

# Synthesis and structure of $[(C_5H_5)Fe(C_5H_4PS_2OCH_2C_6H_4N_3)]^-$ , a new phosphonodithioate derivative, and its coordination chemistry with rhodium(I) and nickel(II)

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Received 2 April 2001; accepted 2 April 2001

## Abstract

The anion  $[(C_5H_5)Fe(C_5H_4PS_2OCH_2C_6H_4N_3)]^-$  (**1**) was synthesized in two steps from ferrocene,  $P_4S_{10}$  and hydroxymethylbenzotriazole in the presence of triethylamine. The molecular structure of **1**, determined by single-crystal X-ray structure analysis of the triethylammonium salt, shows the rare  $R(R'O)PS_2$  arrangement in the expected tetrahedral geometry; the substituents  $R$  = ferrocenyl and  $R'$  = methylenbenzotriazol impose a certain rigidity on the molecule. Anion **1** reacts with  $[RhCl(cod)]_2$  ( $cod$  = 1,5-cyclooctadiene) to give  $Rh(cod)[(C_5H_5)Fe(C_5H_4PS_2OCH_2C_6H_4N_3)]$  (**2**) and with  $[RhCl(CO)_2]_2$  to give  $Rh(CO)_2[(C_5H_5)Fe(C_5H_4PS_2OCH_2C_6H_4N_3)]$  (**3**). With  $[NiCl_2(C_4Me_4)]_2$  anion **1** gives the analogous nickel complex  $Ni(C_4Me_4)[(C_5H_5)Fe(C_5H_4PS_2OCH_2C_6H_4N_3)]$  (**4**). However, with  $NiCl_2 \cdot 6H_2O$  the anion **1** loses the methylenbenzotriazol unit to give the complex  $Ni[(C_5H_5)Fe(C_5H_4PS_2O)]_2$  (**5**). The expected complex  $Ni[(C_5H_5)Fe(C_5H_4PS_2OCH_2C_6H_4N_3)]_2$  (**6**) was obtained from the room-temperature reaction of **1** with anhydrous  $NiCl_2$  in aqueous acetonitrile. The single-crystal X-ray structure analyses reveal a tetrahedral rhodium coordination geometry for **2** and a square-planar nickel coordination geometry for **5**. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Rhodium; Nickel; Ferrocene; Phosphonodithioates; Benzotriazole

## 1. Introduction

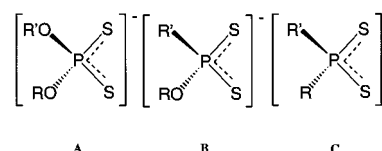
Organodithio derivatives of phosphorus have found important industrial and agricultural applications, e.g. as additives to lubricant oils, solvent extraction reagents for metals, flotation agents for mineral ores, insecticides, rodenticides and pesticides [1]. In recent years substantial progress has been made in the development of the synthesis and coordination chemistry of phosphorodithioate (A) [2] and phosphinodithioate (C) [3] derivatives, however, phosphonodithioates (B) are rare, although a synthetic route to these compounds from Lawesson's reagent and alcohols has been developed recently [4]. Due to the limited access to phosphonodithioates, their coordination chemistry is little explored. In particular, there are no examples of rhodi-

um(I) complexes, a metal system extensively studied with other chelating ligands (Scheme 1).

In this paper we report the synthesis of the anion  $[(C_5H_5)Fe(C_5H_4PS_2OCH_2C_6H_4N_3)]^-$  (**1**), a new phosphonodithioate derivative of type B, isolated as the triethylammonium salt, its molecular structure and its coordination chemistry with rhodium(I) and nickel(II).

## 2. Results and discussion

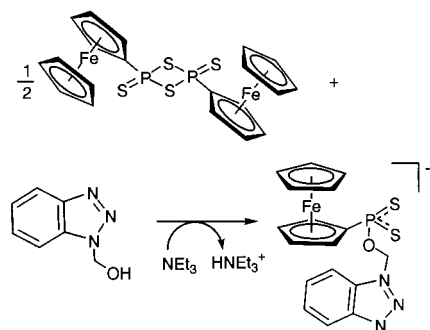
The reaction of the ferrocene derivative of Lawesson's reagent  $[(C_5H_5)_2Fe(C_5H_4)]_2P_2S_4$ , recently reported



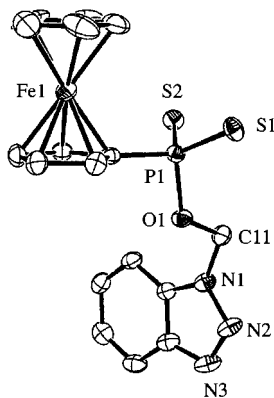
Scheme 1.

