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3-DIPHENYLPHOSPHINOTHIONAPHTHOLATO AS CHELATING LIGAND IN COMPLEXES OF IRON

Hamdi A. M Bennour*

Department of Chemistry, Faculty of Science, Benghazi University, Benghazi, Libya.

ABSTRACT

The work submitted here is concerned with the synthesis and characterization of new $[P,S]$ -chelate complexes of the iron supported by trimethylphosphine ligands and with an investigation of chemical responses of these systems. Among the new compounds of these metal is stable hydrido and methyl metal compounds in low oxidation states which are of particular interest as models for homogeneous catalysis. (3-Diphenylphosphanyl)-2-thionaphthol ($P^{\wedge}nSH$)₂ react with $Fe(PMe_3)_4$ to form monochelate Iron hydride $FeH(P^{\wedge}nS)(PMe_3)_3$ (**1**) or $FeHCO(P^{\wedge}nS)(PMe_3)_2$ (**2**), affords When **1** react with iodomethane to form monochelate $FeI(P^{\wedge}nS)(PMe_3)_3$ (**3**), respectively, and $(P^{\wedge}nS)_2Fe(P^{\wedge}nS)_2$ (**4**). Crystal and molecular structures are given for **1-4**, and dynamic solution spectra are discussed.

Keywords: Synthesis, Characterization, Chelate complex, Phosphine ligands, Dynamic spectra.

INTRODUCTION

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.[1] 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 describes the general formula of a SHOP-active catalyst, consisting of a chelate part and an organo part 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. In the commercially significant Shell Higher Olefin Process (SHOP) [2] hydrido nickel (II)

complexes containing $[P,O]$ -chelate ligands are considered as the active species.[3] Therefore studies on the reactivity of $[Ni-H]$ units are of great importance. Some reports on 2-(diphenylphosphino) thiophenol as a chelating ligand have been published. Most of these studies are concerned with bis- and tris-chelate complexes of 3d, 4d, and 5d metals. [4-7] There are few examples of stable mono $[P, S]$ -chelate complexes of 4d and 5d elements.[8,9] (2-Diphenylphosphino)-thiophenol is an already well-examined ligand system in the literature. However, one finds predominantly bischelate- $[P, S]$ complexes of 3d, 4d, and 5d metals. [10-13] Stable monochelate complexes are known only in the 4d and 5d row. A recent account by Heinicke et al. summarizes the development concerning the syntheses and structural aspects of neutral and cationic organonickel and palladium(2-phosphanyl)phenol(ate) complexes and catalysts for ethylene-coupling reactions.[14] Klein and coworkers reported on the synthesis and characterization of cobalt complexes containing chelating (2-diphenylphosphanyl)phenolato ligands. They obtained cobalt(I) complexes containing one chelating ligand and cobalt(II) complexes bearing two chelating ligands.

Mao could show that phosphinophenols smoothly reacted with tetrakis (trimethylphosphine) iron (0) forming *fac* – hydrido – [P, O] –chelate -iron (II) complexes. [15]. 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. [16] 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.

EXPERIMENTAL

General procedures and materials

All synthesis and manipulations were carried out under an inert atmosphere of argon or nitrogen by using modified Schlenk techniques. [17] 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). [18] 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. Trimethylphosphine PMe_3 [19], $\text{Fe}(\text{PMe}_3)_4$ [20], $\text{FeMe}_2(\text{PMe}_3)_4$ [21], (3-Diphenylphosphino)-2-thionaphthol [22,23] and were synthesized according to literature procedures. C, H, P, N analyses of air sensitive solids were carried by H. Kolbe micro-analytical laboratory, Mulheim /Ruhr. Infrared spectra ($4000\text{--}400\text{ cm}^{-1}$), as obtained from Nujol mulls between KBr discs, were recorded on a Bruker FRA106 spectrometer. ^1H , ^{13}C and ^{31}P NMR spectra were obtained from Bruker AVANCE 500, ARX 300 and AM 200 spectrometers. ^{13}C and ^{31}P NMR resonances were obtained with broad-band proton decoupling. Assignment of ^{13}C signals was supported by DEPT trace. Melting points were measured in capillaries sealed under argon atmosphere.

