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# Syntheses and properties of molecular nickel(II) hydride, methyl, and nickel(I) complexes supported by trimethylphosphane and (2-diphenylphosphanyl)thiophenolato and -naphtholato ligands

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ABSTRACT

(2-Diphenylphosphanyl)thiophenol (P^pSH) or (3-diphenylphosphanyl)-2-thionaphthol (P^nSH) react with $Ni(PMe_3)_4$ to form $NiH(P^pS)(PMe_3)_2$ (**1**) or $NiH(P^nS)(PMe_3)_2$ (**2**). 1,3-Bis(diphenylphosphanyl)propane (P^P) replaces the monodentate phosphane ligands to give NiH(P^pS)(P^P) (**3**). $NiMe(OMe)(PMe_3)$ or $NiMe_2(PMe_3)_3$ react with P^pSH to form $NiMe(P^pS)(PMe_3)$ (**4**) and $NiMe(P^pS)(PMe_3)_2$ (**5**), respectively, and P^nSH affords $NiMe(P^nS)(PMe_3)_2$ (**6**), $NiMe(P^nS)(PMe_3)$ (**7**). Dissociation of $PMe_3$ ligands induces transformation of **1** to $Ni(P^pS)(PMe_3)_2$ (**8**) and $Ni(P^pS)_2$. Crystal and molecular structures are given for **1**, **5**–**8,** and dynamic solution spectra (NMR, EPR) are discussed.



## 1. Introduction

Although numerous examples of hydridonickel(II) complexes have been described [1] no molecular compound of the type $NiH(X)(D)_3$ is known to date with X as anionic and D as neutral donor ligands. Such species have been proposed as key intermediates in homogeneous catalysis (isomerisation and oligomerisation of olefins), and the type $NiH(X)(D)_2$ with [O,P]-chelating $(OC(CF_3)_2CH_2PPh_2)$ is represented by a crystal and molecular structure [2,3]. This line of investigation is also prompted by the industrial application of chelate chalcogenic ligands in SHOP-type processes [4–6]. Using trimethylphosphane and chelating (2-diphenylphosphanyl)thiophenolato ligands we have found an easy access to the title compounds and report here on their characterisation and reactivity. Closely related methylnickel complexes were also part of the study. Most authors, proposing mechanisms for the reactions catalyzed with nickel complexes, avoid introducing odd-electron species into the catalytic cycle. This reluctance is understandable as long as transformation of nickel(0) and nickel(II) states into that of nickel(I) is poorly understood.

The fundamental possibility of nickel(I) complex formation through the symproportionation of Ni(0) and (II) complexes was showed by Heimbach [7]. Others have considered the mechanism of how cationic nickel complexes arise from $Ni(PPh_3)_4$ and boron trifluoride etherate [8]. Symproportionation of phosphine complexes of Ni(0) and Ni(II) is regarded to be the key step. Also the possibility of disproportionation of Ni(II) hydride complexes giving Ni(I) species was shown for the systems $Ni(PPh_3)_4$ – Brønsted acid. Chelate chalcogenic ligands allow one to prepare stable and readily crystallized Ni(II) hydrides and Ni(II) alkyl complexes [9] as well. These compounds can be good models to gain an insight into the intrigue of how the elusive Ni(I) complexes come to exist. Besides, there is an interesting and insufficiently explored question on the possible formation of nickel(I) complexes in the systems with chelating ligands. This question is topical since nickel(I) species are supposed to be involved in catalytic olefin oligomerisation reactions [10–12]. The system under investigation is shown to contain several molecular Ni(I) compounds. One of them could be isolated and its molecular structure elucidated.

## 2. Results and discussion

Reacting pentane solutions of $Ni(PMe_3)_4$ with (2-diphenylphosphanyl)thiophenol (Eq. (1)) gives a red solution from which upon cooling deep red rectangular plates of **1** are grown in 10% yield. With a fivefold excess of $PMe_3$ improved yields of 30–40% are reproducibly obtained, also with Ni(1,5-cyclooctadiene)$(PMe_3)_2$

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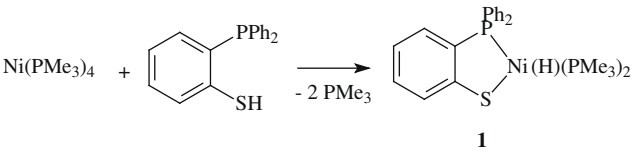
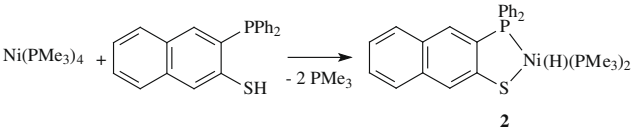
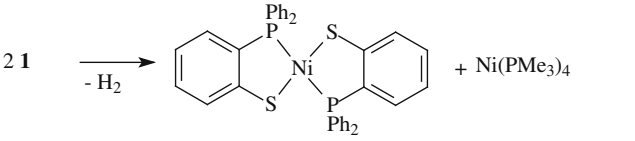
as Ni(0) reagent. Crystals of **1** are stable in air at 20 °C for at least three days. Solutions of **1** in absolute pentane rapidly deposit green Ni(P^pS)$_2$ [13,14] with evolution of $H_2$ but retain their red colour to some degree (Eq. (3)). Under 1 bar of ethene the dismutation of **1** in solution is accelerated, and under 1 bar of carbon monoxide the red colour disappears. In a similar synthesis using (3-diphenylphosphanyl)2-thionaphthol (Eq. (2)) sparingly soluble **2** was isolated showing similar chemical and spectral properties.




**1** (1)




**2** (2)




(3)

The NiH function is recognized in the infrared spectra by conspicuous $\nu$(NiH) bands (**1**: 1893 cm$^{-1}$, **2**: 1883 cm$^{-1}$) which in the $^1$H NMR spectra correspond with doublet resonances (**1**: $^2J_{HP}$ = 41 Hz) indicating dissociation of trimethylphosphane ligands. At 203 K the signal becomes a doublet of triplets suggesting a trigonal bipyramidal molecular geometry. This is confirmed in the $^{31}$P spectrum of **1** and **2** recorded at 203 K where three P atoms display two doublets of doublets. With the known angular dependence of P,P coupling they appear to reside in a trigonal plane leaving apical positions for S and H atoms. This molecular structure is also observed in the crystal of **1** (Fig. 1). The most significant bond length (Ni–H 1.503(32) Å) lies in the expected range, while Ni–P and Ni–S bond lengths are found on the short side. The chelate ring shows a relaxed bite angle (P1–Ni–S = 90.58(3)°) and with a sum of internal angles (539.9°) close to the ideal value (540°) is planar.

