# Synthesis, Reactions, and Properties of Iron, Cobalt, and Nickel Complexes Containing some [*P,S*]-chelating Ligands and Trimethylphosphine

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*To my mother, my daughter*

*and*

*all the faithful of my friends around me*

*who gave me generous support and encouragement*

*during my PhD work*

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## List of Abbreviations

| | |
|---|---|
| Fig | figure |
| Bu | butyl |
| d | doublet |
| dd | doublet of doublets |
| ddd | doublet of doublets of doublets |
| δ | chemical shift (NMR) |
| dec. | decomposition |
| TMEDA | N,N,N,N-tetramethyl-1,2-ethylenediamine |
| SHOP | Shell Higher Olefin Process |
| dt | doublet of triplets |
| eq | equation |
| h | hour |
| IR | Infrared |
| J | coupling constant |
| L | generalized ligand |
| m | medium(IR); multiplet (NMR) |
| M | molecular mass |
| Me | methyl |
| BuLi | butyl lithium |
| MeLi | methyl lithium |
| NMR | Nuclear magnetic resonance |
| MS | Mass spectroscopy |
| ν | frequency |
| Ph | phenyl |
| q | quartet |

| | |
|---|---|
| t | triplet |
| td | triplet of doublets |
| ether | diethyl ether |
| THF | tetrahydrofuran |
| tert | tertiary |
| vs | very strong |
| vw | very weak |
| w | weak |
| X | halide |

# 1 INTRODUCTION

## 1.1 The role of iron, cobalt and nickel complexes in organometallic catalysis

Transition metal organometallic chemistry lies at the interface between classical organic and inorganic chemistry because it looks at the interaction between inorganic metal ions and organic molecules. The field has provided some powerful new synthetic methods in organic chemistry and is beginning to make links with biochemistry with the discovery of several metallo- enzymes that involve organometallic intermediates.[1-4]Organometallic ideas have been useful in interpreting the chemistry of metal surfaces and of metal colloids. The controlled pyrolysis of organometallic species has proved to be a useful way of preparing solid-state material with unusual properties. [5-6]

Public concern for the environment has led to the rise of "green chemistry", the purpose of which is to minimize the production of chemical waste in industry and commerce. One way to do this is to use catalysts rather than stoichiometric reagents to bring about reactions. Many commercially important processes that rely on transition metal organometallic complexes as catalysts have been developed, and such applications are likely to gain more importance in the future. [7]

In the chemical technology of production processes as well as in preparative organic chemistry transition metal-catalyzed processes gain ever more significance. About two thirds of all industry and fine chemicals at any time come into contact with a catalyst. Substrate molecules are usually coordinated first and brought then to reaction with one another. A substantial characteristic of the metal centre in the catalyst is its ability to attain several stable oxidation states and can oscillate between them during the reaction. New developments shift a reaction into the

homogeneous phase if the task consists of achieving a higher selectivity than in heterogeneously catalyzed reactions. Thus the original Ziegler-Natta process for the polymerization of ethene [9] muddled as heterogeneously catalyzed was replaced by the development of high-activity metallocenes[10], which permit homogeneous reaction guidance. In order to replace the frequently used, very reactive precious metal complexes the lower-priced metals of the 3d row, as for example iron, cobalt or nickel, are increasingly used. By consistent continuation of the fundamental work of *Wilke* and his group, the Shell Higher Olefin Process (SHOP) for the oligomerization and/or polymerization of ethene became one of the world-wide largest homogeneous-catalyzed processes. Fig. 1.1 describes the general formula of a SHOP-active catalyst, consisting of a chelate part and an organopart around a square-planar coordinated nickel centre. The chelate part stabilizes the nickel centre and steers the reaction sequence in the opposite positions of the organo part.

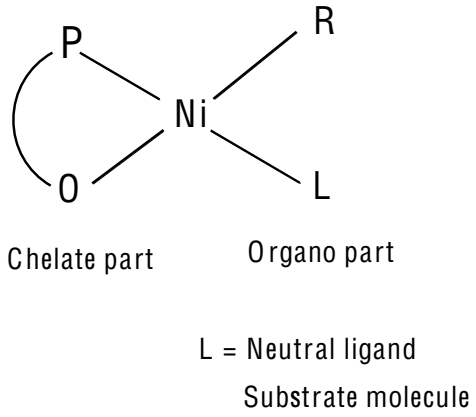



Fig.1.1 General Formula of an SHOP - Catalysts

A typical representative of a SHOP catalyst precursor [16] is shown in Fig.1.2 As reactive intermediate a hydridonickel chelate [*P,O*]- complex was assumed, which is supported by a structurally characterized hydridonickel species B which however proved catalytically inactive[17,18].

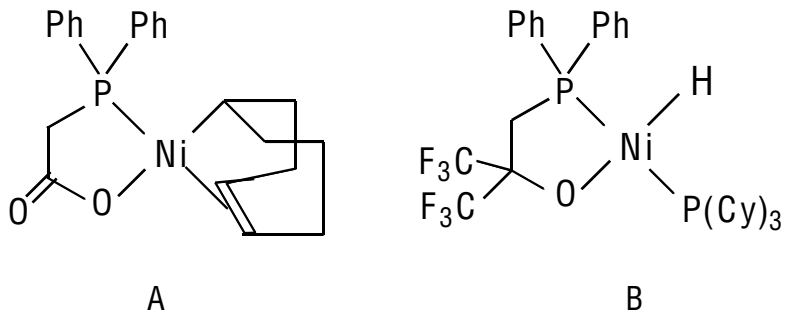



Fig.1.2 A: typical SHOP precursor, B model of active species

The postulated mechanism of the SHOP is shown in Fig 1.3 as a reaction cycle. The initial step of the catalytic cycle generates an under-coordinated hydridonickel species capable of coordinating ethene. Formal insertion of an olefin leads to an ethyl nickel function that can either coordinate another substrate molecule resulting in chain-growth or undergo β-H elimination with formation of an 1-olefin regenerating the hydridonickel species [19].

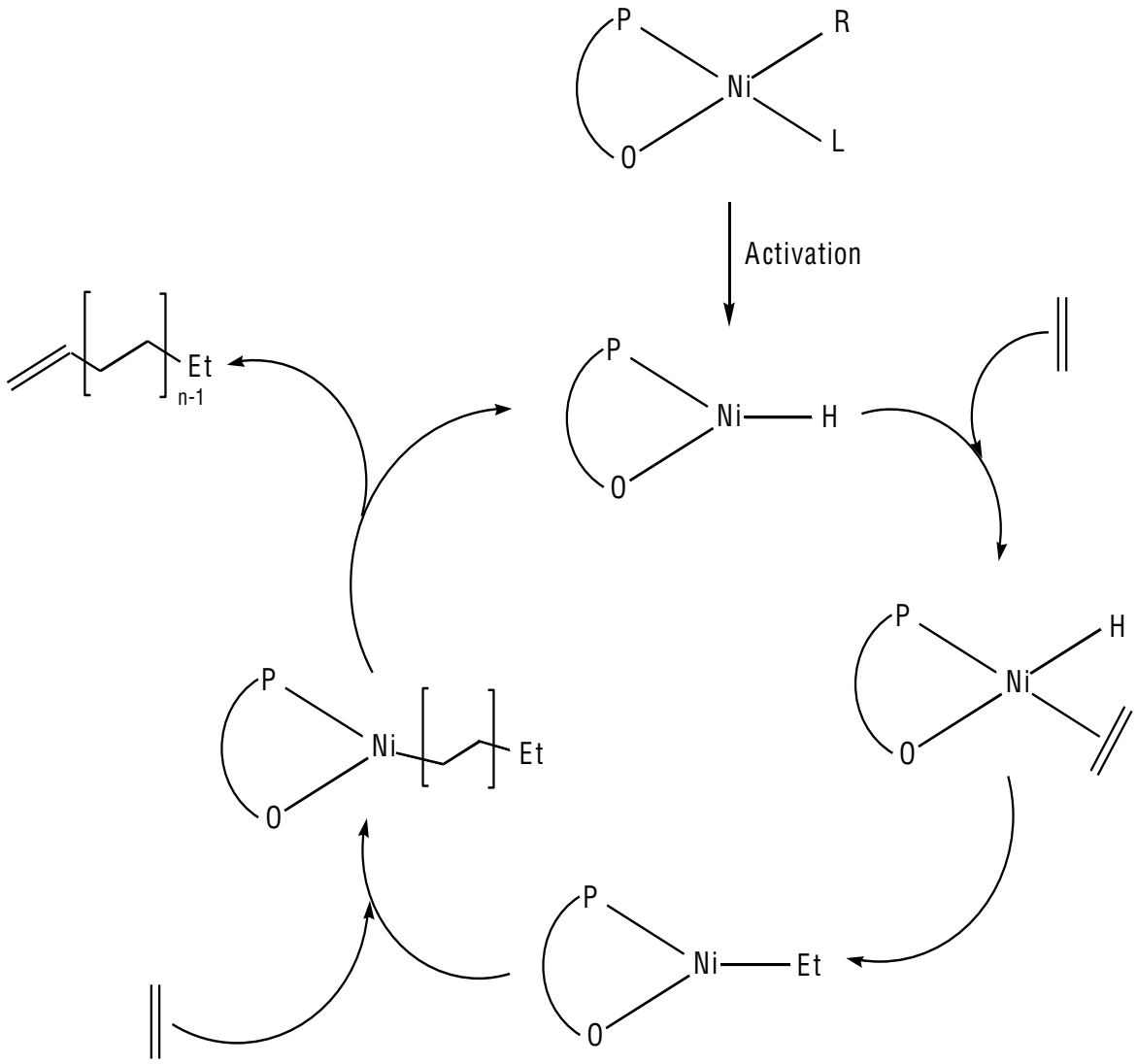



Fig.1.3 Schematic representation of the postulated SHOP

Mean while the chemical industry demands for ever better control of the properties of oligomers and polymers and needs more selective catalysts that tolerate many functional groups. In recent years new catalysts were developed with later transition metals of the 3d series (Fig. 1.4). *Brookhart et al.* [20, 21] described diimino complexes of iron and cobalt that selectively oligomerize ethene to α-olefins up to high molecular weight polymers [22-24]. Fig.1.4 shows the

catalyst types which are usually combined with excess methylalumoxan (MAO) in analogy with the metallocenes [25].

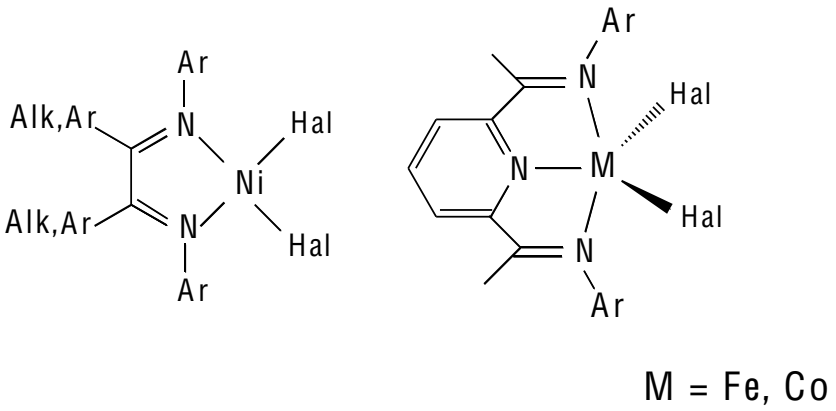



Fig.1.4 Brookhart-type diimino catalyst systems

Low-valent cobalt supported by carbonyl and triorganophosphine ligands catalyzes the old oxo-synthesis (Roelen 1938) [26] which was mechanistically explored by Heck and Breslow [27]. The steering properties of triorganophosphine ligands at cobalt or rhodium centres towards linear aldehydes have been investigated [28, 29]. Generally it seems useful to explore new ligands and metal complexes that show structural relationship to active catalysts of today. As a guideline the structural similarity [30] between (2-diphenylphosphino) phenol and diphenyl-phosphinoacetic acid as an active SHOP-catalyst (Fig. 1.5) was used in preceding doctoral work of *Brand, Dal, Hetche, and Mao*. [31-34]

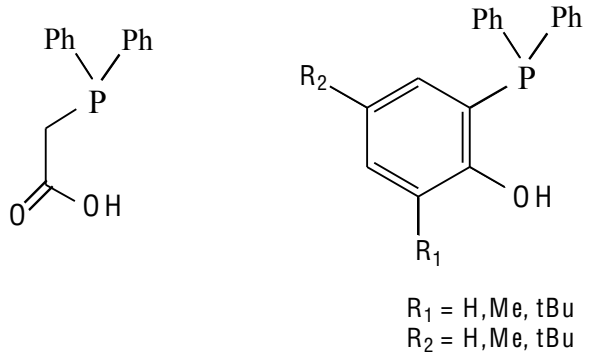



Fig.1.5 Prechelate ligands (diphenyl phosphino)-acetic acid and (2-diphenylphosphino)-phenol

First, orienting experiments of Dal and Hetche for the catalytic activity of chelate-[*P,O*]nickel complexes showed catalytic potential without additional activation by MAO. Therefore they behave as single-component catalysts. Thus the logical extension to (2-diphenylphosphino)thiophenols as higher homologues of prechelate-[*P,O*] ligands represents a big step in terms of changed properties. The new complexes presented in this work exhibit therefore at least some model character of homogeneous catalysts, not only of the SHOP type.

## 1.2 [*P,S*]-chelating ligands in complexes of transition metals

In recent years much interest was focussed on the coordination chemistry of polydentate ligands containing both thiolate and tertiary phosphine donor functions, as their combination is likely to confer unusual structures and reactivities on their metal compounds. Some of these complexes have been used as models for biologically active centers in metalloproteins such as ferredoxins, nitrogenase, blue copper proteins and metallothioneins or as model for the design of complexes with potential application as radiopharmaceuticals. These complexes have exhibited an intriguing variety of structures or unusual oxidation states and have an enhanced solubility which makes them excellent candidates for further studies.[36]

(2-Diphenylphosphino)-thiophenol is a already well-examined ligand system in the literature. However, one finds predominantly bischelate-[*P,S*] complexes of 3d, 4d, and 5d metals.[37-40] Stable monochelate complexes are known only in the 4d and 5d row. As examples some examples from the work of *Dahlenburg and Dilworth*[41, 42] are shown in Fig. 1.6.

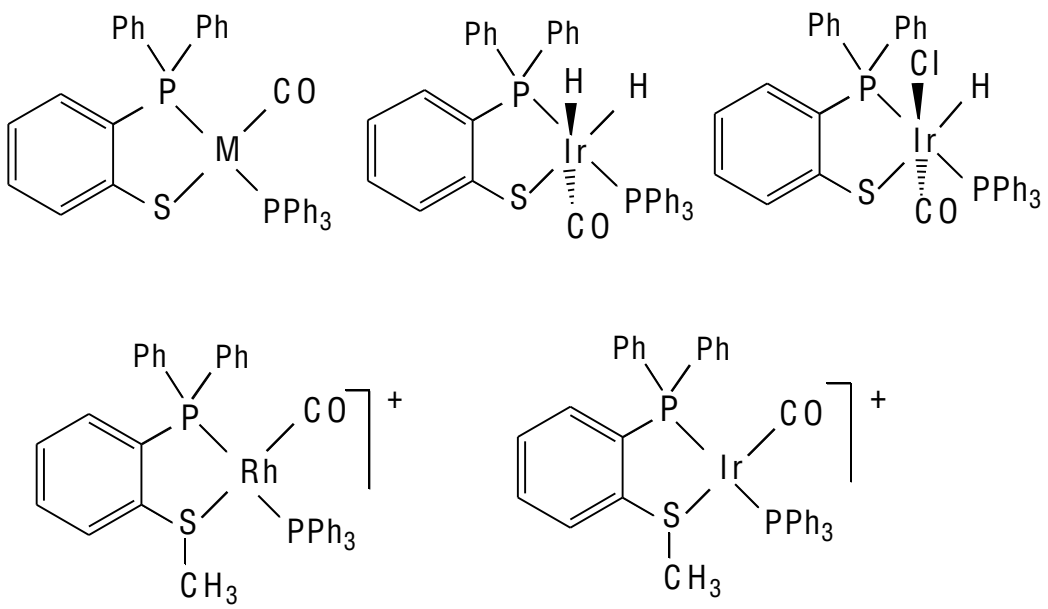



Fig.1.6 Monochelate-[*P,S*]-complexes of 4d and 5d metals

*Levason and co workers*[43] succeeded in isolating thermally stable [*P,S*]-nickel(III) and palladium(IV) complexes by oxidation with bromine (Fig.1.7).

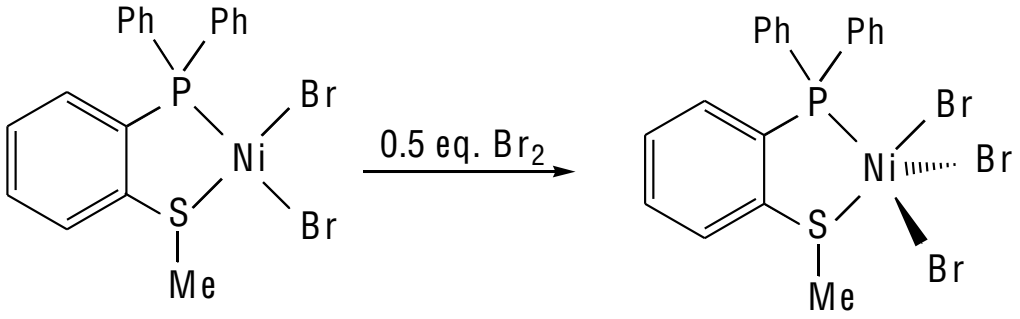



Fig.1.7 Unusual oxidation state of [*P,S*]-nickel(III)

In order to suppress the formation of bis or trischelate species one finds in the literature very frequently systems with two and three thiophenolato donors (Fig. 1.8).

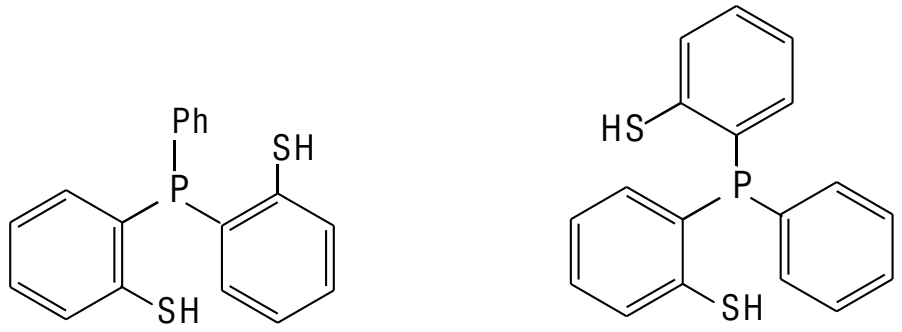



Fig.1.8 Prechelate ligand with two (*PSS*) and three (*PSSS*) sulfur donor atoms

With the ligand shown in Fig.1.8 the conversion of $CoMe(PMe_3)_4$ to a hydrido{chelate-[*P,S*]}cobalt(III) complex is shown (Fig. 1.9).

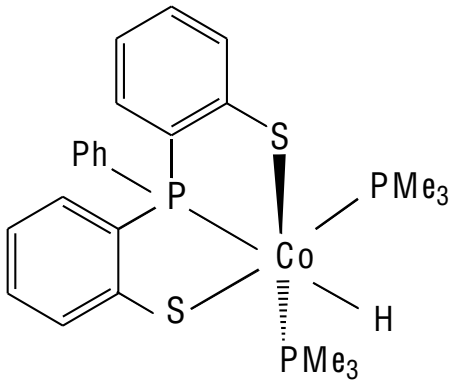



Fig.1.9 Hydrido-[*P,S,S*]-cobalt (III)-complex

Also with (PSSS) ligands complexes with rare oxidation levels of the central atom are accessible. So *Koch and Münck*[46] found an electro-chemical way for reversibly adjusting a [*P,S,S,S*]-iron(II) / (III) system.

Regarding investigations of catalytic properties of chelate-[*P,S*] complexes information in the literature is scarce.

*Gibson et al.* [47] described a chelate-[*P,S*] nickel complex featuring a 1,1-disubstituted ferrocenyl chelate-[*P,S*] unit in a square planar metal geometry.

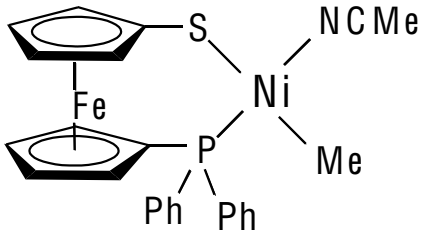



Fig.1.10 New [P, S] substituted ferrocenediyl nickel complex

From the work of *Brookhart* [48] we are aware of half-sandwich systems with cobalt and nickel (Fig.1.11).

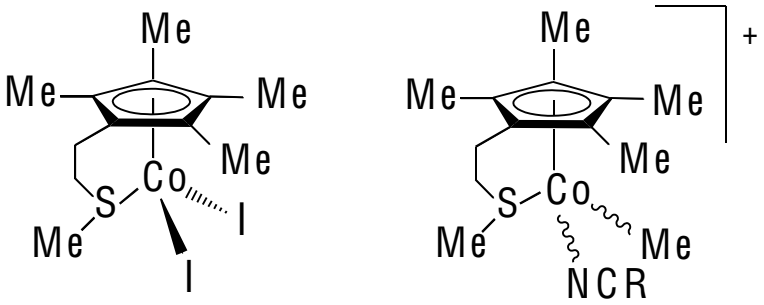



Fig. 1.11 New catalysts for ethene polymerization

The cobalt and nickel complexes show high activities in the polymerization of ethene.

## 1.3 Trimethylphosphine as supporting ligand

Triorganophosphines ($PR_3$) are well known for stabilizing transition metal centers in high and low formal oxidation states. Trimethylphosphine as the simplest trialkylphosphine, with its low steric demand, carries some advantages with itself. Thus it facilitates the evaluation of spectroscopic data (IR, NMR) even in complex connections because of its high local symmetry (local $C_{3v}$). Trimethylphosphine is a good σ-donor in high-valent and also a pronounced π-acceptor in low-valent metal compounds. The spatial requirement of triorganophosphines is described by the so-called *Tolman –angle*. This is defined by the opening angle of a cone with the apex at the metal that encloses the van der Waals boundaries of the substituents. This ligand is particularly useful in the interception of intermediates in catalytic processes.

## 1.4 Aims of the investigation at hand

Little information about monochelate-[*P, S*] complexes with iron, cobalt and nickel as central atom can be extracted from the literature. For the reactivity of these compounds, which can be understood as modified SHOP catalysts, one does not find any references.

The present study consists of the following tasks:

1. Synthesis of new trimethylphosphine supported (3-diphenylphosphino)-2-thionaphtholato-[*P, S*] complexes of iron, cobalt and nickel.
2. Characterization of the isolated species and studies of their properties and

characteristic reactions.

3. Structural investigations on single crystals obtained from these synthesis and comparison of solid state data with solution spectra.
4. Behaviour in solution under 1 bar of carbon monoxide.
5. Comparison of the [*P,S*] systems with the isoelectronic [*P,O*]systems.

# 2 RESULTS AND DISCUSSION

This chapter covers the synthesis and principal properties in subsequent reactions of (3-diphenylphosphino)-2-thionaphtholato complexes of iron, cobalt and nickel.

## 2.1 The prechelate systems (3-diphenylphosphino)-2-thionaphthol and (2-diphenylphosphino)-3-methylthionaphthalene

No procedure to synthesize phosphinothionaphthol and phosphino(methylthio)-naphthalene ligands are known. However since other [*P,S*] ligands are accessible a modified route is derived from the literature [50,51]and is briefly given here. The preparation of (3-diphenylphosphino)-2-thionaphthol achieved by *ortho*–metalation of 2-thionaphthol using *n*-BuLi /TMEDA in cyclohexane solution. The reaction was continued with addition of chlorodiphenylphosphine and subsequent hydrolysis with acetic acid. Extraction with toluene and crystallization from ethanol gave the phosphinothionaphthol in 21.3% yield.

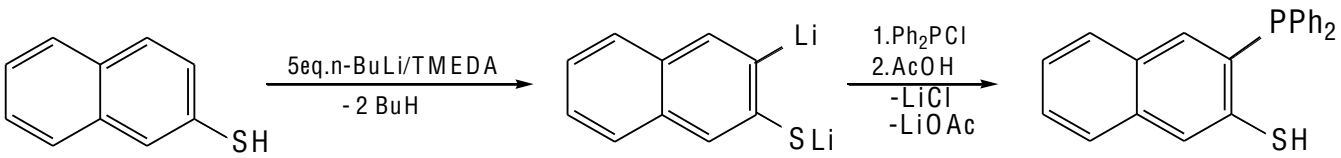



Fig. 2.1 Synthesis of (3-diphenylphosphino)-2-thionaphthol

The synthesis of the phosphino(methylthio) naphthalene is carried out by deprotonation of the 2-thionaphthol with *n*-BuLi and subsequent reaction with methyl iodide. The raw product is extracted as before with toluene and purified

by crystallization from ethanol to yield the phosphinothioether in 61% yield in the form of pale yellow micro needles.

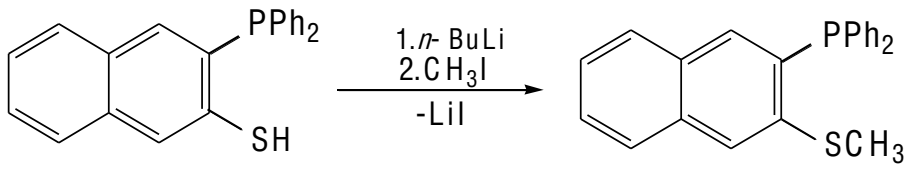



Fig. 2.2 Preparation of (2-diphenylphosphino)(3-methylthio)naphthalene

## 2.2 Synthesis of {(3-Diphenylphosphino)-2thionaphtholato –[*P,S*]}-iron(II) Complexes

### 2.2.1 Synthesis of hydrido-{(3-diphenylphosphino)-2 thionaphtholato -[*P,S*]}-tris(trimethylphosphine)-iron(II) (1)

*Mao* could show that phosphinophenols smoothly reacted with tetrakis (trimethylphosphine) iron (0) forming *fac* –hydrido - [*P, O*] –chelate -iron(II) complexes [34]. Higher yields and faster reactions of phosphinophenols were observed with electron-rich alkyl substituents in the aromatic backbone. Therefore *ortho*-phosphinothiophenol as higher homolog has been successfully used by *Frey* [44]. 3-Phosphino-2-thionaphthol reacted in a similar way by oxidative addition at the iron (0) - center to form the hydrido-iron (II) complexes. The softer sulfur donor when attached to electron-rich metal centers should provide a more stable coordination.

## Synthesis and characterization

(3-Diphenylphosphino)-2-thionaphthol dissolved in THF was reacted with mole-equivalent amounts of tetrakis (trimethylphosphine) iron (0) in THF to give almost quantitatively the red hydrido-iron complex 1. When crystallized from ether at -27° C only a few of the some strongly deformed crystal plates are formed that decomposed during an X-Ray diffraction experiment. In addition, the product can also be obtained by washing the raw product with a little pentane as analytically pure red powder which in dry air remains unreacted for a few minutes, but in solution decomposes within seconds. In pentane at room temperature the [*P,S*] ligand is poorly soluble which makes the reaction time 16h and 30h on a 10-20 g scale.

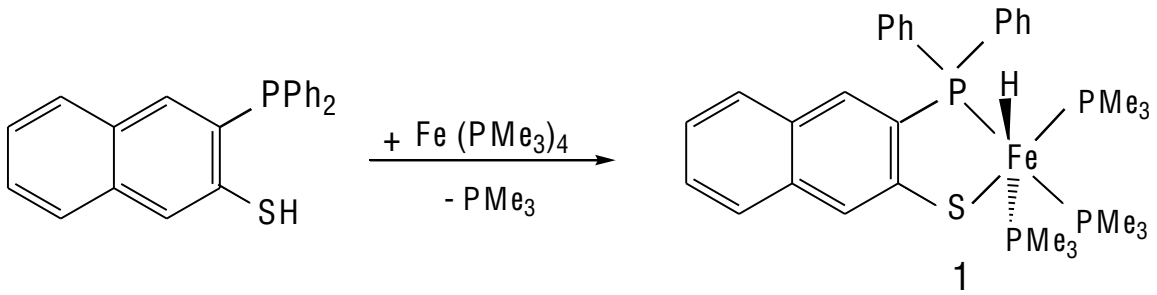



Fig.2.3 Synthesis of complex 1

## Spectroscopic investigation

IR spectra of compound 1 give evidence for the presence of a Fe-H function through a typical ν(Fe-H) stretching frequency at 1842 $cm^{-1}$ (Fig. 2.4). In addition, the characteristic bands of the [*P,S*] ligand at 3051$cm^{-1}$ ν(CH) and 1571, 1617 $cm^{-1}$ (C=C skeleton vibrations), and a strong $\rho_1$-band of coordinated trimethylphosphine at 945 $cm^{-1}$.

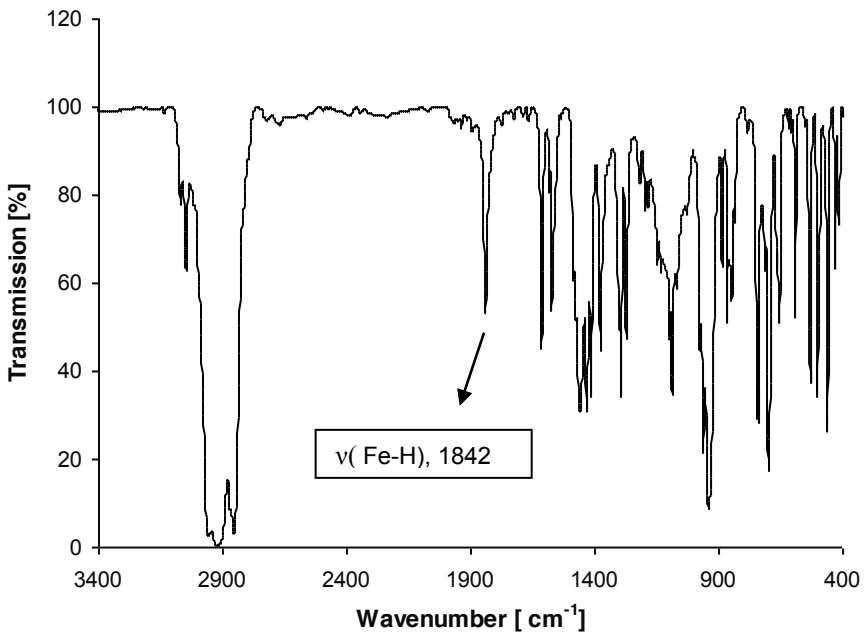



Fig. 2.4 IR- Spectrum of Complex 1

The coordination geometry of 1 can be derived from the $^{1}$H and $^{31}$P NMR spectra. In the $^{1}$H spectrum the hydride resonance appears at -12.8 ppm as four doublets through splitting by four chemically different phosphorus nuclei, which is only compatible with a facial arrangement of ligands. The signals of the three trimethylphosphine ligands appear as sharp doublets at 0.89, 1.23 and 1.64 ppm while the protons of the aromatic part lie in the range of 6.75 to 8.24 ppm. In the $^{31}$P-NMR spectrum three resonances at 27.6, 13.3 and 5.3 ppm are assigned to coordinated trimethylphosphines and a fourth signal with a typical shift at 88.0 ppm to the chelate-P nucleus (Fig. 2.5). Each resonance shows a ddd coupling which confirms the facial configuration of 1. [35] The signal at 13.3 ppm with a large *trans*-coupling constant of 95 Hz is assigned to the phosphine ligand in opposite position to the chelate-P donor. The remaining P-P-couplings lie between 13 and 48 Hz corresponding to *cis*-PP coupling. Fig. 2.5 shows the complete assignment.

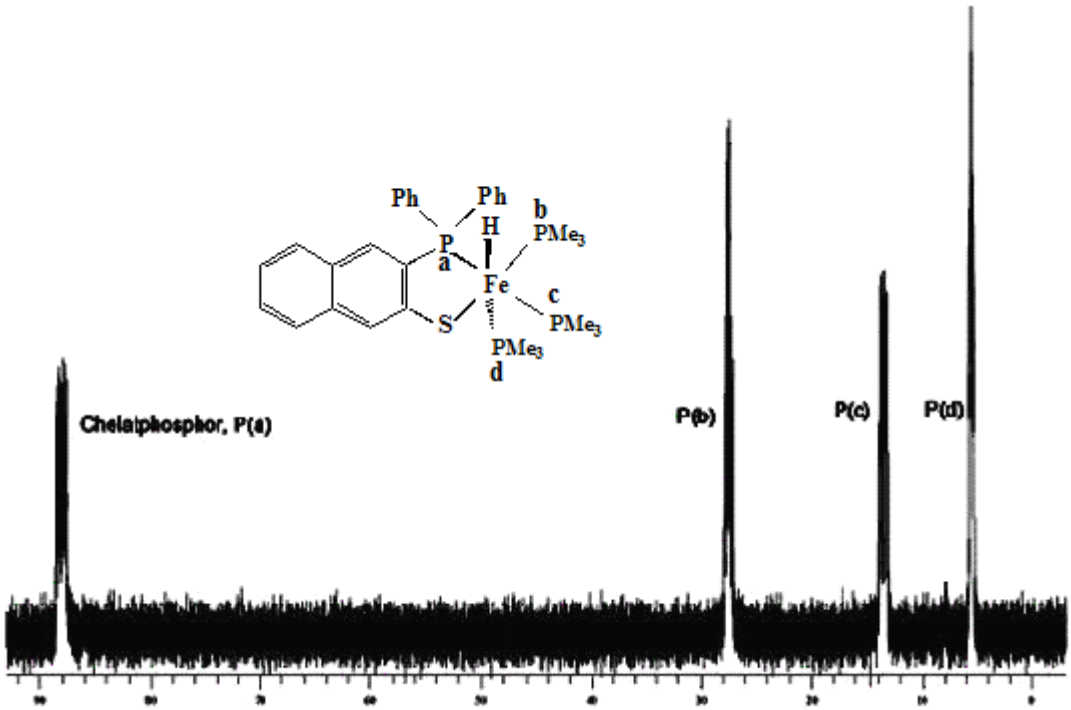



Fig. 2.5 31P-NMR Spectrum of 1

## Discussion

(3-Diphenylphosphino)-2-thionaphthol oxidatively adds to $Fe(PMe_3)_4$forming the hydridoiron(II)complex 1. In solution only the isomer with a *facial* configuration is present (Fig. 2.5) which is in agreement with the results of Mao and Frey. [33, 34]

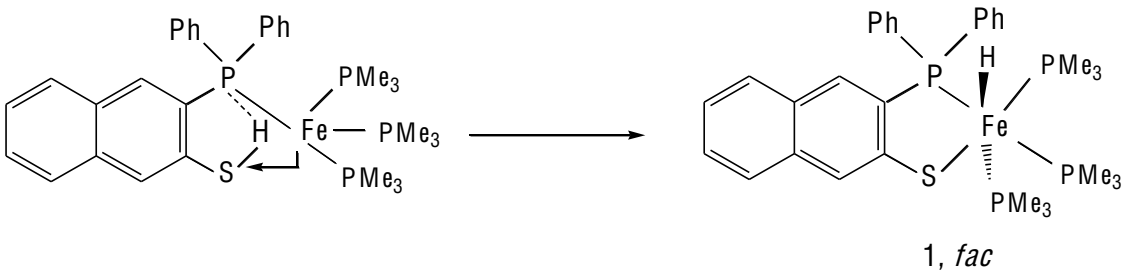



Fig.2.6 Mechanism of formation of the fac-isomer of 1

This suggests that among the stable conformations (Fig. 2.7) the *trans*-bisectional arrangement is favored in an oxidative addition with a weak intramolecular

hydrogen bridge.A crystal structure analysis of a corresponding phosphinophenol by *Hetche* has confirmed the *trans*-bisectional conformation for the solid state. [35]

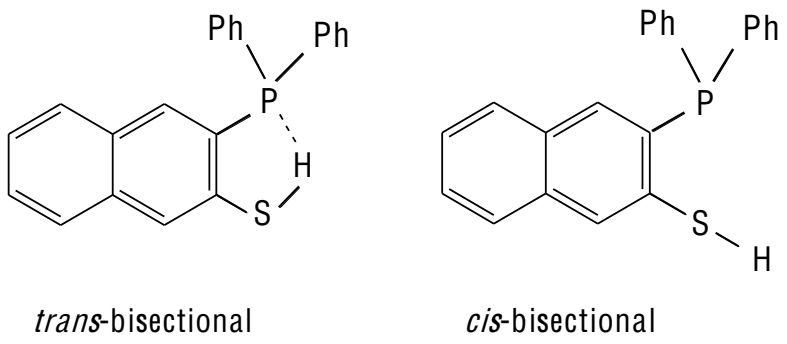
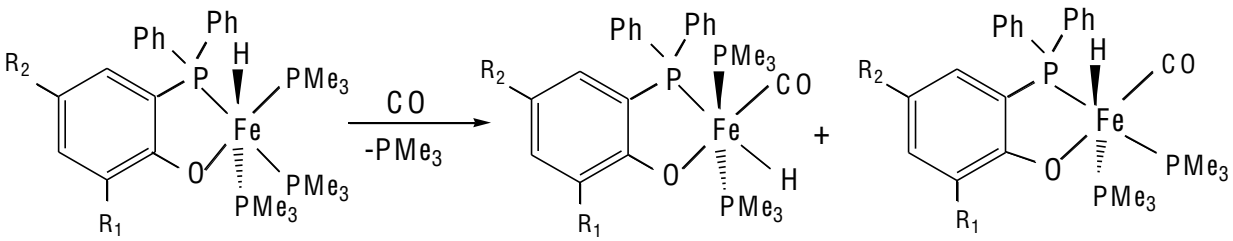



Fig. 2.7 Stable conformations of [*P, S*] ligands

### 2.2.2 Reaction of complex 1 with carbon monoxide

Carbon monoxide as strong π-acceptor ligand is expected to displace at least one of the trimethylphosphine donors as shown by *Mao*. [34] Which alkyl substituents attached to the backbone of the [*P, O*]-ligand, monosubstitution is achieved in hydridoiron (II) complexes, when the reaction was carried out at 1 bar CO pressure (Fig. 2.8).




R1 = Me ,*t*Bu
R2 = Me ,*t*Bu

Fig.2.8 Synthesis of hydrido (carbonyl)-[*P, O*] iron (II)-complexes

The unsubstituted phosphinophenolato iron (II) complex failed to react with carbon monoxide (Fig. 2.9).

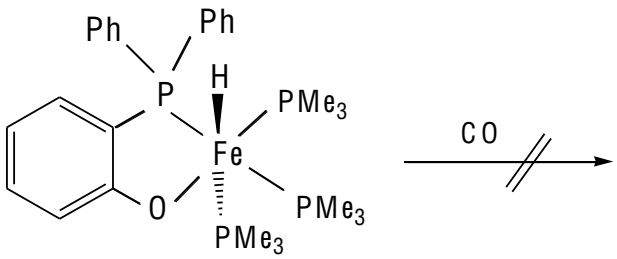



Fig. 2.9 The unsubstituted hydrido-[P, O] iron complex with carbonmonoxide

An interesting possibility after a simple ligand substitution in the [*P,S*] system would be an insertion of CO into the Fe-H bond leading to a formyl complex (Fig. 2.9). Examples are known especially for 4d and 5d metals. [54-56]

## Synthesis and Characterization

At room temperature under a CO atmosphere in THF or ether (much slower in pentane) **1** reacts to form a monocarbonyl complex as mixture of isomers **2a** and **2b** (Fig. 2.10). From ether at room temperature yellow to amber-colored cubes and thin plates are crystallized and isolated in 90% combined yield which reflect daylight with greenish-yellow shimmering and are air-stable for several weeks.

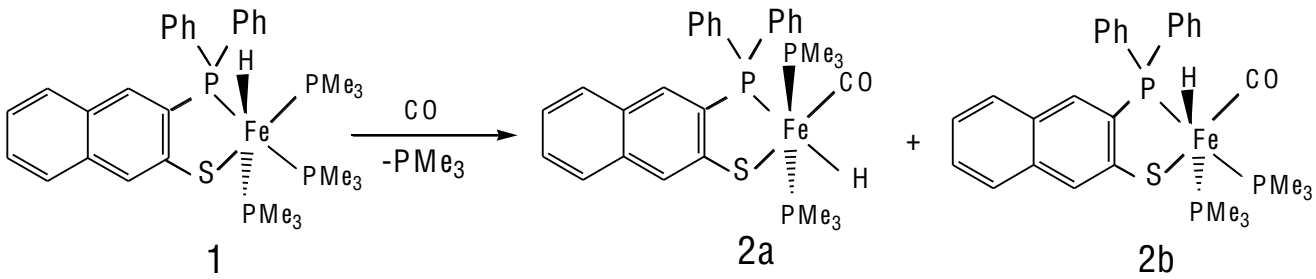



Fig. 2.10 Reaction scheme for the formation of **2a** and **b**

## Spectroscopic investigations

In the IR besides the typical bands of the coordinated phosphinothionaphthol and trimethylphosphine, very strong and sharp stretching absorptions at 1933 and 1889 $cm^{-1}$of terminal carbonyl ligands are registered which are at lower energies than in free CO (2149 $cm^{-1}$). Broad Fe-H valence vibrations absorbs at 1847 $cm^{-1}$. Already at first sight two isomers of complex 2 are present. In the $^{1}H$- NMR spectrum two hydride resonances at -9.8 ppm with a dt splitting for 2a and at -10.8 with a ddd splitting for 2b are registered with an intensity ratio of 2:1 (Fig.2.11).

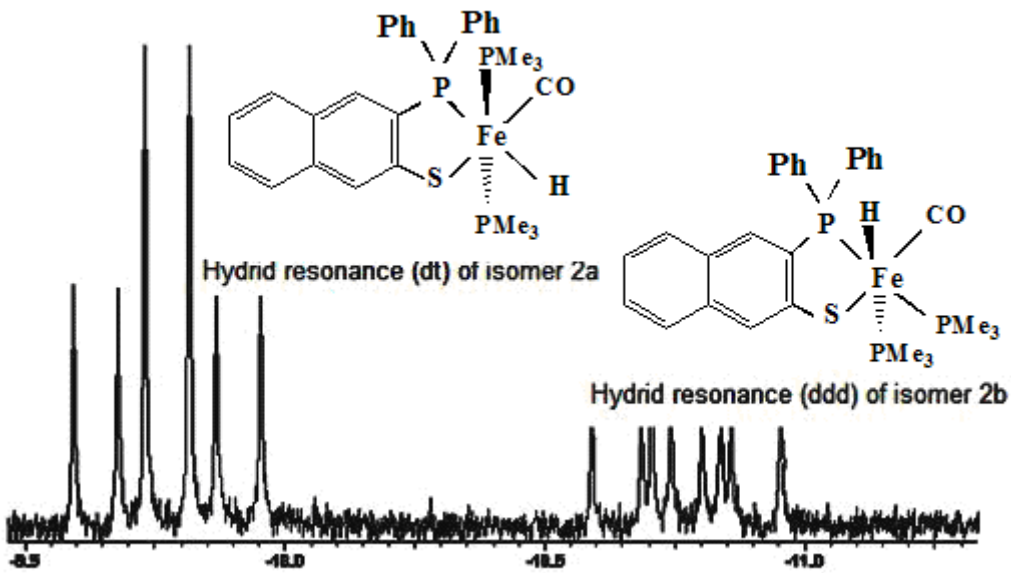



Fig.2.11 Hydrid resonance of 2a and 2b

In the $^{31}P$ NMR spectrum two sets signals with 2:1 intensities are assigned to the two isomers 2a and 2b (Fig. 2.12). The chelate phosphorus of 2a is represented by a triplet at 85.9 pm, caused by splitting with two isochronous trimethylphosphine-P nuclei that appear as doublet at 15.3 ppm. The signals at 93.0 (doublet of doublet of the chelate phosphorus), 19.7 ppm (dd, $PMe_3$ *trans* to the chelate phosphorus) and 5.2 ppm (dd, $PMe_3$) can be clearly assigned to isomer 2b.

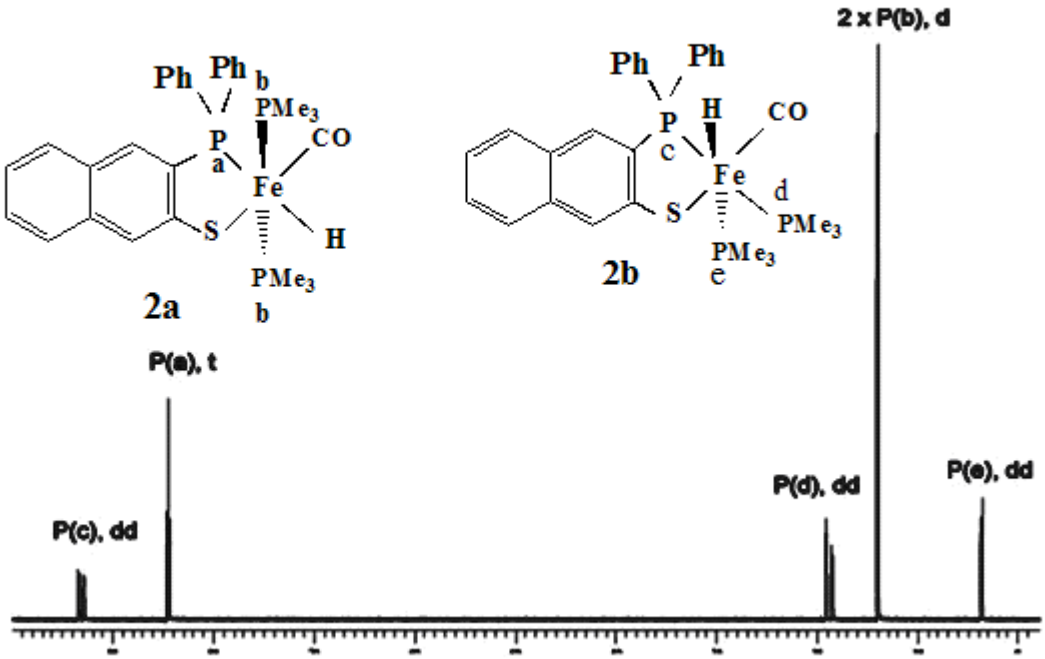



Fig. 2.12 $^{31}$P NMR spectrum of 2a, 2b

## Molecular Structure of 2a

An X-ray diffraction analysis was performed on a rectangular crystal (0.28 mm x 0.16 mm x 0.16 mm). The structure was solved in a monoclinic crystal system crystal with space group P21/c and a final$R_1$ value of 0.0284. All non-hydrogen atoms were refined anisotropically, hydrogen atoms with riding model at idealized positions and with isotropic parameters. An ORTEP drawing of the molecular structure of 2a is shown in Figure 2.13 that gives a view of the molecular geometry with selected bonding parameters. Data are specified in the appendix 8.1.

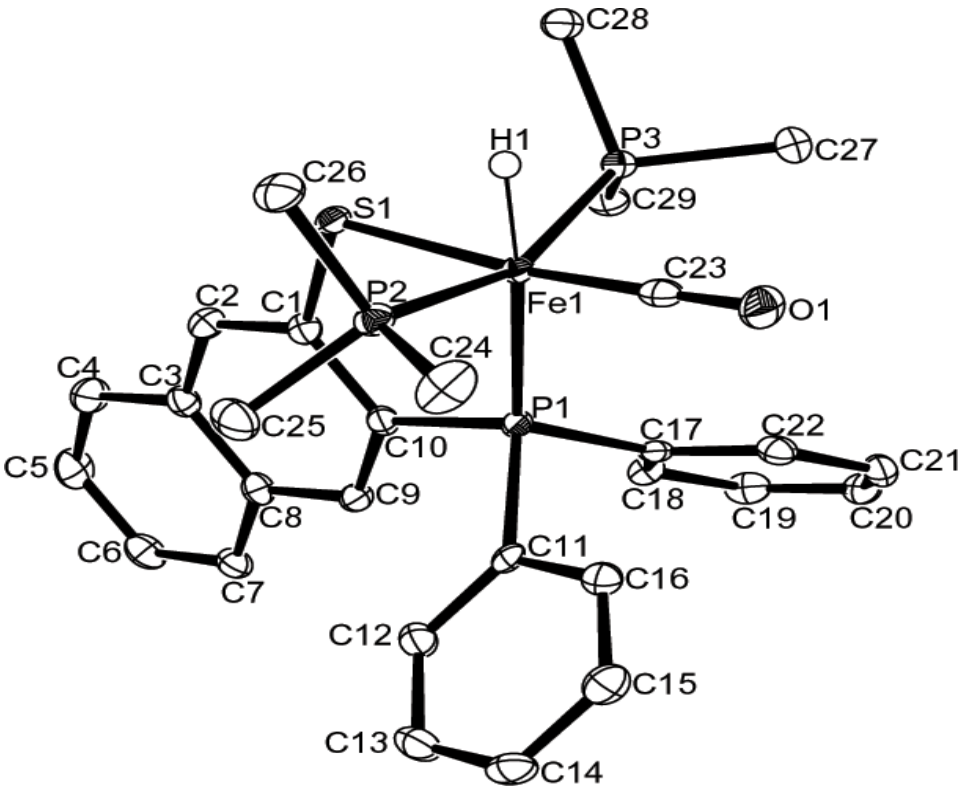



Fig. 2.13 Molecular structure of 2a (ORTEP plot with hydrogen atoms omitted); selected bond lengths [Å] and angles [°]: Fe-H1 1.42(3), Fe1-C23 1.72(2), C23-O1 1.17(2), Fe1-S1 2.31(6), Fe1-P1 2.21(8), Fe1-P2 2.23(6), Fe1-P3 2.22(6); P1-Fe1-S1 88.24(2), P1-Fe1-H1 174.7(11), P2-Fe1-H1 78.4(11), P3-Fe1-H1 81.9(11), S1-Fe1-C23 173.2(7), P2-Fe1-P3 158.6(2).