(3-Diphenylphosphino)-2-thionaphthol

To a stirred solution of 200 mL cyclohexane/TMEDA (1:1) at 0°C were added 2.5M *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 [24, 25] was formed and filtered off as pale yellow powder. This was dissolved in 100 mL of cyclohexane/TMEDA (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*. (21%, melting point at $165\text{--}168^\circ\text{C}$). ^1H 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

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

1.02 g (2.83 mmol) of $\text{Fe}(\text{PMe}_3)_4$ in THF were combined with 0.98 g (2.83 mmol) of 3-diphenylphosphino-2-thionaphthol to afford 1 as red powder, yield 1.61 g (81%); M.P. $181\text{--}184^\circ\text{C}$. (dec.). IR (Nujol) 3051 w, $\nu(\text{H-C=})$, 1842 m, $\nu(\text{FeH})$, 1617 m, $\nu(\text{C=C})$, 1571 m, $\nu(\text{C=C})$, 1295 m, $\nu(\text{PCH}_3)$, 1089 m, $\nu(\text{PPh})$, 945 s, $\nu_{\text{P}1}(\text{PCH}_3)$, 888 m, $\nu_{\text{P}2}(\text{PCH}_3)$, 663 m, $\nu(\text{PC}_3)$. ^1H NMR (500 MHz, $\text{d}_8\text{-THF}$, 300 K): 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, $^2J(\text{PH}) = 9.0\text{ Hz}$, 9H, PCH_3); 1.23 (d, $^2J(\text{PH}) = 9.0\text{ Hz}$, 9H, PCH_3); 0.89 (d, $^2J(\text{PH}) = 9.0\text{ Hz}$, 9H, PCH_3); -12.8 (dddd, $^2J(\text{PH}) = 85\text{ Hz}$, $^2J(\text{PH}) = 60\text{ Hz}$, $^2J(\text{PH}) = 50\text{ Hz}$, $^2J(\text{PH}) = 30\text{ Hz}$, 1H FeH). ^{13}C NMR (125 MHz, $\text{d}_8\text{-THF}$, 300 K): δ : 166.9 (s, C); 156.7 (d, $^3J(\text{PC}) = 8.8\text{ Hz}$, C); 150.2 (d, $^4J(\text{PC}) = 8.8\text{ Hz}$, C); 144.6 (d, $^1J(\text{PC}) = 7.5\text{ Hz}$, C); 140.3 (d, $^2J(\text{PC}) = 8.8\text{ Hz}$, CH); 133.2 (d, $^2J(\text{PC}) = 10\text{ Hz}$, CH); 132.2 (d, $^2J(\text{PC}) = 8.8\text{ Hz}$, CH); 130.1 (s, CH); 128.4 (d, $^1J(\text{PC}) = 8.8\text{ Hz}$, CH); 127.9 (d, $^2J(\text{PC}) = 10\text{ Hz}$, CH); 127.7 (d, $^3J(\text{PC}) = 5.0\text{ Hz}$, CH); 126.3 (s CH); 125.5 (d, $^3J(\text{PC}) = 7.5\text{ Hz}$, CH); 121.7 (s, CH); 24.4 (d, $^1J(\text{PC}) = 18.9\text{ Hz}$, PCH_3); 22.6 (d, $^1J(\text{PC}) = 18.9\text{ Hz}$, PCH_3); 20.8 (d, $^1J(\text{PC}) = 17.6\text{ Hz}$, PCH_3). ^{31}P NMR (202 MHz, $\text{d}_8\text{-THF}$, 296 K): δ : 88.0 (ddd, $^2J(\text{P}_{\text{Ph}}\text{P}_{\text{Me}}) = 95\text{ Hz}$, $^2J(\text{P}_{\text{Ph}}\text{P}_{\text{Me}}) = 42\text{ Hz}$, $^2J(\text{P}_{\text{Me}}\text{P}_{\text{Me}}) = 25\text{ Hz}$, 1P, PPh); 27.6 (ddd, $^2J(\text{P}_{\text{Me}}\text{P}_{\text{Ph}}) = 42\text{ Hz}$, $^2J(\text{P}_{\text{Me}}\text{P}_{\text{Me}}) = 48\text{ Hz}$, $^2J(\text{P}_{\text{Me}}\text{P}_{\text{Me}}) = 34\text{ Hz}$, 1P, PMe); 13.3 (ddd, $^2J(\text{P}_{\text{Me}}\text{P}_{\text{Ph}}) = 95\text{ Hz}$, $^2J(\text{P}_{\text{Me}}\text{P}_{\text{Me}}) = 48\text{ Hz}$, $^2J(\text{P}_{\text{Me}}\text{P}_{\text{Me}}) = 13\text{ Hz}$, 1P, PMe); (5.3 ddd, $^2J(\text{P}_{\text{Me}}\text{P}_{\text{Ph}}) = 25\text{ Hz}$, $^2J(\text{P}_{\text{Me}}\text{P}_{\text{Me}}) = 34\text{ Hz}$, $^2J(\text{P}_{\text{Me}}\text{P}_{\text{Me}}) = 13\text{ Hz}$, 1P, PMe). $\text{C}_{31}\text{H}_{44}\text{FeP}_4\text{S}$ (628.49): Calc.: C, 59.24; H, 7.06; S 5.10; P 19.71 Found: C, 58.57; H, 6.73; S 5.17; P 20.14%.