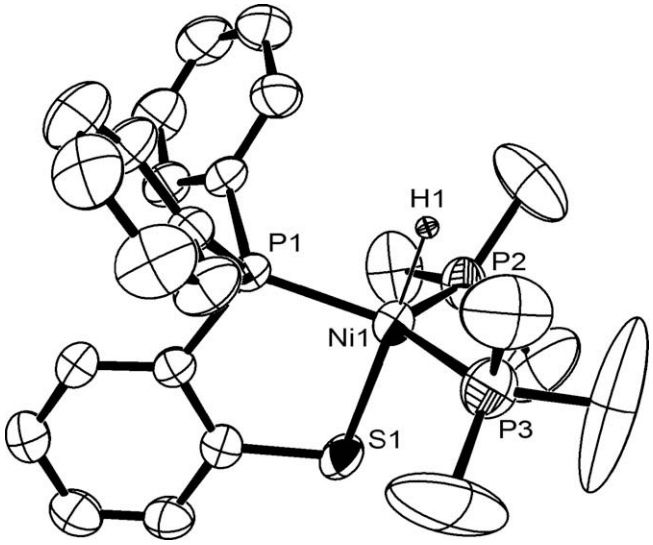
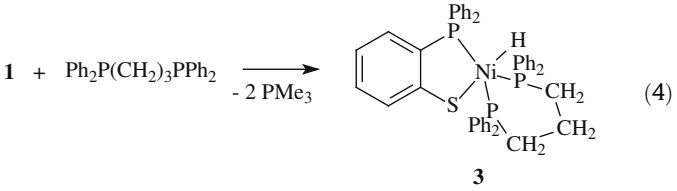
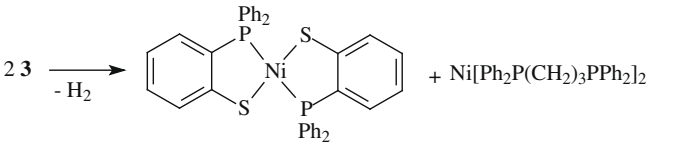



**Fig. 1.** Molecular structure of **1** (ORTEP plot with hydrogen atoms omitted); selected bond lengths [Å] and angles [°]: Ni–H 1.46(3), Ni–S 2.237(9), Ni–P1 2.1465(8), Ni–P2 2.2132(9), Ni–P3 2.183(10); P1–Ni–S1 90.61(3), S1–Ni–H 174.6(12), P1–Ni–P2 116.05(3), P1–Ni–P3 127.09(4), P2–Ni–P3 115.47(4), P2–Ni–H 90.5(12), P3–Ni–H 83.2(12).

An improved stability of the nickel hydride was attempted by introducing 1,3-bis(diphenylphosphanyl)propane as a chelating phosphane. In THF containing a fivefold excess of trimethylphosphane ligand displacement (Eq. (4)) is complete after five minutes, and sparingly soluble **3** is isolated as orange solid in 90% yield. When compared with **1** the $\nu$(NiH) band of **3** is shifted to higher wavenumbers by 17 cm$^{-1}$, and the NiH resonance experiences a low-field shift by 3 ppm. Both values are compatible with a reduced polarisation Ni$^+$H$^-$ and a more covalent NiH bond in **3** arising from the stronger π-accepting diphosphane ligand. In THF solution dismutation of **3** (Eq. (5)) starts after 20 minutes at 20 °C and appears to be only marginally slower than that of Eq. (3), and again under 1 bar of ethene formation of Ni(P^pS)$_2$ is accelerated. From the mother liquor Ni[Ph$_2$P(CH$_2$)$_3$PPh$_2$]$_2$ [15] is crystallised in 64% yield. While the chelate bite (~90°) of the anionic (P^pS) and (P^nS) ligands raises the thermal stability of hydridonickel(II) compounds with 18 metal valence electrons, the diphosphane does not, because in its stable conformation the P-donor atoms cannot span equatorial positions (~120°).

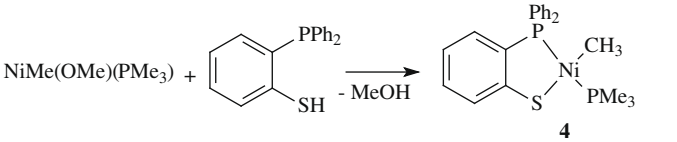



**3** (4)

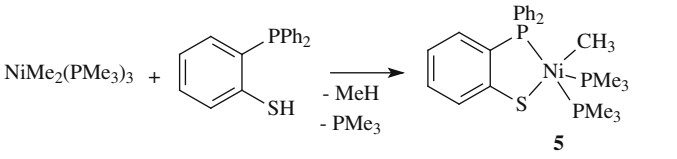



(5)

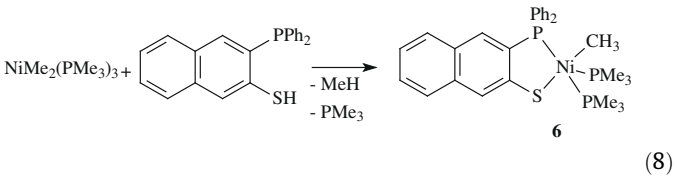
With information of the new hydridonickel compounds at hand methylnickel complexes are expected to exist in similar composition. Syntheses as described earlier make these model compounds readily accessible. (2-Diphenylphosphanyl)thiophenol reacts with NiMe(OMe)(PMe$_3$) (Eq. (6)) or NiMe$_2$(PMe$_3$)$_3$ (Eq. (7)) to afford methylnickel complexes **4** and **5** depending on the concentration of trimethylphosphane in solution during synthesis and workup. Yields are generally higher than with hydride **1** and accordingly are subject to a concurring formation of Ni(P^pS)$_2$. Sparingly soluble **6** and **7** were obtained in a similar way (Eqs. (8) and (9)). The orange crystals of **4,** the red needles of **5,** the red microcrystals of **6,** and orange prismatic crystals are stable in air for at least two weeks, as after that time characteristic infrared bands $\delta$(NiCH$_3$) at 1184 cm$^{-1}$ (**4**), at 1158 cm$^{-1}$ (**5**), at 1157 cm$^{-1}$ (**6**), and at 1219 cm$^{-1}$ (**7**) and in the $^1$H NMR at 20 °C doublets for NiCH$_3$ groups (**4**: −0.37 ppm, $^3J$(PH) = 8 Hz; **5**: −0.33 ppm, $^3J$(PH) = 9 Hz; **6**: −0.20 ppm, $^3J$(PH) = 10 Hz; **7**: −0.29 ppm, $^3J$(PH) = 10.5 Hz) are fully present. Additional coupling with PMe$_3$ phosphorus nuclei is observed at 203 K indicating the expected ligand dynamics.



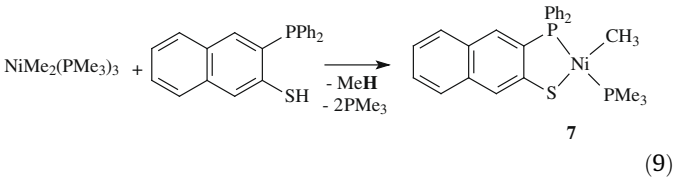

**4** (6)




(7)




(8)




(9)

As compounds **5, 6**, and **7** form crystals suitable for X-ray diffraction we can compare the molecular structures (Figs. 2–4) of closely related methylnickel complexes with 16 and 18 metal valence electrons.