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Scheme 2.

Fig. 1. ORTEP drawing and atom-labeling scheme for compound **1**, hydrogen atoms are omitted for clarity.Table 1  
Selected bond lengths (Å) and angles (°) for compound **1**

Bond lengths			
C(1)–P(1)	1.784(3)	O(1)–P(1)	1.645(2)
P(1)–S(1)	1.9739(10)	P(1)–S(2)	1.9811(10)
Bond angles			
C(2)–C(1)–P(1)	125.5(2)	C(5)–C(1)–P(1)	127.5(2)
C(11)–O(1)–P(1)	118.77(18)	O(1)–P(1)–C(1)	96.78(12)
O(1)–P(1)–S(1)	108.64(9)	C(1)–P(1)–S(1)	112.06(10)
O(1)–P(1)–S(2)	108.07(9)	C(1)–P(1)–S(2)	111.90(10)
S(1)–P(1)–S(2)	117.29(5)		

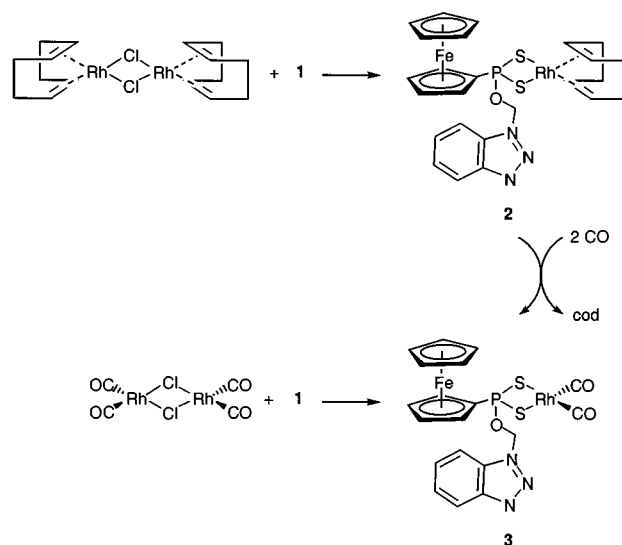
by Woollins et al. [5], with hydroxymethylbenzotriazole leads, in the presence of triethylamine, to the formation of the anion  $[(C_5H_5)Fe(C_5H_4PS_2OCH_2C_6H_4N_3)]^-$  (**1**) which is obtained as the triethylammonium salt. The phosphorus atom of the OPS<sub>2</sub> moiety gives rise to a signal at 110.2 ppm in the <sup>31</sup>P{<sup>1</sup>H}-NMR spectrum. The <sup>1</sup>H-NMR spectrum of the triethylammonium salt of **1** shows the expected signals for the ferrocenyl and the benzotriazole groups, the signal of the methylene protons ( $\delta = 6.4$  ppm) shows up as a doublet because of the coupling with the phosphorus atom ( $J_{PH} = 8.8$  Hz) (Scheme 2).

The single-crystal X-ray structure analysis of the triethylammonium salt of **1** reveals a distorted tetrahe-

dral geometry of the phosphorus atom, the angles S(1)–P(1)–S(2), S(1)–P(1)–C(1), S(1)–P(1)–O(1), S(2)–P(1)–C(1), S(2)–P(1)–O(1), and O(1)–P(1)–C(1) being 117.29(5), 112.06(10), 108.64(9), 111.90(10), 108.67(9), and 96.78(12)°, respectively. The two PS bonds are equal in length [P(1)–S(1) 1.9739(10), P(1)–S(2) 1.9811(10) Å] and have a partial  $\pi$  character, in agreement with those found [1.989(1) and 2.000(1) Å] for the amido derivative  $[PrNH_3][(MeOC_6H_4)P(PrNH)S_2]$  [4]. The molecular structure of **1** is shown in Fig. 1, and important bond lengths and angles are given in Table 1.