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

A sample of 1 (500 mg, 0.79 mmol) in THF was stirred under 1 bar CO to provide a yellow crystals of 2 which crystallize from ether at room temperature, yield 430 mg (86%); M.P. $179\text{--}182^\circ\text{C}$. (dec.). IR (Nujol) 3054 m $\nu(\text{H-C=})$, 1933 m $\nu_{\text{as}}(\text{CO})$, 1889 s $\nu_{\text{s}}(\text{CO})$, 1847 w $\nu(\text{Fe-H})$, 1621 w $\nu(\text{C=C})$, 1567 w $\nu(\text{C=C})$, 1464 w $\delta_{\text{s}}(\text{PCH}_3)$, 1297 m $\nu_{\text{s}}(\text{PCH}_3)$, 1092 m $\delta(\text{PPh})$, 945 s $\nu_{\text{P}1}(\text{PCH}_3)$, 859 w $\nu_{\text{P}2}(\text{PCH}_3)$, 704 m $\nu_{\text{as}}(\text{PC}_3)$, 680 w $\nu_{\text{s}}(\text{PC}_3)$. ^1H NMR (500 MHz, $\text{d}_8\text{-THF}$, 300 K): 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, $^2J(\text{PH}) = 10\text{ Hz}$, 9H, PCH_3); 0.97 (t', $|^2J(\text{PH}) + J(\text{PH})| = 5.0\text{ Hz}$, 18H, PCH_3);

0,82 (dd, $^2J(\text{PH}) = 5,0$ Hz, $^2J(\text{PH}) = 10$ Hz, 9H, PCH_3); -9,8 (dt, $^2J(\text{PH}) = 70$ Hz, $^2J(\text{PH}) = 45$ Hz, 1H, FeH); -10,9 (ddd, $^2J(\text{PH}) = 45$ Hz, $^2J(\text{PH}) = 20$ Hz, $^2J(\text{PH}) = 20$ Hz, 1H, FeH). ^{31}P NMR (202 MHz, d_8 -THF, 300 K): δ 93 (dd, $^2J(\text{P}_{\text{Ph}}\text{P}_{\text{Me}}) = 119$ Hz, $^2J(\text{P}_{\text{Ph}}\text{P}_{\text{Me}}) = 24$ Hz, 1P, PPh); 85,9 (t, $^2J(\text{P}_{\text{Ph}}\text{P}_{\text{Me}}) = 28$ Hz, 1P, PPh); 19,7 (dd, $^2J(\text{P}_{\text{Me}}\text{P}_{\text{Ph}}) = 120$ Hz, $^2J(\text{P}_{\text{Me}}\text{P}_{\text{Me}}) = 16$ Hz, 1P, PMe); 15,3 (d, $^2J(\text{P}_{\text{Me}}\text{P}_{\text{Ph}}) = 28$ Hz, 2P, PMe_3); 5,2 (dd, $^2J(\text{P}_{\text{Me}}\text{P}_{\text{Ph}}) = 24$ Hz, $^2J(\text{P}_{\text{Me}}\text{P}_{\text{Me}}) = 16$ Hz, 1P, PMe). $\text{C}_{29}\text{H}_{35}\text{FeOP}_3\text{S}$ (580.43): Calc.: C, 60.01; H, 6.07; P 16.00 Found: C, 59.46; H, 6.11; P 16.34%.