Methylnickel complex **7** adopts a square planar geometry with the methyl group trans to the sulfur donor (Fig. 2) while **5** and **6** show a trigonal bypyramidal arrangement with three equatorial P donor atoms. NiC, NiS, and NiP bond lengths in **7** are on the short side of expected values indicating the absence of steric crowding and a balanced *trans* influence of the $NiCH_3$ group. The sums of internal angles in the three metallacycles (**5**: 537.8°, **6**: 525.7°, **7**: 538.5°) indicate planarity, and the bite angles are smaller than in **1**. The NiS bond lengths in **5** and **6** are elongated by 8 pm when compared with that in **7** and exceed that in **1** by 3 pm while the angles $SNiCH_3$ or SNiH show no significant difference. This observation suggests stronger NiS $\pi$-bonding in **7** than in **1** or **5, 6**.

The present studies allow a conclusion of the most reasonable ways to the alkyl and hydride nickel(II) complexes with thiophenolato and thionaphtholato ligands. Our experience in complex syntheses led us to test compounds **1** and **5** for generating Ni(I) complexes. When the temperature was carefully controlled dihydrogen began evolving at −10 °C and a green solid of $Ni(P\hat{}pS)_2$ precipitated. Filtering a decomposed solution of **1** affords microcrystalline $Ni(P\hat{}pS)_2$ and a red solution containing free trimethylphosphine that on cooling yields red crystals of the composition $Ni(P\hat{}pS)(PMe_3)_2$ (**8**). These are air-sensitive and under argon decompose above −10 °C. In the solid state and in solution **8** is paramagnetic. In the studied system (Eq. (10)) complex **8** gives a strong EPR signal (Fig. 5). In the "parallel" region of the spectrum one can see a resolved HFS for three $^{31}P$ nuclei, with two of them

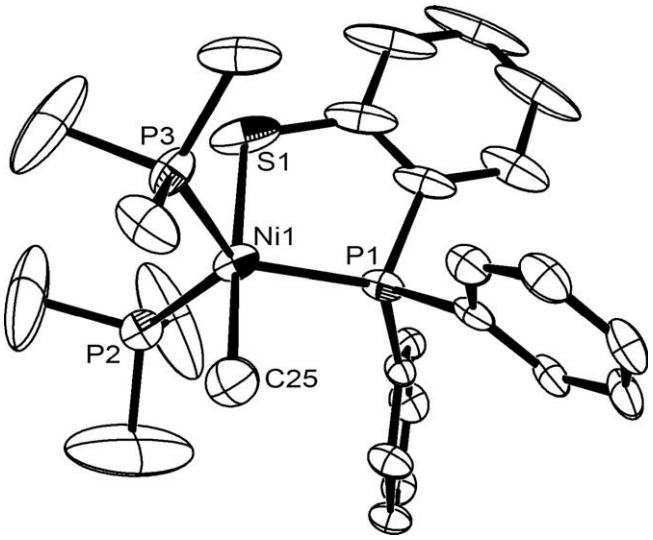



**Fig. 2.** Molecular structure of **5** (ORTEP plot with hydrogen atoms omitted); selected bond lengths [Å] and angles [°]: Ni–C25 2.007(5), Ni–S1 2.261(1), Ni–P1 2.164(1), Ni–P2 2.226 (1), Ni–P3 2.210 (1); P1–Ni–S1 88.47(5), P1–Ni–P2 115.62(4), P1–Ni–P3 125.75(5), P2–Ni–P3 118.62(4), P1–Ni–C25 99.2(2), P2–Ni–C25 89.4(2), P3–Ni–C25 89.8(2), S1–Ni–C25 177.2(2).

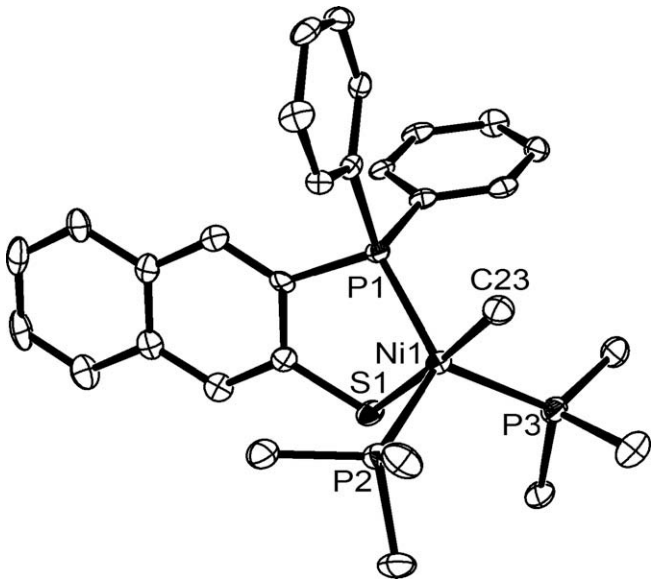



**Fig. 3.** Molecular structure of **6** (ORTEP plot with hydrogen atoms omitted); selected bond lengths [Å] and angles [°]: Ni–C23 1.977(5), Ni–S1 2.281(1), Ni–P1 2.186(1), Ni–P2 2.243(1), Ni–P3 2.253(1); P1–Ni–S1 84.18(5), P1–Ni–P2 120.36(5), P1–Ni–P3 127.61(5), P2–Ni–P3 111.73(5), P1–Ni–C23 92.72(15), P2–Ni–C23 90.86(15), P3–Ni–C23 91.73(15), S1–Ni–C23 176.61(15).

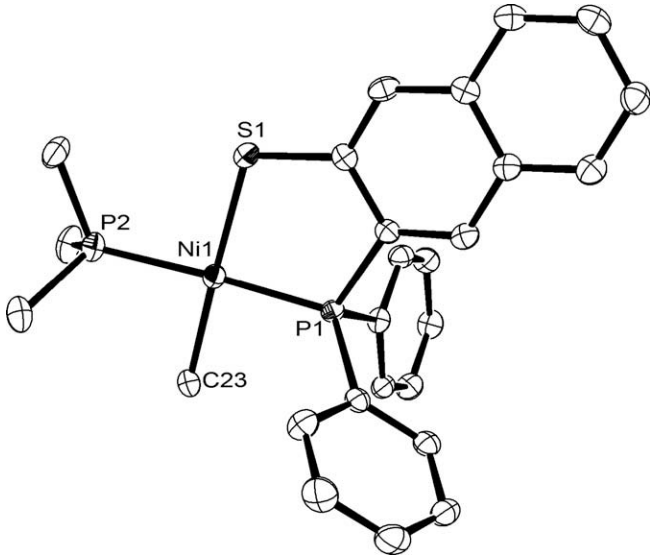



**Fig. 4.** Molecular structure of **7** (ORTEP plot with hydrogen atoms omitted); selected bond lengths [Å] and angles [°]: Ni–S1 2.1997(7), Ni–P1 2.1403(7), Ni–P2 2.1888(8), C23–Ni 1.975(3); P1–Ni–P2 177.37(3), P1–Ni–S1 89.14(3), P2–Ni–S1 93.37(3), C23–Ni–S1 178.32(8), C23–Ni–P1 89.20(8), C23–Ni–P2 88.28(8).