Complex 2a is shown to possess an octahedral coordination of the iron centre, in which the two *trans*-phosphine ligands P2 and P3 are bent toward the hydride ligand which resides in a position bisecting the largest angle (P3-Fe1-P2 = 158.6º).The bond length of the hydride(H1-Fe1=1.42(3) Å) corresponds with expectations for hydridoiron(II) complexes. This minor distortion is also indicated by the angles P2-Fe1-H1 of 78.4º and P3-Fe1-H1 of 81.9º. This is explainable through the lower spatial requirements of the hydride ligand. The remaining four ligand positions come close to ideal geometry. Thus P1-Fe1-H1 forms an angle of 174.7º and S1-Fe1-C23 attains 173.2º. The sum of internal angles in the five-membered ring is close to the ideal value of 540º. The bond length of the chelate

phosphorus (P1-Fe1 = 2.21(8) Å) is enlarged through the *trans*-influence of hydride while other Fe-P distances are in the typical range of 2.18 – 2.22 Å [57]. The bonding situation of the CO ligand corresponds to a terminal coordination. The distance (C23-O1=1.17(2) Å) is normal for a weakened triple bond.

### Discussion

The reaction of 1 with carbon monoxide proceeds under mild conditions by substitution of one trimethylphosphine ligand and terminal coordination of CO that effectively stabilizes the complex. The hydrido (carbonyl) complex 2 is isolated in high yield and its crystals show a high thermal stability even in air. In compound 2 CO occupies a position opposite to the softest donor atom which is sulphur as expected. Thereby the number of isomers is restricted to the pair of 2a and 2b. Further possible isomers of 2 have not been detected. The ratio of isomers 2a/2b in THF is 2:1 as shown by NMR in $d_8$-THF. Of the crystals grown from ether a crystal structure analysis showed only isomer 2a, and by preparing a fresh solution at -30 °C in the NMR experiment a ratio of 3:1 was found. This observation is in favour of a rapid equilibration in solution. In view of the usually rigid octahedral coordination of iron (II) and with no indication of ligand dissociation a reversible insertion of CO into the Fe-H bond forming an intermediate formyliron complex seems likely. A corresponding set of isomers was found by *Mao* [34] with a ratio of isomers 4:1 reflecting the different electronic properties of [*P,O*] ligands.

### 2.2.3 Reaction of 1 with Iodomethane

Oxidative addition of iodomethane constitutes an elegant way to introduce a methyl group at metal centres of low oxidation states. Thus, for example tetrakis(trimethylphosphine)iron(0) is transformed into a iron (II) derivative. [58] Even iron(II) complexes can react with iodomethane. Thus

*Mao* showed that hydrido-{(2-diphenylphosphino)phenolato[*P,O*]}iron (II) compounds with iodomethane are transformed to the corresponding iodoiron (II)complexes.[34] No indication of an intermediate iron(IV) species was obtained.

## Synthesis and Characterization

At room temperature complex 1 in the presence of iodomethane is very slowly but quantitatively converted into the iodo species 3. A yellow powder is isolated which is air-stable for several days and only moderately dissolves in THF. The reaction is visibly followed starting with a strong red THF solution of 1 and ending with a bright orange-yellow suspension of 3 (Fig. 2.14). For the observation of a gas (methane) the process is too slow.

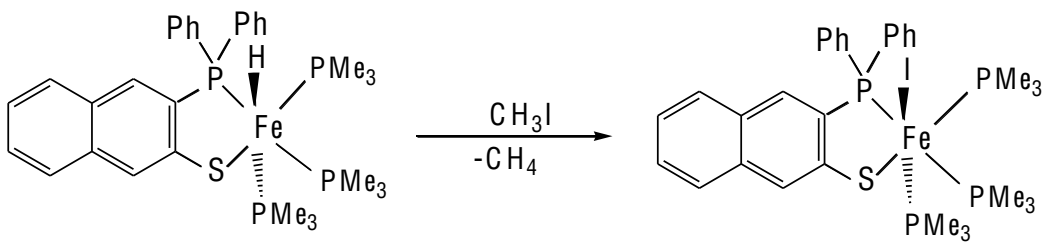



Fig.2.14 Reaction scheme for the synthesis of 3

## Spectroscopic Investigation

The complete transformation of 1 into the iodo complex 3 can be monitored in the IR spectrum by the disappearance of the Fe-H band at 1842 $cm^{-1}$. Clearly visible are the characteristic bands of the [*P,S*] ligands and the coordinated trimethylphosphines with typical wave numbers. Also the hydride resonance in the $^{1}H$ NMR spectrum at -12.8 ppm has disappeared while the facial coordination geometry is preserved as shown by three doublets at 1.12, 1.26 and 1.73 ppm in the ratio 1:1:1 corresponding to three chemically non-equivalent trimethylphosphine ligands. The protons of aromatic ligand systems are to be seen in the range between 7.42 to 8.39 ppm. The $^{31}P$ NMR spectrum is very similar to that of complex 1 but displays a shift of the four phosphorus

resonances. The signal of the chelate-phosphorus appears at 92.4 ppm and the three trimethylphosphine ligands are found at 22.3, 13.1 and -0.8 ppm.

## Discussion

Like with the hydridoiron-[*P,O*] -chelate complexes homologues of 1 can be by obtained by reaction with iodomethane to form the iodo-[*P,S*]-chelate complex 3 whereby the facial configuration is retained. This is clearly seen in the $^{31}$P NMR spectrum where four different phosphorus resonances are found. Instead of an oxidative substitution of two phosphine ligands forming an intermediate iron (IV) species which then reductively eliminates methane to form a four-coordinatediron (II)-species and finally takes up two phosphines to generate 3 a gradual transfer of a methyl group is possible. Consistent with the selective formation of a facial isomer a plausible reaction path is shown in Fig. 2.15.

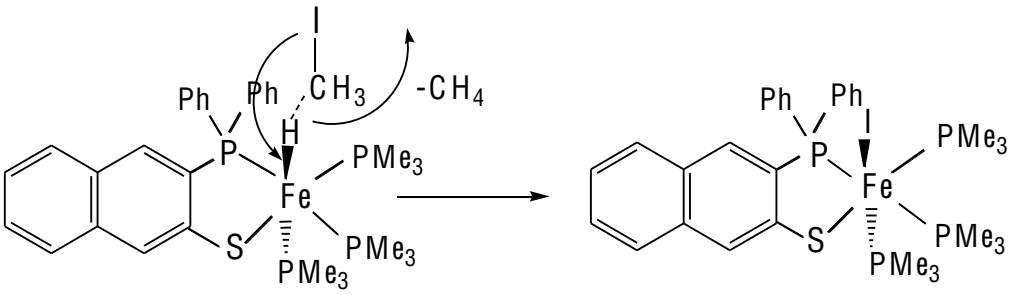



Fig 2.15 Proposed mechanism of formation of the *fac*-isomer of 3

Iodo-iron (II) complexes are interesting as versatile nucleophiles with applications in organometallic and organic synthesis. Recent reports by Brookhart and Gibson on five-coordinate Fe(II) dihalide complexes as precatalysts for the polymerization of ethylene and α-olefines suggest the idea that iron (II), when in an appropriate coordination environment, may be an active catalyst for C-C and C-H bond forming reactions.[59-61] Iron is an attractive

metal for this purpose because of its low cost and relatively low risk of toxicity.

### 2.2.4 Reaction of Dicarbonyl tris(trimethylphosphine)iron(0)with (3-diphenylphosphino)-2-thionaphthol

This experiment is a test for a direct route to the carbonyl derivative 2 without starting from complex 1. There is also a chance to generate a dicarbonyl derivative that cannot be obtained by carbonylation of 2.

#### Synthesis and Characterization

When dicarbonyl-tris(trimethylphosphine)-iron (0) in THF at -78 ºC was combined with the phosphinothionaphthol (Fig. 2.16) and was warmed up the color changed rapidly to yellow. From pentane at room temperature red crystals of 4 were grown, that were found difficult to dissolve in THF and under argon decomposed above 200ºC.The yield varied between 60 and 70%. The crystals were found air stable for several days, but dilute THF solutions rapidly decomposed if air was admitted.

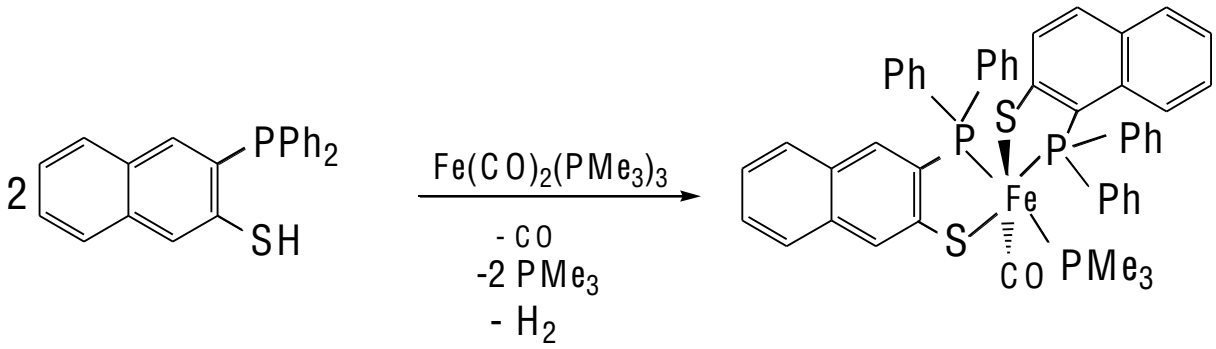



Fig. 2.16 Reaction scheme for complex 4

### Spectroscopic Investigation

The IR spectrum of complex 4 shows the typical bands of coordinated ligands, and it contains a very strong stretching absorption of terminal CO at 1931 $cm^{-1}$. A hydride function cannot be detected. The $^{1}H$ NMR spectrum shows the signal of the nine trimethylphosphine protons as a doublet at 1.26 ppm with a coupling constant of 9 Hz, and the 32 protons of two [*P,S*]-ligands are recognized within the range of 6.90 to 8.28 ppm. The $^{31}P$ NMR spectrum shows two signals for the chelate-phosphorus nuclei at 83.1 ppm (dd, $^{cis}J_{PP}$ = 37 and 45 Hz) and at 3.6 ppm (dd, $^{cis}J_{PP}$ = 45 and $^{trans}J_{PP}$ = 201 Hz) The large coupling of 201 Hz arises from a *trans*-trimethylphosphine, whereby structures with coplanar [*P,S*] ligands are excluded. Considering that the carbonyl ligand prefers to reside in *trans*-position to the sulfur donor there remains as only possible configuration the structure given in Fig. 2.16.

### Discussion

Reaction of two mole equivalents of (3-diphenylphosphino)-2-thionaphthol with $Fe(CO)_2(PMe_3)_3$ affords the octahedral bischelate 4. The absence of a Fe-H function can be demonstrated by spectroscopy. Monitoring the reaction by means of $^{1}H$ NMR spectroscopy provides no evidence of an intermediate hydride that could arise from an oxidative addition of a SH intermediate. Changing the stoichiometry to 1:1 also afforded complex 4 exclusively.

## 2.2.5 Reaction of $FeMe_2(PMe_3)_4$ with (3-diphenylphosphino)-2-thionaphthol

Five coordinated bischelate-[*P,O*] complexes of iron with coordinated trimethylphosphine have been obtained by *Mao* [34] by reaction of dimethyltetrakis(trimethylphosphine)iron(II) with two mole equivalents of phosphinophenol. Alternatively reactions of deprotonated phosphinophenol with dichlorobis(trimethylphosphine)iron(II) require a more complex processing of the product.

## Synthesis and Characterization

The reaction of $FeMe_2(PMe_3)_4$ in THF at -78 ºC with two mole equivalents of (3-diphenylphosphino)-2-thionaphthol (Fig. 2.17) gives good yields of the red-brown bischelate complex 5 when isolated as powder. Crystallization experiments from different solvents under selected conditions remained unsuccessful.

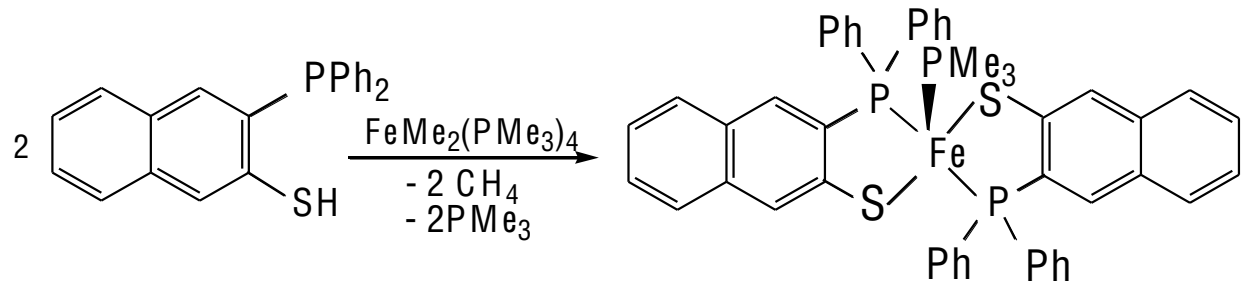



Fig. 2.17 Synthesis of the bischelate complex 5

## Spectroscopic Identification

Compound 5 is a paramagnetic substance. From NMR spectra no detailed information could be obtained. The IR spectrum shows the typical ν (C=C) absorption bands expected for [*P,S*] ligands in the region 1566 – 1615 $cm^{-1}$ and the characteristic $\rho_1$-band of coordinated trimethylphosphine is detected at 946 $cm^{-1}$.

## Discussion

Due to the penta-coordination around the iron atom in the paramagnetic bischelate complex 5 NMR spectroscopy allows no precise statements about its configuration. The one given in Fig. 2.17 is supported by a structure obtained by *Mao*[34] from X-ray work that demonstrated the square pyramidal coordination geometry of the corresponding bischelate-[*P,O*] complexes that contain two [*P,O*] ligands in mutual *trans*-positions. In addition, the composition of 5 is confirmed by elemental analysis.

## 2.3 Synthesis of chelate-[*P,S*]-cobalt complexes in oxidation states II and III

### 2.3.1 Preparation of hydrido-bis {(3-diphenylphosphino)-2-thiophenolato-[*P, S*]}-(trimethylphosphine)-cobalt (III)

#### Synthesis and Characterization

The hydrido bischelate-cobalt (III) complex **6** was synthesized with a stoichiometry of 2:1 (ligand to cobalt). In a 1:1 stoichiometry methane was eliminated, and after two hours the second equivalent of ligand was added. The mixture was kept stirring at 20ºC for 16 h. The volatiles were then removed in vacuo and the residue was washed in 30 ml of pentane. The hydrido-bischelate - cobalt complex was extracted with ether and the combined solution was cooled at -27 º C to afford brown cubic crystals of **6** in a 67 % yield which proved stable in air for several weeks.

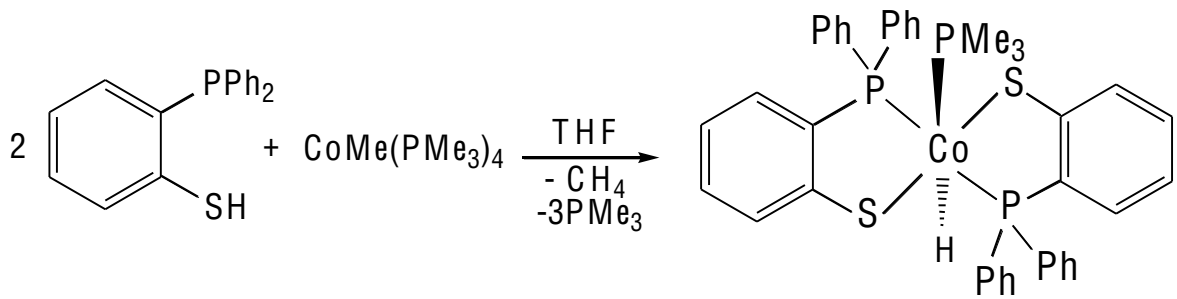



Fig. 2.18 Synthesis of bischelate-cobalt (III) complex **6**

#### Spectroscopic Investigation

In the IR spectrum (Fig. 2.19) the coordination of a hydrido ligand is indicated by a strong band at 1948 $cm^{-1}$. All characteristic bands of the [*P,S*] ligand in addition to the $\rho_1$-band of coordinated trimethylphosphine at 954 $cm^{-1}$ were detected.

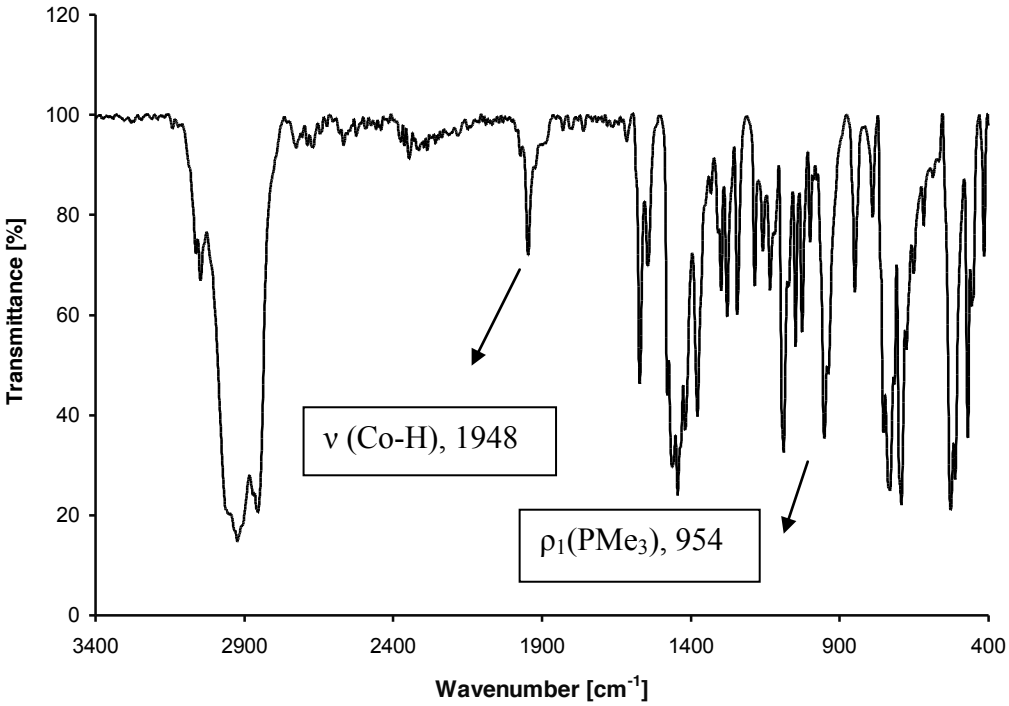



Fig. 2.19 IR spectrum of complex 6

The $^{1}$H NMR spectrum of 6 shows two hydride resonances, one at -11.06 ppm as doublet of doublets of doublets (6a) due to *cis*-coupling of hydride with the ligand-P nuclei and another at -12.72 ppm as doublet of triplets (6b) due to *trans*-disposed chelate-P nuclei. The multiplicities indicate that the cobalt centres have an octahedral coordination (Fig. 2.19). The intensity ratio is 1:2 for 6a/6b. In the $^{31}$P NMR spectrum a broad singlet at 69.2 ppm is assigned to the chelate-P of 6b while at 65 ppm a doublet ($^{2}J_{P,P}$=295.4 Hz) indicates *trans*-coupling in 6a as in the resonance at - 0.63 ppm (d, $^{2}J_{P,P}$ = 255 Hz, 1P, $PMe_3$) while the $PMe_3$ signal at -12 ppm remains a singlet.

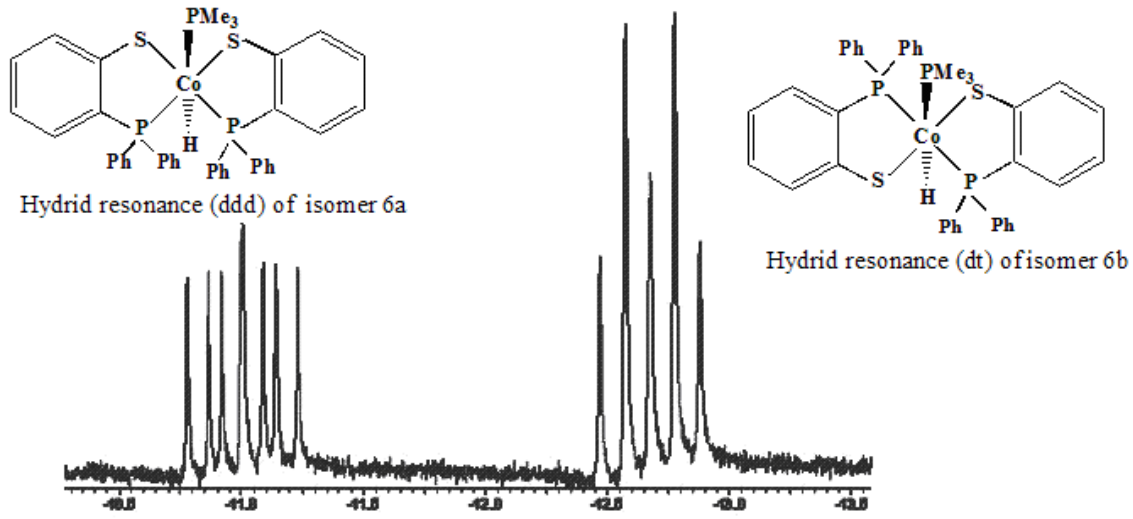



Fig. 2.20 Hydrid resonance of 6a and 6b

## Molecular Structure of Complex 6b

The octahedral configuration of 6b has been confirmed in the crystal. The structure was solved in the monoclinic crystal system, and the space group was determined as P21/c. The refinement resulted in an R value of 0.0552. Fig. 2.21 shows the molecular structure. The two *trans*-standing phosphorus atoms of the bischelate-cobalt unit P1 and P2 are slightly bent toward the hydride position with an angle P1-Co-P2 of 146.3º. This distortion is also illustrated by the angles P1-Co-H1 of 74.6º and P2-Co-H1 of 71.8º and can be explained by the lower space requirement for the hydride ligand. There is no bending of the S-donor atoms (S1-Co1-S2 = 178.6º). The sum of internal angles in both chelate rings approaches 540º.

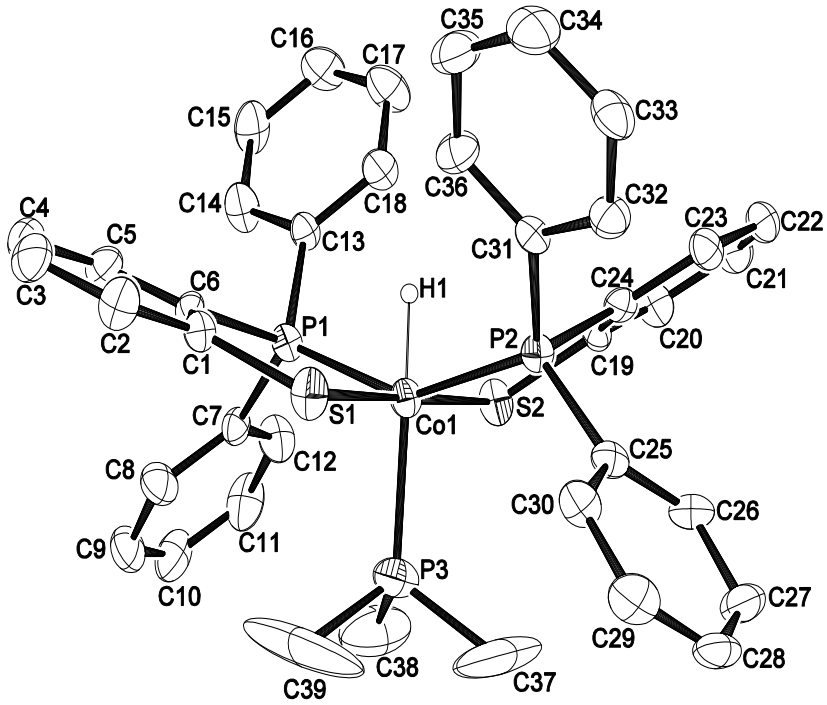



Fig.2.21 Molecular structure of 6b (ORTEP plot with CH-hydrogen atoms omitted). Selected bond lengths [Å] and angles [°]: Co–H 1.31(4), Co–S2 2.259(16), Co–P1 2.1796(16), Co–P2 2.1830(16), Co–P3 2.2597(18); P1–Co–S1 89.58(6), S1–Co–H 86.8(15), P1–Co–P2 146.29(7), P1–Co–P3 105.04(7), P2–Co–P3 108.67(7), P2–Co–H 71.8(15), P3–Co–H 178.0(15).

## Discussion

Hydrido(acyl)cobalt(III) species stabilized by a (2-acyl)-phenolato chelating ligand and supported by trimethylphosphine ligands were studied by Klein and co-workers.[62-66] The influences of chelating ligands containing hard/soft donor atoms on the stability of the complexes in different oxidation states are discussed with respect to the HSAB concept. In the present study [*P,S*]-chelating ligands contain soft/soft donor atoms that are expected to change the properties of metal centres substantially. Complex 6 was synthesized by an oxidative substitution reaction of CoMe $(PMe_3)_4$ with two mole equivalents of thiophenol ligand. A hydridocobalt (III) complex is isolated as brown cubic crystals which are stable under argon below 240°C. X-ray diffraction analysis confirms the

octahedral coordination geometry for the solid state. Complex 6 is probably formed through elimination of methane to generate a monochelate-cobalt (I) intermediate that undergoes a second oxidative substitution reaction. A reaction mechanism is suggested in Fig.2.22.

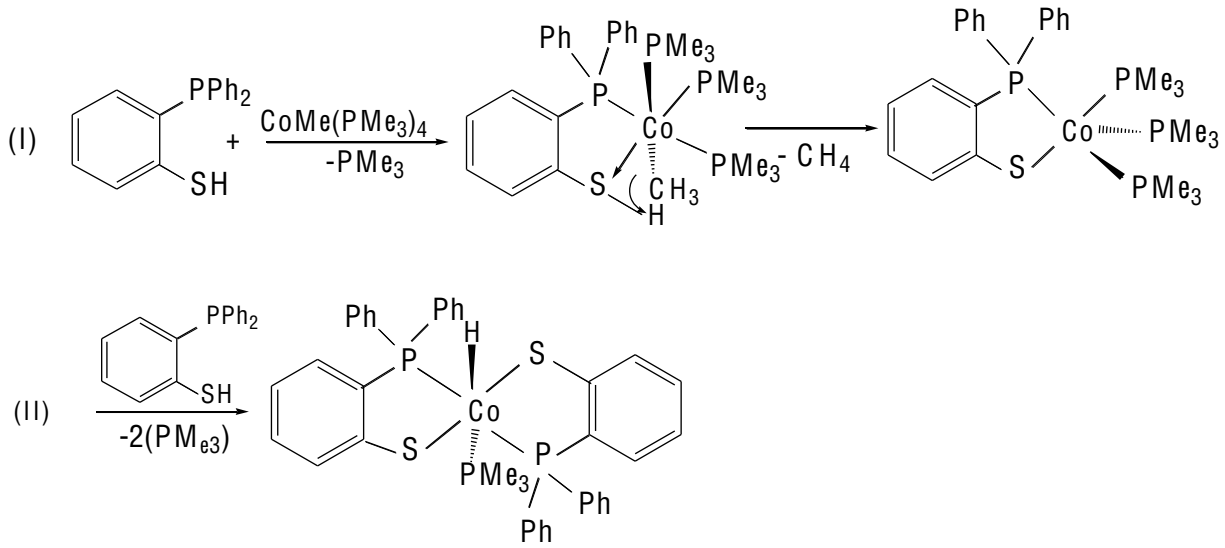



Fig. 2.22 Stepwise formation of hydrido-bischelate complex 6

In the crystal the cobalt atom is in a meridional configuration of P-donor atoms that corresponds with isomer 6a in solution (Fig.2.20).

### 2.3.2 Synthesis of *trans*-bis{(3-diphenylphosphino)-2-thiophenolato -[*P,S*]}-(trimethylphosphine)-cobalt(II)

#### Synthesis and Characterization

The synthesis of bischelate 7 succeeded by combining $CoMe_2(PMe_3)_3$ with two mole equivalents of thiophenol in THF solution (Fig. 2.23). After removal of the volatile components and washing with 30 mL of pentane the bischelate complex 7 was crystallized in ether at -27ºC as brown crystals in 67 % yield.

A specimen was suitable for X-ray diffraction when drying in a dynamic vacuum was avoided. Reversible dissociation of trimethylphosphine ligands and transformation to a tetra-coordinate square planar bischelate complex (Fig. 2.23) is known in the literature. [44]

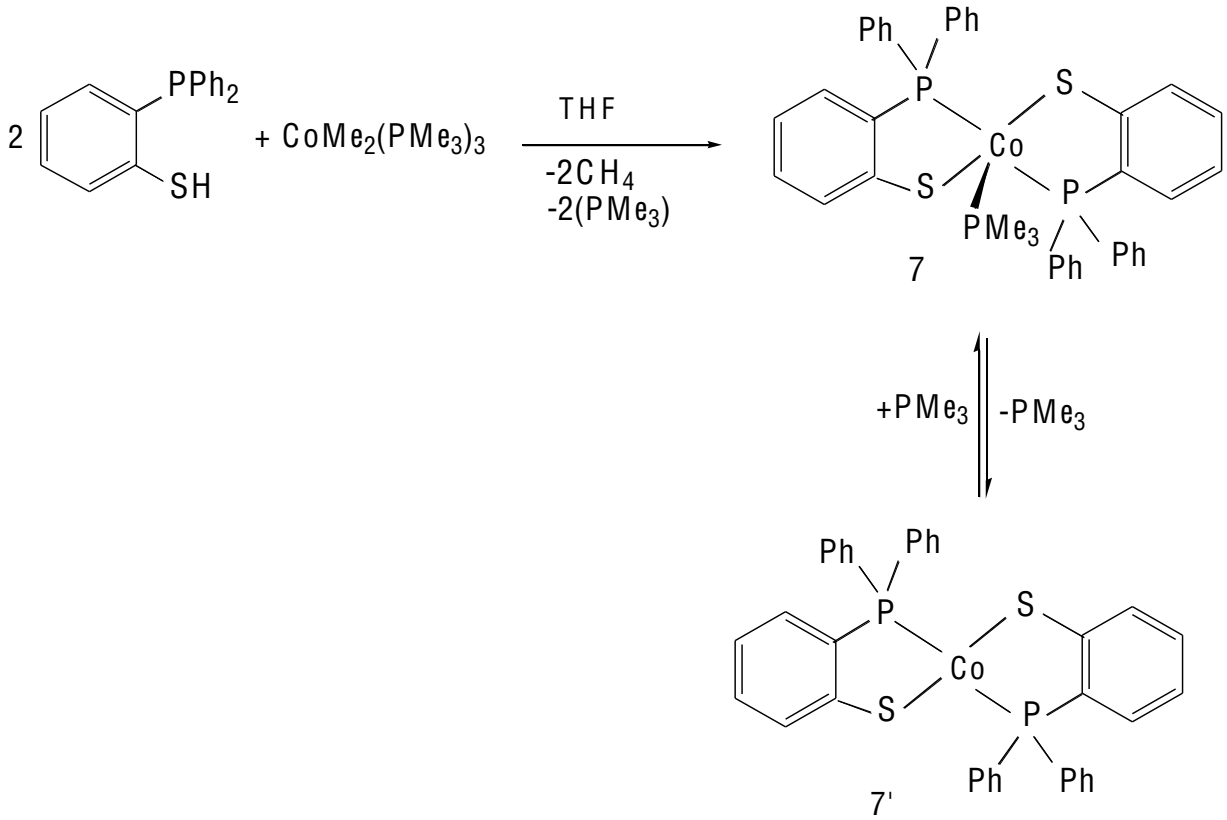



Fig. 2.23 Synthesis of complex 7

## Spectroscopic Investigations

Little information on the composition of the bischelate complex 7 is extracted from the IR spectrum which appears as a collection of typical bands of the aromatic ligand backbone and coordinated trimethylphosphine.

## Molecular Structure of Complex 7

An X-ray structure determination was performed on a single crystal of compound 7 that includes one ether molecule per Co atom from the mother liquor. The structure was solved in the monoclinic crystal system with a space group of

P21/n. The refinement resulted in an $R_1$ value of 0.0403. A penta-coordinate cobalt (II) complex with two [*P,S*] – chelating ligands (see Figure 2.24) shows the expected square-pyramidal geometry of complex 7. The P donor atoms of the bis-chelate unit adopt mutually *trans* positions and are arranged around the cobalt atom with bond lengths P1-Co1 = 2.19(8) Å) and P2-Co1 = 2.20(8)Å) whereas the trimethylphosphine ligand occupies an apical position (P3-Co1 = 2.28(8) Å) and the angles between three P ligands become narrow (P1-Co1-P3 = 101.73(3)º, P2-Co1-P3 = 101.81(3)º). However, the angles for *trans*-arrangements deviate from linearity (S2-Co1-S1 161.46(3)º and P1-Co1-P2 =156.35(3)º). The main feature of this structure is the five-membered metallacycle of the bischelate-[*P,S*] ligand forming bite angles P1-Co1-S1 = 83.35(3)º and P2- Co1-S2 = 87.50(3)º. The sums of internal angles in the five-membered rings approach 540º indicating planarity.

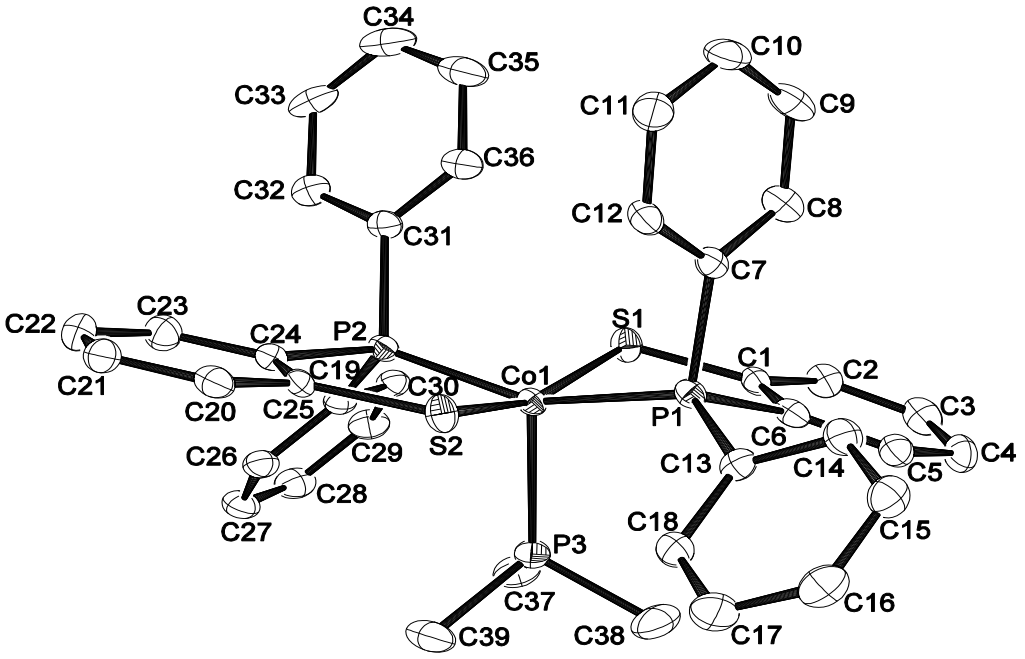



Fig.2.24 Molecular structure of 7 (ORTEP plot with hydrogen atoms omitted). Selected bond lengths [Å] and angles [°]: P2–Co1 2.2010(8), P1–Co1 2.1937(8), S1–Co1 2.2795(7), S2–Co1 2.2177(7), P3–Co1 2.2840(8), P1–Co1–P2 156.35(3), P2–Co1–S1 92.22(3), P1–Co1–S1 83.35(3), P2–Co1–S 287.50(3), P1–Co1–S 289.50(3), S2–Co1–S1 161.46(3), P2-Co1-P3 101.81(3), P1-Co1-P3 101.73(3), S1-Co1-P3 95.50(3), S2-Co1-P3 102.70(3).

### Discussion

The paramagnetic properties of 7 prevent NMR spectroscopic studies. Its IR spectrum gives an indication of the composition based on the characteristic bands for the [*P,S*] ligands and the coordinated trimethylphosphine. Such composition is determined by the elemental analysis. Also from an X-ray analysis of single crystal of complex 7 shows a cobalt atom surrounded by *trans*-bischelate-[*P,S*] ligands and one P-donor of a timethylphosphine ligand which is located at the apex of a square pyramid. By comparison with literature on known [*P,S*]-bischelate complexes the new cobalt complex 7 conforms by its molecular structure.[44,45] As for the related [*P,O*]-cobalt compounds a *cis*-configuration was found.[31]

## 2.3.3 Synthesis of methyl{(3-diphenylphosphino)-2- thionaphtholato-[*P,S*]}-bis(trimethylphosphine)-cobalt(II)

### Synthesis and Characterization

The methylcobalt (II) complex 8 can be synthesized by two different ways, as described in Fig.2.25. According to path (a) $CoMe_2(PMe_3)_3$ in pentane reacts with phosphinothionaphthol under elimination of methane generating the cobalt(II) complex 8. Limiting factor of this synthesis is the poor solubility of the ligand in pentane. To accelerate the reaction THF was used although at the expense of yields. A second and more elegant method for the synthesis of 8 is the oxidative substitution of a methylthioether to $Co(PMe_3)_4$ depicted as path (b). In a smooth reaction yields between 65and 67 % were achieved. Complex 8 was isolated as a dark brown powder. Crystallization from pentane at under selected conditions was unsuccessful.

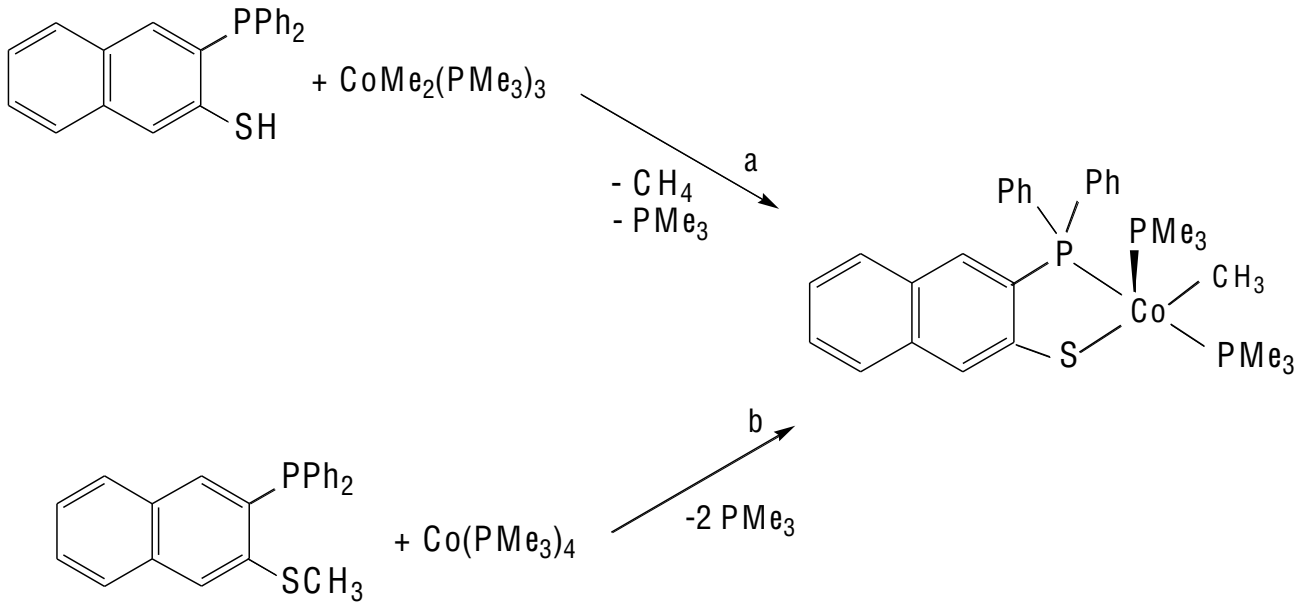



Fig. 2.25 Synthesis of the methylcobalt (II) complex 8

## Spectroscopic Investigations

In the infrared spectrum of 8 shows in addition to the bands of trimethylphosphine only coordinated [*P,S*]-chelate ligands. Furthermore, a weak absorption is registered at 1164 $cm^{-1}$ that is assigned to a deformation mode of a methylcobalt group. Broad and grossly shifted resonances in the NMR indicate a paramagnetic system. The elemental analysis (C, H, P) agrees with calculated values.

## Discussion

A pentacoordinated methylcobalt(II) complex 8 is obtained either by reaction of (3-diphenylphosphino)-2-thionaphthol with $CoMe_2(PMe_3)_3$ or by reaction of (2-diphenylphosphino)-3-methylthionaphthalene with $Co(PMe_3)_4$ (Fig.2.25).The reaction medium must be strictly unpolar since donor solvents such as ether or THF induce rapid decomposition. The bischelate-cobalt(II) complex 9 was identified as one of the decomposition products. The reaction via oxidative addition of the S-$CH_3$ bond gives better yield and is a more elegant alternative

method. A related methylcobalt (II) complex containing a [*P,O*]-chelating ligand presented by *Beck* [67] shows a square pyramidal coordination geometry, which was established by an X-ray structure. A [*P,O*]-methyl cobalt(II)-system is not known.

### 2.3.4 Synthesis of *trans*-bis{(3-diphenylphosphino)-2- thionaphtholato-[*P,S*]}-cobalt(II)

In THF solution with an admixture of methanol anhydrous $CoCl_2$ and (3-diphenylphosphino)-2-thionaphthol react forming a red suspension via route (a). Filtration gave a red powder of complex 9 that is stable in air, the yield was 71%. Complex 9 may also be prepared from anhydrous $CoCl_2$ and sodium-(3-diphenylphosphino)-thionaphtholate in THF via route (b), the yield was 58%. Both reactions proceed also in diethyl ether but with much longer reaction times and with lower yields of 38 - 41 %.

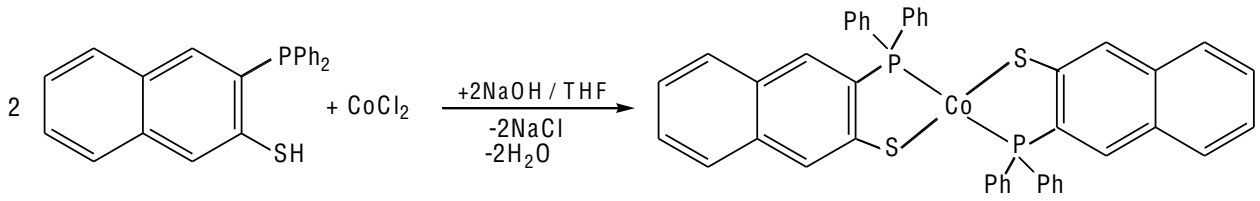



Fig. 2.26 Route (a) fort he synthesis of complex 9

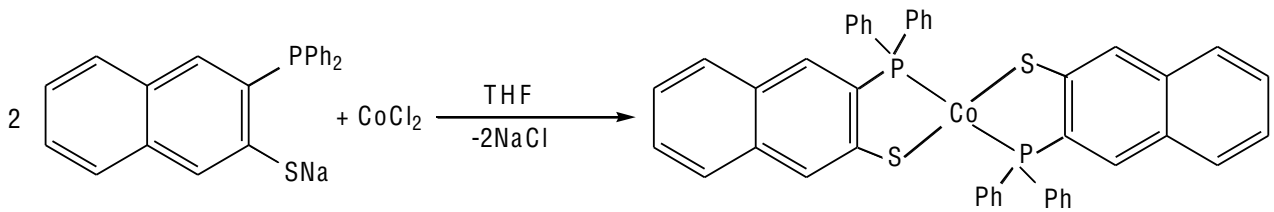



Fig. 2.27 Route (b) fort he synthesis of complex 9

## Spectroscopic Investigations

The consistently paramagnetic compounds ($d^7$, high-spin) do not allow NMR spectroscopic investigation. Information on the combined set is obtained from the IR spectra using low-intensity bands. Striking in the bis-chelate-[*P,S*]-cobalt(II) complex 9 is the absence of typical bands of coordinated trimethylphosphine. The elemental analysis (C, H, P) agree with the calculated values. The MS analysis is presented in Fig. 2.28. It shows the molecular ion and all the molecular fragments of the bis-chelate-[*P,S*] -cobalt(II) complex.

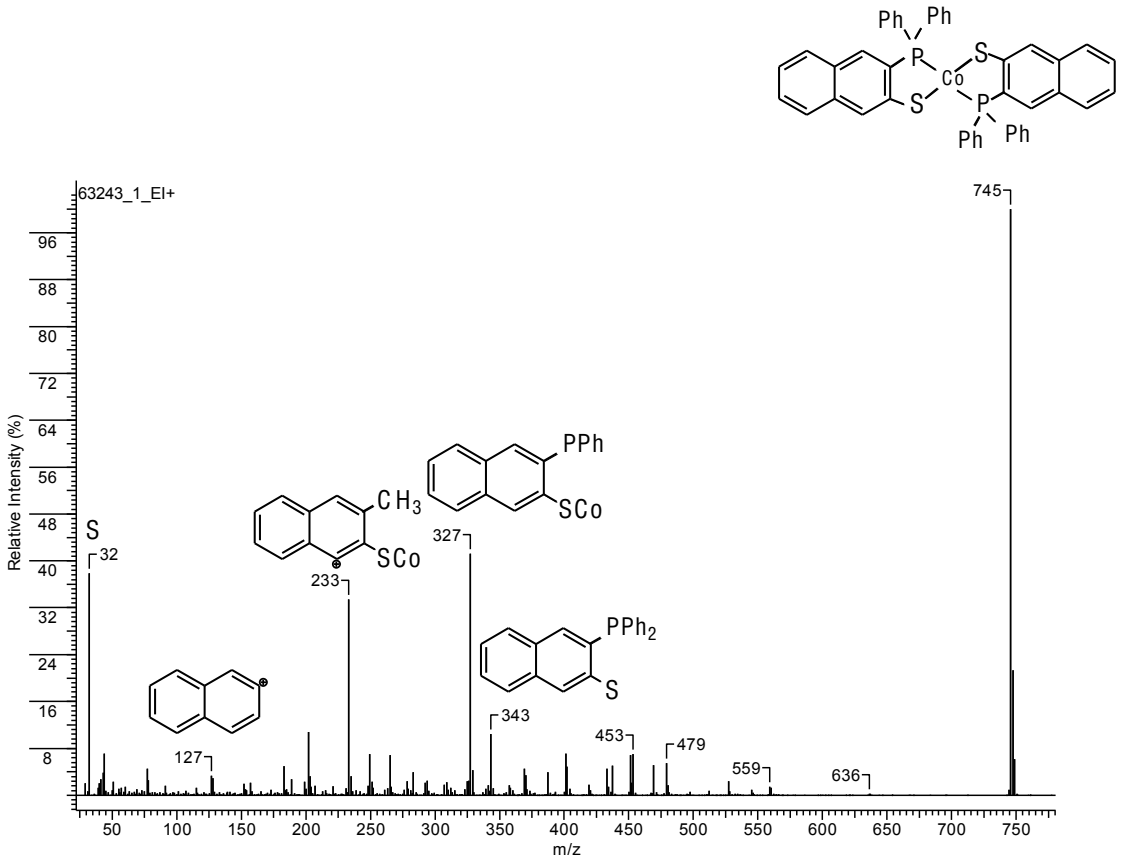



Fig. 2.28. The MS of the complex 9. MS (70 eV) : m/z (%) = 32(38), 44(7), 51(4), 77(8), 91(5), 127(9), 157(2.5), 183(8), 202(12.5), 233(35.5), 249(11), 265(6.5), 294(1.5), 327(44), 343(11.5), 369(6), 401(5.5), 451(6.9), 479(4.2), 527(1.8), 559(1), 745(100).

The ESR spectra of tetra-coordinate complex 9 can be compared with complex 7´(Fig. 2.29) in a polycrystalline state (powder) at T = 77 K as both show

asymmetric signals without hyperfine structure (HFS). They are characteristic of the magneto concentrated samples with a strong exchange interaction between identically directed paramagnetic particles.[70] A profound rhombic anisotropy of the g-tensor (7´: $g_1 = 2.72$, $g_2 = 2.31$, $g_3 = 1.99$; 9: $g_1 = 2.65$, $g_2 = 2.26$, $g_3 = 1.99$) implies a *trans*-arrangement of the planar complex in the crystalline state. The average value of the g-tensor for complex 9 ($g_{av.}=1/3(g_1+g_2+g_3)$ is in closer proximity to the ordinary spin value ($g_e$=2.0023), than that for complex 7´. It seems to result from a greater degree of delocalization of the uncoupled electron in complex 9 in comparison with complex 7`.