The complex  $[RhCl(cod)]_2$  (cod = 1,5-cyclooctadiene) reacts with two equivalents of **1** in dichloromethane to give  $Rh(cod)[(C_5H_5)Fe(C_5H_4PS_2OCH_2C_6H_4N_3)]$  (**2**) in quantitative yield. Similarly, the reaction of  $[RhCl(CO)_2]_2$  with two equivalents of **1** affords  $Rh(CO)_2[(C_5H_5)Fe(C_5H_4PS_2OCH_2C_6H_4N_3)]$  (**3**). Complex **3** exhibits two strong  $\nu(CO)$  absorptions in the IR spectrum, as expected for a *cis*-dicarbonyl arrangement [6]. Both compounds show characteristic doublet resonances in their <sup>31</sup>P-NMR spectra (see Section 4) due to coupling of the phosphorus atoms to <sup>103</sup>Rh ( $I = 1/2$ ), indicating that they are mononuclear in solution [7]. This is in line with the findings for the analogous dithiocarbamate derivative  $Rh(S_2CNMe_2)(CO)_2$  [8]. Carbon monoxide reacts in dichloromethane with **2** to give quantitatively **3** (Scheme 3).

The single-crystal X-ray structure analysis of **2** shows that the complex is indeed mononuclear. The metal atom is in a tetrahedral environment and is coordinated by the two S atoms of one *S,S*-bidentate ligand. The two PS bonds are equal in length [P(1)–S(1) 1.991(2), P(1)–S(2) 2.003(2) Å] and have a partial  $\pi$  character; they are, however, longer than in the free ligand **1**. The molecular structure of **2** is depicted in Fig. 2, and important bond lengths and angles are given in Table 2.



Scheme 3.

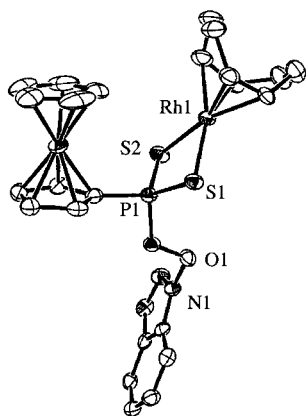
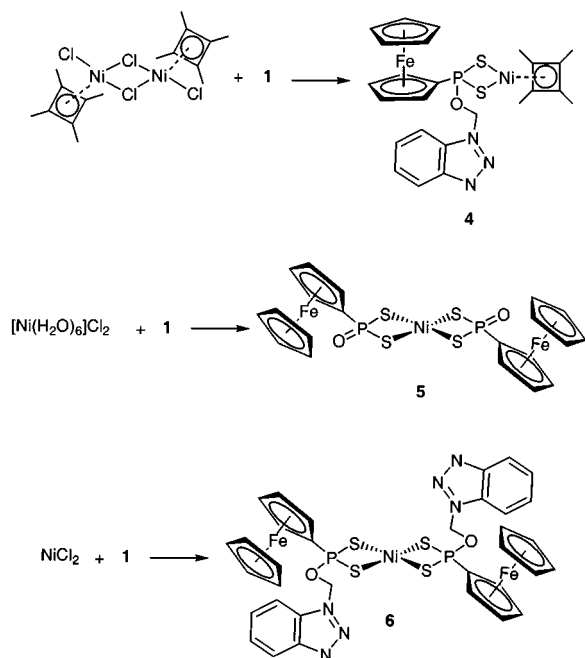


Fig. 2. ORTEP drawing and atom-labeling scheme for compound **2**, hydrogen atoms are omitted for clarity.

Table 2  
Selected bond lengths (Å) and angles (°) for compound **2**

Bond lengths			
C(11)–Rh(1)	2.157(6)	P(1)–S(1)	1.991(2)
C(12)–Rh(1)	2.141(6)	P(1)–S(2)	2.003(2)
C(15)–Rh(1)	2.159(6)	S(1)–Rh(1)	2.3817(16)
C(16)–Rh(1)	2.149(5)	S(2)–Rh(1)	2.4219(13)
O(1)–P(1)	1.609(3)		
Bond angles			
P(1)–S(1)–Rh(1)	84.98(7)	C(15)–Rh(1)–S(1)	94.8(2)
P(1)–S(2)–Rh(1)	83.68(7)	C(12)–Rh(1)–S(2)	93.50(17)
C(12)–Rh(1)–C(16)	98.6(2)	C(11)–Rh(1)–S(2)	96.03(16)
C(16)–Rh(1)–C(11)	82.4(2)	S(1)–Rh(1)–S(2)	83.47(5)
C(12)–Rh(1)–C(15)	82.4(3)		
C(11)–Rh(1)–C(15)	90.2(2)		
C(16)–Rh(1)–S(1)	91.56(18)		



Scheme 4.