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

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 as yellow powder, yield 950 mg (71%); M.P 225–227 °C (dec.) IR (Nujol) 3048 w $\nu(\text{H-C}=\text{C})$, 1617 s $\nu(\text{C}=\text{C})$, 1575 s $\nu(\text{C}=\text{C})$, 1445 s $\delta_{\text{as}}(\text{PCH}_3)$, 1290 w $\delta_{\text{s}}(\text{PCH}_3)$, 952 s $\rho_1(\text{PCH}_3)$, 848 w $\rho_2(\text{PCH}_3)$, 663 w $\nu_{\text{s}}(\text{PC}_3)$. ^1H NMR (500 MHz, d_8 -THF, 300 K): 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, $^2J(\text{PH}) = 6.1$ Hz, 9H, PCH_3); 1.26 (d, $^2J(\text{PH}) = 4.1$ Hz, 9H, PCH_3); 1.12 (d, $^2J(\text{PH}) = 6.7$ Hz, 9H, PCH_3). ^{31}P NMR (202 MHz, d_8 -THF, 300 K): δ : 9.4 (ddd, $^2J(\text{P}_{\text{Ph}}\text{P}_{\text{Me}}) = 16$ Hz, $^2J(\text{P}_{\text{Ph}}\text{P}_{\text{Me}}) = 53$ Hz, $^2J(\text{P}_{\text{Ph}}\text{P}_{\text{Me}}) = 69$ Hz, 1P, PPh); 22.3 (ddd, $^2J(\text{P}_{\text{Me}}\text{P}_{\text{Ph}}) = 53$ Hz, $^2J(\text{P}_{\text{Me}}\text{P}_{\text{Me}}) = 45$ Hz, $^2J(\text{P}_{\text{Me}}\text{P}_{\text{Me}}) = 54$ Hz, 1P, PMe_3); 13 (ddd, $^2J(\text{P}_{\text{Me}}\text{P}_{\text{Ph}}) = 69$ Hz, $^2J(\text{P}_{\text{Me}}\text{P}_{\text{Me}}) = 54$ Hz, $^2J(\text{P}_{\text{Me}}\text{P}_{\text{Me}}) = 35$ Hz, 1P, PMe); -0,8 (ddd, $^2J(\text{P}_{\text{Me}}\text{P}_{\text{Ph}}) = 16$ Hz, $^2J(\text{P}_{\text{Me}}\text{P}_{\text{Me}}) = 35$ Hz, $^2J(\text{P}_{\text{Me}}\text{P}_{\text{Me}}) = 45$ Hz, 1P, PMe). $\text{C}_{31}\text{H}_{43}\text{FeIP}_4\text{S}$ (754.39). Calc.: C, 49.36; H, 5.74; P 16.42 Found: C, 48.53; H, 6.28; P 15.86%.

Trans-Bis(3-diphenylphosphino)-2-thionaphtholato-[P,S]-(trimethylphosphine)iron(II) (4)

900 mg (2.3 mmol) of $\text{FeMe}_2(\text{PMe}_3)_4$ in THF were combined with 1.59 g (4.6 mmol) of (3-diphenylphosphino)-2-thionaphthol. By extraction with ether the complex **4** were obtained as brown powder. Yield 1.75 g (71%); M.P > 236°C (dec). IR (Nujol) 3054 w $\nu(\text{H-C}=\text{C})$, 1615 s $\nu(\text{C}=\text{C})$, 1566 s $\nu(\text{C}=\text{C})$, 1437 vs $\delta_{\text{as}}(\text{PCH}_3)$, 1297 m $\delta_{\text{s}}(\text{PCH}_3)$, 1086 s $\delta(\text{Ph})$, 946 s $\rho_1(\text{PCH}_3)$, 843 w $\rho_2(\text{PCH}_3)$, 695 vs $\nu_{\text{as}}(\text{PC}_3)$, 667 w $\nu_{\text{s}}(\text{PC}_3)$. $\text{C}_{47}\text{H}_{41}\text{FeP}_3\text{S}_2$ (818.74) Calc.: C, 68.95; H, 5.05; P 11.35 Found: C, 68.21; H, 5.63; P 11.51%.