*Where 7´ = [P,S] bis-chelate thiophenol; 9 = [P,S] bis-chelate thionaphthol*

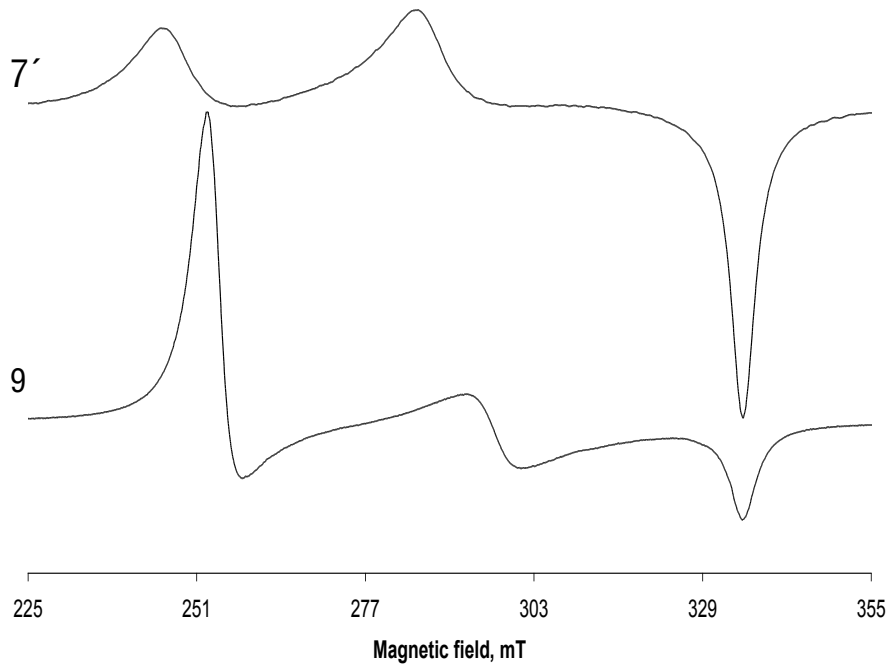



Fig. 2.29 ESR spectra of complexes 7´ and 9. Powders, T=77 K

Complex 9 in a nonpolar solvent e.g. toluene, at T = 77K gives no ESR signals. An abrupt time shortening of spin-lattice relaxation, when crystalline phase alternates with a dissolved state, may be brought about by a tetrahedral distortion

of the flat structure of the complex (the planes of the chelate ligands turn in the opposite directions)[71].

### Discussion

In an altered stoichiometry of ligand to cobalt complex (2:1) the tetra-coordinate bischelate 9 was obtained .Paramagnetic characterization of complex 9 prevents routine NMR-spectroscopic studies, whereas the IR spectrum gives an indication of the composition based on characteristic bands for the [*P,S*] ligands. Mass spectroscopy shows the molecular ions and molecular fragments of the bischelate-[*P,S*]-cobalt (II) complex. ESR spectroscopy identifies characteristic magneto properties of complex 9.

## 2.3.5 Synthesis of hydrido-bis{(3-diphenylphosphino)-2-thionaphtholato-[*P,S*]}-(trimethylphosphine)-cobalt(III)

### Synthesis and characterization

Combining two mole equivalents of the thionaphthol ligand with $CoMe(PMe_3)_4$ in THF at -70 ºC (Fig. 2.30) after 16 h afforded the octahedral Co(III) complex 10 which was isolated as red brown crystals in 43% yield. Crystals of 10 are air-stable and under argon decompose above 230ºC.

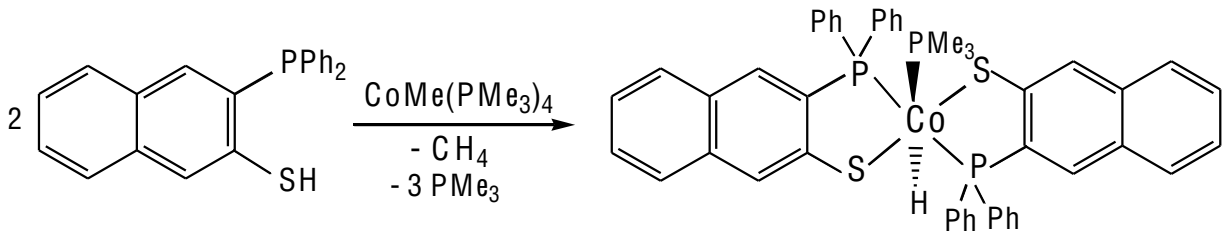



Fig.2.30 Synthesis of complex 10

## Spectroscopic investigation

The IR spectrum of compound **10** contains a conspicuous ν(Co-H) band at 1930 $cm^{-1}$, the characteristic bands of [*P,S*] ligands at 3048 $cm^{-1}$ ν( =C-H), and 1613, 1563 $cm^{-1}$ ν( C=C). In addition to the typical bands of the aromatic ligand backbone still a $\rho_1$ - band of coordinated trimethylphosphine at 950 $cm^{-1}$ was detected. The elemental analysis differs from calculated values due to the presence of a by-product. The $^1$H-NMR spectrum of **10** in $d_8$-THF exhibits two hydride resonances at -12.5 ppm as doublet of triplets (**10b**) due to the coupling of hydride with *trans*-disposed chelate-P nuclei and at -10.8 ppm as doublet of doublets of doublets (**10a**) with *cis*-coupling of hydride with three an isochronic P nuclei. The two resonances indicate an octahedral coordination around the cobalt (Fig.2.31) and exhibit an intensity ratio of 2:1 in favor of **10b**. In the $^{31}$P-NMR spectrum a broad singlet at 65.9 ppm for the chelate-P is observed while at 63.1 ppm a doublet shows *trans*-coupling ($^2J_{P,P}$=309 Hz) and the doublet at -0.87 ppm shows *cis*-coupling ($^2J_{P,P}$=175.2 Hz). Spectroscopic data are thus consistent with an octahedral coordination around the cobalt atom.

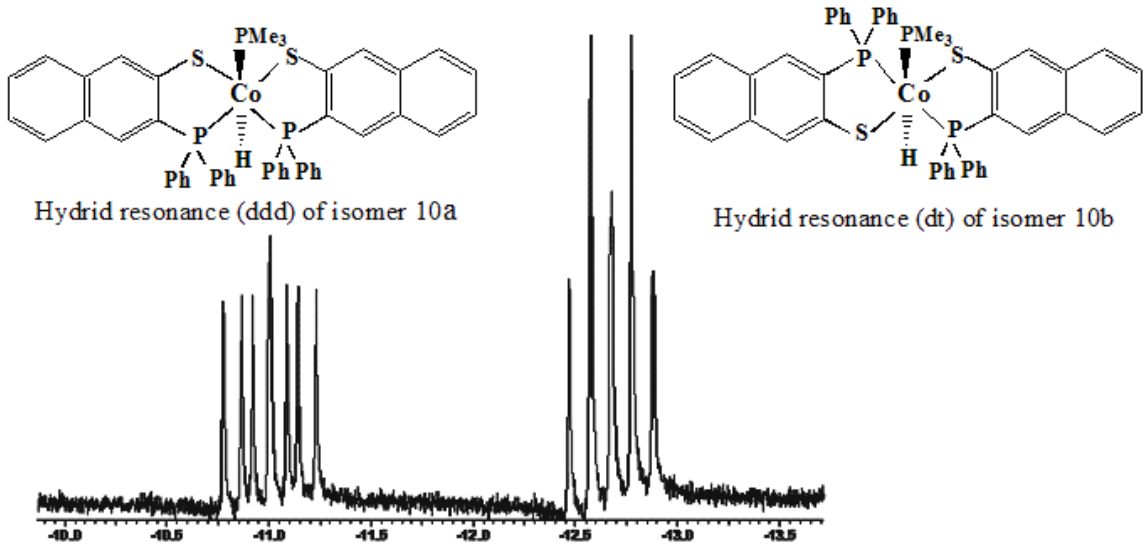



Fig. 2.31 Hydrid resonance of **10a** and **10b**

## Discussion

A thermally stable hydrido-bischelate-cobalt(III) complex 10 was obtained through successive reductive elimination and oxidative addition reactions as discussed for complex 6. The coordination geometry is the same in both complexes. The crystals of complex 10 were found to be intimately mixed with an unknown a co-product and could not be separated by fractional crystallization or be separated manually due to the same appearance of crystal color and shape. The mixture gave no satisfactory elemental analysis.

## 2.3.6 Synthesis of *trans*-bis{(3-diphenylphosphino)-2- thionaphthato-[*P,S*]}-(trimethylphosphine)-cobalt(II)

## Synthesis and Characterization

When two mole equivalents of (3-Diphenylphosphino)-2-thionaphthol were added to a THF solution of $CoMe_2(PMe_3)_3$ at -70ºC elimination of methane to afforded the penta coordinate bischelate [*P,S*] cobalt(II) complex 11 (see Fig.2.32).

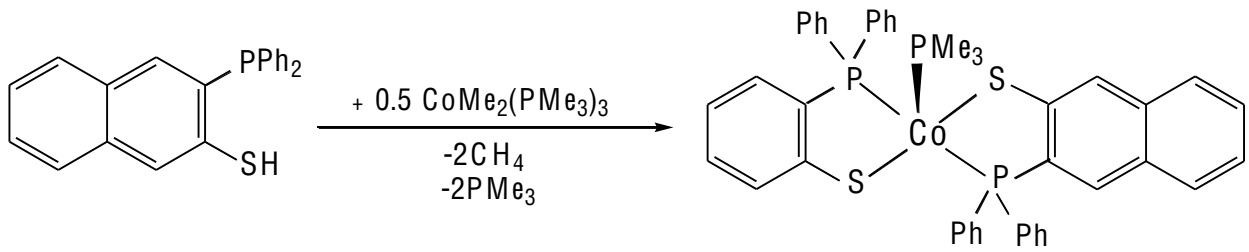



Fig.2.32 Synthesis of complex 11

While brown solution of 11 in ether deposite crystals at -27ºC as dark brown cubic, isolated in 58% yield and decomposes above 230ºC. Elemental composition shows that the loss of methane molecule and one

trimethylphosphine group during the reaction also the presence of ether within the crystal.

### Spectroscopic Investigations

Compound 11 is a paramagnetic substance. The IR spectrum shows the typical absorption bands in the region for (νC=C) at 1615 and 1566 $cm^{-1}$ respectively with $\rho_1$-band of the coordinated ligand trimethylphosphine at 950$cm^{-1}$ detected.

### Molecular Structure of 11

Crystals of 11 proved to be stable in air for several days and could thus be mounted on an X- ray diffractometer without inert gas protection. The molecular structure (Fig. 2.33) confirms the configuration of 11 as derived from the spectroscopic data.It was solved in a triclinic crystal system and the space group was determined as $P^{-}1$.The refinement resulted in an R value of 0.0363. X-ray diffraction analysis of 11 indicates that the penta - coordinate cobalt (II) complex with two [*P,S*]–chelating ligands and one trimethylphosphine group shows the expected square - pyramidal geometry. The P donor atoms of bischelates adopt mutually *trans* positions and are arranged around the cobalt atom with similar bond lengths P1-Co1 of 2.20(7) Å and P2-Co1 of 2.21(7) Å whereas the trimethylphosphine ligand occupies an apical position (P3-Co1= 2.27(7) Å) with slightly different angles between the three P ligands (P1-Co1-P3=103.2 (3)º), P2-Co1-P3 = 106.60(3)º. However, the angles for *trans*-ligands (S1-Co1-S2 = 168.17(3) º, P1-Co1-P2 = 150.07(3)º).are displaced from an axis. The main feature of this structure are the five-membered metallacycles with bite angles P1- Co1-S1 = 85.66(3)ºand P2- Co1-S2 = 84.36(3)º. The sum of internal angles in both five-membered rings (539.39º) equals that of a regular pentagon.

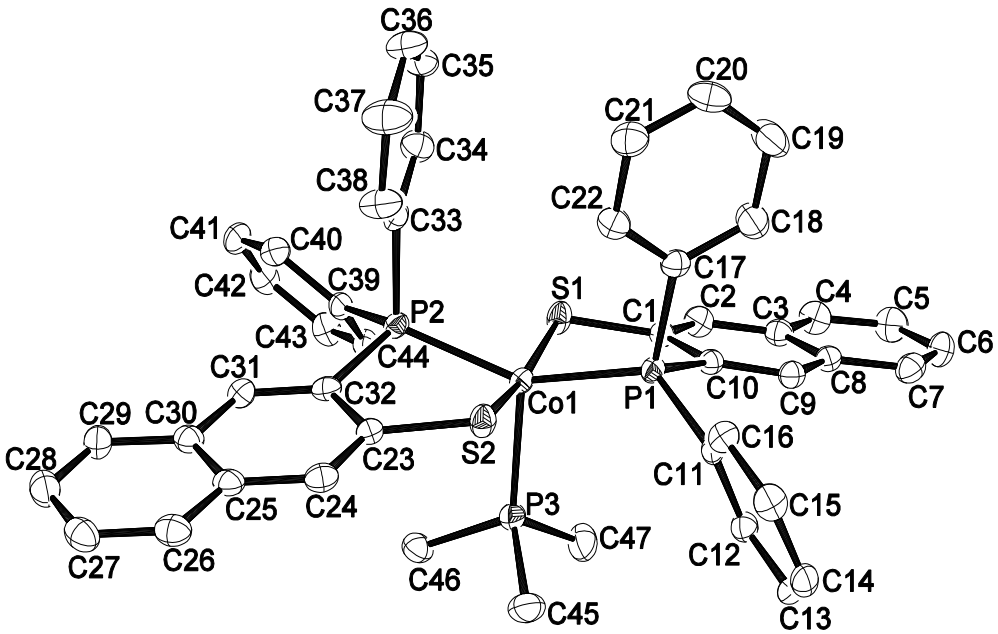



Figure 2.33 Molecular structure of 11 (ORTEP plot with hydrogen atoms omitted). Selected bond lengths [Å] and angles [°]: P2–Co1 2.21 (7), P1–Co1 2.20(7), S1–Co1 2.23(7), S2–Co1 2.25(7), P3–Co1 2.27(7), P1–Co1–P2 150.07(3), P2–Co1–S1 92.61(3), P1–Co1–S1 85.66(3), P2–Co1–S2 84.36(3), P1–Co1–S2 91.26(3), S2–Co1–S1 168.17(3), P2-Co1-P3 106.60(3), P1-Co1-P3 103.19(3) ,S1-Co1-P3 98.76(3), S2-Co1-P3 93.06(3).

## Discussion

Similar to the compound 7 as already observed reacts $CoMe_2(PMe_3)_3$ under methane elimination with phosphinothionaphthol to produce cobalt (II) complex of 11$^{th}$. The paramagnetic property of 11 complicates analysis by NMR spectroscopy. Only the IR spectrum gives an indication of the composition on the basis of characteristic bands for the [*P,S*] ligands and the coordinated trimethylphosphine. Such a composition is determined by elemental analysis and by the X-ray analysis are confirmed the [*P,S*] bischelate cobalt II and the presence of ether within the crystal. The square-pyramidal structure of 11 with trans permanent bischelate ligands around cobalt atom detected.

## 2.4 Synthesis of (3-diphenylphosphino)-2-thionaphtholato-[*P,S*]-nickel(II)complexes

### 2.4.1 Synthesis of hydrido-(3-diphenylphosphino)-2-thionaphtholato-[*P,S*]-bis(trimethylphosphine)-nickel(II) (12)

Protonation of compounds $NiL_4$ (L = $PR_3$) is a general method for generating cationic hydridonickel compounds. *Dal* has synthesized the cation $NiH(PMe_3)_4^+$ by protonation of $Ni(PMe_3)_4$ with phenolic derivatives.[32] Transformation to neutral hydridonickel(II) species is a difficult task. Phosphinothionaphthol with its soft sulfur donor provides a promising possibility for the generation of SHOP-type molecular [*P,S*]-hydrido nickel(II)-compounds which are likely to be obtained by oxidative addition of a SH group to the electron-rich nickel(0) center.

#### Synthesis and Characterization

Combining ether solutions of $Ni(PMe_3)_4$ with one mole equivalent of [*P,S*] ligand at -70ºC (Fig. 2.34) caused a color change from light yellow to orange red. In the presence of a fivefold excess of trimethylphosphine crystallization at -27ºC afforded complex 12 as orange red powder (95%) and orange crystals (less than 5%) that were isolated and kept under paraffin oil as a protection against humidity. A rapid decomposition is observed upon removal of all volatile components which leaves a light green *trans*-bischelate-nickel complex as major by-product. However, in the presence of excess trimethylphosphine 12 is quite stable under argon atmosphere at 20ºC, but survives only a few seconds in ether solution.

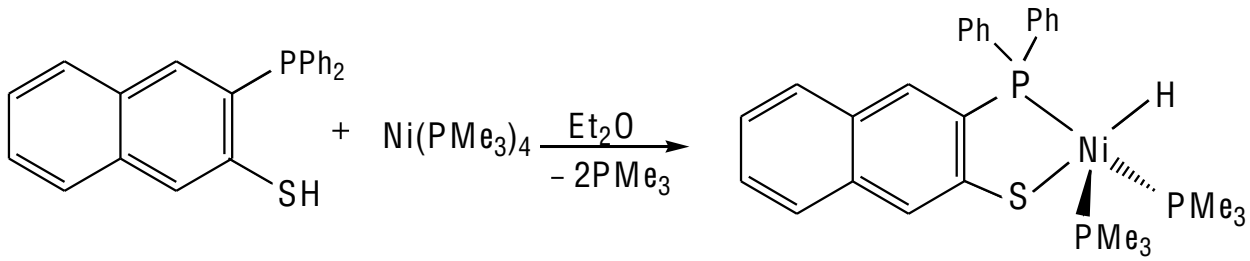



Fig.2.34 Synthesis of complex 12

## Spectroscopic Investigation

In the IR spectrum of 12 (Fig. 2.35), the NiH function is readily recognized by a strong ν(Ni-H) band at 1883 $cm^{-1}$. In addition, the characteristic absorptions of the coordinated ligands are recorded.

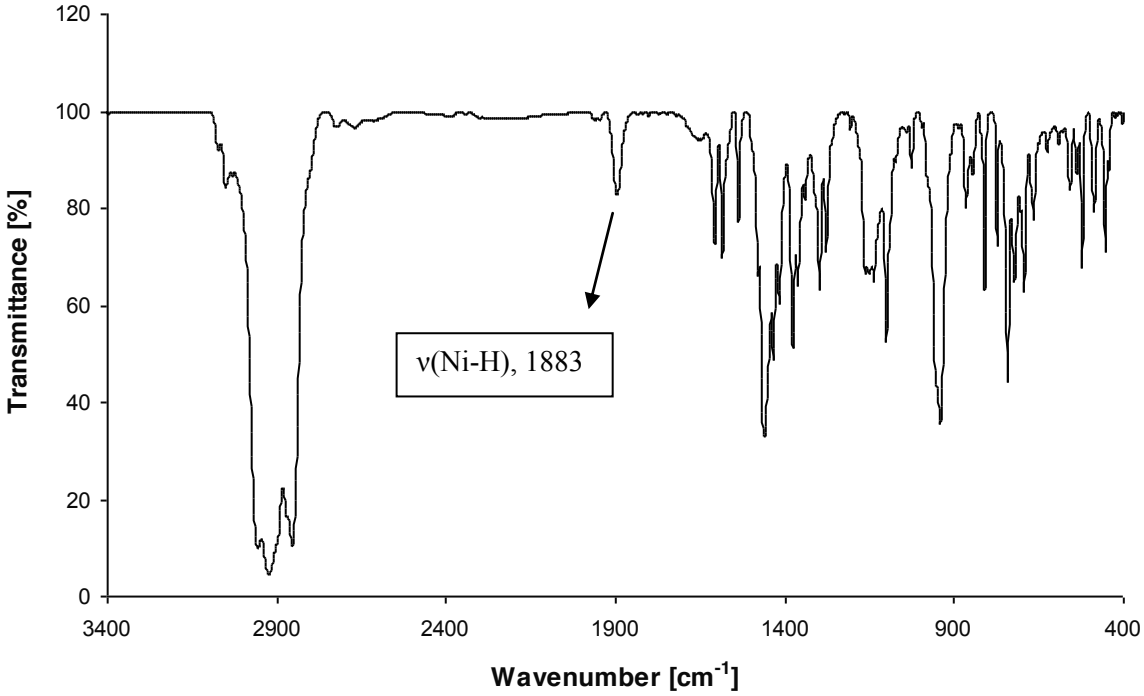



Fig.2.35 IR-Spectrum of 12

In the $^{1}H$ NMR spectrum the resonance of the hydride at -19.91 ppm as doublet indicates dissociation of trimethylphosphine ligands and sole coupling with the chelate-P nucleus with a coupling constant $^{2}J$(HP) = 40 Hz. At 203 K the signal becomes a doublet of triplets suggesting a trigonal bipyramidal molecular

geometry. At 190º K the ligand exchange is slowed so far that the signal becomes a well-resolved doublet of triplets with coupling constants $^2J$ (PH) = 40 Hz and 50 Hz. The $^{31}$P NMR spectrum confirmed the trigonal bipyramidal configuration of 12 with three phosphorus donor atoms in the trigonal plane. The resonance of the chelate phosphorus is at 46.4 ppm as triplet of doublets with $^2J(P_{ph}.P_{eq})$ = 35 Hz and 152 Hz. A doublet of doublets at -22.0 ppm with the same coupling constants is assigned to the two phosphine ligands.

## Discussion

$Ni(PMe_3)_4$ when combined with 2-phosphinothionaphthol undergoed an oxidative addition and is transformed to a neutral Ni-H complex. The M-H bond plays a very important role in organometallic chemistry because metal hydrides can undergo insertion with a wide variety of unsaturated compounds to give stable species or reaction intermediates containing a M-C bond.[77] A great number of catalytic reactions involve hydride insertion as the key step.[78-80] The hydridonickel(II) complex 12 was generated in a solution that contains a high trimethylphosphine concentration in order to suppress decomposition reaction to the bis-chelate-nickel. SHOP activity of compound 12 is doubtful because it is not stable under conditions of catalysis. The decomposition cycle is illustrated in Fig. 2.36.

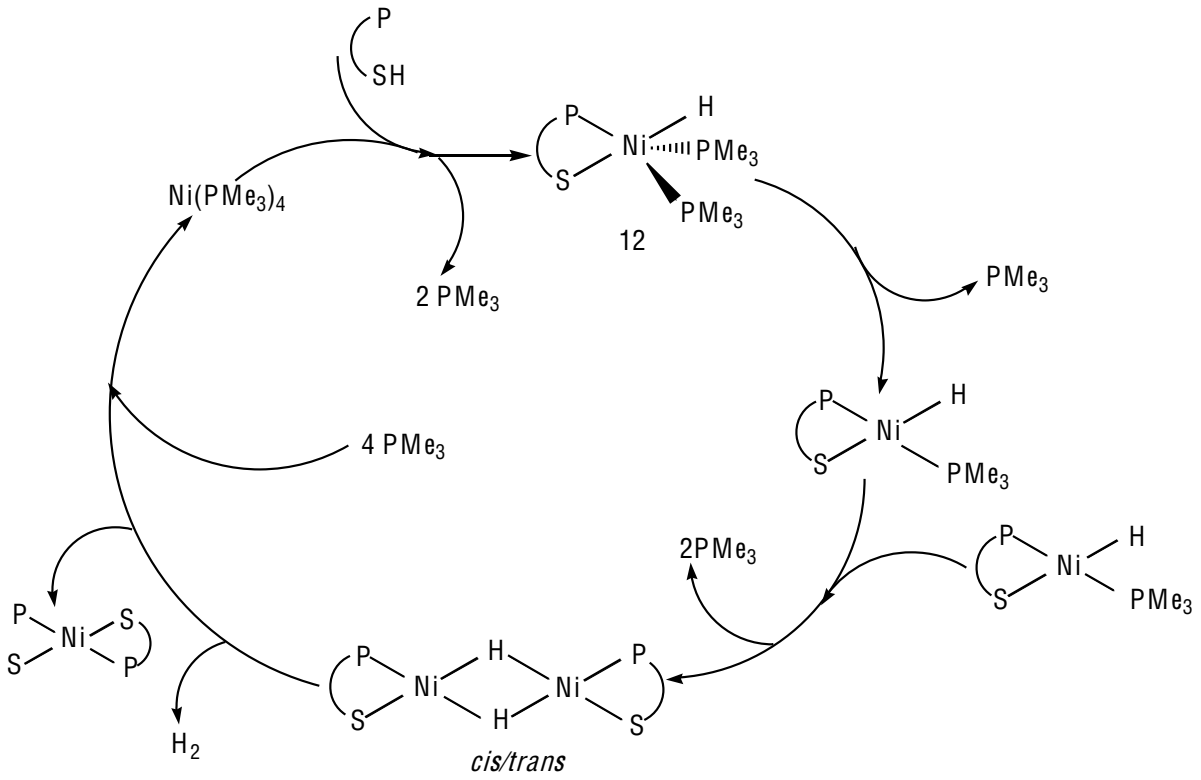



Fig.2.36 postulated decomposition cycle of 12

The sequence starts with dissociation of a trimethylphosphine. The square planar nickel species associate to form a hydrido-bridged dimer in *cis* or *trans* configuration with loss of more trimethylphosphine. Elimination of dihydrogen leaves the *trans*-bischelate complex and "naked Ni" which associates with four trimethylphosphine ligands to form $Ni(PMe_3)_4$ and close the cycle. Elemental analysis and spectral data prove the suggested composition and structure for compound 12. IR studies show Ni-H stretching frequency in the range of typical M-H frequencies (1500-2200 $cm^{-1}$).[82] Hydrides in diamagnetic compounds are conveniently detected by $^1H$ NMR at high field in a region normally free of other ligand resonances. 12 shows such $^1H$ NMR resonances around -19 ppm. The coupling with three phosphine-P nuclei is useful for determining the stereochemistry of the complex in solution.

### 2.4.2 Reaction of 12 with 1,3-bis(diphenylphosphino)propane

In order to protect the sensitive complex 12 in solution from decomposition exchange of two phosphine ligands by the chelating ligand 1,3-bis(diphenylphosphino)propane was attempted.

#### Synthesis and Characterization

The ligand exchange upon addition of dppp was readily achived according to Fig. 2.37 but still needed the presence of a fivefold excess of trimethylphosphine to prevent decomposition. After five minutes of reaction time are all volatile components were removed in a vacuum and the hydrido(dppp)-nickel complex 13 was isolated as orange powder in 63% yield which is only sparingly soluble in THF. Similar to the hydrido-nickel (II) complex 12, it is stable under at 20ºC but decomposes within a few seconds in ether solution.

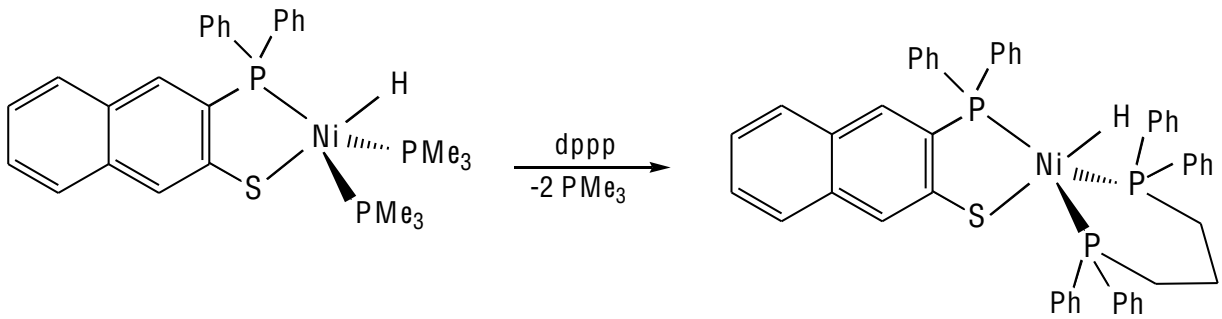



Fig.2.37 Synthesis of 13

#### Spectroscopic Investigation

When comparing the IR spectra of 13 and 12 we recognize two significant differences. First,the characteristic$\rho_1$-band of coordinated trimethylphosphine has disappeared and, secondly, the ν(Ni-H) band around 1900 $cm^{-1}$ is recorded at higher wave numbers which must be due to the higher acceptor property of the dppp ligand. In the $^1$H NMR spectrum at 300º K a doublet of triplets is registered at -17.0 ppm with coupling parameters $^2J$(PH) of 25 and 50 Hz. The $^{31}$P NMR spectrum shows the typical splitting pattern with three phosphorus ligands in the

trigonal plane of a trigonal bipyramide as triplet at 52.3 ppm for the chelate-phosphorus and as a doublet at 6.5 ppm for the isochronous phosphorus nuclei of the [*P,P*] ligand.

## Discussion

An improved stability of the nickel hydride was attempted by introducing 1.3-bis(diphenylphosphanyl)propane as a chelating phosphine. In THF containing a fivefold excess of trimethylphosphine ligand displacement is complete after five minutes (Fig. 2.37), and sparingly soluble **13** is isolated as orange solid in 63% yield. The stabilization of the [*P,P*]-chelating ligand is only marginally achieved, since also for **13 a** cycle of decomposition applies as shown in Fig. 2.33 for complex **12**. However, this transformation takes at 20 °C about 20 minutes as judged by progressive green coloring from the bis-chelate. The $^{31}$P NMR spectrum shows a singlet at -13 ppm that arises from the Ni(0) analog $Ni(dppp)_2$. The dppp-ligand dynamics is slow enough only at -30ºC to achieve in the $^{1}$H NMR hydride resonance at -17.0 ppm resolution of a doublet of triplets. The stronger electron acceptor character of the dppp ligand shifts the ν(Ni-H) IR-band by 41 $cm^{-1}$ to higher wave numbers and in the $^{1}$H NMR spectrum the hydride resonance by 2.91 ppm to lower field. Thus the stronger hydride character in **12** is changed to a more covalent bonding in **13**. While the chelate bite (~90°) of the anionic [*P,S*] ligand raises the thermal stability of hydridonickel(II) compounds with 18 metal valence electrons, the diphosphine dppp does not, because in its stable conformation the P-donor atoms cannot span equatorial positions (~120°).

## Behaviour of hydridonickel complexes under ethene and CO

In order to improve the stability of Hydridonickel complexes **12** and **13** in pentane solution an atmosphere of ethene is not sufficient because decomposition is rapid as in pure pentane under argon. Carbon monoxide is observed to

accelerate the precipitation of the green solid of the *trans*-bischelate complex.

### 2.4.3 Synthesis of methyl-(3-diphenylphosphino)-2-thionaphtholato [*P,S*]-nickel(II)complexes containing one and two trimethyl – phosphines

Besides the hydridonickel complexes, the methylnickel complexes are regarded as model compounds for catalytic reactions. [*P,S*] ligands are expected to stabilize this type of complex very effectively.

#### Synthesis and Characterization

Through reaction of methylnickel (II) compounds with the phosphino-thionaphthol in THF at -78°C the [*P,S*]-methylnickel(II)-complexes 14 and 15 are generated (Fig. 2.38 and 2.39). Phosphine content of solvents was monitored by a quaternization reaction with iodomethane. Thus with $NiMe_2(PMe_3)_3$ and one equivalent of ligand and by crystallization from pentane at -27 °C in the presence of trimethyl-phosphine the trigonal bipyramidal methyl nickel ( II)-complex 15 in the form of dark red needles was obtained, whereas starting from $NiClMe(PMe_3)_2$ and the lithium salt of the [*P,S*] ligand and by crystallization from pentane at room temperature the square planar complex 14 in the form of orange rhombic crystals was isolated. The yields are 59 % of complex 14 and 44% of the complex 15. The lower yield is due to a competing formation of the bischelate-nickel complex which can be suppressed only by high phosphine concentrations. Both solids are characterized by a high air-stability. Complex 14 remains unchanged for several months while 14 survives at least several weeks in air.

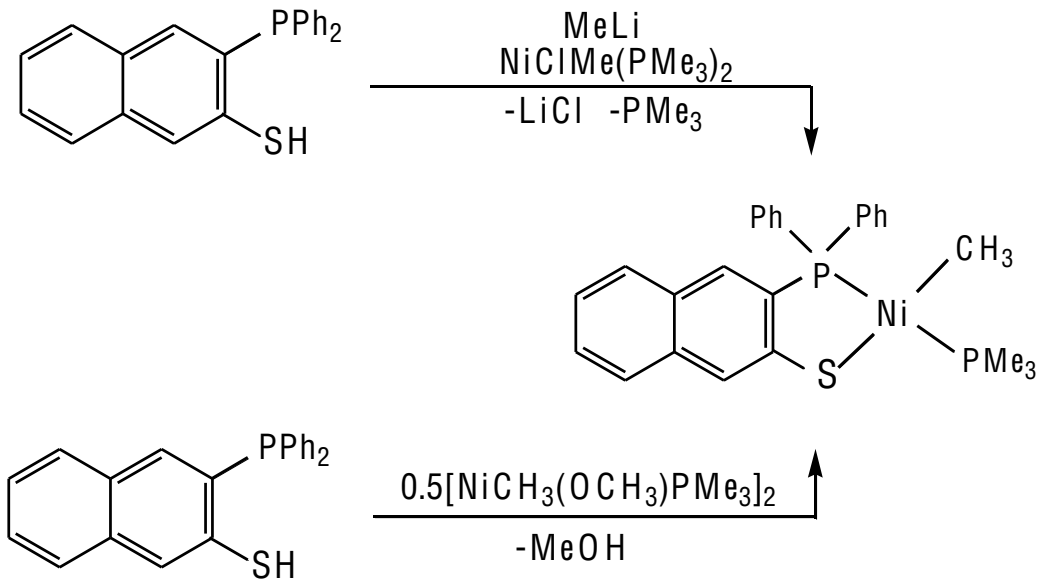



Fig. 2.38 Reaction pattern to the synthesis of 14

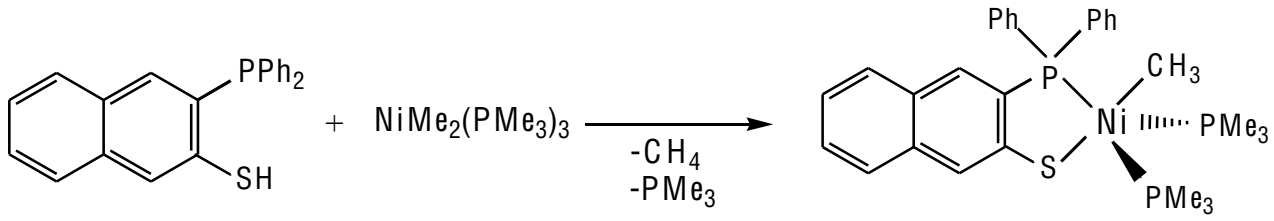



Fig. 2.39 Synthesis of 15

Complex 14 can be reversibly converted into 15 by addition of trimethylphosphine, and 15 from phosphine-free solvents crystallizes as 14 (Fig. 2.40).

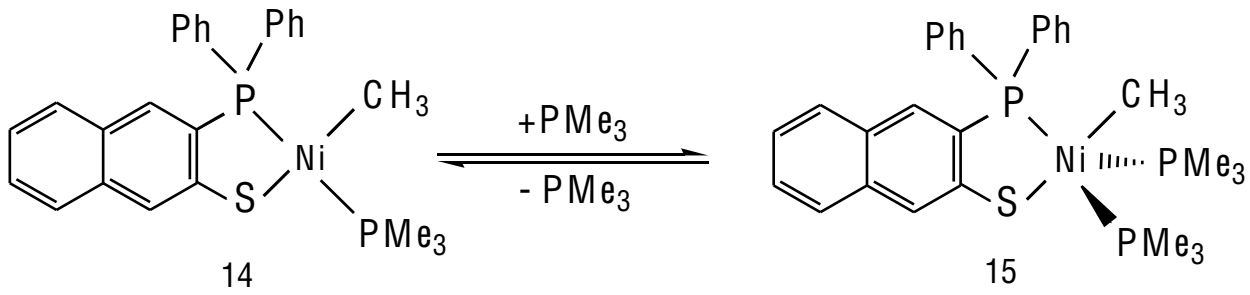



Fig. 2.40 Dissociation equilibrium with methylnickel complexes 14 and 15

## Spectroscopic Investigation

The IR spectra of 14 and 15 only differ in the intensities of the trimethylphosphine bands. They show different frequencies for the Ni-$CH_3$ deformation vibrations at 1219 $cm^{-1}$ (14) and at 1222 $cm^{-1}$ (15). Fig. 2.41 shows the IR spectrum of the penta-coordinate methylnickel complex.

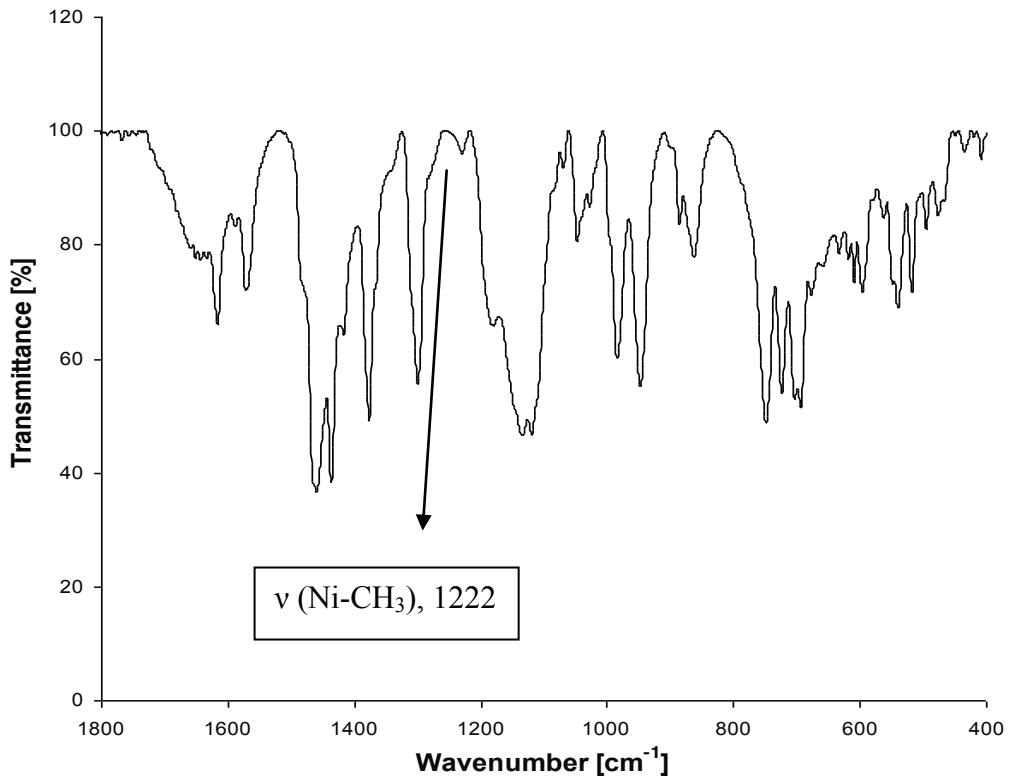



Fig. 2.41 IR-Spectrum of 15

Both complexes show at room temperature fast exchange of trimethyl- phosphine as the $NiCH_3$ group in the $^1H$ NMR spectrum even at 190 K was recorded as a doublet through coupling with the chelate-P nucleus only. (14: -0.29 ppm, d, $^3J_{PH}$ = 10.5 Hz and 15: -0.20 ppm, d, $^3J_{PH}$ = 10 Hz). In the $^{31}P$ NMR spectrum of 14 at 190º K a doublet for the chelate-P resonance at 50 ppm and doublet of doublets at -22.28 ppm for trimethylphosphine were recorded with a P,P-coupling constant of 45 Hz, which is the expected value for trans-coupling in square planar

complexes at the slow exchange limit. The $^{31}$P-NMR spectrum of 15 under these conditions contained two singlets due to a faster exchange of trimetylphosphine.

### Molecular structure of 14

Compound 14 as obtained from pentane formed orange rhombic crystals (0.32 mm x 0.28 mm x 0.14 mm). A suitable specimen in a Mark tube was sealed under argon. The crystal structure was solved in the monoclinic crystal system, and the space group was determined as P21/ n. The refinement resulted in an R1 value of 0.0355. Heavy atoms were refined anisotropically, hydrogen atoms were fixed in idealized positions with isotropic temperature factors. Further information on measurement and structure solution are in the Appendix in Tables (8.5). Fig. 2.42 gives an ORTEP plot of the molecular structure of 14. The coordination sphere around the central nickel is square planar wit the chelate-S atom *trans* to the methyl group.

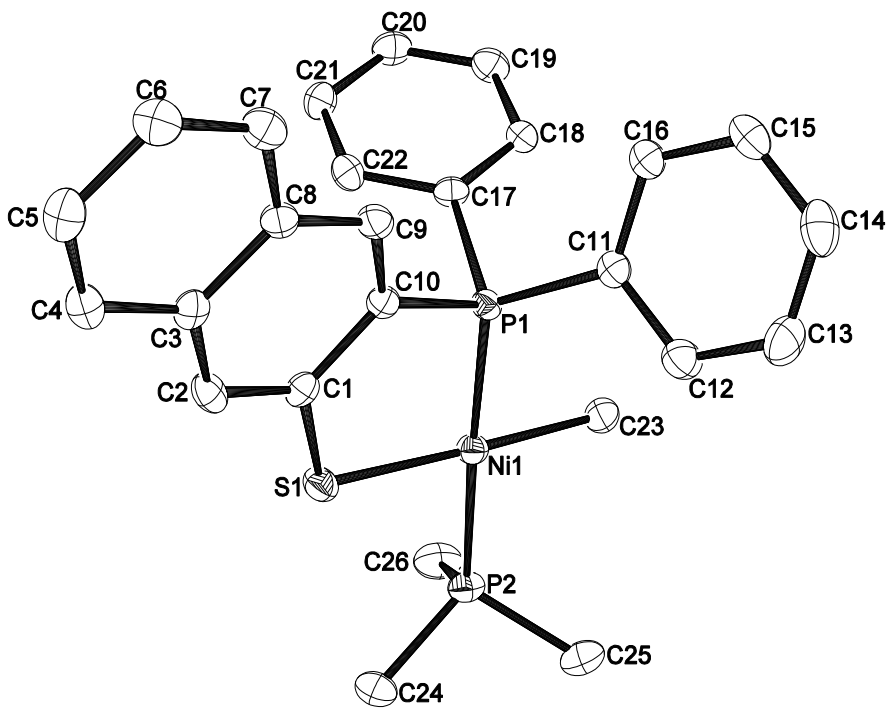



Figure2.42Molecular structure of 14 (ORTEP plot with hydrogen atoms omitted); selected bond lengths [Å] and angles [°]:Ni–S1 2.1997(7), Ni–P1 2.1403(7), Ni–P2 2.1888(8), C23-Ni 1.975(3); P1–Ni–P2 177.37(3), P1-Ni-S1 89.14(3), P2-Ni-S1 93.37(3), C23-Ni-S1 178.32(8), C23-Ni-P1 89.20(8), C23-Ni-P2 88.28(8).

The angles C23-Ni1-S1 and P1-Ni1-P2 with 178.32(8)º and 177.37(3)º, respectively, correspond well with a linear arrangement. The bite angle of the chelating thionaphthol ligand (P1-Ni-S1=89.14(3)º) meets expectation. The Ni-P bond lengths (Ni-P1 2.1403(7) Å), Ni-P2 2.1888(8) Å) as well as the C-Ni bond (C23-Ni 1.975(3) Å) fall in the expected range. They indicate the absence of steric crowding. The sum of the internal angles in the five-membered metallacycle (538.45º) approaches that of a regular pentagon (540 °) suggesting a stable coordination.

### Molecular structure of 15

A dark red crystal of 15 (0.16 mm x 0.16 mm x 0.08 mm) was mounted on a glass thread. The structure was solved in the monoclinic crystal system using direct and Fourier methods with space group P21/n. Heavy atoms Ni, S, P, and C were refined anisotropically, and H atoms were fixed in idealized positions with isotropic temperature factors. The final R1 value was 0.0684. Selected bond lengths and angles are given with the molecular structure (Fig. 2.43). More details such as atomic coordinates and displacement parameters are given in Tables listed in the Appendix (8.6).

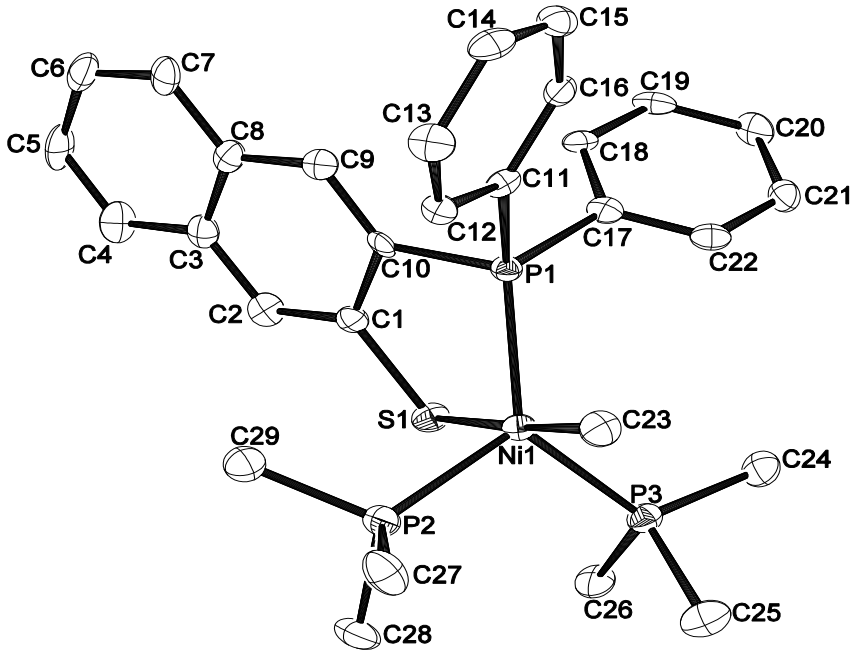



Figure2.43Molecular structure of 15 (ORTEP plot with hydrogen atoms omitted); selected bond lengths [Å] and angles [°]: Ni–C23 1.977(5), Ni–S1 2.281(1), Ni–P1 2.186(1), Ni–P2 2.243(1), Ni–P3 2.253(1); P1–Ni–S1 84.18(5), P1–Ni–P2 120.36(5), P1–Ni–P3 127.61(5), P2–Ni–P3 111.73(5), P1–Ni–C23 92.72(15), P2–Ni–C23 90.86(15), P3–Ni–C23 91.73(15), S1–Ni–C23 176.61(15).

Complex 15 shows a trigonal bipyramidal arrangement of ligands around the central nickel atom with three equatorial P donor atoms and the chelate sulfur *trans* to the methyl group. The bite angle (P1-Ni1-S1 = 84.2º) corresponds with expectations and the sum of internal angles (525.7°) is less than that of a regular pentagon (540º) indicating steric crowding. The Ni-P bond lengths (Ni-P1 2.186(1) Å), Ni-P2 2.243(1) Å), Ni-P3 2.253(1) Å) are longer than in 14 which is in line with expectation. The Ni-C distance (Ni-C23 = 1.977(5) Aº) resembles that in 14 while the Ni-S bond length appears elongated (Ni1-S1 = 2.281(1) Aº). Again the methyl group with the strongest *trans*-influence is seen in a position *trans* to sulfur.

## Discussion

The methyl nickel (II) compounds 14 and 15 arise from a smooth reaction of methyl nickel educts with one mole equivalent of [*P,S*] ligand. The formation of product depends on the phosphine concentration. Complexes 14 and 15 are interconverted by association or dissociation of trimethylphosphine and differ slightly by their colors. A competing side-reaction leading to the bischelate-nickel (II) complex can be suppressed only with difficulty as recognized by the emergence of a bright green solid. At variance with the cis/trans isomerism as observed for the isoelectronic [*P,N*]- and [*P,O*]-methyl nickel(II) systems by Beck[67] and Hetche[33] isomers could not be detected with methyl nickel complex 14. The reason is the soft character of the sulfur donor which exclusively resides *trans* to the Me-Ni Group.

# 3 EXPERIMENTAL PART

## 3.1 Working Techniques

All syntheses and manipulations were carried out under an inert atmosphere of argon or nitrogen by using modified Schlenk techniques. [83] This type of apparatus offers an opportunity of carrying out a complete synthesis in a closed system, and in one run. Synthesis, transport and storage of chemicals were done under an atmosphere of purified Argon (BTS catalyst). [84] Solvents (THF, diethyl ether, pentane) were dried according to known procedures and were freshly distilled prior to use. All reagents (Aldrich, Acros, Fluka, or Lancaster) were used as purchased without further purification.

## 3.2 Identification of substances

### 3.2.1 Elemental analyses

Air-sensitive samples were provided in capillaries sealed under vacuum and were analyzed by H. Kolbe microanalytical laboratory, Mülheim/Ruhr. C, H, N analyses as identification of composition of air stable substances were performed in the microanalytical laboratory of Clemens-Schöpf Institute for Organic Chemistry and Biochemistry at TU Darmstadt.

### 3.2.2 X-Ray crystallography

Single crystals were sealed under Argon in glass capillaries whereas air-stable crystals were mounted on a glass rod. Crystallographic data were collected on STOEIPDS (Eduard-Zintl Institute of TU Darmstadt) and Bruker AX SMART APEX CCD diffractometers (University of Paderborn). Reflections were collected (**ω**- scans) by use of graphite-monochromated Mo-$K_{\alpha}$ radiation, and

Lorentz polarization, and absorption corrections based on ψ-scans were applied. The structures were solved by direct and conventional Fourier methods. All non-hydrogen atoms were treated anisotropically. MH hydrogen atoms were refined separately; all other hydrogen atoms fixed in idealized positions were treated with a riding model. [85, 86]

### 3.2.3 Infrared spectrometry

IR spectra were obtained from Nujol mulls between KBr plates using a Bruker, type FRA 106, spectrophotometer and were recorded in the range from 4000 to 400 $cm^{-1}$. The spectrum was worked with the help of OPUS IR software.

### 3.2.4 Nuclear Magnetic Resonance spectrometry

$^{1}H$, $^{13}C$ and $^{31}P$ NMR spectra were recorded on Bruker ARX 300 and Bruker DRX 500 spectrometers at the Organic Chemistry Institute of TU Darmstadt. $^{1}H$ and $^{13}C$ chemical shifts were referenced to external TMS, and $^{31}P$ chemical shifts were referenced to external $H_3PO_4$ 85%. C and P resonances were obtained with broad-band proton decoupling.

### 3.2.5 Melting and decomposition points

All melting and decomposition points were measured on a Büchi 510 melting point apparatus and are uncorrected. Air-sensitive substances were sealed in capillaries under 1 bar argon.