The analogous reaction of the tetramethylcyclobutadiene complex  $[\text{NiCl}_2(\text{C}_4\text{Me}_4)]_2$  with two equivalents of **1** in dichloromethane gives the nickel complex  $\text{Ni}(\text{C}_4\text{Me}_4)[(\text{C}_5\text{H}_5)\text{Fe}(\text{C}_5\text{H}_4\text{PS}_2\text{OCH}_2\text{C}_6\text{H}_4\text{N}_3)]$  (**4**) in good yield. Complex **4** shows the expected signal at  $\delta$  104.1 ppm in the  $^{31}\text{P}$ -NMR spectrum. With  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ , anion **1** reacts to give the complex  $\text{Ni}[(\text{C}_5\text{H}_5)\text{Fe}(\text{C}_5\text{H}_4\text{PS}_2\text{O})]_2$  (**5**), in which the methylenebenzotriazol unit of the ligand has been lost. This is presumably due to the oxophilicity of phosphorus. This is in line with the findings that the complexes *cis*- $\text{M}[\text{S}_2\text{P}(\text{S})-(\text{C}_6\text{H}_4\text{OMe})](\text{PPh}_3)_2$  [ $\text{M} = \text{Ni}(\text{II}), \text{Pd}(\text{II})$  and  $\text{Pt}(\text{II})$ ] are readily oxidized in solution to give  $\text{M}[\text{S}_2\text{P}(\text{O})-(\text{C}_6\text{H}_4\text{OMe})](\text{PPh}_3)_2$  [**9**] (Scheme 4).

The single-crystal X-ray structure analysis of **5** reveals that the complex is square-planar. The metal is coordinated by the four S atoms of the two ligands. The four nickel–sulfur bonds are not equivalent, each ligand is coordinated by a shorter and a longer Ni–S bond [ $\text{Ni}–\text{S}(1) = \text{Ni}–\text{S}(1a)$  2.2203(9),  $\text{Ni}–\text{S}(2) = \text{Ni}–\text{S}(2a)$  2.2387(8) Å]. The two phosphorus atoms have a pseudo-tetrahedral geometry, the four P–S bonds being very similar [ $\text{P}(1)–\text{S}(1) = \text{P}(1)–\text{S}(1a)$  2.2203(9),  $\text{Ni}–\text{S}(2) = \text{Ni}–\text{S}(2a)$  2.2387(8) Å]. The molecular structure of **5** is depicted in Fig. 3, and important bond lengths and angles are given in Table 3.

The expected nickel complex  $\text{Ni}[(\text{C}_5\text{H}_5)\text{Fe}(\text{C}_5\text{H}_4\text{PS}_2\text{OCH}_2\text{C}_6\text{H}_4\text{N}_3)]_2$  (**6**) could be obtained from the room-temperature reaction of **1** with anhydrous nickel(II) chloride in aqueous acetonitrile from which it precipitates quantitatively. It is soluble in dimethylsulfoxide and is characterized by correct NMR and micro-analytical data. The mass spectrum (electrospray) shows the expected molecular peak at  $m/z$  915.

### 3. Conclusion

The aim of this work was the synthesis of a new phosphonodithioate ligand and to study its ability to coordinate as ligand to transition metals. A high-yield route was developed to synthesize the anion (**1**) which crystallizes as the triethylammonium salt. The coordination chemistry of **1** studied with Rh(I) and Ni(II) centers shows that **1** behaves as a typical chelating ligand using the two sulfur atoms of the  $\text{PS}_2$  unit for coordination. Since **1** also contains nitrogen atoms in the benzotriazol unit, it may be possible to use **1** for the build-up of multinuclear complexes.

### 4. Experimental

Solvents were dried and distilled under nitrogen prior to use. All reactions were carried out under nitrogen, using standard Schlenk techniques. The compounds

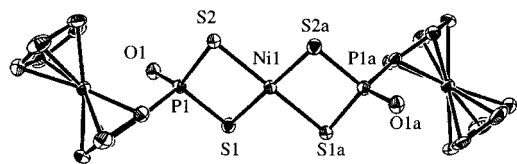


Fig. 3. ORTEP drawing and atom-labeling scheme for compound **5**, hydrogen atoms are omitted for clarity.