RESULTS AND DISCUSSION

Mao could show that phosphinophenols smoothly reacted with tetrakis (trimethylphosphine) iron (0) forming *fac* – hydrido – [P,O] – chelate -iron (II) complexes [26]. 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* [27] 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.

(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 analytically pure pentane, the red powder which when dry remains unreactive for a few minutes, but in solution decomposes within seconds. In pentane and at room temperature the [P,S] ligand is poorly soluble that makes the reaction takes 16 to 30 h on a 10–20 g scale.

The coordination geometry of **1** can be derived from the ^1H and ^{31}P NMR spectra. In the ^1H 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.4). Each resonance shows a ddd coupling which confirms the facial configuration of **1**. [28] 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. 4 shows the complete assignment.

(3-Diphenylphosphino)-2-thionaphthol oxidatively additions to $\text{Fe}(\text{PMe}_3)_4$ forming the hydrido iron (II) complex **1**. In solution only the isomer with a *facial* configuration is present (Fig. 5) which is in agreement with the results of *Mao and Frey*. [26 27]

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. 6). 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.

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 absorb at 1847 cm^{-1} . Already at first sight two isomers of complex 2 are present. In the ^1H -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.7).

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 8 that gives a view of the molecular geometry with selected bonding parameters.

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 ($\text{P3-Fe1-P2} = 158.6^\circ$). The bond length of the hydride ($\text{H1-Fe1} = 1.42(3) \text{ \AA}$) corresponds with expectations for hydridoiron(II) complexes. This minor distortion is also indicated by the angles P2-Fe1-H1 of 78.4° and P3-Fe1-H1 of 81.9° . 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 174.7° and S1-Fe1-C23 attains 173.2° . The sum of internal angles in the five-membered ring is close to the ideal value of 540° . The bond length of the chelate phosphorus ($\text{P1-Fe1} = 2.21(8) \text{ \AA}$) is enlarged through the *trans*-influence of hydride while other Fe-P distances are in the typical range of $2.18 - 2.22 \text{ \AA}$ [57]. The bonding situation of the CO ligand corresponds to a terminal coordination. The distance ($\text{C23-O1} = 1.17(2) \text{ \AA}$) is normal for a weakened triple bond. 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 iron complex seems likely. A corresponding set of isomers was found by Mao, with a

ratio of isomers 4:1 reflecting the different electronic properties of [P,O] ligands. 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 an iron (II) derivative. [29] Even iron(II) complexes can react with iodomethane. Thus Mao showed that hydrido-{(2-diphenyl phosphino) phenolato[P,O]}iron (II) compounds with iodomethane are transformed to the corresponding iodoiron (II) complexes. [26] No indication of an intermediate iron(IV) species was obtained. 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. 9). For the observation of a gas (methane) the process is too slow.

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 ^1H 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. Like with the hydridoiron-[P,O]-chelate complexes homologues of 1 can be 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-coordinated iron (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. 10.

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 -olefins 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.[30-32] Iron is an attractive metal for this purpose because of its low cost and relatively low risk of toxicity. Five coordinated bischelate- $[P,O]$ complexes of iron with coordinated trimethylphosphine have been obtained by reaction of dimethyltetakis (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. The reaction of $\text{FeMe}_2(\text{PMe}_3)_4$ in THF at -78°C with two mole equivalents of (3-diphenylphosphino)-2-thionaphthol (Fig.11) gives good yields of the red-brown bischelate complex 4 when isolated as powder. Crystallization experiments from different solvents under selected conditions remained unsuccessful. Compound 4 is a paramagnetic substance. From NMR spectra no detailed information could be obtained. The IR spectrum shows the typical $\nu(\text{C}=\text{C})$ absorption bands expected for $[P,S]$ ligands in the region $1566 - 1615\text{ cm}^{-1}$ and the characteristic band of coordinated trimethylphosphine is detected at 946 cm^{-1} . Due to the penta-coordination around the iron atom in the paramagnetic bischelate complex 4 NMR spectroscopy allows no precise statements about its configuration. The one given in Fig. 11 is supported by a structure obtained by Mao [26] 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 4 is confirmed by elemental analysis.