## 3.3 Preparation of educts

### 3.3.1 Trimethylphosphine - [$PMe_3$]

Trimethylphosphine was synthesized in ether from methylmagnesium chloride and triphenylphosphite according to a modified procedure given by Wolfsberger and Schmidbaur which allows repeated syntheses in yields from 85 to 92 %.[87]

### 3.3.2 Dichlorobis(trimethylphosphine)iron(II) - [$FeCl_2(PMe_3)_2$]

Anhydrous $FeCl_3$ was reduced to $FeCl_2$ in THF solution with a slight excess of elemental iron (powder). Upon addition of two equivalents of trimethylphosphine the solution was evaporated to afford a light gray powder of $FeCl_2(PMe_3)_2$ in 90% yield.[88]

### 3.3.3 Dimethyltetrakis(trimethylphosphine)iron(II) - [$FeMe_2(PMe_3)_4$]

To a THF solution of $FeCl_2(PMe_3)_2$ containing two mole equivalents of trimethylphosphine were added at -70°C two mole equivalents of 1.6 M methyl lithium (in ether). $FeMe_2(PMe_3)_4$ was obtained from pentane as brown powder in 80% yield.[58]

### 3.3.4 Tetrakis(trimethylphosphine)iron(0) - [$Fe(PMe_3)_4$]

Reduction of $FeCl_2$ with magnesium turnings in THF with the presence of excess trimethylphosphine afforded a dark brown solid of $Fe(PMe_3)_4$ in 86% yield. [89]

### 3.3.5 Tetrakis(trimethylphosphine)cobalt(0) - [$Co(PMe_3)_4$]

$Co(PMe_3)_4$ was synthesized by reduction of anhydrous cobalt dichloride with magnesium in THF containing four equivalents of trimethylphosphine as brown solid in 80-90% yield.[90]

### 3.3.6 Methyl-tetrakis(trimetylphosphine)cobalt(I) - [$CoMe(PMe_3)_4$]

Reaction of $CoCl(PMe_3)_3$ with MeLi in the presence of excess trimethylphosphine gave $CoMe(PMe_3)_4$ as orange-red powder in 90-95% yield.[90]

### 3.3.7 Dichloro-tris(trimethylphosphine)cobalt(II) - [$CoCl_2(PMe_3)_3$]

$CoCl_2(PMe_3)_3$ was synthesized by reacting of anhydrous $CoCl_2$ in THF with three equivalents of trimethylphosphine and was obtained quantitatively as dark violet crystals.[91]

### 3.3.8 Dimethyl-tris(trimethylphosphine)cobalt(II) - [$CoMe_2(PMe_3)_3$]

$CoMe_2(PMe_3)_3$ was synthesized by reacting $CoCl_2(PMe_3)_3$ in diethyl ether with two equivalents of 1.6 M MeLi and was obtained as orange-brown powder in 78% yield.[91]

### 3.3.9 Chloro-tris(trimethylphosphine)cobalt(I) - [$CoCl(PMe_3)_3$]

The comproportination reaction between $CoCl_2(PMe_3)_3$ and $Co(PMe_3)_4$ in diethyl ether gave shiny blue crystals of $CoCl(PMe_3)_3$ in 90% yield.[92]

### 3.3.10 *trans*-Dichloro-bis(trimethylphosphine)nickel(II) - [$NiCl_2(PMe_3)_2$]

After removing water from a mixture of $NiCl_2 \times 6H_2O$ and two equivalents of trimethylphosphine in THF solution deep red crystals of $NiCl_2(PMe_3)_2$ were obtained in 96%.[93]

### 3.3.11 *trans*-Chloro(methyl)bis(trimethylphosphine)nickel(II) [$NiClMe(PMe_3)_2$]

To a solution of $NiCl_2(PMe_3)_2$ in THF at -80 °C stoichiometric amounts of 1.6 M solution MeLi in ether were added to give orange-golden leafs of $NiClMe(PMe_3)_2$ in 97% yield.[94]

### 3.3.12 *trans*-Dimethyl-tris(trimethylphosphine)nickel(II) [$NiMe_2(PMe_3)_3$]

$NiCl_2(PMe_3)_2$ in THF was methylated at -70 °C by two mole equivalents of 1.6 M MeLi to afford an orange solid of $NiMe_2(PMe_3)_3$ in 96% yield.[95]

### 3.3.13 Tetrakis(trimethylphosphine)nickel(0) - [$Ni(PMe_3)_4$]

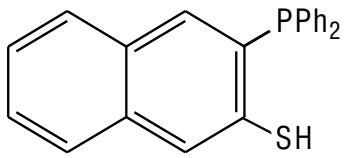
Anhydrous nickel chloride in THF containing four mole equivalents of trimethylphosphine was reduced with magnesium turnings that were activated by a small grain of potassium metal. $Ni(PMe_3)_4$ was obtained as yellow solid in 93% yield.[96]

### 3.3.14 Di-μ-methoxo-bis[cis-methyl(trimethylphosphine)nickel(II)] [$Ni(OMe)Me(PMe_3)]_2$

$[Ni(OMe)Me(PMe_3)]_2$ was synthesized by reaction of $NiClMe(PMe_3)_2$ with sodium methoxide in ether as dark brown crystals in 97% yield.[94]

## 3.4 Ligand Synthesis

### 3.4.1 (3-Diphenylphosphino)-2-thionaphthol




To a stirred solution of 200 mL cyclohexane/TMEDA (1:1) at 0°C were .added 2.5 M n-BuLi in hexane (249 mL, 624 mmol) and 2-thionaphthol (20 g, 124.8

mmol).The cooling bath was removed. After 24 h at 20 °C the dilithium salt [97, 98] was formed and filtered off as pale yellow powder. This was dissolved in 100 mL of cyclohexane/TEMDA (1:1). At 0°C chlorodiphenylphosphine (22.4 mL, 124.8 mmol) in 50 mL cyclohexane was added dropwise under stirring within 1 h. After 16 h at 25 °C the mixture was hydrolyzed with water (30 mL) and toluene (200 mL) was added. The organic layer was washed with three portions (200 mL) of 5% acetic acid. After phase separation the volatiles were removed in vacuo and the residue was dissolved in warm ethanol (60 mL). Pale yellow microcrystals were formed that were isolated by filtration and drying in vacuo. [50, 51]

**Yield:** 10.1 g (21% th.)

**Melting point:** 165 – 168 °C.

**Elemental analysis:** $C_{22}H_{17}PS$, M 344.41 g/mol

| % | C | H | P | S |
|---|---|---|---|---|
| Calculated | 76. 72 | 4.97 | 8. 99 | 9. 31 |
| Found | 76. 58 | 4.99 | 8. 35 | 8. 73 |

**IR** (Nujol, 4000–1700 $cm^{-1}$):

2547 w ν(S-H).

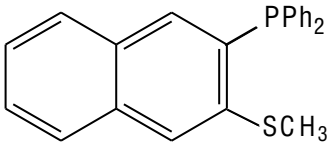
**$^1$H NMR** (200 MHz, $CDCl_3$, 296 K, ppm):

δ: 7.87–7.25 (m, 16 H, CH); 4.11 (s, 1H, SH).

**$^{31}$P NMR** (81 MHz, $CDCl_3$, 296 K, ppm):

δ: - 11.4 s PPh.

### 3.4.2 (2-Diphenylphosphino)-3-methylthionaphthalene




To a solution of (3-diphenylphosphino)-2-thionaphthol (4.6 g, 13.4 mmol) in THF (60 mL) were slowly added 5.5 mL of 2.5 M n-BuLi (13.4 mmol) in hexane at -60 °C. Deprotonation proceeded with a change of color from colorless to yellow. Then iodomethane (0.83 mL, 13.4 mmol) was added dropwise at the same temperature. The mixture was stirred at 20 °C for 4 h. After that the reaction mixture contained solid lithium iodide. The mixture was hydrolyzed with 10 mL of water and was extracted with 250 mL of toluene. Remaining salt was removed by washing with 2% acetic acid (3×200 mL). The organic phase was collected and the solvent was removed in vacuo. (2-Diphenylphosphino)(3-methylthio) naphthalene was crystallized from 50 mL of hot ethanol as pale yellow microcrystals.

**Yield:** 3.3 g (61% th.)

**Melting point:** 175 – 177 °C

**Elemental analysis:** $C_{23}H_{19}PS$, M 358.44 g/mol.

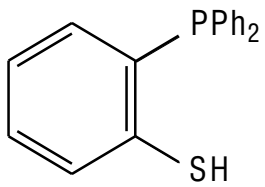
| % | C | H | P | S |
|---|---|---|---|---|
| Calculated | 77. 07 | 5.34 | 8. 64 | 9. 50 |
| Found | 77.02 | 5.38 | 8. 59 | 9.01 |

$^{1}$H NMR (300 MHz, $CDCl_3$, 300 K, ppm):

δ: 7.66 – 7.22 (m, 16H, CH); 2.52 (s, 3H, $CH_3$).

$^{31}$P NMR (121 MHz, $CDCl_3$, 300 K, ppm):
- 13.48 (s, PPh).

### 3.4.3 (2-Diphenylphosphino)-thiophenol




TMEDA (24.2 mL, 0.160 mol) and 65 mL of 2.5 M n-BuLi (0.160 mol) in hexane were mixed at -10 – 0 °C. After 10 min. were added 200 mL of pentane, and then thiophenol (7.7 mL, 0.075 mol) of in 30 mL of pentane was added dropwise under stirring. The cooling bath was removed and the mixture stirred at room temperature for 24 h. The mixture contains a white suspension of the dilithium salt. Finally at 0 °C chlorodiphenyl-phosphine (13.5 mL, 0.075 mol) in 30 mL of pentane was added dropwise within 30 min. After 16 h at 25 °C the mixture was hydrolyzed with 30 mL of water and toluene (200 mL) was added. The organic layer was washed with three portions (200 mL) of 5% acetic acid. After phase separation the volatiles were removed in vacuo. The phosphinothiophenol was crystallized from 60 mL of ethanol. White microcrystals were formed that were isolated by filtration and drying in vacuo. [50, 51]

**Yield:** 14.8 g (68% th.)

**Melting point:** 97– 98 °C.

**Elemental analysis:** $C_{18}H_{15}PS$, M 294.36 g/mol

| % | C | H | P | S |
|---|---|---|---|---|
| Calculated | 73.45 | 5.14 | 10.52 | 10.89 |
| Found | 73.27 | 5.29 | 10.77 | 10.65 |

**IR** (Nujol, 4000 – 1700 $cm^{-1}$):
2493 w ν(S-H).

$^{1}$**H NMR** (200 MHz, $CDCl_3$, 293 K, ppm):

δ: 7.38 – 6.76 (m, 14H, CH); 4.05 (s, 1H, SH).

$^{31}$**P NMR** (81 MHz, $CDCl_3$, 293 K, ppm):

δ: -12.5 (s, 1P, PPh).

## 3.5 Synthesis of New Complexes

### 3.5.1 Synthesis of iron complexes: Procedure A

$Fe(PMe_3)_4$ or $FeMe_2(PMe_3)_4$ in THF were combined with stoichiometric amounts of [*P,S*] ligand at -70 ºC. After removing the cooling bath the mixture was kept stirring at 20 ºC for 16 h. The volatiles were then removed in vacuo and the residue was extracted with ether or pentane. Combined solutions were cooled or concentrated at room temperature to afford crystalline or microcrystalline material.

### 3.5.2 Synthesis of cobalt complexes: Procedure B

$Co(PMe_3)_4$ or $CoMe(PMe_3)_4$ in THF was combined with stoichiometric amounts of [*P,S*] ligand at -70 ºC. The mixture was warmed to 20ºC and kept stirring for 16 h. The volatiles were then removed in vacuo. The residue was extracted with ether, and combined solutions were cooled or concentrated at room temperature to afford crystalline material Alternatively, filtration and drying in vacuo afforded powdery material.

### 3.5.3 Synthesis of nickel complexes: Procedure C

$Ni(PMe_3)_4$, $Ni(CH_3)_2(PMe_3)_3$ and $NiClCH_3(PMe_3)_2$ in THF Solution were combined with stoichiometric amounts of [*P,S*] ligands at-70ºC. The mixture was warmed to 20ºC and kept stirring for 16h. The volatiles were then removed in vacuo. The residue was extracted with ether or pentane and combined solutions were cooled or at room temperature to afford crystalline or alternatively, the product also means filtration and drying on vacuo as a powdery substance to be fixed material.

### 3.5.4 Reactions with carbon monoxide: Procedure D

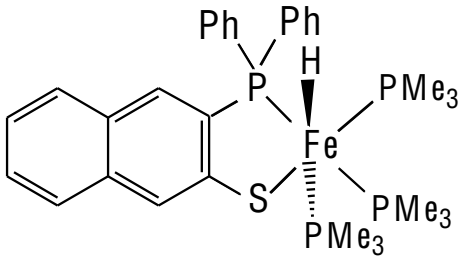
A sample of a thionaphthol complex was stirred under 1 bar of CO for 10 h. The volatiles were then removed in vacuo. The residue was extracted with ether at room temperature to afford crystalline material.

### 3.5.5 Reactions with iodomethane: Procedure E

Iodomethane was added to a sample of a thionaphthol complex in THF at room temperature. After 10 h stirring the volatiles were removed in vacuo. The residue was isolated as powder.

## 3.6 New Complexes

### 3.6.1 Hydrido-[(3-diphenylphosphino)-2-thionaphtholato]-[P,S]-tris(trimethylphosphine)-iron(II) (1)




Procedure A:

1.02 g (2.83 mmol) of $Fe(PMe_3)_4$ in THF were combined with 0.98 g (2.83 mmol) of 3-diphenylphosphino-2-thionaphthol to afford 1.61 g of 1 as red powder.

Yield: 81%

Melting point: 181 – 184 °C (dec.)

Elemental analysis: $C_{31}H_{44}FeP_4S$, M 628.49g/mol

| % | C | H | P | S |
|---|---|---|---|---|
| Calculated | 59.24 | 7.06 | 19.71 | 5.10 |
| Found | 58.57 | 6.73 | 20.14 | 5.17 |

IR (Nujol, 4000–400 $cm^{-1}$):

3051 w ν(H-C=), 1842 m ν(FeH), 1617 m ν(C=C), 1571 m ν(C=C), 1295 m $\delta_s$ ($PCH_3$), 1089 m δ(PPh), 945 s $\rho_1$($PCH_3$), 888 m $\rho_2$($PCH_3$), 663 m ν($PC_3$).

$^{1}$H NMR (500 MHz, $d_8$-THF, 300 K, ppm):

δ: 8.24 m (1H, CH); 7.77–7.30 m (4H, CH); 7.24–7.17 m (7H, CH); 6.91– 6.75 m (4H, CH); 1.64 (d, $^{2}J$(PH) = 9.0 Hz, 9H, $PCH_3$); 1.23 (d,$^{2}J$(PH) = 9.0 Hz, 9H, $PCH_3$); 0.89 (d, $^{2}J$(PH) = 9.0 Hz, 9H, $PCH_3$); -12.8 (dddd, $^{2}J$(PH) = 85 Hz, $^{2}J$(PH) = 60 Hz, $^{2}J$(PH) = 50 Hz, $^{2}J$(PH) = 30 Hz, 1H FeH).

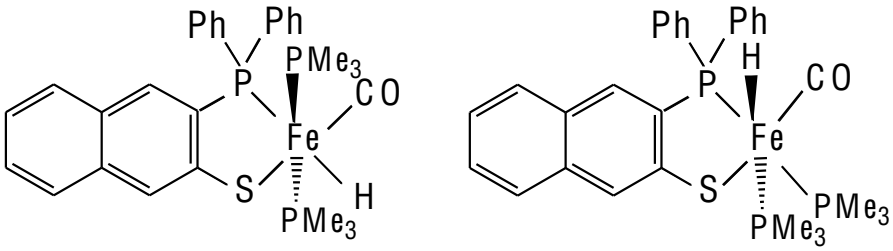
$^{13}$C NMR (125 MHz, $d_8$-THF, 300 K, ppm):

δ: 166.9 (s, C); 156.7 (d, $^{3}J$(PC) = 8.8 Hz, C); 150.2 (d, $^{4}J$(PC) = 8.8 Hz, C); 144.6 (d, $^{1}J$(PC) = 7.5 Hz, C); 140.3 (d, $^{2}J$(PC) = 8.8 Hz, CH); 133.2 (d, $^{2}J$(PC) = 10 Hz, CH); 132.2 (d, $^{2}J$(PC) = 8.8 Hz, CH); 130.1 (s, CH); 128.4 (d, $^{1}J$(PC) = 8.8 Hz, CH); 127.9 (d, $^{2}J$(PC) = 10 Hz, CH); 127.7 (d, $^{3}J$(PC) = 5.0 Hz, CH); 126.3 (s CH) ; 125.5 (d, $^{3}J$(PC) = 7.5 Hz, CH); 121.7 (s, CH); 24.4 (d,$^{1}J$(PC) = 18.9 Hz, $PCH_3$); 22.6 (d, $^{1}J$(PC) = 18.9 Hz, $PCH_3$); 20.8 (d, $^{1}J$(PC) = 17.6 Hz, $PCH_3$).

$^{31}$P NMR (202 MHz, $d_8$-THF, 296 K, ppm):

δ: 88.0 (ddd, $^{2}J(P_{Ph}P_{Me})$ = 95 Hz, $^{2}J(P_{Ph}P_{Me})$ = 42 Hz, $^{2}J$ $(P_{Ph}P_{Me})$ = 25 Hz, 1P, PPh); 27.6 (ddd, $^{2}J(P_{Me}P_{Ph})$ = 42 Hz, $^{2}J(P_{Me}P_{Me})$ = 48 Hz, $^{2}J(P_{Me}P_{Me})$ = 34 Hz, 1P, PMe); 13.3 (ddd, $^{2}J(P_{Me}P_{Ph})$ = 95 Hz, $^{2}J(P_{Me}P_{Me})$ = 48 Hz, $^{2}J(P_{Me}P_{Me})$ = 13 Hz, 1P, PMe); (5.3 ddd, $^{2}J(P_{Me}P_{Ph})$ = 25 Hz, $^{2}J(P_{Me}P_{Me})$ = 34 Hz, $^{2}J(P_{Me}P_{Me})$ = 13 Hz, 1P, PMe).

### 3.6.2 Hydrido-{(3-diphenylphosphino)-2-thionaphtholato-[P,S]} (carbonyl)-bis(trimethylphosphine)-iron(II) (2)




2a 2b

**Procedure D:**

A sample of 1 ( 500 mg, 0.79 mmol) in THF was stirred under 1 bar CO to provide 430 mg of yellow crystals of 2 which crystallize from ether at room temperature.

**Yield:** 86%

**Melting point:** 179 – 182 °C (dec. >200 °C)

**Elemental analysis:** $C_{29}H_{35}FeOP_3S$, M 580.43g/mol

| % | C | H | P |
|---|---|---|---|
| Calculated | 60.01 | 6.07 | 16.00 |
| Found | 59.46 | 6.11 | 16.34 |

**IR** (Nujol, 4000–400 $cm^{-1}$):

3054 m ν(H-C=), 1933 m $\nu_{as}$(CO), 1889 s $\nu_s$(CO), 1847 w ν(Fe-H), 1621 w ν(C=C), 1567 w ν(C=C), 1464 w $\delta_{as}(PCH_3)$, 1297 m $\delta_s(PCH_3)$, 1092 m δ(PPh), 945 s $\rho_1(PCH_3)$, 859 w $\rho_2(PCH_3)$, 704 m $\nu_{as}(PC_3)$, 680 w $\nu_s(PC_3)$.

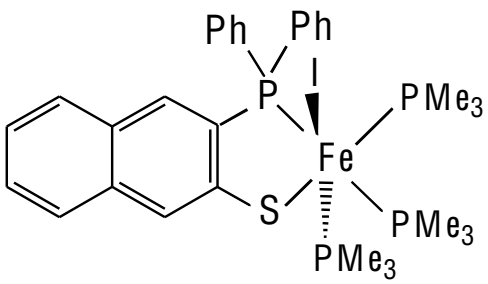
$^{1}$H NMR (500 MHz, $d_8$-THF, 300 K, ppm):

δ: 7.99–7.96 (m, 1H, CH); 7.73–7.70 (m, 2H, CH); 7.45–7.35 (m, 3H, CH); 7.34–7.24 (m, 5H, CH); 7.23–7.22 (m, 16H, CH); 7.21–7,19 (m, 1H, CH); 7.06–6,92 (m, 4H, CH); 1.5 (d, $^{2}J$(PH) = 10 Hz, 9H, $PCH_3$); 0.97 (t', $|^{2}J$ (PH) + $^{4}J$(PH)$|$ = 5,0 Hz, 18H, $PCH_3$); 0,82 (dd, $^{2}J$(PH) = 5,0 Hz, $^{2}J$(PH) = 10 Hz, 9H, $PCH_3$); - 9,8 (dt, $^{2}J$(PH) = 70 Hz, $^{2}J$(PH) = 45 Hz, 1H, FeH) ; -10,9 (ddd, $^{2}J$(PH) = 45 Hz, $^{2}J$(PH) = 20 Hz, $^{2}J$(PH) = 20 Hz, 1H, FeH).

$^{31}$P NMR (121 MHz, $d_8$-THF, 300 K, ppm):

δ: 93 (dd, $^{2}J(P_{Ph}P_{Me})$ = 119 Hz, $^{2}J(P_{Ph}P_{Me})$ = 24 Hz, 1P, PPh); 85,9 (t, $^{2}J(P_{Ph}\ P_{Me})$ = 28 Hz, 1P, PPh); 19,7 (dd, $^{2}J(P_{Me}P_{Ph})$ = 120 Hz, $^{2}J(P_{Me}P_{Me})$ = 16 Hz, 1P, PMe); 15.3 (d, $^{2}J(P_{Me}P_{Ph})$ = 28 Hz, 2P, $PMe_3$); 5.2 (dd, $^{2}J(P_{Me}P_{Ph})$ = 24 Hz, $^{2}J(P_{Me}P_{Me})$ = 16 Hz, 1P, PMe).

### 3.6.3 Iodo-(3-diphenylphosphino)-2-thionaphtholato- [*P,S*]-tris(trimethylphosphine)iron(II) (3)




Procedure E:

1.10 g (1.75 mmol) of 1 in THF were combined with 249 mg (1.77 mmol) of iodomethane. After 10 h the volatiles were removed in vacuo and the residue was collected to afford 950 mg of complex 3 as yellow powder.

**Yield:** 71%

**Melting point:** 225 – 227 °C (dec.)

**Elemental analysis:** $C_{31}H_{43}FeIP_4S$, M 754.39 g/mol

| % | C | H | P |
|---|---|---|---|
| Calculated | 49.36 | 5.74 | 16.42 |
| Found | 48.53 | 6.28 | 15.86 |

**IR** (Nujol, 4000 – 400 $cm^{-1}$):

3048 w ν(H-C=), 1617 s ν(C=C), 1575 s ν(C=C), 1445 s $\delta_{as}(PCH_3)$,1290 w $\delta_s(PCH_3)$, 952 s $\rho_1(PCH_3)$, 848 w $\rho_2(PCH_3)$, 663 w $\nu_s(PC_3)$.

$^1$**H NMR** (500 MHz, $d_8$-THF, 300 K, ppm):

δ: 8.39 (m, 2H, CH); 8.45 (m, 2H, CH); 7.87 (m, 2H, CH); 7.72 (m, 2H, CH); 7.65 (m, 6H, CH); 7.42 (m 2H, CH); 1.73 (d, $^2$J(PH) = 6.1 Hz, 9H, $PCH_3$); 1.26 (d, $^2$J(PH) = 4.1 Hz, 9H, $PCH_3$); 1.12 (d, $^2$J(PH) = 6.7 Hz, 9H, $PCH_3$).

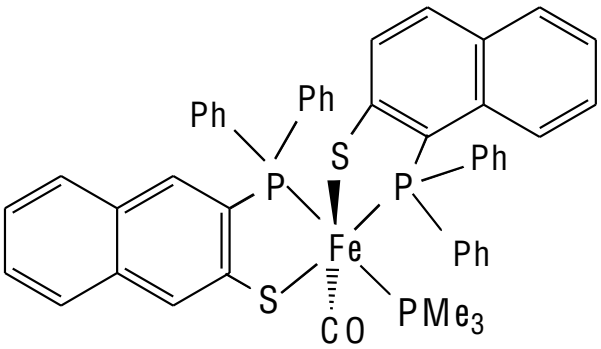
$^{13}$**C NMR** (125 MHz, $d_8$-THF, 300 K, ppm):

δ: 165.9 (s, C); 151.3 (s, C); 150.7 (d, $^3J$(PC) = 10.2 Hz, C); 150.2 (d, $^4J$(PC) = 8.8 Hz, C); 147.6 (d, $^2J$(PC) = 7.5 Hz, C); 140.3 (d, $^2J$(PC) = 31.4 Hz, CH); 133.2 (d, $^2J$(PC) = 18.2 Hz, CH); 132.2 (s, CH); 131.5 (s, CH); 130.1 (s, CH); 128.4 (d, $^4J$(PC) = 5.2 Hz, CH); 127.9 (d, $^2J$(PC) = 10 Hz, CH); 127.7 (d, $^3J$(PC) = 5.0 Hz, CH); 126.3 (s, CH); 24.4 (d, $^1J$(PC) =18.4 Hz, $PCH_3$); 22.6 (d, $^1J$ (PC) = 15.1 Hz, $PCH_3$); 20.8 (d, $^1J$(PC) = 20.7 Hz, $PCH_3$).

$^{31}$P NMR (202 MHz, $d_8$-THF, 300 K, ppm):

δ: 9.4 (ddd, $^2J(P_{Ph}\ P_{Me})$ = 16 Hz, $^2J(P_{Ph}P_{Me})$ = 53 Hz, $^2J(P_{Ph}P_{Me})$ = 69 Hz, 1P, PPh); 22.3 (ddd, $^2J(P_{Me}P_{Ph})$ = 53 Hz, $^2J(P_{Me}P_{Me})$ = 45 Hz, $^2J(P_{Me}P_{Me})$ = 54 Hz, 1P, $PMe_3$); 13 (ddd, $^2J(P_{Me}P_{Ph})$ = 69 Hz, $^2J(P_{Me}P_{Me})$ = 54 Hz, $^2J(P_{Me}P_{Me})$ = 35 Hz, 1P, PMe); -0,8 (ddd, $^2J(P_{Me}P_{Ph})$ = 16 Hz, $^2J(P_{Me}P_{Me})$ = 35 Hz, $^2J(P_{Me}P_{Me})$ = 45 Hz, 1P, PMe).

### 3.6.4 Bis (3-diphenylphosphino)-2-thionaphtholato-[*P,S*]-(carbonyl)-(trimethylphosphine)iron (II) (4)




Procedure A:

520 mg (1.53 mmol) of $Fe(CO)_2(PMe_3)_3$ in THF were combined with 1.05 g (3.06 mmol) of (3-diphenylphosphino)-2-thionaphthol. Red cubic crystals were obtained at room temperature to afford 1.1g of 4.

Yield: 70%

Melting point: 175 – 177 °C, (dec. > 200 °C)

Elemental analysis: $C_{48}H_{41}FeOP_3S_2$, M 846.75 g/mol

| % | C | H | P |
|---|---|---|---|
| Calculated | 68.08 | 4.88 | 10.97 |
| Found | 67.35 | 5.55 | 11.87 |

IR (Nujol, 4000 – 400 $cm^{-1}$):

3053 w ν(H-C=), 2012 w $\nu_{as}$(CO), 1931 s $\nu_s$(CO), 1734 w ν(CO), 1618 m ν(C=C), 1563 m ν(C=C), 1297 w $\delta_s(PCH_3)$, 1092 w δ(PPh), 955 s $\rho_1(PCH_3)$, 879 w $\rho_2(PCH_3)$, 698 m $\nu_{as}(PC_3)$, 670 w $\nu_s(PC_3)$.

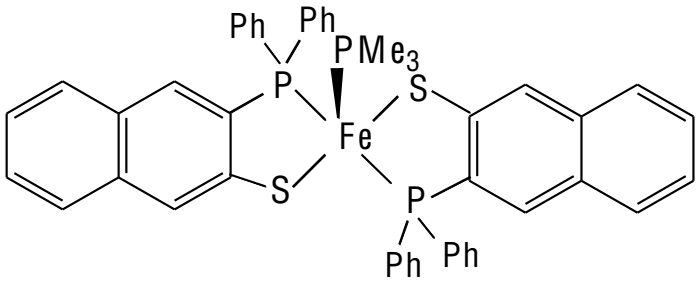
$^1$H NMR (500 MHz, $d_8$-THF, 300 K, ppm):

δ: 8. 28 – 6.90 (m, 32H, CH); 1.26 (d, $^2J$ (PH) = 9 Hz, 9H, $PCH_3$).

$^{31}$P NMR (202 MHz, $d_8$-THF, 300 K, ppm):

δ: 83.1 (dd, $^2J(P_{Ph}P_{Ph})$ = 37 Hz, $^2J$ $(P_{Ph}P_{Me})$ = 45 Hz, 1P, PPh); 55.2 (dd, $^2J(P_{Ph}P_{Ph})$ = 37 Hz, $^2J(P_{Ph}P_{Me})$ = 201 Hz, 1P, PPh); 3.6 (dd, $^2J(P_{Me}P_{Ph})$ = 201 Hz; $^2J$ $(P_{Me}P_{ph})$ = 45 Hz, 1P, PMe).

### 3.6.5. *trans*- Bis(3-diphenylphosphino)-2-thionaphtholato-[*P,S*]-(trimethylphosphine)iron(II) (5)




Procedure A:

900 mg (2.3 mmol) of $FeMe_2(PMe_3)_4$ in THF were combined with 1.59 g (4.6 mmol) of (3-diphenylphosphino)-2-thionaphthol. By extraction with ether 1.75 g of 5 were obtained as brown powder.

Yield: 71%

**Melting point:** 225 – 227 °C (dec.)

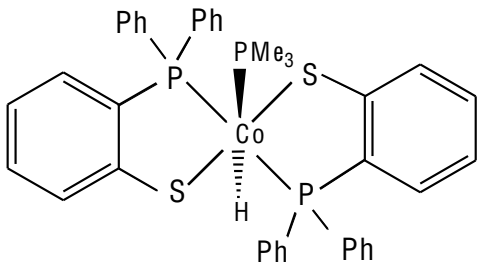
**Elemental analysis:** $C_{47}H_{41}FeP_3S_2$, M 818.74 g/mol

| % | C | H | P |
|---|---|---|---|
| Calculated | 68.95 | 5.05 | 11.35 |
| Found | 68.21 | 5.63 | 11.51 |

**IR** (Nujol, 4000 – 400 $cm^{-1}$):

3054 w ν(H-C=), 1615 s ν(C=C), 1566 s ν(C=C), 1437 vs $\delta_{as}(PCH_3)$, 1297 m $\delta_s(PCH_3)$, 1086 s δ(Ph), 946 s $\rho_1(PCH_3)$, 843 w $\rho_2(PCH_3)$, 695 vs $\nu_{as}(PC_3)$, 667 w $\nu_s(PC_3)$.

### 3.6.6 Hydrido-*bis*(2-diphenylphosphino)thiophenolato-[*P,S*]-(trimethylphosphine)cobalt(III)(6)




**Procedure B:**

1.02 g (2.7 mmol) of $CoMe(PMe_3)_4$ in THF were combined with 1.56 g (5.3 mmol) of (2-diphenylphosphino)thiophenol to afford 1.75 g of **6** as red brown cubic crystals which were crystallized from ether.

**Yield:** 67 %

**Melting point:** > 240 °C

**Elemental Analysis:** $C_{39}H_{38}CoP_3S_2$, M 722.72 g/mol

| % | C | H | P | S |
|---|---|---|---|---|
| Calculated | 64.81 | 5.30 | 12.86 | 8.87 |
| Found | 64.75 | 5.24 | 12.75 | 8.72 |

**IR** (Nujol, 4000 – 400 $cm^{-1}$):

3049 w ν(H-C=), 1948 m ν(Co-H), 1574 m ν(C=C), 1443 s $\delta_{as}(PCH_3)$, 1281 m $\delta_s(PCH_3)$, 1091 s δ(PPh), 954 s $\rho_1(PCH_3)$, 862 w $\rho_2(PCH_3)$, 697 vs $\nu_{as}(PC_3)$, 663 w $\nu_s(PC_3)$.

**$^1$H NMR** (500 MHz, $d_8$-THF, 300 K, ppm):

δ: 7.8 – 7.6 (m, 4H, CH); 7.4 – 7.3 (m, 5H, CH); 7.2 – 7.0 (m, 11H, CH); 6.9 – 6.7 (m, 4H, CH); 6.6 – 6.4 (m, 4H, CH); 0.92 (d, $^2J$(PH) = 10 Hz, 9H, $PCH_3$); -11.06 (ddd, $^2J$(PH) = 45 Hz, $^2J$(PH) = 40 Hz, $^2J$(PH) = 40 Hz 1H, Co-H); -12,72 (dt, $^2J$ (PH) = 55 Hz, $^2J$ (PH) = 50 Hz, 1H, Co-H).

**$^{13}$C NMR** (125 MHz, $d_8$-THF, 300 K, ppm):

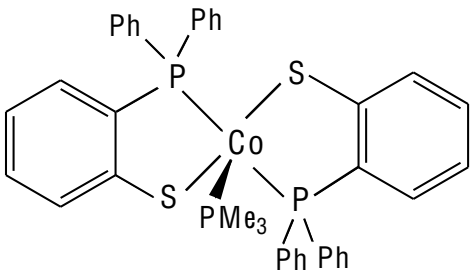
δ: 163.6 (d, $^2J$(PC) = 44 Hz, C); 161.5 (d, $^1J$(PC) = 25 Hz, C); 138.8 (s, CH); 134.2, $^2J$(PC) = 9 Hz, d, CH); 131.8 (d, $^3J$(PC) = 10 Hz, CH); 128.9 (d, $^2J$(PC) = 19 Hz, CH); 128.1 (s, CH); 127.2 d, $^4J$(PC) = 5 Hz, CH); 126.9 d, $^2J$(PC) = 9 Hz, CH; 119.7 (s, CH); 13.4 (d, $^1J$(PC) = 23.9 Hz $PCH_3$).

$^{31}$P NMR (202 MHz, $d_8$-THF, 300 K, ppm):

δ: 69.2 (s, PPh) ; 65.0 (d, $^2J$ ($P_{Ph}P_{Me}$) = 295.4 Hz, 1P, PPh); 46.0 (s, PPh);

- 0.63 (d, $^2J$ ($P_{Me}P_{Ph}$) = 255.3 Hz, 1P, PMe); -11.7 (s, PMe).

### 3.6.7 *trans*-Bis-(2-diphenylphosphino)thiophenolato-[*P, S*]-(trimethylphosphine)cobalt(II) (7)




Procedure B:

770 mg (2.4 mmol) of $CoMe_2(PMe_3)_3$ in THF were combined with 1.4 g (4.75 mmol) of (2-diphenylphosphino)thiophenol. After removing the volatile components and washing with pentane the solid residue was extracted with ether to afford 1.45 g of 7 as brown prismatic crystals.

Yield: 67 %

Melting point: 130 – 133°C (dec.>230°C)

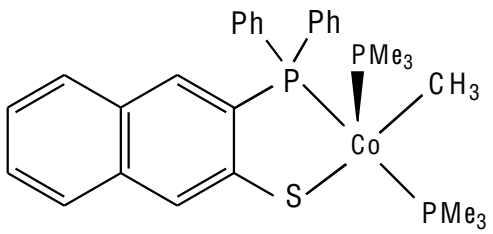
Elemental analysis: $C_{43}H_{47}CoOP_3S_2$, M 795.83 g/mol

| % | C | H | P |
|---|---|---|---|
| Calculated | 64.90 | 5.95 | 11.68 |
| Found | 64.75 | 5. 78 | 12.23 |

IR (Nujol, 4000 – 400 $cm^{-1}$):

3044 w ν(H-C), 1570 m ν(C=C), 1435 vs $\delta_{as}(PCH_3)$, 1422 vs $\delta_{as}(PCH_3)$, 1281m $\delta_s(PCH_3)$, 1093 s δ(PPh), 949 s $\rho_1(PCH_3)$, 863 w $\rho_2(PCH_3)$, 694 vs $\nu_{as}(PC_3)$, 663 w $\nu_s(PC_3)$.

### 3.6.8 Methyl-(3-diphenylphosphino)-2-thionaphtholato-[*P,S*]-bis (trimethylphosphine)cobalt(II) (8)




Procedure B:

580 mg (1.59 mmol) of $Co(PMe_3)_4$ in THF were mixed with 572 mg (1.59 mmol) of (2-diphenylphosphino)-2-methylthionaphthalene. Extraction with pentane afforded 760 mg of 8 as red brown powder.

Yield: 67 %

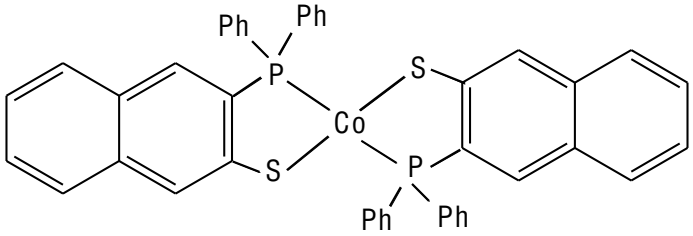
Melting point: 101 – 105 °C (dec. >110 °C.

Elemental analysis: $C_{29}H_{37}CoP_3S$, M 569.53 g/mol.

| % | C | H | P |
|---|---|---|---|
| Calculated | 61.16 | 6.55 | 16.31 |
| Found | 60.77 | 6.96 | 16.34 |

IR (Nujol, 400 – 4000 $cm^{-1}$):
3047 w ν(H-C=), 1613 m ν(C=C), 1570 m ν(C=C), 1461 s $\delta_{as}(PCH_3)$, 1422 w $\delta_{as}(PCH_3)$, 1296 m $\delta_s(PCH_3)$, 1164 w $\delta_s(CoCH_3)$, 1095 s δ(PPh), 948 vs $\rho_1(PCH_3)$, 887w $\rho_2(PCH_3)$, 697 m $\nu_{as}(PC_3)$, 670 w $\nu_s(PC_3)$.

### 3.6.9 *trans*-Bis(3-diphenylphosphino)-2-thionaphtholato-[*P,S*]-cobalt(II) (9)




Procedure B:

1.0 g (2.9 mmol) of (3-diphenylphosphino)-2-thionaphthol in THF were combined with 1.33 g of sodium methoxide. After 15 min. stirring 190 mg (1.45 mmol) of anhydrous cobalt chloride were added. The volatiles were removed in vacuo and the residue was washed with THF and water to afford 850 mg of 9 as red powder.

Yield: 71 %

Melting point: dec. > 240 °C

Mass spectrum (m/Z+): 745 (2M - PSCo); 327 (M - S - Co).

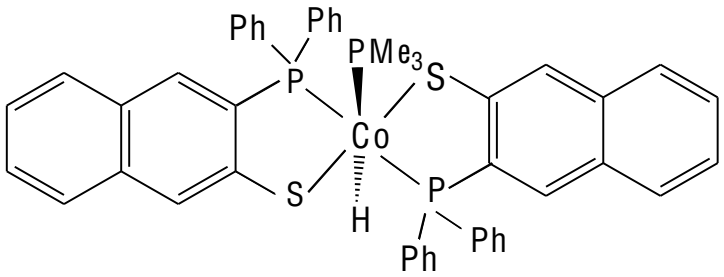
Elemental analysis: $C_{44}H_{32}CoP_2S_2$, M 745.75 g/mol.

| % | C | H | P | S |
|---|---|---|---|---|
| Calculated | 70.87 | 4.32 | 8.31 | 8.60 |
| Found | 71.63 | 4.36 | 7.83 | 9.06 |

IR (Nujol, 4000 - 400 $cm^{-1}$):

3050 w ν(H-C=), 1617 m ν(C=C), 1570 m ν(C=C), 1096 s δ(PPh),751 m $\nu_{as}(PC_3)$, 694 m $\nu_s(PC_3)$.

### 3.6.10 Hydrido-bis(3-diphenylphosphino)-2-thionaphtholato-[*P, S*]-(trimethylphosphine)cobalt(III) (10)




Procedure B:

750 mg (1.98 mmol) of $CoMe(PMe_3)_4$ in THF were combined with 1.35 g (392 mmol) of (3-diphenylphosphino)-2-thionaphthol to give 900 mg of red brown crystals of 10 which were crystallized from ether at -27 °C.

Yield: 900 mg (43% th.)

Melting point: > 230 °C

Elemental analysis: $C_{47}H_{42}CoP_3S_2$, M 822.84 g/mol.

| % | C | H | P |
|---|---|---|---|
| Calculated | 68.61 | 5.14 | 11.29 |
| Found | 70.20 | 6.09 | 12.18 |

IR (Nujol, 4000 – 400 $cm^{-1}$):

3048 w ν(H-C=), 1930 m ν(Co – H), 1613 m ν(C=C), 1563 m ν(C=C), 1463 s $\delta_{as}(PCH_3)$, 1443 s $\delta_{as}(PCH_3)$, 1281 m $\delta_s(PCH_3)$, 1092 s δ( Ph), 950 s $\rho_1(PCH_3)$, 885 w $\rho_2(PCH_3)$, 695 vs $\nu_{as}(PC_3)$, 669 w $\nu_s(PC_3)$.

$^1$H NMR (500 MHz, $d_8$-THF, 300 K, ppm) :

δ: 7.91 – 7.8 (m, 4H, CH); 7.7 – 7.6 (m, 6H, CH); 7.5 – 7.4 (m, 5H, CH); 7.4 – 7.3 ( m, 12H, CH); 7.2 -7.1 (m, 5H, CH); 1.09 (d, $^2J$(PH) = 10 Hz, 9H, $PCH_3$); -10,8 (ddd, $^2J$(PH) = 44 Hz, $^2J$(PH) = 40 Hz, $^2J$(PH) = 40 Hz, 1H, CoH); -12.5 (dt, $^2J$(PH) = 50 Hz, $^2J$(PH) = 50 Hz, 1H, CoH).

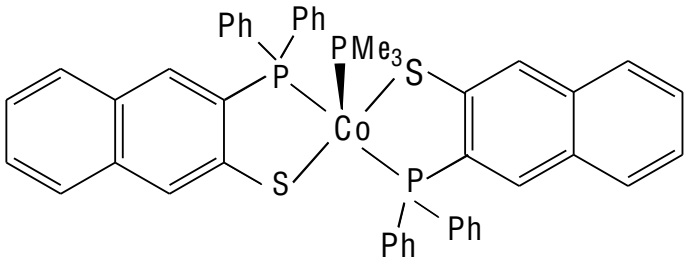
$^{13}$C NMR (125 MHz, $d_8$-THF, 300 K, ppm):

δ: 156.3 (s, C); 139.2 (s, C); 131.1 (d, $^3J$(PC) = 38 Hz, C); 133.0 (d, $^4J$(PC) = 36.5 Hz, C); 130.0 (d, $^2J$(PC) = 21.4 Hz, C); 128.8 (s, C); 128.5 (d, $^3J$(PC) = 13.8 Hz, CH); 128.2 (d, $^2J$(PC) = 5.0 Hz, CH); 127.9 d, $^4J$(PC) = 27.7 Hz, CH); 127.7 (d, $^2J$(PC) = 27.6 Hz, CH); 125.7 (d, $^4J$(PC) = 15.1 Hz, CH); 123.4 (s, C); 122.1 (s, C); 121.3 (s, C); 14.1 (d, $^1J$(PC) = 23.9 Hz, $PCH_3$).

$^{31}$P NMR (202 MHz, $d_8$-THF, 300 K, ppm):

δ: 65.9 (s, 1P, PPh); 63.1 (d, $^2J(P_{Ph}\ P_{Me})$ = 309 Hz, 1P, PPh); 45.4 (s, 1P, PPh); -0.87 (d, $^2J(P_{Me}P_{Ph})$ = 175.2 Hz, 1P, $PMe_3$); - 11.8 (s, 1P, $PMe_3$).

### 3.6.11 *trans*-Bis{(3-diphenylphosphino)-thionaphtholato-[*P,S*]}-(trimethylphosphine)cobalt(II) (11)




Procedure B:

590 mg (1.9 mmol) of $CoMe_2(PMe_3)_3$ in THF were combined with 1.3 g (3.8 mmol) of (3-diphenylphosphino)-2-thionaphthol. After removing all volatile components and washing the solid residue with pentane extraction with ether afforded 1.10 g of 7 as dark brown cubes.

Yield: 58 %

Melting point: 175 – 177 °C (dec. >230 °C)

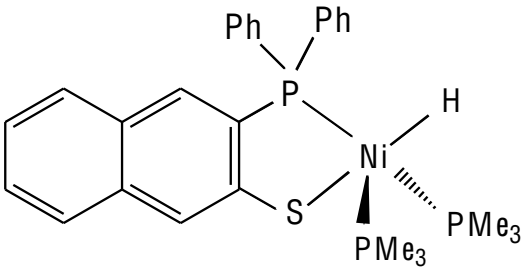
Elemental analysis: $C_{51}H_{51}CoOP_3S_2$, M 895.95 g/mol

| % | C | H | P |
|---|---|---|---|
| Calculated | 68.37 | 5.74 | 10.37 |
| Found | 67.68 | 5. 49 | 11.23 |

IR (Nujol, 4000 – 400 $cm^{-1}$):

3056 w ν(H-C), 1615 m ν(C=C), 1566 m ν(C=C), 1436 vs $\delta_{as}(PCH_3)$, 1411 vs $\delta_{as}(PCH_3)$, 1288 w $\delta_s(PCH_3)$, 1094 s δ(PPh), 950 s $\rho_1(PCH_3)$, 870 w $\rho_2(PCH_3)$, 698 vs $\nu_{as}(PC_3)$, 669 w $\nu_s(PC_3)$.

### 3.6.12 Hydrido-(3-diphenylphosphino)-2-thionaphtholato-[P, S]-bis (trimethylphosphine)nickel(II) (12)




Procedure C:

430 mg (1.18 mmol) of $Ni(PMe_3)_4$ in ether were combined with 408 mg (1.18 mmol) of (3-diphenylphosphino)-2-thionaphthol in the presence of a five-fold excess of trimethylphosphine (500 mg). Filtration and crystallization at -27 °C afforded 560 mg of 12. The main part was collected as light red powder a few red crystals.

Yield: 42 %

Melting point: 273 – 275 °C (dec. > 270 °C)

Elemental analysis: $C_{28}H_{35}NiP_3S$, M 554.71 g/mol

| % | C | H | P | S |
|---|---|---|---|---|
| Calculated | 60.63 | 6.36 | 16.75 | 5.78 |
| Found | 60.13 | 6.95 | 16.81 | 5.56 |

IR (Nujol, 4000 – 400 $cm^{-1}$):

3054w ν(H-C=), 1883 s ν(Ni-H), 1617 s ν(C=C), 1564 s ν(C=C), 1463 vs $\delta_{as}(PCH_3)$, 1435 s $\delta_{as}(PCH_3)$, 1300 s $\delta_s(PCH_3)$, 1092 s δ(PPh), 845 m $\rho_2(PCH_3)$, 943 vs $\rho_1(PCH_3)$, 698 s $\nu_{as}(PC_3)$, 664 m $\nu_s(PC_3)$.

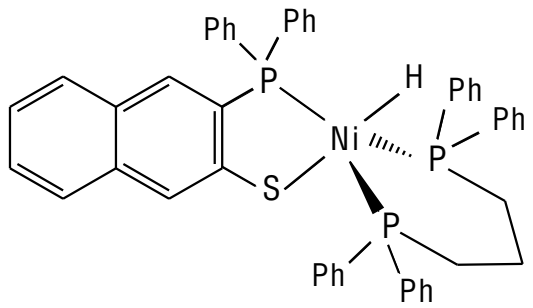
$^1$H NMR (500 MHz, $d_8$-THF, 190 K, ppm):

δ : 7. 73 – 7. 24 (m, 16H, CH); 1.01(s, 18H, $PCH_3$); -19.91(dt, $^2J$(PH) = 40 Hz, $^2J$(PH) = 50 Hz, 1H, NiH).

$^{31}$P NMR (202 MHz, $d_8$-THF, 190 K, ppm):

δ: 47.5 (dd, $^2J(P_{Ph}P_{Me})$ =152 Hz, $^2J(P_{Ph}P_{Me})$ =35.4 Hz, 1P, PPh); - 22.0 (dd, $^2J(P_{Me}P_{Ph})$ = 152 Hz, $^2J(P_{Me}P_{Ph})$ = 35.4 Hz, 2P, PMe).

### 3.6.13 Hydrido-(3-diphenylphosphino)-2-thionaphtholato-[*P,S*]-[bis(diphenylphosphino)propane]nickel(II) (13)




Procedure C:

620 mg (1.71 mmol) of $Ni(PMe_3)_4$ in THF were combined with 590 mg (1.71 mmol) of (3-diphenylphosphino)-2-thionaphthol in the presence of 650 mg of trimethylphosphine. After 30 min. 700 mg (1.71 mmol) of dppp was added at

20°C. The volatiles were removed and the residue was washed with pentane to afford 1.2 g of **13** as orange powder.

**Yield:** 63 %

**Melting point:** > 112°C (dec.)

**Elemental analysis:** $C_{49}H_{43}NiP_3S$, M 815.56 g/mol

| % | C | H | P |
|---|---|---|---|
| Calculated | 72.22 | 5.31 | 11.39 |
| Found | 71.98 | 4.94 | 11.61 |

**IR** (Nujol, 4000 – 400 $cm^{-1}$):

3051w ν(H-C=);1924 m ν(Ni-H);1616 s ν(C=C); 1571 s ν(C=C);1097 vs δ(Ph).

