
C(33)-P(3)-C(32)	99.90(9)	H(5B)-C(5)-H(5C)	109.5
C(31)-P(3)-C(32)	96.43(9)	C(4)-C(6)-H(6A)	109.5
C(33)-P(3)-Co(1)	116.97(7)	C(4)-C(6)-H(6B)	109.5

H(6A)-C(6)-H(6B)	109.5
C(4)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
P(1)-C(11)-H(11A)	109.5
P(1)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
P(1)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
P(1)-C(12)-H(12A)	109.5
P(1)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
P(1)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
P(1)-C(13)-H(13A)	109.5
P(1)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
P(1)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
P(2)-C(21)-H(21A)	109.5
P(2)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
P(2)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
P(2)-C(22)-H(22A)	109.5
P(2)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
P(2)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
P(2)-C(23)-H(23A)	109.5
P(2)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
P(2)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
P(3)-C(31)-H(31A)	109.5
P(3)-C(31)-H(31B)	109.5
H(31A)-C(31)-H(31B)	109.5
P(3)-C(31)-H(31D)	109.5
H(31A)-C(31)-H(31D)	109.5
H(31B)-C(31)-H(31D)	109.5
P(3)-C(32)-H(32A)	109.5
P(3)-C(32)-H(32D)	109.5
H(32A)-C(32)-H(32D)	109.5
P(3)-C(32)-H(32B)	109.5
H(32A)-C(32)-H(32B)	109.5
H(32D)-C(32)-H(32B)	109.5
P(3)-C(33)-H(33D)	109.5
P(3)-C(33)-H(33A)	109.5
H(33D)-C(33)-H(33A)	109.5
P(3)-C(33)-H(33B)	109.5
H(33D)-C(33)-H(33B)	109.5
H(33A)-C(33)-H(33B)	109.5

Table B-2.5. Anisotropic displacement parameters ($Å^2 \times 10^3$) for Compound 6. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Co(1)	9(1)	9(1)	11(1)	1(1)	0(1)	-1(1)
P(1)	15(1)	11(1)	15(1)	2(1)	-1(1)	0(1)
P(2)	13(1)	13(1)	12(1)	-1(1)	1(1)	-2(1)
P(3)	10(1)	15(1)	14(1)	1(1)	1(1)	0(1)
O(1)	17(1)	17(1)	23(1)	0(1)	1(1)	3(1)
C(1)	12(1)	13(1)	17(1)	-1(1)	-5(1)	-2(1)
C(2)	12(1)	14(1)	12(1)	-1(1)	-5(1)	4(1)
C(3)	13(1)	17(1)	12(1)	1(1)	0(1)	2(1)
C(4)	18(1)	17(1)	11(1)	2(1)	-4(1)	1(1)
C(5)	25(1)	17(1)	17(1)	-5(1)	-4(1)	3(1)
C(6)	22(1)	17(1)	24(1)	4(1)	0(1)	-1(1)
C(11)	31(1)	12(1)	26(1)	0(1)	-3(1)	0(1)
C(12)	21(1)	20(1)	23(1)	7(1)	4(1)	-2(1)
C(13)	23(1)	21(1)	21(1)	7(1)	-3(1)	4(1)
C(21)	17(1)	21(1)	19(1)	-3(1)	2(1)	3(1)
C(22)	18(1)	25(1)	13(1)	-3(1)	0(1)	0(1)
C(23)	35(1)	15(1)	21(1)	-5(1)	3(1)	-7(1)
C(31)	14(1)	44(1)	23(1)	5(1)	-3(1)	-6(1)
C(32)	14(1)	20(1)	27(1)	2(1)	4(1)	-2(1)
C(33)	19(1)	20(1)	31(1)	-2(1)	8(1)	4(1)

Table B-2.6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for Compound 6.

	x	y	z	U(eq)
H(5A)	3263	1061	-316	30
H(5B)	3920	471	521	30
H(5C)	5063	1064	-3	30
H(6A)	4292	4554	812	32
H(6B)	4803	4021	-62	32
H(6C)	5794	3980	925	32
H(11A)	4520	-681	2719	35
H(11B)	5421	-305	1874	35
H(11C)	3597	-186	1886	35
H(12A)	3255	102	3962	32
H(12B)	2321	809	3376	32
H(12C)	3486	1057	4248	32
H(13A)	6138	-117	4060	33
H(13B)	6664	826	4239	33
H(13C)	7364	299	3417	33
H(21A)	2655	3413	4053	28
H(21B)	2264	2460	3821	28
H(21C)	2022	3149	3015	28
H(22A)	5328	3087	4842	28
H(22B)	6722	2638	4369	28
H(22C)	5280	2105	4663	28
H(23A)	5057	4212	3678	35
H(23B)	4564	4150	2578	35
H(23C)	6288	3929	2958	35
H(31A)	9832	1888	2857	40
H(31B)	8522	1555	3495	40
H(31D)	8713	2531	3327	40

H(32A)	9361	2741	1393	30
H(32D)	7948	3313	1653	30
H(32B)	7831	2777	706	30
H(33D)	9361	1147	1320	34
H(33A)	7736	988	755	34
H(33B)	8137	532	1739	34
H(1A)	2280(20)	1102(10)	1739(13)	20(5)
H(1B)	2090(20)	2090(10)	1776(13)	16(5)
H(3)	5310(20)	2516(11)	396(12)	11(5)

Table B-2.7. Torsion angles [°] for Compound 6.

C(2)-Co(1)-P(1)-C(11)	25.51(10)	C(2)-Co(1)-P(2)-C(22)	162.82(10)
C(1)-Co(1)-P(1)-C(11)	62.01(9)	C(1)-Co(1)-P(2)-C(22)	128.55(9)
C(3)-Co(1)-P(1)-C(11)	16.46(13)	C(3)-Co(1)-P(2)-C(22)	-157.88(9)
P(3)-Co(1)-P(1)-C(11)	-91.27(8)	P(1)-Co(1)-P(2)-C(22)	39.80(8)
P(2)-Co(1)-P(1)-C(11)	164.25(8)	P(3)-Co(1)-P(2)-C(22)	-60.28(8)
C(2)-Co(1)-P(1)-C(12)	-92.05(9)	C(2)-Co(1)-P(2)-C(23)	-76.28(11)
C(1)-Co(1)-P(1)-C(12)	-55.55(9)	C(1)-Co(1)-P(2)-C(23)	-110.54(10)
C(3)-Co(1)-P(1)-C(12)	-101.10(12)	C(3)-Co(1)-P(2)-C(23)	-36.97(10)
P(3)-Co(1)-P(1)-C(12)	151.17(7)	P(1)-Co(1)-P(2)-C(23)	160.71(8)
P(2)-Co(1)-P(1)-C(12)	46.69(7)	P(3)-Co(1)-P(2)-C(23)	60.63(8)
C(2)-Co(1)-P(1)-C(13)	147.36(10)	C(2)-Co(1)-P(3)-C(33)	-50.54(10)
C(1)-Co(1)-P(1)-C(13)	-176.14(10)	C(1)-Co(1)-P(3)-C(33)	-35.92(15)
C(3)-Co(1)-P(1)-C(13)	138.31(12)	C(3)-Co(1)-P(3)-C(33)	-87.50(9)
P(3)-Co(1)-P(1)-C(13)	30.58(8)	P(1)-Co(1)-P(3)-C(33)	61.34(8)
P(2)-Co(1)-P(1)-C(13)	-73.90(8)	P(2)-Co(1)-P(3)-C(33)	163.41(8)
C(2)-Co(1)-P(2)-C(21)	43.09(10)	C(2)-Co(1)-P(3)-C(31)	-173.37(10)
C(1)-Co(1)-P(2)-C(21)	8.83(9)	C(1)-Co(1)-P(3)-C(31)	-158.75(14)
C(3)-Co(1)-P(2)-C(21)	82.40(9)	C(3)-Co(1)-P(3)-C(31)	149.67(10)
P(1)-Co(1)-P(2)-C(21)	-79.92(7)	P(1)-Co(1)-P(3)-C(31)	-61.49(9)
P(3)-Co(1)-P(2)-C(21)	180.00(7)	P(2)-Co(1)-P(3)-C(31)	40.58(9)

C(2)-Co(1)-P(3)-C(32)	68.70(9)	P(1)-Co(1)-C(2)-C(5)	-55.87(17)
C(1)-Co(1)-P(3)-C(32)	83.33(14)	P(3)-Co(1)-C(2)-C(5)	50.11(17)
C(3)-Co(1)-P(3)-C(32)	31.75(9)	P(2)-Co(1)-C(2)-C(5)	-176.24(13)
P(1)-Co(1)-P(3)-C(32)	-179.42(8)	C(1)-C(2)-C(3)-C(4)	-38.1(3)
P(2)-Co(1)-P(3)-C(32)	-77.34(8)	C(5)-C(2)-C(3)-C(4)	136.02(19)
C(3)-Co(1)-C(1)-C(2)	35.35(10)	Co(1)-C(2)-C(3)-C(4)	-99.62(18)
P(1)-Co(1)-C(1)-C(2)	-120.44(10)	C(1)-C(2)-C(3)-Co(1)	61.48(13)
P(3)-Co(1)-C(1)-C(2)	-20.61(18)	C(5)-C(2)-C(3)-Co(1)	-124.36(16)
P(2)-Co(1)-C(1)-C(2)	140.07(9)	C(1)-Co(1)-C(3)-C(2)	-35.71(11)
Co(1)-C(1)-C(2)-C(3)	-62.79(13)	P(1)-Co(1)-C(3)-C(2)	13.30(16)
Co(1)-C(1)-C(2)-C(5)	123.30(17)	P(3)-Co(1)-C(3)-C(2)	122.24(10)
C(3)-Co(1)-C(2)-C(1)	-123.44(15)	P(2)-Co(1)-C(3)-C(2)	-133.24(9)
P(1)-Co(1)-C(2)-C(1)	64.05(10)	C(2)-Co(1)-C(3)-C(4)	122.40(18)
P(3)-Co(1)-C(2)-C(1)	170.04(9)	C(1)-Co(1)-C(3)-C(4)	86.69(14)
P(2)-Co(1)-C(2)-C(1)	-56.31(12)	P(1)-Co(1)-C(3)-C(4)	135.70(11)
C(1)-Co(1)-C(2)-C(3)	123.44(15)	P(3)-Co(1)-C(3)-C(4)	-115.37(13)
P(1)-Co(1)-C(2)-C(3)	-172.51(9)	P(2)-Co(1)-C(3)-C(4)	-10.84(14)
P(3)-Co(1)-C(2)-C(3)	-66.52(11)	C(2)-C(3)-C(4)-O(1)	7.4(3)
P(2)-Co(1)-C(2)-C(3)	67.13(12)	Co(1)-C(3)-C(4)-O(1)	-67.0(2)
C(1)-Co(1)-C(2)-C(5)	-119.9(2)	C(2)-C(3)-C(4)-C(6)	-170.47(17)
C(3)-Co(1)-C(2)-C(5)	116.6(2)	Co(1)-C(3)-C(4)-C(6)	115.15(15)

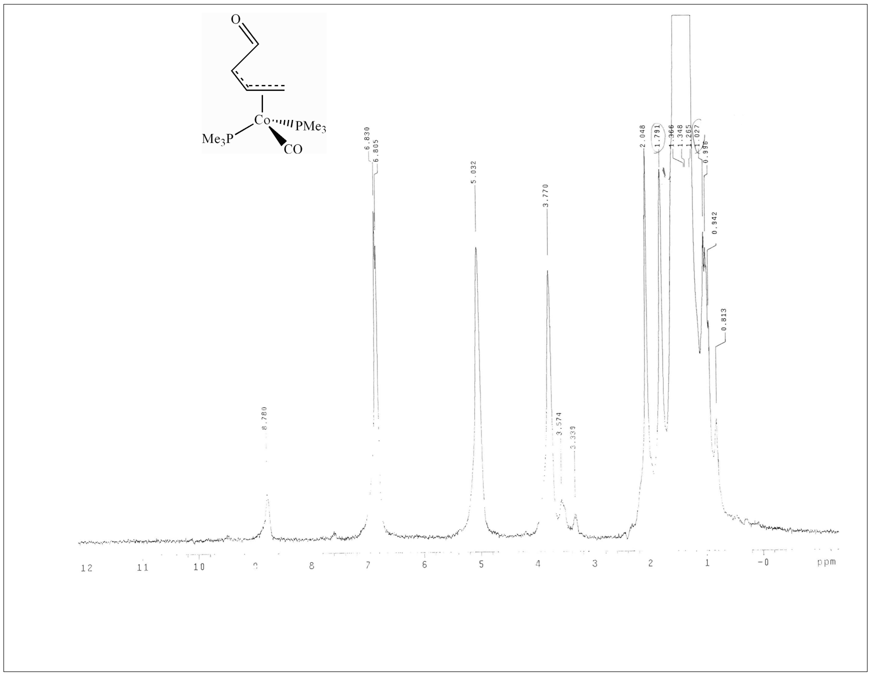

Figure B-15. ^{1}H NMR of Compound 7.

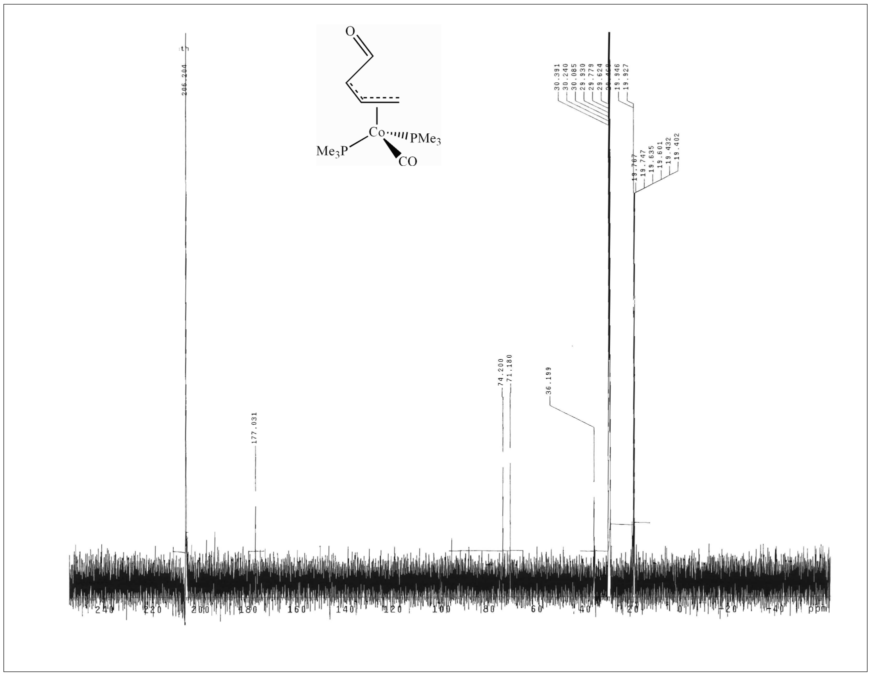

Figure B-16. ^{13}C NMR Spectrum of Compound 7.

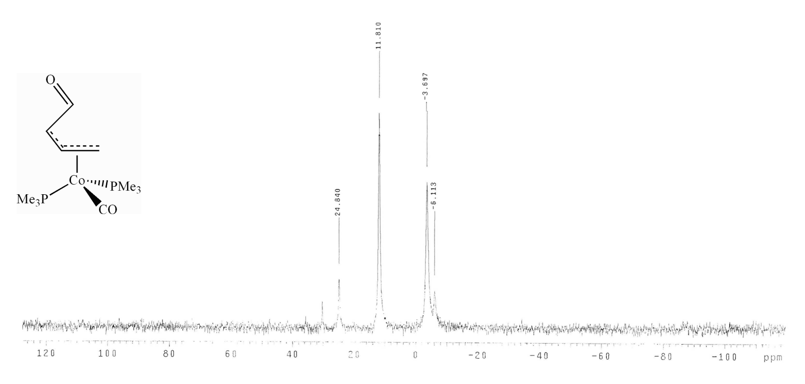

Figure B-17. ^{31}P NMR Spectrum of Compound 7.

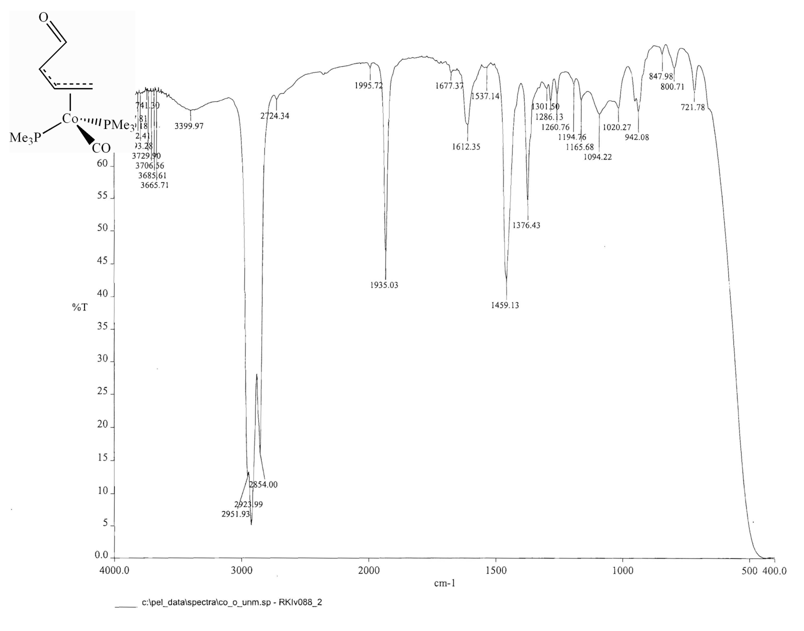

Figure B-18. IR Spectrum of Compound 7.

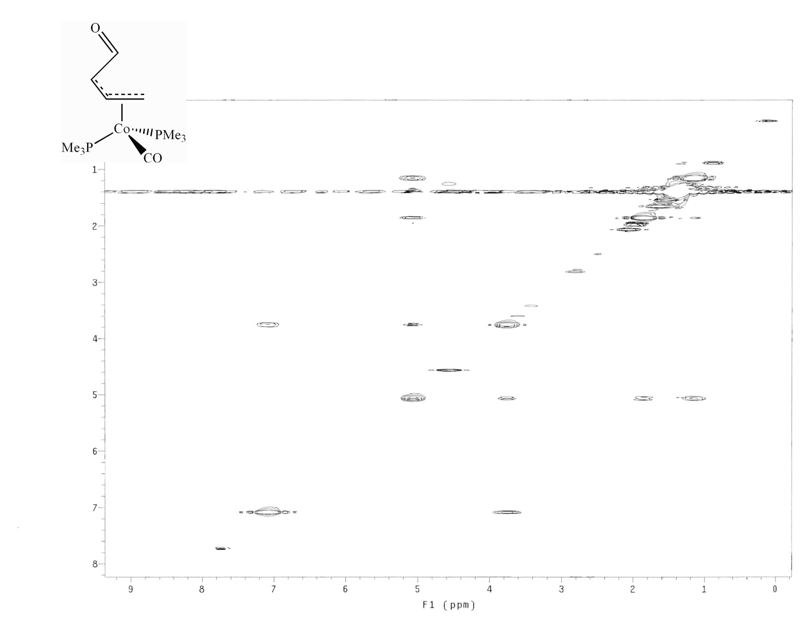

Figure B-19. COSY Spectrum of Compound 7.

Table B-3.1. Crystal data and structure refinement for Compound 7.

Empirical formula	C11 H23 Co O2 P2	
Formula weight	308.16	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 9.7576(7) Å	α= 90°.
	b = 11.1403(8) Å	β= 100.413(3)°.
	c = 14.0125(10) Å	γ = 90°.
Volume	1498.11(19) $Å^3$	
Z	4	
Density (calculated)	1.366 Mg/m^3	
Absorption coefficient	1.345 mm^{-1}	
F(000)	648	
Crystal size	0.47 x 0.33 x 0.26 mm^3	
Theta range for data collection	2.80 to 35.73°.	
Index ranges	$-15 \leq h \leq 15$, $-18 \leq k \leq 16$, $-22 \leq l \leq 22$	
Reflections collected	65934	
Independent reflections	6931 [R(int) = 0.0313]	
Completeness to theta = 35.73°	99.5 %	
Absorption correction	Numerical	
Max. and min. transmission	0.7230 and 0.5700	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6931 / 0 / 171	
Goodness-of-fit on F^2	1.051	
Final R indices [I>2sigma(I)]	R1 = 0.0304, wR2 = 0.0726	
R indices (all data)	R1 = 0.0409, wR2 = 0.0772	
Largest diff. peak and hole	0.784 and -0.649 $e.Å^{-3}$	

Table B-3.2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3)for Compound 7. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Co(1)	7833(1)	13059(1)	-103(1)	14(1)
P(1)	8662(1)	12547(1)	-1385(1)	16(1)
P(2)	5626(1)	12491(1)	-497(1)	16(1)
O(1)	8039(1)	9866(1)	410(1)	37(1)
O(2)	7757(1)	15539(1)	-717(1)	36(1)
C(1)	7905(1)	13424(1)	1344(1)	29(1)
C(2)	9167(1)	12937(1)	1132(1)	27(1)
C(3)	9139(1)	11774(1)	717(1)	25(1)
C(4)	8085(1)	10891(1)	786(1)	29(1)
C(5)	7799(1)	14557(1)	-454(1)	22(1)
C(11)	10437(2)	13018(2)	-1384(1)	43(1)
C(12)	8755(2)	10967(1)	-1653(1)	40(1)
C(13)	7724(2)	13128(2)	-2520(1)	42(1)
C(21)	5163(1)	11085(1)	-1144(1)	24(1)
C(22)	4526(1)	13561(1)	-1272(1)	26(1)
C(23)	4633(1)	12350(1)	484(1)	25(1)

Table B-3.3. Bond lengths [Å] for Compound 7.

Co(1)-C(5)	1.7387(12)
Co(1)-C(2)	1.9734(12)
Co(1)-C(1)	2.0569(12)
Co(1)-C(3)	2.1134(12)
Co(1)-P(1)	2.1750(3)
Co(1)-P(2)	2.2167(3)
P(1)-C(13)	1.8049(14)
P(1)-C(12)	1.8057(14)
P(1)-C(11)	1.8094(14)
P(2)-C(21)	1.8246(12)
P(2)-C(22)	1.8254(12)
P(2)-C(23)	1.8254(11)
O(1)-C(4)	1.2541(18)
O(2)-C(5)	1.1528(15)
C(1)-C(2)	1.425(2)
C(1)-H(1A)	1.02(2)
C(1)-H(1B)	1.002(18)
C(2)-C(3)	1.4183(19)
C(2)-H(2)	0.969(18)
C(3)-C(4)	1.4385(18)
C(3)-H(3)	0.998(18)
C(4)-H(4)	0.995(16)
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800

Table B-3.4. Bond angles [°] for Compound 7.

C(5)-Co(1)-C(2)	106.86(5)
C(5)-Co(1)-C(1)	94.86(6)
C(2)-Co(1)-C(1)	41.35(6)
C(5)-Co(1)-C(3)	141.52(5)
C(2)-Co(1)-C(3)	40.43(5)
C(1)-Co(1)-C(3)	71.81(6)
C(5)-Co(1)-P(1)	90.48(4)
C(2)-Co(1)-P(1)	114.93(4)
C(1)-Co(1)-P(1)	156.12(4)
C(3)-Co(1)-P(1)	89.66(4)
C(5)-Co(1)-P(2)	103.65(4)
C(2)-Co(1)-P(2)	130.98(4)
C(1)-Co(1)-P(2)	99.23(4)
C(3)-Co(1)-P(2)	113.91(4)
P(1)-Co(1)-P(2)	102.083(12)
C(13)-P(1)-C(12)	101.67(8)
C(13)-P(1)-C(11)	103.28(9)
C(12)-P(1)-C(11)	101.46(8)
C(13)-P(1)-Co(1)	115.38(5)
C(12)-P(1)-Co(1)	117.87(5)
C(11)-P(1)-Co(1)	114.98(5)
C(21)-P(2)-C(22)	101.49(6)
C(21)-P(2)-C(23)	100.54(6)
C(22)-P(2)-C(23)	99.74(6)
C(21)-P(2)-Co(1)	120.71(4)
C(22)-P(2)-Co(1)	113.68(4)
C(23)-P(2)-Co(1)	117.46(4)
C(2)-C(1)-Co(1)	66.18(7)
C(2)-C(1)-H(1A)	119.6(11)
Co(1)-C(1)-H(1A)	122.2(11)
C(2)-C(1)-H(1B)	119.4(10)
Co(1)-C(1)-H(1B)	108.8(10)
H(1A)-C(1)-H(1B)	112.8(14)
C(3)-C(2)-C(1)	118.70(12)
C(3)-C(2)-Co(1)	75.10(7)
C(1)-C(2)-Co(1)	72.47(7)
C(3)-C(2)-H(2)	117.4(11)
C(1)-C(2)-H(2)	123.0(11)
Co(1)-C(2)-H(2)	114.2(10)
C(2)-C(3)-C(4)	123.92(12)
C(2)-C(3)-Co(1)	64.47(7)
C(4)-C(3)-Co(1)	97.53(8)
C(2)-C(3)-H(3)	121.4(11)
C(4)-C(3)-H(3)	113.8(11)
Co(1)-C(3)-H(3)	119.3(10)
O(1)-C(4)-C(3)	124.48(13)
O(1)-C(4)-H(4)	120.7(10)
C(3)-C(4)-H(4)	114.8(10)
O(2)-C(5)-Co(1)	177.80(11)
P(1)-C(11)-H(11A)	109.5
P(1)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
P(1)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
P(1)-C(12)-H(12A)	109.5
P(1)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
P(1)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
P(1)-C(13)-H(13A)	109.5

P(1)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
P(1)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
P(2)-C(21)-H(21A)	109.5
P(2)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
P(2)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
P(2)-C(22)-H(22A)	109.5
P(2)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
P(2)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
P(2)-C(23)-H(23A)	109.5
P(2)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
P(2)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5

Table B-3.5. Anisotropic displacement parameters ($\AA^2 \times 10^3$) for Compound 7. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\,h^2\,a^{*2}U^{11} + ... + 2\,h\,k\,a^*\,b^*\,U^{12}\,]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Co(1)	13(1)	17(1)	13(1)	0(1)	1(1)	-1(1)
P(1)	13(1)	17(1)	16(1)	-1(1)	3(1)	0(1)
P(2)	12(1)	20(1)	16(1)	2(1)	3(1)	-1(1)
O(1)	33(1)	25(1)	50(1)	11(1)	2(1)	-2(1)
O(2)	40(1)	18(1)	48(1)	1(1)	3(1)	1(1)
C(1)	31(1)	37(1)	17(1)	-3(1)	2(1)	-4(1)
C(2)	24(1)	35(1)	19(1)	2(1)	-6(1)	-3(1)
C(3)	20(1)	30(1)	23(1)	8(1)	-1(1)	1(1)
C(4)	23(1)	33(1)	29(1)	13(1)	0(1)	0(1)
C(5)	21(1)	21(1)	23(1)	-3(1)	1(1)	0(1)
C(11)	25(1)	65(1)	42(1)	-18(1)	18(1)	-18(1)
C(12)	53(1)	25(1)	47(1)	-11(1)	20(1)	3(1)
C(13)	45(1)	66(1)	18(1)	11(1)	10(1)	30(1)
C(21)	21(1)	26(1)	25(1)	-2(1)	2(1)	-8(1)
C(22)	17(1)	31(1)	28(1)	8(1)	2(1)	4(1)
C(23)	20(1)	32(1)	25(1)	3(1)	10(1)	-1(1)

Table B-3.6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for Compound 7.

	x	y	z	U(eq)
H(11A)	11049	12686	-813	64
H(11B)	10488	13897	-1364	64
H(11C)	10735	12727	-1974	64
H(12A)	7839	10598	-1668	60
H(12B)	9442	10580	-1151	60
H(12C)	9033	10866	-2286	60
H(13A)	8143	12819	-3055	63
H(13B)	7771	14006	-2512	63
H(13C)	6748	12873	-2607	63
H(21A)	4166	10929	-1181	36
H(21B)	5703	10426	-796	36
H(21C)	5370	11145	-1801	36
H(22A)	4889	13677	-1874	38
H(22B)	4528	14331	-932	38
H(22C)	3572	13251	-1426	38
H(23A)	3672	12119	214	38
H(23B)	4633	13121	821	38
H(23C)	5060	11735	943	38
H(1A)	7890(20)	14282(18)	1603(14)	45(5)
H(1B)	7232(19)	12883(16)	1597(13)	32(4)
H(2)	10007(19)	13407(16)	1154(12)	31(4)
H(3)	9953(19)	11450(17)	460(13)	36(5)
H(4)	7379(17)	11141(15)	1178(12)	27(4)

Table B-3.7. Torsion angles [°] for Compound 7.