Table 3  
Selected bond lengths (Å) and angles (°) for compound **5**

Bond lengths			
P(1)–S(2)	2.0300(13)	S(2)–Ni(1)	2.2387(8)
P(1)–S(1)	2.0420(12)	Ni(1)–S(1) # 1	2.2203(9)
S(1)–Ni(1)	2.2203(9)	Ni(1)–S(2) # 1	2.2387(8)
Bond angles			
C(5)–C(1)–P(1)	124.8(3)	S(2)–P(1)–S(1)	98.40(5)
C(2)–C(1)–P(1)	127.8(3)	P(1)–S(1)–Ni(1)	86.53(4)
O(1)–P(1)–C(1)	107.63(13)	P(1)–S(2)–Ni(1)	86.33(4)
O(1)–P(1)–S(2)	117.90(10)	S(1) # 1–Ni(1)–S(2) # 1	87.47(3)
C(1)–P(1)–S(2)	108.64(12)	S(1)–Ni(1)–S(2) # 1	92.53(3)
O(1)–P(1)–S(1)	114.65(10)	S(1) # 1–Ni(1)–S(2)	92.53(3)
C(1)–P(1)–S(1)	109.15(11)	S(1)–Ni(1)–S(2)	87.47(3)

[RhCl(cod)]<sub>2</sub> [10], [RhCl(CO)<sub>2</sub>]<sub>2</sub> [11] and [(C<sub>4</sub>Me<sub>4</sub>)NiCl<sub>2</sub>]<sub>2</sub> [12] were prepared as described previously. All other reagents were purchased (Fluka) and used as received. Nuclear magnetic resonance spectra were recorded using a Varian Gemini 200 BB instrument or a Bruker AMX 400 spectrometer and referenced by using the resonances of residual protons in the deuterated solvents. <sup>1</sup>H-NMR: internal standard solvent, external standard TMS; <sup>13</sup>C-NMR: internal standard solvent, external standard TMS; <sup>31</sup>P-NMR: external standard 85% H<sub>3</sub>PO<sub>4</sub>. Infrared spectra were recorded with a Perkin–Elmer 1720X FTIR spectrometer. Microanalyses were carried out by the Laboratory of Pharmaceutical Chemistry, University of Geneva, Switzerland.

#### 4.1. [HNEt<sub>3</sub>][(C<sub>5</sub>H<sub>5</sub>)Fe(C<sub>5</sub>H<sub>4</sub>PS<sub>2</sub>OCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>N<sub>3</sub>)] (anion **1**)

A solution of [(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Fe(C<sub>5</sub>H<sub>4</sub>)<sub>2</sub>P<sub>2</sub>S<sub>4</sub>] (2.6 g, 4.6 mmol), hydroxymethylbenzotriazole (1.4 g, 9.3 mmol) and Et<sub>3</sub>N (1.3 ml, 9.3 mmol) in THF (50 ml) was stirred at room temperature (r.t.). After 3 h the solvent was removed under reduced pressure. The resulting yellow–green solid was washed with acetone (2 × 25 ml), toluene (10 ml) and dried under vacuum (2.3 g, 94%). Crystals suitable for X-ray diffraction analysis were grown by slow evaporation of a 1:1 CH<sub>2</sub>Cl<sub>2</sub>–pentane solution. Anal. Found: C, 52.3; H, 5.9. Calc. for C<sub>23</sub>H<sub>31</sub>Fe<sub>1</sub>N<sub>4</sub>O<sub>1</sub>P<sub>1</sub>S<sub>2</sub> (530.5): C, 52.1; H, 5.9%. FTIR

(4000–400 cm<sup>-1</sup>): 3062vw, 2940w, 1609w, 1495m, 1469m, 1455m, 1382m, 1313m, 1269m, 1173m, 1162m, 1130w, 1106m, 1039vs, 1016s, 925w, 896vw, 808vs, 753s, 665vs, 636m, 588s, 502m, 483m, 452m, 433w cm<sup>-1</sup>. <sup>31</sup>P-NMR (CDCl<sub>3</sub>): δ = 110.16 (s). <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ = 7.99 (d, 1H), δ = 7.77 (d, 1H), δ = 7.44 (t, 1H), δ = 7.34 (t, 1H), δ = 6.42 (d, 2H), δ = 4.65 (s, 2H), δ = 4.30 (s, 2H), δ = 4.26 (s, 5H), δ = 3.20 (q, 6H), δ = 1.33 (t, 9H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>): δ = 146.51, 133.38, 127.94, 124.59, 119.90, 111.38, 72.20, 72.05, 71.18, 71.15, 70.91, 70.80, 46.50, 9.05.