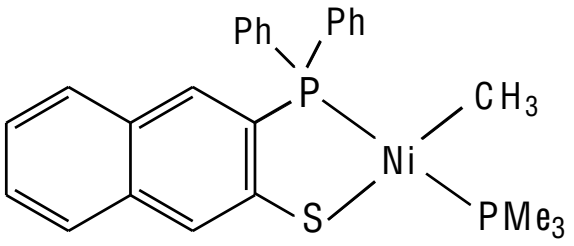
**$^1$H NMR** (500 MHz, $d_8$-THF, 300 K, ppm):

δ: 7.64- 6.86 (m, 36 H, CH);1.24 - 0.97(m, 6H, $CH_2$); -17.0(dt,$^2J$(PH) = 50 Hz, $^2J$(PH) = 25 Hz, 1H, Ni-H).

**$^{31}$P NMR** (202 Hz, $d_8$-THF, 300 K, ppm):

δ: 52.3 (t, $^2J(P_{Ph}P_{Me})$ = 118 Hz, 1P, PPh); 6.5 (d, $^2J(P_{Me}P_{Ph})$ =118 Hz, 2P, PPh).

### 3.6.14 *trans*-Methyl{(3-diphenylphosphino)-2-thionaphtholato-[*P,S*]}-(trimethylphosphine)-nickel(II) (14)




**Procedure C:**

700 mg (1.94 mmol) of $[Ni(OMe)Me(PMe_3)]_2$ in THF were combined with 1.31 g (3.80 mmol) of (3-diphenylphosphino)-2-thionaphthol. After 10 min. the solvent was removed in vacuo and the residue was extracted with pentane. Crystallization at room temperature afforded 880 mg of **14** as orange prismatic rods.

**Yield:** 44 %

**Melting point:** 139 – 142°C

**Elemental analysis:** $C_{26}H_{28}NiP_2S$, M 493.21 g/mol.

| % | C | H | P | S |
|---|---|---|---|---|
| Calculated | 63.31 | 5.72 | 12.56 | 6.50 |
| Found | 63.69 | 5.31 | 11.67 | 6.77 |

IR (Nujol, 4000 – 400 $cm^{-1}$):

3050 m ν(H-C=), 1615 w ν(C=C), 1570 w ν(C=C), 1435 vs $\delta_{as}(PCH_3)$, 1417 vs $\delta_{as}(PCH_3)$, 1305 m $\delta_s(PCH_3)$, 1219 m $\delta(NiCH_3)$, 1096 s δ(PPh), 950 vs $\rho_1(PCH_2)$, 870 w $\rho_2(PCH_2)$, 693 s ν(PC).

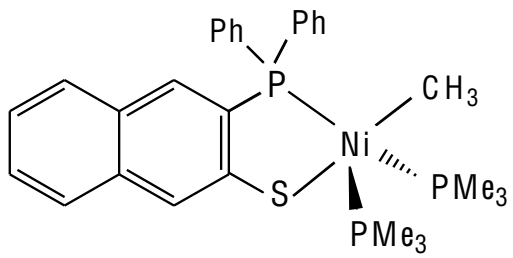
$^1$H NMR (500 MHz, $d_8$-THF, 190 K, ppm):

δ: 7.60–7.52 (m, 4H, CH); 7.39–7.31 (m, 9H, CH); 7.28–7.26 (m, 2H, CH); 7.19 (m, 1H, CH); 1.08 (d, $^2J$(PH) = 7,0 Hz, 9H, $PCH_3$); - 0.29 (d, $^3J$(PH) = 10,5 Hz, 3H, $NiCH_3$).

$^{31}$P NMR (202 MHz, $d_8$-THF, 190 K, ppm):

δ: 50.0 (d, ,$^2J(P_{Ph}P_{Me})$ = 34.4 Hz, 1P, PPh); -21.9 (d, $^2J$ $(P_{Me}P_{Ph})$ = 45.5 Hz, 1P, PMe); -22.7 (d, $^2J(P_{Me}P_{Ph})$ = 45.5 Hz, 1P, PMe).

### 3.6. 15 Methyl-(3-diphenylphosphino)-2-thionaphtholato-[*P, S*]-bis (trimethylphosphine)nickel(II) (15)




Procedure C:

720 mg (2.3 mmol) of $NiMe_2(PMe_3)_3$ in THF were combined with 790 mg (2.3 mmol) of (3-diphenylphosphino)-2-thionaphthol. After 10 min. the solvent was removed in vacuo and the residue was extracted with pentane containing 600 mg of trimethylphosphine to afford 890 mg of complex 15 as dark red crystals.

**Yield:** 59 %

**Melting point:** 101 – 103 °C

**Elemental analysis:** $C_{29}H_{37}NiP_3S$, M 569.29 g/mol

| % | C | H | P | S |
|---|---|---|---|---|
| Calculated | 61.18 | 6.55 | 16.34 | 5.64 |
| Found | 60.63 | 6.47 | 17.09 | 4.98 |

**IR** (Nujol, 4000 – 400 $cm^{-1}$):

3054 w ν(H-C=), 1612 w ν(C=C), 1566 w ν(C=C), 1430 w $\delta_{as}(PCH_3)$, 1303 w $\delta_s(PCH_3)$, 1222 m δ(NiMe), 1093 m $\rho_1$(PPh), 942 vs $\rho_1(PCH_3)$, 871 w $\rho_2(PCH_3)$, 697 s $\nu_{as}(PC_3)$, 666 w $\nu_s(PC_3)$.

**$^1$H NMR** (500 MHz, $d_8$-THF, 190 K, ppm):

δ: 7.8 (s, 1H, CH); 7.45 – 7.6 (m, 8H, CH); 7.37 – 7.32 (m, 4H, CH); 7.30 – 7.1 (m, 3H, CH); 1.1 (d, $^2J$(PH) = 7 Hz, 18H, $PCH_3$); -0.20 (d, $^3J$(PH) = 10 Hz, 3H, $NiCH_3$).

**$^{13}$C NMR** (125 MHz, $d_8$-THF, 190 K, ppm):

δ: 156.5 (s, C); 155.7 (d, $^3J$(PC) = 45.3 Hz, C); 139.7 (d, $^1J$(PC) = 46.5 Hz, C); 135.6 (d, $^2J$(PC) = 25.2 Hz, C); 134.2 (s, CH); 131.8 (d, $^3J$(PC) = 11.3 Hz, CH); 128.4 (d, $^2J$(PC) = 40.2 Hz, CH); 127.8 (d, $^1J$(PC) = 7.55 Hz, CH); 127.7 (d, $^2J$(PC) = 15.1 Hz, CH); 127.5 (s, C); 126.3 (s, C); 124.7 (s, C); 123.3 (d, $^4J$(PC) = 11.3 Hz, CH); 122.0 (s, C); 23.8 (d, $^1J$(PC) = 20.1 Hz, $PCH_3$); 13.8 (d, $^1J$(PC) = 11.3 Hz, $PCH_3$); -10.6 (d, $^2J$(PC) = 18.9 Hz, $NiCH_3$).

$^{31}$P NMR (202 MHz, $d_8$-THF, 190 K, ppm):

δ: 36.9 (s, 1P, PPh); -25.3 (s, 2P, $PMe_3$).

# 4 Summary

The work submitted here is concerned with the synthesis and characterization of new [*P,S*]-chelate complexes of the iron, cobalt and nickel, supported by trimethylphosphine ligands and with an investigation of chemical responses of these systems. Among the new compounds of these metals are stable hydrido and methyl metal compounds in low and high oxidation states which are of particular interest as models for homogeneous catalysis.

## [*P, S*]-chelate-iron(II) complexes

Formulae and reaction pattern of the new [*P,S*]-iron(II) compounds are shown in Fig. 4.1. A hydridoiron(II) species **1** is smoothly generated by reaction of $Fe(PMe_3)_4$ with (3-diphenylphosphino)-2-thionaphthol through an oxidative substitution of a trimethylphosphine ligand. The molecular structure shows the iron atom attain a *mer*-octahedral coordination geometry.

Introducing carbon monoxide as strong π-acceptor ligand preserves the Fe-H function, and the respective hydrido(carbonyl)-iron(II) complex is accessible in two isomeric forms **2a**, **2b**. CO-insertion is not observed. The reaction of **1** with iodomethane proceeds with elimination of methane and yields the iodo-iron (II) derivative**3**.Starting from $Fe(CO)_2(PMe_3)_3$the reaction with (3-diphenylphosphino)-2-thionaphthol selectively furnishes an octahedral bischelate-iron(II) compound **4**, which is diamagnetic. Monitoring this reaction by means of $^1H$ NMR spectroscopy no indication of a hydridoiron(II) intermediate was obtained. The bischelate-iron(II) complex **5** which is generated by reacting a dimethyl iron complex with two equivalents of (3-diphenylphosphino) 2-thionaphthol remains penta-coordinate and paramagnetic even in the presence of a fivefold excess of trimethylphosphine which is probably due to steric congestion.

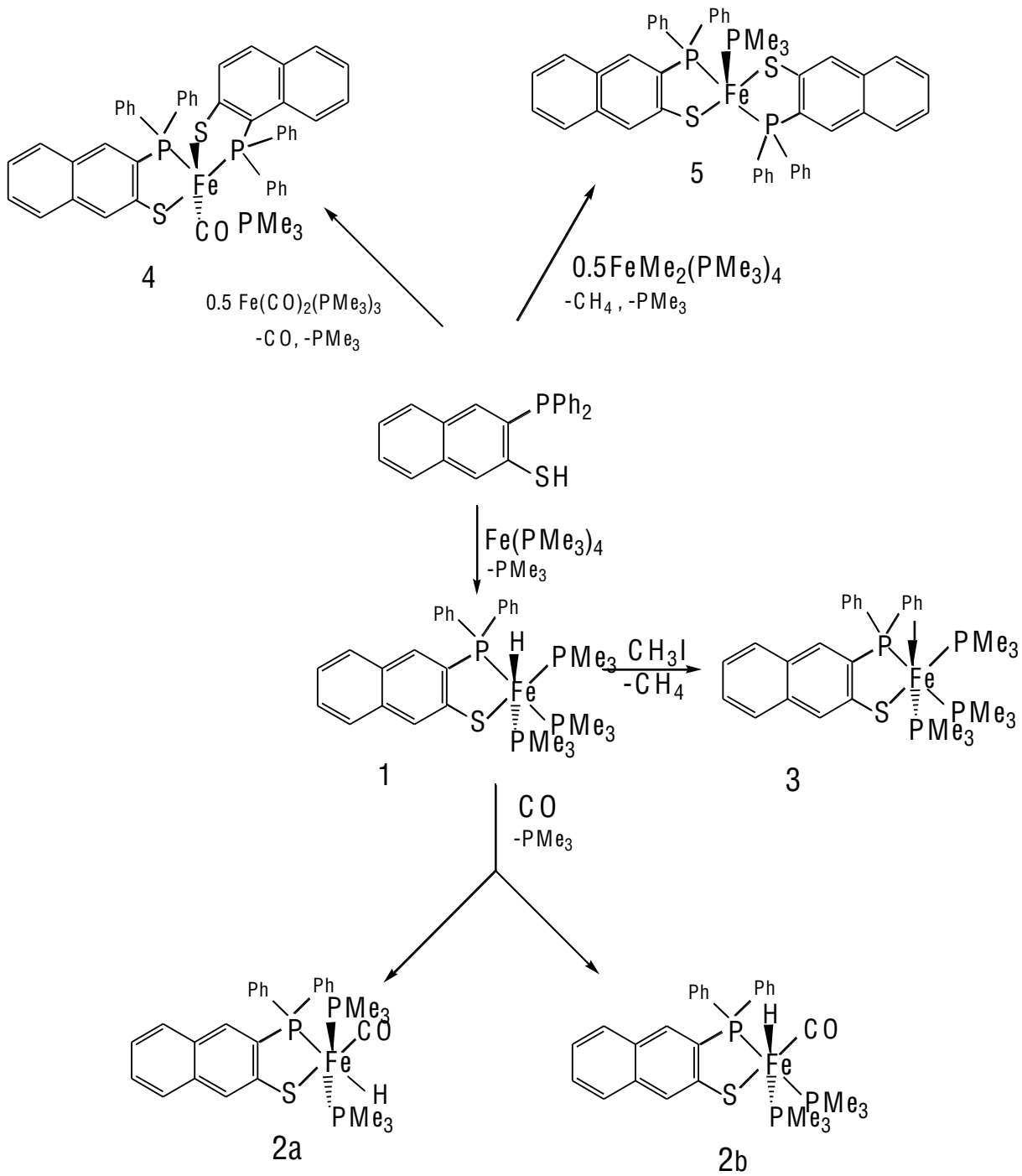



Fig.4.1 Reaction scheme of [*P, S*]-iron (II) complexes

## [*P,S*]-chelate-cobalt complexes in oxidation states II and III

An overview of the new thiophenolato-cobalt complexes is given in the reaction scheme (Fig. 4.2).

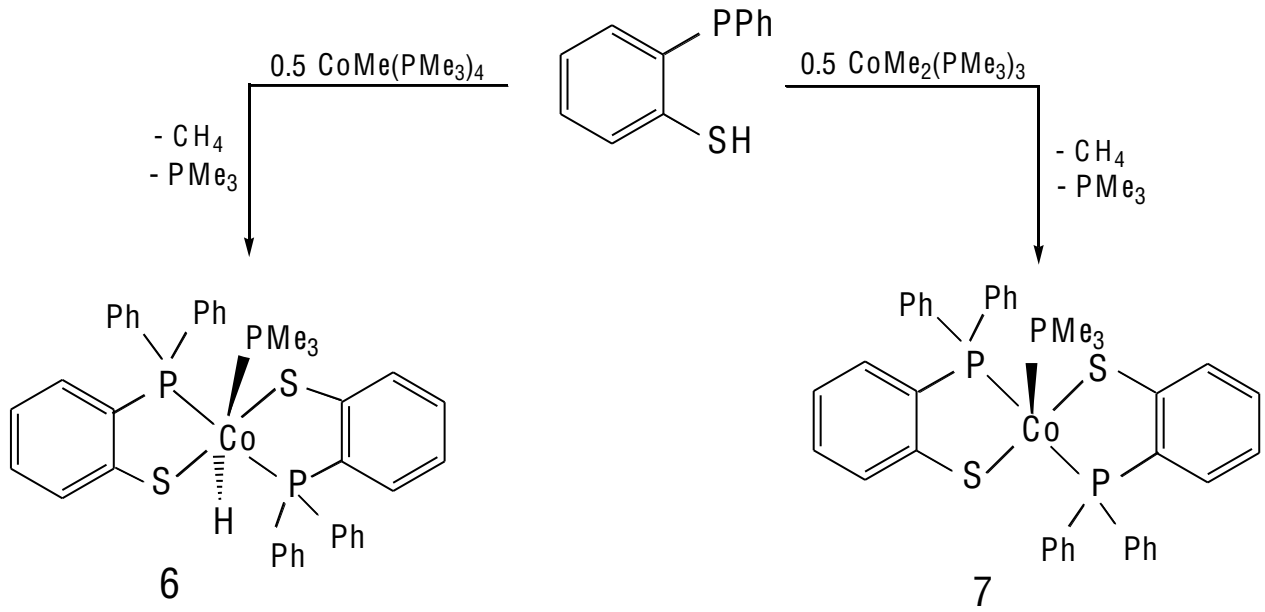



Fig. 4.2 Reaction scheme of thiophenolato cobalt complexes

The hydridocobalt (III) complex **6** is obtained from a reaction of $CoMe(PMe_3)_4$ with two equivalents of chelating thiophenol. The octahedral coordination geometry in the molecular structure of **6** is formed in two steps: the first proceeds via oxidative addition with elimination of methane and the second as addition only (Fig. 4.3).

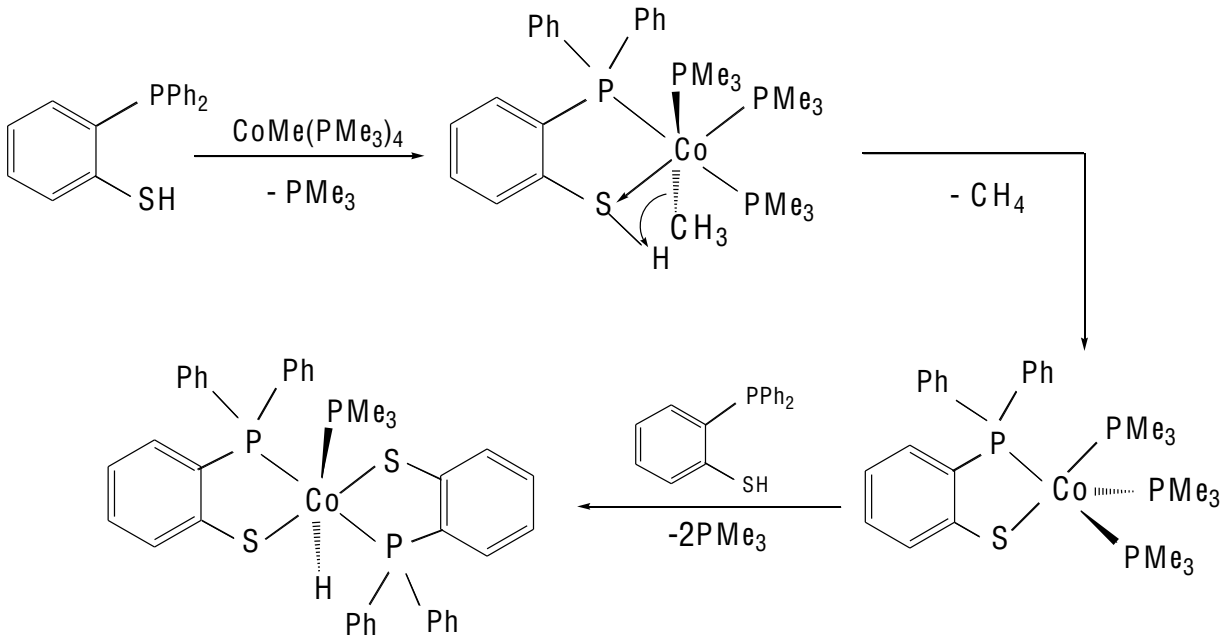



Fig.4.3 Reaction mechanism for the formation of 6 from $CoMe(PMe_3)_4$

$CoMe_2(PMe_3)_4$ is a useful starting material giving access to the paramagnetic bischelate-cobalt(II) 7 which as found in 6 attains a *trans*-configuration of the bischelate unit in its molecular structure. The chelating thionaphtholato ligand shows similar reactivity and is particularly suited in the synthesis of the methylcobalt complex 8 (Fig. 4.4). A second and more elegant access is provided by the reaction of $Co(PMe_3)_4$ with(2-diphenylphosphino)-(3-methylthio) naphthalene that involves the first oxidative addition of an aromatic $SCH_3$ substituent to a cobalt(0) center.

The *trans*-bis(chelate-[*P,S*])cobalt(II) complex 9 was successfully synthesized from $CoMe_2(PMe_3)_3$ and (2-diphenylphosphino)-thiophenol in ether with good yield and attains a square pyramidal coordination geometry as in the molecular structure of the derivative 11 with coordinated trimethylphosphine. In a two step reaction as with thiophenol the thionaphtholato ligand provides a hydrido-bischelate-cobalt(III) compound 10 by reaction of $CoMe(PMe_3)_4$ with (3-diphenylphosphino)-2-thionaphthol in ether (Fig. 4.4).

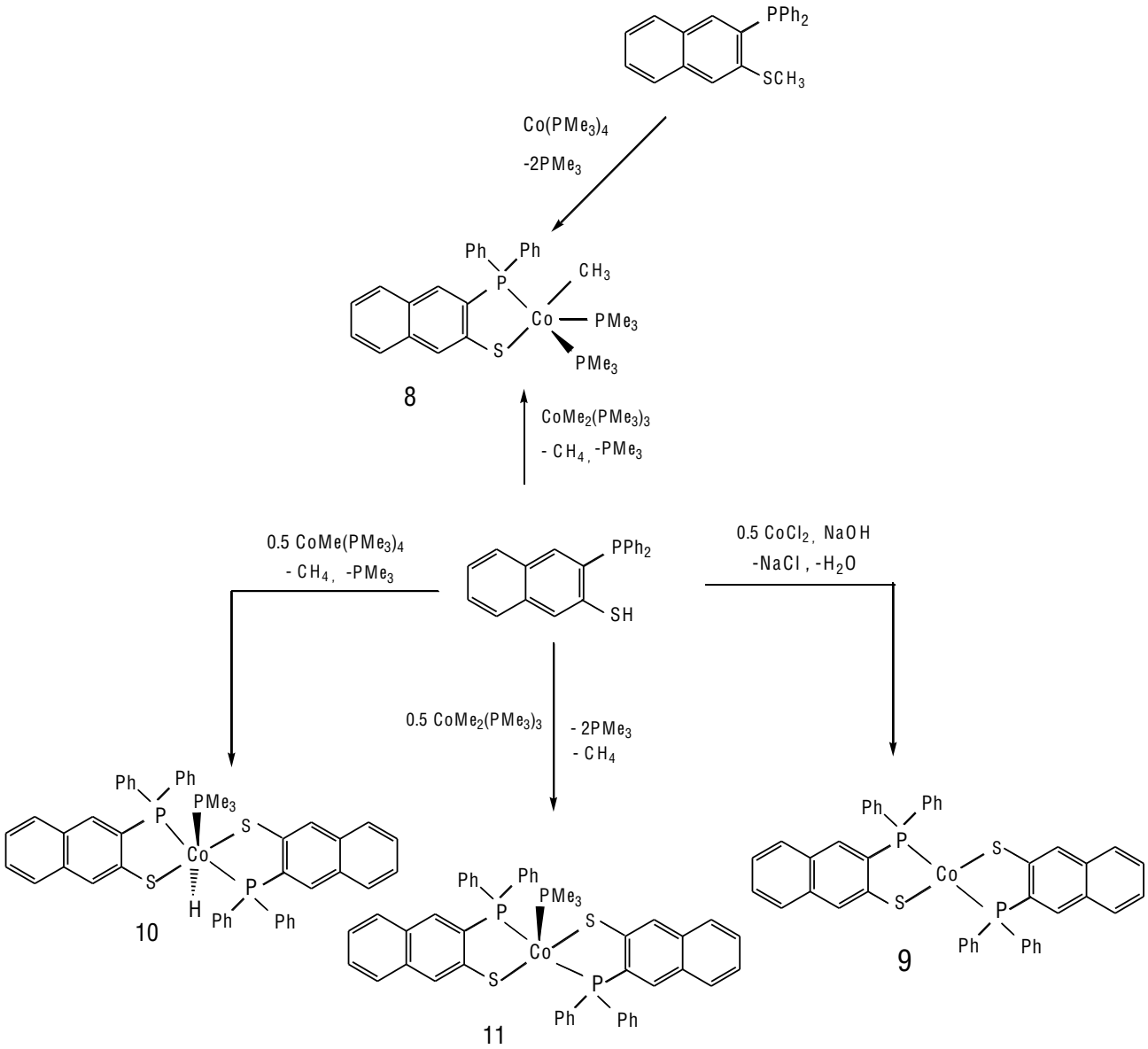



Fig.4.4 Reaction scheme of thionaphtholato cobalt complexes

## [*P, S*]-chelate-nickel(II) complexes

The new [*P,S*]-nickel(II) complexes are presented in the reaction scheme (Fig. 4.5).

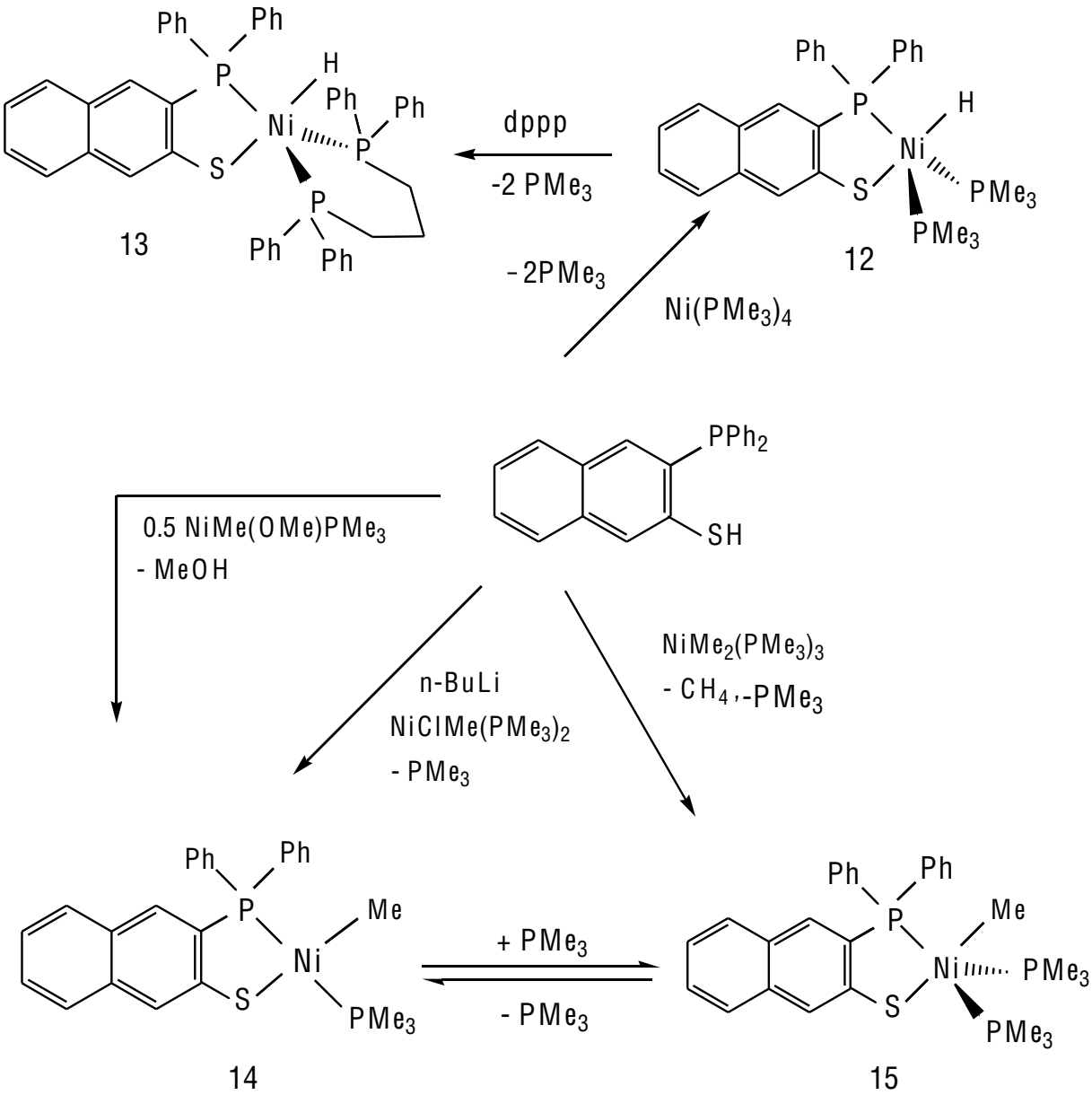



Fig. 4.5 Reaction scheme of [*P,S*]- nickel (II) complexes

By reaction of $Ni(PMe_3)_4$ with (3-diphenylphosphino)-2-thionaphthol in the presence of a fivefold excess of trimethylphosphine, the sufficiently stable hydridonickel (II) complex 12 was synthesized and characterized by NMR.

Without free phosphine in solution 12 decomposes rapidly. This property is not altered after substitution with the chelating 1,3-bis(diphenylphosphino) -propane ligand in a derivative 13 (Fig.4.5), From dimethylnickel educts and (3-diphenylphosphino)-2-thionaphthol a pair of methyl-[*P,S*]-chelate-nickel(II) complexes 14 and 15 is obtained where the S-donor stabilizes the trans-$NiCH_3$ group.

# 5 Zusammenfassung

Die hier vorgelegte Arbeit beschreibt Synthesen und Charakterisierung neuer [*P,S*]-chelate von Eisen, Cobalt und Nickel, die von Trimethylphosphin-Liganden gestützt werden, und die Untersuchung derchemischen Eigenschaften dieser Systeme. Unter den neuen Verbindungen ragen stabile Hydrido- und Methylmetall-Komplexe in hohen und niedrigen Oxidationsstufen heraus, die als Modellverbindungen für die Homogene Katalyse von besonderem Interesse sind.

## [*P,S*]-Chelat-eisen(II) –Komplexe

Strukturformeln und ein Reaktionsschema für die neuen [*P,S*]-eisen(II)-Verbindungen zeigt Abb.5.1. Eine Hydridoeisen(II)-spezies 1 wird glatt gebildet in der Reaktion von $Fe(PMe_3)_4$ mit (3-diphenylphosphino)-2-thionaphthol durch eine oxidative Substitution eines Trimethylphosphin- Liganden durch die S-H Funktion. In der Molekülstruktur nimmt das Eisen eine *mer*-oktaedrische Koordinationsgeometrie an.

Führt man durch Substitution CO als starken π-Akzeptor-Liganden ein, dann bleibt die Fe-H Funktion erhalten, und ein strukturell entsprechender Hydrido(carbonyl)eisen-Komplex entsteht in zwei isomeren Formen 2a, 2b. CO-Insertion wird nicht beobachtet. Die Reaktion von 1 mit Iodomethan verläuft mit Eliminierung von Methan und ergibt das Iodo-Derivat 3. Ausgehend von $Fe(CO)_2(PMe_3)_3$ führt die Reaktion selektiv zu einer oktaedrischen Bischelat-eisen(II)-Verbindung 4, die diamagnetisch ist. Beim Verfolgen der Reaktion mittels $^1$H-NMR-Spektroskopie wird kein Hinweis auf ein Hydridoeisen(II)-Intermediat erhalten. Der Bischelat-eisen(II)-Komplex 5, den die Reaktion einer Dimethyleisen-Verbindung mit zwei Moläquivalenten von (3-Diphenylphosphino)-2-thionaphthol liefert, bleibt pentakoordiniert und

paramagnetisch selbst mit fünffachem Überschuss an Trimethylphosphin, wofür eine hohe sterische Belastung der Grund sein dürfte.

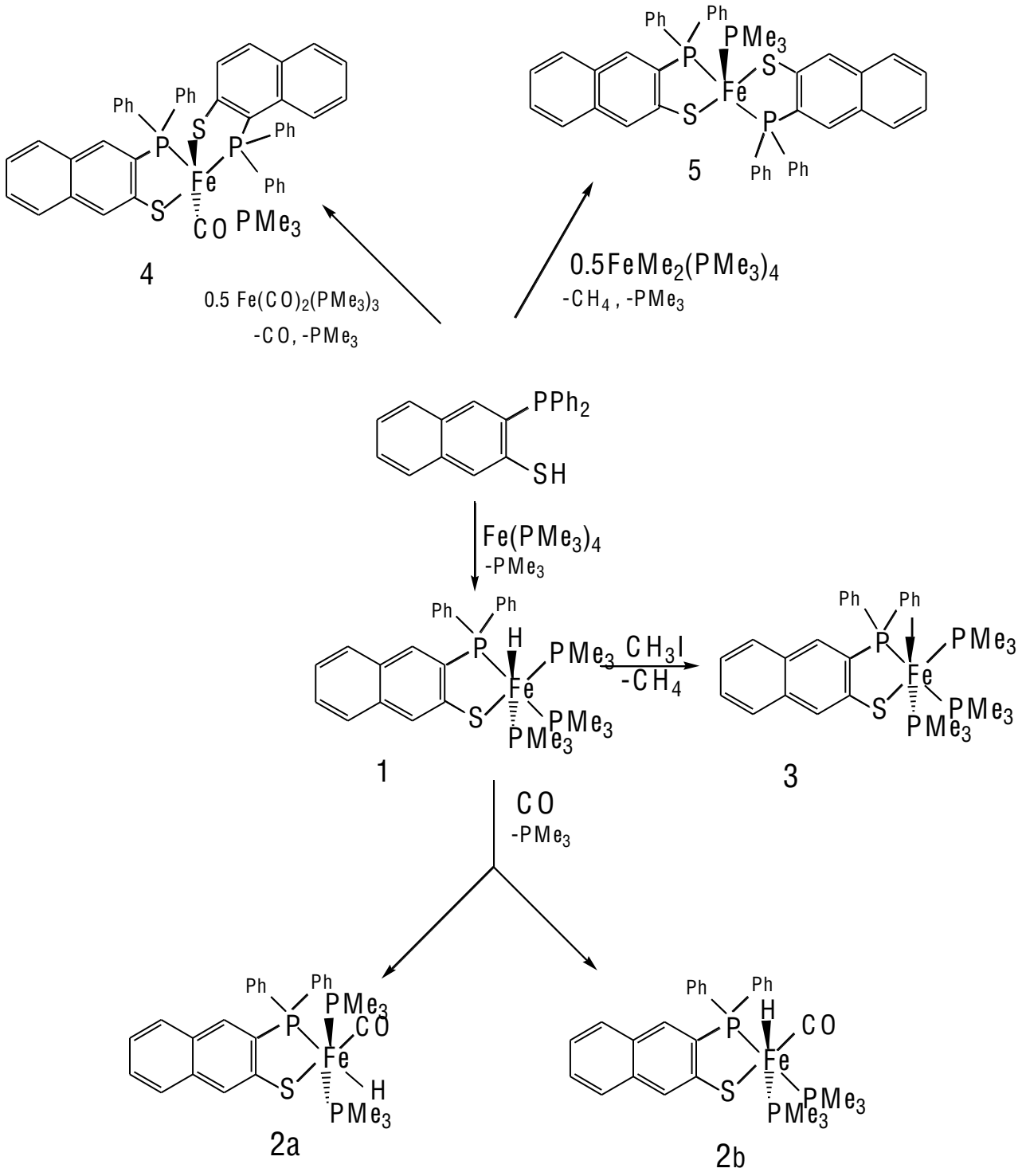



Abb.5.1Reaktionsschema der [*P,S*]-Eisen(II)-Komplexe

## [*P, S*]-Chelat-Cobalt-Komplexe in den Oxidationsstufen II und III

Eine Übersicht der neuen Thiophenolato-Cobalt-Komplexe gibt ein Reaktionsschema (Abb.5.2).

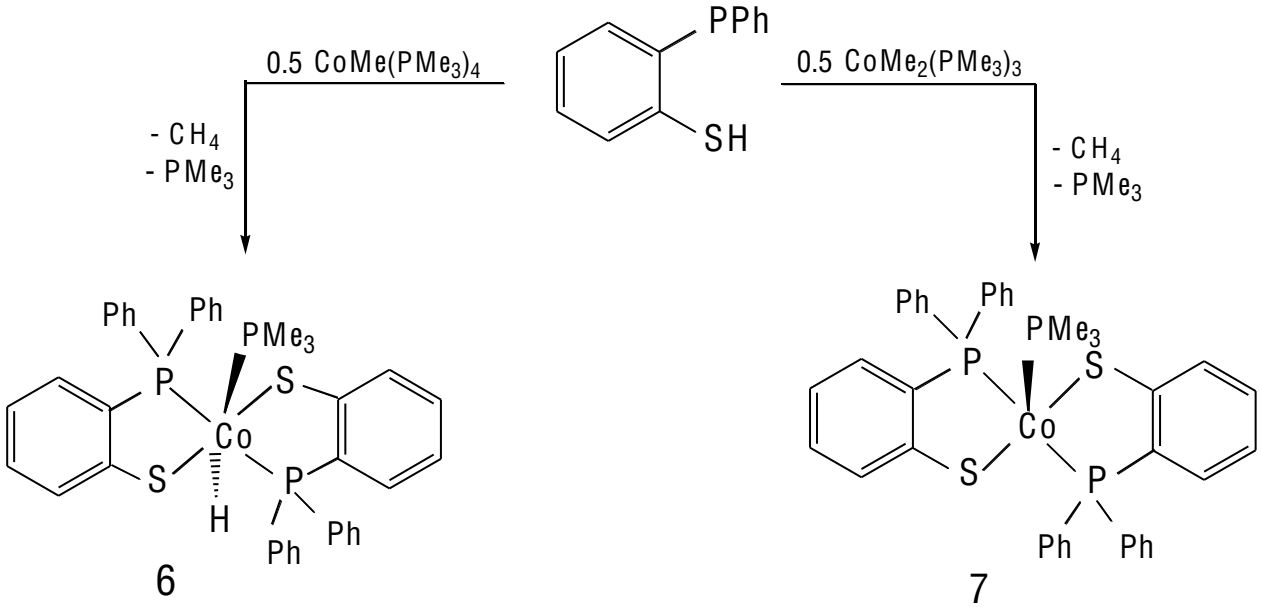



Abb.5.2 Reaktionsschema Thiophenolato cobalt-Komplexe

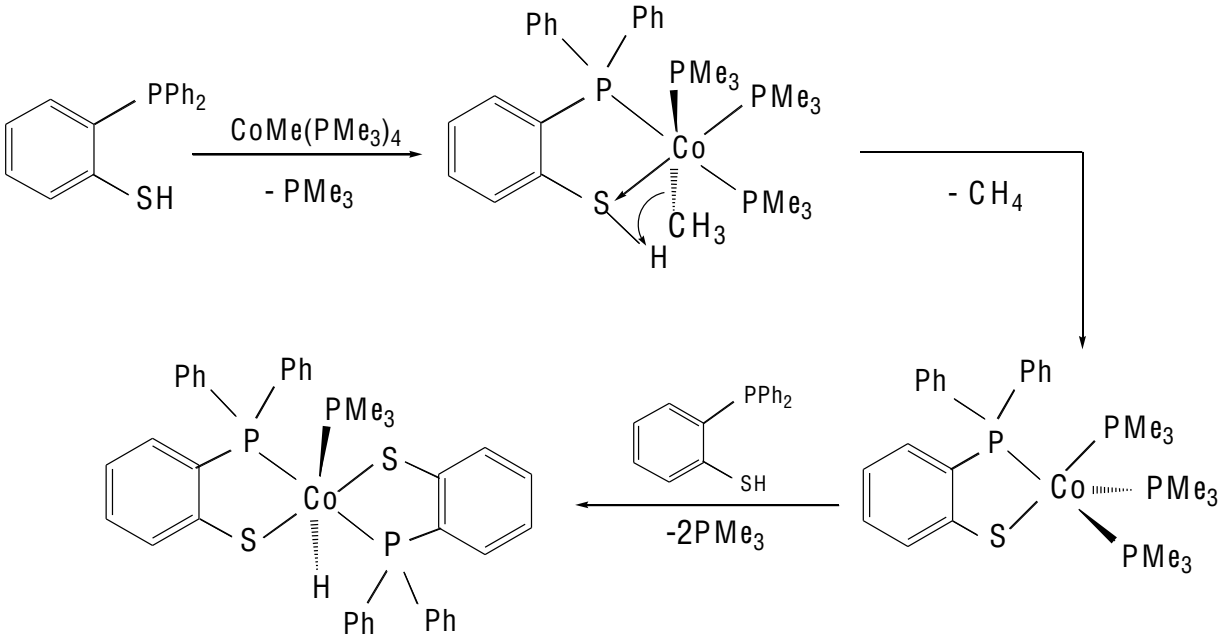



Abb.5.3Reaktionsmechanismus für die Bildung von 6 aus $CoMe(PMe_3)_4$

Der Hydridocobalt(III)-Komplex 6 entsteht in einer Reaktion von $CoMe(PMe_3)_4$ mit zwei Moläquivalenten des chelatisierenden Thiophenols. Die oktaedrische Koordination in der Molekülstruktur von 6 bildet sich in zwei Schritten aus: der erste verläuft unter oxidativer Addition mit Eliminierung von Methan und der zweite nur unter Addition (Abb.5.3).$CoMe_2(PMe_3)_4$ ist eine nützliche Ausgangsverbindung für den Zugang zu dem paramagnetischen Bischelat-Cobalt-Komplex 7, der in seiner Molekülstruktur eine *trans*-Konfiguration der Bischelat-Einheit annimmt, die auch in 6 gefunden wurde. Der chelatisierende Thionaphtholato-Ligand zeigt eine ähnliche Reaktivität und eignet sich besonders für die Synthese des Methylcobalt-Komplexes 8 (Abb.5.4). Einen zweiten und viel eleganteren Zugang ermöglicht die Reaktion von $Co(PMe_3)_4$ mit(2-Diphenylphosphino)-(3-methylthio)naphthalin, die erstmals die oxidative Addition eines aromatischen $SCH_3$-Substituenten an einem Cobalt(0)- zentrum demonstriert.

Eine Darstellung des *trans*-Bis(chelat-[*P,S*])cobalt(II)-Komplexes 9 gelang ausgehend von $CoMe_2(PMe_3)_3$ und (2-Diphenylphosphino)-thiophenol in Ether in hohen Ausbeuten. Dieser enthält eine quadratisch pyramidale Koordinationsgeometrie wie in der Molekülstruktur des Derivates 11, das einen zusätzlichen Trimethylphosphin-Liganden enthält. In einer zweistufigen Reaktion wie mit dem Thiophenol liefert auch der Naphtholato-Ligand einen Hydrido(bischelat)cobalt(III)-Komplex 10 durch Reaktion von $CoMe(PMe_3)_4$ mit (3-Diphenylphosphino)-2-thionaphthol in Ether (Abb.5.4).

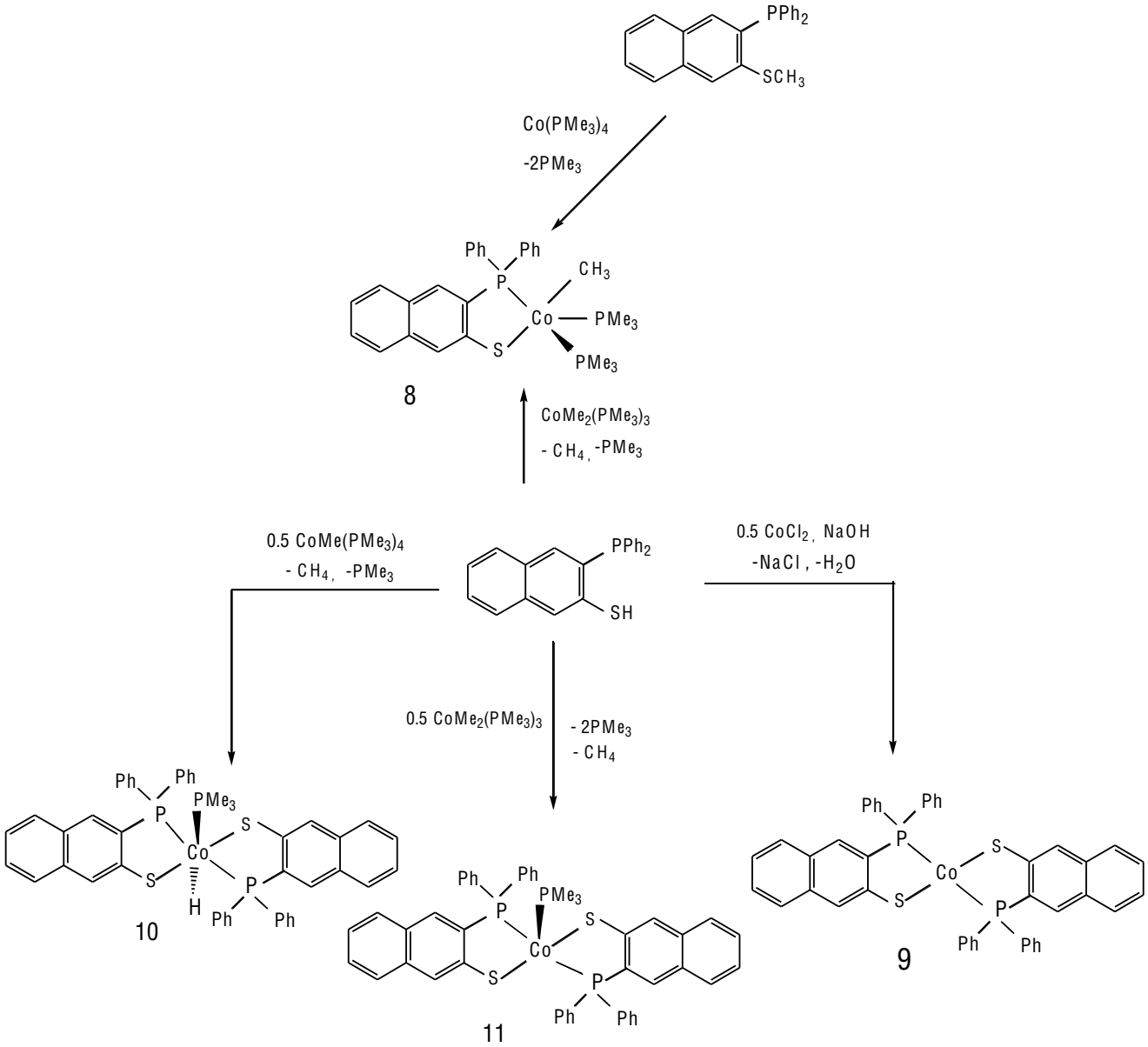



Abb.5.4 Reaktionsschema der Thionaphtholatocobalt-Komplexe

# [*P, S*]-Chelat-Nickel(II)-Komplexe

Die neuen [*P,S*]-Nickel(II)-Komplexe sind in einem Reaktionsschema zusammengefasst (Abb.5.5).

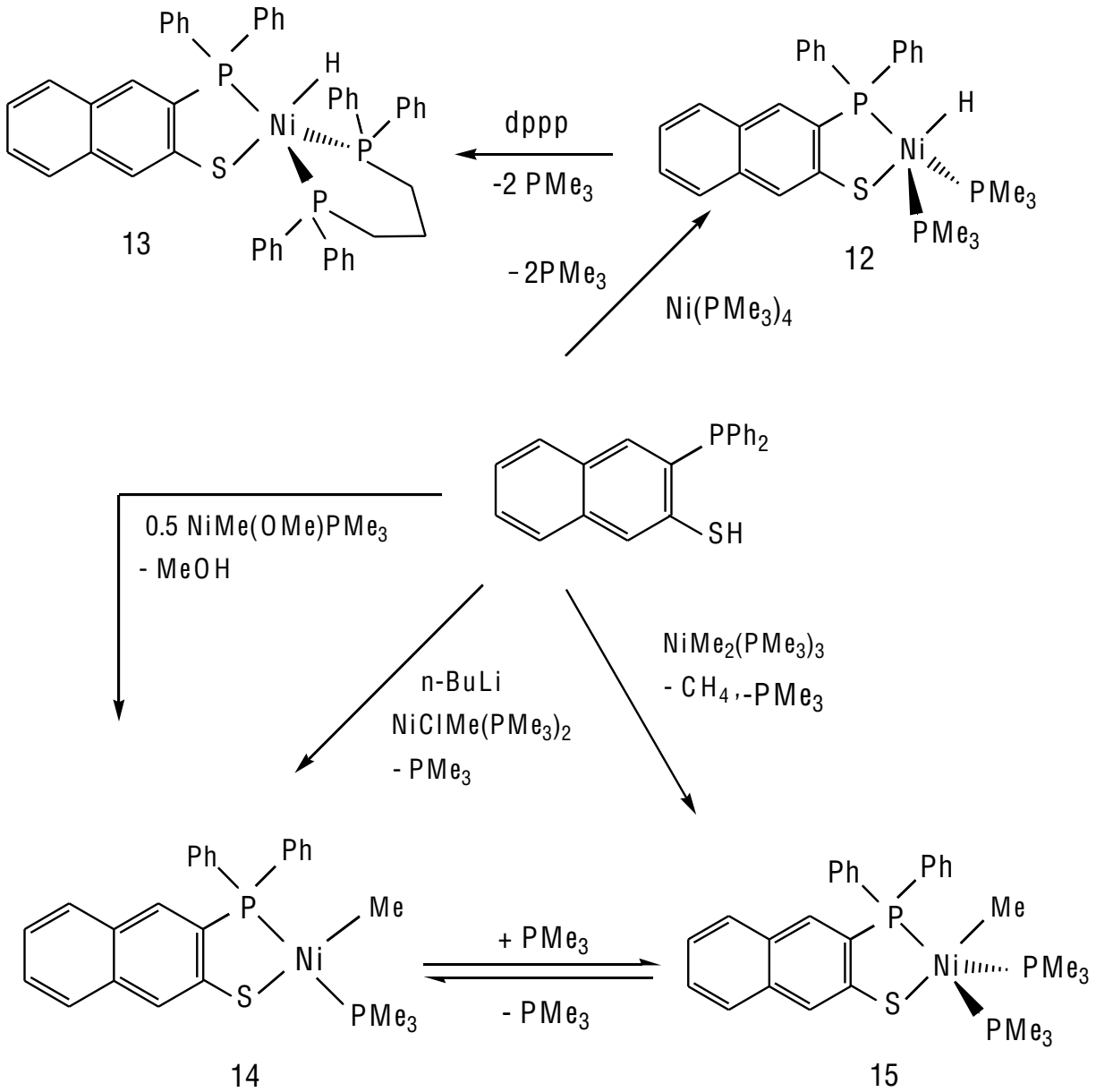



Abb.5.5 Reaktionsschema für [*P,S*]- Nickel(II)-Komplexe

Durch Reaktion von $Ni(PMe_3)_4$ mit (3-Diphenylphosphino)-2-thionaphthol in Gegenwart eines fünffachen Überschusses von Trimethylphosphin wird der

hinreichend stabile Hydridonickel-Komlex 12 synthetisiert und mit NMR-Spektroskopie charakterisiert. In Abwesenheit von freiem Trimethylphosphin zersetzt sich 12 in Lösung rasch. An dieser Eigenschaft ändert sich wenig, wenn man die einzähnigen Phosphine durch das chelatisierende 1,3 (Diphenylphosphino)propan im Derivat 13 ersetzt (Abb.5.5). Ausgehend von Dimethylnickel-Edukten and (3-Diphenylphosphino)-2-thionaphthol wird das Paar von Methyl-[*P, S*]-chelat-nickel(II)-Complexen 14 and 15 erhalten, in denen der S-Donor die *trans*-ständige $NiCH_3$-Gruppe stabilisiert.