Table 1. Crystal data for compound 2

Empirical formula	$\text{C}_{29}\text{H}_{35}\text{FeO}_3\text{P}_3\text{S}$
Formula weight	580.39
Temperature	100(2) K
Wavelength	0.71073 \AA
Crystal system	Monoclinic
Space group	P21/c
Unit cell dimensions	$a = 9.1746(3)\text{ \AA}$ $\alpha = 90^\circ$ $b = 17.827(6)\text{ \AA}$ $\beta = 97.776(4)^\circ$ $c = 17.2726(7)\text{ \AA}$ $\gamma = 90^\circ$
Volume	$2799.0(10)\text{ \AA}^3$
Z	4
Density (calculated)	1.377 Mg/m^3
Absorption coefficient	0.806 mm^{-1}
F	(000) 1216
Crystal size	$0.28 \times 0.16 \times 0.16\text{ mm}$
Theta range for data collection	2.24 to 26.37°
Index ranges	$-11 \leq h \leq 9$, $-21 \leq k \leq 22$, $-21 \leq l \leq 19$
Reflections collected	21039
Independent reflections	5710 [R (int) = 0.0266]
Completeness to	$2\theta = 26.37^\circ$ 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)	$R1 = 0.0453$, $wR2 = 0.0787$

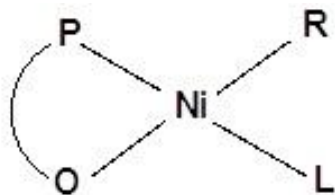
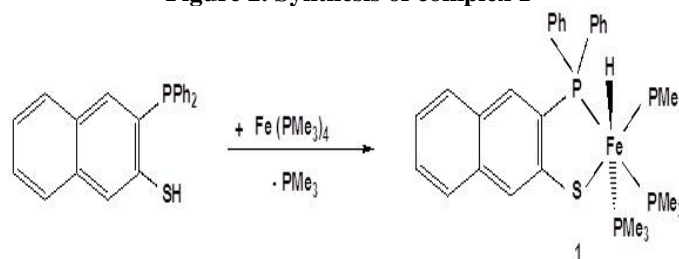
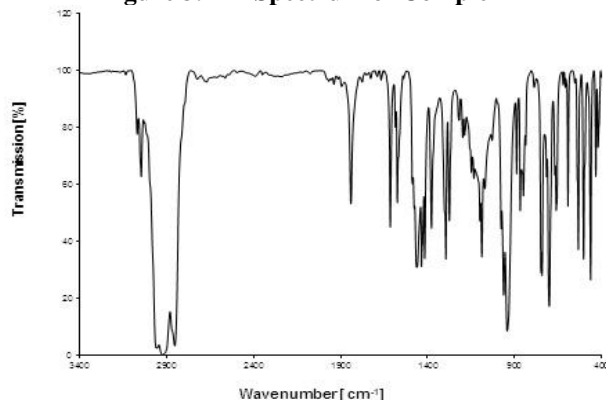
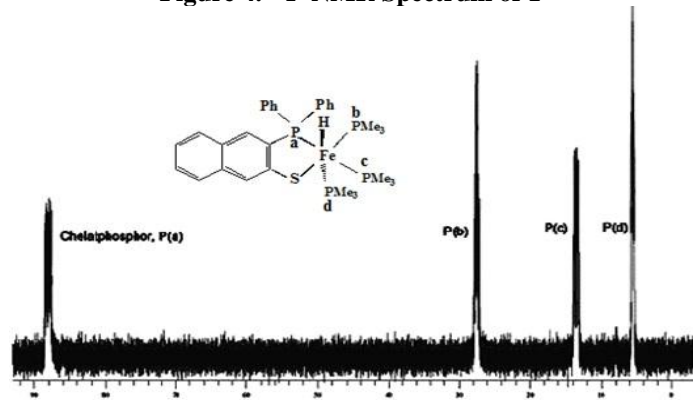
Figure 1. General Formula of an SHOP – Catalysts**Chelating part****Organic part****Figure 2. Synthesis of complex 1****Figure 3. IR- Spectrum of Complex 1****Figure 4. ^{31}P -NMR Spectrum of 1**