#### 4.2. Rh(cod)[(C<sub>5</sub>H<sub>5</sub>)Fe(C<sub>5</sub>H<sub>4</sub>PS<sub>2</sub>OCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>N<sub>3</sub>)] (**2**)

100 mg (0.2 mmol) of [RhCl(cod)]<sub>2</sub> and 320 mg (0.5 mmol) of [NEt<sub>3</sub>H]**1** were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (20 ml). The resulting solution was stirred at r.t. for 2 h, then the solvent was removed under reduced pressure. The residue was extracted Et<sub>2</sub>O (20 ml), the solution was filtered and then the solvent was evaporated to dryness. The remaining orange solid was washed with hexane (10 ml) and dried in vacuo (105 mg, 82%). Crystals suitable for X-ray diffraction analysis were grown by slow evaporation of a 1:3 CH<sub>2</sub>Cl<sub>2</sub>–pentane solution. Anal. Found: C, 46.9; H, 4.6. Calc. for C<sub>25</sub>H<sub>27</sub>Fe<sub>1</sub>N<sub>3</sub>O<sub>1</sub>P<sub>1</sub>Rh<sub>1</sub>S<sub>2</sub> (639.4): C, 46.9; H, 4.2%. <sup>31</sup>P-NMR (acetone-*d*<sub>6</sub>): δ = 110.1 (d). <sup>1</sup>H-NMR (acetone-*d*<sub>6</sub>): δ = 8.17 (d, 1H), δ = 8.13 (d, 1H), δ = 7.73 (t, 1H), δ = 7.52 (t, 1H), δ = 6.76 (d, 2H), δ = 4.30–4.59 (m, 9H). <sup>13</sup>C-NMR (acetone-*d*<sub>6</sub>): δ = 146.55, 133.35, 128.65, 127.04, 124.78, 120.10, 111.08, 72.40, 72.15, 71.38, 71.17, 71.01, 70.83, 29.05.

#### 4.3. Rh(CO)<sub>2</sub>[(C<sub>5</sub>H<sub>5</sub>)Fe(C<sub>5</sub>H<sub>4</sub>PS<sub>2</sub>OCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>N<sub>3</sub>)] (**3**)

A solution of [RhCl(CO)<sub>2</sub>]<sub>2</sub> (100 mg, 0.26 mmol) and [NEt<sub>3</sub>H]**1** (410 mg, 0.65 mmol) in MeCN (20 ml) was stirred at r.t. for 2 h. Then the solvent was removed under reduced pressure. The residue was dissolved in acetone (10 ml), the solution was filtered then evaporated to dryness. The resulting orange solid was washed with hexane (10 ml) and dried under vacuum (115 mg, 76%). Anal. Found: C, 38.6; H, 2.8. Calc. for C<sub>19</sub>H<sub>15</sub>Fe<sub>1</sub>N<sub>3</sub>O<sub>3</sub>P<sub>1</sub>Rh<sub>1</sub>S<sub>2</sub> (587.2): C, 38.9; H, 2.6%. FTIR (4000–400 cm<sup>-1</sup>): 3067vw, 2953w, 1614w, 1494m, 1454m, 1388m, 1289m, 1187m, 1151m, 1000vs, 970s, 858s, 753s, 601m, 583m, 503m, 481m, 452m, 432 w cm<sup>-1</sup>. <sup>31</sup>P-NMR (acetone-*d*<sub>6</sub>): δ = 123.1 (d). <sup>1</sup>H-NMR (acetone-*d*<sub>6</sub>): δ = 8.17 (d, 1H), δ = 8.13 (d, 1H), δ = 7.76 (t, 1H), δ = 7.59 (t, 1H), δ = 6.88 (d, 2H), δ = 4.59 (m, 4H), δ = 4.18 (s, 5H). <sup>13</sup>C-NMR (acetone-*d*<sub>6</sub>): δ = 184.29 (d), 182.44 (d), 146.60, 133.33, 128.84, 125.19, 120.20, 111.05, 72.91, 72.78, 71.64, 71.46, 71.32, 71.29, 70.76.