C(5)-Co(1)-P(1)-C(13)	-50.28(8)
C(2)-Co(1)-P(1)-C(13)	-159.17(9)
C(1)-Co(1)-P(1)-C(13)	-153.48(13)
C(3)-Co(1)-P(1)-C(13)	168.20(8)
P(2)-Co(1)-P(1)-C(13)	53.79(8)
C(5)-Co(1)-P(1)-C(12)	-170.56(8)
C(2)-Co(1)-P(1)-C(12)	80.55(8)
C(1)-Co(1)-P(1)-C(12)	86.24(13)
C(3)-Co(1)-P(1)-C(12)	47.92(8)
P(2)-Co(1)-P(1)-C(12)	-66.49(7)
C(5)-Co(1)-P(1)-C(11)	69.82(8)
C(2)-Co(1)-P(1)-C(11)	-39.07(9)
C(1)-Co(1)-P(1)-C(11)	-33.39(13)
C(3)-Co(1)-P(1)-C(11)	-71.70(8)
P(2)-Co(1)-P(1)-C(11)	173.89(7)
C(5)-Co(1)-P(2)-C(21)	133.25(6)
C(2)-Co(1)-P(2)-C(21)	-99.42(7)
C(1)-Co(1)-P(2)-C(21)	-129.40(6)
C(3)-Co(1)-P(2)-C(21)	-55.29(6)
P(1)-Co(1)-P(2)-C(21)	39.77(5)
C(5)-Co(1)-P(2)-C(22)	12.36(6)
C(2)-Co(1)-P(2)-C(22)	139.68(7)
C(1)-Co(1)-P(2)-C(22)	109.70(6)
C(3)-Co(1)-P(2)-C(22)	-176.19(6)
P(1)-Co(1)-P(2)-C(22)	-81.13(5)
C(5)-Co(1)-P(2)-C(23)	-103.49(6)
C(2)-Co(1)-P(2)-C(23)	23.83(7)
C(1)-Co(1)-P(2)-C(23)	-6.15(7)
C(3)-Co(1)-P(2)-C(23)	67.96(6)
P(1)-Co(1)-P(2)-C(23)	163.02(5)
C(5)-Co(1)-C(1)-C(2)	-110.12(8)
C(3)-Co(1)-C(1)-C(2)	32.92(8)
P(1)-Co(1)-C(1)-C(2)	-7.82(16)
P(2)-Co(1)-C(1)-C(2)	145.18(7)
Co(1)-C(1)-C(2)-C(3)	-61.29(10)
C(5)-Co(1)-C(2)-C(3)	-154.90(8)
C(1)-Co(1)-C(2)-C(3)	127.24(12)
P(1)-Co(1)-C(2)-C(3)	-56.24(8)
P(2)-Co(1)-C(2)-C(3)	78.95(8)
C(5)-Co(1)-C(2)-C(1)	77.86(9)
C(3)-Co(1)-C(2)-C(1)	-127.24(12)
P(1)-Co(1)-C(2)-C(1)	176.52(7)
P(2)-Co(1)-C(2)-C(1)	-48.29(10)
C(1)-C(2)-C(3)-C(4)	-21.66(18)
Co(1)-C(2)-C(3)-C(4)	-81.59(11)
C(1)-C(2)-C(3)-Co(1)	59.93(10)
C(5)-Co(1)-C(3)-C(2)	40.72(12)
C(1)-Co(1)-C(3)-C(2)	-33.61(8)
P(1)-Co(1)-C(3)-C(2)	131.07(7)
P(2)-Co(1)-C(3)-C(2)	-125.85(7)
C(5)-Co(1)-C(3)-C(4)	164.83(9)
C(2)-Co(1)-C(3)-C(4)	124.11(12)
C(1)-Co(1)-C(3)-C(4)	90.49(9)
P(1)-Co(1)-C(3)-C(4)	-104.83(8)
P(2)-Co(1)-C(3)-C(4)	-1.75(9)
C(2)-C(3)-C(4)-O(1)	178.94(12)
Co(1)-C(3)-C(4)-O(1)	114.73(12)
C(2)-Co(1)-C(5)-O(2)	164(3)
C(1)-Co(1)-C(5)-O(2)	-156(3)
C(3)-Co(1)-C(5)-O(2)	137(3)
P(1)-Co(1)-C(5)-O(2)	47(3)
P(2)-Co(1)-C(5)-O(2)	-55(3)

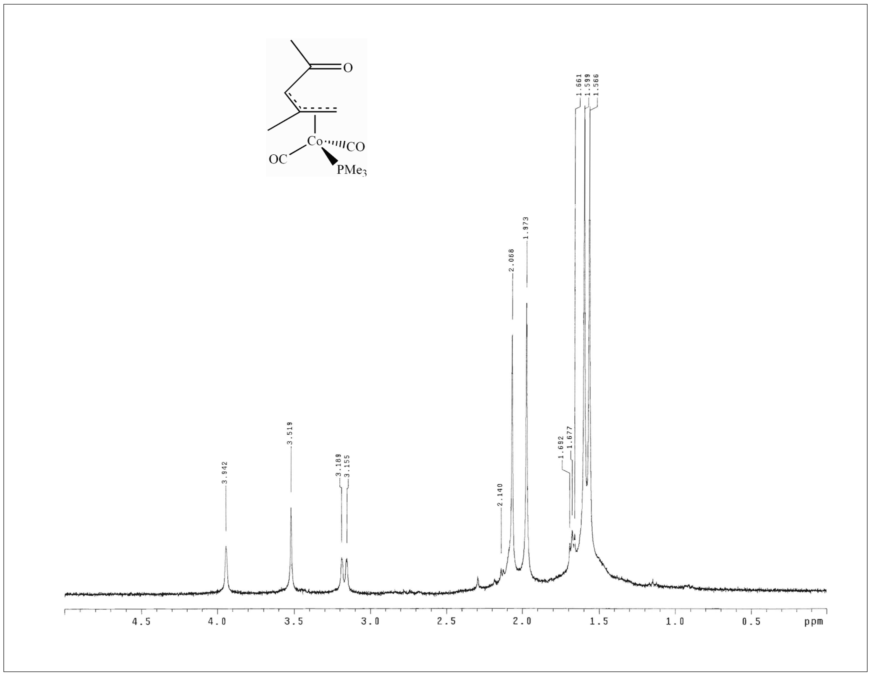

Figure B-20. ^{1}H NMR Spectrum of Compound 8.

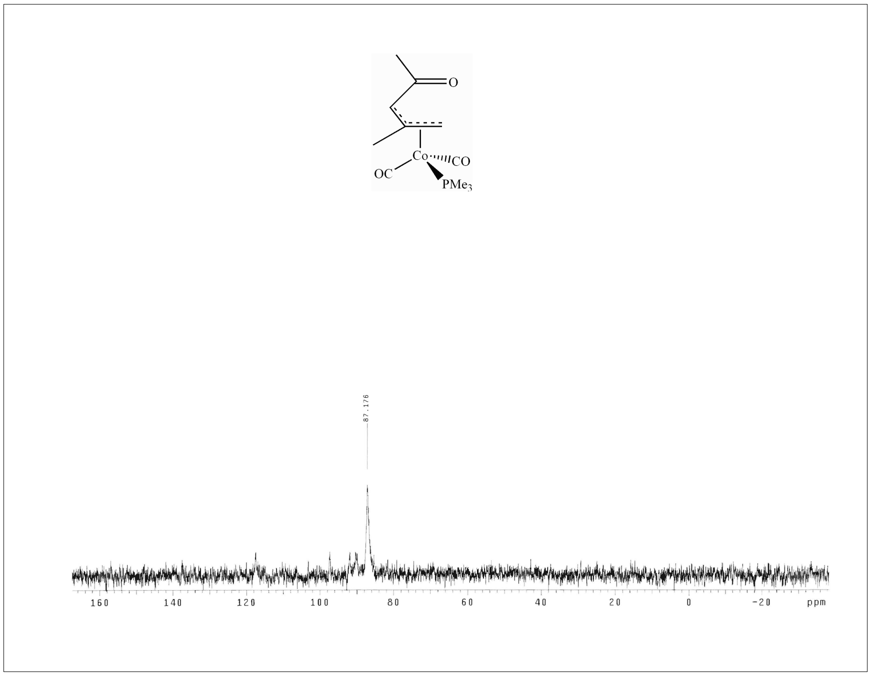

Figure B-21. ^{31}P NMR Spectrum of Compound 8.

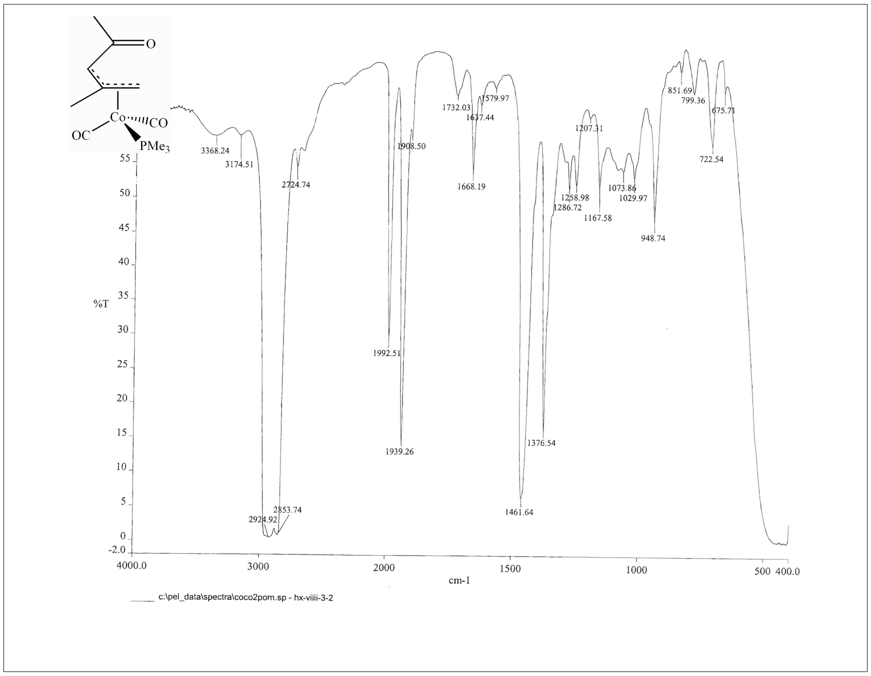

Figure B-22. IR Spectrum of Compound 8.

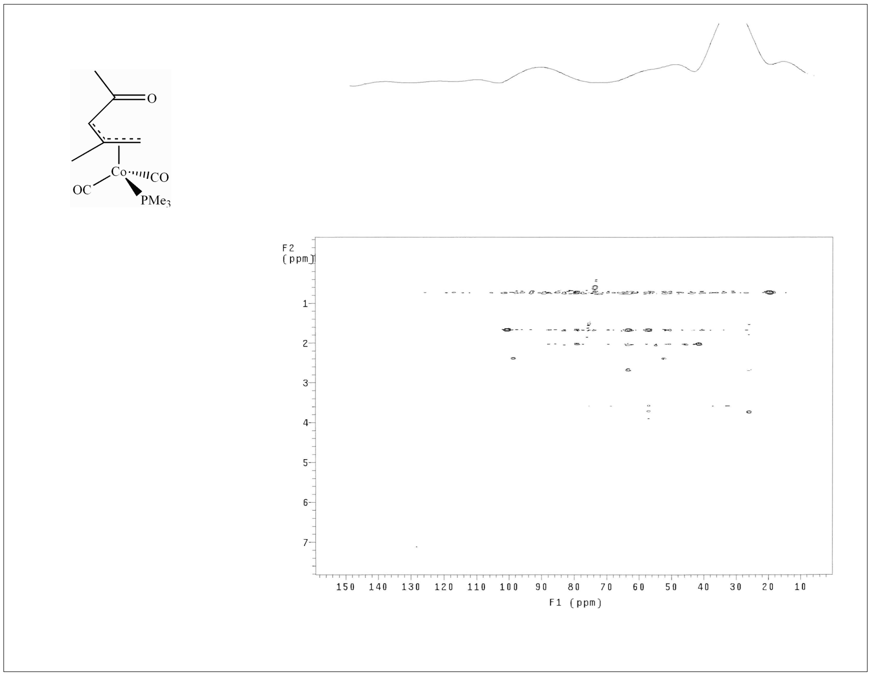

Figure B-23. HMBC Spectrum of Compound 8.

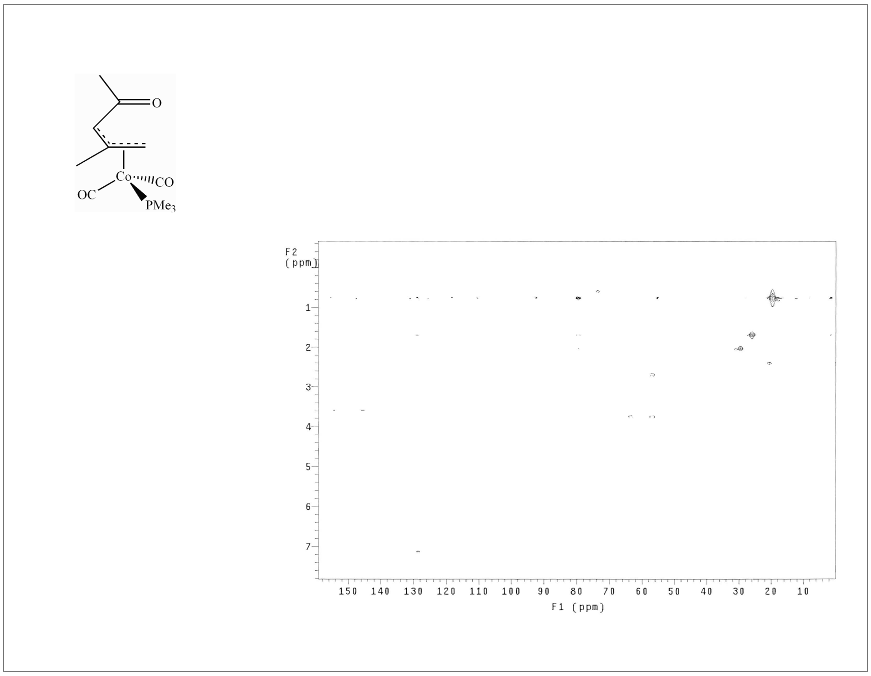

Figure B-24. HMQC Spectrum of Compound 8.

Table B-4.1. Crystal data and structure refinement for Compound 8.

Empirical formula	$C_{11} H_{18} Co O_3 P$	
Formula weight	288.15	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 6.2947(18) Å	α= 90°.
	b = 13.870(4) Å	β= 95.183(14)°.
	c = 16.203(5) Å	γ = 90°.
Volume	1408.9(7) $Å^3$	
Z	4	
Density (calculated)	1.359 Mg/m^3	
Absorption coefficient	1.322 mm^{-1}	
F(000)	600	
Crystal size	0.20 x 0.12 x 0.11 mm^3	
Theta range for data collection	2.52 to 25.42°.	
Index ranges	$-7\le h\le 7$, $-16\le k\le 16$, $-19\le l\le 19$	
Reflections collected	20800	
Independent reflections	2576 [R(int) = 0.0739]	
Completeness to theta = 25.00°	99.8 %	
Absorption correction	Numerical	
Max. and min. transmission	0.8661 and 0.7817	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2576 / 0 / 150	
Goodness-of-fit on F^2	1.058	
Final R indices [I>2sigma(I)]	R1 = 0.0395, wR2 = 0.0996	
R indices (all data)	R1 = 0.0568, wR2 = 0.1099	
Largest diff. peak and hole	0.596 and -0.403 e.$Å^{-3}$	

Table B-4.2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for Compound 8. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Co(1)	227(1)	2037(1)	1228(1)	18(1)
P(1)	1775(1)	1042(1)	2123(1)	21(1)
O(1)	724(4)	4498(2)	1065(1)	33(1)
O(2)	-2027(4)	3054(2)	2475(2)	32(1)
O(3)	-2202(4)	531(2)	306(2)	39(1)
C(1)	3255(5)	2677(2)	1137(2)	26(1)
C(2)	2063(5)	2596(2)	371(2)	25(1)
C(3)	26(5)	3059(2)	279(2)	24(1)
C(4)	-526(5)	3992(2)	630(2)	25(1)
C(5)	2782(6)	1985(3)	-323(2)	38(1)
C(6)	-2791(5)	4331(2)	412(2)	31(1)
C(7)	-1102(5)	2677(2)	1985(2)	21(1)
C(8)	-1223(5)	1124(2)	663(2)	24(1)
C(11)	3227(6)	1620(3)	3009(2)	33(1)
C(12)	-60(6)	257(3)	2600(2)	40(1)
C(13)	3700(6)	205(3)	1767(2)	38(1)

Table B-4.3. Bond lengths [Å] for Compound 8.

Co(1)-C(8)	1.766(3)	C(3)-H(3A)	1.0000
Co(1)-C(7)	1.784(4)	C(4)-C(6)	1.512(5)
Co(1)-C(2)	2.039(3)	C(5)-H(5A)	0.9800
Co(1)-C(3)	2.087(3)	C(5)-H(5B)	0.9800
Co(1)-C(1)	2.120(3)	C(5)-H(5C)	0.9800
Co(1)-P(1)	2.1673(10)	C(6)-H(6A)	0.9800
P(1)-C(13)	1.810(4)	C(6)-H(6B)	0.9800
P(1)-C(12)	1.811(4)	C(6)-H(6C)	0.9800
P(1)-C(11)	1.817(3)	C(11)-H(11A)	0.9800
O(1)-C(4)	1.228(4)	C(11)-H(11B)	0.9800
O(2)-C(7)	1.151(4)	C(11)-H(11C)	0.9800
O(3)-C(8)	1.152(4)	C(12)-H(12A)	0.9800
C(1)-C(2)	1.396(4)	C(12)-H(12B)	0.9800
C(1)-H(1A)	0.9900	C(12)-H(12C)	0.9800
C(1)-H(1B)	0.9900	C(13)-H(13A)	0.9800
C(2)-C(3)	1.430(5)	C(13)-H(13B)	0.9800
C(2)-C(5)	1.510(5)	C(13)-H(13C)	0.9800
C(3)-C(4)	1.468(4)		

Table B-4.4. Bond angles [°] for Compound 8.

C(8)-Co(1)-C(7)	117.43(14)	C(3)-Co(1)-C(1)	70.08(13)
C(8)-Co(1)-C(2)	102.58(14)	C(8)-Co(1)-P(1)	94.06(11)
C(7)-Co(1)-C(2)	127.53(15)	C(7)-Co(1)-P(1)	93.85(10)
C(8)-Co(1)-C(3)	96.36(14)	C(2)-Co(1)-P(1)	116.73(10)
C(7)-Co(1)-C(3)	99.63(13)	C(3)-Co(1)-P(1)	156.76(10)
C(2)-Co(1)-C(3)	40.53(13)	C(1)-Co(1)-P(1)	87.74(9)
C(8)-Co(1)-C(1)	133.62(14)	C(13)-P(1)-C(12)	102.78(18)
C(7)-Co(1)-C(1)	108.64(14)	C(13)-P(1)-C(11)	103.36(17)
C(2)-Co(1)-C(1)	39.18(12)	C(12)-P(1)-C(11)	102.85(18)

C(13)-P(1)-Co(1)	117.93(12)
C(12)-P(1)-Co(1)	113.77(12)
C(11)-P(1)-Co(1)	114.32(12)
C(2)-C(1)-Co(1)	67.28(18)
C(2)-C(1)-H(1A)	117.0
Co(1)-C(1)-H(1A)	117.0
C(2)-C(1)-H(1B)	117.0
Co(1)-C(1)-H(1B)	117.0
H(1A)-C(1)-H(1B)	114.0
C(1)-C(2)-C(3)	117.4(3)
C(1)-C(2)-C(5)	122.3(3)
C(3)-C(2)-C(5)	120.1(3)
C(1)-C(2)-Co(1)	73.54(19)
C(3)-C(2)-Co(1)	71.54(19)
C(5)-C(2)-Co(1)	121.3(2)
C(2)-C(3)-C(4)	126.7(3)
C(2)-C(3)-Co(1)	67.93(17)
C(4)-C(3)-Co(1)	108.3(2)
C(2)-C(3)-H(3A)	114.5
C(4)-C(3)-H(3A)	114.5
Co(1)-C(3)-H(3A)	114.5
O(1)-C(4)-C(3)	124.3(3)
O(1)-C(4)-C(6)	119.9(3)
C(3)-C(4)-C(6)	115.8(3)
C(2)-C(5)-H(5A)	109.5
C(2)-C(5)-H(5B)	109.5
H(5A)-C(5)-H(5B)	109.5
C(2)-C(5)-H(5C)	109.5
H(5A)-C(5)-H(5C)	109.5
H(5B)-C(5)-H(5C)	109.5
C(4)-C(6)-H(6A)	109.5
C(4)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5
C(4)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
O(2)-C(7)-Co(1)	176.7(3)
O(3)-C(8)-Co(1)	178.6(3)
P(1)-C(11)-H(11A)	109.5
P(1)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
P(1)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
P(1)-C(12)-H(12A)	109.5
P(1)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
P(1)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
P(1)-C(13)-H(13A)	109.5
P(1)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
P(1)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5

Table B-4.5. Anisotropic displacement parameters ($Å^2 x 10^3$) for Compound 8. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Co(1)	20(1)	21(1)	13(1)	0(1)	0(1)	-2(1)
P(1)	22(1)	23(1)	18(1)	2(1)	-1(1)	-1(1)
O(1)	41(2)	28(1)	28(1)	1(1)	-2(1)	-8(1)
O(2)	36(2)	36(1)	24(1)	-3(1)	8(1)	3(1)
O(3)	34(2)	39(2)	42(2)	-16(1)	-2(1)	-9(1)
C(1)	24(2)	29(2)	26(2)	9(2)	3(2)	-5(2)
C(2)	28(2)	29(2)	19(2)	7(2)	5(1)	-6(2)
C(3)	32(2)	29(2)	11(2)	3(1)	0(1)	-4(2)
C(4)	34(2)	26(2)	17(2)	7(1)	5(2)	-8(2)
C(5)	43(2)	46(2)	26(2)	2(2)	14(2)	4(2)
C(6)	34(2)	28(2)	33(2)	4(2)	11(2)	4(2)
C(7)	22(2)	23(2)	17(2)	5(1)	-3(1)	-3(1)
C(8)	21(2)	29(2)	23(2)	2(2)	2(1)	2(2)
C(11)	43(2)	37(2)	17(2)	0(2)	-9(2)	1(2)
C(12)	30(2)	39(2)	49(3)	24(2)	1(2)	0(2)
C(13)	44(2)	40(2)	29(2)	0(2)	-2(2)	14(2)

Table B-4.6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for Compound 8.

	x	y	z	U(eq)
H(1A)	3471	3334	1367	31
H(1B)	4517	2253	1235	31
H(3A)	-899	2865	-228	29
H(5A)	3536	2390	-697	57
H(5B)	1535	1691	-632	57
H(5C)	3740	1477	-91	57
H(6A)	-3048	4918	725	47
H(6B)	-3788	3827	553	47
H(6C)	-3006	4468	-183	47
H(11A)	3866	1125	3386	49
H(11B)	2243	2015	3301	49
H(11C)	4353	2029	2819	49
H(12A)	-774	-167	2178	60
H(12B)	-1128	647	2852	60
H(12C)	729	-134	3029	60
H(13A)	4253	-208	2228	57
H(13B)	4880	565	1558	57
H(13C)	3011	-195	1322	57

Table B-4.7. Torsion angles [°] for Compound 8.