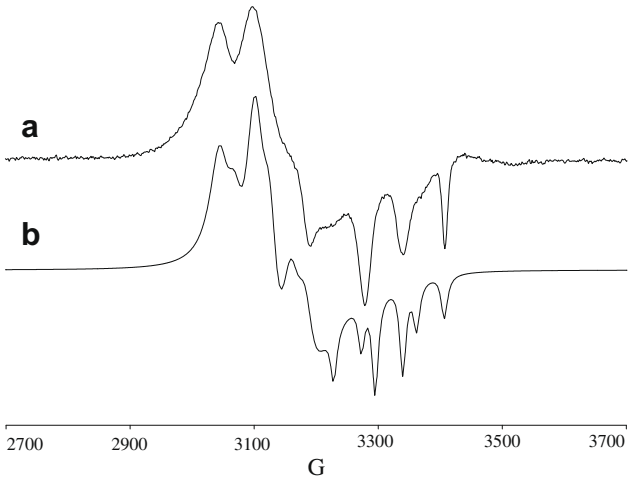



**Fig. 5.** Experimental (a) and model (b) EPR spectra of **8**, solid state (powder), $T = 77$ K. $g_{\|} = 2.008$, $g_{\perp} = 2.140$, $A_{\|}$ (1P) = 45 G, $A_{\perp}$ (1P) $\leqslant$ 23 G, $A_{\|}$ (2P) = 67 G, $A_{\perp}$ (2P) = 57 G, $T = 77$ K.

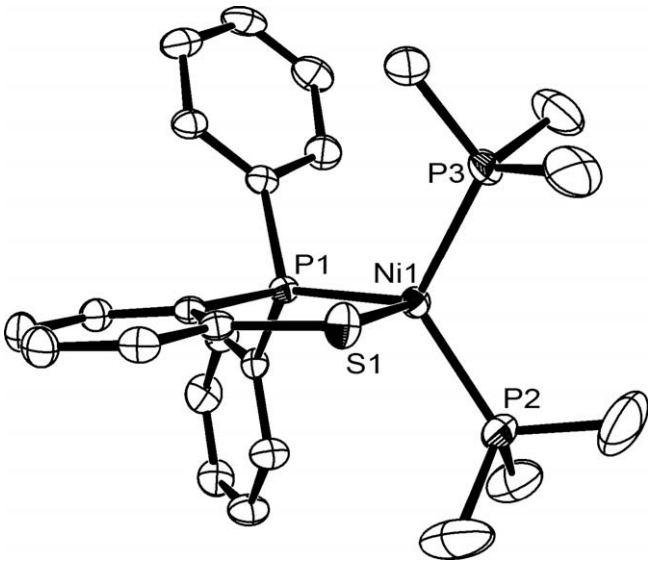
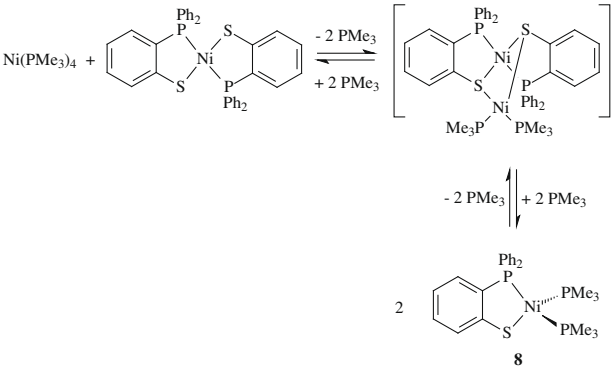



**Fig. 6.** Molecular structure of **8** (ORTEP plot with hydrogen atoms omitted); selected bond lengths [Å] and angles [°]: Ni–S1 2.241(1), Ni–P1 2.147(9), Ni–P2 2.184(1), Ni–P3 2.199(1); P1–Ni–S1 91.07(3), P1–Ni–P2 123.91(3), P1–Ni–P3 116.02(4), P2–Ni–P3 118.57(4), P1–Ni–S1 91.08(3), P2–Ni–S1 97.01(4), P3–Ni–S1 94.04(4).

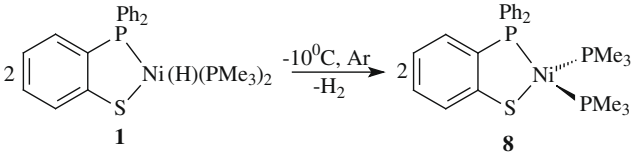
being equivalent. The lines are non-uniformly broadened which seems to result from a statistic dispersion of the geometric parameters of the Ni(I) complex included in a diamagnetic crystalline matrix. In a monocrystalline state complex **8** gives almost no EPR signal up to $T = 5$ K which is indicative of the antiferromagnetic character of the exchange interaction between Ni(I) ions in the crystal. In a powdered state complex **8** gives an intensive EPR signal even at $T = 77$ K. Hence the presence of HFS in the EPR spectrum for a solid sample of complex **8** is attributable to a diamagnetic dilution of the system with monocrystals of complex **8**. The ratio between the components of the $g$-factor $g_{\perp} > g_{\|} \sim 2$ is characteristic of tetrahedral Ni(I) complexes with a trigonal distortion [10]. The EPR based conclusion on the geometrical structure of complex **8** is in excellent agreement with the X-ray data (see Fig. 6 ).

A rational synthesis proceeds by shifting an equilibrium towards formation of **8** by adding trimethylphosphine to a mixture of $Ni(PMe_3)_4$ and freshly prepared $Ni(P^{\wedge}pS)_2$ in THF. Although all attempts to isolate the dinickel intermediate (Eq. (10)) have so far failed, the effect of excess trimethylphosphine points to its presence.




(10)

To elucidate whether Ni(I) complex **8** can be obtained directly from Ni(II) hydride **1** we examined transformations of dissolved complex **1**. A diethyl ether solution of complex **1**, stable in a solid form, was prepared at −10 °C (Method d, Section 3). After twenty minutes, the EPR signal of complex **8** was recorded, after 2 h the signal intensity peaked. Thus, complex **8** can be also prepared by the slow disproportionation of hydride **1** at −10 °C in a diethyl ether solution under argon (Eq. (11)). This fact allows one to conclude that in the systems based on chelating P,S ligands nickel(I) complexes are formed as decomposition products of nickel hydrides. The disproportionation appears to go through a dinickel intermediate as shown in Eq. (10).



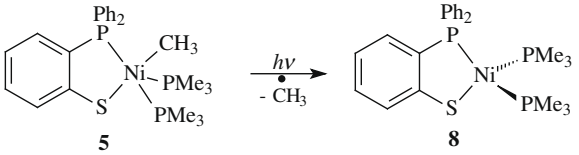

(11)

A similar disproportionation of the nickel hydride(II) $NiH(CH_3COO)(PPh_3)_2$ giving a nickel(I) complex is known for the system $Ni(PPh_3)_4/CH_3COOH$ [8]. Despite a great number of publications devoted to nickel complex catalysts, the question of the structure of the active species remains open. The majority of researchers traditionally assume that the oligomerization of olefins is performed by Ni(II) hydride complexes and follows a Ni–H addition/elimination course. These assumptions are based on the classic works of Tolman [16,17] and others concerned with NMR identification of Ni(II) hydride model complexes [3–6]. On the other hand, according to the EPR data, the process of formation of the nickel complex catalysts includes the generation and stabilization of Ni(I) complexes, independent of the metal valence state in the initial compound [8–12].