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# 8 SUPPLEMENTRY DATA

## 8.1 Crystallographic data of 2

### 8.1.1 Crystal data and structure refinement

| | | |
|---|---|---|
| Empirical formula | C29 H35 Fe O P3 S | |
| Formula weight | 580.39 | |
| Temperature | 100(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P21/c | |
| Unit cell dimensions | a = 9.1746(3) Å | α = 90 º. |
| | b = 17.827(6) Å | β =97.776(4)º. |
| | c = 17.2726(7) | γ = 90 º. |
| Volume | 2799.0(10) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.377 $Mg/m^3$ | |
| Absorption coefficient | 0.806 $mm^{-1}$ | |
| F (000) | 1216 | |
| Crystal size | 0.28 x 0.16 x 0.16 mm | |
| Theta range for data collection | 2.24 to 26.37º. | |
| Index ranges | -11<=h<=9, -21<=k<=22, -21<=l<=19 | |
| Reflections collected | 21039 | |
| Independent reflections | 5710 [R (int) = 0.0266] | |
| Completeness to 2theta = 26.37º | 99.9% | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 5710 / 0 / 320 | |
| Goodness-of-fit on $F^2$ | 1.044 | |
| Final R indices [I>2sigma (I)] | R1 = 0.0284, wR2 = 0.0692 | |
| R indices (all data) | R1 = 0.0453, wR2 = 0.0787 | |

Largest diff. peak and hole 0.392 and -0.307 e. Å-3

## 8.1.2 Atomic coordinates (x 10^4) and equivalent isotropic Displacement parameters (A^2 x 10^3)

| | x | y | z | U(eq) |
|---|---|---|---|---|
| C(1) | 6236(2) | 776(1) | 6692(1) | 15(1) |
| C(2) | 5105(2) | 641(1) | 6090(1) | 17(1) |
| C(3) | 4490(2) | 1214(1) | 5589(1) | 16(1) |
| C(4) | 3323(2) | 1084(1) | 4969(1) | 23(1) |
| C(5) | 2764(2) | 1658(1) | 4495(1) | 25(1) |
| C(6) | 3334(2) | 2390(1) | 4603(1) | 22(1) |
| C(7) | 4454(2) | 2538(1) | 5186(1) | 18(1) |
| C(8) | 5060(2) | 1957(1) | 5694(1) | 16(1) |
| C(9) | 6215(2) | 2090(1) | 6307(1) | 14(1) |
| C(10) | 6806(2) | 1523(1) | 6801(1) | 14(1) |
| C(11) | 9810(2) | 2113(1) | 7180(1) | 13(1) |
| C(12) | 9730(2) | 2372(1) | 6418(1) | 18(1) |
| C(13) | 10948(2) | 2713(1) | 6156(1) | 22(1) |
| C(14) | 12243(2) | 2803(1) | 6656(1) | 21(1) |
| C(15) | 12340(2) | 2542(1) | 7415(1) | 21(1) |
| C(16) | 11142(2) | 2196(1) | 7671(1) | 18(1) |
| C(17) | 7743(2) | 2437(1) | 8201(1) | 13(1) |
| C(18) | 6472(2) | 2865(1) | 8014(1) | 16(1) |
| C(19) | 6135(2) | 3447(1) | 8499(1) | 20(1) |
| C(20) | 7064(2) | 3612(1) | 9173(1) | 20(1) |
| C(21) | 8338(2) | 3193(1) | 9368(1) | 20(1) |
| C(22) | 8664(2) | 2606(1) | 8893(1) | 17(1) |
| C(23) | 10193(2) | 832(1) | 8882(1) | 16(1) |
| C(24) | 12264(2) | 269(1) | 7656(2) | 29(1) |
| C(25) | 10045(3) | 319(1) | 6360(1) | 26(1) |
| C(26) | 10292(2) | -929(1) | 7379(1) | 23(1) |
| C(27) | 7755(2) | 871(1) | 10006(1) | 20(1) |
| C(28) | 6367(2) | -365(1) | 9169(1) | 19(1) |
| C(29) | 5450(2) | 1110(1) | 8766(1) | 19(1) |
| O(1) | 11160(2) | 1004(1) | 9363(1) | 24(1) |
| P(1) | 8295(1) | 1646(1) | 7603(1) | 11(1) |
| P(2) | 10307(1) | 89(1) | 7401(1) | 16(1) |
| P(3) | 7130(1) | 560(1) | 9007(1) | 14(1) |
| S(1) | 6933(1) | 33(1) | 7302(1) | 15(1) |
| Fe(1) | 8785(1) | 552(1) | 8182(1) | 12(1) |

## 8.1.3 Bond lengths [Å] and angles [°]

| | |
|---|---|
| C(1)-C(2) | 1.386(3) |
| C(1)-C(10) | 1.434(3) |
| C(1)-S(1) | 1.758(2) |
| C(2)-C(3) | 1.407(3) |
| C(2)-H(2) | 0.9500 |
| C(3)-C(8) | 1.426(3) |
| C(3)-C(4) | 1.427(3) |
| C(4)-C(5) | 1.366(3) |
| C(4)-H(4) | 0.9500 |
| C(5)-C(6) | 1.410(3) |
| C(5)-H(5) | 0.9500 |
| C(6)-C(7) | 1.363(3) |
| C(6)-H(6) | 0.9500 |
| C(7)-C(8) | 1.422(3) |
| C(7)-H(7) | 0.9500 |
| C(8)-C(9) | 1.413(3) |
| C(9)-C(10) | 1.385(3) |
| C(9)-H(9) | 0.9500 |
| C(10)-P(1) | 1.8229(19) |
| C(11)-C(12) | 1.388(3) |
| C(11)-C(16) | 1.398(3) |
| C(11)-P(1) | 1.8529(19) |
| C(12)-C(13) | 1.400(3) |
| C(12)-H(12) | 0.9500 |
| C(13)-C(14) | 1.380(3) |
| C(13)-H(13) | 0.9500 |
| C(14)-C(15) | 1.384(3) |
| C(14)-H(14) | 0.9500 |
| C(15)-C(16) | 1.383(3) |
| C(15)-H(15) | 0.9500 |
| C(16)-H(16) | 0.9500 |
| C(17)-C(18) | 1.394(3) |
| C(17)-C(22) | 1.399(3) |
| C(17)-P(1) | 1.859(2) |
| C(18)-C(19) | 1.395(3) |
| C(18)-H(18) | 0.9500 |
| C(19)-C(20) | 1.377(3) |
| C(19)-H(19) | 0.9500 |
| C(20)-C(21) | 1.389(3) |
| C(20)-H(20) | 0.9500 |
| C(21)-C(22) | 1.387(3) |
| C(21)-H(21) | 0.9500 |
| C(22)-H(22) | 0.9500 |
| C(23)-O(1) | 1.171(2) |
| C(23)-Fe(1) | 1.720(2) |
| C(24)-P(2) | 1.818(2) |
| C(24)-H(24A) | 0.9800 |
| C(24)-H(24B) | 0.9800 |
| C(24)-H(24C) | 0.9800 |
| C(25)-P(2) | 1.828(2) |
| C(25)-H(25A) | 0.9800 |
| C(25)-H(25B) | 0.9800 |
| C(25)-H(25C) | 0.9800 |
| C(26)-P(2) | 1.814(2) |
| C(26)-H(26A) | 0.9800 |
| C(26)-H(26B) | 0.9800 |
| C(26)-H(26C) | 0.9800 |

| | |
|---|---|
| C(27)-P(3) | 1.830(2) |
| C(27)-H(27A) | 0.9800 |
| C(27)-H(27B) | 0.9800 |
| C(27)-H(27C) | 0.9800 |
| C(28)-P(3) | 1.827(2) |
| C(28)-H(28A) | 0.9800 |
| C(28)-H(28B) | 0.9800 |
| C(28)-H(28C) | 0.9800 |
| C(29)-P(3) | 1.826(2) |
| C(29)-H(29A) | 0.9800 |
| C(29)-H(29B) | 0.9800 |
| C(29)-H(29C) | 0.9800 |
| P(1)-Fe(1) | 2.2109(8) |
| P(2)-Fe(1) | 2.2278(6) |
| P(3)-Fe(1) | 2.2177(6) |
| S(1)-Fe(1) | 2.3141(6) |
| Fe(1)-H(1) | 1.42(3) |

| | |
|---|---|
| C(2)-C(1)-C(10) | 118.83(17) |
| C(2)-C(1)-S(1) | 119.54(15) |
| C(10)-C(1)-S(1) | 121.63(14) |
| C(1)-C(2)-C(3) | 122.22(19) |
| C(1)-C(2)-H(2) | 118.9 |
| C(3)-C(2)-H(2) | 118.9 |
| C(2)-C(3)-C(8) | 119.02(18) |
| C(2)-C(3)-C(4) | 122.81(19) |
| C(8)-C(3)-C(4) | 118.17(18) |
| C(5)-C(4)-C(3) | 120.7(2) |
| C(5)-C(4)-H(4) | 119.7 |
| C(3)-C(4)-H(4) | 119.7 |
| C(4)-C(5)-C(6) | 120.9(2) |
| C(4)-C(5)-H(5) | 119.6 |
| C(6)-C(5)-H(5) | 119.6 |
| C(7)-C(6)-C(5) | 120.33(19) |
| C(7)-C(6)-H(6) | 119.8 |
| C(5)-C(6)-H(6) | 119.8 |
| C(6)-C(7)-C(8) | 120.6(2) |
| C(6)-C(7)-H(7) | 119.7 |
| C(8)-C(7)-H(7) | 119.7 |
| C(9)-C(8)-C(7) | 122.08(18) |
| C(9)-C(8)-C(3) | 118.49(17) |
| C(7)-C(8)-C(3) | 119.43(18) |
| C(10)-C(9)-C(8) | 122.01(18) |
| C(10)-C(9)-H(9) | 119.0 |
| C(8)-C(9)-H(9) | 119.0 |
| C(9)-C(10)-C(1) | 119.43(17) |
| C(9)-C(10)-P(1) | 124.83(15) |
| C(1)-C(10)-P(1) | 115.74(14) |
| C(12)-C(11)-C(16) | 118.02(18) |
| C(12)-C(11)-P(1) | 125.26(15) |
| C(16)-C(11)-P(1) | 116.71(14) |
| C(11)-C(12)-C(13) | 120.58(19) |
| C(11)-C(12)-H(12) | 119.7 |
| C(13)-C(12)-H(12) | 119.7 |
| C(14)-C(13)-C(12) | 120.40(19) |
| C(14)-C(13)-H(13) | 119.8 |
| C(12)-C(13)-H(13) | 119.8 |
| C(13)-C(14)-C(15) | 119.55(19) |
| C(13)-C(14)-H(14) | 120.2 |
| C(15)-C(14)-H(14) | 120.2 |
| C(16)-C(15)-C(14) | 120.0(2) |

| | |
|---|---|
| C(16)-C(15)-H(15) | 120.0 |
| C(14)-C(15)-H(15) | 120.0 |
| C(15)-C(16)-C(11) | 121.40(19) |
| C(15)-C(16)-H(16) | 119.3 |
| C(11)-C(16)-H(16) | 119.3 |
| C(18)-C(17)-C(22) | 118.03(18) |
| C(18)-C(17)-P(1) | 124.65(15) |
| C(22)-C(17)-P(1) | 117.32(14) |
| C(17)-C(18)-C(19) | 120.97(19) |
| C(17)-C(18)-H(18) | 119.5 |
| C(19)-C(18)-H(18) | 119.5 |
| C(20)-C(19)-C(18) | 120.18(19) |
| C(20)-C(19)-H(19) | 119.9 |
| C(18)-C(19)-H(19) | 119.9 |
| C(19)-C(20)-C(21) | 119.69(19) |
| C(19)-C(20)-H(20) | 120.2 |
| C(21)-C(20)-H(20) | 120.2 |
| C(22)-C(21)-C(20) | 120.2(2) |
| C(22)-C(21)-H(21) | 119.9 |
| C(20)-C(21)-H(21) | 119.9 |
| C(21)-C(22)-C(17) | 120.92(19) |
| C(21)-C(22)-H(22) | 119.5 |
| C(17)-C(22)-H(22) | 119.5 |
| O(1)-C(23)-Fe(1) | 178.32(18) |
| P(2)-C(24)-H(24A) | 109.5 |
| P(2)-C(24)-H(24B) | 109.5 |
| H(24A)-C(24)-H(24B) | 109.5 |
| P(2)-C(24)-H(24C) | 109.5 |
| H(24A)-C(24)-H(24C) | 109.5 |
| H(24B)-C(24)-H(24C) | 109.5 |
| P(2)-C(25)-H(25A) | 109.5 |
| P(2)-C(25)-H(25B) | 109.5 |
| H(25A)-C(25)-H(25B) | 109.5 |
| P(2)-C(25)-H(25C) | 109.5 |
| H(25A)-C(25)-H(25C) | 109.5 |
| H(25B)-C(25)-H(25C) | 109.5 |
| P(2)-C(26)-H(26A) | 109.5 |
| P(2)-C(26)-H(26B) | 109.5 |
| H(26A)-C(26)-H(26B) | 109.5 |
| P(2)-C(26)-H(26C) | 109.5 |
| H(26A)-C(26)-H(26C) | 109.5 |
| H(26B)-C(26)-H(26C) | 109.5 |
| P(3)-C(27)-H(27A) | 109.5 |
| P(3)-C(27)-H(27B) | 109.5 |
| H(27A)-C(27)-H(27B) | 109.5 |
| P(3)-C(27)-H(27C) | 109.5 |
| H(27A)-C(27)-H(27C) | 109.5 |
| H(27B)-C(27)-H(27C) | 109.5 |
| P(3)-C(28)-H(28A) | 109.5 |
| P(3)-C(28)-H(28B) | 109.5 |
| H(28A)-C(28)-H(28B) | 109.5 |
| P(3)-C(28)-H(28C) | 109.5 |
| H(28A)-C(28)-H(28C) | 109.5 |
| H(28B)-C(28)-H(28C) | 109.5 |
| P(3)-C(29)-H(29A) | 109.5 |
| P(3)-C(29)-H(29B) | 109.5 |
| H(29A)-C(29)-H(29B) | 109.5 |
| P(3)-C(29)-H(29C) | 109.5 |
| H(29A)-C(29)-H(29C) | 109.5 |
| H(29B)-C(29)-H(29C) | 109.5 |
| C(10)-P(1)-C(11) | 106.21(9) |

| | |
|---|---|
| C(10)-P(1)-C(17) | 106.34(9) |
| C(11)-P(1)-C(17) | 98.87(8) |
| C(10)-P(1)-Fe(1) | 108.85(7) |
| C(11)-P(1)-Fe(1) | 117.21(6) |
| C(17)-P(1)-Fe(1) | 118.18(6) |
| C(26)-P(2)-C(24) | 100.75(11) |
| C(26)-P(2)-C(25) | 101.79(10) |
| C(24)-P(2)-C(25) | 101.11(12) |
| C(26)-P(2)-Fe(1) | 112.29(7) |
| C(24)-P(2)-Fe(1) | 117.86(8) |
| C(25)-P(2)-Fe(1) | 120.16(7) |
| C(29)-P(3)-C(28) | 100.99(10) |
| C(29)-P(3)-C(27) | 101.49(10) |
| C(28)-P(3)-C(27) | 101.90(10) |
| C(29)-P(3)-Fe(1) | 119.16(7) |
| C(28)-P(3)-Fe(1) | 113.74(7) |
| C(27)-P(3)-Fe(1) | 116.94(7) |
| C(1)-S(1)-Fe(1) | 105.54(7) |
| C(23)-Fe(1)-P(1) | 98.56(7) |
| C(23)-Fe(1)-P(3) | 93.51(7) |
| P(1)-Fe(1)-P(3) | 99.79(2) |
| C(23)-Fe(1)-P(2) | 93.46(7) |
| P(1)-Fe(1)-P(2) | 99.14(2) |
| P(3)-Fe(1)-P(2) | 158.60(2) |
| C(23)-Fe(1)-S(1) | 173.21(7) |
| P(1)-Fe(1)-S(1) | 88.24(2) |
| P(3)-Fe(1)-S(1) | 85.35(2) |
| P(2)-Fe(1)-S(1) | 85.34(2) |
| C(23)-Fe(1)-H(1) | 86.3(11) |
| P(1)-Fe(1)-H(1) | 174.7(11) |
| P(3)-Fe(1)-H(1) | 81.9(11) |
| P(2)-Fe(1)-H(1) | 78.4(11) |
| S(1)-Fe(1)-H(1) | 86.9(11) |

### 8.1.4 Anisotropic displacement parameters (A^2 x 10^3)

| | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| C(1) | 15(1) | 15(1) | 14(1) | 0(1) | 2(1) | 2(1) |
| C(2) | 17(1) | 16(1) | 19(1) | -2(1) | 1(1) | -3(1) |
| C(3) | 14(1) | 21(1) | 13(1) | 0(1) | 1(1) | -1(1) |
| C(4) | 21(1) | 25(1) | 21(1) | -1(1) | -3(1) | -5(1) |
| C(5) | 19(1) | 34(1) | 19(1) | -1(1) | -6(1) | -1(1) |
| C(6) | 21(1) | 27(1) | 17(1) | 6(1) | 1(1) | 6(1) |
| C(7) | 21(1) | 18(1) | 15(1) | 2(1) | 4(1) | 2(1) |
| C(8) | 15(1) | 19(1) | 14(1) | -1(1) | 3(1) | 2(1) |
| C(9) | 15(1) | 13(1) | 15(1) | 0(1) | 1(1) | -1(1) |
| C(10) | 13(1) | 16(1) | 12(1) | -1(1) | 2(1) | -1(1) |
| C(11) | 15(1) | 7(1) | 16(1) | -3(1) | 3(1) | 0(1) |
| C(12) | 19(1) | 20(1) | 15(1) | 0(1) | 2(1) | -1(1) |
| C(13) | 26(1) | 24(1) | 18(1) | 3(1) | 9(1) | -1(1) |
| C(14) | 19(1) | 20(1) | 28(1) | 1(1) | 11(1) | -4(1) |
| C(15) | 15(1) | 22(1) | 26(1) | -2(1) | 1(1) | -2(1) |
| C(16) | 21(1) | 16(1) | 17(1) | 2(1) | 1(1) | -2(1) |
| C(17) | 16(1) | 10(1) | 14(1) | 1(1) | 5(1) | -3(1) |
| C(18) | 15(1) | 15(1) | 19(1) | -1(1) | 2(1) | -2(1) |
| C(19) | 18(1) | 16(1) | 28(1) | 1(1) | 9(1) | 4(1) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(20) | 30(1) | 12(1) | 21(1) | -4(1) | 12(1) | 1(1) |
| C(21) | 32(1) | 15(1) | 13(1) | -1(1) | 3(1) | -1(1) |
| C(22) | 20(1) | 14(1) | 17(1) | 4(1) | 4(1) | 2(1) |
| C(23) | 19(1) | 12(1) | 18(1) | 4(1) | 4(1) | 1(1) |
| C(24) | 17(1) | 26(1) | 46(2) | -10(1) | 10(1) | 0(1) |
| C(25) | 37(1) | 22(1) | 22(1) | 1(1) | 13(1) | 7(1) |
| C(26) | 29(1) | 14(1) | 28(1) | -2(1) | 10(1) | 4(1) |
| C(27) | 25(1) | 21(1) | 15(1) | -2(1) | 3(1) | -2(1) |
| C(28) | 23(1) | 16(1) | 19(1) | 1(1) | 6(1) | -1(1) |
| C(29) | 17(1) | 20(1) | 21(1) | 2(1) | 7(1) | -1(1) |
| O(1) | 23(1) | 24(1) | 23(1) | 1(1) | -8(1) | -3(1) |
| P(1) | 12(1) | 10(1) | 12(1) | 0(1) | 0(1) | -1(1) |
| P(2) | 17(1) | 12(1) | 19(1) | -1(1) | 5(1) | 0(1) |
| P(3) | 16(1) | 13(1) | 14(1) | 1(1) | 3(1) | -1(1) |
| S(1) | 17(1) | 11(1) | 15(1) | 1(1) | -2(1) | -2(1) |
| Fe(1) | 13(1) | 10(1) | 12(1) | 0(1) | 1(1) | 0(1) |

## 8.1.5 Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3).

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(2) | 4734 | 146 | 6014 | 21 |
| H(4) | 2931 | 593 | 4885 | 27 |
| H(5) | 1981 | 1562 | 4088 | 30 |
| H(6) | 2936 | 2783 | 4267 | 26 |
| H(7) | 4833 | 3033 | 5253 | 21 |
| H(9) | 6598 | 2584 | 6382 | 17 |
| H(12) | 8840 | 2318 | 6071 | 22 |
| H(13) | 10883 | 2883 | 5631 | 26 |
| H(14) | 13062 | 3044 | 6479 | 25 |
| H(15) | 13230 | 2599 | 7761 | 25 |
| H(16) | 11226 | 2012 | 8191 | 22 |
| H(18) | 5827 | 2759 | 7549 | 20 |
| H(19) | 5261 | 3732 | 8365 | 24 |
| H(20) | 6835 | 4009 | 9502 | 24 |
| H(21) | 8988 | 3309 | 9829 | 24 |
| H(22) | 9524 | 2315 | 9038 | 20 |
| H(24A) | 12471 | 795 | 7548 | 35 |
| H(24B) | 12821 | -56 | 7344 | 35 |
| H(24C) | 12556 | 165 | 8212 | 35 |
| H(25A) | 10668 | -7 | 6087 | 31 |
| H(25B) | 10315 | 844 | 6291 | 31 |
| H(25C) | 9011 | 242 | 6146 | 31 |
| H(26A) | 10703 | -1123 | 7894 | 28 |
| H(26B) | 10887 | -1106 | 6986 | 28 |
| H(26C) | 9279 | -1107 | 7247 | 28 |
| H(27A) | 8489 | 517 | 10258 | 24 |
| H(27B) | 6916 | 891 | 10301 | 24 |
| H(27C) | 8196 | 1370 | 9994 | 24 |
| H(28A) | 5568 | -314 | 9489 | 23 |
| H(28B) | 7140 | -686 | 9441 | 23 |
| H(28C) | 5985 | -592 | 8666 | 23 |
| H(29A) | 5689 | 1645 | 8805 | 23 |
| H(29B) | 4758 | 986 | 9132 | 23 |

| | | | | |
|---|---|---|---|---|
| H(29C) | 5002 | 992 | 8232 | 23 |
| H(1) | 9040(30) | -185(15) | 8490(16) | 51(8) |

## 8.2 Crystallographic data of 6

### 8.2.1 Crystal data and structure refinement

| | | |
|---|---|---|
| Empirical formula | C39 H38 Co P3 S2 | |
| Formula weight | 722.65 | |
| Temperature | 301(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P21/c | |
| Unit cell dimensions | a = 10.324(3) Å | α = 90º. |
| | b = 37.315(9) Å | β = 115.93(2)º. |
| | c = 10.237(2) Å | γ = 90º. |
| Volume | 3546.7(15) $Å^3$ | |
| Z | 4 | |
| Density (Calculated) | 1.353 Mg/m3 | |
| Absorption coefficient | 0.764 $mm^{-1}$ | |
| F (000) | 1504 | |
| Crystal size | 0.32 x 0.10 x 0.04 mm | |
| Theta range for data collection | 2.40 to 23.26º. | |

| | |
|---|---|
| Index ranges | -11<=h<=11,-41<=k<=41, 11<=l<=11 |
| Reflections collected | 37756 |
| Independent reflections | 5098 [R (int) = 0.1552] |
| Completeness to2theta =23.26 | 99.9% |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 5098 / 0 / 413 |

| | |
|---|---|
| Goodness-of-fit on $F^2$ | 0.955 |
| Final R indices [I>2sigma (I)] | R1 = 0.0552, wR2 = 0.0868 |
| R indices (all data) | R1 = 0.1413, wR2 = 0.1080 |
| Largest diff. peak and hole | 0.497 and -0.304 e. Å-3 |

## 8.2.2 Atomic coordinates (x 10^4) and equivalent isotropic Displacement parameters (A^2 x 10^3)

| | x | y | z | U(eq) |
|---|---|---|---|---|
| C(1) | 11375(5) | 862(1) | 5674(6) | 37(1) |
| C(2) | 12661(6) | 784(2) | 5602(6) | 53(2) |
| C(3) | 13813(6) | 652(2) | 6774(8) | 58(2) |
| C(4) | 13735(6) | 594(2) | 8057(7) | 54(2) |
| C(5) | 12499(6) | 677(1) | 8153(6) | 45(2) |
| C(6) | 11312(5) | 816(1) | 6980(6) | 34(1) |
| C(7) | 9085(5) | 514(2) | 7602(5) | 39(2) |
| C(8) | 9540(6) | 181(2) | 7398(6) | 59(2) |
| C(9) | 9048(7) | -133(2) | 7732(8) | 75(2) |
| C(10) | 8074(7) | -111(2) | 8277(8) | 79(2) |
| C(11) | 7592(7) | 211(2) | 8528(7) | 76(2) |
| C(12) | 8100(6) | 521(2) | 8184(6) | 59(2) |
| C(13) | 10096(5) | 1202(2) | 8639(6) | 37(1) |
| C(14) | 10785(6) | 1050(2) | 10004(7) | 58(2) |
| C(15) | 11217(6) | 1254(2) | 11249(7) | 66(2) |
| C(16) | 10958(7) | 1615(2) | 11153(7) | 64(2) |
| C(17) | 10246(7) | 1770(2) | 9811(8) | 67(2) |
| C(18) | 9824(6) | 1565(2) | 8568(6) | 47(2) |
| C(19) | 6215(5) | 1763(1) | 5184(5) | 37(1) |
| C(20) | 5427(6) | 1968(2) | 5727(6) | 51(2) |
| C(21) | 5138(6) | 2322(2) | 5362(6) | 50(2) |
| C(22) | 5651(6) | 2485(2) | 4464(6) | 49(2) |
| C(23) | 6425(6) | 2286(2) | 3925(6) | 42(2) |
| C(24) | 6731(5) | 1928(2) | 4289(5) | 33(1) |
| C(25) | 6461(6) | 1609(1) | 1648(5) | 36(1) |
| C(26) | 4987(6) | 1672(1) | 1130(6) | 44(2) |
| C(27) | 4064(6) | 1613(2) | -299(7) | 55(2) |
| C(28) | 4564(8) | 1495(2) | -1262(6) | 56(2) |
| C(29) | 6011(8) | 1437(2) | -778(7) | 57(2) |
| C(30) | 6938(6) | 1488(1) | 659(7) | 45(2) |
| C(31) | 9100(6) | 1929(1) | 3580(6) | 34(1) |
| C(32) | 8857(6) | 2173(2) | 2482(6) | 45(2) |
| C(33) | 9900(7) | 2409(2) | 2541(7) | 52(2) |
| C(34) | 11225(8) | 2404(2) | 3700(9) | 66(2) |
| C(35) | 11496(6) | 2163(2) | 4812(7) | 64(2) |
| C(36) | 10452(6) | 1929(2) | 4755(6) | 50(2) |
| C(37) | 5254(11) | 801(2) | 2042(8) | 248(7) |
| C(38) | 5966(8) | 424(2) | 4433(7) | 129(3) |
| C(39) | 7582(11) | 363(3) | 2998(16) | 319(10) |
| P(1) | 9620(1) | 925(1) | 7023(2) | 37(1) |
| P(2) | 7670(1) | 1640(1) | 3571(1) | 35(1) |
| P(3) | 6819(2) | 703(1) | 3611(2) | 58(1) |
| S(1) | 9913(2) | 1019(1) | 4133(2) | 49(1) |

| | | | | |
|---|---|---|---|---|
| S(2) | 6547(2) | 1306(1) | 5648(2) | 48(1) |
| Co(1) | 8246(1) | 1158(1) | 4912(1) | 37(1) |

## 8.2.3 Bond lengths [Å] and angles [°]

| | |
|---|---|
| C(1)-C(6) | 1.377(6) |
| C(1)-C(2) | 1.391(6) |
| C(1)-S(1) | 1.740(5) |
| C(2)-C(3) | 1.360(7) |
| C(2)-H(2) | 0.9300 |
| C(3)-C(4) | 1.367(7) |
| C(3)-H(3) | 0.9300 |
| C(4)-C(5) | 1.358(6) |
| C(4)-H(4) | 0.9300 |
| C(5)-C(6) | 1.388(6) |
| C(5)-H(5) | 0.9300 |
| C(6)-P(1) | 1.812(5) |
| C(7)-C(8) | 1.376(7) |
| C(7)-C(12) | 1.385(6) |
| C(7)-P(1) | 1.815(5) |
| C(8)-C(9) | 1.379(7) |
| C(8)-H(8) | 0.9300 |
| C(9)-C(10) | 1.349(8) |
| C(9)-H(9) | 0.9300 |
| C(10)-C(11) | 1.369(8) |
| C(10)-H(10) | 0.9300 |
| C(11)-C(12) | 1.377(7) |
| C(11)-H(11) | 0.9300 |
| C(12)-H(12) | 0.9300 |
| C(13)-C(18) | 1.378(6) |
| C(13)-C(14) | 1.382(6) |
| C(13)-P(1) | 1.828(5) |
| C(14)-C(15) | 1.380(7) |
| C(14)-H(14) | 0.9300 |
| C(15)-C(16) | 1.368(7) |
| C(15)-H(15) | 0.9300 |
| C(16)-C(17) | 1.370(7) |
| C(16)-H(16) | 0.9300 |
| C(17)-C(18) | 1.380(7) |
| C(17)-H(17) | 0.9300 |
| C(18)-H(18) | 0.9300 |
| C(19)-C(24) | 1.390(6) |
| C(19)-C(20) | 1.398(6) |
| C(19)-S(2) | 1.761(5) |
| C(20)-C(21) | 1.369(7) |
| C(20)-H(20) | 0.9300 |
| C(21)-C(22) | 1.384(7) |
| C(21)-H(21) | 0.9300 |
| C(22)-C(23) | 1.371(6) |
| C(22)-H(22) | 0.9300 |
| C(23)-C(24) | 1.385(6) |
| C(23)-H(23) | 0.9300 |
| C(24)-P(2) | 1.805(5) |
| C(25)-C(30) | 1.382(6) |
| C(25)-C(26) | 1.396(6) |
| C(25)-P(2) | 1.816(5) |
| C(26)-C(27) | 1.370(6) |

| | |
|---|---|
| C(26)-H(26) | 0.9300 |
| C(27)-C(28) | 1.370(7) |
| C(27)-H(27) | 0.9300 |
| C(28)-C(29) | 1.369(7) |
| C(28)-H(28) | 0.9300 |
| C(29)-C(30) | 1.373(7) |
| C(29)-H(29) | 0.9300 |
| C(30)-H(30) | 0.9300 |
| C(31)-C(32) | 1.380(6) |
| C(31)-C(36) | 1.388(6) |
| C(31)-P(2) | 1.826(5) |
| C(32)-C(33) | 1.372(6) |
| C(32)-H(32) | 0.9300 |
| C(33)-C(34) | 1.364(7) |
| C(33)-H(33) | 0.9300 |
| C(34)-C(35) | 1.380(7) |
| C(34)-H(34) | 0.9300 |
| C(35)-C(36) | 1.369(7) |
| C(35)-H(35) | 0.9300 |
| C(36)-H(36) | 0.9300 |
| C(37)-P(3) | 1.747(7) |
| C(37)-H(37A) | 0.9600 |
| C(37)-H(37B) | 0.9600 |
| C(37)-H(37C) | 0.9600 |
| C(38)-P(3) | 1.794(6) |
| C(38)-H(38A) | 0.9600 |
| C(38)-H(38B) | 0.9600 |
| C(38)-H(38C) | 0.9600 |
| C(39)-P(3) | 1.748(7) |
| C(39)-H(39C) | 0.9600 |
| C(39)-H(39B) | 0.9600 |
| C(39)-H(39A) | 0.9600 |
| P(1)-Co(1) | 2.1796(16) |
| P(2)-Co(1) | 2.1830(16) |
| P(3)-Co(1) | 2.2597(18) |
| S(1)-Co(1) | 2.2506(15) |
| S(2)-Co(1) | 2.2598(16) |
| Co(1)-H(1) | 1.31(4) |

| | |
|---|---|
| C(6)-C(1)-C(2) | 118.5(5) |
| C(6)-C(1)-S(1) | 122.0(4) |
| C(2)-C(1)-S(1) | 119.5(4) |
| C(3)-C(2)-C(1) | 121.1(5) |
| C(3)-C(2)-H(2) | 119.5 |
| C(1)-C(2)-H(2) | 119.5 |
| C(2)-C(3)-C(4) | 120.5(5) |
| C(2)-C(3)-H(3) | 119.7 |
| C(4)-C(3)-H(3) | 119.7 |
| C(5)-C(4)-C(3) | 119.0(6) |
| C(5)-C(4)-H(4) | 120.5 |
| C(3)-C(4)-H(4) | 120.5 |
| C(4)-C(5)-C(6) | 121.7(5) |
| C(4)-C(5)-H(5) | 119.2 |
| C(6)-C(5)-H(5) | 119.2 |
| C(1)-C(6)-C(5) | 119.1(5) |
| C(1)-C(6)-P(1) | 116.8(4) |
| C(5)-C(6)-P(1) | 124.0(4) |
| C(8)-C(7)-C(12) | 116.4(5) |
| C(8)-C(7)-P(1) | 122.7(5) |
| C(12)-C(7)-P(1) | 120.7(5) |
| C(7)-C(8)-C(9) | 122.9(6) |

| | |
|---|---|
| C(7)-C(8)-H(8) | 118.5 |
| C(9)-C(8)-H(8) | 118.5 |
| C(10)-C(9)-C(8) | 118.2(6) |
| C(10)-C(9)-H(9) | 120.9 |
| C(8)-C(9)-H(9) | 120.9 |
| C(9)-C(10)-C(11) | 121.9(7) |
| C(9)-C(10)-H(10) | 119.0 |
| C(11)-C(10)-H(10) | 119.0 |
| C(10)-C(11)-C(12) | 118.6(6) |
| C(10)-C(11)-H(11) | 120.7 |
| C(12)-C(11)-H(11) | 120.7 |
| C(11)-C(12)-C(7) | 121.9(6) |
| C(11)-C(12)-H(12) | 119.1 |
| C(7)-C(12)-H(12) | 119.1 |
| C(18)-C(13)-C(14) | 117.4(5) |
| C(18)-C(13)-P(1) | 122.7(5) |
| C(14)-C(13)-P(1) | 119.9(5) |
| C(15)-C(14)-C(13) | 121.5(6) |
| C(15)-C(14)-H(14) | 119.3 |
| C(13)-C(14)-H(14) | 119.3 |
| C(16)-C(15)-C(14) | 120.2(6) |
| C(16)-C(15)-H(15) | 119.9 |
| C(14)-C(15)-H(15) | 119.9 |
| C(15)-C(16)-C(17) | 119.2(6) |
| C(15)-C(16)-H(16) | 120.4 |
| C(17)-C(16)-H(16) | 120.4 |
| C(16)-C(17)-C(18) | 120.4(6) |
| C(16)-C(17)-H(17) | 119.8 |
| C(18)-C(17)-H(17) | 119.8 |
| C(13)-C(18)-C(17) | 121.3(5) |
| C(13)-C(18)-H(18) | 119.4 |
| C(17)-C(18)-H(18) | 119.4 |
| C(24)-C(19)-C(20) | 118.4(5) |
| C(24)-C(19)-S(2) | 121.5(4) |
| C(20)-C(19)-S(2) | 120.2(4) |
| C(21)-C(20)-C(19) | 121.1(5) |
| C(21)-C(20)-H(20) | 119.4 |
| C(19)-C(20)-H(20) | 119.4 |
| C(20)-C(21)-C(22) | 120.1(5) |
| C(20)-C(21)-H(21) | 119.9 |
| C(22)-C(21)-H(21) | 119.9 |
| C(23)-C(22)-C(21) | 119.3(5) |
| C(23)-C(22)-H(22) | 120.3 |
| C(21)-C(22)-H(22) | 120.3 |
| C(22)-C(23)-C(24) | 121.2(5) |
| C(22)-C(23)-H(23) | 119.4 |
| C(24)-C(23)-H(23) | 119.4 |
| C(23)-C(24)-C(19) | 119.8(5) |
| C(23)-C(24)-P(2) | 124.4(4) |
| C(19)-C(24)-P(2) | 115.6(4) |
| C(30)-C(25)-C(26) | 117.1(5) |
| C(30)-C(25)-P(2) | 121.3(4) |
| C(26)-C(25)-P(2) | 121.3(4) |
| C(27)-C(26)-C(25) | 120.8(5) |
| C(27)-C(26)-H(26) | 119.6 |
| C(25)-C(26)-H(26) | 119.6 |
| C(26)-C(27)-C(28) | 121.0(6) |
| C(26)-C(27)-H(27) | 119.5 |
| C(28)-C(27)-H(27) | 119.5 |
| C(29)-C(28)-C(27) | 119.0(6) |
| C(29)-C(28)-H(28) | 120.5 |

| | |
|---|---|
| C(27)-C(28)-H(28) | 120.5 |
| C(28)-C(29)-C(30) | 120.4(6) |
| C(28)-C(29)-H(29) | 119.8 |
| C(30)-C(29)-H(29) | 119.8 |
| C(29)-C(30)-C(25) | 121.7(5) |
| C(29)-C(30)-H(30) | 119.2 |
| C(25)-C(30)-H(30) | 119.2 |
| C(32)-C(31)-C(36) | 117.5(5) |
| C(32)-C(31)-P(2) | 121.8(4) |
| C(36)-C(31)-P(2) | 120.6(4) |
| C(33)-C(32)-C(31) | 121.8(5) |
| C(33)-C(32)-H(32) | 119.1 |
| C(31)-C(32)-H(32) | 119.1 |
| C(34)-C(33)-C(32) | 120.0(6) |
| C(34)-C(33)-H(33) | 120.0 |
| C(32)-C(33)-H(33) | 120.0 |
| C(33)-C(34)-C(35) | 119.4(6) |
| C(33)-C(34)-H(34) | 120.3 |
| C(35)-C(34)-H(34) | 120.3 |
| C(36)-C(35)-C(34) | 120.6(6) |
| C(36)-C(35)-H(35) | 119.7 |
| C(34)-C(35)-H(35) | 119.7 |
| C(35)-C(36)-C(31) | 120.7(6) |
| C(35)-C(36)-H(36) | 119.6 |
| C(31)-C(36)-H(36) | 119.6 |
| 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(39C) | 109.5 |
| P(3)-C(39)-H(39B) | 109.5 |
| H(39C)-C(39)-H(39B) | 109.5 |
| P(3)-C(39)-H(39A) | 109.5 |
| H(39C)-C(39)-H(39A) | 109.5 |
| H(39B)-C(39)-H(39A) | 109.5 |
| C(6)-P(1)-C(7) | 104.7(2) |
| C(6)-P(1)-C(13) | 105.5(2) |
| C(7)-P(1)-C(13) | 100.5(3) |
| C(6)-P(1)-Co(1) | 106.34(19) |
| C(7)-P(1)-Co(1) | 120.09(17) |
| C(13)-P(1)-Co(1) | 118.2(2) |
| C(24)-P(2)-C(25) | 104.0(2) |
| C(24)-P(2)-C(31) | 102.9(2) |
| C(25)-P(2)-C(31) | 102.3(2) |
| C(24)-P(2)-Co(1) | 106.42(18) |
| C(25)-P(2)-Co(1) | 119.90(17) |
| C(31)-P(2)-Co(1) | 119.13(19) |
| C(37)-P(3)-C(39) | 101.7(6) |
| C(37)-P(3)-C(38) | 96.1(4) |
| C(39)-P(3)-C(38) | 97.9(5) |
| C(37)-P(3)-Co(1) | 119.2(3) |
| C(39)-P(3)-Co(1) | 118.4(3) |
| C(38)-P(3)-Co(1) | 119.1(2) |

| | |
|---|---|
| C(1)-S(1)-Co(1) | 104.53(19) |
| C(19)-S(2)-Co(1) | 103.65(19) |
| P(1)-Co(1)-P(2) | 146.29(7) |
| P(1)-Co(1)-S(1) | 89.58(6) |
| P(2)-Co(1)-S(1) | 90.43(6) |
| P(1)-Co(1)-P(3) | 105.04(7) |
| P(2)-Co(1)-P(3) | 108.67(7) |
| S(1)-Co(1)-P(3) | 91.19(7) |
| P(1)-Co(1)-S(2) | 91.78(6) |
| P(2)-Co(1)-S(2) | 88.21(6) |
| S(1)-Co(1)-S(2) | 178.58(6) |
| P(3)-Co(1)-S(2) | 88.84(7) |
| P(1)-Co(1)-H(1) | 74.6(15) |
| P(2)-Co(1)-H(1) | 71.8(15) |
| S(1)-Co(1)-H(1) | 86.8(15) |
| P(3)-Co(1)-H(1) | 178.0(15) |
| S(2)-Co(1)-H(1) | 93.2(15) |

## 8.2.4 Anisotropic displacement parameters (A^2 x 10^3)

| | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| C(1) | 37(4) | 36(4) | 39(4) | 3(3) | 19(3) | 5(3) |
| C(2) | 51(4) | 72(5) | 40(4) | 2(4) | 25(4) | 11(4) |
| C(3) | 38(4) | 71(5) | 68(5) | -10(4) | 26(4) | 3(4) |
| C(4) | 48(4) | 60(5) | 46(4) | 2(4) | 13(4) | 9(3) |
| C(5) | 35(4) | 59(4) | 42(4) | -8(3) | 16(4) | -2(3) |
| C(6) | 23(3) | 33(4) | 43(4) | 4(3) | 11(3) | 0(3) |
| C(7) | 36(4) | 39(4) | 37(4) | 11(3) | 12(3) | 6(3) |
| C(8) | 59(4) | 40(4) | 80(5) | 6(4) | 32(4) | -3(4) |
| C(9) | 59(5) | 38(5) | 121(6) | 9(4) | 33(5) | 2(4) |
| C(10) | 52(5) | 67(6) | 100(6) | 47(5) | 17(5) | -1(4) |
| C(11) | 54(5) | 94(6) | 96(6) | 39(5) | 46(4) | 12(5) |
| C(12) | 62(4) | 54(5) | 75(5) | 16(4) | 42(4) | 5(4) |
| C(13) | 46(4) | 35(4) | 32(4) | 5(3) | 19(3) | 6(3) |
| C(14) | 80(5) | 59(5) | 39(4) | 6(4) | 30(4) | 23(4) |
| C(15) | 80(5) | 80(6) | 33(4) | 12(4) | 20(4) | 28(4) |
| C(16) | 85(5) | 65(5) | 48(5) | -15(4) | 36(4) | -2(4) |
| C(17) | 105(6) | 51(5) | 53(5) | -4(4) | 42(5) | 1(4) |
| C(18) | 63(4) | 46(5) | 31(4) | 2(4) | 19(3) | 4(4) |
| C(19) | 40(4) | 32(4) | 37(4) | -4(3) | 15(3) | 7(3) |
| C(20) | 56(4) | 50(4) | 58(4) | 3(4) | 37(4) | 4(4) |
| C(21) | 43(4) | 53(5) | 59(5) | -10(4) | 26(4) | 7(3) |
| C(22) | 49(4) | 39(4) | 57(5) | -8(4) | 21(4) | 12(3) |
| C(23) | 55(4) | 37(4) | 36(4) | 7(3) | 20(3) | 3(3) |
| C(24) | 40(4) | 38(4) | 20(3) | 0(3) | 11(3) | -1(3) |
| C(25) | 44(4) | 30(3) | 38(4) | 3(3) | 22(3) | -8(3) |
| C(26) | 47(4) | 48(4) | 41(4) | -13(3) | 22(4) | -14(3) |
| C(27) | 48(4) | 59(5) | 44(5) | -6(4) | 6(4) | -12(3) |
| C(28) | 78(6) | 43(4) | 29(4) | -2(3) | 6(4) | -19(4) |
| C(29) | 85(5) | 57(5) | 35(5) | -2(4) | 33(4) | -4(4) |
| C(30) | 61(4) | 43(4) | 39(4) | 0(3) | 28(4) | 3(3) |
| C(31) | 42(4) | 28(4) | 37(4) | -1(3) | 22(3) | 0(3) |
| C(32) | 44(4) | 44(4) | 46(4) | 3(3) | 20(3) | -5(3) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(33) | 61(5) | 35(4) | 70(5) | 11(4) | 37(4) | -2(4) |
| C(34) | 56(5) | 58(5) | 95(6) | -4(5) | 42(5) | -16(4) |
| C(35) | 46(5) | 69(5) | 66(5) | -3(4) | 14(4) | -15(4) |
| C(36) | 37(4) | 59(5) | 56(4) | -3(4) | 21(4) | -6(4) |
| C(37) | 291(13) | 128(9) | 111(7) | 45(7) | -111(8) | -137(9) |
| C(38) | 140(7) | 129(8) | 99(6) | -1(6) | 34(5) | -69(6) |
| C(39) | 232(12) | 229(12) | 640(30) | -347(16) | 327(16) | -167(10) |
| P(1) | 42(1) | 34(1) | 38(1) | 3(1) | 21(1) | 5(1) |
| P(2) | 37(1) | 37(1) | 31(1) | 2(1) | 17(1) | 2(1) |
| P(3) | 72(1) | 48(1) | 53(1) | -7(1) | 26(1) | -12(1) |
| S(1) | 54(1) | 60(1) | 43(1) | 8(1) | 29(1) | 14(1) |
| S(2) | 53(1) | 48(1) | 57(1) | 12(1) | 36(1) | 9(1) |
| Co(1) | 41(1) | 37(1) | 36(1) | 4(1) | 19(1) | 4(1) |

## 8.2.5 Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3).

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(2) | 12732 | 823 | 4739 | 63 |
| H(3) | 14661 | 600 | 6703 | 70 |
| H(4) | 14517 | 499 | 8852 | 65 |
| H(5) | 12447 | 640 | 9027 | 55 |
| H(8) | 10208 | 167 | 7018 | 71 |
| H(9) | 9379 | -354 | 7585 | 90 |
| H(10) | 7719 | -321 | 8489 | 95 |
| H(11) | 6934 | 221 | 8922 | 92 |
| H(12) | 7773 | 741 | 8346 | 71 |
| H(14) | 10961 | 805 | 10085 | 69 |
| H(15) | 11685 | 1146 | 12155 | 79 |
| H(16) | 11261 | 1754 | 11989 | 76 |
| H(17) | 10046 | 2014 | 9736 | 81 |
| H(18) | 9346 | 1674 | 7665 | 57 |
| H(20) | 5094 | 1863 | 6346 | 61 |
| H(21) | 4596 | 2454 | 5718 | 60 |
| H(22) | 5472 | 2726 | 4230 | 59 |
| H(23) | 6750 | 2393 | 3304 | 51 |
| H(26) | 4626 | 1755 | 1762 | 53 |
| H(27) | 3084 | 1655 | -621 | 66 |
| H(28) | 3930 | 1455 | -2229 | 67 |
| H(29) | 6366 | 1363 | -1426 | 68 |
| H(30) | 7912 | 1439 | 974 | 54 |
| H(32) | 7962 | 2177 | 1680 | 54 |
| H(33) | 9703 | 2572 | 1791 | 62 |
| H(34) | 11940 | 2562 | 3740 | 79 |
| H(35) | 12396 | 2160 | 5608 | 77 |
| H(36) | 10651 | 1768 | 5512 | 61 |
| H(37A) | 4649 | 956 | 2284 | 298 |
| H(37B) | 4747 | 583 | 1631 | 298 |
| H(37C) | 5506 | 918 | 1350 | 298 |
| H(38A) | 5560 | 217 | 3835 | 155 |
| H(38B) | 5215 | 556 | 4530 | 155 |
| H(38C) | 6665 | 349 | 5376 | 155 |
| H(39C) | 8484 | 291 | 3771 | 383 |
| H(39B) | 7740 | 450 | 2197 | 383 |
| H(39A) | 6941 | 161 | 2688 | 383 |
| H(1) | 9110(40) | 1416(10) | 5660(40) | 32(12) |

## 8.3 Crystallographic data of 7

### 8.3.1 Crystal data and structure refinement

| | |
|---|---|
| Empirical formula | C43 H47 Co O P3 S2 |
| Formula weight | 795.77 |
| Temperature | 100(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Monoclinic |
| Space group | P21/n |
| Unit cell dimensions | a = 17.6863(8) Å α = 90º. |
| | b = 11.9369(5) Å β = 96.266(4) º. |
| | c = 18.7112(8) Å γ = 90º. |
| Volume | 3926.7(3) $Å^3$ |
| Z | 4 |
| Density (Calculated) | 1.346 $Mg/m^3$ |
| Absorption coefficient | 0.699 $mm^{-1}$ |
| F(000) | 1668 |
| Crystal size | 0.40 x 0.36 x 0.28 mm |
| Theta range for data collection | 2.19 to 26.37 º. |
| Index ranges | -18<=h<=22,-14<=k<=14,23<=l<=23 |
| Reflections collected | 28759 |
| Independent reflections | 8007 [R (int) = 0.0457] |
| Completeness to 2theta = 26.37 | 99.8% |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 8007 / 0 / 456 |
| Goodness-of-fit on $F^2$ | 1.058 |

| | |
|---|---|
| Final R indices [I>2sigma (I)] | R1 = 0.0403, wR2 = 0.1038 |
| R indices (all data) | R1 = 0.0676, wR2 = 0.1220 |
| Largest diff. peak and hole | 0.834 and -0.466 e. Å-3 |