4.4.  $Ni(C_4Me_4)[(C_5H_5)Fe(C_5H_4PS_2OCH_2C_6H_4N_3)]$  (**4**)

A solution of  $[NiCl_2(C_4Me_4)]_2$  (100 mg, 0.21 mmol) in chloroform (10 ml) was added dropwise to a solution of the triethylammonium salt of **1** (300 mg, 0.47 mmol) in the same solvent (10 ml). The resulting solution was stirred at r.t. for 2 h, then the solvent was removed under reduced pressure. The residue was extracted with acetone (10 ml), the solution was filtered and then the solvent was evaporated to dryness. The remaining purple solid was washed with hexane (20 ml) and dried in vacuo (94 mg, 75%). Anal. Found: C, 50.1; H, 4.6. Calc. for  $C_{25}H_{27}Fe_1N_3Ni_1O_1P_1S_2$  (595.1): C, 50.4; H, 4.5%.  $^{31}P$ -NMR ( $CDCl_3$ ):  $\delta = 104.1$  (s).  $^1H$ -NMR ( $CDCl_3$ ):  $\delta = 8.18$  (d, 1H),  $\delta = 8.04$  (d, 1H),  $\delta = 7.55$  (t, 1H),  $\delta = 7.38$  (t, 1H),  $\delta = 6.73$  (d, 2H),  $\delta = 4.44$  (s, 2H),  $\delta = 4.37$  (s, 2H),  $\delta = 4.01$  (s, 5H).  $^{13}C$ -NMR ( $CDCl_3$ ):  $\delta = 146.45$ , 133.25, 128.50, 124.87, 120.04, 111.60, 105.62, 72.07, 71.94, 71.23, 71.07, 70.44, 31.37, 11.18.

4.5.  $Ni[(C_5H_5)Fe(C_5H_4PS_2O)]_2$  (**5**)

100 mg (0.77 mmol) of  $NiCl_2$  and 1.02 g (1.93 mmol) of  $[NEt_3H]1$  were dissolved in MeCN– $H_2O$  (1:1, 20 ml). After heating at reflux for 1 h, the resulting brownish solution was filtered and then the solvent was evaporated to dryness. The remaining brown–orange solid was washed with the same mixture of solvents and dried in vacuo (388 mg, 59%). Crystals suitable for X-ray diffraction analysis were grown by slow evapora-

tion of a 1:3 acetone–pentane solution. Anal. Found: C, 44.6; H, 5.6. Calc. for  $C_{32}H_{50}Fe_2N_2Ni_1O_2P_2S_4$  (855.3): C, 44.9; H, 5.9%.  $^{31}P$ -NMR ( $CDCl_3$ ):  $\delta = 107.3$  (s).  $^1H$ -NMR ( $CDCl_3$ ):  $\delta = 7.98$  (dd, 2H),  $\delta = 7.49$  (t, 1H),  $\delta = 7.37$  (t, 1H),  $\delta = 6.31$  (d, 2H),  $\delta = 4.37$  (s, 2H),  $\delta = 4.14$  (s, 2H),  $\delta = 4.12$  (s, 5H).  $^{13}C$ -NMR ( $CDCl_3$ ):  $\delta = 146.45$ , 133.25, 128.50, 124.87, 120.04, 111.60, 105.62, 72.07, 71.94, 71.23, 71.07, 70.44, 31.37, 11.18.

4.6.  $Ni[(C_5H_5)Fe(C_5H_4PS_2OCH_2C_6H_4N_3)]_2$  (**6**)

A solution of  $NiCl_2$  (100 mg, 0.77 mmol) and  $[NEt_3H]1$  (1.02 g, 1.93 mmol) in MeCN– $H_2O$  (1:1, 30 ml) was stirred at r.t. for 2 h. The red–brown precipitate was isolated by filtration, washed with MeCN (10 ml) and dried in vacuo (625 mg, 89%). Anal. Found: C, 44.2; H, 3.5. Calc. for  $C_{34}H_{30}Fe_2N_6Ni_1O_2P_2S_4$  (915.2): C, 44.6; H, 3.3%.  $^{31}P$ -NMR (DMSO):  $\delta = 107.3$  (s).  $^1H$ -NMR ( $Me_2SO-d_6$ ):  $\delta = 7.98$  (dd, 2H),  $\delta = 7.49$  (t, 1H),  $\delta = 7.37$  (t, 1H),  $\delta = 6.31$  (d, 2H),  $\delta = 4.37$  (s, 2H),  $\delta = 4.14$  (s, 2H),  $\delta = 4.12$  (s, 5H).  $^{13}C$ -NMR ( $Me_2SO-d_6$ ):  $\delta = 146.38$ , 133.48, 128.24, 124.92, 119.83, 112.35, 72.26, 72.05, 70.70, 70.15, 70.05.