C(8)-Co(1)-P(1)-C(13)	68.14(18)
C(7)-Co(1)-P(1)-C(13)	-173.98(17)
C(2)-Co(1)-P(1)-C(13)	-38.13(19)
C(3)-Co(1)-P(1)-C(13)	-48.4(3)
C(1)-Co(1)-P(1)-C(13)	-65.44(18)
C(8)-Co(1)-P(1)-C(12)	-52.33(18)
C(7)-Co(1)-P(1)-C(12)	65.56(19)
C(2)-Co(1)-P(1)-C(12)	-158.60(18)
C(3)-Co(1)-P(1)-C(12)	-168.9(3)
C(1)-Co(1)-P(1)-C(12)	174.09(18)
C(8)-Co(1)-P(1)-C(11)	-170.09(17)
C(7)-Co(1)-P(1)-C(11)	-52.21(17)
C(2)-Co(1)-P(1)-C(11)	83.64(18)
C(3)-Co(1)-P(1)-C(11)	73.4(3)
C(1)-Co(1)-P(1)-C(11)	56.33(17)
C(8)-Co(1)-C(1)-C(2)	46.1(3)
C(7)-Co(1)-C(1)-C(2)	-127.1(2)
C(3)-Co(1)-C(1)-C(2)	-33.4(2)
P(1)-Co(1)-C(1)-C(2)	139.6(2)
Co(1)-C(1)-C(2)-C(3)	58.3(3)
Co(1)-C(1)-C(2)-C(5)	-117.1(3)
C(8)-Co(1)-C(2)-C(1)	-147.7(2)
C(7)-Co(1)-C(2)-C(1)	72.3(2)
C(3)-Co(1)-C(2)-C(1)	127.3(3)
P(1)-Co(1)-C(2)-C(1)	-46.5(2)
C(8)-Co(1)-C(2)-C(3)	85.1(2)
C(7)-Co(1)-C(2)-C(3)	-55.0(2)
C(1)-Co(1)-C(2)-C(3)	-127.3(3)
P(1)-Co(1)-C(2)-C(3)	-173.78(15)
C(8)-Co(1)-C(2)-C(5)	-29.5(3)
C(7)-Co(1)-C(2)-C(5)	-169.5(3)
C(3)-Co(1)-C(2)-C(5)	-114.5(3)
C(1)-Co(1)-C(2)-C(5)	118.2(4)
P(1)-Co(1)-C(2)-C(5)	71.7(3)
C(1)-C(2)-C(3)-C(4)	37.6(5)
C(5)-C(2)-C(3)-C(4)	-146.9(3)
Co(1)-C(2)-C(3)-C(4)	96.9(3)
C(1)-C(2)-C(3)-Co(1)	-59.3(3)
C(5)-C(2)-C(3)-Co(1)	116.1(3)
C(8)-Co(1)-C(3)-C(2)	-101.9(2)
C(7)-Co(1)-C(3)-C(2)	138.8(2)
C(1)-Co(1)-C(3)-C(2)	32.33(19)
P(1)-Co(1)-C(3)-C(2)	14.2(3)
C(8)-Co(1)-C(3)-C(4)	135.1(2)
C(7)-Co(1)-C(3)-C(4)	15.8(3)
C(2)-Co(1)-C(3)-C(4)	-123.0(3)
C(1)-Co(1)-C(3)-C(4)	-90.7(2)
P(1)-Co(1)-C(3)-C(4)	-108.8(3)
C(2)-C(3)-C(4)-O(1)	-0.8(5)
Co(1)-C(3)-C(4)-O(1)	74.9(4)
C(2)-C(3)-C(4)-C(6)	178.0(3)
Co(1)-C(3)-C(4)-C(6)	-106.3(3)
C(8)-Co(1)-C(7)-O(2)	22(5)
C(2)-Co(1)-C(7)-O(2)	157(5)
C(3)-Co(1)-C(7)-O(2)	124(5)
C(1)-Co(1)-C(7)-O(2)	-164(5)
P(1)-Co(1)-C(7)-O(2)	-75(5)
C(7)-Co(1)-C(8)-O(3)	-10(12)
C(2)-Co(1)-C(8)-O(3)	-155(12)
C(3)-Co(1)-C(8)-O(3)	-114(12)
C(1)-Co(1)-C(8)-O(3)	177(100)
P(1)-Co(1)-C(8)-O(3)	87(12)

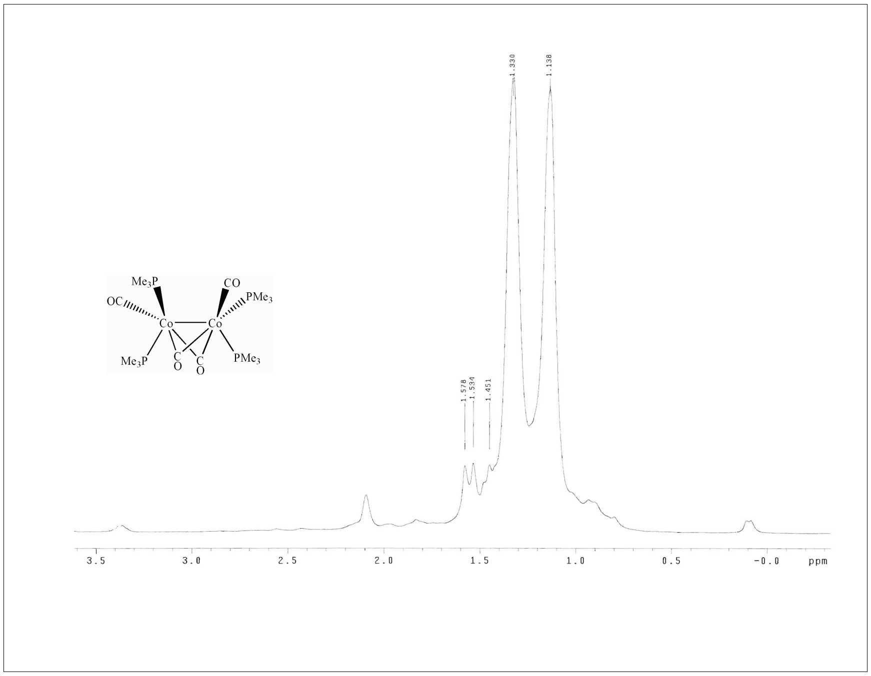

Figure B-25. ^{1}H NMR Spectrum of Compound 9.

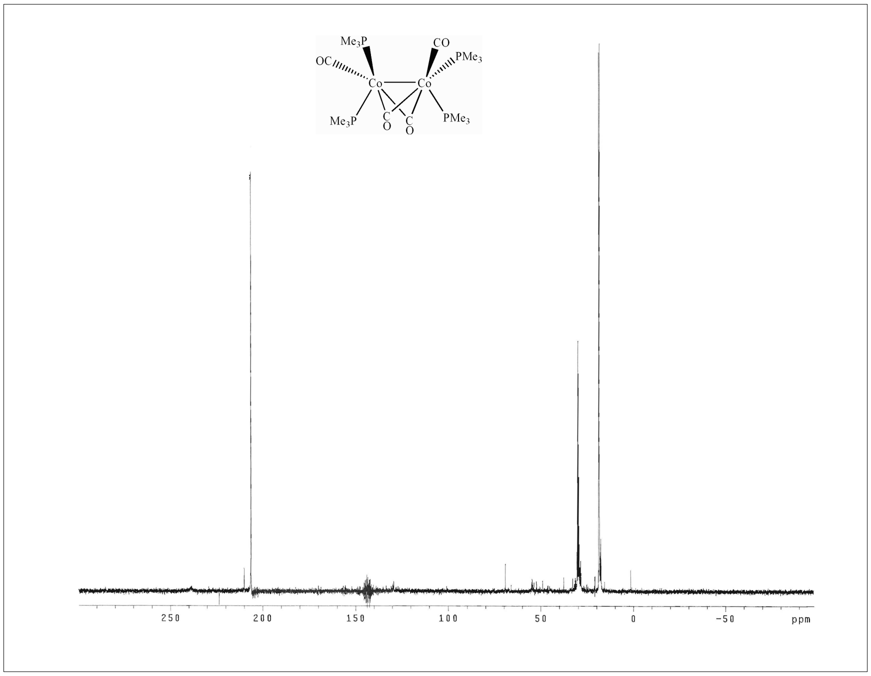

Figure B-26. ^{13}C NMR Spectrum of Compound 9.

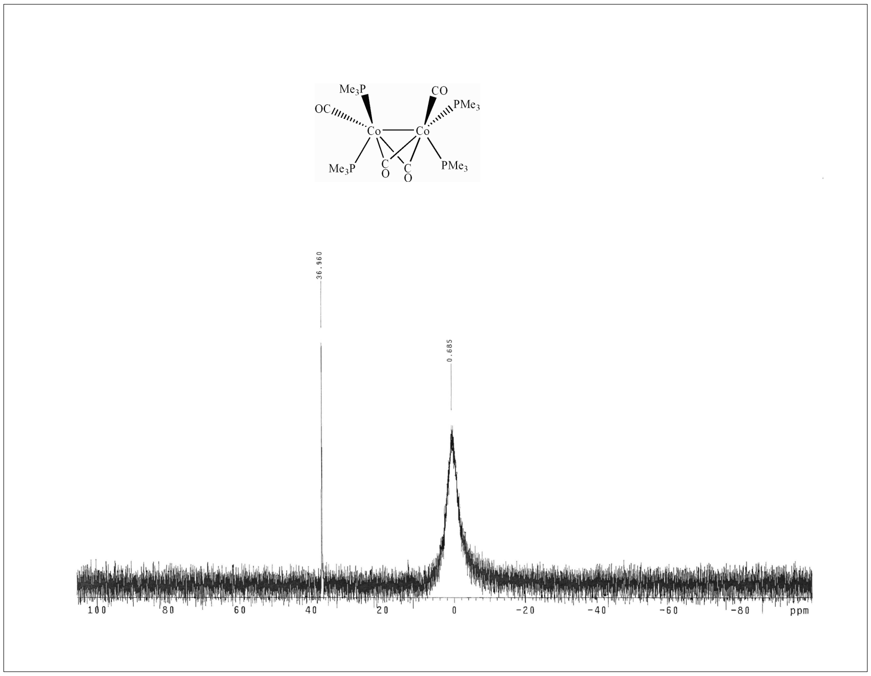

Figure B-27. ^{31}P NMR Spectrum of Compound 9.

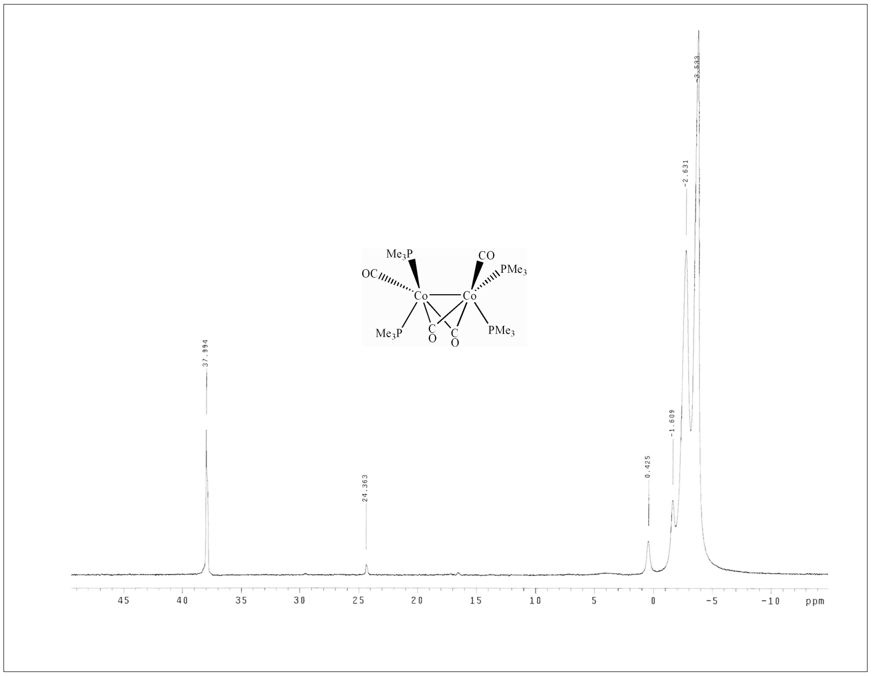

Figure B-28. ^{31}P NMR Spectrum of Compound 9 at -70 C.

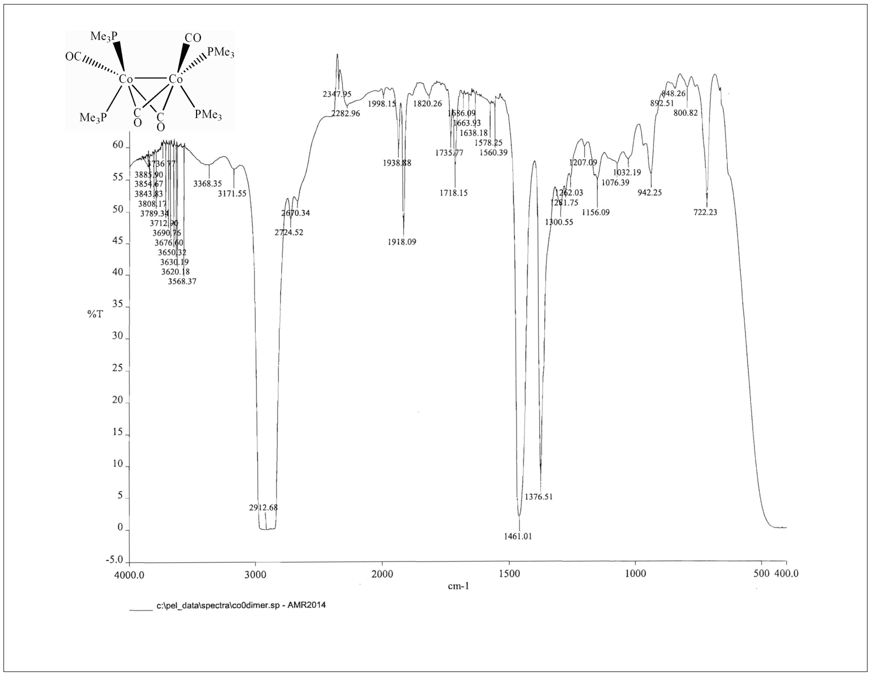

Figure B-29. IR Spectrum of Compound 9.

Table 1. Crystal data and structure refinement for Compound 9.

Empirical formula	$C_{16} H_{36} Co_2 O_4 P_4$	
Formula weight	534.19	
Temperature	140(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 10.9720(9) Å	α= 90°.
	b = 13.2483(11) Å	β= 107.156(4)°.
	c = 18.0190(15) Å	γ = 90°.
Volume	2502.7(4) Å^3	
Z	4	
Density (calculated)	1.418 Mg/m^3	
Absorption coefficient	1.598 mm^{-1}	
F(000)	1112	
Crystal size	0.34 x 0.18 x 0.17 mm^3	
Theta range for data collection	3.00 to 25.48°.	
Index ranges	-13≤h≤13, -15≤k≤16, -21≤l≤21	
Reflections collected	39554	
Independent reflections	4598 [R(int) = 0.092]	
Completeness to theta = 25.48°	99.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7762 and 0.6110	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4598 / 0 / 247	
Goodness-of-fit on F^2	1.026	
Final R indices [I>2sigma(I)]	R1 = 0.0476, wR2 = 0.1134	
R indices (all data)	R1 = 0.0772, wR2 = 0.1345	
Largest diff. peak and hole	1.289 and -0.720 e.Å^{-3}	

Table B-5.2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for Compound 9. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Co(1)	8220(1)	8696(1)	1920(1)	24(1)
Co(2)	6656(1)	7315(1)	1327(1)	24(1)
P(1)	8935(1)	8882(1)	3177(1)	29(1)
P(2)	9844(1)	8648(1)	1428(1)	29(1)
P(3)	5151(1)	7853(1)	285(1)	28(1)
P(4)	5632(1)	6377(1)	1934(1)	33(1)
O(1)	7675(3)	10809(3)	1518(2)	46(1)
O(2)	9083(3)	6635(2)	2361(2)	34(1)
O(3)	5667(3)	9013(2)	2017(2)	39(1)
O(4)	7404(3)	5687(3)	465(2)	46(1)
C(1)	7890(4)	9964(4)	1639(3)	33(1)
C(2)	8333(4)	7257(3)	2045(3)	27(1)
C(3)	6467(4)	8543(3)	1842(2)	28(1)
C(4)	7128(4)	6362(3)	794(3)	31(1)
C(11)	7963(5)	8304(4)	3718(3)	38(1)
C(12)	9035(5)	10179(4)	3525(3)	44(1)
C(13)	10505(5)	8407(4)	3710(3)	50(1)
C(21)	10310(5)	9856(4)	1110(3)	40(1)
C(22)	11366(4)	8136(4)	2003(3)	45(1)
C(23)	9594(5)	7908(4)	552(3)	46(1)
C(31)	5667(5)	8851(3)	-243(3)	36(1)
C(32)	4496(5)	6957(4)	-495(3)	44(1)
C(33)	3680(4)	8365(4)	416(3)	37(1)
C(41)	4436(6)	5543(4)	1321(4)	62(2)
C(42)	4701(5)	6936(4)	2509(3)	52(1)
C(43)	6622(5)	5515(5)	2638(4)	86(3)

Table B-5.3. Bond lengths [Å] for Compound 9.

Co(1)-C(1)	1.761(5)
Co(1)-C(3)	1.897(4)
Co(1)-C(2)	1.920(4)
Co(1)-P(1)	2.1800(13)
Co(1)-P(2)	2.2136(13)
Co(1)-Co(2)	2.5209(8)
Co(2)-C(4)	1.753(5)
Co(2)-C(2)	1.914(4)
Co(2)-C(3)	1.916(4)
Co(2)-P(4)	2.1742(13)
Co(2)-P(3)	2.2199(13)
P(1)-C(11)	1.814(5)
P(1)-C(13)	1.819(5)
P(1)-C(12)	1.822(5)
P(2)-C(23)	1.809(5)
P(2)-C(22)	1.817(5)
P(2)-C(21)	1.823(5)
P(3)-C(31)	1.814(4)
P(3)-C(32)	1.818(5)
P(3)-C(33)	1.829(5)
P(4)-C(43)	1.812(5)
P(4)-C(42)	1.814(5)
P(4)-C(41)	1.819(5)
O(1)-C(1)	1.151(5)
O(2)-C(2)	1.185(5)
O(3)-C(3)	1.192(5)
O(4)-C(4)	1.161(5)
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800
C(31)-H(31A)	0.9800
C(31)-H(31B)	0.9800
C(31)-H(31C)	0.9800
C(32)-H(32A)	0.9800
C(32)-H(32B)	0.9800
C(32)-H(32C)	0.9800
C(33)-H(33A)	0.9800
C(33)-H(33B)	0.9800
C(33)-H(33C)	0.9800
C(41)-H(41A)	0.9800
C(41)-H(41B)	0.9800
C(41)-H(41C)	0.9800
C(42)-H(42A)	0.9800
C(42)-H(42B)	0.9800
C(42)-H(42C)	0.9800
C(43)-H(43A)	0.9800
C(43)-H(43B)	0.9800

C(43)-H(43C)	0.9800

Table B-5.4. Bond angles [°] for Compound 9.

C(1)-Co(1)-C(3)	87.9(2)
C(1)-Co(1)-C(2)	169.0(2)
C(3)-Co(1)-C(2)	86.11(18)
C(1)-Co(1)-P(1)	99.93(15)
C(3)-Co(1)-P(1)	97.79(14)
C(2)-Co(1)-P(1)	89.97(13)
C(1)-Co(1)-P(2)	91.89(15)
C(3)-Co(1)-P(2)	152.32(14)
C(2)-Co(1)-P(2)	89.18(13)
P(1)-Co(1)-P(2)	109.48(5)
C(1)-Co(1)-Co(2)	120.94(15)
C(3)-Co(1)-Co(2)	48.94(13)
C(2)-Co(1)-Co(2)	48.78(13)
P(1)-Co(1)-Co(2)	120.93(4)
P(2)-Co(1)-Co(2)	109.65(4)
C(4)-Co(2)-C(2)	87.76(19)
C(4)-Co(2)-C(3)	165.6(2)
C(2)-Co(2)-C(3)	85.75(19)
C(4)-Co(2)-P(4)	98.30(15)
C(2)-Co(2)-P(4)	99.99(13)
C(3)-Co(2)-P(4)	95.46(14)
C(4)-Co(2)-P(3)	92.02(15)
C(2)-Co(2)-P(3)	155.72(13)
C(3)-Co(2)-P(3)	88.67(13)
P(4)-Co(2)-P(3)	104.05(5)
C(4)-Co(2)-Co(1)	118.75(15)
C(2)-Co(2)-Co(1)	48.99(13)
C(3)-Co(2)-Co(1)	48.29(13)
P(4)-Co(2)-Co(1)	126.09(5)
P(3)-Co(2)-Co(1)	111.63(4)
C(11)-P(1)-C(13)	100.7(2)
C(11)-P(1)-C(12)	101.4(2)
C(13)-P(1)-C(12)	101.1(3)
C(11)-P(1)-Co(1)	114.99(16)
C(13)-P(1)-Co(1)	120.29(18)
C(12)-P(1)-Co(1)	115.50(17)
C(23)-P(2)-C(22)	100.0(3)
C(23)-P(2)-C(21)	100.7(2)
C(22)-P(2)-C(21)	102.2(2)
C(23)-P(2)-Co(1)	115.63(17)
C(22)-P(2)-Co(1)	119.69(17)
C(21)-P(2)-Co(1)	115.72(17)
C(31)-P(3)-C(32)	100.6(2)
C(31)-P(3)-C(33)	102.8(2)
C(32)-P(3)-C(33)	100.3(2)
C(31)-P(3)-Co(2)	114.09(16)
C(32)-P(3)-Co(2)	117.98(18)
C(33)-P(3)-Co(2)	118.35(16)
C(43)-P(4)-C(42)	100.3(3)
C(43)-P(4)-C(41)	102.6(3)
C(42)-P(4)-C(41)	99.7(3)
C(43)-P(4)-Co(2)	114.86(18)
C(42)-P(4)-Co(2)	121.1(2)
C(41)-P(4)-Co(2)	115.4(2)
O(1)-C(1)-Co(1)	174.2(4)
O(2)-C(2)-Co(2)	138.2(4)
O(2)-C(2)-Co(1)	139.4(4)
Co(2)-C(2)-Co(1)	82.24(18)

O(3)-C(3)-Co(1)	137.2(4)
O(3)-C(3)-Co(2)	139.9(4)
Co(1)-C(3)-Co(2)	82.78(17)
O(4)-C(4)-Co(2)	175.6(4)
P(1)-C(11)-H(11A)	109.5
P(1)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
P(1)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
P(1)-C(12)-H(12A)	109.5
P(1)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
P(1)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
P(1)-C(13)-H(13A)	109.5
P(1)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
P(1)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
P(2)-C(21)-H(21A)	109.5
P(2)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
P(2)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
P(2)-C(22)-H(22A)	109.5
P(2)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
P(2)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
P(2)-C(23)-H(23A)	109.5
P(2)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
P(2)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
P(3)-C(31)-H(31A)	109.5
P(3)-C(31)-H(31B)	109.5
H(31A)-C(31)-H(31B)	109.5
P(3)-C(31)-H(31C)	109.5
H(31A)-C(31)-H(31C)	109.5
H(31B)-C(31)-H(31C)	109.5
P(3)-C(32)-H(32A)	109.5
P(3)-C(32)-H(32B)	109.5
H(32A)-C(32)-H(32B)	109.5
P(3)-C(32)-H(32C)	109.5
H(32A)-C(32)-H(32C)	109.5
H(32B)-C(32)-H(32C)	109.5
P(3)-C(33)-H(33A)	109.5
P(3)-C(33)-H(33B)	109.5
H(33A)-C(33)-H(33B)	109.5
P(3)-C(33)-H(33C)	109.5
H(33A)-C(33)-H(33C)	109.5
H(33B)-C(33)-H(33C)	109.5
P(4)-C(41)-H(41A)	109.5
P(4)-C(41)-H(41B)	109.5
H(41A)-C(41)-H(41B)	109.5
P(4)-C(41)-H(41C)	109.5
H(41A)-C(41)-H(41C)	109.5
H(41B)-C(41)-H(41C)	109.5
P(4)-C(42)-H(42A)	109.5
P(4)-C(42)-H(42B)	109.5

H(42A)-C(42)-H(42B)	109.5	P(4)-C(43)-H(43B)	109.5
P(4)-C(42)-H(42C)	109.5	H(43A)-C(43)-H(43B)	109.5
H(42A)-C(42)-H(42C)	109.5	P(4)-C(43)-H(43C)	109.5
H(42B)-C(42)-H(42C)	109.5	H(43A)-C(43)-H(43C)	109.5
P(4)-C(43)-H(43A)	109.5	H(43B)-C(43)-H(43C)	109.5

Table B-5.5. Anisotropic displacement parameters ($Å^2$x 10^3) for Compound 9. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Co(1)	26(1)	25(1)	24(1)	0(1)	10(1)	1(1)
Co(2)	24(1)	24(1)	28(1)	1(1)	13(1)	1(1)
P(1)	30(1)	33(1)	26(1)	0(1)	11(1)	2(1)
P(2)	29(1)	32(1)	29(1)	-3(1)	15(1)	-6(1)
P(3)	28(1)	31(1)	27(1)	0(1)	10(1)	0(1)
P(4)	25(1)	35(1)	43(1)	11(1)	16(1)	1(1)
O(1)	57(2)	29(2)	50(2)	8(2)	11(2)	10(2)
O(2)	30(2)	31(2)	41(2)	10(2)	11(2)	4(2)
O(3)	29(2)	44(2)	45(2)	-11(2)	14(2)	9(2)
O(4)	49(2)	40(2)	53(2)	-14(2)	22(2)	4(2)
C(1)	34(3)	39(3)	25(3)	0(2)	7(2)	0(2)
C(2)	32(2)	27(2)	29(3)	5(2)	18(2)	-1(2)
C(3)	31(2)	32(2)	22(2)	0(2)	12(2)	2(2)
C(4)	32(3)	32(3)	31(3)	1(2)	10(2)	-3(2)
C(11)	53(3)	40(3)	26(3)	6(2)	18(2)	1(2)
C(12)	58(3)	43(3)	35(3)	-7(2)	20(3)	-6(3)
C(13)	40(3)	76(4)	30(3)	2(3)	5(2)	7(3)
C(21)	47(3)	44(3)	33(3)	-1(2)	20(2)	-17(2)
C(22)	34(3)	57(3)	52(3)	5(3)	25(3)	-1(2)

C(23)	49(3)	51(3)	50(3)	-18(3)	33(3)	-13(3)
C(31)	40(3)	37(3)	34(3)	8(2)	16(2)	2(2)
C(32)	46(3)	55(3)	34(3)	-4(2)	15(2)	-7(3)
C(33)	28(3)	47(3)	38(3)	6(2)	13(2)	4(2)
C(41)	76(4)	51(4)	72(4)	-13(3)	42(4)	-31(3)
C(42)	46(3)	72(4)	49(3)	-4(3)	32(3)	-13(3)
C(43)	43(4)	80(5)	138(7)	83(5)	32(4)	13(3)

Table B-5.6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for Compound 9.

	x	y	z	U(eq)
H(11A)	8013	7567	3685	58
H(11B)	7074	8519	3500	58
H(11C)	8275	8512	4264	58
H(12A)	8196	10500	3333	66
H(12B)	9654	10552	3335	66
H(12C)	9309	10182	4094	66
H(13A)	10621	8462	4269	75
H(13B)	11161	8805	3575	75
H(13C)	10578	7698	3574	75
H(21A)	11043	9757	912	59
H(21B)	10543	10325	1550	59
H(21C)	9595	10135	698	59
H(22A)	11229	7478	2215	68
H(22B)	11760	8599	2431	68
H(22C)	11929	8055	1675	68
H(23A)	10354	7946	374	69
H(23B)	8857	8174	148	69
H(23C)	9433	7203	659	69

H(31A)	6343	8596	-447	55
H(31B)	5995	9419	108	55
H(31C)	4943	9077	-674	55
H(32A)	3843	7291	-914	66
H(32B)	4114	6389	-296	66
H(32C)	5180	6708	-695	66
H(33A)	3124	8602	-84	56
H(33B)	3887	8930	783	56
H(33C)	3242	7837	620	56
H(41A)	4805	5179	965	93
H(41B)	3705	5942	1020	93
H(41C)	4154	5058	1646	93
H(42A)	4270	6402	2712	78
H(42B)	4063	7395	2184	78
H(42C)	5266	7314	2943	78
H(43A)	7250	5900	3038	129
H(43B)	7065	5057	2377	129
H(43C)	6086	5121	2881	129

Table B-5.7. Torsion angles [°] for Compound 9.