Our research shows that the Ni(II) hydride complexes readily turn into Ni(I) complexes that remain intact in solution. Consequently, one should not neglect the chance that Ni(I) complexes are directly relevant to the catalytic conversions of olefinic hydrocarbons.

Photoactivation is one of activation methods for nickel complex catalytic systems. A possibility of photoactivation of the nickel(II) catalytic system in catalytic acetylene cyclotrimerization and ethylene dimerization was demonstrated [18]. The formation of Ni(I) species in this system was detected with EPR spectroscopy. Fourteen different complexes [19] were obtained when Ni(II) complexes were gamma-irradiated (2). Noteworthy, all the data were

gained for complex systems without isolation. As to information on the possible photoreduction of Ni(II) organometallic complexes into those of Ni(I), we failed to find it. In this connection, we studied the UV photoreduction of complex **5**. A toluene solution of complex **5** in a sealed quartz ampoule was UV-irradiated (Method b, Section 3). After 2 h the EPR signal of Ni(I) complex **8** appeared. It peaked after 8 h of the irradiation. Thus we also obtained the Ni(I) complex through the photoreduction of Ni(II) alkyl complex **5** (Eq. (12)).




**5** **8** (12)

In closing we would like to point out that we did not anticipate Ni(I) species to be formed so readily in the examined systems as it proved to occur. Our study shows that chelate chalcogenic ligands facilitate the generation of Ni(I) complexes.

The monovalent oxidation state of nickel has received increasing attention in recent years, in part due to its active role in a number of catalytic processes including biochemical reactions [26–39,40], nickel mediated cross-coupling reactions to make new C–C bonds [39,40–46], alkene oligomerization by heterogeneous [47–60] and homogeneous nickel catalysts [61–62], and other processes [63–67]. We hope that the results presented here will help to appreciate the role of Ni(I) in these processes.

## 3. Experimental

### 3.1. General procedures and materials

Standard vacuum techniques were used in manipulations of volatile and air-sensitive materials. $Ni(PMe_3)_4$ [20], $NiMe_2(PMe_3)_3$ [21], NiMe(OMe)($PMe_3$) [22], (2-diphenylphosphanyl)thiophenol [23], (3-diphenylphosphanyl)2-thionaphthol [23] and were synthesized according to literature procedures. C, H, P, S analyses of air-sensitive solids were carried by H. Kolbe microanalytical laboratory, Mülheim/Ruhr. Infrared spectra (4000–400 $cm^{-1}$), as obtained from Nujol mulls between KBr discs, were recorded on a Bruker FRA 106 spectrometer. Mass spectra were obtained on a Varian MAT spectrometer. EPR spectra were recorded with Bruker ESP 300E. The EPR spectra were simulated with our own program [24], in which the hyperfine interaction (HFI) is limited to the second-order term and where the main axes of the g-tensor and the HFI tensors coincide.

$^1H$, $^{13}C$ 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 and are uncorrected.

### 3.2. (3-Diphenylphosphanyl)2-thionaphthol

2-Thionaphthol (20 g, 125 mmol) in 200 mL of TMEDA/cyclohexane (1:1) was dilithiated [10] using nBuLi (2.5 **M**) (249 mL, 624 mmol) at 25 °C. After cooling to 0 °C chlorodiphenylphosphane (22.4 mL, 125 mmol) in cyclohexane (50 mL) was added dropwise under stirring within 1 h. After 16 h at 25 °C the mixture was hydrolised with water (30 mL), and toluene (200 mL) was added. The organic layer was washed with three portions (200 mL) of acetic acid (5%). 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. Yield 10.1 g (21%); m.p. 165–168 °C. IR (Nujol) $\nu$ = 2547 $cm^{-1}$(SH). $^1H$ NMR (200 MHz, $CDCl_3$, 296 K): $\delta$ 7.87–7.24 (m, 16H, CH), 4.10 (s, 1H, SH) ppm. $^{31}P$ NMR (81 MHz, $CDCl_3$, 296 K): $\delta$ −11.7 (s). $C_{22}H_{17}PS$ (344.4): Calc.: C, 76.72; H, 4.97. Found: C, 76.58; H, 4.99%.

### 3.3. Hydrido(2-diphenylphosphanyl)thiophenolato[P,S]bis(trimethylphosphane)nickel (**1**) [25]

$Ni(PMe_3)_4$ (1.30 g, 3.60 mmol) in pentane (80 mL) containing 1.4 g of trimethylphosphane was combined with (2-diphenylphosphanyl)thiophenol (1.05 g, 3.60 mmol) and stirred for 30 min. The red solution was filtered and cooled to −27 °C to form light red plates of **1**. Yield 670 mg (37%); decomp. >65 °C. IR (Nujol) $\nu$ = 1893 $cm^{-1}$(NiH). $^1H$ NMR (500 MHz, [$D_8$]THF, 203 K): $\delta$ 7.71–6.86 (m, 14H, CH), 1.15 (s, 18H, $PCH_3$), −19.9 (dt, $^2J_{P,H}$ = 45 and 54 Hz, 1H, NiH) ppm. $^{13}C$ NMR (125 MHz, [$D_8$]THF, 203 K): $\delta$ 163.6 (d, $^2J_{P,C}$ = 51 Hz, C1), 140.6 (dt, $^1J_{P,C}$ = 34 Hz, $^3J_{P,C}$ = 10 Hz, C2), 136.7 (d, $^1J_{P,C}$ = 44.9 Hz, C3), 133.8 (s, CH4), 133.1 (d, $^3J_{P,C}$ = 12.1 Hz, CH5), 130.1 (d, $^3J_{P,C}$ = 16.8 Hz, CH6), 129.3 (s, CH7), 129.1 (d, $^3J_{P,C}$ = 8.0 Hz, CH8), 128.9 (d, $^2J_{P,C}$ = 8.6 Hz, CH9), 120.0 (s, CH10), 15.6 (s, $PCH_3$) ppm.

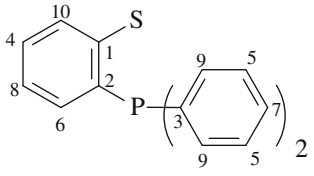
$^{31}P$ NMR (202 MHz, [$D_8$]THF, 203 K): $\delta$ = 57.5 (t, $^2J_{P,P}$ = 154 Hz, 1P, PPh), −14.4 (d, $^2J_{P,P}$ = 154 Hz, 2P, PMe) ppm. $C_{24}H_{33}NiP_3S$ (505.2): Calc.: C, 57.06; H, 6.58; P, 18.39. Found: C, 57.80; H, 6.95; P, 17.81% (see Scheme 1).