Figure 5. Mechanism of formation of the fac-isomer of 1

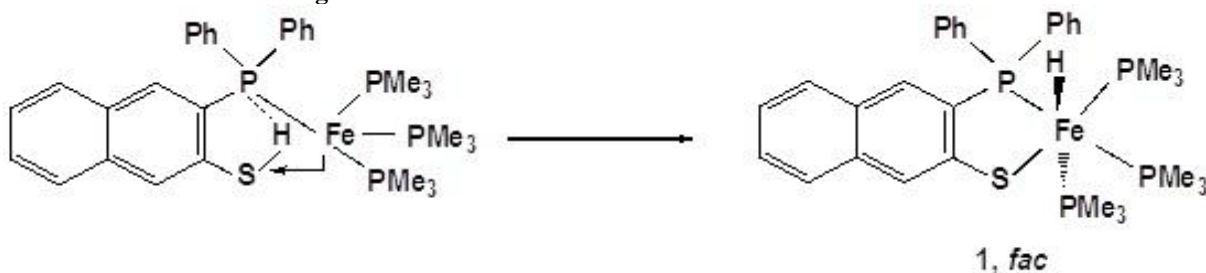


Figure 6. Reaction scheme for the formation of 2a and b

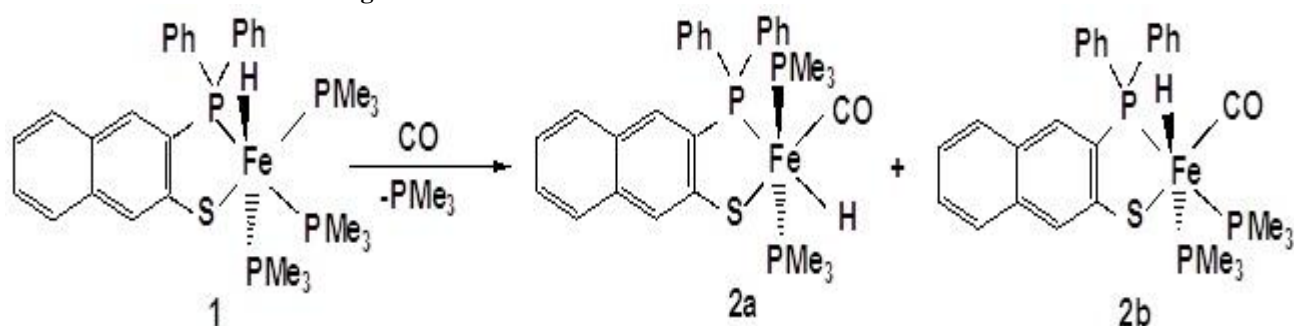


Figure 7. Hydrid resonance of 2a and 2b

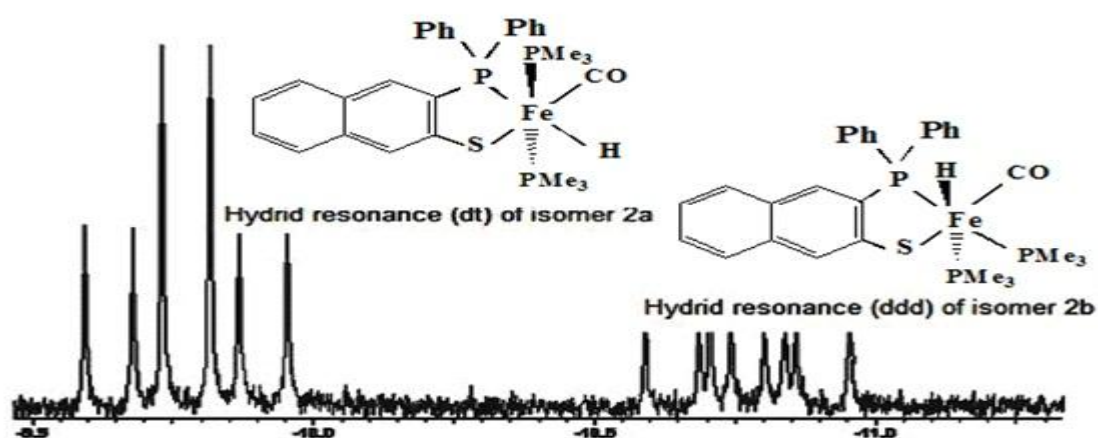


Figure 8. Molecular structure of 2a (ORTEP plot with hydrogen atoms omitted); selected bond lengths [Å] and angles [°]: Fe-H1 1.42(3), Fe1-C23 1.72(2), C23-O1 1.17(2), Fe1-S1 2.31(6), Fe1-P1 2.21(8), Fe1-P2 2.23(6), Fe1-P3 2.22(6); P1-Fe1-S1 88.24(2), P1-Fe1-H1 174.7(11), P2-Fe1-H1 78.4(11), P3-Fe1-H1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