C(1)-Co(1)-Co(2)-C(4)	117.7(2)	P(1)-Co(1)-Co(2)-C(3)	71.79(18)
C(3)-Co(1)-Co(2)-C(4)	172.4(2)	P(2)-Co(1)-Co(2)-C(3)	-159.39(18)
C(2)-Co(1)-Co(2)-C(4)	-57.6(2)	C(1)-Co(1)-Co(2)-P(4)	-115.13(18)
P(1)-Co(1)-Co(2)-C(4)	-115.85(17)	C(3)-Co(1)-Co(2)-P(4)	-60.52(18)
P(2)-Co(1)-Co(2)-C(4)	12.96(17)	C(2)-Co(1)-Co(2)-P(4)	69.55(17)
C(1)-Co(1)-Co(2)-C(2)	175.3(2)	P(1)-Co(1)-Co(2)-P(4)	11.28(7)
C(3)-Co(1)-Co(2)-C(2)	-130.1(2)	P(2)-Co(1)-Co(2)-P(4)	140.09(6)
P(1)-Co(1)-Co(2)-C(2)	-58.27(17)	C(1)-Co(1)-Co(2)-P(3)	12.63(18)
P(2)-Co(1)-Co(2)-C(2)	70.54(17)	C(3)-Co(1)-Co(2)-P(3)	67.24(18)
C(1)-Co(1)-Co(2)-C(3)	-54.6(2)	C(2)-Co(1)-Co(2)-P(3)	-162.69(17)
C(2)-Co(1)-Co(2)-C(3)	130.1(2)	P(1)-Co(1)-Co(2)-P(3)	139.03(5)

P(2)-Co(1)-Co(2)-P(3)	-92.15(5)
C(1)-Co(1)-P(1)-C(11)	115.3(2)
C(3)-Co(1)-P(1)-C(11)	26.1(2)
C(2)-Co(1)-P(1)-C(11)	-60.0(2)
P(2)-Co(1)-P(1)-C(11)	-149.09(18)
Co(2)-Co(1)-P(1)-C(11)	-20.20(19)
C(1)-Co(1)-P(1)-C(13)	-124.1(3)
C(3)-Co(1)-P(1)-C(13)	146.7(3)
C(2)-Co(1)-P(1)-C(13)	60.6(3)
P(2)-Co(1)-P(1)-C(13)	-28.5(2)
Co(2)-Co(1)-P(1)-C(13)	100.4(2)
C(1)-Co(1)-P(1)-C(12)	-2.4(2)
C(3)-Co(1)-P(1)-C(12)	-91.6(2)
C(2)-Co(1)-P(1)-C(12)	-177.7(2)
P(2)-Co(1)-P(1)-C(12)	93.2(2)
Co(2)-Co(1)-P(1)-C(12)	-137.88(19)
C(1)-Co(1)-P(2)-C(23)	-108.5(3)
C(3)-Co(1)-P(2)-C(23)	-19.4(4)
C(2)-Co(1)-P(2)-C(23)	60.6(2)
P(1)-Co(1)-P(2)-C(23)	150.3(2)
Co(2)-Co(1)-P(2)-C(23)	15.5(2)
C(1)-Co(1)-P(2)-C(22)	131.9(3)
C(3)-Co(1)-P(2)-C(22)	-139.0(4)
C(2)-Co(1)-P(2)-C(22)	-59.0(2)
P(1)-Co(1)-P(2)-C(22)	30.7(2)
Co(2)-Co(1)-P(2)-C(22)	-104.2(2)
C(1)-Co(1)-P(2)-C(21)	8.9(2)
C(3)-Co(1)-P(2)-C(21)	98.0(3)
C(2)-Co(1)-P(2)-C(21)	178.0(2)
P(1)-Co(1)-P(2)-C(21)	-92.30(18)
Co(2)-Co(1)-P(2)-C(21)	132.85(18)
C(4)-Co(2)-P(3)-C(31)	-92.2(2)
C(2)-Co(2)-P(3)-C(31)	-3.2(4)
C(3)-Co(2)-P(3)-C(31)	73.5(2)
P(4)-Co(2)-P(3)-C(31)	168.74(18)
Co(1)-Co(2)-P(3)-C(31)	29.94(18)
C(4)-Co(2)-P(3)-C(32)	25.6(2)
C(2)-Co(2)-P(3)-C(32)	114.6(4)
C(3)-Co(2)-P(3)-C(32)	-168.8(2)
P(4)-Co(2)-P(3)-C(32)	-73.52(19)
Co(1)-Co(2)-P(3)-C(32)	147.67(18)
C(4)-Co(2)-P(3)-C(33)	146.7(2)
C(2)-Co(2)-P(3)-C(33)	-124.3(4)
C(3)-Co(2)-P(3)-C(33)	-47.7(2)
P(4)-Co(2)-P(3)-C(33)	47.63(19)
Co(1)-Co(2)-P(3)-C(33)	-91.18(19)
C(4)-Co(2)-P(4)-C(43)	67.5(3)
C(2)-Co(2)-P(4)-C(43)	-21.7(3)
C(3)-Co(2)-P(4)-C(43)	-108.3(3)
P(3)-Co(2)-P(4)-C(43)	161.7(3)
Co(1)-Co(2)-P(4)-C(43)	-67.6(3)
C(4)-Co(2)-P(4)-C(42)	-171.9(3)
C(2)-Co(2)-P(4)-C(42)	99.0(3)
C(3)-Co(2)-P(4)-C(42)	12.3(3)
P(3)-Co(2)-P(4)-C(42)	-77.7(2)
Co(1)-Co(2)-P(4)-C(42)	53.1(2)
C(4)-Co(2)-P(4)-C(41)	-51.6(3)
C(2)-Co(2)-P(4)-C(41)	-140.8(3)
C(3)-Co(2)-P(4)-C(41)	132.6(3)
P(3)-Co(2)-P(4)-C(41)	42.6(2)
Co(1)-Co(2)-P(4)-C(41)	173.3(2)
C(3)-Co(1)-C(1)-O(1)	78(4)
C(2)-Co(1)-C(1)-O(1)	135(4)
P(1)-Co(1)-C(1)-O(1)	-19(4)
P(2)-Co(1)-C(1)-O(1)	-130(4)
Co(2)-Co(1)-C(1)-O(1)	116(4)

C(4)-Co(2)-C(2)-O(2)	-43.4(5)
C(3)-Co(2)-C(2)-O(2)	149.4(5)
P(4)-Co(2)-C(2)-O(2)	54.6(5)
P(3)-Co(2)-C(2)-O(2)	-133.4(4)
Co(1)-Co(2)-C(2)-O(2)	-175.6(6)
C(4)-Co(2)-C(2)-Co(1)	132.21(18)
C(3)-Co(2)-C(2)-Co(1)	-34.95(16)
P(4)-Co(2)-C(2)-Co(1)	-129.75(10)
P(3)-Co(2)-C(2)-Co(1)	42.3(4)
C(1)-Co(1)-C(2)-O(2)	153.9(9)
C(3)-Co(1)-C(2)-O(2)	-149.1(5)
P(1)-Co(1)-C(2)-O(2)	-51.3(5)
P(2)-Co(1)-C(2)-O(2)	58.2(5)
Co(2)-Co(1)-C(2)-O(2)	175.5(6)
C(1)-Co(1)-C(2)-Co(2)	-21.6(11)
C(3)-Co(1)-C(2)-Co(2)	35.34(17)
P(1)-Co(1)-C(2)-Co(2)	133.15(11)
P(2)-Co(1)-C(2)-Co(2)	-117.37(11)
C(1)-Co(1)-C(3)-O(3)	-42.6(5)
C(2)-Co(1)-C(3)-O(3)	146.6(5)
P(1)-Co(1)-C(3)-O(3)	57.1(5)
P(2)-Co(1)-C(3)-O(3)	-132.7(4)
Co(2)-Co(1)-C(3)-O(3)	-178.2(6)
C(1)-Co(1)-C(3)-Co(2)	135.59(19)
C(2)-Co(1)-C(3)-Co(2)	-35.24(17)
P(1)-Co(1)-C(3)-Co(2)	-124.67(11)
P(2)-Co(1)-C(3)-Co(2)	45.5(4)
C(4)-Co(2)-C(3)-O(3)	150.1(7)
C(2)-Co(2)-C(3)-O(3)	-146.5(6)
P(4)-Co(2)-C(3)-O(3)	-46.9(6)
P(3)-Co(2)-C(3)-O(3)	57.1(5)
Co(1)-Co(2)-C(3)-O(3)	178.1(6)
C(4)-Co(2)-C(3)-Co(1)	-28.0(9)
C(2)-Co(2)-C(3)-Co(1)	35.39(16)
P(4)-Co(2)-C(3)-Co(1)	135.04(11)
P(3)-Co(2)-C(3)-Co(1)	-120.97(12)
C(2)-Co(2)-C(4)-O(4)	98(5)
C(3)-Co(2)-C(4)-O(4)	161(5)
P(4)-Co(2)-C(4)-O(4)	-2(5)
P(3)-Co(2)-C(4)-O(4)	-107(5)
Co(1)-Co(2)-C(4)-O(4)	137(5)

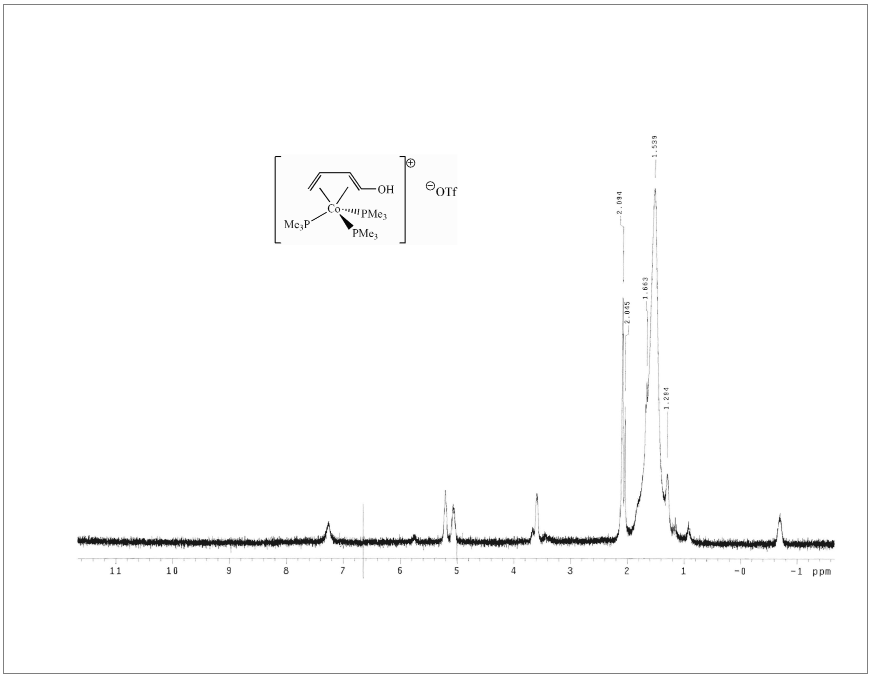

Figure B-30. ^{1}H NMR Spectrum of Compound 10.

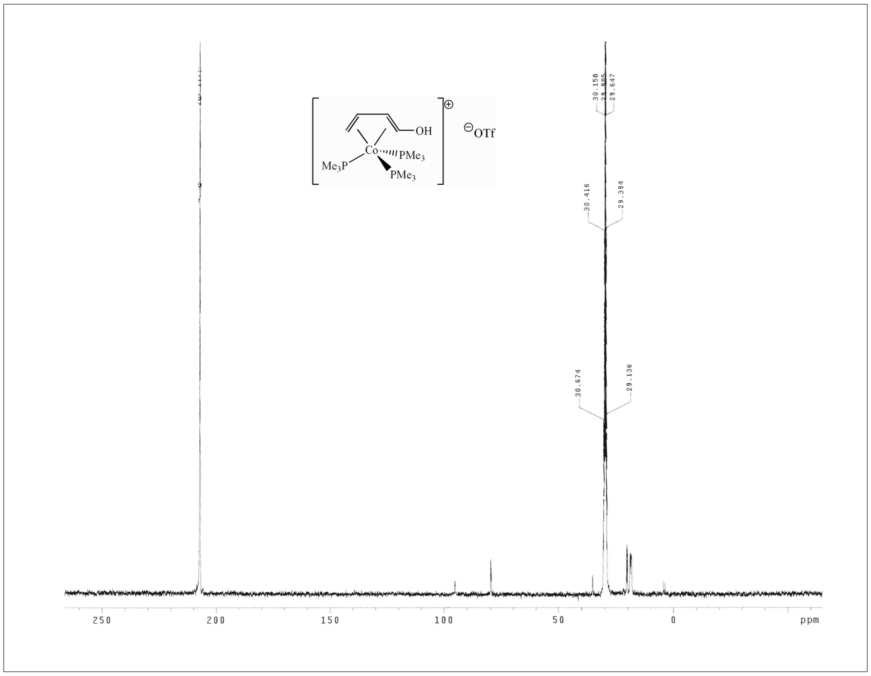

Figure B-31. ^{13}C NMR of Compound 10.

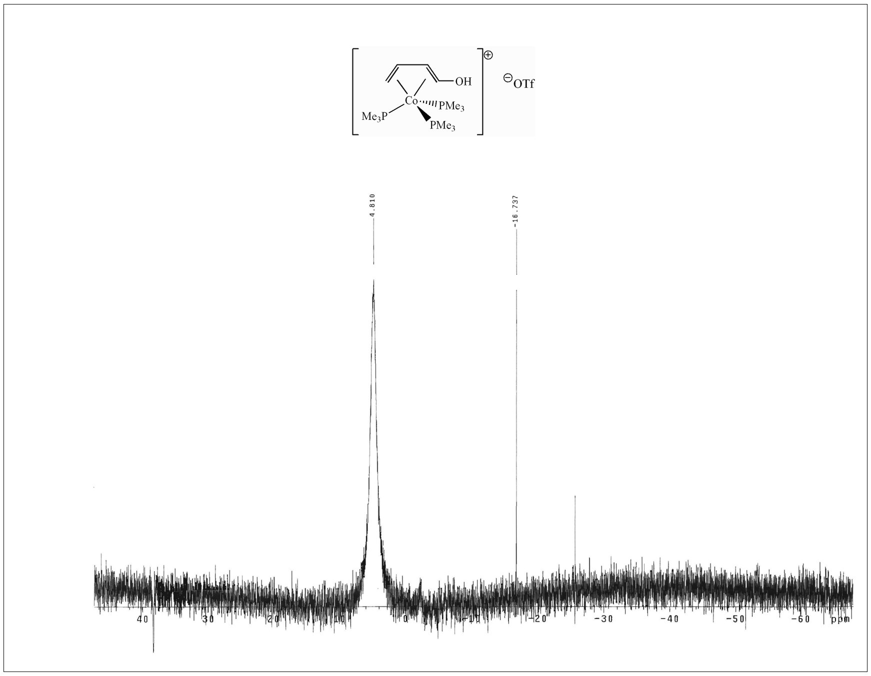

Figure B-32. ^{31}P NMR Spectrum of Compound 10.

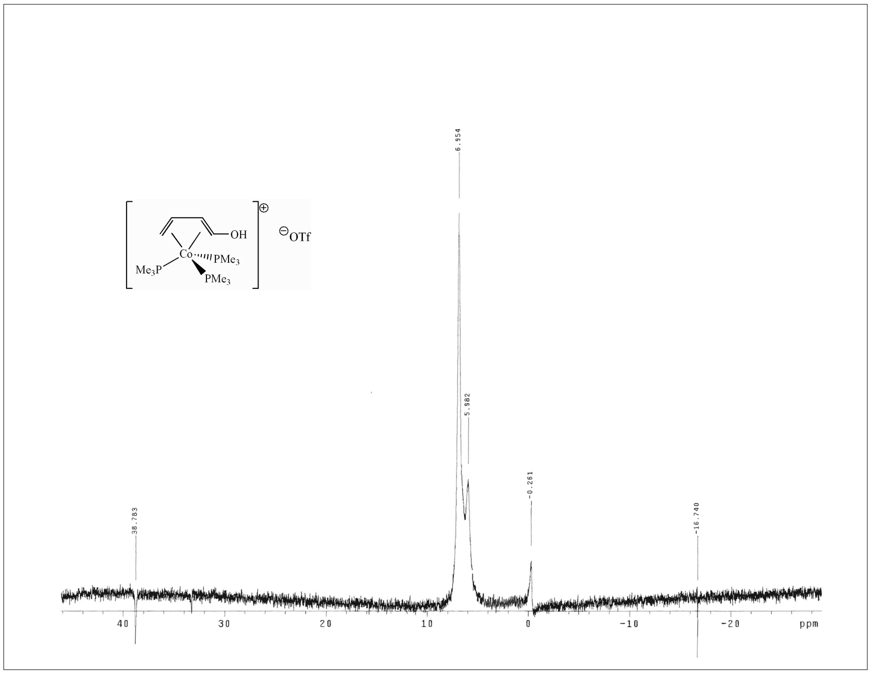

Figure B-33. ^{31}P NMR Spectrum of Compound 10 at -70 C.

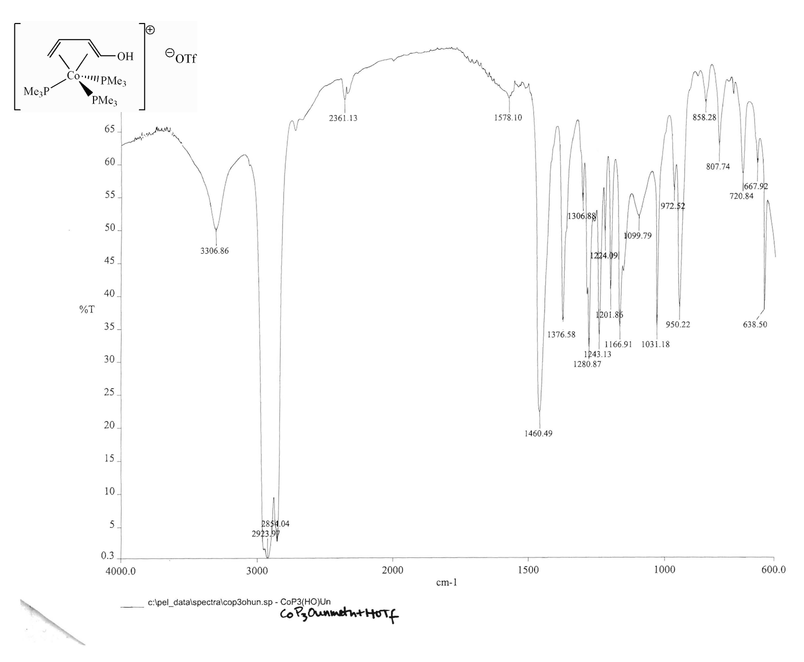

Figure B-34. IR Spectrum of Compound 10.

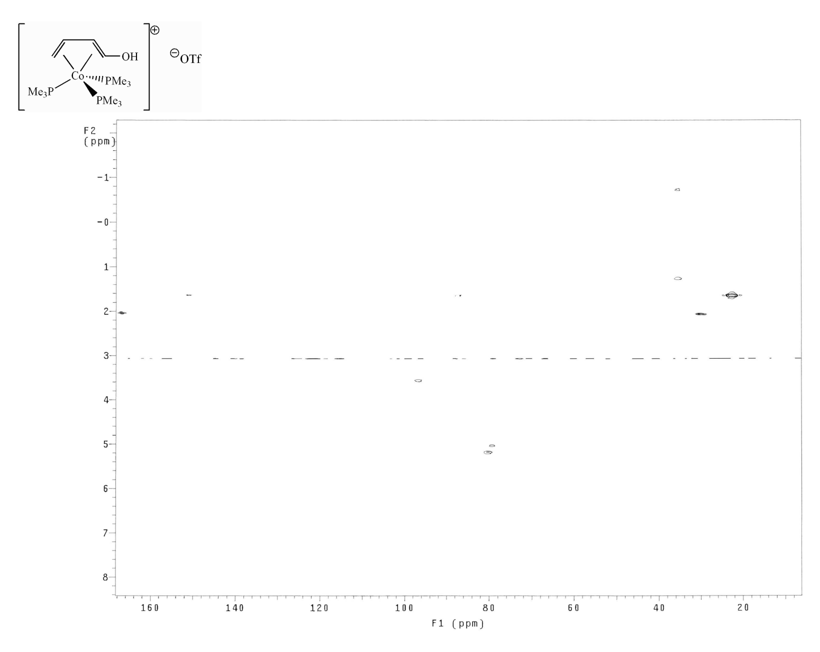

Figure B-35. HMQC Spectrum of Compound 10.

Table B-6.1. Crystal data and structure refinement for Compound 10.

Empirical formula	$C_{14} H_{33} Co F_3 O_4 P_3 S$	
Formula weight	506.30	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.4154(6) Å	α= 90.567(4)°.
	b = 10.1041(6) Å	β= 98.475(4)°.
	c = 13.1407(10) Å	γ = 92.082(4)°.
Volume	1104.29(13) $Å^3$	
Z	2	
Density (calculated)	1.523 Mg/m^3	
Absorption coefficient	1.130 mm^{-1}	
F(000)	528	
Crystal size	0.27 x 0.13 x 0.09 mm^3	
Theta range for data collection	1.57 to 28.97°.	
Index ranges	$-11 \le h \le 11$, $-13 \le k \le 13$, $0 \le l \le 17$	
Reflections collected	56729	
Independent reflections	5786 [R(int) = 0.0000]	
Completeness to theta = 25.00°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9071 and 0.7479	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5786 / 1 / 263	
Goodness-of-fit on F^2	1.087	
Final R indices [I>2sigma(I)]	R1 = 0.0307, wR2 = 0.0712	
R indices (all data)	R1 = 0.0389, wR2 = 0.0751	
Largest diff. peak and hole	0.543 and -0.413 $e.Å^{-3}$	

Table B-6.2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for Compound 10. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Co(1)	1620(1)	7472(1)	2347(1)	8(1)
S(1)	5444(1)	2294(1)	2350(1)	12(1)
P(1)	2588(1)	7405(1)	4003(1)	11(1)
P(2)	-60(1)	5752(1)	2242(1)	10(1)
P(3)	2(1)	9145(1)	2512(1)	11(1)
F(1)	2922(2)	2087(1)	915(1)	23(1)
F(2)	4816(2)	3404(2)	552(1)	36(1)
F(3)	5060(2)	1291(2)	483(1)	32(1)
O(1)	5030(2)	6132(2)	2694(1)	18(1)
O(2)	4749(2)	3429(2)	2774(1)	21(1)
O(3)	4929(2)	1039(2)	2722(1)	22(1)
O(4)	7135(2)	2457(2)	2292(1)	20(1)
C(1)	1253(3)	7523(2)	759(2)	15(1)
C(2)	2474(3)	8460(2)	1195(2)	15(1)
C(3)	3780(3)	7963(2)	1850(2)	14(1)
C(4)	3791(3)	6584(2)	1992(2)	14(1)
C(5)	4522(3)	2272(2)	1006(2)	18(1)
C(11)	1391(3)	7926(2)	4976(2)	17(1)
C(12)	3145(3)	5792(2)	4526(2)	17(1)
C(13)	4446(3)	8386(2)	4394(2)	19(1)
C(21)	-1831(3)	5800(2)	1260(2)	17(1)
C(22)	-1043(3)	5299(2)	3348(2)	16(1)
C(23)	743(3)	4178(2)	1922(2)	18(1)
C(31)	957(3)	10667(2)	3115(2)	18(1)
C(32)	-1026(3)	9811(2)	1318(2)	20(1)
C(33)	-1744(3)	8901(2)	3178(2)	16(1)

Table B-6.3. Bond lengths [Å] for Compound 10.