### 3.4. Hydrido(3-diphenylphosphanyl)2-thionaphtholato[P,S]bis(trimethylphosphane)nickel (**2**)

$Ni(PMe_3)_4$ (430 mg, 1.18 mmol) in diethyl ether (30 mL) containing 0.5 g of trimethylphosphane at −30 °C was combined with (3-diphenylphosphanyl)2-thionaphthol (408 mg, 1.18 mmol) in diethyl ether (50 mL). On warming, the mixture turned orange red and was stirred at 20 °C for 16 h and filtered. From the filtrate at −27 °C red crystals of **2** were obtained. Yield 560 mg (63%); decomp. >75 °C. IR (Nujol) $\nu$ = 1883 $cm^{-1}$(NiH). $^1H$ NMR (500 MHz, [$D_8$]THF, 190 K): $\delta$ 7.73–6.24 (m, 16H, CH), 1.01 (s, 18H, $PCH_3$), −19.9 (dt, $^2J_{P,H}$ = 40 and 50 Hz, 1H, NiH) ppm. $^{31}P$ NMR (202 MHz, [$D_8$]THF, 190 K): $\delta$ 46.8 (t, $^2J_{P,P}$ = 152 Hz, 1P, PPh), −22.2 (d, $^2J_{P,P}$ = 152 Hz, 2P, PMe) ppm. $C_{28}H_{35}NiP_3S$ (554.7): Calc.: C, 60.63, H, 6.36; P, 16.75; S, 5.78. Found: C, 60.13, H, 6.95; P, 16.81%.

### 3.5. Hydrido(2-diphenylphosphanyl)thiophenolato[P,S]-1,3-bis[(diphenylphosphanyl)-propane]nickel (**3**) [25]

$Ni(PMe_3)_4$ (840 mg, 2.31 mmol) in THF (60 mL) containing 880 mg of trimethylphosphane was combined with (2-diphenylphosphanyl)thiophenol (670 mg, 2.30 mmol) and stirred for 5 min. 1,3-Bis(diphenylphosphanyl)propane (950 mg, 2.30 mmol) in THF (30 mL) was added, and the volatiles were removed in vacuo. The orange residue was washed with two 20 mL portions of pentane and dried in vacuo. Yield 1.57 g (89%); decomp. >91 °C. IR (Nujol) $\nu$ = 1910 $cm^{-1}$ (NiH). $^1H$ NMR (200 MHz, [$D_8$]THF, 296 K): $\delta$ 7.65–6.61 (m, 34H, CH), 2.62–0.94 (m, 6H, $CH_2$), −16.9




**Scheme 1.** Assignment of aromatic $^{13}C$ signals in **1, 3** and **4**.

(dt, $^2J_{P,H}$ = 59 and 22 Hz, 1H, NiH) ppm. $^{31}$P NMR (81 MHz, [$D_8$]THF, 243 K): $\delta$ 61.9 (t, $^2J_{P,P}$ = 74 Hz, 1P, PPh), −14.2 (d, $^2J_{P,P}$ = 74 Hz, 2P, $PCH_2$) ppm. $C_{45}H_{41}NiP_3S$ (765.5): Calc.: C, 70.61; H, 5.40; P, 12.14. Found: C, 70.64; H, 5.99; P, 11.70%.

### 3.6. Methyl(2-diphenylphosphanyl)thiophenolato[P,S](trimethylphosphane)nickel (**4**) [25]

NiMe(OMe)($PMe_3$) (1.35 g, 7.40 mmol) in THF (50 mL) was combined with (2-diphenylphosphanyl)thiophenol (2.14 g, 7.30 mmol) in THF (30 mL). After stirring for 10 min the volatiles were evaporated and the residue was extracted with two 50 mL portions of pentane over a glass-sinter disc (G3). Crystallisation afforded orange prisms of **4**. Yield 1.77 g (54%); m.p. 117–119 °C, decomp. >125 °C. IR (Nujol) $\nu$ = 1183 cm$^{-1}$($\delta$NiCH$_3$). $^1$H NMR (200 MHz, [$D_8$]THF, 223 K): $\delta$ 7.60–6.71 (m, 14H, CH), 1.35 d, $^2J_{P,H}$ = 8.5 Hz, 9 H, $PCH_3$), −0.37 (d,d $^3J_{P,H}$ = 9.4 and 8.5 Hz, 3H, $NiCH_3$) ppm. $^{13}$C NMR (125 MHz, [$D_8$]THF, 300 K): $\delta$ 161.3 (d, $^2J_{P,C}$ = 39.0 Hz, C1), 136.8 (d, $^1J_{P,C}$ = 55.3 Hz, C2), 134.1 (d, $^3J_{P,C}$ = 10.1 Hz, C4), 133.7 (s, C3), 132.6 (s, CH5), 131.1 (s, CH6), 130.7 (s, CH7), 129.8 (d, $^3J_{P,C}$ = 12.6 Hz, CH8), 129.1 (d, $^2J_{P,C}$ = 10.1 Hz, CH9), 121.4 (d, $^3J_{P,C}$ = 5.0 Hz, CH10), 13.3 (d, $^1J_{P,C}$ = 26.4 Hz, $PCH_3$), −7.6 (d, $^2J_{P,C}$ = 22.6 Hz, $NiCH_3$) ppm. $^{31}$P NMR (81 MHz, [$D_8$]THF, 203 K): $\delta$ 62.6 (d, $^2J_{P,P}$ = 301 Hz, 1P, PPh), −1.3 (d, $^2J_{P,P}$ = 301 Hz, 1P, $PCH_2$) ppm. $C_{22}H_{26}NiP_2S$ (443.2): Calc.: C, 59.63; H, 5.91; P, 13.98. Found: C, 59.68; H, 5.80; P, 13.91%.