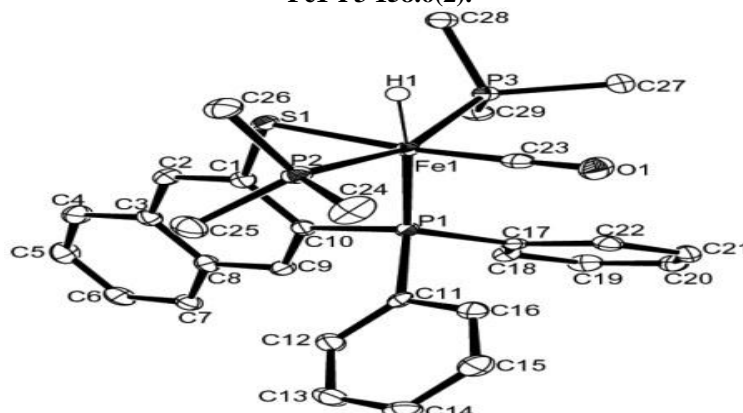


Figure 9. Reaction scheme for the synthesis of 3

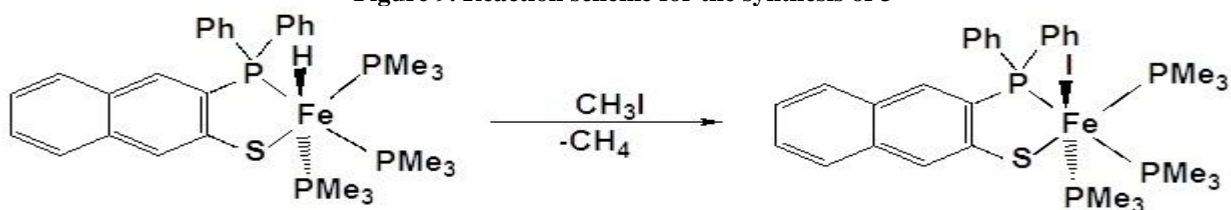


Figure 10. Proposed mechanism formation of the fac-isomer of 3

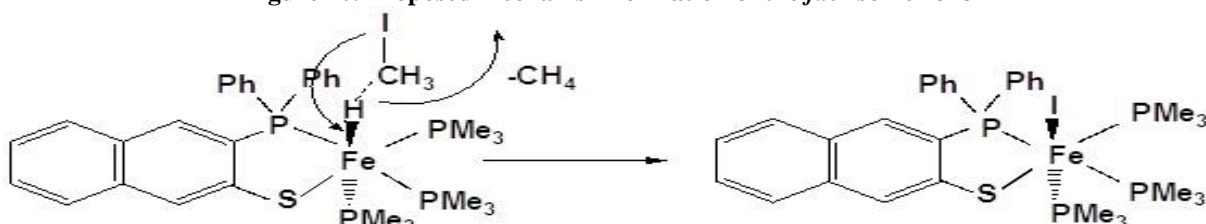
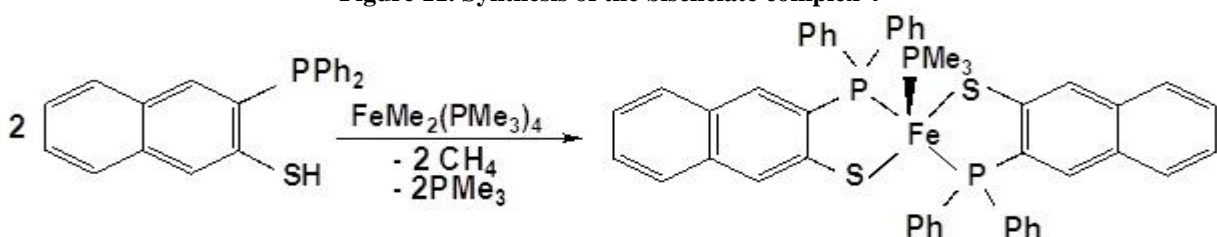


Figure 11. Synthesis of the bischelate complex 4



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