Co(1)-C(2)	2.026(2)
Co(1)-C(1)	2.065(2)
Co(1)-C(3)	2.066(2)
Co(1)-C(4)	2.173(2)
Co(1)-P(2)	2.1898(6)
Co(1)-P(1)	2.2108(7)
Co(1)-P(3)	2.2371(6)
S(1)-O(3)	1.4381(17)
S(1)-O(4)	1.4405(17)
S(1)-O(2)	1.4493(17)
S(1)-C(5)	1.821(3)
P(1)-C(12)	1.825(2)
P(1)-C(13)	1.825(2)
P(1)-C(11)	1.825(2)
P(2)-C(23)	1.820(2)
P(2)-C(21)	1.824(2)
P(2)-C(22)	1.828(2)
P(3)-C(32)	1.824(2)
P(3)-C(31)	1.827(2)
P(3)-C(33)	1.828(2)
F(1)-C(5)	1.340(3)
F(2)-C(5)	1.328(3)
F(3)-C(5)	1.330(3)
O(1)-C(4)	1.380(3)
O(1)-H(1)	0.77(3)
C(1)-C(2)	1.423(3)
C(1)-H(1A)	0.90(2)
C(1)-H(1B)	0.90(2)
C(2)-C(3)	1.404(3)
C(2)-H(2)	1.02(3)
C(3)-C(4)	1.408(3)
C(3)-H(3)	0.92(3)
C(4)-H(4)	0.92(3)
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800
C(31)-H(31A)	0.9800
C(31)-H(31B)	0.9800
C(31)-H(31C)	0.9800
C(32)-H(32A)	0.9800
C(32)-H(32B)	0.9800
C(32)-H(32C)	0.9800
C(33)-H(33A)	0.9800
C(33)-H(33B)	0.9800
C(33)-H(33C)	0.9800

Table B-6.4. Bond angles [°] for Compound 10.

C(2)-Co(1)-C(1)	40.69(9)	C(13)-P(1)-Co(1)	115.18(8)
C(2)-Co(1)-C(3)	40.11(9)	C(11)-P(1)-Co(1)	120.80(8)
C(1)-Co(1)-C(3)	71.28(10)	C(23)-P(2)-C(21)	100.61(11)
C(2)-Co(1)-C(4)	69.69(9)	C(23)-P(2)-C(22)	101.33(11)
C(1)-Co(1)-C(4)	78.83(9)	C(21)-P(2)-C(22)	99.19(11)
C(3)-Co(1)-C(4)	38.69(8)	C(23)-P(2)-Co(1)	115.93(8)
C(2)-Co(1)-P(2)	128.67(7)	C(21)-P(2)-Co(1)	116.58(8)
C(1)-Co(1)-P(2)	88.24(7)	C(22)-P(2)-Co(1)	119.97(8)
C(3)-Co(1)-P(2)	137.05(7)	C(32)-P(3)-C(31)	99.80(11)
C(4)-Co(1)-P(2)	101.64(6)	C(32)-P(3)-C(33)	98.25(11)
C(2)-Co(1)-P(1)	129.93(7)	C(31)-P(3)-C(33)	102.44(11)
C(1)-Co(1)-P(1)	167.10(7)	C(32)-P(3)-Co(1)	116.17(8)
C(3)-Co(1)-P(1)	96.28(7)	C(31)-P(3)-Co(1)	116.45(8)
C(4)-Co(1)-P(1)	89.33(7)	C(33)-P(3)-Co(1)	120.27(8)
P(2)-Co(1)-P(1)	99.25(2)	C(4)-O(1)-H(1)	107(2)
C(2)-Co(1)-P(3)	88.97(6)	C(2)-C(1)-Co(1)	68.19(13)
C(1)-Co(1)-P(3)	93.68(7)	C(2)-C(1)-H(1A)	120.4(17)
C(3)-Co(1)-P(3)	116.26(7)	Co(1)-C(1)-H(1A)	106.8(18)
C(4)-Co(1)-P(3)	154.95(6)	C(2)-C(1)-H(1B)	118.3(18)
P(2)-Co(1)-P(3)	101.99(2)	Co(1)-C(1)-H(1B)	121.9(18)
P(1)-Co(1)-P(3)	95.00(2)	H(1A)-C(1)-H(1B)	113(2)
O(3)-S(1)-O(4)	115.85(10)	C(3)-C(2)-C(1)	116.8(2)
O(3)-S(1)-O(2)	114.35(11)	C(3)-C(2)-Co(1)	71.49(13)
O(4)-S(1)-O(2)	114.50(10)	C(1)-C(2)-Co(1)	71.12(13)
O(3)-S(1)-C(5)	103.54(11)	C(3)-C(2)-H(2)	117.5(15)
O(4)-S(1)-C(5)	103.27(11)	C(1)-C(2)-H(2)	125.6(15)
O(2)-S(1)-C(5)	102.99(11)	Co(1)-C(2)-H(2)	124.2(15)
C(12)-P(1)-C(13)	101.19(11)	C(2)-C(3)-C(4)	117.4(2)
C(12)-P(1)-C(11)	98.44(11)	C(2)-C(3)-Co(1)	68.40(12)
C(13)-P(1)-C(11)	100.76(11)	C(4)-C(3)-Co(1)	74.77(13)
C(12)-P(1)-Co(1)	117.14(8)	C(2)-C(3)-H(3)	119.6(16)

C(4)-C(3)-H(3)	122.8(17)
Co(1)-C(3)-H(3)	122.5(17)
O(1)-C(4)-C(3)	116.1(2)
O(1)-C(4)-Co(1)	126.37(15)
C(3)-C(4)-Co(1)	66.54(12)
O(1)-C(4)-H(4)	119.0(16)
C(3)-C(4)-H(4)	118.4(17)
Co(1)-C(4)-H(4)	99.2(16)
F(2)-C(5)-F(3)	108.3(2)
F(2)-C(5)-F(1)	107.41(19)
F(3)-C(5)-F(1)	106.94(18)
F(2)-C(5)-S(1)	111.43(16)
F(3)-C(5)-S(1)	111.29(16)
F(1)-C(5)-S(1)	111.26(17)
P(1)-C(11)-H(11A)	109.5
P(1)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
P(1)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
P(1)-C(12)-H(12A)	109.5
P(1)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
P(1)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
P(1)-C(13)-H(13A)	109.5
P(1)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
P(1)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
P(2)-C(21)-H(21A)	109.5
P(2)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
P(2)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
P(2)-C(22)-H(22A)	109.5
P(2)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
P(2)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
P(2)-C(23)-H(23A)	109.5
P(2)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
P(2)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
P(3)-C(31)-H(31A)	109.5
P(3)-C(31)-H(31B)	109.5
H(31A)-C(31)-H(31B)	109.5
P(3)-C(31)-H(31C)	109.5
H(31A)-C(31)-H(31C)	109.5
H(31B)-C(31)-H(31C)	109.5
P(3)-C(32)-H(32A)	109.5
P(3)-C(32)-H(32B)	109.5
H(32A)-C(32)-H(32B)	109.5
P(3)-C(32)-H(32C)	109.5
H(32A)-C(32)-H(32C)	109.5
H(32B)-C(32)-H(32C)	109.5
P(3)-C(33)-H(33A)	109.5
P(3)-C(33)-H(33B)	109.5
H(33A)-C(33)-H(33B)	109.5
P(3)-C(33)-H(33C)	109.5

H(33A)-C(33)-H(33C) 109.5 | H(33B)-C(33)-H(33C) 109.5

Table B-6.5. Anisotropic displacement parameters ($Å^2$x 10^3) for Compound 10. The anisotropic displacement factor exponent takes the form: $-2\pi^2$[h^2 $a^{*2}U^{11}$ + ... + 2 h k a* b* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Co(1)	9(1)	9(1)	8(1)	0(1)	2(1)	1(1)
S(1)	12(1)	11(1)	13(1)	-1(1)	0(1)	2(1)
P(1)	10(1)	14(1)	10(1)	0(1)	1(1)	1(1)
P(2)	10(1)	10(1)	11(1)	0(1)	1(1)	0(1)
P(3)	12(1)	10(1)	12(1)	1(1)	3(1)	3(1)
F(1)	15(1)	27(1)	25(1)	-3(1)	-6(1)	1(1)
F(2)	43(1)	36(1)	24(1)	16(1)	-7(1)	-12(1)
F(3)	29(1)	44(1)	23(1)	-16(1)	6(1)	4(1)
O(1)	13(1)	17(1)	24(1)	-2(1)	3(1)	4(1)
O(2)	21(1)	19(1)	22(1)	-5(1)	-1(1)	7(1)
O(3)	23(1)	17(1)	24(1)	5(1)	1(1)	-1(1)
O(4)	11(1)	21(1)	26(1)	-3(1)	1(1)	-1(1)
C(1)	18(1)	17(1)	12(1)	2(1)	5(1)	3(1)
C(2)	18(1)	13(1)	15(1)	3(1)	8(1)	1(1)
C(3)	13(1)	18(1)	14(1)	-1(1)	8(1)	-2(1)
C(4)	12(1)	16(1)	13(1)	-2(1)	6(1)	1(1)
C(5)	17(1)	17(1)	17(1)	-1(1)	0(1)	-2(1)
C(11)	19(1)	22(1)	12(1)	1(1)	4(1)	4(1)
C(12)	17(1)	18(1)	14(1)	4(1)	-1(1)	5(1)
C(13)	17(1)	23(1)	16(1)	-2(1)	-1(1)	-5(1)
C(21)	15(1)	20(1)	15(1)	1(1)	-2(1)	0(1)
C(22)	14(1)	18(1)	14(1)	2(1)	2(1)	-3(1)
C(23)	19(1)	11(1)	26(1)	-2(1)	6(1)	1(1)
C(31)	20(1)	13(1)	22(1)	-2(1)	6(1)	0(1)

C(32)	28(1)	20(1)	14(1)	2(1)	1(1)	11(1)
C(33)	12(1)	19(1)	19(1)	2(1)	3(1)	4(1)

Table B-6.6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for Compound 10.

	x	y	z	U(eq)
H(1)	5030(40)	5380(30)	2630(20)	27
H(1A)	1520(30)	6730(20)	530(20)	18
H(1B)	340(30)	7830(30)	400(20)	18
H(2)	2440(30)	9460(30)	1110(20)	17
H(3)	4530(30)	8540(30)	2210(20)	17
H(4)	3350(30)	6040(30)	1460(20)	16
H(11A)	1998	7808	5662	26
H(11B)	386	7388	4905	26
H(11C)	1145	8861	4882	26
H(12A)	3819	5359	4084	25
H(12B)	2171	5240	4554	25
H(12C)	3744	5910	5221	25
H(13A)	4736	8355	5144	29
H(13B)	4288	9306	4185	29
H(13C)	5310	8024	4064	29
H(21A)	-1493	5874	580	25
H(21B)	-2460	6565	1389	25
H(21C)	-2492	4985	1284	25
H(22A)	-1711	4488	3183	23
H(22B)	-1720	6018	3509	23
H(22C)	-225	5147	3943	23
H(23A)	1632	3961	2456	27
H(23B)	1136	4245	1257	27

H(23C)	-105	3481	1879	27
H(31A)	164	11358	3081	28
H(31B)	1841	10959	2751	28
H(31C)	1379	10502	3836	28
H(32A)	-1725	9117	943	31
H(32B)	-229	10125	893	31
H(32C)	-1675	10551	1477	31
H(33A)	-1385	8663	3894	25
H(33B)	-2452	8188	2835	25
H(33C)	-2332	9722	3163	25

Table B-6.7. Torsion angles [°] for Compound 10.

C(2)-Co(1)-P(1)-C(12)	-118.99(12)
C(1)-Co(1)-P(1)-C(12)	-79.7(3)
C(3)-Co(1)-P(1)-C(12)	-94.68(11)
C(4)-Co(1)-P(1)-C(12)	-56.54(11)
P(2)-Co(1)-P(1)-C(12)	45.14(9)
P(3)-Co(1)-P(1)-C(12)	148.17(9)
C(2)-Co(1)-P(1)-C(13)	-0.17(12)
C(1)-Co(1)-P(1)-C(13)	39.1(3)
C(3)-Co(1)-P(1)-C(13)	24.14(11)
C(4)-Co(1)-P(1)-C(13)	62.27(11)
P(2)-Co(1)-P(1)-C(13)	163.95(9)
P(3)-Co(1)-P(1)-C(13)	-93.01(9)
C(2)-Co(1)-P(1)-C(11)	121.18(12)
C(1)-Co(1)-P(1)-C(11)	160.4(3)
C(3)-Co(1)-P(1)-C(11)	145.49(11)
C(4)-Co(1)-P(1)-C(11)	-176.37(11)
P(2)-Co(1)-P(1)-C(11)	-74.69(9)
P(3)-Co(1)-P(1)-C(11)	28.34(9)
C(2)-Co(1)-P(2)-C(23)	73.47(12)
C(1)-Co(1)-P(2)-C(23)	78.50(12)
C(3)-Co(1)-P(2)-C(23)	18.78(14)
C(4)-Co(1)-P(2)-C(23)	0.28(12)
P(1)-Co(1)-P(2)-C(23)	-90.94(10)
P(3)-Co(1)-P(2)-C(23)	171.89(9)
C(2)-Co(1)-P(2)-C(21)	-44.70(12)
C(1)-Co(1)-P(2)-C(21)	-39.67(11)
C(3)-Co(1)-P(2)-C(21)	-99.39(13)
C(4)-Co(1)-P(2)-C(21)	-117.89(11)
P(1)-Co(1)-P(2)-C(21)	150.88(9)
P(3)-Co(1)-P(2)-C(21)	53.72(9)
C(2)-Co(1)-P(2)-C(22)	-164.35(12)
C(1)-Co(1)-P(2)-C(22)	-159.32(11)
C(3)-Co(1)-P(2)-C(22)	140.96(13)
C(4)-Co(1)-P(2)-C(22)	122.46(11)
P(1)-Co(1)-P(2)-C(22)	31.24(9)
P(3)-Co(1)-P(2)-C(22)	-65.93(9)
C(2)-Co(1)-P(3)-C(32)	43.38(12)
C(1)-Co(1)-P(3)-C(32)	2.94(12)
C(3)-Co(1)-P(3)-C(32)	73.86(13)
C(4)-Co(1)-P(3)-C(32)	74.22(18)

P(2)-Co(1)-P(3)-C(32)	-86.04(10)
P(1)-Co(1)-P(3)-C(32)	173.39(10)
C(2)-Co(1)-P(3)-C(31)	-73.77(11)
C(1)-Co(1)-P(3)-C(31)	-114.21(11)
C(3)-Co(1)-P(3)-C(31)	-43.29(12)
C(4)-Co(1)-P(3)-C(31)	-42.93(18)
P(2)-Co(1)-P(3)-C(31)	156.81(9)
P(1)-Co(1)-P(3)-C(31)	56.23(9)
C(2)-Co(1)-P(3)-C(33)	161.54(12)
C(1)-Co(1)-P(3)-C(33)	121.10(12)
C(3)-Co(1)-P(3)-C(33)	-167.98(12)
C(4)-Co(1)-P(3)-C(33)	-167.61(18)
P(2)-Co(1)-P(3)-C(33)	32.12(10)
P(1)-Co(1)-P(3)-C(33)	-68.45(10)
C(3)-Co(1)-C(1)-C(2)	-32.38(13)
C(4)-Co(1)-C(1)-C(2)	-71.75(13)
P(2)-Co(1)-C(1)-C(2)	-173.98(12)
P(1)-Co(1)-C(1)-C(2)	-48.1(4)
P(3)-Co(1)-C(1)-C(2)	84.12(12)
Co(1)-C(1)-C(2)-C(3)	56.74(18)
C(1)-Co(1)-C(2)-C(3)	-128.06(19)
C(4)-Co(1)-C(2)-C(3)	-31.53(13)
P(2)-Co(1)-C(2)-C(3)	-120.34(12)
P(1)-Co(1)-C(2)-C(3)	39.43(15)
P(3)-Co(1)-C(2)-C(3)	135.08(12)
C(3)-Co(1)-C(2)-C(1)	128.06(19)
C(4)-Co(1)-C(2)-C(1)	96.53(14)
P(2)-Co(1)-C(2)-C(1)	7.72(16)
P(1)-Co(1)-C(2)-C(1)	167.49(11)
P(3)-Co(1)-C(2)-C(1)	-96.85(12)
C(1)-C(2)-C(3)-C(4)	1.9(3)
Co(1)-C(2)-C(3)-C(4)	58.47(18)
C(1)-C(2)-C(3)-Co(1)	-56.56(18)
C(1)-Co(1)-C(3)-C(2)	32.82(13)
C(4)-Co(1)-C(3)-C(2)	128.3(2)
P(2)-Co(1)-C(3)-C(2)	98.51(14)
P(1)-Co(1)-C(3)-C(2)	-150.66(12)
P(3)-Co(1)-C(3)-C(2)	-51.92(14)
C(2)-Co(1)-C(3)-C(4)	-128.3(2)
C(1)-Co(1)-C(3)-C(4)	-95.50(15)
P(2)-Co(1)-C(3)-C(4)	-29.81(18)
P(1)-Co(1)-C(3)-C(4)	81.02(13)
P(3)-Co(1)-C(3)-C(4)	179.76(11)
C(2)-C(3)-C(4)-O(1)	-175.70(19)
Co(1)-C(3)-C(4)-O(1)	-120.48(18)
C(2)-C(3)-C(4)-Co(1)	-55.22(18)
C(2)-Co(1)-C(4)-O(1)	138.6(2)
C(1)-Co(1)-C(4)-O(1)	180.0(2)
C(3)-Co(1)-C(4)-O(1)	106.0(2)
P(2)-Co(1)-C(4)-O(1)	-94.21(18)
P(1)-Co(1)-C(4)-O(1)	5.10(18)
P(3)-Co(1)-C(4)-O(1)	105.5(2)
C(2)-Co(1)-C(4)-C(3)	32.62(14)
C(1)-Co(1)-C(4)-C(3)	73.93(15)
P(2)-Co(1)-C(4)-C(3)	159.77(13)
P(1)-Co(1)-C(4)-C(3)	-100.92(13)
P(3)-Co(1)-C(4)-C(3)	-0.5(2)
O(3)-S(1)-C(5)-F(2)	176.93(17)
O(4)-S(1)-C(5)-F(2)	-61.91(19)
O(2)-S(1)-C(5)-F(2)	57.54(19)
O(3)-S(1)-C(5)-F(3)	-62.07(18)
O(4)-S(1)-C(5)-F(3)	59.10(18)
O(2)-S(1)-C(5)-F(3)	178.54(16)
O(3)-S(1)-C(5)-F(1)	57.08(18)
O(4)-S(1)-C(5)-F(1)	178.25(15)
O(2)-S(1)-C(5)-F(1)	-62.31(18)

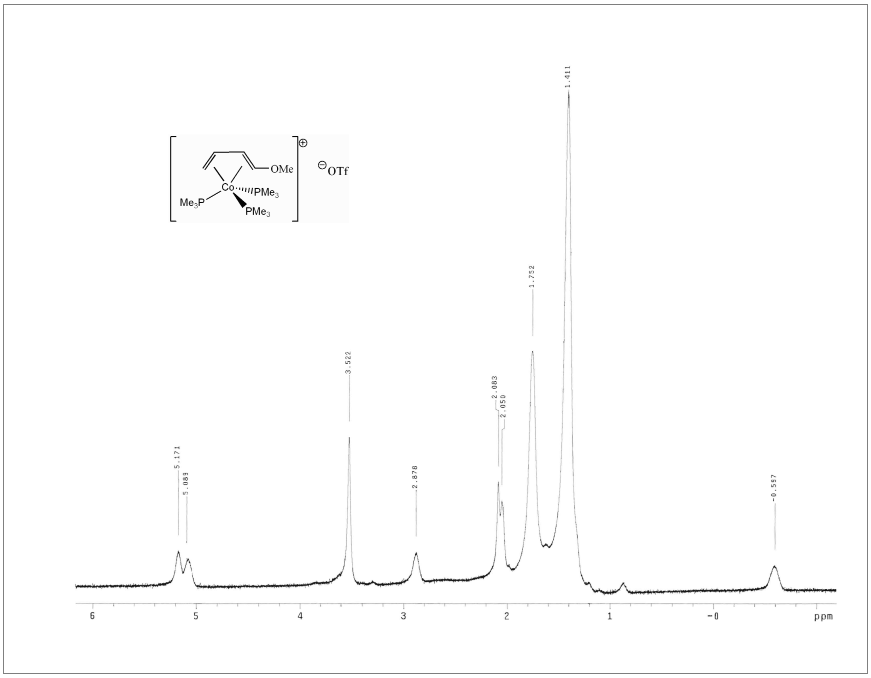

Figure B-36. ^{1}H NMR Spectrum of Compound 11.

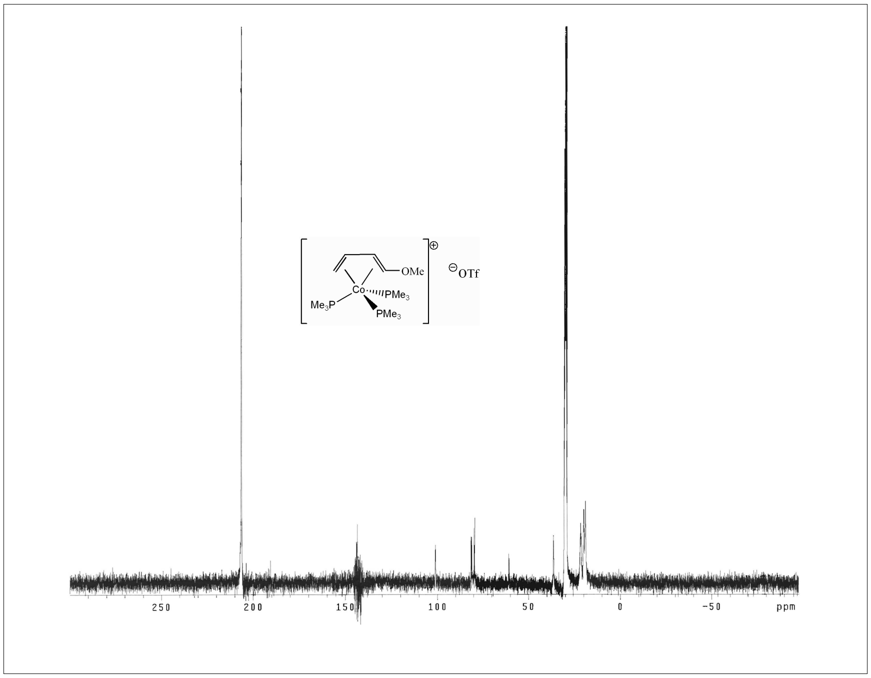

Figure B-37. ^{13}C NMR Spectrum of Compound 11.

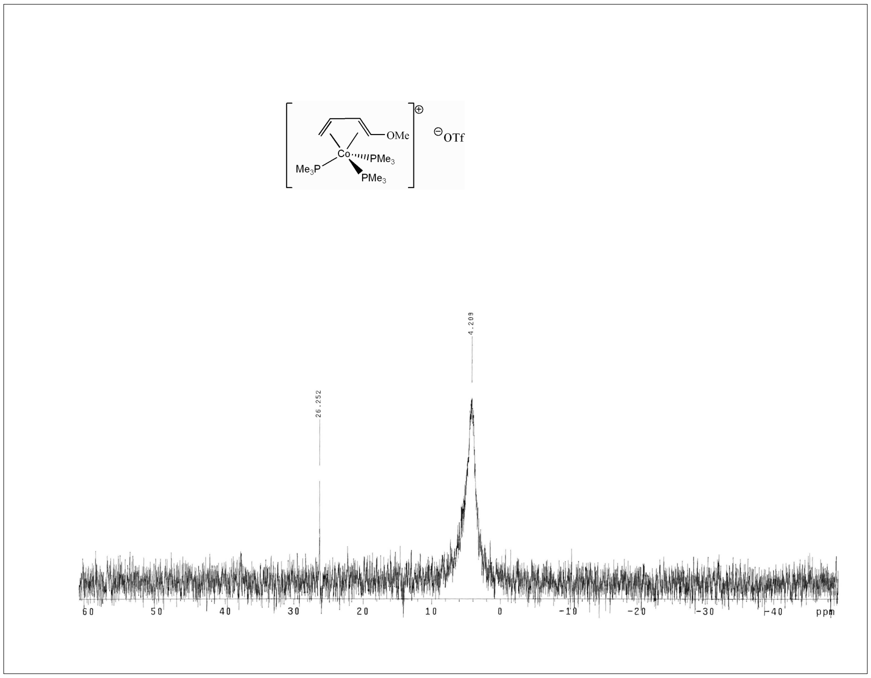

Figure B-38. ^{31}P NMR Spectrum of Compound 11.