### 3.7. Methyl(2-diphenylphosphanyl)thiophenolato[P,S]bis(trimethylphosphane)nickel(**5**) [25]

$NiMe_2(PMe_3)_3$ (1.20 g, 3.70 mmol) in diethyl ether (50 mL) was combined with (2-diphenylphosphanyl)thiophenol (1.07 g, 3.66 mmol) in diethyl ether (50 mL) and stirred for 15 min. The volatiles were evaporated and the residue was extracted with 50 mL of pentane containing 0.5 g of trimethylphosphane, and the red solution was kept at −27 °C to yield dark red needles of **5**. Yield 1.29 g (67%); m.p. 118–123 °C, decomp. >132 °C. IR (Nujol) $\nu$ = 1158 cm$^{-1}$($\delta$NiCH$_3$). $^1$H NMR (500 MHz, [$D_8$]THF, 297 K): $\delta$ 7.55–6.69 (m, 14H, CH), 1.13 (d, $^2J_{P,H}$ = 6 Hz, 18H, $PCH_3$), −0.33 (d, $^3J_{P,H}$ = 9 Hz, 3H, $NiCH_3$) ppm. $^{13}$C NMR (75 MHz, [$D_8$]THF, 297 K): $\delta$ 159.5 (d, $^2J_{P,C}$ = 41.5 Hz, C1), 135.4 (d, $^1J_{P,C}$ = 52.3 Hz, C2), 133.1 (d, $^1J_{P,C}$ = 36.7 Hz, C3), 132.7 (d, $^3J_{P,C}$ = 6.3 Hz, CH4), 132.1 (d, $^3J_{P,C}$ = 11.5 Hz, CH5), 130.9 (s, CH6), 129.5 (s, CH7), 128.7 (s, CH8), 127.8 (d, $^2J_{P,C}$ = 13.0 Hz, CH9), 119.3 (d, $^4J_{P,C}$ = 4.6 Hz, CH10), 13.3 (d, $^1J_{P,C}$ = 9.3 Hz, $PCH_3$), −8.3 (d, $^2J_{P,C}$ = 21.5 Hz, $NiCH_3$) ppm. $^{31}$P NMR (81 MHz, [$D_8$]THF, 193 K): $\delta$ 45.8 (t, $^2J_{P,P}$ = 179 Hz, 1P, PPh), −17.3 (d, $^2J_{P,P}$ = 179 Hz, 2P, $PCH_3$) ppm. $C_{25}H_{35}NiP_3S$ (519.2): Calc.: C, 57.83; H, 6.79; P, 17.90. Found: C, 57.68; H, 6.83; P, 17.86%.

### 3.8. Methyl(3-diphenylphosphanyl)-2-thionaphtholato[P,S]bis(trimethylphosphane)nickel (**6**)

$NiMe_2(PMe_3)_3$ (720 mg, 2.30 mmol) in THF (30 mL) at −30 °C was combined with (3-diphenylphosphanyl)-2-thionaphthol (790 mg, 2.30 mmol) in THF (30 mL) and stirred for 15 min at 20 °C. The volatiles were evaporated and the residue was extracted with 80 mL of pentane containing 0.6 g of trimethylphosphane, and the red solution was kept at −27 °C to yield dark red plates of **6**. Yield 890 mg (59%); m.p. 101–103 °C. IR (Nujol) $\nu$ = 1157 cm$^{-1}$ ($\delta$NiCH$_3$). $^1$H NMR (500 MHz, [$D_8$]THF, 190 K): $\delta$ = 7.8–7.2 (m, 16H, CH), 1.10 (d, $^2J_{P,H}$ = 7 Hz, 18H, $PCH_3$), −0.20 (d, $^3J_{P,H}$ = 10 Hz, 3H, $NiCH_3$) ppm. $^{31}$P NMR (202 MHz, [$D_8$]THF, 193 K): $\delta$ 36.9 (s(br), 1P, PPh), −25.3 (s(br), 2P, $PCH_3$) ppm. $C_{29}H_{37}NiP_3S$ (569.3): Calc.: C, 61.18; H, 6.55; P, 16.34; S, 5.64. Found: C, 60.63; H, 6.47; P, 17.09; S, 4.98%.

### 3.9. Methyl(3-diphenylphosphanyl)-2-thionaphtholato[P,S](trimethylphosphane)nickel (**7**)

700 mg (3.88 mmol) of NiMe(OMe)($PMe_3$) in THF were combined with 1.31 g (3.80 mmol) of (3-diphenylphosphino)-2-thionaphthol. After 10 min. the volatiles were removed in vacuo and the residue was extracted with pentane. Crystallization at room temperature afforded 880 mg of methylnickel complex **7** as orange prismatic rods. Yield: 44%. m.p. 139–142 °C. IR (Nujol) $\nu$ = 1219 cm$^{-1}$($\delta$NiCH$_3$). $^1$H NMR (500 MHz, [$D_8$]THF, 190 K): $\delta$ *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 (s(br), 9H, $PCH_3$); −0.29 (d, $^3J_{P,H}$ = 10.5 Hz, 3H, $NiCH_3$) ppm. $^{31}$P NMR (202 MHz, [$D_8$]THF, 193 K): $\delta$ 50.02 (d, $^2J_{P,H}$ = 31.4 Hz, 1P, $PPh_2$); −22.7 (d, $^2J_{PMe,PPh}$ = 46.9 Hz, 1P, $PCH_3$) ppm. $C_{26}H_{28}NiP_2S$ (493.2): Calc.: C, 63.31; H, 5.72; P, 12.56; S, 6.50. Found: C, 63.69; H, 5.31; P, 11.67; S, 6.77%.

### 3.10. (2-Diphenylphosphanyl)thiophenolato[P,S]bis(trimethylphosphane)nickel (**8**)

#### 3.10.1. Method a

Ni($PMe_3$)$_4$ (1.50 g, 4.10 mmol) in diethyl ether (50 mL) containing 1.0 g of trimethylphosphane was combined with (2-diphenylphosphanyl)thiophenol (1.22 g, 4.10 mmol) and stirred for 60 min at −50 °C. The resulting red solution was filtered at −50 °C. Then it was carefully warmed to −10 °C and kept at this temperature for 2 h. Warming was accompanied by evolving gaseous dihydrogen and forming a small amount of green thinly dispersed precipitate. During this the solution slightly changed its colour keeping within red gamut. The solution was filtered at −10 °C, and cooling to −27 °C gave red crystals of **8**. Yield 250 mg (12%). Decomp. 42–47 °C. IR (Nujol) $\nu$ = 934 cm$^{-1}$($\rho$PCH$_3$). MS (70 eV): *m*/*z* (%) = 58(4), 77(3), 109(5), 183(17.2), 215(24.5), 293(59), 337(20.4), 369(37), 428(2), 644(100). MS of Ni(P^pS)$_2$ (70 eV): *m*/*z* (%) = 58(3.3), 77(3.3), 107(5.8), 152(10), 183(72.5), 215(26.6), 243(7.5), 293(32.5), 337(5.8), 369(17.5), 428(5), 644 (100). EPR (X-Band, $T$ = 77 K) $g_{\|}$ = 2.008, $g_{\perp}$ = 2.140, $A_{\|}$ (1P) = 45 G, $A_{\perp}$ (1P) $\leqslant$ 23 G, $A_{\|}$ (2P) = 67 G, $A_{\perp}$ (2P) = 57 G.

#### 3.10.2. Method b

Complex **8** was prepared in situ by photochemical reduction of **5** in an EPR ampoule. Complex **5** (50 mg) in 1.5 mL of toluene was sealed in an EPR ampoule which was irradiated by light of wavelengths 20000–24000 cm$^{-1}$ with the EPR signal intensity being measured every 2 h. After 8 h the intensity reached its maximum. The resulting solution was deep red, attempts to crystallise the product failed.

#### 3.10.3. Method c

Ni($PMe_3$)$_4$ (1.50 g, 4.10 mmol) in THF (50 mL) containing 1.0 g of trimethylphosphane was combined with Ni(P^pS)$_2$ (2.7 g, 4.10 mmol) and stirred for 3 h at −10 °C. The volatiles were evaporated, and the residue was extracted with 30 mL of diethyl ether containing 0.5 g of trimethylphosphane. The red solution at −27 °C gave red crystals of **8** (IR, EPR). Yield 270 mg (12%).