## 8.3.2 Atomic coordinates (x 10^4) and equivalent isotropic Displacement parameters (A^2 x 10^3)

| | x | y | z | U(eq) |
|---|---|---|---|---|
| C(1) | 1062(2) | 2339(2) | 920(2) | 18(1) |
| C(2) | 477(2) | 1895(2) | 1272(2) | 22(1) |
| C(3) | -269(2) | 1931(2) | 952(2) | 28(1) |
| C(4) | -449(2) | 2429(2) | 285(2) | 26(1) |
| C(5) | 123(2) | 2937(2) | -50(2) | 22(1) |
| C(6) | 872(2) | 2900(2) | 265(1) | 19(1) |
| C(7) | 1761(2) | 4912(2) | 446(1) | 17(1) |
| C(8) | 1314(2) | 5123(2) | 999(1) | 23(1) |
| C(9) | 1419(2) | 6098(2) | 1406(2) | 29(1) |
| C(10) | 1975(2) | 6851(2) | 1270(2) | 29(1) |
| C(11) | 2421(2) | 6653(2) | 719(2) | 27(1) |
| C(12) | 2313(2) | 5683(2) | 311(2) | 21(1) |
| C(13) | 1398(2) | 4029(2) | -973(1) | 17(1) |
| C(14) | 830(2) | 4836(2) | -1111(2) | 22(1) |
| C(15) | 589(2) | 5153(2) | -1809(2) | 24(1) |
| C(16) | 922(2) | 4691(2) | -2373(2) | 27(1) |
| C(17) | 1492(2) | 3906(3) | -2245(2) | 30(1) |
| C(18) | 1727(2) | 3570(2) | -1544(1) | 23(1) |
| C(19) | 4330(2) | 3332(2) | -132(1) | 17(1) |
| C(20) | 4880(2) | 3846(2) | -507(2) | 21(1) |
| C(21) | 5642(2) | 3724(2) | -276(2) | 26(1) |
| C(22) | 5878(2) | 3088(3) | 329(2) | 29(1) |
| C(23) | 5345(2) | 2595(2) | 709(2) | 25(1) |
| C(24) | 4565(2) | 2710(2) | 487(1) | 19(1) |
| C(25) | 4013(2) | 795(2) | 1255(1) | 18(1) |
| C(26) | 4500(2) | 123(2) | 902(1) | 22(1) |
| C(27) | 4596(2) | -996(2) | 1085(2) | 27(1) |
| C(28) | 4218(2) | -1453(2) | 1625(2) | 29(1) |
| C(29) | 3735(2) | -797(2) | 1980(2) | 26(1) |
| C(30) | 3631(2) | 323(2) | 1793(1) | 21(1) |
| C(31) | 3956(2) | 3008(2) | 1831(1) | 19(1) |
| C(32) | 4541(2) | 2707(2) | 2351(2) | 23(1) |
| C(33) | 4658(2) | 3291(3) | 2991(2) | 30(1) |
| C(34) | 4197(2) | 4189(3) | 3116(2) | 36(1) |
| C(35) | 3622(2) | 4519(3) | 2596(2) | 35(1) |
| C(36) | 3501(2) | 3929(2) | 1953(2) | 25(1) |
| C(37) | 2454(2) | -373(2) | 271(2) | 30(1) |
| C(38) | 1504(2) | 785(3) | -736(2) | 37(1) |
| C(39) | 3073(2) | 550(3) | -921(2) | 33(1) |
| C(40) | -1406(3) | -417(4) | 2736(2) | 76(1) |
| C(41) | -1228(3) | 815(4) | 2683(2) | 58(1) |
| C(42) | -1696(2) | 2467(3) | 2127(2) | 43(1) |
| C(43) | -2172(2) | 2903(3) | 1461(2) | 55(1) |
| O(1) | -1720(1) | 1282(2) | 2091(1) | 44(1) |
| S(1) | 2027(1) | 2205(1) | 1274(1) | 20(1) |

| | | | | |
|---|---|---|---|---|
| S(2) | 3359(1) | 3517(1) | -422(1) | 20(1) |
| P(1) | 1691(1) | 3580(1) | -49(1) | 15(1) |
| P(2) | 3792(1) | 2239(1) | 978(1) | 16(1) |
| P(3) | 2451(1) | 928(1) | -244(1) | 19(1) |
| Co(1) | 2702(1) | 2594(1) | 333(1) | 15(1) |

## 8.3.3 Bond lengths [Å] and angles [º]

| | |
|---|---|
| C(1)-C(2) | 1.390(4) |
| C(1)-C(6) | 1.407(4) |
| C(1)-S(1) | 1.769(3) |
| C(2)-C(3) | 1.387(4) |
| C(2)-H(2) | 0.9500 |
| C(3)-C(4) | 1.388(4) |
| C(3)-H(3) | 0.9500 |
| C(4)-C(5) | 1.387(4) |
| C(4)-H(4) | 0.9500 |
| C(5)-C(6) | 1.390(4) |
| C(5)-H(5) | 0.9500 |
| C(6)-P(1) | 1.813(3) |
| C(7)-C(12) | 1.386(4) |
| C(7)-C(8) | 1.392(4) |
| C(7)-P(1) | 1.837(3) |
| C(8)-C(9) | 1.392(4) |
| C(8)-H(8) | 0.9500 |
| C(9)-C(10) | 1.377(4) |
| C(9)-H(9) | 0.9500 |
| C(10)-C(11) | 1.385(4) |
| C(10)-H(10) | 0.9500 |
| C(11)-C(12) | 1.389(4) |
| C(11)-H(11) | 0.9500 |
| C(12)-H(12) | 0.9500 |
| C(13)-C(18) | 1.384(4) |
| C(13)-C(14) | 1.394(4) |
| C(13)-P(1) | 1.831(3) |
| C(14)-C(15) | 1.382(4) |
| C(14)-H(14) | 0.9500 |
| C(15)-C(16) | 1.378(4) |
| C(15)-H(15) | 0.9500 |
| C(16)-C(17) | 1.379(4) |
| C(16)-H(16) | 0.9500 |
| C(17)-C(18) | 1.392(4) |
| C(17)-H(17) | 0.9500 |
| C(18)-H(18) | 0.9500 |
| C(19)-C(24) | 1.399(4) |
| C(19)-C(20) | 1.401(4) |
| C(19)-S(2) | 1.758(3) |
| C(20)-C(21) | 1.377(4) |
| C(20)-H(20) | 0.9500 |
| C(21)-C(22) | 1.390(4) |
| C(21)-H(21) | 0.9500 |
| C(22)-C(23) | 1.373(4) |
| C(22)-H(22) | 0.9500 |
| C(23)-C(24) | 1.404(4) |
| C(23)-H(23) | 0.9500 |
| C(24)-P(2) | 1.819(3) |

| | |
|---|---|
| C(25)-C(30) | 1.392(4) |
| C(25)-C(26) | 1.395(4) |
| C(25)-P(2) | 1.830(3) |
| C(26)-C(27) | 1.385(4) |
| C(26)-H(26) | 0.9500 |
| C(27)-C(28) | 1.383(4) |
| C(27)-H(27) | 0.9500 |
| C(28)-C(29) | 1.382(4) |
| C(28)-H(28) | 0.9500 |
| C(29)-C(30) | 1.389(4) |
| C(29)-H(29) | 0.9500 |
| C(30)-H(30) | 0.9500 |
| C(31)-C(32) | 1.388(4) |
| C(31)-C(36) | 1.396(4) |
| C(31)-P(2) | 1.836(3) |
| C(32)-C(33) | 1.381(4) |
| C(32)-H(32) | 0.9500 |
| C(33)-C(34) | 1.382(4) |
| C(33)-H(33) | 0.9500 |
| C(34)-C(35) | 1.385(5) |
| C(34)-H(34) | 0.9500 |
| C(35)-C(36) | 1.391(4) |
| C(35)-H(35) | 0.9500 |
| C(36)-H(36) | 0.9500 |
| C(37)-P(3) | 1.826(3) |
| C(37)-H(37A) | 0.9800 |
| C(37)-H(37B) | 0.9800 |
| C(37)-H(37C) | 0.9800 |
| C(38)-P(3) | 1.829(3) |
| C(38)-H(38A) | 0.9800 |
| C(38)-H(38B) | 0.9800 |
| C(38)-H(38C) | 0.9800 |
| C(39)-P(3) | 1.824(3) |
| C(39)-H(39A) | 0.9800 |
| C(39)-H(39B) | 0.9800 |
| C(39)-H(39C) | 0.9800 |
| C(40)-C(41) | 1.509(6) |
| C(40)-H(40A) | 0.9800 |
| C(40)-H(40B) | 0.9800 |
| C(40)-H(40C) | 0.9800 |
| C(41)-O(1) | 1.443(4) |
| C(41)-H(41A) | 0.9900 |
| C(41)-H(41B) | 0.9900 |
| C(42)-O(1) | 1.417(4) |
| C(42)-C(43) | 1.518(5) |
| C(42)-H(42A) | 0.9900 |
| C(42)-H(42B) | 0.9900 |
| C(43)-H(43A) | 0.9800 |
| C(43)-H(43B) | 0.9800 |
| C(43)-H(43C) | 0.9800 |
| S(1)-Co(1) | 2.2795(7) |
| S(2)-Co(1) | 2.2177(7) |
| P(1)-Co(1) | 2.1937(8) |
| P(2)-Co(1) | 2.2010(8) |
| P(3)-Co(1) | 2.2840(8) |

| | |
|---|---|
| C(2)-C(1)-C(6) | 118.3(2) |
| C(2)-C(1)-S(1) | 121.8(2) |
| C(6)-C(1)-S(1) | 119.9(2) |
| C(3)-C(2)-C(1) | 120.4(3) |
| C(3)-C(2)-H(2) | 119.8 |

| | |
|---|---|
| C(1)-C(2)-H(2) | 119.8 |
| C(2)-C(3)-C(4) | 121.1(3) |
| C(2)-C(3)-H(3) | 119.5 |
| C(4)-C(3)-H(3) | 119.5 |
| C(5)-C(4)-C(3) | 119.0(3) |
| C(5)-C(4)-H(4) | 120.5 |
| C(3)-C(4)-H(4) | 120.5 |
| C(4)-C(5)-C(6) | 120.3(3) |
| C(4)-C(5)-H(5) | 119.9 |
| C(6)-C(5)-H(5) | 119.9 |
| C(5)-C(6)-C(1) | 120.7(2) |
| C(5)-C(6)-P(1) | 127.4(2) |
| C(1)-C(6)-P(1) | 111.8(2) |
| C(12)-C(7)-C(8) | 119.0(2) |
| C(12)-C(7)-P(1) | 119.5(2) |
| C(8)-C(7)-P(1) | 121.3(2) |
| C(9)-C(8)-C(7) | 120.3(3) |
| C(9)-C(8)-H(8) | 119.8 |
| C(7)-C(8)-H(8) | 119.8 |
| C(10)-C(9)-C(8) | 120.0(3) |
| C(10)-C(9)-H(9) | 120.0 |
| C(8)-C(9)-H(9) | 120.0 |
| C(9)-C(10)-C(11) | 120.1(3) |
| C(9)-C(10)-H(10) | 119.9 |
| C(11)-C(10)-H(10) | 119.9 |
| C(10)-C(11)-C(12) | 119.8(3) |
| C(10)-C(11)-H(11) | 120.1 |
| C(12)-C(11)-H(11) | 120.1 |
| C(7)-C(12)-C(11) | 120.7(3) |
| C(7)-C(12)-H(12) | 119.6 |
| C(11)-C(12)-H(12) | 119.6 |
| C(18)-C(13)-C(14) | 119.0(2) |
| C(18)-C(13)-P(1) | 120.9(2) |
| C(14)-C(13)-P(1) | 120.1(2) |
| C(15)-C(14)-C(13) | 120.4(3) |
| C(15)-C(14)-H(14) | 119.8 |
| C(13)-C(14)-H(14) | 119.8 |
| C(16)-C(15)-C(14) | 120.1(3) |
| C(16)-C(15)-H(15) | 120.0 |
| C(14)-C(15)-H(15) | 120.0 |
| C(15)-C(16)-C(17) | 120.3(3) |
| C(15)-C(16)-H(16) | 119.9 |
| C(17)-C(16)-H(16) | 119.9 |
| C(16)-C(17)-C(18) | 119.8(3) |
| C(16)-C(17)-H(17) | 120.1 |
| C(18)-C(17)-H(17) | 120.1 |
| C(13)-C(18)-C(17) | 120.4(3) |
| C(13)-C(18)-H(18) | 119.8 |
| C(17)-C(18)-H(18) | 119.8 |
| C(24)-C(19)-C(20) | 119.2(2) |
| C(24)-C(19)-S(2) | 120.9(2) |
| C(20)-C(19)-S(2) | 119.9(2) |
| C(21)-C(20)-C(19) | 120.4(3) |
| C(21)-C(20)-H(20) | 119.8 |
| C(19)-C(20)-H(20) | 119.8 |
| C(20)-C(21)-C(22) | 120.6(3) |
| C(20)-C(21)-H(21) | 119.7 |
| C(22)-C(21)-H(21) | 119.7 |
| C(23)-C(22)-C(21) | 119.7(3) |
| C(23)-C(22)-H(22) | 120.2 |
| C(21)-C(22)-H(22) | 120.2 |

| | |
|---|---|
| C(22)-C(23)-C(24) | 120.8(3) |
| C(22)-C(23)-H(23) | 119.6 |
| C(24)-C(23)-H(23) | 119.6 |
| C(19)-C(24)-C(23) | 119.4(3) |
| C(19)-C(24)-P(2) | 114.3(2) |
| C(23)-C(24)-P(2) | 126.1(2) |
| C(30)-C(25)-C(26) | 119.0(2) |
| C(30)-C(25)-P(2) | 118.7(2) |
| C(26)-C(25)-P(2) | 122.1(2) |
| C(27)-C(26)-C(25) | 120.2(3) |
| C(27)-C(26)-H(26) | 119.9 |
| C(25)-C(26)-H(26) | 119.9 |
| C(28)-C(27)-C(26) | 120.3(3) |
| C(28)-C(27)-H(27) | 119.8 |
| C(26)-C(27)-H(27) | 119.8 |
| C(29)-C(28)-C(27) | 120.1(3) |
| C(29)-C(28)-H(28) | 120.0 |
| C(27)-C(28)-H(28) | 120.0 |
| C(28)-C(29)-C(30) | 119.8(3) |
| C(28)-C(29)-H(29) | 120.1 |
| C(30)-C(29)-H(29) | 120.1 |
| C(29)-C(30)-C(25) | 120.6(3) |
| C(29)-C(30)-H(30) | 119.7 |
| C(25)-C(30)-H(30) | 119.7 |
| C(32)-C(31)-C(36) | 119.2(3) |
| C(32)-C(31)-P(2) | 121.0(2) |
| C(36)-C(31)-P(2) | 119.8(2) |
| C(33)-C(32)-C(31) | 120.5(3) |
| C(33)-C(32)-H(32) | 119.7 |
| C(31)-C(32)-H(32) | 119.7 |
| C(32)-C(33)-C(34) | 120.2(3) |
| C(32)-C(33)-H(33) | 119.9 |
| C(34)-C(33)-H(33) | 119.9 |
| C(33)-C(34)-C(35) | 120.2(3) |
| C(33)-C(34)-H(34) | 119.9 |
| C(35)-C(34)-H(34) | 119.9 |
| C(34)-C(35)-C(36) | 119.7(3) |
| C(34)-C(35)-H(35) | 120.2 |
| C(36)-C(35)-H(35) | 120.2 |
| C(35)-C(36)-C(31) | 120.2(3) |
| C(35)-C(36)-H(36) | 119.9 |
| C(31)-C(36)-H(36) | 119.9 |
| 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(41)-C(40)-H(40A) | 109.5 |

| | |
|---|---|
| C(41)-C(40)-H(40B) | 109.5 |
| H(40A)-C(40)-H(40B) | 109.5 |
| C(41)-C(40)-H(40C) | 109.5 |
| H(40A)-C(40)-H(40C) | 109.5 |
| H(40B)-C(40)-H(40C) | 109.5 |
| O(1)-C(41)-C(40) | 108.3(3) |
| O(1)-C(41)-H(41A) | 110.0 |
| C(40)-C(41)-H(41A) | 110.0 |
| O(1)-C(41)-H(41B) | 110.0 |
| C(40)-C(41)-H(41B) | 110.0 |
| H(41A)-C(41)-H(41B) | 108.4 |
| O(1)-C(42)-C(43) | 107.0(3) |
| O(1)-C(42)-H(42A) | 110.3 |
| C(43)-C(42)-H(42A) | 110.3 |
| O(1)-C(42)-H(42B) | 110.3 |
| C(43)-C(42)-H(42B) | 110.3 |
| H(42A)-C(42)-H(42B) | 108.6 |
| C(42)-C(43)-H(43A) | 109.5 |
| C(42)-C(43)-H(43B) | 109.5 |
| H(43A)-C(43)-H(43B) | 109.5 |
| C(42)-C(43)-H(43C) | 109.5 |
| H(43A)-C(43)-H(43C) | 109.5 |
| H(43B)-C(43)-H(43C) | 109.5 |
| C(42)-O(1)-C(41) | 109.7(3) |
| C(1)-S(1)-Co(1) | 104.96(9) |
| C(19)-S(2)-Co(1) | 107.67(9) |
| C(6)-P(1)-C(13) | 106.40(12) |
| C(6)-P(1)-C(7) | 103.65(12) |
| C(13)-P(1)-C(7) | 102.64(12) |
| C(6)-P(1)-Co(1) | 107.85(9) |
| C(13)-P(1)-Co(1) | 127.02(9) |
| C(7)-P(1)-Co(1) | 106.99(9) |
| C(24)-P(2)-C(25) | 106.56(12) |
| C(24)-P(2)-C(31) | 103.19(12) |
| C(25)-P(2)-C(31) | 102.49(12) |
| C(24)-P(2)-Co(1) | 108.96(9) |
| C(25)-P(2)-Co(1) | 118.99(9) |
| C(31)-P(2)-Co(1) | 115.22(9) |
| C(39)-P(3)-C(37) | 100.85(15) |
| C(39)-P(3)-C(38) | 102.43(15) |
| C(37)-P(3)-C(38) | 97.88(15) |
| C(39)-P(3)-Co(1) | 116.27(10) |
| C(37)-P(3)-Co(1) | 120.16(10) |
| C(38)-P(3)-Co(1) | 116.08(10) |
| P(1)-Co(1)-P(2) | 156.35(3) |
| P(1)-Co(1)-S(2) | 89.50(3) |
| P(2)-Co(1)-S(2) | 87.50(3) |
| P(1)-Co(1)-S(1) | 83.35(3) |
| P(2)-Co(1)-S(1) | 92.22(3) |
| S(2)-Co(1)-S(1) | 161.46(3) |
| P(1)-Co(1)-P(3) | 101.73(3) |
| P(2)-Co(1)-P(3) | 101.81(3) |
| S(2)-Co(1)-P(3) | 102.70(3) |
| S(1)-Co(1)-P(3) | 95.50(3) |

## 8.3.4 Anisotropic displacement parameters (A^2 x 10^3)

| | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| C(1) | 16(1) | 15(1) | 22(1) | -2(1) | 6(1) | 0(1) |
| C(2) | 25(2) | 17(1) | 26(2) | 5(1) | 6(1) | -1(1) |
| C(3) | 27(2) | 20(2) | 39(2) | 1(1) | 14(2) | -2(1) |
| C(4) | 17(2) | 25(2) | 38(2) | -2(1) | 7(1) | -2(1) |
| C(5) | 21(2) | 20(2) | 24(2) | -1(1) | 4(1) | 1(1) |
| C(6) | 22(2) | 16(1) | 21(1) | -2(1) | 8(1) | 1(1) |
| C(7) | 19(1) | 17(1) | 15(1) | 2(1) | 0(1) | 5(1) |
| C(8) | 29(2) | 21(2) | 21(2) | 3(1) | 7(1) | 4(1) |
| C(9) | 40(2) | 27(2) | 20(2) | -1(1) | 9(1) | 12(1) |
| C(10) | 37(2) | 20(2) | 28(2) | -8(1) | -5(1) | 9(1) |
| C(11) | 24(2) | 20(2) | 36(2) | 1(1) | 1(1) | 0(1) |
| C(12) | 20(2) | 18(1) | 26(2) | -1(1) | 7(1) | 3(1) |
| C(13) | 17(1) | 19(1) | 16(1) | 2(1) | 3(1) | -5(1) |
| C(14) | 22(2) | 20(1) | 24(2) | 1(1) | 3(1) | 2(1) |
| C(15) | 25(2) | 23(2) | 25(2) | 5(1) | -2(1) | 4(1) |
| C(16) | 30(2) | 31(2) | 18(2) | 6(1) | -2(1) | -4(1) |
| C(17) | 32(2) | 40(2) | 18(2) | -3(1) | 5(1) | -1(2) |
| C(18) | 20(2) | 27(2) | 21(2) | -2(1) | 3(1) | 1(1) |
| C(19) | 14(1) | 15(1) | 23(1) | -5(1) | 4(1) | 1(1) |
| C(20) | 25(2) | 18(1) | 22(2) | -3(1) | 8(1) | -2(1) |
| C(21) | 22(2) | 27(2) | 30(2) | -8(1) | 12(1) | -9(1) |
| C(22) | 17(2) | 38(2) | 31(2) | -7(1) | 0(1) | -1(1) |
| C(23) | 23(2) | 32(2) | 22(2) | -1(1) | 4(1) | 0(1) |
| C(24) | 18(2) | 20(1) | 20(1) | -6(1) | 4(1) | 0(1) |
| C(25) | 20(2) | 15(1) | 18(1) | -1(1) | 0(1) | 1(1) |
| C(26) | 24(2) | 22(2) | 19(1) | -3(1) | -1(1) | 1(1) |
| C(27) | 29(2) | 23(2) | 28(2) | -8(1) | 0(1) | 7(1) |
| C(28) | 35(2) | 19(2) | 32(2) | -2(1) | -6(2) | 4(1) |
| C(29) | 34(2) | 20(2) | 24(2) | 1(1) | 2(1) | -4(1) |
| C(30) | 22(2) | 23(2) | 17(1) | -3(1) | -2(1) | 2(1) |
| C(31) | 22(2) | 20(1) | 16(1) | -1(1) | 8(1) | -5(1) |
| C(32) | 26(2) | 22(2) | 21(1) | 2(1) | 2(1) | -4(1) |
| C(33) | 40(2) | 31(2) | 19(2) | 1(1) | -4(1) | -18(2) |
| C(34) | 55(2) | 30(2) | 24(2) | -8(1) | 10(2) | -20(2) |
| C(35) | 46(2) | 25(2) | 36(2) | -12(1) | 16(2) | -5(2) |
| C(36) | 30(2) | 22(2) | 23(2) | -4(1) | 5(1) | -1(1) |
| C(37) | 39(2) | 19(2) | 32(2) | -1(1) | 1(2) | -9(1) |
| C(38) | 39(2) | 25(2) | 44(2) | -9(2) | -13(2) | -2(1) |
| C(39) | 42(2) | 28(2) | 30(2) | -10(1) | 12(2) | -3(2) |
| C(40) | 107(4) | 57(3) | 65(3) | 18(2) | 21(3) | 21(3) |
| C(41) | 79(3) | 66(3) | 29(2) | 5(2) | 6(2) | 12(2) |
| C(42) | 50(2) | 41(2) | 40(2) | -6(2) | 10(2) | -2(2) |
| C(43) | 53(3) | 55(3) | 57(3) | 8(2) | 4(2) | 3(2) |
| O(1) | 55(2) | 41(1) | 38(1) | 6(1) | 11(1) | 5(1) |
| S(1) | 18(1) | 25(1) | 19(1) | 5(1) | 5(1) | 2(1) |
| S(2) | 18(1) | 22(1) | 21(1) | 5(1) | 6(1) | 1(1) |
| P(1) | 17(1) | 15(1) | 15(1) | 1(1) | 5(1) | 0(1) |
| P(2) | 17(1) | 16(1) | 16(1) | -2(1) | 4(1) | 1(1) |
| P(3) | 22(1) | 16(1) | 20(1) | -1(1) | 2(1) | -1(1) |
| Co(1) | 15(1) | 15(1) | 15(1) | 0(1) | 4(1) | 1(1) |

## 8.3.5 Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3).

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(2) | 588 | 1565 | 1733 | 27 |
| H(3) | -661 | 1611 | 1194 | 34 |
| H(4) | -958 | 2421 | 61 | 32 |
| H(5) | 3 | 3311 | -496 | 26 |
| H(8) | 935 | 4599 | 1100 | 28 |
| H(9) | 1107 | 6243 | 1778 | 34 |
| H(10) | 2053 | 7509 | 1554 | 35 |
| H(11) | 2799 | 7179 | 620 | 32 |
| H(12) | 2622 | 5546 | -65 | 25 |
| H(14) | 607 | 5168 | -723 | 26 |
| H(15) | 195 | 5691 | -1900 | 29 |
| H(16) | 757 | 4915 | -2852 | 32 |
| H(17) | 1724 | 3595 | -2635 | 35 |
| H(18) | 2115 | 3022 | -1456 | 27 |
| H(20) | 4726 | 4282 | -922 | 26 |
| H(21) | 6010 | 4078 | -534 | 31 |
| H(22) | 6405 | 2996 | 480 | 34 |
| H(23) | 5507 | 2170 | 1127 | 30 |
| H(26) | 4767 | 434 | 535 | 26 |
| H(27) | 4923 | -1453 | 838 | 32 |
| H(28) | 4290 | -2220 | 1751 | 35 |
| H(29) | 3476 | -1111 | 2351 | 32 |
| H(30) | 3295 | 772 | 2035 | 25 |
| H(32) | 4862 | 2095 | 2267 | 28 |
| H(33) | 5057 | 3076 | 3346 | 36 |
| H(34) | 4274 | 4580 | 3559 | 43 |
| H(35) | 3312 | 5145 | 2679 | 42 |
| H(36) | 3107 | 4153 | 1596 | 30 |
| H(37A) | 2256 | -984 | -46 | 36 |
| H(37B) | 2133 | -285 | 662 | 36 |
| H(37C) | 2976 | -548 | 472 | 36 |
| H(38A) | 1120 | 800 | -397 | 44 |
| H(38B) | 1472 | 73 | -999 | 44 |
| H(38C) | 1414 | 1406 | -1078 | 44 |
| H(39A) | 2872 | -117 | -1182 | 39 |
| H(39B) | 3585 | 393 | -686 | 39 |
| H(39C) | 3097 | 1173 | -1259 | 39 |
| H(40A) | -1290 | -799 | 2297 | 91 |
| H(40B) | -1947 | -513 | 2793 | 91 |
| H(40C) | -1098 | -740 | 3152 | 91 |
| H(41A) | -1314 | 1199 | 3136 | 69 |
| H(41B) | -689 | 917 | 2601 | 69 |
| H(42A) | -1165 | 2736 | 2139 | 52 |
| H(42B) | -1906 | 2733 | 2566 | 52 |
| H(43A) | -2688 | 2596 | 1441 | 66 |
| H(43B) | -1941 | 2672 | 1031 | 66 |
| H(43C) | -2195 | 3723 | 1480 | 66 |

## 8.4 Crystallographic data of 11

### 8.4.1 Crystal data and structure refinement

| | |
|---|---|
| Empirical formula | C51 H51 Co O P3 S2 |
| Formula weight | 895.88 |
| Temperature | 100(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Triclinic |
| Space group | P-1 |
| Unit cell dimensions | a = 11.0280(10) Å α = 102.662(7) º. |
| | b = 14.0190(10) Å β = 95.242(6) º. |
| | c = 15.5330(10) Å γ = 109.627(7) º. |
| Volume | 2171.0(3) $Å^3$ |
| Z | 2 |
| Density (calculated) | 1.370 $Mg/m^3$ |
| Absorption coefficient | 0.641 $mm^{-1}$ |
| F (000) | 938 |
| Crystal size | 0.50 x 0.24 x 0.12 mm |
| Theta range for data collection | 2.36 to 26.37 º. |
| Index ranges | -13<=h<=13,-17<=k<=17,-18<=l<=19 |
| Reflections collected | 27327 |
| Independent reflections | 8817 [R (int) = 0.0274] |
| Completeness to 2theta = 26.37 | 99.2% |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 8817 / 0 / 528 |
| Goodness-of-fit on $F^2$ | 1.030 |
| Final R indices [I>2sigma (I)] | R1 = 0.0363, wR2 = 0.0915 |

| | |
|---|---|
| R indices (all data) | R1 = 0.0603, wR2 = 0.1040 |
| Largest diff. peak and hole | 0.499 and -0.594 e. Å-3 |

## 8.4.2 Atomic coordinates (x 10^4) and equivalent isotropic Displacement parameters (A^2 x 10^3)

| | x | y | z | U(eq) |
|---|---|---|---|---|
| C(1) | 1310(2) | 4664(2) | 3208(2) | 19(1) |
| C(2) | 372(2) | 3944(2) | 3507(2) | 25(1) |
| C(3) | 561(2) | 3065(2) | 3709(2) | 23(1) |
| C(4) | -406(3) | 2293(2) | 3992(2) | 29(1) |
| C(5) | -211(3) | 1431(2) | 4134(2) | 33(1) |
| C(6) | 974(3) | 1286(2) | 4036(2) | 29(1) |
| C(7) | 1946(3) | 2023(2) | 3798(2) | 27(1) |
| C(8) | 1767(2) | 2917(2) | 3613(2) | 21(1) |
| C(9) | 2734(2) | 3680(2) | 3329(2) | 20(1) |
| C(10) | 2524(2) | 4514(2) | 3119(2) | 18(1) |
| C(11) | 5257(2) | 5509(2) | 3019(2) | 18(1) |
| C(12) | 5651(2) | 5515(2) | 3898(2) | 21(1) |
| C(13) | 6904(2) | 5554(2) | 4177(2) | 22(1) |
| C(14) | 7777(2) | 5606(2) | 3586(2) | 25(1) |
| C(15) | 7397(2) | 5618(2) | 2719(2) | 26(1) |
| C(16) | 6139(2) | 5569(2) | 2434(2) | 21(1) |
| C(17) | 3291(2) | 4776(2) | 1442(2) | 20(1) |
| C(18) | 2952(3) | 3700(2) | 1159(2) | 34(1) |
| C(19) | 2727(3) | 3191(2) | 255(2) | 40(1) |
| C(20) | 2852(3) | 3757(2) | -373(2) | 32(1) |
| C(21) | 3189(3) | 4832(2) | -100(2) | 30(1) |
| C(22) | 3404(3) | 5338(2) | 805(2) | 26(1) |
| C(23) | 4775(2) | 9024(2) | 2465(2) | 19(1) |
| C(24) | 5846(2) | 9889(2) | 2478(2) | 22(1) |
| C(25) | 5728(2) | 10854(2) | 2452(2) | 22(1) |
| C(26) | 6814(3) | 11749(2) | 2447(2) | 26(1) |
| C(27) | 6672(3) | 12675(2) | 2430(2) | 27(1) |
| C(28) | 5436(3) | 12755(2) | 2390(2) | 28(1) |
| C(29) | 4362(3) | 11903(2) | 2378(2) | 25(1) |
| C(30) | 4477(2) | 10941(2) | 2424(2) | 21(1) |
| C(31) | 3384(2) | 10041(2) | 2409(2) | 21(1) |
| C(32) | 3515(2) | 9114(2) | 2419(2) | 20(1) |
| C(33) | 1775(2) | 7328(2) | 1057(2) | 20(1) |
| C(34) | 557(3) | 6573(2) | 666(2) | 28(1) |
| C(35) | 254(3) | 6134(2) | -257(2) | 31(1) |
| C(36) | 1169(3) | 6416(2) | -786(2) | 35(1) |
| C(37) | 2396(3) | 7147(3) | -396(2) | 42(1) |
| C(38) | 2696(3) | 7612(2) | 516(2) | 33(1) |
| C(39) | 758(2) | 8163(2) | 2549(2) | 20(1) |
| C(40) | 118(2) | 8562(2) | 1983(2) | 25(1) |
| C(41) | -974(3) | 8782(2) | 2184(2) | 29(1) |
| C(42) | -1442(3) | 8587(2) | 2952(2) | 29(1) |
| C(43) | -825(3) | 8189(2) | 3515(2) | 27(1) |
| C(44) | 273(2) | 7972(2) | 3311(2) | 23(1) |
| C(45) | 5549(3) | 8202(2) | 4703(2) | 36(1) |
| C(46) | 3382(3) | 8801(2) | 4803(2) | 27(1) |
| C(47) | 3236(3) | 6849(2) | 5088(2) | 38(1) |

| | | | | |
|---|---|---|---|---|
| C(48) | 10267(4) | 1268(4) | 1442(3) | 103(2) |
| C(49) | 9260(4) | 976(3) | 704(3) | 70(1) |
| C(50) | 7130(4) | -186(4) | 1(4) | 91(2) |
| C(51) | 5945(4) | -940(3) | 87(2) | 57(1) |
| O(1) | 8155(2) | 128(2) | 688(2) | 55(1) |
| P(1) | 3612(1) | 5469(1) | 2639(1) | 17(1) |
| P(2) | 2193(1) | 7861(1) | 2281(1) | 18(1) |
| P(3) | 3778(1) | 7654(1) | 4324(1) | 22(1) |
| S(1) | 1070(1) | 5748(1) | 2921(1) | 23(1) |
| S(2) | 4894(1) | 7797(1) | 2448(1) | 22(1) |
| Co(1) | 3037(1) | 6849(1) | 2838(1) | 17(1) |

## 8.4.3 Bond lengths [Å] and angles [º]

| | |
|---|---|
| C(1)-C(2) | 1.377(3) |
| C(1)-C(10) | 1.437(3) |
| C(1)-S(1) | 1.767(3) |
| C(2)-C(3) | 1.411(4) |
| C(2)-H(2) | 0.9500 |
| C(3)-C(4) | 1.422(4) |
| C(3)-C(8) | 1.429(4) |
| C(4)-C(5) | 1.357(4) |
| C(4)-H(4) | 0.9500 |
| C(5)-C(6) | 1.404(4) |
| C(5)-H(5) | 0.9500 |
| C(6)-C(7) | 1.359(4) |
| C(6)-H(6) | 0.9500 |
| C(7)-C(8) | 1.417(4) |
| C(7)-H(7) | 0.9500 |
| C(8)-C(9) | 1.416(3) |
| C(9)-C(10) | 1.365(3) |
| C(9)-H(9) | 0.9500 |
| C(10)-P(1) | 1.820(2) |
| C(11)-C(16) | 1.386(3) |
| C(11)-C(12) | 1.391(3) |
| C(11)-P(1) | 1.834(2) |
| C(12)-C(13) | 1.389(3) |
| C(12)-H(12) | 0.9500 |
| C(13)-C(14) | 1.385(4) |
| C(13)-H(13) | 0.9500 |
| C(14)-C(15) | 1.380(4) |
| C(14)-H(14) | 0.9500 |
| C(15)-C(16) | 1.390(4) |
| C(15)-H(15) | 0.9500 |
| C(16)-H(16) | 0.9500 |
| C(17)-C(18) | 1.382(4) |
| C(17)-C(22) | 1.383(4) |
| C(17)-P(1) | 1.838(2) |
| C(18)-C(19) | 1.385(4) |
| C(18)-H(18) | 0.9500 |
| C(19)-C(20) | 1.375(4) |
| C(19)-H(19) | 0.9500 |
| C(20)-C(21) | 1.379(4) |
| C(20)-H(20) | 0.9500 |
| C(21)-C(22) | 1.388(4) |

| | |
|---|---|
| C(21)-H(21) | 0.9500 |
| C(22)-H(22) | 0.9500 |
| C(23)-C(24) | 1.374(3) |
| C(23)-C(32) | 1.433(3) |
| C(23)-S(2) | 1.764(3) |
| C(24)-C(25) | 1.411(4) |
| C(24)-H(24) | 0.9500 |
| C(25)-C(26) | 1.416(4) |
| C(25)-C(30) | 1.424(4) |
| C(26)-C(27) | 1.364(4) |
| C(26)-H(26) | 0.9500 |
| C(27)-C(28) | 1.401(4) |
| C(27)-H(27) | 0.9500 |
| C(28)-C(29) | 1.365(4) |
| C(28)-H(28) | 0.9500 |
| C(29)-C(30) | 1.413(4) |
| C(29)-H(29) | 0.9500 |
| C(30)-C(31) | 1.416(3) |
| C(31)-C(32) | 1.358(4) |
| C(31)-H(31) | 0.9500 |
| C(32)-P(2) | 1.821(2) |
| C(33)-C(34) | 1.381(4) |
| C(33)-C(38) | 1.389(4) |
| C(33)-P(2) | 1.837(3) |
| C(34)-C(35) | 1.391(4) |
| C(34)-H(34) | 0.9500 |
| C(35)-C(36) | 1.370(4) |
| C(35)-H(35) | 0.9500 |
| C(36)-C(37) | 1.376(4) |
| C(36)-H(36) | 0.9500 |
| C(37)-C(38) | 1.380(4) |
| C(37)-H(37) | 0.9500 |
| C(38)-H(38) | 0.9500 |
| C(39)-C(44) | 1.385(4) |
| C(39)-C(40) | 1.397(4) |
| C(39)-P(2) | 1.830(2) |
| C(40)-C(41) | 1.385(4) |
| C(40)-H(40) | 0.9500 |
| C(41)-C(42) | 1.387(4) |
| C(41)-H(41) | 0.9500 |
| C(42)-C(43) | 1.378(4) |
| C(42)-H(42) | 0.9500 |
| C(43)-C(44) | 1.391(4) |
| C(43)-H(43) | 0.9500 |
| C(44)-H(44) | 0.9500 |
| C(45)-P(3) | 1.826(3) |
| C(45)-H(45A) | 0.9800 |
| C(45)-H(45B) | 0.9800 |
| C(45)-H(45C) | 0.9800 |
| C(46)-P(3) | 1.827(3) |
| C(46)-H(46A) | 0.9800 |
| C(46)-H(46B) | 0.9800 |
| C(46)-H(46C) | 0.9800 |
| C(47)-P(3) | 1.818(3) |
| C(47)-H(47A) | 0.9800 |
| C(47)-H(47B) | 0.9800 |
| C(47)-H(47C) | 0.9800 |
| C(48)-C(49) | 1.404(5) |
| C(48)-H(48A) | 0.9800 |
| C(48)-H(48B) | 0.9800 |
| C(48)-H(48C) | 0.9800 |

| | |
|---|---|
| C(49)-O(1) | 1.381(4) |
| C(49)-H(49A) | 0.9900 |
| C(49)-H(49B) | 0.9900 |
| C(50)-O(1) | 1.361(4) |
| C(50)-C(51) | 1.417(5) |
| C(50)-H(50A) | 0.9900 |
| C(50)-H(50B) | 0.9900 |
| C(51)-H(51A) | 0.9800 |
| C(51)-H(51B) | 0.9800 |
| C(51)-H(51C) | 0.9800 |
| P(1)-Co(1) | 2.2000(7) |
| P(2)-Co(1) | 2.2131(7) |
| P(3)-Co(1) | 2.2720(7) |
| S(1)-Co(1) | 2.2345(7) |
| S(2)-Co(1) | 2.2534(7) |

| | |
|---|---|
| C(2)-C(1)-C(10) | 118.2(2) |
| C(2)-C(1)-S(1) | 122.7(2) |
| C(10)-C(1)-S(1) | 119.17(18) |
| C(1)-C(2)-C(3) | 122.1(2) |
| C(1)-C(2)-H(2) | 118.9 |
| C(3)-C(2)-H(2) | 118.9 |
| C(2)-C(3)-C(4) | 123.2(2) |
| C(2)-C(3)-C(8) | 119.4(2) |
| C(4)-C(3)-C(8) | 117.4(2) |
| C(5)-C(4)-C(3) | 121.3(3) |
| C(5)-C(4)-H(4) | 119.3 |
| C(3)-C(4)-H(4) | 119.3 |
| C(4)-C(5)-C(6) | 121.1(3) |
| C(4)-C(5)-H(5) | 119.5 |
| C(6)-C(5)-H(5) | 119.5 |
| C(7)-C(6)-C(5) | 119.7(3) |
| C(7)-C(6)-H(6) | 120.2 |
| C(5)-C(6)-H(6) | 120.2 |
| C(6)-C(7)-C(8) | 121.1(3) |
| C(6)-C(7)-H(7) | 119.4 |
| C(8)-C(7)-H(7) | 119.4 |
| C(9)-C(8)-C(7) | 122.8(2) |
| C(9)-C(8)-C(3) | 117.8(2) |
| C(7)-C(8)-C(3) | 119.4(2) |
| C(10)-C(9)-C(8) | 122.0(2) |
| C(10)-C(9)-H(9) | 119.0 |
| C(8)-C(9)-H(9) | 119.0 |
| C(9)-C(10)-C(1) | 120.5(2) |
| C(9)-C(10)-P(1) | 126.29(19) |
| C(1)-C(10)-P(1) | 113.01(18) |
| C(16)-C(11)-C(12) | 119.2(2) |
| C(16)-C(11)-P(1) | 119.77(19) |
| C(12)-C(11)-P(1) | 121.04(18) |
| C(13)-C(12)-C(11) | 120.3(2) |
| C(13)-C(12)-H(12) | 119.9 |
| C(11)-C(12)-H(12) | 119.9 |
| C(14)-C(13)-C(12) | 120.2(2) |
| C(14)-C(13)-H(13) | 119.9 |
| C(12)-C(13)-H(13) | 119.9 |
| C(15)-C(14)-C(13) | 119.7(2) |
| C(15)-C(14)-H(14) | 120.1 |
| C(13)-C(14)-H(14) | 120.1 |
| C(14)-C(15)-C(16) | 120.3(2) |
| C(14)-C(15)-H(15) | 119.9 |
| C(16)-C(15)-H(15) | 119.9 |

| | |
|---|---|
| C(11)-C(16)-C(15) | 120.4(2) |
| C(11)-C(16)-H(16) | 119.8 |
| C(15)-C(16)-H(16) | 119.8 |
| C(18)-C(17)-C(22) | 118.7(2) |
| C(18)-C(17)-P(1) | 121.5(2) |
| C(22)-C(17)-P(1) | 119.8(2) |
| C(17)-C(18)-C(19) | 120.8(3) |
| C(17)-C(18)-H(18) | 119.6 |
| C(19)-C(18)-H(18) | 119.6 |
| C(20)-C(19)-C(18) | 120.1(3) |
| C(20)-C(19)-H(19) | 120.0 |
| C(18)-C(19)-H(19) | 120.0 |
| C(19)-C(20)-C(21) | 119.8(3) |
| C(19)-C(20)-H(20) | 120.1 |
| C(21)-C(20)-H(20) | 120.1 |
| C(20)-C(21)-C(22) | 120.0(3) |
| C(20)-C(21)-H(21) | 120.0 |
| C(22)-C(21)-H(21) | 120.0 |
| C(17)-C(22)-C(21) | 120.6(3) |
| C(17)-C(22)-H(22) | 119.7 |
| C(21)-C(22)-H(22) | 119.7 |
| C(24)-C(23)-C(32) | 118.7(2) |
| C(24)-C(23)-S(2) | 122.0(2) |
| C(32)-C(23)-S(2) | 119.24(18) |
| C(23)-C(24)-C(25) | 121.4(2) |
| C(23)-C(24)-H(24) | 119.3 |
| C(25)-C(24)-H(24) | 119.3 |
| C(24)-C(25)-C(26) | 122.4(2) |
| C(24)-C(25)-C(30) | 119.5(2) |
| C(26)-C(25)-C(30) | 118.1(2) |
| C(27)-C(26)-C(25) | 121.1(3) |
| C(27)-C(26)-H(26) | 119.4 |
| C(25)-C(26)-H(26) | 119.4 |
| C(26)-C(27)-C(28) | 120.6(2) |
| C(26)-C(27)-H(27) | 119.7 |
| C(28)-C(27)-H(27) | 119.7 |
| C(29)-C(28)-C(27) | 120.0(3) |
| C(29)-C(28)-H(28) | 120.0 |
| C(27)-C(28)-H(28) | 120.0 |
| C(28)-C(29)-C(30) | 121.0(3) |
| C(28)-C(29)-H(29) | 119.5 |
| C(30)-C(29)-H(29) | 119.5 |
| C(29)-C(30)-C(31) | 122.6(2) |
| C(29)-C(30)-C(25) | 119.1(2) |
| C(31)-C(30)-C(25) | 118.3(2) |
| C(32)-C(31)-C(30) | 121.3(2) |
| C(32)-C(31)-H(31) | 119.3 |
| C(30)-C(31)-H(31) | 119.3 |
| C(31)-C(32)-C(23) | 120.8(2) |
| C(31)-C(32)-P(2) | 126.44(19) |
| C(23)-C(32)-P(2) | 112.57(18) |
| C(34)-C(33)-C(38) | 118.8(2) |
| C(34)-C(33)-P(2) | 119.9(2) |
| C(38)-C(33)-P(2) | 121.17(19) |
| C(33)-C(34)-C(35) | 120.2(3) |
| C(33)-C(34)-H(34) | 119.9 |
| C(35)-C(34)-H(34) | 119.9 |
| C(36)-C(35)-C(34) | 120.7(3) |
| C(36)-C(35)-H(35) | 119.7 |
| C(34)-C(35)-H(35) | 119.7 |
| C(35)-C(36)-C(37) | 119.3(3) |

| | |
|---|---|
| C(35)-C(36)-H(36) | 120.3 |
| C(37)-C(36)-H(36) | 120.3 |
| C(36)-C(37)-C(38) | 120.6(3) |
| C(36)-C(37)-H(37) | 119.7 |
| C(38)-C(37)-H(37) | 119.7 |
| C(37)-C(38)-C(33) | 120.5(3) |
| C(37)-C(38)-H(38) | 119.8 |
| C(33)-C(38)-H(38) | 119.8 |
| C(44)-C(39)-C(40) | 119.0(2) |
| C(44)-C(39)-P(2) | 119.94(19) |
| C(40)-C(39)-P(2) | 121.0(2) |
| C(41)-C(40)-C(39) | 120.8(3) |
| C(41)-C(40)-H(40) | 119.6 |
| C(39)-C(40)-H(40) | 119.6 |
| C(40)-C(41)-C(42) | 119.2(3) |
| C(40)-C(41)-H(41) | 120.4 |
| C(42)-C(41)-H(41) | 120.4 |
| C(43)-C(42)-C(41) | 120.7(2) |
| C(43)-C(42)-H(42) | 119.7 |
| C(41)-C(42)-H(42) | 119.7 |
| C(42)-C(43)-C(44) | 119.9(3) |
| C(42)-C(43)-H(43) | 120.0 |
| C(44)-C(43)-H(43) | 120.0 |
| C(39)-C(44)-C(43) | 120.3(2) |
| C(39)-C(44)-H(44) | 119.8 |
| C(43)-C(44)-H(44) | 119.8 |
| P(3)-C(45)-H(45A) | 109.5 |
| P(3)-C(45)-H(45B) | 109.5 |
| H(45A)-C(45)-H(45B) | 109.5 |
| P(3)-C(45)-H(45C) | 109.5 |
| H(45A)-C(45)-H(45C) | 109.5 |
| H(45B)-C(45)-H(45C) | 109.5 |
| P(3)-C(46)-H(46A) | 109.5 |
| P(3)-C(46)-H(46B) | 109.5 |
| H(46A)-C(46)-H(46B) | 109.5 |
| P(3)-C(46)-H(46C) | 109.5 |
| H(46A)-C(46)-H(46C) | 109.5 |
| H(46B)-C(46)-H(46C) | 109.5 |
| P(3)-C(47)-H(47A) | 109.5 |
| P(3)-C(47)-H(47B) | 109.5 |
| H(47A)-C(47)-H(47B) | 109.5 |
| P(3)-C(47)-H(47C) | 109.5 |
| H(47A)-C(47)-H(47C) | 109.5 |
| H(47B)-C(47)-H(47C) | 109.5 |
| C(49)-C(48)-H(48A) | 109.5 |
| C(49)-C(48)-H(48B) | 109.5 |
| H(48A)-C(48)-H(48B) | 109.5 |
| C(49)-C(48)-H(48C) | 109.5 |
| H(48A)-C(48)-H(48C) | 109.5 |
| H(48B)-C(48)-H(48C) | 109.5 |
| O(1)-C(49)-C(48) | 115.1(4) |
| O(1)-C(49)-H(49A) | 108.5 |
| C(48)-C(49)-H(49A) | 108.5 |
| O(1)-C(49)-H(49B) | 108.5 |
| C(48)-C(49)-H(49B) | 108.5 |
| H(49A)-C(49)-H(49B) | 107.5 |
| O(1)-C(50)-C(51) | 116.4(4) |
| O(1)-C(50)-H(50A) | 108.2 |
| C(51)-C(50)-H(50A) | 108.2 |
| O(1)-C(50)-H(50B) | 108.2 |
| C(51)-C(50)-H(50B) | 108.2 |

| | |
|---|---|
| H(50A)-C(50)-H(50B) | 107.3 |
| C(50)-C(51)-H(51A) | 109.5 |
| C(50)-C(51)-H(51B) | 109.5 |
| H(51A)-C(51)-H(51B) | 109.5 |
| C(50)-C(51)-H(51C) | 109.5 |
| H(51A)-C(51)-H(51C) | 109.5 |
| H(51B)-C(51)-H(51C) | 109.5 |
| C(50)-O(1)-C(49) | 118.4(3) |
| C(10)-P(1)-C(11) | 105.04(11) |
| C(10)-P(1)-C(17) | 103.43(11) |
| C(11)-P(1)-C(17) | 102.36(11) |
| C(10)-P(1)-Co(1) | 108.24(8) |
| C(11)-P(1)-Co(1) | 124.73(8) |
| C(17)-P(1)-Co(1) | 110.99(8) |
| C(32)-P(2)-C(39) | 106.57(12) |
| C(32)-P(2)-C(33) | 102.49(11) |
| C(39)-P(2)-C(33) | 102.37(11) |
| C(32)-P(2)-Co(1) | 107.40(8) |
| C(39)-P(2)-Co(1) | 127.42(9) |
| C(33)-P(2)-Co(1) | 107.95(8) |
| C(47)-P(3)-C(45) | 101.72(15) |
| C(47)-P(3)-C(46) | 101.42(13) |
| C(45)-P(3)-C(46) | 99.71(13) |
| C(47)-P(3)-Co(1) | 116.32(10) |
| C(45)-P(3)-Co(1) | 116.98(10) |
| C(46)-P(3)-Co(1) | 117.82(9) |
| C(1)-S(1)-Co(1) | 106.77(8) |
| C(23)-S(2)-Co(1) | 105.82(8) |
| P(1)-Co(1)-P(2) | 150.07(3) |
| P(1)-Co(1)-S(1) | 85.66(3) |
| P(2)-Co(1)-S(1) | 92.61(3) |
| P(1)-Co(1)-S(2) | 91.26(3) |
| P(2)-Co(1)-S(2) | 84.36(3) |
| S(1)-Co(1)-S(2) | 168.17(3) |
| P(1)-Co(1)-P(3) | 103.19(3) |
| P(2)-Co(1)-P(3) | 106.60(3) |
| S(1)-Co(1)-P(3) | 98.76(3) |
| S(2)-Co(1)-P(3) | 93.06(3) |