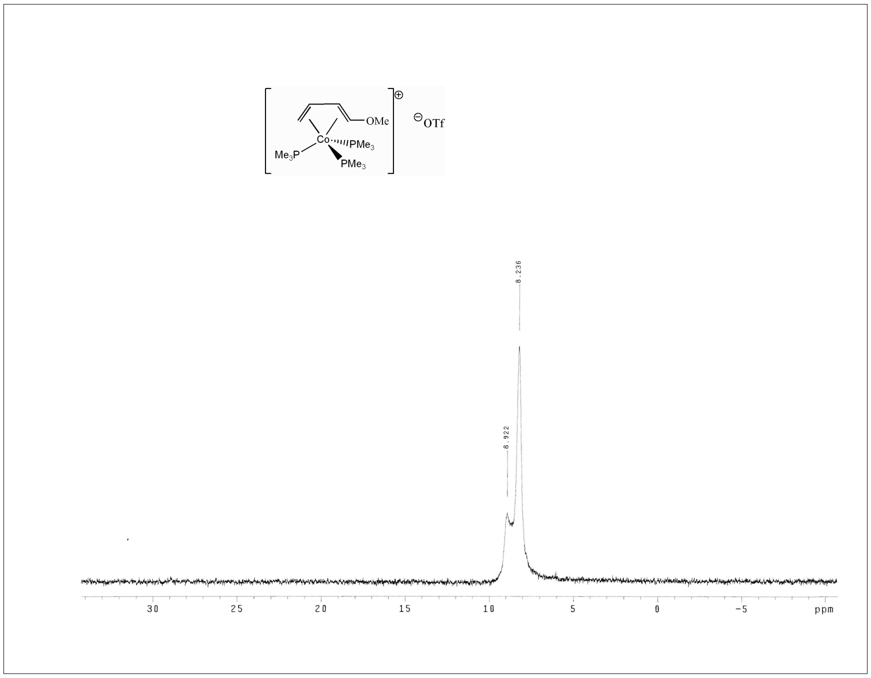

Figure B-39. ^{31}P NMR Spectrum of Compound 11 at -70 C.

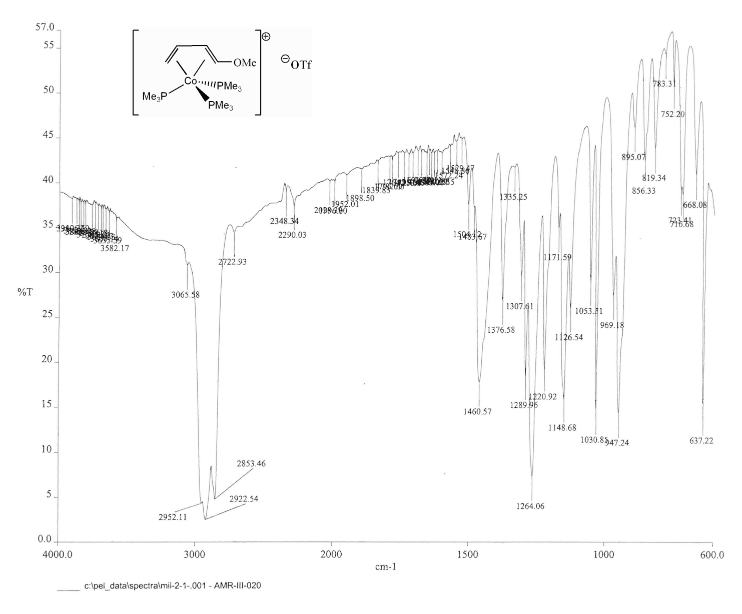

Figure B-40. IR Spectrum of Compound 11.

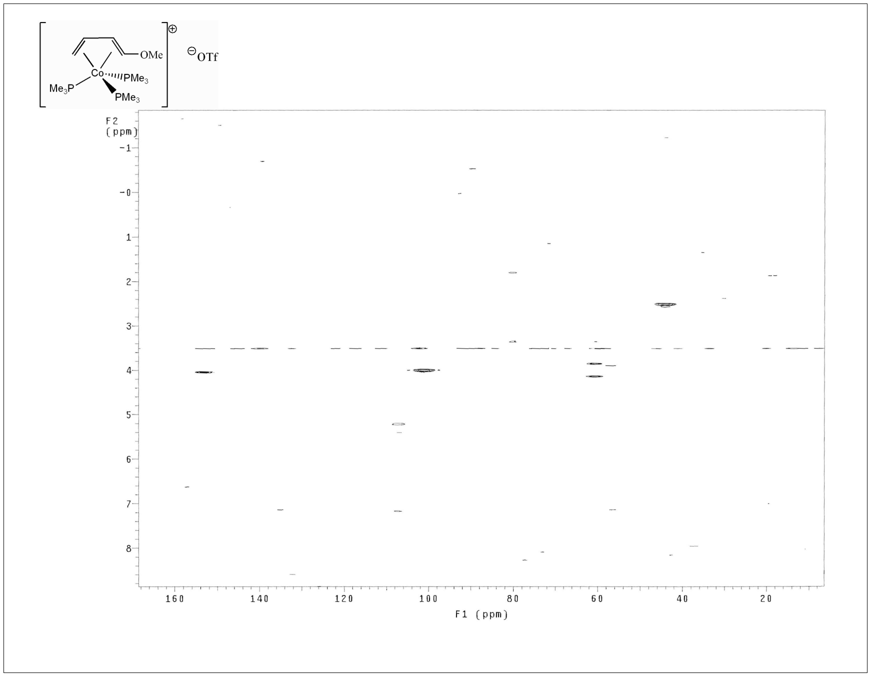

Figure B-41. HMQC Spectrum of Compound 11.

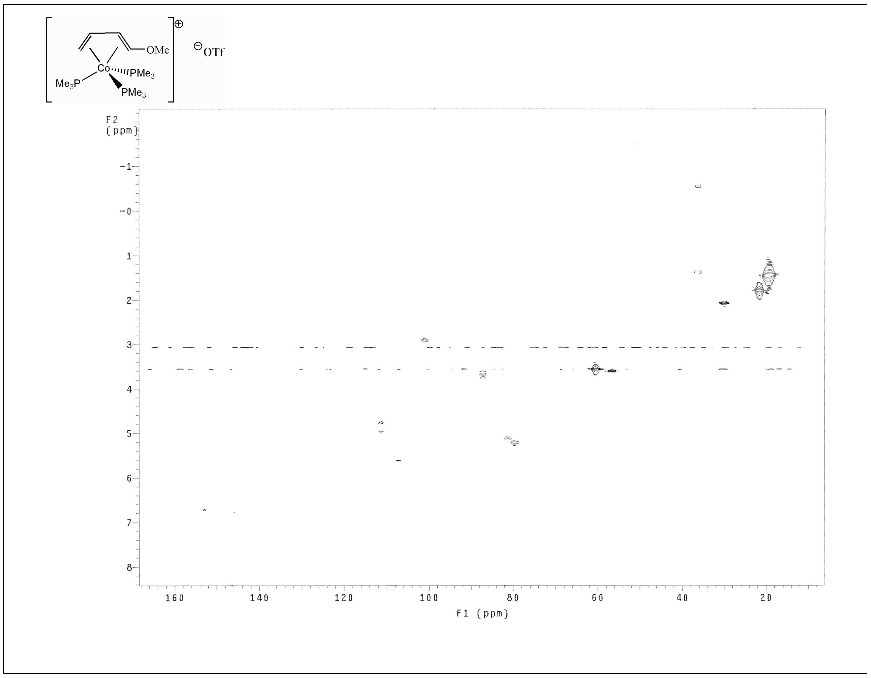

Figure B-41. HMBC Spectrum of Compound 11.

Table B-7.1. Crystal data and structure refinement for Compound 11.

Empirical formula	$C_{15} H_{35} Co F_3 O_4 P_3 S$	
Formula weight	520.33	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 16.5274(11) Å	α= 90°.
	b = 15.3020(11) Å	β= 90.855(3)°.
	c = 18.7319(12) Å	γ = 90°.
Volume	4736.8(6) $Å^3$	
Z	8	
Density (calculated)	1.459 Mg/m^3	
Absorption coefficient	1.056 mm^{-1}	
F(000)	2176	
Crystal size	0.24 x 0.19 x 0.17 mm^3	
Theta range for data collection	1.23 to 36.48°.	
Index ranges	$-27 \leq h \leq 27$, $-25 \leq k \leq 25$, $-31 \leq l \leq 31$	
Reflections collected	214380	
Independent reflections	22719 [R(int) = 0.0556]	
Completeness to theta = 25.00°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8426 and 0.7880	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	22719 / 0 / 507	
Goodness-of-fit on F^2	1.013	
Final R indices [I>2sigma(I)]	R1 = 0.0321, wR2 = 0.0642	
R indices (all data)	R1 = 0.0576, wR2 = 0.0729	
Largest diff. peak and hole	0.598 and -0.569 $e.Å^{-3}$	

Table B-7.2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for Compound 11. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Co(1)	3338(1)	1380(1)	2166(1)	9(1)
Co(2)	1553(1)	6487(1)	2962(1)	11(1)
P(1)	3588(1)	115(1)	2691(1)	13(1)
P(2)	4076(1)	1282(1)	1200(1)	14(1)
P(3)	4148(1)	2114(1)	2918(1)	13(1)
P(1')	1450(1)	5113(1)	3332(1)	15(1)
P(2')	752(1)	6505(1)	2017(1)	14(1)
P(3')	726(1)	6998(1)	3797(1)	13(1)
S(1)	1550(1)	2150(1)	4667(1)	18(1)
S(1')	3471(1)	7123(1)	5425(1)	14(1)
F(1)	1534(1)	1128(1)	5790(1)	38(1)
F(2)	1508(1)	447(1)	4782(1)	56(1)
F(3)	2614(1)	1026(1)	5164(1)	50(1)
F(1')	2892(1)	8604(1)	4931(1)	34(1)
F(2')	3865(1)	8082(1)	4312(1)	28(1)
F(3')	4120(1)	8688(1)	5326(1)	36(1)
O(1)	1888(1)	58(1)	1781(1)	19(1)
O(2)	681(1)	2167(1)	4712(1)	30(1)
O(3)	1855(1)	2019(1)	3961(1)	32(1)
O(4)	1959(1)	2805(1)	5088(1)	31(1)
O(1')	3078(1)	5410(1)	2392(1)	18(1)
O(2')	3041(1)	7369(1)	6057(1)	23(1)
O(3')	3012(1)	6620(1)	4912(1)	26(1)
O(4')	4289(1)	6827(1)	5546(1)	21(1)
C(1)	2832(1)	2516(1)	1758(1)	17(1)
C(2)	2448(1)	2235(1)	2393(1)	15(1)

C(3)	2120(1)	1391(1)	2388(1)	14(1)
C(4)	2190(1)	901(1)	1749(1)	15(1)
C(5)	1784(1)	-346(1)	1098(1)	24(1)
C(6)	1811(1)	1136(1)	5124(1)	30(1)
C(11)	2874(1)	-177(1)	3383(1)	22(1)
C(12)	3553(1)	-849(1)	2126(1)	21(1)
C(13)	4556(1)	-101(1)	3144(1)	22(1)
C(21)	3621(1)	811(1)	398(1)	23(1)
C(22)	5036(1)	683(1)	1222(1)	26(1)
C(23)	4401(1)	2330(1)	845(1)	27(1)
C(31)	5244(1)	1981(1)	2855(1)	20(1)
C(32)	4111(1)	3307(1)	2873(1)	23(1)
C(33)	3956(1)	1986(1)	3870(1)	19(1)
C(1')	1925(1)	7728(1)	2681(1)	17(1)
C(2')	2379(1)	7386(1)	3272(1)	16(1)
C(3')	2781(1)	6590(1)	3165(1)	16(1)
C(4')	2710(1)	6216(1)	2477(1)	15(1)
C(5')	3141(1)	5157(1)	1663(1)	23(1)
C(6')	3596(1)	8174(1)	4977(1)	21(1)
C(11')	535(1)	4706(1)	3761(1)	24(1)
C(12')	1538(1)	4258(1)	2659(1)	24(1)
C(13')	2228(1)	4773(1)	3973(1)	25(1)
C(21')	193(1)	7523(1)	1891(1)	26(1)
C(22')	-75(1)	5717(1)	1925(1)	23(1)
C(23')	1213(1)	6394(1)	1145(1)	24(1)
C(31')	638(1)	8184(1)	3887(1)	22(1)
C(32')	-349(1)	6726(1)	3735(1)	20(1)
C(33')	987(1)	6719(1)	4719(1)	20(1)

Table B-7.3. Bond lengths [Å] for Compound 11.

Co(1)-C(2)	2.0188(11)
Co(1)-C(3)	2.0629(10)
Co(1)-C(1)	2.0702(11)
Co(1)-C(4)	2.1693(11)
Co(1)-P(2)	2.2026(3)
Co(1)-P(1)	2.2070(3)
Co(1)-P(3)	2.2307(3)
Co(2)-C(2')	2.0165(11)
Co(2)-C(3')	2.0652(11)
Co(2)-C(1')	2.0679(11)
Co(2)-C(4')	2.1688(11)
Co(2)-P(2')	2.1956(3)
Co(2)-P(1')	2.2201(4)
Co(2)-P(3')	2.2345(3)
P(1)-C(12)	1.8154(12)
P(1)-C(11)	1.8223(12)
P(1)-C(13)	1.8301(12)
P(2)-C(21)	1.8192(12)
P(2)-C(23)	1.8208(14)
P(2)-C(22)	1.8313(13)
P(3)-C(33)	1.8261(12)
P(3)-C(31)	1.8280(12)
P(3)-C(32)	1.8284(13)
P(1')-C(13')	1.8214(13)
P(1')-C(12')	1.8242(13)
P(1')-C(11')	1.8326(12)
P(2')-C(23')	1.8205(13)
P(2')-C(21')	1.8248(13)
P(2')-C(22')	1.8287(13)
P(3')-C(33')	1.8238(12)
P(3')-C(32')	1.8258(12)
P(3')-C(31')	1.8284(13)
S(1)-O(3)	1.4370(10)
S(1)-O(4)	1.4379(10)
S(1)-O(2)	1.4400(10)
S(1)-C(6)	1.8212(16)
S(1')-O(3')	1.4378(10)
S(1')-O(2')	1.4398(9)
S(1')-O(4')	1.4404(9)
S(1')-C(6')	1.8282(13)
F(1)-C(6)	1.3338(17)
F(2)-C(6)	1.3269(19)
F(3)-C(6)	1.3387(18)
F(1')-C(6')	1.3372(15)
F(2')-C(6')	1.3378(15)
F(3')-C(6')	1.3341(16)
O(1)-C(4)	1.3849(14)
O(1)-C(5)	1.4283(15)
O(1')-C(4')	1.3851(14)
O(1')-C(5')	1.4239(15)
C(1)-C(2)	1.4231(16)
C(1)-H(1A)	0.9900
C(1)-H(1B)	0.9900
C(2)-C(3)	1.4008(16)
C(2)-H(2)	1.0000
C(3)-C(4)	1.4177(15)
C(3)-H(3)	1.0000
C(4)-H(4)	1.0000
C(5)-H(5A)	0.9800
C(5)-H(5B)	0.9800
C(5)-H(5C)	0.9800
C(11)-H(11A)	0.9800

C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800
C(31)-H(31A)	0.9800
C(31)-H(31B)	0.9800
C(31)-H(31C)	0.9800
C(32)-H(32A)	0.9800
C(32)-H(32B)	0.9800
C(32)-H(32C)	0.9800
C(33)-H(33A)	0.9800
C(33)-H(33B)	0.9800
C(33)-H(33C)	0.9800
C(1')-C(2')	1.4277(16)
C(1')-H(1'1)	0.9900
C(1')-H(1'2)	0.9900
C(2')-C(3')	1.4031(17)
C(2')-H(2')	1.0000
C(3')-C(4')	1.4129(16)
C(3')-H(3')	1.0000
C(4')-H(4')	1.0000
C(5')-H(5'1)	0.9800
C(5')-H(5'2)	0.9800
C(5')-H(5'3)	0.9800
C(11')-H(11D)	0.9800
C(11')-H(11E)	0.9800
C(11')-H(11F)	0.9800
C(12')-H(12D)	0.9800
C(12')-H(12E)	0.9800
C(12')-H(12F)	0.9800
C(13')-H(13D)	0.9800
C(13')-H(13E)	0.9800
C(13')-H(13F)	0.9800
C(21')-H(21D)	0.9800
C(21')-H(21E)	0.9800
C(21')-H(21F)	0.9800
C(22')-H(22D)	0.9800
C(22')-H(22E)	0.9800
C(22')-H(22F)	0.9800
C(23')-H(23D)	0.9800
C(23')-H(23E)	0.9800
C(23')-H(23F)	0.9800
C(31')-H(31D)	0.9800
C(31')-H(31E)	0.9800
C(31')-H(31F)	0.9800
C(32')-H(32D)	0.9800
C(32')-H(32E)	0.9800
C(32')-H(32F)	0.9800
C(33')-H(33D)	0.9800
C(33')-H(33E)	0.9800
C(33')-H(33F)	0.9800

Table B-7.4. Bond angles [°] for Compound 11.

C(2)-Co(1)-C(3)	40.13(5)
C(2)-Co(1)-C(1)	40.71(5)
C(3)-Co(1)-C(1)	71.15(5)
C(2)-Co(1)-C(4)	69.99(4)
C(3)-Co(1)-C(4)	39.04(4)
C(1)-Co(1)-C(4)	78.67(5)
C(2)-Co(1)-P(2)	129.17(3)
C(3)-Co(1)-P(2)	136.08(3)
C(1)-Co(1)-P(2)	88.84(3)
C(4)-Co(1)-P(2)	99.98(3)
C(2)-Co(1)-P(1)	127.34(3)
C(3)-Co(1)-P(1)	95.38(3)
C(1)-Co(1)-P(1)	166.53(3)
C(4)-Co(1)-P(1)	91.18(3)
P(2)-Co(1)-P(1)	101.746(13)
C(2)-Co(1)-P(3)	88.47(3)
C(3)-Co(1)-P(3)	116.56(3)
C(1)-Co(1)-P(3)	92.66(4)
C(4)-Co(1)-P(3)	155.58(3)
P(2)-Co(1)-P(3)	102.648(13)
P(1)-Co(1)-P(3)	93.109(13)
C(2')-Co(2)-C(3')	40.19(5)
C(2')-Co(2)-C(1')	40.90(5)
C(3')-Co(2)-C(1')	71.44(5)
C(2')-Co(2)-C(4')	69.76(5)
C(3')-Co(2)-C(4')	38.89(4)
C(1')-Co(2)-C(4')	78.57(5)
C(2')-Co(2)-P(2')	128.34(4)
C(3')-Co(2)-P(2')	136.59(3)
C(1')-Co(2)-P(2')	87.72(3)
C(4')-Co(2)-P(2')	100.92(3)
C(2')-Co(2)-P(1')	127.65(4)
C(3')-Co(2)-P(1')	95.46(3)
C(1')-Co(2)-P(1')	166.89(3)
C(4')-Co(2)-P(1')	91.27(3)
P(2')-Co(2)-P(1')	102.461(13)
C(2')-Co(2)-P(3')	88.76(3)
C(3')-Co(2)-P(3')	117.05(3)
C(1')-Co(2)-P(3')	92.50(3)
C(4')-Co(2)-P(3')	155.89(3)
P(2')-Co(2)-P(3')	101.050(13)
P(1')-Co(2)-P(3')	93.592(12)
C(12)-P(1)-C(11)	101.55(6)
C(12)-P(1)-C(13)	98.26(6)
C(11)-P(1)-C(13)	101.32(6)
C(12)-P(1)-Co(1)	116.71(5)
C(11)-P(1)-Co(1)	114.41(4)
C(13)-P(1)-Co(1)	121.39(4)
C(21)-P(2)-C(23)	99.69(7)
C(21)-P(2)-C(22)	99.66(6)
C(23)-P(2)-C(22)	100.90(7)
C(21)-P(2)-Co(1)	118.57(4)
C(23)-P(2)-Co(1)	114.16(5)
C(22)-P(2)-Co(1)	120.39(5)
C(33)-P(3)-C(31)	103.73(6)
C(33)-P(3)-C(32)	98.41(6)
C(31)-P(3)-C(32)	98.04(6)
C(33)-P(3)-Co(1)	116.82(4)
C(31)-P(3)-Co(1)	119.26(4)
C(32)-P(3)-Co(1)	117.03(4)
C(13')-P(1')-C(12')	100.80(7)
C(13')-P(1')-C(11')	101.13(7)

C(12')-P(1')-C(11')	97.69(6)
C(13')-P(1')-Co(2)	114.80(5)
C(12')-P(1')-Co(2)	117.12(5)
C(11')-P(1')-Co(2)	121.78(4)
C(23')-P(2')-C(21')	100.49(7)
C(23')-P(2')-C(22')	100.14(6)
C(21')-P(2')-C(22')	100.05(7)
C(23')-P(2')-Co(2)	117.79(4)
C(21')-P(2')-Co(2)	114.43(4)
C(22')-P(2')-Co(2)	120.57(5)
C(33')-P(3')-C(32')	102.87(6)
C(33')-P(3')-C(31')	99.44(6)
C(32')-P(3')-C(31')	98.86(6)
C(33')-P(3')-Co(2)	116.19(4)
C(32')-P(3')-Co(2)	118.70(4)
C(31')-P(3')-Co(2)	117.54(4)
O(3)-S(1)-O(4)	115.64(7)
O(3)-S(1)-O(2)	114.86(6)
O(4)-S(1)-O(2)	114.64(7)
O(3)-S(1)-C(6)	103.31(7)
O(4)-S(1)-C(6)	103.32(7)
O(2)-S(1)-C(6)	102.54(7)
O(3')-S(1')-O(2')	115.32(6)
O(3')-S(1')-O(4')	114.95(6)
O(2')-S(1')-O(4')	115.23(5)
O(3')-S(1')-C(6')	103.06(6)
O(2')-S(1')-C(6')	101.95(6)
O(4')-S(1')-C(6')	103.70(6)
C(4)-O(1)-C(5)	113.82(10)
C(4')-O(1')-C(5')	113.04(9)
C(2)-C(1)-Co(1)	67.70(6)
C(2)-C(1)-H(1A)	116.9
Co(1)-C(1)-H(1A)	116.9
C(2)-C(1)-H(1B)	116.9
Co(1)-C(1)-H(1B)	116.9
H(1A)-C(1)-H(1B)	113.9
C(3)-C(2)-C(1)	116.75(10)
C(3)-C(2)-Co(1)	71.63(6)
C(1)-C(2)-Co(1)	71.59(6)
C(3)-C(2)-H(2)	121.5
C(1)-C(2)-H(2)	121.5
Co(1)-C(2)-H(2)	121.5
C(2)-C(3)-C(4)	117.15(10)
C(2)-C(3)-Co(1)	68.24(6)
C(4)-C(3)-Co(1)	74.54(6)
C(2)-C(3)-H(3)	121.2
C(4)-C(3)-H(3)	121.2
Co(1)-C(3)-H(3)	121.2
O(1)-C(4)-C(3)	114.96(10)
O(1)-C(4)-Co(1)	127.82(8)
C(3)-C(4)-Co(1)	66.42(6)
O(1)-C(4)-H(4)	112.9
C(3)-C(4)-H(4)	112.9
Co(1)-C(4)-H(4)	112.9
O(1)-C(5)-H(5A)	109.5
O(1)-C(5)-H(5B)	109.5
H(5A)-C(5)-H(5B)	109.5
O(1)-C(5)-H(5C)	109.5
H(5A)-C(5)-H(5C)	109.5
H(5B)-C(5)-H(5C)	109.5
F(2)-C(6)-F(1)	108.17(13)
F(2)-C(6)-F(3)	107.07(13)
F(1)-C(6)-F(3)	107.46(12)
F(2)-C(6)-S(1)	111.40(11)
F(1)-C(6)-S(1)	111.39(10)
F(3)-C(6)-S(1)	111.15(11)

P(1)-C(11)-H(11A)	109.5
P(1)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
P(1)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
P(1)-C(12)-H(12A)	109.5
P(1)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
P(1)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
P(1)-C(13)-H(13A)	109.5
P(1)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
P(1)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
P(2)-C(21)-H(21A)	109.5
P(2)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
P(2)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
P(2)-C(22)-H(22A)	109.5
P(2)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
P(2)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
P(2)-C(23)-H(23A)	109.5
P(2)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
P(2)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
P(3)-C(31)-H(31A)	109.5
P(3)-C(31)-H(31B)	109.5
H(31A)-C(31)-H(31B)	109.5
P(3)-C(31)-H(31C)	109.5
H(31A)-C(31)-H(31C)	109.5
H(31B)-C(31)-H(31C)	109.5
P(3)-C(32)-H(32A)	109.5
P(3)-C(32)-H(32B)	109.5
H(32A)-C(32)-H(32B)	109.5
P(3)-C(32)-H(32C)	109.5
H(32A)-C(32)-H(32C)	109.5
H(32B)-C(32)-H(32C)	109.5
P(3)-C(33)-H(33A)	109.5
P(3)-C(33)-H(33B)	109.5
H(33A)-C(33)-H(33B)	109.5
P(3)-C(33)-H(33C)	109.5
H(33A)-C(33)-H(33C)	109.5
H(33B)-C(33)-H(33C)	109.5
C(2')-C(1')-Co(2)	67.62(6)
C(2')-C(1')-H(1'1)	116.9
Co(2)-C(1')-H(1'1)	116.9
C(2')-C(1')-H(1'2)	116.9
Co(2)-C(1')-H(1'2)	116.9
H(1'1)-C(1')-H(1'2)	113.9
C(3')-C(2')-C(1')	116.94(11)
C(3')-C(2')-Co(2)	71.77(7)
C(1')-C(2')-Co(2)	71.49(6)
C(3')-C(2')-H(2')	121.4
C(1')-C(2')-H(2')	121.4
Co(2)-C(2')-H(2')	121.4