4.7. X-ray structure determination of **1** (triethylammonium salt), **2**, and **5**

Crystallographic and experimental details of the data collection and refinement of the structures of **1** (triethylammonium salt), **2**, and **5** are reported in Table 4,

Table 4  
Summary of X-ray single-crystal data and structure refinement parameters for the compounds **1**, **2**, and **5**

	<b>1</b>	<b>2</b>	<b>5</b>
Empirical formula	$C_{23}H_{31}Fe_1N_4OPS_2$	$C_{26}H_{29}Cl_2Fe_1N_5O_1P_1RhS_2$	$C_{32}H_{50}Fe_2N_2NiO_2P_2S_4$
Molecular mass	530.46	724.27	855.33
Temperature (K)	153(2)	153(2)	153(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/c$	$P2_1/c$
$a$ (Å)	11.9317(7)	6.3599(4)	8.9648(8)
$b$ (Å)	10.4665(9)	20.1621(13)	17.0764(13)
$c$ (Å)	39.806(2)	22.3423(15)	12.0475(10)
$\alpha$ (°)	90	90	90
$\beta$ (°)	95.054(7)	97.011(8)	90.991(10)
$\gamma$ (°)	90	90	90
$V$ (Å <sup>3</sup> )	4951.7(6)	2843.5(3)	1844.0(3)
$Z$	8	4	2
$D_{calc}$ (g cm <sup>-3</sup> )	1.423	1.692	1.540
Wavelength (Å)	0.71073(Mo– $K_{\alpha}$ )	0.71073(Mo– $K_{\alpha}$ )	0.71073(Mo– $K_{\alpha}$ )
$\mu$ (min <sup>-1</sup> )	0.866	1.508	1.627
$F(000)$	2224	1464	892
$\theta$ Range (°)	2.15–22.50	2.15–25.08	2.07–25.85
Unique reflections with $I > 2\sigma(I)$	2944	5346	3348
Final $R_1$ , $wR_2$ (observed data)	0.0330, 0.0856	0.0445, 0.0995	0.0309, 0.0569
Number of variables	293	334	305
Goodness-of-fit	1.009	0.857	0.836
Residual density (max/min) (e Å <sup>-3</sup> )	0.343/–0.288	0.731/–1.279	0.319/–0.371

$$R_1 = [\Sigma(|F_o| - |F_c|) / \Sigma|F_o|]; \omega R^2 = \{[\Sigma(\omega(F_o^2 - F_c^2)^2) / \Sigma(\omega F_o^4)]^{1/2}\}.$$

while the molecular structures are depicted in Figs. 1–3. Crystals of compound **1**, **2** and **5** were mounted on a Stoe Imaging Plate Diffractometer System (Stoe & Cie, 1995) equipped with a one-circle  $\varphi$  goniometer and a graphite-monochromator. Data collection was performed at  $-120\text{ }^{\circ}\text{C}$  using Mo- $K_{\alpha}$  radiation ( $\lambda = 0.71073\text{ \AA}$ ). For **1**, 180 exposures (2 min per exposure) were obtained at an image plate distance of 90 mm with  $0 < \varphi < 180^{\circ}$  and with the crystal oscillating through  $1^{\circ}$  in  $\varphi$ . The resolution was  $D_{\min} - D_{\max}$  16.00–0.93  $\text{\AA}$ . For **2**, 180 exposures (3 min per exposure) were obtained at an image plate distance of 70 mm with  $0 < \varphi < 180^{\circ}$  and with the crystal oscillating through  $1^{\circ}$  in  $\varphi$ . The resolution was  $D_{\min} - D_{\max}$  12.45–0.81  $\text{\AA}$ . For **5**, 133 exposures (3 min per exposure) were obtained at an image plate distance of 70 mm with  $0 < \varphi < 200^{\circ}$  and with the crystal oscillating through  $1.5^{\circ}$  in  $\varphi$ . The resolution was  $D_{\min} - D_{\max}$  12.45–0.81  $\text{\AA}$ . The structures were solved by direct methods using the program SHELXS-97 [13] and refined by full-matrix least-squares on  $F^2$  with SHELXL-97 [14]. The hydrogen atoms of **1** and **2** were included in calculated positions and treated as riding atoms using SHELXL-97 default parameters. For **2**, an empirical absorption correction was applied using DIFABS [15] ( $T_{\min} = 0.226$ ,  $T_{\max} = 0.689$ ). The hydrogen atoms of **5** were located from difference Fourier maps and refined isotropically.

## 5. Supplementary material

Lists of atomic coordinates, anisotropic displacement parameters and crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 157385 (**1** triethylammonium salt), 157386 (**2**) and 157387 (**5**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

## Acknowledgements

Financial support (Project no 20-61227.00) of this work from the Swiss National Science Foundation is gratefully acknowledged.

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