## 8.4.4 Anisotropic displacement parameters (A^2 x 10^3)

| | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| C(1) | 20(1) | 20(1) | 18(1) | 4(1) | 2(1) | 8(1) |
| C(2) | 19(1) | 28(2) | 28(2) | 7(1) | 7(1) | 9(1) |
| C(3) | 24(1) | 24(1) | 20(1) | 5(1) | 4(1) | 8(1) |
| C(4) | 24(1) | 32(2) | 32(2) | 11(1) | 10(1) | 8(1) |
| C(5) | 32(2) | 32(2) | 33(2) | 15(1) | 11(1) | 6(1) |
| C(6) | 35(2) | 27(2) | 32(2) | 15(1) | 7(1) | 13(1) |
| C(7) | 29(2) | 32(2) | 22(1) | 9(1) | 4(1) | 14(1) |
| C(8) | 25(1) | 21(1) | 17(1) | 5(1) | 2(1) | 9(1) |
| C(9) | 18(1) | 23(1) | 20(1) | 4(1) | 4(1) | 10(1) |
| C(10) | 19(1) | 19(1) | 16(1) | 4(1) | 3(1) | 7(1) |
| C(11) | 18(1) | 14(1) | 22(1) | 4(1) | 2(1) | 7(1) |
| C(12) | 23(1) | 21(1) | 21(1) | 6(1) | 4(1) | 10(1) |
| C(13) | 26(1) | 20(1) | 20(1) | 5(1) | -3(1) | 9(1) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(14) | 17(1) | 19(1) | 37(2) | 6(1) | -1(1) | 7(1) |
| C(15) | 20(1) | 26(1) | 31(2) | 7(1) | 9(1) | 8(1) |
| C(16) | 20(1) | 24(1) | 21(1) | 8(1) | 5(1) | 7(1) |
| C(17) | 17(1) | 25(1) | 19(1) | 4(1) | 3(1) | 9(1) |
| C(18) | 50(2) | 27(2) | 25(2) | 7(1) | 6(1) | 14(1) |
| C(19) | 57(2) | 25(2) | 29(2) | 1(1) | 7(1) | 9(1) |
| C(20) | 30(2) | 37(2) | 20(1) | 0(1) | 6(1) | 6(1) |
| C(21) | 34(2) | 35(2) | 22(1) | 10(1) | 8(1) | 11(1) |
| C(22) | 28(1) | 26(1) | 23(1) | 4(1) | 5(1) | 10(1) |
| C(23) | 22(1) | 19(1) | 16(1) | 5(1) | 1(1) | 7(1) |
| C(24) | 16(1) | 28(1) | 21(1) | 6(1) | 3(1) | 7(1) |
| C(25) | 24(1) | 23(1) | 15(1) | 4(1) | 1(1) | 6(1) |
| C(26) | 25(1) | 29(2) | 20(1) | 6(1) | 4(1) | 6(1) |
| C(27) | 32(2) | 23(1) | 23(1) | 5(1) | 7(1) | 3(1) |
| C(28) | 36(2) | 22(1) | 27(2) | 8(1) | 7(1) | 11(1) |
| C(29) | 29(2) | 22(1) | 26(1) | 7(1) | 4(1) | 11(1) |
| C(30) | 23(1) | 22(1) | 17(1) | 4(1) | 3(1) | 7(1) |
| C(31) | 20(1) | 23(1) | 21(1) | 7(1) | 3(1) | 9(1) |
| C(32) | 20(1) | 23(1) | 14(1) | 4(1) | 1(1) | 6(1) |
| C(33) | 23(1) | 22(1) | 20(1) | 8(1) | 1(1) | 12(1) |
| C(34) | 24(1) | 29(2) | 28(2) | 5(1) | 4(1) | 9(1) |
| C(35) | 26(2) | 29(2) | 30(2) | 1(1) | -6(1) | 7(1) |
| C(36) | 36(2) | 42(2) | 20(1) | 6(1) | -3(1) | 11(1) |
| C(37) | 37(2) | 54(2) | 25(2) | 10(1) | 6(1) | 4(2) |
| C(38) | 27(2) | 41(2) | 22(1) | 8(1) | 0(1) | 3(1) |
| C(39) | 16(1) | 17(1) | 25(1) | 4(1) | 1(1) | 7(1) |
| C(40) | 24(1) | 26(1) | 24(1) | 6(1) | 2(1) | 9(1) |
| C(41) | 22(1) | 28(2) | 37(2) | 8(1) | -3(1) | 14(1) |
| C(42) | 18(1) | 25(1) | 41(2) | 3(1) | 5(1) | 10(1) |
| C(43) | 24(1) | 24(1) | 34(2) | 7(1) | 9(1) | 8(1) |
| C(44) | 23(1) | 20(1) | 27(1) | 6(1) | 2(1) | 9(1) |
| C(45) | 32(2) | 39(2) | 33(2) | -3(1) | -8(1) | 18(1) |
| C(46) | 28(2) | 26(1) | 25(1) | 0(1) | 3(1) | 11(1) |
| C(47) | 64(2) | 32(2) | 24(2) | 9(1) | 8(1) | 25(2) |
| C(48) | 71(3) | 116(4) | 67(3) | 35(3) | -16(2) | -33(3) |
| C(49) | 52(2) | 63(3) | 91(3) | 38(2) | -1(2) | 8(2) |
| C(50) | 50(3) | 100(4) | 113(4) | 70(3) | -24(3) | -2(2) |
| C(51) | 53(2) | 69(3) | 41(2) | 10(2) | 3(2) | 15(2) |
| O(1) | 46(1) | 64(2) | 40(1) | 19(1) | -5(1) | 3(1) |
| P(1) | 17(1) | 19(1) | 17(1) | 5(1) | 3(1) | 8(1) |
| P(2) | 15(1) | 20(1) | 19(1) | 6(1) | 1(1) | 7(1) |
| P(3) | 28(1) | 22(1) | 18(1) | 4(1) | 1(1) | 12(1) |
| S(1) | 16(1) | 23(1) | 34(1) | 12(1) | 6(1) | 9(1) |
| S(2) | 17(1) | 21(1) | 30(1) | 9(1) | 5(1) | 9(1) |
| Co(1) | 16(1) | 18(1) | 18(1) | 6(1) | 2(1) | 8(1) |

## 8.4.5 Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3).

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(2) | -427 | 4042 | 3579 | 30 |
| H(4) | -1205 | 2383 | 4083 | 35 |
| H(5) | -886 | 916 | 4303 | 39 |
| H(6) | 1096 | 677 | 4135 | 35 |

| | | | | |
|---|---|---|---|---|
| H(7) | 2759 | 1938 | 3756 | 32 |
| H(9) | 3555 | 3610 | 3283 | 24 |
| H(12) | 5062 | 5494 | 4309 | 25 |
| H(13) | 7162 | 5544 | 4774 | 27 |
| H(14) | 8634 | 5633 | 3778 | 30 |
| H(15) | 7997 | 5661 | 2314 | 31 |
| H(16) | 5884 | 5576 | 1836 | 26 |
| H(18) | 2872 | 3304 | 1589 | 41 |
| H(19) | 2486 | 2450 | 69 | 47 |
| H(20) | 2707 | 3410 | -992 | 38 |
| H(21) | 3274 | 5225 | -532 | 36 |
| H(22) | 3630 | 6078 | 989 | 31 |
| H(24) | 6684 | 9835 | 2504 | 26 |
| H(26) | 7655 | 11704 | 2454 | 31 |
| H(27) | 7419 | 13272 | 2447 | 33 |
| H(28) | 5346 | 13400 | 2370 | 34 |
| H(29) | 3525 | 11959 | 2338 | 30 |
| H(31) | 2542 | 10087 | 2392 | 25 |
| H(34) | -75 | 6353 | 1029 | 33 |
| H(35) | -597 | 5635 | -524 | 37 |
| H(36) | 959 | 6110 | -1416 | 41 |
| H(37) | 3042 | 7332 | -758 | 50 |
| H(38) | 3539 | 8129 | 774 | 39 |
| H(40) | 436 | 8685 | 1454 | 30 |
| H(41) | -1398 | 9062 | 1801 | 34 |
| H(42) | -2195 | 8730 | 3091 | 34 |
| H(43) | -1149 | 8064 | 4042 | 33 |
| H(44) | 692 | 7691 | 3696 | 28 |
| H(45A) | 5749 | 8535 | 5349 | 44 |
| H(45B) | 5952 | 8726 | 4385 | 44 |
| H(45C) | 5898 | 7638 | 4577 | 44 |
| H(46A) | 3665 | 9318 | 4458 | 33 |
| H(46B) | 3833 | 9113 | 5428 | 33 |
| H(46C) | 2435 | 8586 | 4780 | 33 |
| H(47A) | 3558 | 7284 | 5708 | 45 |
| H(47B) | 3581 | 6281 | 4990 | 45 |
| H(47C) | 2278 | 6547 | 4978 | 45 |
| H(48A) | 9891 | 1242 | 1988 | 123 |
| H(48B) | 10876 | 1983 | 1504 | 123 |
| H(48C) | 10736 | 782 | 1349 | 123 |
| H(49A) | 9002 | 1587 | 698 | 84 |
| H(49B) | 9609 | 810 | 148 | 84 |
| H(50A) | 7397 | -480 | -557 | 109 |
| H(50B) | 6955 | 442 | -71 | 109 |
| H(51A) | 6113 | -1544 | 211 | 69 |
| H(51B) | 5312 | -1173 | -473 | 69 |
| H(51C) | 5590 | -624 | 580 | 69 |

## 8.5 Crystallographic data of 14

### 8.5.1 Crystal data and structure refinement

| | |
|---|---|
| Empirical formula | C26 H28 Ni P2 S |
| Formula weight | 493.19 |
| Temperature | 100(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Monoclinic |
| Space group | P21/n |
| Unit cell dimensions | a = 9.0995(6) Å α = 90 º. |
| | b = 12.8266(4) Å β = 96.155(4) º. |
| | c = 20.6562(6) Å γ = 90 º. |
| Volume | 2397.00(19) $Å^3$ |
| Z | 4 |
| Density (calculated) | 1.367 $Mg/m^3$ |
| Absorption coefficient | 1.041 $mm^{-1}$ |
| F(000) | 1032 |
| Crystal size | 0.32 x 0.28 x 0.14 mm |
| Theta range for data collection | 2.36 to 26.37 º. |
| Index ranges | -11<=h<=11,-15<=k<=16,-25<=l<=25 |
| Reflections collected | 20568 |
| Independent reflections | 4899 [R (int) = 0.0414] |
| Completeness to 2theta = 26.37 | 99.8% |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 4899 / 0 / 275 |
| Goodness-of-fit on $F^2$ | 1.049 |
| Final R indices [I>2sigma (I)] | R1 = 0.0355, wR2 = 0.0876 |
| R indices (all data) | R1 = 0.0603, wR2 = 0.1039 |
| Largest diff. peak and hole | 0.791 and -0.291 e. $Å^{-3}$ |

## 8.5.2 Atomic coordinates (x 10^4) and equivalent isotropic Displacement parameters (A^2 x 10^3)

| | x | y | z | U(eq) |
|---|---|---|---|---|
| C(1) | 4922(3) | 5094(2) | 3108(1) | 17(1) |
| C(2) | 5281(3) | 5225(2) | 3765(1) | 21(1) |
| C(3) | 4974(3) | 6157(2) | 4086(1) | 18(1) |
| C(4) | 5290(3) | 6298(2) | 4767(1) | 21(1) |
| C(5) | 4954(3) | 7205(2) | 5062(1) | 25(1) |
| C(6) | 4313(3) | 8046(2) | 4693(1) | 25(1) |
| C(7) | 4006(3) | 7942(2) | 4033(1) | 23(1) |
| C(8) | 4296(3) | 7005(2) | 3716(1) | 19(1) |
| C(9) | 3918(3) | 6861(2) | 3044(1) | 20(1) |
| C(10) | 4189(3) | 5938(2) | 2746(1) | 16(1) |
| C(11) | 4013(3) | 6843(2) | 1464(1) | 18(1) |
| C(12) | 5366(3) | 6918(2) | 1207(1) | 26(1) |
| C(13) | 5757(3) | 7827(2) | 910(1) | 31(1) |
| C(14) | 4789(3) | 8652(2) | 849(1) | 31(1) |
| C(15) | 3447(3) | 8592(2) | 1098(1) | 24(1) |
| C(16) | 3055(3) | 7690(2) | 1407(1) | 20(1) |
| C(17) | 1654(3) | 5477(2) | 1853(1) | 17(1) |
| C(18) | 707(3) | 5716(2) | 1303(1) | 20(1) |
| C(19) | -794(3) | 5484(2) | 1279(1) | 24(1) |
| C(20) | -1340(3) | 5006(2) | 1801(1) | 24(1) |
| C(21) | -400(3) | 4749(2) | 2348(1) | 23(1) |
| C(22) | 1084(3) | 4988(2) | 2375(1) | 21(1) |
| C(23) | 4096(3) | 4490(2) | 726(1) | 23(1) |
| C(24) | 7041(3) | 2133(2) | 1973(1) | 30(1) |
| C(25) | 6838(3) | 2922(2) | 685(1) | 30(1) |
| C(26) | 4504(3) | 1716(2) | 1104(2) | 34(1) |
| S(1) | 5322(1) | 3938(1) | 2702(1) | 21(1) |
| P(1) | 3663(1) | 5639(1) | 1895(1) | 16(1) |
| P(2) | 5751(1) | 2775(1) | 1368(1) | 22(1) |
| Ni(1) | 4696(1) | 4211(1) | 1657(1) | 18(1) |

## 8.5.3 Bond lengths [Å] and angles [º]

| | |
|---|---|
| C(1)-C(2) | 1.372(4) |
| C(1)-C(10) | 1.437(3) |
| C(1)-S(1) | 1.761(3) |
| C(2)-C(3) | 1.410(4) |
| C(2)-H(2) | 0.9500 |
| C(3)-C(4) | 1.418(3) |
| C(3)-C(8) | 1.431(3) |
| C(4)-C(5) | 1.364(4) |
| C(4)-H(4) | 0.9500 |
| C(5)-C(6) | 1.410(4) |
| C(5)-H(5) | 0.9500 |
| C(6)-C(7) | 1.369(4) |
| C(6)-H(6) | 0.9500 |

| | |
|---|---|
| C(7)-C(8) | 1.408(4) |
| C(7)-H(7) | 0.9500 |
| C(8)-C(9) | 1.405(4) |
| C(9)-C(10) | 1.369(4) |
| C(9)-H(9) | 0.9500 |
| C(10)-P(1) | 1.813(2) |
| C(11)-C(16) | 1.390(3) |
| C(11)-C(12) | 1.395(4) |
| C(11)-P(1) | 1.827(3) |
| C(12)-C(13) | 1.382(4) |
| C(12)-H(12) | 0.9500 |
| C(13)-C(14) | 1.374(4) |
| C(13)-H(13) | 0.9500 |
| C(14)-C(15) | 1.376(4) |
| C(14)-H(14) | 0.9500 |
| C(15)-C(16) | 1.386(4) |
| C(15)-H(15) | 0.9500 |
| C(16)-H(16) | 0.9500 |
| C(17)-C(18) | 1.385(3) |
| C(17)-C(22) | 1.394(4) |
| C(17)-P(1) | 1.832(2) |
| C(18)-C(19) | 1.394(4) |
| C(18)-H(18) | 0.9500 |
| C(19)-C(20) | 1.379(4) |
| C(19)-H(19) | 0.9500 |
| C(20)-C(21) | 1.383(4) |
| C(20)-H(20) | 0.9500 |
| C(21)-C(22) | 1.381(3) |
| C(21)-H(21) | 0.9500 |
| C(22)-H(22) | 0.9500 |
| C(23)-Ni(1) | 1.975(3) |
| C(23)-H(23A) | 0.9800 |
| C(23)-H(23B) | 0.9800 |
| C(23)-H(23C) | 0.9800 |
| C(24)-P(2) | 1.818(3) |
| C(24)-H(24A) | 0.9800 |
| C(24)-H(24B) | 0.9800 |
| C(24)-H(24C) | 0.9800 |
| C(25)-P(2) | 1.818(3) |
| C(25)-H(25A) | 0.9800 |
| C(25)-H(25B) | 0.9800 |
| C(25)-H(25C) | 0.9800 |
| C(26)-P(2) | 1.817(3) |
| C(26)-H(26A) | 0.9800 |
| C(26)-H(26B) | 0.9800 |
| C(26)-H(26C) | 0.9800 |
| S(1)-Ni(1) | 2.1997(7) |
| P(1)-Ni(1) | 2.1403(7) |
| P(2)-Ni(1) | 2.1888(8) |

| | |
|---|---|
| C(2)-C(1)-C(10) | 118.1(2) |
| C(2)-C(1)-S(1) | 122.3(2) |
| C(10)-C(1)-S(1) | 119.64(19) |
| C(1)-C(2)-C(3) | 122.0(2) |
| C(1)-C(2)-H(2) | 119.0 |
| C(3)-C(2)-H(2) | 119.0 |
| C(2)-C(3)-C(4) | 123.0(2) |
| C(2)-C(3)-C(8) | 119.3(2) |
| C(4)-C(3)-C(8) | 117.7(2) |
| C(5)-C(4)-C(3) | 121.4(2) |
| C(5)-C(4)-H(4) | 119.3 |

| | |
|---|---|
| C(3)-C(4)-H(4) | 119.3 |
| C(4)-C(5)-C(6) | 120.7(2) |
| C(4)-C(5)-H(5) | 119.6 |
| C(6)-C(5)-H(5) | 119.6 |
| C(7)-C(6)-C(5) | 119.5(3) |
| C(7)-C(6)-H(6) | 120.2 |
| C(5)-C(6)-H(6) | 120.2 |
| C(6)-C(7)-C(8) | 121.2(2) |
| C(6)-C(7)-H(7) | 119.4 |
| C(8)-C(7)-H(7) | 119.4 |
| C(9)-C(8)-C(7) | 122.3(2) |
| C(9)-C(8)-C(3) | 118.3(2) |
| C(7)-C(8)-C(3) | 119.4(2) |
| C(10)-C(9)-C(8) | 121.4(2) |
| C(10)-C(9)-H(9) | 119.3 |
| C(8)-C(9)-H(9) | 119.3 |
| C(9)-C(10)-C(1) | 120.9(2) |
| C(9)-C(10)-P(1) | 125.24(19) |
| C(1)-C(10)-P(1) | 113.86(18) |
| C(16)-C(11)-C(12) | 119.0(2) |
| C(16)-C(11)-P(1) | 124.2(2) |
| C(12)-C(11)-P(1) | 116.78(19) |
| C(13)-C(12)-C(11) | 120.5(3) |
| C(13)-C(12)-H(12) | 119.8 |
| C(11)-C(12)-H(12) | 119.8 |
| C(14)-C(13)-C(12) | 119.8(3) |
| C(14)-C(13)-H(13) | 120.1 |
| C(12)-C(13)-H(13) | 120.1 |
| C(13)-C(14)-C(15) | 120.5(3) |
| C(13)-C(14)-H(14) | 119.7 |
| C(15)-C(14)-H(14) | 119.7 |
| C(14)-C(15)-C(16) | 120.1(3) |
| C(14)-C(15)-H(15) | 120.0 |
| C(16)-C(15)-H(15) | 120.0 |
| C(15)-C(16)-C(11) | 120.1(3) |
| C(15)-C(16)-H(16) | 120.0 |
| C(11)-C(16)-H(16) | 120.0 |
| C(18)-C(17)-C(22) | 118.9(2) |
| C(18)-C(17)-P(1) | 122.9(2) |
| C(22)-C(17)-P(1) | 117.82(19) |
| C(17)-C(18)-C(19) | 120.3(2) |
| C(17)-C(18)-H(18) | 119.9 |
| C(19)-C(18)-H(18) | 119.9 |
| C(20)-C(19)-C(18) | 120.0(2) |
| C(20)-C(19)-H(19) | 120.0 |
| C(18)-C(19)-H(19) | 120.0 |
| C(19)-C(20)-C(21) | 120.2(2) |
| C(19)-C(20)-H(20) | 119.9 |
| C(21)-C(20)-H(20) | 119.9 |
| C(22)-C(21)-C(20) | 119.8(3) |
| C(22)-C(21)-H(21) | 120.1 |
| C(20)-C(21)-H(21) | 120.1 |
| C(21)-C(22)-C(17) | 120.8(2) |
| C(21)-C(22)-H(22) | 119.6 |
| C(17)-C(22)-H(22) | 119.6 |
| Ni(1)-C(23)-H(23A) | 109.5 |
| Ni(1)-C(23)-H(23B) | 109.5 |
| H(23A)-C(23)-H(23B) | 109.5 |
| Ni(1)-C(23)-H(23C) | 109.5 |
| H(23A)-C(23)-H(23C) | 109.5 |
| H(23B)-C(23)-H(23C) | 109.5 |

| | |
|---|---|
| P(2)-C(24)-H(24A) | 109.5 |
| P(2)-C(24)-H(24B) | 109.5 |
| H(24A)-C(24)-H(24B) | 109.5 |
| P(2)-C(24)-H(24C) | 109.5 |
| H(24A)-C(24)-H(24C) | 109.5 |
| H(24B)-C(24)-H(24C) | 109.5 |
| P(2)-C(25)-H(25A) | 109.5 |
| P(2)-C(25)-H(25B) | 109.5 |
| H(25A)-C(25)-H(25B) | 109.5 |
| P(2)-C(25)-H(25C) | 109.5 |
| H(25A)-C(25)-H(25C) | 109.5 |
| H(25B)-C(25)-H(25C) | 109.5 |
| P(2)-C(26)-H(26A) | 109.5 |
| P(2)-C(26)-H(26B) | 109.5 |
| H(26A)-C(26)-H(26B) | 109.5 |
| P(2)-C(26)-H(26C) | 109.5 |
| H(26A)-C(26)-H(26C) | 109.5 |
| H(26B)-C(26)-H(26C) | 109.5 |
| C(1)-S(1)-Ni(1) | 106.75(9) |
| C(10)-P(1)-C(11) | 104.62(11) |
| C(10)-P(1)-C(17) | 103.18(11) |
| C(11)-P(1)-C(17) | 107.35(12) |
| C(10)-P(1)-Ni(1) | 109.06(8) |
| C(11)-P(1)-Ni(1) | 120.52(9) |
| C(17)-P(1)-Ni(1) | 110.62(8) |
| C(26)-P(2)-C(24) | 101.79(14) |
| C(26)-P(2)-C(25) | 102.57(14) |
| C(24)-P(2)-C(25) | 102.47(14) |
| C(26)-P(2)-Ni(1) | 115.69(10) |
| C(24)-P(2)-Ni(1) | 117.60(10) |
| C(25)-P(2)-Ni(1) | 114.58(10) |
| C(23)-Ni(1)-P(1) | 89.20(8) |
| C(23)-Ni(1)-P(2) | 88.28(8) |
| P(1)-Ni(1)-P(2) | 177.37(3) |
| C(23)-Ni(1)-S(1) | 178.32(8) |
| P(1)-Ni(1)-S(1) | 89.14(3) |
| P(2)-Ni(1)-S(1) | 93.37(3) |

## 8.5.4 Anisotropic displacement parameters (A^2 x 10^3)

| | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| C(1) | 14(1) | 19(1) | 19(1) | -1(1) | 4(1) | -4(1) |
| C(2) | 19(1) | 18(1) | 24(2) | 6(1) | -1(1) | -3(1) |
| C(3) | 13(1) | 21(1) | 20(1) | 1(1) | 2(1) | -6(1) |
| C(4) | 19(1) | 22(2) | 20(1) | 3(1) | -2(1) | -5(1) |
| C(5) | 25(2) | 29(2) | 20(1) | -2(1) | 0(1) | -8(1) |
| C(6) | 26(2) | 24(2) | 26(2) | -4(1) | 0(1) | 0(1) |
| C(7) | 20(1) | 23(2) | 26(2) | 0(1) | -1(1) | -1(1) |
| C(8) | 13(1) | 23(1) | 21(1) | 2(1) | 1(1) | -1(1) |
| C(9) | 14(1) | 22(1) | 23(1) | 3(1) | 1(1) | 0(1) |
| C(10) | 13(1) | 20(1) | 16(1) | -1(1) | 0(1) | -1(1) |
| C(11) | 20(1) | 19(1) | 14(1) | -2(1) | 0(1) | -1(1) |
| C(12) | 24(2) | 22(2) | 31(2) | 4(1) | 2(1) | 0(1) |
| C(13) | 30(2) | 30(2) | 35(2) | 2(1) | 11(1) | -8(1) |
| C(14) | 47(2) | 20(2) | 26(2) | 2(1) | 5(1) | -8(1) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(15) | 32(2) | 18(1) | 21(1) | -1(1) | -5(1) | 1(1) |
| C(16) | 21(1) | 22(1) | 15(1) | -2(1) | -2(1) | -1(1) |
| C(17) | 13(1) | 18(1) | 21(1) | -2(1) | 0(1) | -1(1) |
| C(18) | 20(1) | 19(1) | 21(1) | 2(1) | 3(1) | 2(1) |
| C(19) | 19(1) | 27(2) | 27(2) | 1(1) | -3(1) | 1(1) |
| C(20) | 15(1) | 26(2) | 31(2) | -2(1) | 2(1) | -2(1) |
| C(21) | 22(1) | 24(2) | 25(2) | 3(1) | 6(1) | -4(1) |
| C(22) | 22(1) | 21(1) | 19(1) | 1(1) | -2(1) | 0(1) |
| C(23) | 28(2) | 22(2) | 19(1) | -3(1) | 6(1) | 4(1) |
| C(24) | 30(2) | 24(2) | 36(2) | 3(1) | 4(1) | 10(1) |
| C(25) | 24(2) | 33(2) | 33(2) | -7(1) | 8(1) | 3(1) |
| C(26) | 27(2) | 24(2) | 49(2) | -8(1) | 3(1) | 0(1) |
| S(1) | 24(1) | 19(1) | 21(1) | 1(1) | 1(1) | 4(1) |
| P(1) | 15(1) | 16(1) | 16(1) | 1(1) | 0(1) | 0(1) |
| P(2) | 18(1) | 20(1) | 27(1) | -2(1) | 4(1) | 2(1) |
| Ni(1) | 17(1) | 17(1) | 19(1) | 0(1) | 2(1) | 1(1) |

## 8.5.5 Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3).

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(2) | 5752 | 4670 | 4012 | 25 |
| H(4) | 5746 | 5748 | 5024 | 25 |
| H(5) | 5153 | 7271 | 5521 | 30 |
| H(6) | 4097 | 8679 | 4902 | 30 |
| H(7) | 3590 | 8514 | 3785 | 28 |
| H(9) | 3465 | 7416 | 2792 | 23 |
| H(12) | 6023 | 6341 | 1238 | 31 |
| H(13) | 6692 | 7882 | 747 | 37 |
| H(14) | 5047 | 9270 | 634 | 37 |
| H(15) | 2789 | 9169 | 1057 | 29 |
| H(16) | 2130 | 7651 | 1579 | 24 |
| H(18) | 1082 | 6039 | 941 | 24 |
| H(19) | -1442 | 5656 | 902 | 29 |
| H(20) | -2365 | 4853 | 1784 | 29 |
| H(21) | -774 | 4408 | 2705 | 28 |
| H(22) | 1725 | 4818 | 2754 | 25 |
| H(23A) | 3245 | 4962 | 683 | 27 |
| H(23B) | 3826 | 3833 | 502 | 27 |
| H(23C) | 4920 | 4812 | 531 | 27 |
| H(24A) | 7879 | 2597 | 2099 | 36 |
| H(24B) | 7399 | 1488 | 1790 | 36 |
| H(24C) | 6540 | 1967 | 2358 | 36 |
| H(25A) | 7200 | 2237 | 563 | 35 |
| H(25B) | 7679 | 3383 | 809 | 35 |
| H(25C) | 6219 | 3223 | 314 | 35 |
| H(26A) | 3977 | 1487 | 1468 | 40 |
| H(26B) | 5073 | 1131 | 953 | 40 |
| H(26C) | 3789 | 1956 | 746 | 40 |

## 8.6 Crystallographic data of 15

### 8.6.1 Crystal data and structure refinement

| | |
|---|---|
| Empirical formula | C29 H37 Ni P3 S |
| Formula weight | 569.27 |
| Temperature | 100(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Monoclinic |
| Space group | P21/n |
| Unit cell dimensions | a = 13.5939(8) Å α = 90 º. |
| | b = 13.9297(7) Å β = 94.366(5) º. |
| | c = 15.0138(8) Å γ = 90 º. |
| Volume | 2834.7(3) $Å^3$ |
| Z | 4 |
| Density (calculated) | 1.334 $Mg/m^3$ |
| Absorption coefficient | 0.944 $mm^{-1}$ |
| F(000) | 1200 |
| Crystal size | 0.16 x 0.16 x 0.08 mm |
| Theta range for data collection | 2.44 to 26.37º. |
| Index ranges | -15<=h<=16,-17<=k<=17,-18<=l<=18 |
| Reflections collected | 23007 |
| Independent reflections | 5783 [R (int) = 0.0943] |
| Completeness to 2theta = 26.37 | 99.7% |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 5783 / 0 / 313 |
| Goodness-of-fit on $F^2$ | 1.097 |

| | |
|---|---|
| Final R indices [I>2sigma (I)] | R1 = 0.0684, wR2 = 0.0955 |
| R indices (all data) | R1 = 0.1430, wR2 = 0.1206 |
| Largest diff. peak and hole | 0.737 and -0.556 e. Å $^{-3}$ |

## 8.6.2 Atomic coordinates (x 10^4) and equivalent isotropic Displacement parameters (A^2 x 10^3)

| | x | y | z | U(eq) |
|---|---|---|---|---|
| C(1) | 3591(3) | 659(3) | 2716(3) | 17(1) |
| C(2) | 4331(3) | 736(3) | 3391(3) | 21(1) |
| C(3) | 5275(3) | 323(3) | 3324(3) | 21(1) |
| C(4) | 6039(4) | 377(4) | 4011(4) | 28(1) |
| C(5) | 6936(4) | -21(4) | 3924(4) | 30(1) |
| C(6) | 7123(4) | -501(4) | 3126(4) | 32(1) |
| C(7) | 6403(4) | -584(3) | 2449(3) | 24(1) |
| C(8) | 5465(3) | -174(3) | 2521(3) | 19(1) |
| C(9) | 4696(3) | -249(3) | 1828(3) | 18(1) |
| C(10) | 3792(3) | 161(3) | 1914(3) | 15(1) |
| C(11) | 2996(3) | -897(3) | 382(3) | 15(1) |
| C(12) | 2801(3) | -1822(3) | 674(3) | 20(1) |
| C(13) | 2978(4) | -2615(3) | 171(3) | 23(1) |
| C(14) | 3368(3) | -2512(4) | -650(3) | 22(1) |
| C(15) | 3561(3) | -1598(4) | -962(3) | 22(1) |
| C(16) | 3378(3) | -803(3) | -448(3) | 18(1) |
| C(17) | 2941(3) | 1130(3) | 337(3) | 17(1) |
| C(18) | 3858(3) | 1547(3) | 259(3) | 17(1) |
| C(19) | 3967(4) | 2289(3) | -338(3) | 23(1) |
| C(20) | 3167(4) | 2630(3) | -868(3) | 24(1) |
| C(21) | 2252(4) | 2213(3) | -801(3) | 22(1) |
| C(22) | 2141(4) | 1470(3) | -206(3) | 20(1) |
| C(23) | 631(4) | -595(3) | 1002(3) | 23(1) |
| C(24) | 176(4) | 2307(3) | 879(3) | 26(1) |
| C(25) | -1013(4) | 978(4) | 1686(4) | 32(1) |
| C(26) | 274(4) | 2169(4) | 2727(3) | 26(1) |
| C(27) | 429(4) | -1846(4) | 2763(3) | 30(1) |
| C(28) | 645(4) | -270(4) | 3933(3) | 30(1) |
| C(29) | 2318(4) | -1318(4) | 3512(3) | 27(1) |
| P(1) | 2729(1) | 125(1) | 1090(1) | 15(1) |
| P(2) | 1205(1) | -784(1) | 2972(1) | 20(1) |
| P(3) | 260(1) | 1392(1) | 1749(1) | 20(1) |
| S(1) | 2419(1) | 1155(1) | 2798(1) | 20(1) |
| Ni(1) | 1424(1) | 237(1) | 1848(1) | 16(1) |

## 8.6.3 Bond lengths [Å] and angles [°]

| | |
|---|---|
| C(1)-C(2) | 1.376(6) |
| C(1)-C(10) | 1.434(6) |
| C(1)-S(1) | 1.749(5) |
| C(2)-C(3) | 1.417(6) |

| | |
|---|---|
| C(2)-H(2) | 0.9500 |
| C(3)-C(4) | 1.409(7) |
| C(3)-C(8) | 1.430(6) |
| C(4)-C(5) | 1.355(7) |
| C(4)-H(4) | 0.9500 |
| C(5)-C(6) | 1.412(7) |
| C(5)-H(5) | 0.9500 |
| C(6)-C(7) | 1.362(7) |
| C(6)-H(6) | 0.9500 |
| C(7)-C(8) | 1.410(6) |
| C(7)-H(7) | 0.9500 |
| C(8)-C(9) | 1.421(6) |
| C(9)-C(10) | 1.369(6) |
| C(9)-H(9) | 0.9500 |
| C(10)-P(1) | 1.830(5) |
| C(11)-C(16) | 1.392(6) |
| C(11)-C(12) | 1.393(6) |
| C(11)-P(1) | 1.829(4) |
| C(12)-C(13) | 1.371(6) |
| C(12)-H(12) | 0.9500 |
| C(13)-C(14) | 1.386(6) |
| C(13)-H(13) | 0.9500 |
| C(14)-C(15) | 1.388(7) |
| C(14)-H(14) | 0.9500 |
| C(15)-C(16) | 1.383(6) |
| C(15)-H(15) | 0.9500 |
| C(16)-H(16) | 0.9500 |
| C(17)-C(18) | 1.388(6) |
| C(17)-C(22) | 1.392(6) |
| C(17)-P(1) | 1.836(5) |
| C(18)-C(19) | 1.383(6) |
| C(18)-H(18) | 0.9500 |
| C(19)-C(20) | 1.382(7) |
| C(19)-H(19) | 0.9500 |
| C(20)-C(21) | 1.383(7) |
| C(20)-H(20) | 0.9500 |
| C(21)-C(22) | 1.383(6) |
| C(21)-H(21) | 0.9500 |
| C(22)-H(22) | 0.9500 |
| C(23)-Ni(1) | 1.977(5) |
| C(23)-H(23A) | 0.9800 |
| C(23)-H(23B) | 0.9800 |
| C(23)-H(23C) | 0.9800 |
| C(24)-P(3) | 1.822(5) |
| C(24)-H(24A) | 0.9800 |
| C(24)-H(24B) | 0.9800 |
| C(24)-H(24C) | 0.9800 |
| C(25)-P(3) | 1.819(5) |
| C(25)-H(25A) | 0.9800 |
| C(25)-H(25B) | 0.9800 |
| C(25)-H(25C) | 0.9800 |
| C(26)-P(3) | 1.824(5) |
| C(26)-H(26A) | 0.9800 |
| C(26)-H(26B) | 0.9800 |
| C(26)-H(26C) | 0.9800 |
| C(27)-P(2) | 1.830(5) |
| C(27)-H(27A) | 0.9800 |
| C(27)-H(27B) | 0.9800 |
| C(27)-H(27C) | 0.9800 |
| C(28)-P(2) | 1.828(5) |
| C(28)-H(28A) | 0.9800 |

| | |
|---|---|
| C(28)-H(28B) | 0.9800 |
| C(28)-H(28C) | 0.9800 |
| C(29)-P(2) | 1.820(5) |
| C(29)-H(29A) | 0.9800 |
| C(29)-H(29B) | 0.9800 |
| C(29)-H(29C) | 0.9800 |
| P(1)-Ni(1) | 2.1858(13) |
| P(2)-Ni(1) | 2.2433(14) |
| P(3)-Ni(1) | 2.2526(14) |
| S(1)-Ni(1) | 2.2813(14) |

| | |
|---|---|
| C(2)-C(1)-C(10) | 118.8(4) |
| C(2)-C(1)-S(1) | 122.4(4) |
| C(10)-C(1)-S(1) | 118.9(3) |
| C(1)-C(2)-C(3) | 122.0(5) |
| C(1)-C(2)-H(2) | 119.0 |
| C(3)-C(2)-H(2) | 119.0 |
| C(4)-C(3)-C(2) | 123.2(5) |
| C(4)-C(3)-C(8) | 118.2(4) |
| C(2)-C(3)-C(8) | 118.6(4) |
| C(5)-C(4)-C(3) | 121.8(5) |
| C(5)-C(4)-H(4) | 119.1 |
| C(3)-C(4)-H(4) | 119.1 |
| C(4)-C(5)-C(6) | 119.8(5) |
| C(4)-C(5)-H(5) | 120.1 |
| C(6)-C(5)-H(5) | 120.1 |
| C(7)-C(6)-C(5) | 120.5(5) |
| C(7)-C(6)-H(6) | 119.7 |
| C(5)-C(6)-H(6) | 119.7 |
| C(6)-C(7)-C(8) | 120.8(5) |
| C(6)-C(7)-H(7) | 119.6 |
| C(8)-C(7)-H(7) | 119.6 |
| C(7)-C(8)-C(9) | 122.2(4) |
| C(7)-C(8)-C(3) | 118.9(4) |
| C(9)-C(8)-C(3) | 118.9(4) |
| C(10)-C(9)-C(8) | 121.1(4) |
| C(10)-C(9)-H(9) | 119.5 |
| C(8)-C(9)-H(9) | 119.5 |
| C(9)-C(10)-C(1) | 120.6(4) |
| C(9)-C(10)-P(1) | 126.4(4) |
| C(1)-C(10)-P(1) | 112.9(3) |
| C(16)-C(11)-C(12) | 117.4(4) |
| C(16)-C(11)-P(1) | 123.5(4) |
| C(12)-C(11)-P(1) | 119.1(4) |
| C(13)-C(12)-C(11) | 121.8(4) |
| C(13)-C(12)-H(12) | 119.1 |
| C(11)-C(12)-H(12) | 119.1 |
| C(12)-C(13)-C(14) | 120.2(5) |
| C(12)-C(13)-H(13) | 119.9 |
| C(14)-C(13)-H(13) | 119.9 |
| C(13)-C(14)-C(15) | 119.3(4) |
| C(13)-C(14)-H(14) | 120.4 |
| C(15)-C(14)-H(14) | 120.4 |
| C(16)-C(15)-C(14) | 120.0(4) |
| C(16)-C(15)-H(15) | 120.0 |
| C(14)-C(15)-H(15) | 120.0 |
| C(15)-C(16)-C(11) | 121.3(4) |
| C(15)-C(16)-H(16) | 119.3 |
| C(11)-C(16)-H(16) | 119.3 |
| C(18)-C(17)-C(22) | 118.3(4) |
| C(18)-C(17)-P(1) | 123.7(4) |

| | |
|---|---|
| C(22)-C(17)-P(1) | 117.9(4) |
| C(19)-C(18)-C(17) | 120.6(5) |
| C(19)-C(18)-H(18) | 119.7 |
| C(17)-C(18)-H(18) | 119.7 |
| C(20)-C(19)-C(18) | 120.8(5) |
| C(20)-C(19)-H(19) | 119.6 |
| C(18)-C(19)-H(19) | 119.6 |
| C(19)-C(20)-C(21) | 119.1(5) |
| C(19)-C(20)-H(20) | 120.5 |
| C(21)-C(20)-H(20) | 120.5 |
| C(22)-C(21)-C(20) | 120.3(5) |
| C(22)-C(21)-H(21) | 119.9 |
| C(20)-C(21)-H(21) | 119.9 |
| C(21)-C(22)-C(17) | 121.0(5) |
| C(21)-C(22)-H(22) | 119.5 |
| C(17)-C(22)-H(22) | 119.5 |
| Ni(1)-C(23)-H(23A) | 109.5 |
| Ni(1)-C(23)-H(23B) | 109.5 |
| H(23A)-C(23)-H(23B) | 109.5 |
| Ni(1)-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(24)-H(24A) | 109.5 |
| P(3)-C(24)-H(24B) | 109.5 |
| H(24A)-C(24)-H(24B) | 109.5 |
| P(3)-C(24)-H(24C) | 109.5 |
| H(24A)-C(24)-H(24C) | 109.5 |
| H(24B)-C(24)-H(24C) | 109.5 |
| P(3)-C(25)-H(25A) | 109.5 |
| P(3)-C(25)-H(25B) | 109.5 |
| H(25A)-C(25)-H(25B) | 109.5 |
| P(3)-C(25)-H(25C) | 109.5 |
| H(25A)-C(25)-H(25C) | 109.5 |
| H(25B)-C(25)-H(25C) | 109.5 |
| P(3)-C(26)-H(26A) | 109.5 |
| P(3)-C(26)-H(26B) | 109.5 |
| H(26A)-C(26)-H(26B) | 109.5 |
| P(3)-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(11)-P(1)-C(10) | 103.4(2) |
| C(11)-P(1)-C(17) | 100.8(2) |
| C(10)-P(1)-C(17) | 104.0(2) |

| | |
|---|---|
| C(11)-P(1)-Ni(1) | 124.28(15) |
| C(10)-P(1)-Ni(1) | 106.09(14) |
| C(17)-P(1)-Ni(1) | 115.98(15) |
| C(29)-P(2)-C(28) | 101.0(2) |
| C(29)-P(2)-C(27) | 101.2(2) |
| C(28)-P(2)-C(27) | 100.5(2) |
| C(29)-P(2)-Ni(1) | 116.16(17) |
| C(28)-P(2)-Ni(1) | 115.59(18) |
| C(27)-P(2)-Ni(1) | 119.44(17) |
| C(25)-P(3)-C(24) | 100.2(2) |
| C(25)-P(3)-C(26) | 100.4(2) |
| C(24)-P(3)-C(26) | 99.1(2) |
| C(25)-P(3)-Ni(1) | 115.96(18) |
| C(24)-P(3)-Ni(1) | 123.54(16) |
| C(26)-P(3)-Ni(1) | 113.97(17) |
| C(1)-S(1)-Ni(1) | 103.60(16) |
| C(23)-Ni(1)-P(1) | 92.72(15) |
| C(23)-Ni(1)-P(2) | 90.86(15) |
| P(1)-Ni(1)-P(2) | 120.36(5) |
| C(23)-Ni(1)-P(3) | 91.73(15) |
| P(1)-Ni(1)-P(3) | 127.61(5) |
| P(2)-Ni(1)-P(3) | 111.73(5) |
| C(23)-Ni(1)-S(1) | 176.61(15) |
| P(1)-Ni(1)-S(1) | 84.18(5) |
| P(2)-Ni(1)-S(1) | 89.54(5) |
| P(3)-Ni(1)-S(1) | 91.25(5) |

## 8.6.4 Anisotropic displacement parameters (A^2 x 10^3)

| | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| C(1) | 17(3) | 15(3) | 20(3) | 4(2) | 5(2) | -3(2) |
| C(2) | 24(3) | 14(3) | 24(3) | -2(2) | 1(2) | -5(2) |
| C(3) | 20(3) | 19(3) | 24(3) | 5(2) | 0(2) | -5(2) |
| C(4) | 30(3) | 24(3) | 30(3) | -1(3) | -7(3) | -4(3) |
| C(5) | 20(3) | 31(3) | 37(3) | 9(3) | -16(3) | -6(2) |
| C(6) | 20(3) | 29(3) | 45(4) | 19(3) | 2(3) | 6(2) |
| C(7) | 27(3) | 17(3) | 28(3) | 9(2) | -2(3) | 1(2) |
| C(8) | 18(3) | 14(2) | 26(3) | 5(2) | 1(2) | -1(2) |
| C(9) | 23(3) | 11(2) | 22(3) | 0(2) | 5(2) | -1(2) |
| C(10) | 19(3) | 16(2) | 12(2) | 7(2) | 4(2) | -3(2) |
| C(11) | 10(2) | 14(3) | 19(3) | -6(2) | -1(2) | -1(2) |
| C(12) | 20(3) | 25(3) | 15(3) | -1(2) | 3(2) | 3(2) |
| C(13) | 29(3) | 12(3) | 28(3) | -1(2) | 7(2) | -2(2) |
| C(14) | 19(3) | 20(3) | 28(3) | -9(2) | 5(2) | 3(2) |
| C(15) | 18(3) | 31(3) | 16(3) | -6(2) | 2(2) | -1(2) |
| C(16) | 14(3) | 18(3) | 20(3) | 2(2) | 1(2) | 2(2) |
| C(17) | 22(3) | 12(2) | 17(3) | -7(2) | 5(2) | 1(2) |
| C(18) | 14(3) | 21(3) | 18(3) | -5(2) | 6(2) | 0(2) |
| C(19) | 25(3) | 20(3) | 25(3) | -2(2) | 15(2) | -3(2) |
| C(20) | 35(3) | 12(3) | 26(3) | 7(2) | 8(3) | 2(2) |
| C(21) | 27(3) | 19(3) | 19(3) | 1(2) | 1(2) | 7(2) |
| C(22) | 21(3) | 17(3) | 20(3) | -7(2) | 7(2) | -1(2) |
| C(23) | 24(3) | 23(3) | 22(3) | -6(2) | 1(2) | 0(2) |
| C(24) | 27(3) | 22(3) | 29(3) | -1(3) | 2(2) | 7(2) |
| C(25) | 25(3) | 28(3) | 43(4) | -3(3) | 7(3) | 2(2) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(26) | 27(3) | 25(3) | 27(3) | -7(3) | 5(2) | 8(2) |
| C(27) | 39(3) | 27(3) | 25(3) | 6(3) | 2(3) | -9(3) |
| C(28) | 35(3) | 33(3) | 23(3) | 3(3) | 14(2) | 0(3) |
| C(29) | 29(3) | 26(3) | 26(3) | -1(3) | 6(2) | 5(2) |
| P(1) | 16(1) | 15(1) | 15(1) | -1(1) | 3(1) | 1(1) |
| P(2) | 22(1) | 19(1) | 20(1) | 1(1) | 5(1) | 1(1) |
| P(3) | 18(1) | 21(1) | 21(1) | -2(1) | 3(1) | 3(1) |
| S(1) | 20(1) | 19(1) | 22(1) | -6(1) | 4(1) | 1(1) |
| Ni(1) | 16(1) | 16(1) | 18(1) | -2(1) | 4(1) | 1(1) |

## 8.6.5 Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3).

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(2) | 4204 | 1077 | 3919 | 25 |
| H(4) | 5922 | 700 | 4550 | 34 |
| H(5) | 7438 | 23 | 4399 | 36 |
| H(6) | 7757 | -769 | 3062 | 38 |
| H(7) | 6535 | -922 | 1921 | 29 |
| H(9) | 4811 | -588 | 1298 | 22 |
| H(12) | 2537 | -1905 | 1237 | 24 |
| H(13) | 2833 | -3237 | 385 | 27 |
| H(14) | 3502 | -3062 | -996 | 27 |
| H(15) | 3819 | -1519 | -1528 | 26 |
| H(16) | 3516 | -181 | -666 | 21 |
| H(18) | 4415 | 1321 | 619 | 21 |
| H(19) | 4599 | 2568 | -383 | 27 |
| H(20) | 3244 | 3143 | -1274 | 29 |
| H(21) | 1697 | 2438 | -1165 | 26 |
| H(22) | 1509 | 1188 | -167 | 23 |
| H(23A) | 927 | -1236 | 999 | 27 |
| H(23B) | 617 | -318 | 401 | 27 |
| H(23C) | -43 | -642 | 1186 | 27 |
| H(24A) | -348 | 2763 | 995 | 31 |
| H(24B) | 24 | 2001 | 297 | 31 |
| H(24C) | 806 | 2648 | 878 | 31 |
| H(25A) | -1162 | 634 | 1123 | 38 |
| H(25B) | -1455 | 1531 | 1713 | 38 |
| H(25C) | -1107 | 547 | 2188 | 38 |
| H(26A) | -303 | 2593 | 2674 | 31 |
| H(26B) | 877 | 2557 | 2767 | 31 |
| H(26C) | 255 | 1775 | 3266 | 31 |
| H(27A) | -233 | -1646 | 2531 | 36 |
| H(27B) | 384 | -2200 | 3323 | 36 |
| H(27C) | 719 | -2259 | 2325 | 36 |
| H(28A) | 652 | -747 | 4412 | 36 |
| H(28B) | -37 | -84 | 3756 | 36 |
| H(28C) | 1021 | 297 | 4144 | 36 |
| H(29A) | 2588 | -1785 | 3107 | 32 |
| H(29B) | 2158 | -1642 | 4062 | 32 |
| H(29C) | 2808 | -814 | 3657 | 32 |

# CURRICULUM VITAE

| | |
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# Eidesstattliche Erklärung

Ich erkläre hiermit an Eides Statt, dass ich meine Dissertation selbständig und nur mit den angegebenen Hilfsmitteln angefertigt habe.

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# Erklärung

Ich erkläre hiermit, noch keinen Promotionsversuch unternommen zu haben.

H. Bennour