C(2')-C(3')-C(4')	116.65(10)
C(2')-C(3')-Co(2)	68.04(6)
C(4')-C(3')-Co(2)	74.52(6)
C(2')-C(3')-H(3')	121.5
C(4')-C(3')-H(3')	121.5
Co(2)-C(3')-H(3')	121.5
O(1')-C(4')-C(3')	115.82(10)
O(1')-C(4')-Co(2)	127.62(8)
C(3')-C(4')-Co(2)	66.59(6)
O(1')-C(4')-H(4')	112.8
C(3')-C(4')-H(4')	112.8
Co(2)-C(4')-H(4')	112.8
O(1')-C(5')-H(5'1)	109.5
O(1')-C(5')-H(5'2)	109.5
H(5'1)-C(5')-H(5'2)	109.5
O(1')-C(5')-H(5'3)	109.5
H(5'1)-C(5')-H(5'3)	109.5
H(5'2)-C(5')-H(5'3)	109.5
F(3')-C(6')-F(1')	107.53(11)
F(3')-C(6')-F(2')	107.27(10)
F(1')-C(6')-F(2')	107.01(10)
F(3')-C(6')-S(1')	111.72(9)
F(1')-C(6')-S(1')	111.01(9)
F(2')-C(6')-S(1')	112.04(9)
P(1')-C(11')-H(11D)	109.5
P(1')-C(11')-H(11E)	109.5
H(11D)-C(11')-H(11E)	109.5
P(1')-C(11')-H(11F)	109.5
H(11D)-C(11')-H(11F)	109.5
H(11E)-C(11')-H(11F)	109.5
P(1')-C(12')-H(12D)	109.5
P(1')-C(12')-H(12E)	109.5
H(12D)-C(12')-H(12E)	109.5
P(1')-C(12')-H(12F)	109.5
H(12D)-C(12')-H(12F)	109.5
H(12E)-C(12')-H(12F)	109.5
P(1')-C(13')-H(13D)	109.5
P(1')-C(13')-H(13E)	109.5
H(13D)-C(13')-H(13E)	109.5
P(1')-C(13')-H(13F)	109.5
H(13D)-C(13')-H(13F)	109.5
H(13E)-C(13')-H(13F)	109.5
P(2')-C(21')-H(21D)	109.5
P(2')-C(21')-H(21E)	109.5
H(21D)-C(21')-H(21E)	109.5
P(2')-C(21')-H(21F)	109.5
H(21D)-C(21')-H(21F)	109.5
H(21E)-C(21')-H(21F)	109.5
P(2')-C(22')-H(22D)	109.5
P(2')-C(22')-H(22E)	109.5
H(22D)-C(22')-H(22E)	109.5
P(2')-C(22')-H(22F)	109.5
H(22D)-C(22')-H(22F)	109.5
H(22E)-C(22')-H(22F)	109.5
P(2')-C(23')-H(23D)	109.5
P(2')-C(23')-H(23E)	109.5
H(23D)-C(23')-H(23E)	109.5
P(2')-C(23')-H(23F)	109.5
H(23D)-C(23')-H(23F)	109.5
H(23E)-C(23')-H(23F)	109.5
P(3')-C(31')-H(31D)	109.5
P(3')-C(31')-H(31E)	109.5
H(31D)-C(31')-H(31E)	109.5
P(3')-C(31')-H(31F)	109.5
H(31D)-C(31')-H(31F)	109.5
H(31E)-C(31')-H(31F)	109.5

P(3')-C(32')-H(32D)	109.5	P(3')-C(33')-H(33D)	109.5
P(3')-C(32')-H(32E)	109.5	P(3')-C(33')-H(33E)	109.5
H(32D)-C(32')-H(32E)	109.5	H(33D)-C(33')-H(33E)	109.5
P(3')-C(32')-H(32F)	109.5	P(3')-C(33')-H(33F)	109.5
H(32D)-C(32')-H(32F)	109.5	H(33D)-C(33')-H(33F)	109.5
H(32E)-C(32')-H(32F)	109.5	H(33E)-C(33')-H(33F)	109.5

Table B-7.5. Anisotropic displacement parameters ($Å^2$x 10^3) for Compound 11. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Co(1)	8(1)	11(1)	10(1)	0(1)	0(1)	0(1)
Co(2)	9(1)	11(1)	12(1)	0(1)	-2(1)	0(1)
P(1)	14(1)	11(1)	15(1)	0(1)	-1(1)	1(1)
P(2)	11(1)	19(1)	12(1)	-1(1)	2(1)	-1(1)
P(3)	11(1)	13(1)	13(1)	-2(1)	-1(1)	-2(1)
P(1')	13(1)	12(1)	19(1)	2(1)	0(1)	0(1)
P(2')	13(1)	15(1)	14(1)	-1(1)	-4(1)	2(1)
P(3')	11(1)	15(1)	14(1)	-2(1)	-1(1)	0(1)
S(1)	15(1)	28(1)	11(1)	0(1)	-1(1)	0(1)
S(1')	12(1)	18(1)	12(1)	1(1)	-1(1)	-1(1)
F(1)	47(1)	41(1)	25(1)	13(1)	5(1)	0(1)
F(2)	84(1)	27(1)	56(1)	-9(1)	0(1)	-7(1)
F(3)	38(1)	63(1)	49(1)	12(1)	1(1)	27(1)
F(1')	31(1)	36(1)	34(1)	16(1)	8(1)	17(1)
F(2')	25(1)	39(1)	20(1)	13(1)	6(1)	5(1)
F(3')	42(1)	24(1)	42(1)	3(1)	-3(1)	-12(1)
O(1)	17(1)	22(1)	19(1)	-7(1)	0(1)	-6(1)

O(2)	15(1)	54(1)	20(1)	-2(1)	0(1)	6(1)
O(3)	25(1)	58(1)	14(1)	0(1)	5(1)	2(1)
O(4)	37(1)	30(1)	25(1)	0(1)	-6(1)	-11(1)
O(1')	16(1)	20(1)	19(1)	-1(1)	1(1)	4(1)
O(2')	24(1)	28(1)	17(1)	4(1)	7(1)	6(1)
O(3')	24(1)	32(1)	22(1)	-4(1)	-6(1)	-9(1)
O(4')	15(1)	25(1)	22(1)	4(1)	-2(1)	4(1)
C(1)	18(1)	17(1)	17(1)	3(1)	-2(1)	3(1)
C(2)	12(1)	16(1)	16(1)	-1(1)	-1(1)	5(1)
C(3)	8(1)	18(1)	14(1)	-2(1)	0(1)	2(1)
C(4)	10(1)	19(1)	16(1)	-2(1)	-2(1)	0(1)
C(5)	20(1)	28(1)	24(1)	-13(1)	-1(1)	-4(1)
C(6)	34(1)	29(1)	26(1)	0(1)	1(1)	2(1)
C(11)	26(1)	19(1)	21(1)	6(1)	3(1)	-2(1)
C(12)	23(1)	14(1)	26(1)	-5(1)	-1(1)	2(1)
C(13)	20(1)	19(1)	26(1)	1(1)	-7(1)	5(1)
C(21)	21(1)	34(1)	15(1)	-7(1)	1(1)	-2(1)
C(22)	15(1)	40(1)	23(1)	-3(1)	4(1)	6(1)
C(23)	32(1)	27(1)	23(1)	1(1)	12(1)	-8(1)
C(31)	12(1)	26(1)	22(1)	-3(1)	-2(1)	-3(1)
C(32)	25(1)	14(1)	30(1)	-3(1)	-3(1)	-4(1)
C(33)	18(1)	25(1)	15(1)	-4(1)	-1(1)	-2(1)
C(1')	17(1)	14(1)	19(1)	1(1)	0(1)	-3(1)
C(2')	13(1)	17(1)	18(1)	-2(1)	-1(1)	-5(1)
C(3')	10(1)	20(1)	17(1)	1(1)	-2(1)	-2(1)
C(4')	12(1)	16(1)	18(1)	0(1)	0(1)	-1(1)
C(5')	24(1)	23(1)	22(1)	-3(1)	2(1)	3(1)
C(6')	19(1)	24(1)	21(1)	6(1)	1(1)	2(1)
C(11')	22(1)	18(1)	34(1)	2(1)	7(1)	-4(1)
C(12')	23(1)	14(1)	35(1)	-5(1)	2(1)	2(1)
C(13')	24(1)	23(1)	29(1)	9(1)	-6(1)	2(1)
C(21')	30(1)	22(1)	26(1)	-2(1)	-14(1)	10(1)
C(22')	15(1)	27(1)	26(1)	-1(1)	-6(1)	-4(1)

C(23')	21(1)	35(1)	15(1)	1(1)	-2(1)	1(1)
C(31')	24(1)	16(1)	26(1)	-5(1)	4(1)	2(1)
C(32')	11(1)	26(1)	23(1)	-6(1)	0(1)	1(1)
C(33')	18(1)	28(1)	15(1)	-1(1)	-2(1)	1(1)

Table B-7.6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10 ^{3}) for Compound 11.

	x	y	z	U(eq)
H(1A)	3164	3053	1791	20
H(1B)	2516	2463	1307	20
H(2)	2465	2596	2838	18
H(3)	1909	1119	2833	16
H(4)	1997	1228	1317	18
H(5A)	1442	25	792	36
H(5B)	1525	-917	1157	36
H(5C)	2313	-424	878	36
H(11A)	2337	-271	3167	33
H(11B)	2846	297	3734	33
H(11C)	3055	-714	3621	33
H(12A)	3641	-1372	2420	32
H(12B)	3977	-810	1767	32
H(12C)	3023	-886	1887	32
H(13A)	4554	-695	3339	33
H(13B)	4636	320	3533	33
H(13C)	4996	-43	2803	33
H(21A)	3110	1111	288	35
H(21B)	3516	188	477	35
H(21C)	3991	880	-2	35
H(22A)	5329	793	780	39

H(22B)	4928	56	1267	39
H(22C)	5365	880	1631	39
H(23A)	4763	2233	443	41
H(23B)	4688	2659	1220	41
H(23C)	3927	2663	682	41
H(31A)	5512	2314	3238	30
H(31B)	5423	2197	2392	30
H(31C)	5383	1361	2903	30
H(32A)	3556	3506	2952	35
H(32B)	4287	3500	2401	35
H(32C)	4471	3554	3241	35
H(33A)	4004	1367	4001	29
H(33B)	3409	2192	3974	29
H(33C)	4352	2328	4146	29
H(1'1)	2211	7788	2223	20
H(1'2)	1549	8215	2782	20
H(2')	2360	7664	3754	19
H(3')	3048	6269	3570	19
H(4')	2843	6637	2088	18
H(5'1)	2600	5035	1466	34
H(5'2)	3477	4631	1630	34
H(5'3)	3390	5631	1391	34
H(11D)	615	4094	3901	37
H(11E)	76	4747	3426	37
H(11F)	425	5058	4186	37
H(12D)	2074	4287	2444	36
H(12E)	1121	4343	2288	36
H(12F)	1466	3686	2883	36
H(13D)	2104	4185	4147	38
H(13E)	2243	5182	4375	38
H(13F)	2755	4768	3740	38
H(21D)	574	8006	1825	39
H(21E)	-136	7637	2312	39

H(21F)	-161	7474	1468	39
H(22D)	-420	5878	1515	34
H(22E)	-397	5719	2360	34
H(22F)	149	5132	1850	34
H(23D)	803	6491	771	36
H(23E)	1439	5805	1097	36
H(23F)	1647	6826	1099	36
H(31D)	279	8322	4283	33
H(31E)	413	8430	3443	33
H(31F)	1174	8436	3982	33
H(32D)	-410	6096	3658	30
H(32E)	-598	7044	3335	30
H(32F)	-614	6891	4180	30
H(33D)	596	6988	5040	30
H(33E)	1531	6936	4834	30
H(33F)	974	6083	4777	30

Table B-7.7. Torsion angles [°] for Compound 11.

C(2)-Co(1)-P(1)-C(12)	120.41(6)	C(3)-Co(1)-P(1)-C(13)	-146.50(6)
C(3)-Co(1)-P(1)-C(12)	93.80(6)	C(1)-Co(1)-P(1)-C(13)	-144.66(16)
C(1)-Co(1)-P(1)-C(12)	95.65(16)	C(4)-Co(1)-P(1)-C(13)	174.61(6)
C(4)-Co(1)-P(1)-C(12)	54.91(6)	P(2)-Co(1)-P(1)-C(13)	74.17(5)
P(2)-Co(1)-P(1)-C(12)	-45.53(5)	P(3)-Co(1)-P(1)-C(13)	-29.44(5)
P(3)-Co(1)-P(1)-C(12)	-149.14(5)	C(2)-Co(1)-P(2)-C(21)	-75.92(7)
C(2)-Co(1)-P(1)-C(11)	2.07(7)	C(3)-Co(1)-P(2)-C(21)	-21.08(8)
C(3)-Co(1)-P(1)-C(11)	-24.53(6)	C(1)-Co(1)-P(2)-C(21)	-81.95(7)
C(1)-Co(1)-P(1)-C(11)	-22.69(16)	C(4)-Co(1)-P(2)-C(21)	-3.66(6)
C(4)-Co(1)-P(1)-C(11)	-63.42(6)	P(1)-Co(1)-P(2)-C(21)	89.66(6)
P(2)-Co(1)-P(1)-C(11)	-163.87(5)	P(3)-Co(1)-P(2)-C(21)	-174.41(6)
P(3)-Co(1)-P(1)-C(11)	92.52(5)	C(2)-Co(1)-P(2)-C(23)	41.10(7)
C(2)-Co(1)-P(1)-C(13)	-119.89(7)	C(3)-Co(1)-P(2)-C(23)	95.94(7)

C(1)-Co(1)-P(2)-C(23)	35.08(7)
C(4)-Co(1)-P(2)-C(23)	113.36(6)
P(1)-Co(1)-P(2)-C(23)	-153.32(6)
P(3)-Co(1)-P(2)-C(23)	-57.38(6)
C(2)-Co(1)-P(2)-C(22)	161.34(7)
C(3)-Co(1)-P(2)-C(22)	-143.83(7)
C(1)-Co(1)-P(2)-C(22)	155.31(7)
C(4)-Co(1)-P(2)-C(22)	-126.41(7)
P(1)-Co(1)-P(2)-C(22)	-33.09(6)
P(3)-Co(1)-P(2)-C(22)	62.85(6)
C(2)-Co(1)-P(3)-C(33)	72.96(6)
C(3)-Co(1)-P(3)-C(33)	43.24(6)
C(1)-Co(1)-P(3)-C(33)	113.47(6)
C(4)-Co(1)-P(3)-C(33)	45.40(10)
P(2)-Co(1)-P(3)-C(33)	-157.13(5)
P(1)-Co(1)-P(3)-C(33)	-54.35(5)
C(2)-Co(1)-P(3)-C(31)	-161.02(6)
C(3)-Co(1)-P(3)-C(31)	169.26(6)
C(1)-Co(1)-P(3)-C(31)	-120.52(6)
C(4)-Co(1)-P(3)-C(31)	171.41(9)
P(2)-Co(1)-P(3)-C(31)	-31.11(5)
P(1)-Co(1)-P(3)-C(31)	71.66(5)
C(2)-Co(1)-P(3)-C(32)	-43.26(6)
C(3)-Co(1)-P(3)-C(32)	-72.98(6)
C(1)-Co(1)-P(3)-C(32)	-2.75(6)
C(4)-Co(1)-P(3)-C(32)	-70.82(10)
P(2)-Co(1)-P(3)-C(32)	86.65(5)
P(1)-Co(1)-P(3)-C(32)	-170.57(5)
C(2')-Co(2)-P(1')-C(13')	-1.73(7)
C(3')-Co(2)-P(1')-C(13')	24.69(6)
C(1')-Co(2)-P(1')-C(13')	24.59(17)
C(4')-Co(2)-P(1')-C(13')	63.43(6)
P(2')-Co(2)-P(1')-C(13')	164.91(5)
P(3')-Co(2)-P(1')-C(13')	-92.94(5)
C(2')-Co(2)-P(1')-C(12')	-119.68(6)
C(3')-Co(2)-P(1')-C(12')	-93.26(6)
C(1')-Co(2)-P(1')-C(12')	-93.35(16)
C(4')-Co(2)-P(1')-C(12')	-54.51(6)
P(2')-Co(2)-P(1')-C(12')	46.96(5)
P(3')-Co(2)-P(1')-C(12')	149.12(5)
C(2')-Co(2)-P(1')-C(11')	120.71(7)
C(3')-Co(2)-P(1')-C(11')	147.13(7)
C(1')-Co(2)-P(1')-C(11')	147.03(16)
C(4')-Co(2)-P(1')-C(11')	-174.13(7)
P(2')-Co(2)-P(1')-C(11')	-72.65(6)
P(3')-Co(2)-P(1')-C(11')	29.50(6)
C(2')-Co(2)-P(2')-C(23')	68.12(7)
C(3')-Co(2)-P(2')-C(23')	13.65(8)
C(1')-Co(2)-P(2')-C(23')	73.28(6)
C(4')-Co(2)-P(2')-C(23')	-4.62(6)
P(1')-Co(2)-P(2')-C(23')	-98.39(6)
P(3')-Co(2)-P(2')-C(23')	165.38(5)
C(2')-Co(2)-P(2')-C(21')	-49.62(7)
C(3')-Co(2)-P(2')-C(21')	-104.08(8)
C(1')-Co(2)-P(2')-C(21')	-44.46(7)
C(4')-Co(2)-P(2')-C(21')	-122.36(6)
P(1')-Co(2)-P(2')-C(21')	143.87(6)
P(3')-Co(2)-P(2')-C(21')	47.64(6)
C(2')-Co(2)-P(2')-C(22')	-169.02(7)
C(3')-Co(2)-P(2')-C(22')	136.51(7)
C(1')-Co(2)-P(2')-C(22')	-163.86(6)
C(4')-Co(2)-P(2')-C(22')	118.24(6)
P(1')-Co(2)-P(2')-C(22')	24.47(5)
P(3')-Co(2)-P(2')-C(22')	-71.76(5)
C(2')-Co(2)-P(3')-C(33')	-73.68(6)
C(3')-Co(2)-P(3')-C(33')	-44.01(6)

C(1')-Co(2)-P(3')-C(33')	-114.41(6)
C(4')-Co(2)-P(3')-C(33')	-47.23(9)
P(2')-Co(2)-P(3')-C(33')	157.42(5)
P(1')-Co(2)-P(3')-C(33')	53.98(5)
C(2')-Co(2)-P(3')-C(32')	162.80(6)
C(3')-Co(2)-P(3')-C(32')	-167.54(6)
C(1')-Co(2)-P(3')-C(32')	122.06(6)
C(4')-Co(2)-P(3')-C(32')	-170.76(9)
P(2')-Co(2)-P(3')-C(32')	33.89(5)
P(1')-Co(2)-P(3')-C(32')	-69.55(5)
C(2')-Co(2)-P(3')-C(31')	43.87(6)
C(3')-Co(2)-P(3')-C(31')	73.54(6)
C(1')-Co(2)-P(3')-C(31')	3.14(6)
C(4')-Co(2)-P(3')-C(31')	70.31(9)
P(2')-Co(2)-P(3')-C(31')	-85.03(5)
P(1')-Co(2)-P(3')-C(31')	171.53(5)
C(3)-Co(1)-C(1)-C(2)	32.64(7)
C(4)-Co(1)-C(1)-C(2)	72.41(7)
P(2)-Co(1)-C(1)-C(2)	172.83(7)
P(1)-Co(1)-C(1)-C(2)	30.70(19)
P(3)-Co(1)-C(1)-C(2)	-84.56(6)
Co(1)-C(1)-C(2)-C(3)	-57.33(9)
C(1)-Co(1)-C(2)-C(3)	127.62(10)
C(4)-Co(1)-C(2)-C(3)	31.73(6)
P(2)-Co(1)-C(2)-C(3)	118.36(6)
P(1)-Co(1)-C(2)-C(3)	-43.78(8)
P(3)-Co(1)-C(2)-C(3)	-136.52(6)
C(3)-Co(1)-C(2)-C(1)	-127.62(10)
C(4)-Co(1)-C(2)-C(1)	-95.89(7)
P(2)-Co(1)-C(2)-C(1)	-9.26(8)
P(1)-Co(1)-C(2)-C(1)	-171.40(6)
P(3)-Co(1)-C(2)-C(1)	95.86(7)
C(1)-C(2)-C(3)-C(4)	-0.87(15)
Co(1)-C(2)-C(3)-C(4)	-58.18(9)
C(1)-C(2)-C(3)-Co(1)	57.31(9)
C(1)-Co(1)-C(3)-C(2)	-33.08(7)
C(4)-Co(1)-C(3)-C(2)	-128.33(10)
P(2)-Co(1)-C(3)-C(2)	-100.42(7)
P(1)-Co(1)-C(3)-C(2)	146.46(6)
P(3)-Co(1)-C(3)-C(2)	50.26(7)
C(2)-Co(1)-C(3)-C(4)	128.33(10)
C(1)-Co(1)-C(3)-C(4)	95.24(7)
P(2)-Co(1)-C(3)-C(4)	27.91(9)
P(1)-Co(1)-C(3)-C(4)	-85.21(7)
P(3)-Co(1)-C(3)-C(4)	178.59(6)
C(5)-O(1)-C(4)-C(3)	165.60(10)
C(5)-O(1)-C(4)-Co(1)	-115.78(10)
C(2)-C(3)-C(4)-O(1)	177.30(9)
Co(1)-C(3)-C(4)-O(1)	122.33(9)
C(2)-C(3)-C(4)-Co(1)	54.97(8)
C(2)-Co(1)-C(4)-O(1)	-136.68(11)
C(3)-Co(1)-C(4)-O(1)	-104.13(12)
C(1)-Co(1)-C(4)-O(1)	-178.11(10)
P(2)-Co(1)-C(4)-O(1)	95.12(9)
P(1)-Co(1)-C(4)-O(1)	-7.02(9)
P(3)-Co(1)-C(4)-O(1)	-107.19(10)
C(2)-Co(1)-C(4)-C(3)	-32.55(7)
C(1)-Co(1)-C(4)-C(3)	-73.98(7)
P(2)-Co(1)-C(4)-C(3)	-160.75(6)
P(1)-Co(1)-C(4)-C(3)	97.10(7)
P(3)-Co(1)-C(4)-C(3)	-3.06(12)
O(3)-S(1)-C(6)-F(2)	-56.19(12)
O(4)-S(1)-C(6)-F(2)	-177.06(11)
O(2)-S(1)-C(6)-F(2)	63.49(12)
O(3)-S(1)-C(6)-F(1)	-177.06(10)
O(4)-S(1)-C(6)-F(1)	62.07(12)

O(2)-S(1)-C(6)-F(1)	-57.38(12)
O(3)-S(1)-C(6)-F(3)	63.13(12)
O(4)-S(1)-C(6)-F(3)	-57.74(12)
O(2)-S(1)-C(6)-F(3)	-177.19(10)
C(3')-Co(2)-C(1')-C(2')	-32.53(7)
C(4')-Co(2)-C(1')-C(2')	-72.20(7)
P(2')-Co(2)-C(1')-C(2')	-173.82(7)
P(1')-Co(2)-C(1')-C(2')	-32.43(19)
P(3')-Co(2)-C(1')-C(2')	85.21(6)
Co(2)-C(1')-C(2')-C(3')	57.31(9)
C(1')-Co(2)-C(2')-C(3')	-127.82(10)
C(4')-Co(2)-C(2')-C(3')	-31.90(7)
P(2')-Co(2)-C(2')-C(3')	-119.94(6)
P(1')-Co(2)-C(2')-C(3')	43.34(8)
P(3')-Co(2)-C(2')-C(3')	136.92(6)
C(3')-Co(2)-C(2')-C(1')	127.82(10)
C(4')-Co(2)-C(2')-C(1')	95.92(7)
P(2')-Co(2)-C(2')-C(1')	7.88(8)
P(1')-Co(2)-C(2')-C(1')	171.16(5)
P(3')-Co(2)-C(2')-C(1')	-95.25(6)
C(1')-C(2')-C(3')-C(4')	1.21(15)
Co(2)-C(2')-C(3')-C(4')	58.37(9)
C(1')-C(2')-C(3')-Co(2)	-57.16(9)
C(1')-Co(2)-C(3')-C(2')	33.06(7)
C(4')-Co(2)-C(3')-C(2')	127.85(10)
P(2')-Co(2)-C(3')-C(2')	98.48(7)
P(1')-Co(2)-C(3')-C(2')	-146.92(6)
P(3')-Co(2)-C(3')-C(2')	-50.06(7)
C(2')-Co(2)-C(3')-C(4')	-127.85(10)
C(1')-Co(2)-C(3')-C(4')	-94.79(7)
P(2')-Co(2)-C(3')-C(4')	-29.37(9)
P(1')-Co(2)-C(3')-C(4')	85.24(6)
P(3')-Co(2)-C(3')-C(4')	-177.90(6)
C(5')-O(1')-C(4')-C(3')	-167.02(10)
C(5')-O(1')-C(4')-Co(2)	113.60(10)
C(2')-C(3')-C(4')-O(1')	-177.00(9)
Co(2)-C(3')-C(4')-O(1')	-121.97(9)
C(2')-C(3')-C(4')-Co(2)	-55.02(9)
C(2')-Co(2)-C(4')-O(1')	138.29(11)
C(3')-Co(2)-C(4')-O(1')	105.40(12)
C(1')-Co(2)-C(4')-O(1')	179.92(11)
P(2')-Co(2)-C(4')-O(1')	-94.68(10)
P(1')-Co(2)-C(4')-O(1')	8.27(10)
P(3')-Co(2)-C(4')-O(1')	109.97(10)
C(2')-Co(2)-C(4')-C(3')	32.90(7)
C(1')-Co(2)-C(4')-C(3')	74.53(7)
P(2')-Co(2)-C(4')-C(3')	159.93(6)
P(1')-Co(2)-C(4')-C(3')	-97.13(7)
P(3')-Co(2)-C(4')-C(3')	4.57(12)
O(3')-S(1')-C(6')-F(3')	-170.02(9)
O(2')-S(1')-C(6')-F(3')	70.12(10)
O(4')-S(1')-C(6')-F(3')	-49.87(10)
O(3')-S(1')-C(6')-F(1')	69.96(10)
O(2')-S(1')-C(6')-F(1')	-49.90(10)
O(4')-S(1')-C(6')-F(1')	-169.90(9)
O(3')-S(1')-C(6')-F(2')	-49.62(10)
O(2')-S(1')-C(6')-F(2')	-169.48(9)
O(4')-S(1')-C(6')-F(2')	70.52(10)

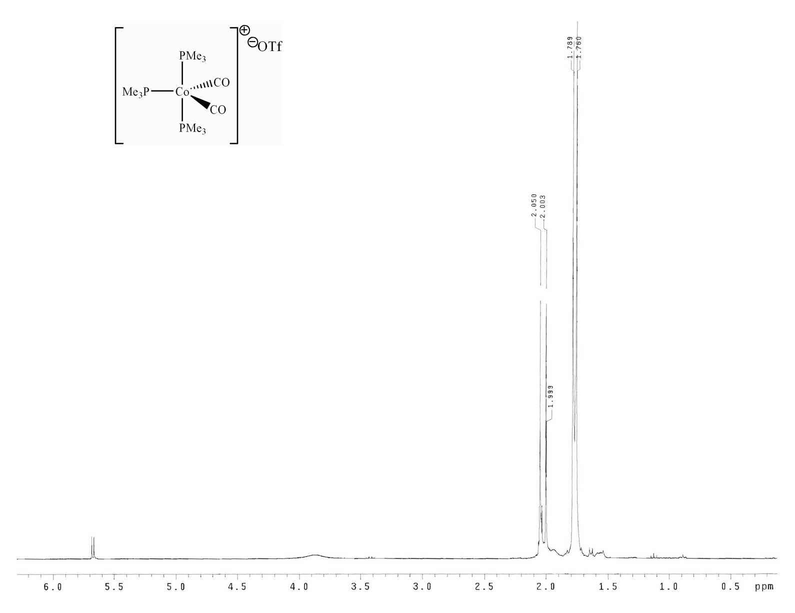

Figure B-43. ^{1}H NMR Spectrum of Compound 12.