#### 3.10.4. Method d

Complex **1** (500 mg, 1 mmol) was dissolved in diethyl ether (20 mL) containing 300 mg of trimethylphosphane at −10 °C. The solution was kept at −10 °C for 2 h and then filtered. The red filtrate was cooled to −27 °C to give red crystals of **8** (IR, EPR). Yield 300 mg (60%).

### 3.11. Crystal structure analyses

Crystal data are presented in Tables 1 and 2. Data collection: Complex **1**: A crystal was sealed under argon in a glass capillary and mounted on an Oxford Xcalibur diffractometer. Reflections were measured using graphite-monochromated Mo Kα radiation; Lp correction and absorption correction based on Ψ-scans were applied. The structure was solved by direct and conventional Fourier methods. All non-hydrogen atoms were treated with a riding model in idealized positions. Complexes **5, 6** and **7**: Selected crystals were kept under paraffin oil for protection against humidity. For single crystal data collection the crystals were placed in premounted Cryoloops from Hampton Research and cooled down to 100 K, covered with a protecting oil film. Data collection was performed using an Xcalibur diffractometer from Oxford Diffraction, equipped with the Enhance source option and Sapphire CCD detector in φ and ω-scan mode, respectively. The structure was solved by direct methods using SHELXS und refined using SHELXL-97. H atoms were added at idealized positions. Complex **8**: A crystal of **8** was mounted on a glass capillary with silicone grease, quickly put into the cold nitrogen stream of the cooling device of the goniometer and measured on a STOE IPDSII diffractometer. An initial structural model was obtained by direct methods using SHELXS-97. The remaining atoms were obtained from difference Fourier maps, followed by least-squares refinement cycles. Refinements were performed using SHELXL-97. After anisotropic refinement of this model, H atoms were added at idealized positions.

**Table 1**
Crystal data for compounds **1** and **8**.

| | **1** | **8** |
|---|---|---|
| Empirical formula | $C_{24}H_{33}NiP_3S$ | $C_{24}H_{32}NiP_3S$ |
| Formula mass | 505.18 | 504.18 |
| Crystal size | 0.50 × 0.36 × 0.02 | 0.36 × 0.20 × 0.1 |
| Crystal system | Triclinic | Triclinic |
| Space group | $P\bar{1}$ | $P\bar{1}$ |
| $a$ (Å) | 9.237(1) | 9.098(7) |
| $b$ (Å) | 11.775(1) | 11.650(9) |
| $c$ (Å) | 13.026(1) | 12.937(8) |
| $\alpha$ (°) | 71.37(1) | 72.533(2) |
| $\beta$ (°) | 80.02(1) | 81.091(3) |
| $\gamma$ (°) | 82.48(1) | 82.969(1) |
| $V$ (Å$^3$) | 1317.9(2) | 1288.29(3) |
| Z | 2 | 2 |
| $D_{calc}$ (g/cm$^3$) | 1.237 | 1.300 |
| $\mu$(Mo Kα) (mm$^{-1}$) | 1.006 | 1.03 |
| Temperature (K) | 301(2) | 150 |
| Data collected range (°) | $8.3 \geqslant 2\Theta \geqslant 52.7$ | $1.9 \geqslant 2\Theta \geqslant 54.2$ |
| $h$ | $-6 \geqslant h \geqslant 11$ | $-11 \geqslant h \geqslant 11$ |
| $k$ | $-14 \geqslant k \geqslant 14$ | $-14 \geqslant k \geqslant 14$ |
| $l$ | $-16 \geqslant l \geqslant 16$ | $-16 \geqslant l \geqslant 16$ |
| No. of reflections measured | 8836 | 19766 |
| No. unique data | 5274 | 5588 ($R_{int}$ = 0.0547) |
| Parameters | 293 | 262 |
| Goodness-of-fit on $F^2$ | 1.351 | 1.027 |
| $R_1$ [$I \geqslant 2\sigma(I)$] | 0.0404 | 0.0398 |
| $wR_2$ (all data) | 0.1316 | 0.0931 |

**Table 2**
Crystal data for compounds **5**–**7**.

| | **5** | **6** | **7** |
|---|---|---|---|
| Empirical formula | $C_{25}H_{35}NiP_3S$ | $C_{29}H_{37}NiP_3S$ | $C_{26}H_{28}NiP_2S$ |
| Formula mass | 519.21 | 569.27 | 493.19 |
| Crystal size (mm) | 0.40 × 0.20 × 0.06 | 0.16 × 0.16 × 0.08 | 0.32 × 0.28 × 0.14 |
| Crystal system | Monoclinic | Monoclinic | Monoclinic |
| Space group | $P2_1/n$ | $P2_1/n$ | $P2_1/n$ |
| $a$ (Å) | 10.465(2) | 13.5939(8) | 9.0995(6) |
| $b$ (Å) | 10.532(2) | 13.9297(7) | 12.8266(4) |
| $c$ (Å) | 24.233(3) | 15.0138(8) | 20.6562(6) |
| $\beta$ (°) | 100.66(1) | 94.366(5) | 96.155(4) |
| $V$ (Å$^3$) | 2624.8(8) | 2834.7(3) | 2397.00(19) |
| Z | 4 | 4 | 4 |
| $D_{calc}$ (g/cm$^3$) | 1.314 | 1.334 | 1.367 |
| $\mu$(Mo Kα) (mm$^{-1}$) | 1.012 | 0.944 | 1.041 |
| Temperature (K) | 100(2) | 100(2) | 100(2) |
| Data collected range (°) | $4.6 \geqslant 2\Theta \geqslant 52.4$ | $4.9 \geqslant 2\Theta \geqslant 52.7$ | $4.72 \geqslant 2\Theta \geqslant 52.72$ |
| $h$ | $-11 \geqslant h \geqslant 13$ | $-15 \geqslant h \geqslant 16$ | $-11 \geqslant h \geqslant 11$ |
| $k$ | $-12 \geqslant k \geqslant 13$ | $-17 \geqslant k \geqslant 17$ | $-15 \geqslant k \geqslant 16$ |
| $l$ | $-30 \geqslant l \geqslant 27$ | $-18 \geqslant l \geqslant 18$ | $-25 \geqslant l \geqslant 25$ |
| No. reflections measured | 21543 | 23007 | 20568 |
| No. unique data | 5350 ($R_{int}$ = 0.0561) | 5783 ($R_{int}$ = 0.0943) | 4899 ($R_{int}$ = 0.0943) |
| Parameters | 278 | 313 | 275 |
| Goodness-of-fit on $F^2$ | 1.040 | 1.097 | 1.049 |
| $R_1$ [$I \geqslant 2\sigma(I)$)] | 0.0502 | 0.0684 | 0.0355 |
| $wR_2$ (all data) | 0.0987 | 0.1206 | 0.1039 |

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## Appendix A. Supplementary material

CCDC 705060, 705061, 705062, 708341 and 705063 contain the supplementary crystallographic data for complexes **1**, **5**, **6**, **7** and **8**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.01.023.

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