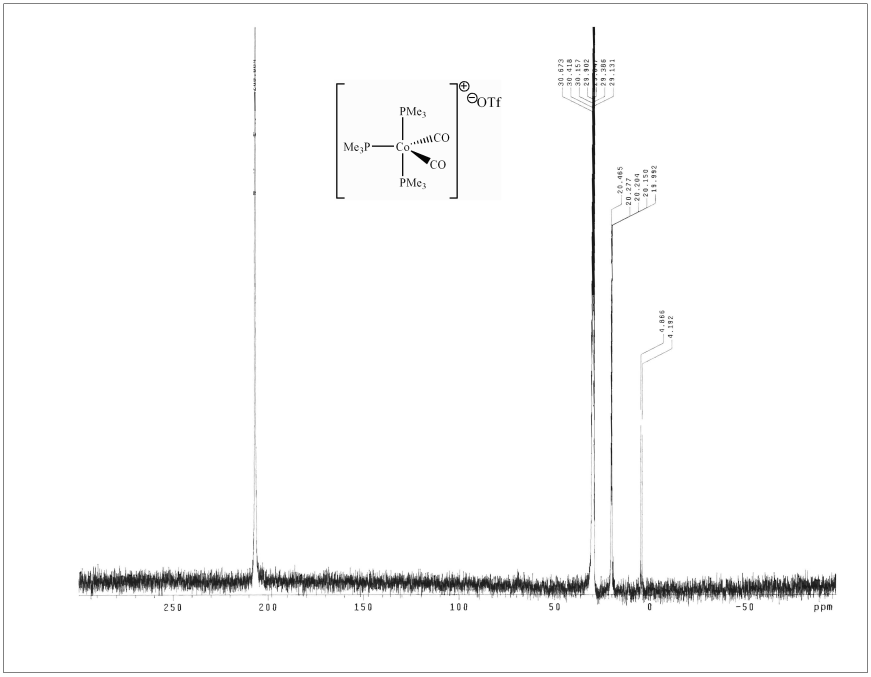

Figure B-44. ^{13}C NMR Spectrum of Compound 12.

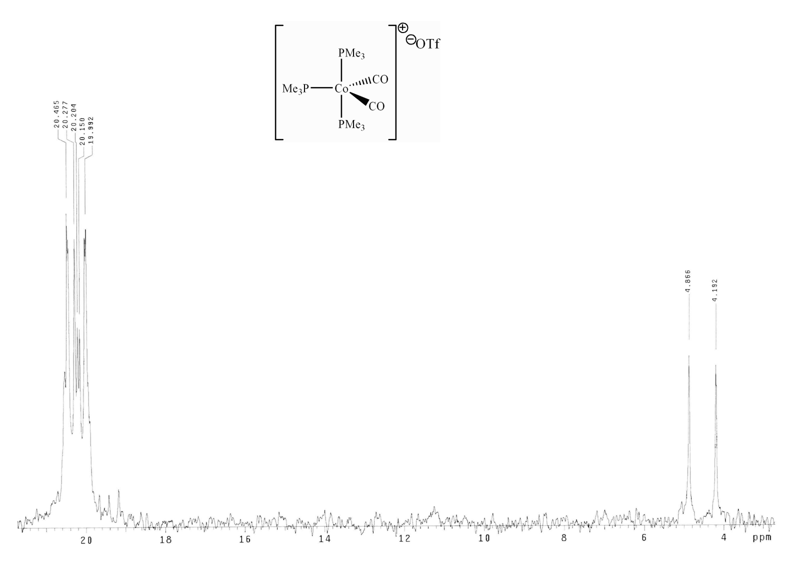

Figure B-45. Expansion of ^{13}C NMR Spectrum of Compound 12.

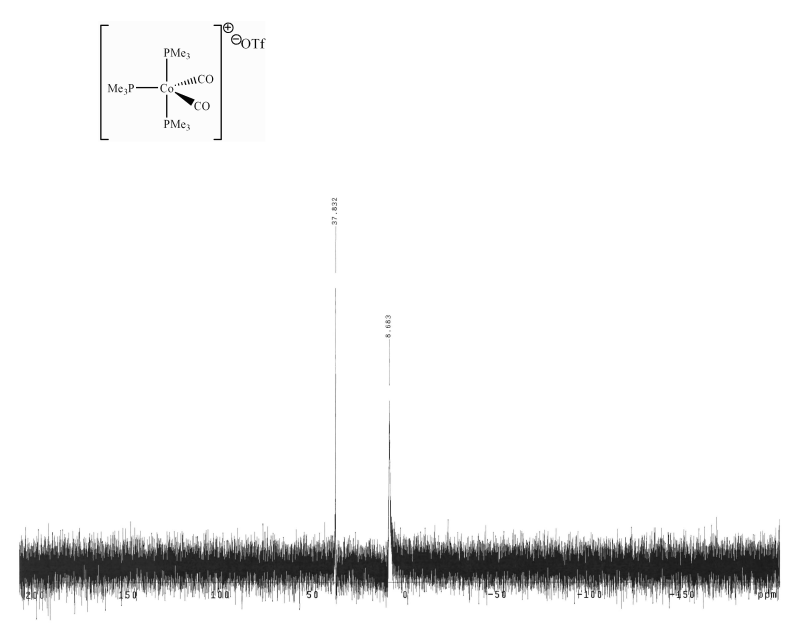

Figure B-46. ^{31}P NMR Spectrum of Compound 12.

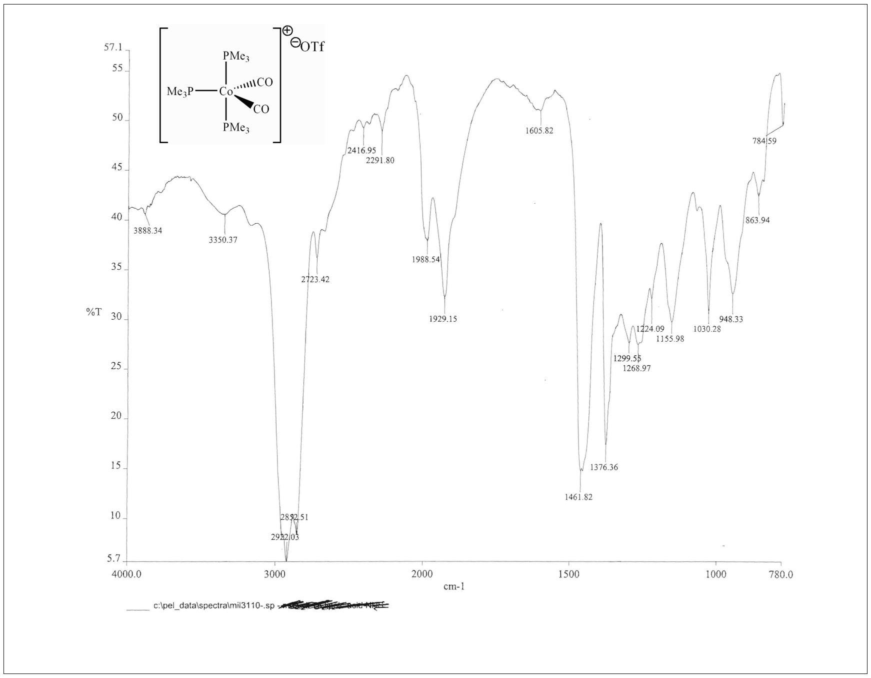

Figure B-47. IR Spectrum of Compound 12.

Table B-8.1. Crystal data and structure refinement for Compound 12.

Empirical formula	$C_{12} H_{27} Co F_3 O_5 P_3 S$	
Formula weight	492.24	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 14.8592(9) Å	α= 90°.
	b = 8.3390(5) Å	β= 107.585(3)°.
	c = 18.0971(11) Å	γ = 90°.
Volume	2137.6(2) $Å^3$	
Z	4	
Density (calculated)	1.529 Mg/m^3	
Absorption coefficient	1.168 mm^{-1}	
F(000)	1016	
Crystal size	0.52 x 0.14 x 0.12 mm^3	
Theta range for data collection	2.36 to 37.30°.	
Index ranges	$-25\leq h\leq 25$, $-14\leq k\leq 14$, $-30\leq l\leq 30$	
Reflections collected	137054	
Independent reflections	11095 [R(int) = 0.0473]	
Completeness to theta = 25.00°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8735 and 0.5801	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11095 / 0 / 235	
Goodness-of-fit on F^2	1.039	
Final R indices [I>2sigma(I)]	R1 = 0.0257, wR2 = 0.0569	
R indices (all data)	R1 = 0.0381, wR2 = 0.0619	
Largest diff. peak and hole	0.540 and -0.352 $e.Å^{-3}$	

Table B-8.2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for Compound 12. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Co(1)	1831(1)	2761(1)	9561(1)	9(1)
S(1)	2950(1)	-3405(1)	7908(1)	16(1)
P(1)	3284(1)	1985(1)	9568(1)	11(1)
P(2)	1037(1)	1328(1)	8555(1)	10(1)
P(3)	2279(1)	4366(1)	10573(1)	12(1)
F(1)	4041(1)	-3767(1)	7018(1)	42(1)
F(2)	4607(1)	-4767(1)	8157(1)	30(1)
F(3)	4611(1)	-2217(1)	7997(1)	39(1)
O(1)	1002(1)	773(1)	10494(1)	48(1)
O(2)	975(1)	5518(1)	8641(1)	21(1)
O(3)	3180(1)	-3147(1)	8731(1)	28(1)
O(4)	2529(1)	-2040(1)	7440(1)	23(1)
O(5)	2529(1)	-4929(1)	7635(1)	31(1)
C(1)	1350(1)	1534(1)	10127(1)	22(1)
C(2)	1349(1)	4446(1)	9003(1)	13(1)
C(3)	4109(1)	-3545(1)	7760(1)	21(1)
C(11)	4248(1)	3406(1)	9912(1)	18(1)
C(12)	3703(1)	253(1)	10188(1)	24(1)
C(13)	3494(1)	1371(1)	8670(1)	19(1)
C(21)	1225(1)	1727(1)	7628(1)	17(1)
C(22)	-220(1)	1642(1)	8349(1)	15(1)
C(23)	1154(1)	-826(1)	8668(1)	19(1)
C(31)	1260(1)	5134(1)	10812(1)	21(1)
C(32)	2881(1)	6209(1)	10482(1)	22(1)
C(33)	2988(1)	3496(1)	11479(1)	18(1)

Table B-8.3. Bond lengths [Å] for Compound 12.

Co(1)-C(1)	1.7470(10)	C(11)-H(11C)	0.9800
Co(1)-C(2)	1.7519(9)	C(12)-H(12A)	0.9800
Co(1)-P(2)	2.1996(3)	C(12)-H(12B)	0.9800
Co(1)-P(3)	2.2029(3)	C(12)-H(12C)	0.9800
Co(1)-P(1)	2.2489(3)	C(13)-H(13A)	0.9800
S(1)-O(5)	1.4363(9)	C(13)-H(13B)	0.9800
S(1)-O(3)	1.4400(8)	C(13)-H(13C)	0.9800
S(1)-O(4)	1.4430(8)	C(21)-H(21A)	0.9800
S(1)-C(3)	1.8250(10)	C(21)-H(21B)	0.9800
P(1)-C(11)	1.8185(9)	C(21)-H(21C)	0.9800
P(1)-C(12)	1.8190(10)	C(22)-H(22A)	0.9800
P(1)-C(13)	1.8192(10)	C(22)-H(22B)	0.9800
P(2)-C(22)	1.8084(9)	C(22)-H(22C)	0.9800
P(2)-C(23)	1.8097(9)	C(23)-H(23A)	0.9800
P(2)-C(21)	1.8132(9)	C(23)-H(23B)	0.9800
P(3)-C(32)	1.8105(10)	C(23)-H(23C)	0.9800
P(3)-C(33)	1.8106(9)	C(31)-H(31A)	0.9800
P(3)-C(31)	1.8132(10)	C(31)-H(31B)	0.9800
F(1)-C(3)	1.3289(12)	C(31)-H(31C)	0.9800
F(2)-C(3)	1.3345(12)	C(32)-H(32A)	0.9800
F(3)-C(3)	1.3310(13)	C(32)-H(32B)	0.9800
O(1)-C(1)	1.1475(13)	C(32)-H(32C)	0.9800
O(2)-C(2)	1.1485(11)	C(33)-H(33A)	0.9800
C(11)-H(11A)	0.9800	C(33)-H(33B)	0.9800
C(11)-H(11B)	0.9800	C(33)-H(33C)	0.9800

Table B-8.4. Bond angles [°] for Compound 12.

C(1)-Co(1)-C(2)	129.69(5)
C(1)-Co(1)-P(2)	87.39(3)
C(2)-Co(1)-P(2)	86.27(3)
C(1)-Co(1)-P(3)	86.70(3)
C(2)-Co(1)-P(3)	87.71(3)
P(2)-Co(1)-P(3)	165.945(10)
C(1)-Co(1)-P(1)	112.98(4)
C(2)-Co(1)-P(1)	117.32(3)
P(2)-Co(1)-P(1)	97.060(10)
P(3)-Co(1)-P(1)	96.987(10)
O(5)-S(1)-O(3)	115.52(6)
O(5)-S(1)-O(4)	115.48(5)
O(3)-S(1)-O(4)	114.46(5)
O(5)-S(1)-C(3)	103.00(5)
O(3)-S(1)-C(3)	102.73(5)
O(4)-S(1)-C(3)	103.01(5)
C(11)-P(1)-C(12)	102.63(5)
C(11)-P(1)-C(13)	99.14(5)
C(12)-P(1)-C(13)	102.00(5)
C(11)-P(1)-Co(1)	118.02(3)
C(12)-P(1)-Co(1)	112.42(4)
C(13)-P(1)-Co(1)	119.97(3)
C(22)-P(2)-C(23)	103.04(5)
C(22)-P(2)-C(21)	102.75(4)
C(23)-P(2)-C(21)	104.46(5)
C(22)-P(2)-Co(1)	110.78(3)
C(23)-P(2)-Co(1)	115.87(3)
C(21)-P(2)-Co(1)	118.14(3)
C(32)-P(3)-C(33)	104.75(5)
C(32)-P(3)-C(31)	101.10(5)
C(33)-P(3)-C(31)	103.00(5)
C(32)-P(3)-Co(1)	118.27(3)
C(33)-P(3)-Co(1)	117.15(3)
C(31)-P(3)-Co(1)	110.41(3)
O(1)-C(1)-Co(1)	177.11(12)
O(2)-C(2)-Co(1)	175.40(8)
F(1)-C(3)-F(3)	107.81(9)
F(1)-C(3)-F(2)	107.34(9)
F(3)-C(3)-F(2)	107.21(8)
F(1)-C(3)-S(1)	111.70(7)
F(3)-C(3)-S(1)	111.18(8)
F(2)-C(3)-S(1)	111.38(7)
P(1)-C(11)-H(11A)	109.5
P(1)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
P(1)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
P(1)-C(12)-H(12A)	109.5
P(1)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
P(1)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
P(1)-C(13)-H(13A)	109.5
P(1)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
P(1)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
P(2)-C(21)-H(21A)	109.5
P(2)-C(21)-H(21B)	109.5

H(21A)-C(21)-H(21B)	109.5
P(2)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
P(2)-C(22)-H(22A)	109.5
P(2)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
P(2)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
P(2)-C(23)-H(23A)	109.5
P(2)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
P(2)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
P(3)-C(31)-H(31A)	109.5
P(3)-C(31)-H(31B)	109.5
H(31A)-C(31)-H(31B)	109.5
P(3)-C(31)-H(31C)	109.5
H(31A)-C(31)-H(31C)	109.5
H(31B)-C(31)-H(31C)	109.5
P(3)-C(32)-H(32A)	109.5
P(3)-C(32)-H(32B)	109.5
H(32A)-C(32)-H(32B)	109.5
P(3)-C(32)-H(32C)	109.5
H(32A)-C(32)-H(32C)	109.5
H(32B)-C(32)-H(32C)	109.5
P(3)-C(33)-H(33A)	109.5
P(3)-C(33)-H(33B)	109.5
H(33A)-C(33)-H(33B)	109.5
P(3)-C(33)-H(33C)	109.5
H(33A)-C(33)-H(33C)	109.5
H(33B)-C(33)-H(33C)	109.5

Table B-8.5. Anisotropic displacement parameters ($Å^2$x 10^3) for Compound 12. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\, h^2\, a^{*2}U^{11} + ... + 2\, h\, k\, a^*\, b^*\, U^{12}\,]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Co(1)	10(1)	9(1)	8(1)	0(1)	2(1)	-1(1)
S(1)	14(1)	15(1)	17(1)	3(1)	4(1)	1(1)
P(1)	10(1)	11(1)	12(1)	1(1)	2(1)	0(1)
P(2)	10(1)	10(1)	11(1)	-2(1)	2(1)	-1(1)
P(3)	13(1)	14(1)	9(1)	-2(1)	3(1)	-1(1)
F(1)	39(1)	70(1)	19(1)	4(1)	15(1)	16(1)
F(2)	22(1)	36(1)	29(1)	4(1)	4(1)	14(1)
F(3)	21(1)	38(1)	56(1)	2(1)	11(1)	-10(1)
O(1)	64(1)	59(1)	24(1)	2(1)	16(1)	-41(1)
O(2)	24(1)	14(1)	22(1)	3(1)	0(1)	2(1)
O(3)	31(1)	37(1)	17(1)	4(1)	10(1)	9(1)
O(4)	21(1)	20(1)	24(1)	7(1)	2(1)	5(1)
O(5)	24(1)	18(1)	47(1)	-2(1)	5(1)	-6(1)
C(1)	26(1)	25(1)	13(1)	-1(1)	5(1)	-13(1)
C(2)	14(1)	12(1)	12(1)	-2(1)	2(1)	-1(1)
C(3)	17(1)	28(1)	17(1)	2(1)	4(1)	2(1)
C(11)	13(1)	21(1)	20(1)	-3(1)	4(1)	-5(1)
C(12)	20(1)	21(1)	29(1)	11(1)	4(1)	5(1)
C(13)	15(1)	24(1)	18(1)	-4(1)	5(1)	2(1)
C(21)	16(1)	23(1)	12(1)	-3(1)	4(1)	-2(1)
C(22)	10(1)	19(1)	16(1)	-1(1)	3(1)	-2(1)
C(23)	21(1)	10(1)	24(1)	-2(1)	4(1)	-1(1)
C(31)	18(1)	30(1)	15(1)	-6(1)	4(1)	6(1)
C(32)	32(1)	17(1)	19(1)	-6(1)	8(1)	-9(1)
C(33)	16(1)	26(1)	10(1)	0(1)	2(1)	0(1)

Table B-8.6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10 ^{3}) for Compound 12.

	x	y	z	U(eq)
H(11A)	4303	3719	10446	27
H(11B)	4122	4358	9580	27
H(11C)	4839	2906	9897	27
H(12A)	3329	-692	9959	36
H(12B)	3636	457	10702	36
H(12C)	4368	59	10235	36
H(13A)	4165	1120	8771	28
H(13B)	3316	2244	8291	28
H(13C)	3115	418	8464	28
H(21A)	1761	1092	7584	25
H(21B)	1358	2870	7590	25
H(21C)	657	1434	7208	25
H(22A)	-561	957	7914	23
H(22B)	-370	2769	8212	23
H(22C)	-408	1370	8808	23
H(23A)	762	-1351	8196	29
H(23B)	948	-1163	9110	29
H(23C)	1816	-1130	8759	29
H(31A)	886	4236	10910	32
H(31B)	872	5775	10378	32
H(31C)	1471	5806	11277	32
H(32A)	2889	6926	10913	34
H(32B)	2548	6732	9990	34
H(32C)	3530	5968	10493	34
H(33A)	3594	3139	11426	27
H(33B)	2654	2578	11610	27
H(33C)	3100	4301	11891	27

Table B-8.7. Torsion angles [°] for Compound 12.

C(1)-Co(1)-P(1)-C(11)	-120.90(5)
C(2)-Co(1)-P(1)-C(11)	59.50(5)
P(2)-Co(1)-P(1)-C(11)	148.94(4)
P(3)-Co(1)-P(1)-C(11)	-31.53(4)
C(1)-Co(1)-P(1)-C(12)	-1.72(6)
C(2)-Co(1)-P(1)-C(12)	178.68(5)
P(2)-Co(1)-P(1)-C(12)	-91.88(4)
P(3)-Co(1)-P(1)-C(12)	87.65(4)
C(1)-Co(1)-P(1)-C(13)	118.12(5)
C(2)-Co(1)-P(1)-C(13)	-61.48(5)
P(2)-Co(1)-P(1)-C(13)	27.96(4)
P(3)-Co(1)-P(1)-C(13)	-152.51(4)
C(1)-Co(1)-P(2)-C(22)	67.45(5)
C(2)-Co(1)-P(2)-C(22)	-62.62(4)
P(3)-Co(1)-P(2)-C(22)	2.22(6)
P(1)-Co(1)-P(2)-C(22)	-179.71(3)
C(1)-Co(1)-P(2)-C(23)	-49.43(6)
C(2)-Co(1)-P(2)-C(23)	-179.50(5)
P(3)-Co(1)-P(2)-C(23)	-114.67(5)
P(1)-Co(1)-P(2)-C(23)	63.41(4)
C(1)-Co(1)-P(2)-C(21)	-174.48(5)
C(2)-Co(1)-P(2)-C(21)	55.46(5)
P(3)-Co(1)-P(2)-C(21)	120.29(5)
P(1)-Co(1)-P(2)-C(21)	-61.63(4)
C(1)-Co(1)-P(3)-C(32)	-178.12(6)
C(2)-Co(1)-P(3)-C(32)	-48.14(5)
P(2)-Co(1)-P(3)-C(32)	-112.81(6)
P(1)-Co(1)-P(3)-C(32)	69.12(5)
C(1)-Co(1)-P(3)-C(33)	54.97(5)
C(2)-Co(1)-P(3)-C(33)	-175.04(5)
P(2)-Co(1)-P(3)-C(33)	120.28(5)
P(1)-Co(1)-P(3)-C(33)	-57.79(4)
C(1)-Co(1)-P(3)-C(31)	-62.44(6)
C(2)-Co(1)-P(3)-C(31)	67.54(5)
P(2)-Co(1)-P(3)-C(31)	2.87(6)
P(1)-Co(1)-P(3)-C(31)	-175.21(4)
C(2)-Co(1)-C(1)-O(1)	-7.4(19)
P(2)-Co(1)-C(1)-O(1)	-90.3(19)
P(3)-Co(1)-C(1)-O(1)	76.9(19)
P(1)-Co(1)-C(1)-O(1)	173.1(19)
C(1)-Co(1)-C(2)-O(2)	-15.9(10)
P(2)-Co(1)-C(2)-O(2)	67.6(10)
P(3)-Co(1)-C(2)-O(2)	-99.7(10)
P(1)-Co(1)-C(2)-O(2)	163.6(10)
O(5)-S(1)-C(3)-F(1)	60.45(9)
O(3)-S(1)-C(3)-F(1)	-179.19(8)
O(4)-S(1)-C(3)-F(1)	-59.98(9)
O(5)-S(1)-C(3)-F(3)	-179.07(8)
O(3)-S(1)-C(3)-F(3)	-58.71(9)
O(4)-S(1)-C(3)-F(3)	60.50(8)
O(5)-S(1)-C(3)-F(2)	-59.56(9)
O(3)-S(1)-C(3)-F(2)	60.80(9)
O(4)-S(1)-C(3)-F(2)	-179.99(7)

THE END