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Synthesis and characterisation of cobalt and nickel compounds with phosphinothiol ligands. Crystal and molecular structures of $[Co\{2\text{-}(Ph_2P)\text{-}6\text{-}(Me_3Si)C_6H_3S)\}_3]$, $[Ni\{2\text{-}(Ph_2P)\text{-}6\text{-}(Me_3Si)C_6H_3S)\}_2]$ and $[Co\{2\text{-}(Ph_2PO)\text{-}6\text{-}(Me_3Si)C_6H_3S\}_2]$

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Abstract—The electrochemical oxidation of anodic metal (cobalt or nickel) in an acetonitrile solution of phosphinothiol ligands, $2\text{-}(Ph_2P)C_6H_4SH$, $2\text{-}(Ph_2P)\text{-}6\text{-}(SiMe_3)C_6H_3SH$, $2\text{-}(Ph_2PO)\text{-}6\text{-}(SiMe_3)C_6H_3SH$, affords $[Co\{2\text{-}(Ph_2P)C_6H_4S)\}_3]$ **1**, $[Ni\{2\text{-}(Ph_2P)C_6H_4S\}_2]$ **2**, $[Co\{2\text{-}(Ph_2P)\text{-}6\text{-}(SiMe_3)C_6H_3S\}_3]$ **3**, $[Ni\{2\text{-}(Ph_2P)\text{-}6\text{-}(SiMe_3)C_6H_3S\}_2]$ **4**, $[Co\{2\text{-}(Ph_2PO)\text{-}6\text{-}(SiMe_3)C_6H_3S\}_2]$ **5**, $[Co\{2\text{-}(Ph_2PO)\text{-}6\text{-}(SiMe_3)C_6H_3S\}_3]$ **6** and $[Ni\{2\text{-}(Ph_2PO)\text{-}6\text{-}(SiMe_3)C_6H_3S\}_2]$ **7**. All compounds have been characterised by microanalysis, IR, UV-visible, FAB and NMR spectroscopic studies and compounds **3**, **4** and **5** by single-crystal X-ray diffraction. © 1998 Elsevier Science Ltd. All rights reserved

Keywords: electrochemical synthesis; crystals structures; cobalt and nickel complexes; phosphinothiol complexes

INTRODUCTION

Interest in the coordination chemistry of metal–sulfur complexes arises from their potential relevance to active sites in metallo-enzymes and also from their ability to adopt various nuclearities and significant structural complexity [1–4]. These features are the result of the tendency of thiolate ligands to bridge metal centres to give polymeric species. Such association phenomena can be controlled by introducing coligands. In this context, the synthesis and characterisation of mixed complexes containing both thiolate and additional donors, such as tertiary phosphines, have been objects of extensive studies [5]. However, ligands containing both phosphorus and sulfur as donor atoms have received far less attention. In the last decade, compounds containing arenophosphinothiolate ligands have been reported by Dilworth and Zubieta, mainly with heavier transition metals, such as molybdenum [6], technetium and rhenium [7], rhodium [8] and iridium [9].

As a result of our continuing interest in the chemistry of monomeric and low molecularity thiolate complexes, we now describe the synthesis of cobalt and nickel compounds with aromatic phosphinothiol ligands, using an electrochemical procedure, where the metal is the anode of a cell containing the ligand in an acetonitrile solution. This method has been successfully used for the synthesis of cobalt and nickel thiolate compounds [10]; and also for metallic compounds with other ligands having weak acid groups,

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such as heterocyclic thiones [11–14]. Although the compounds $[Ni\{2\text{-}(Ph_2P)C_6H_4S\}_2]$ and $[Ni\{2\text{-}(Ph_2PO)\text{-}6\text{-}(SiMe_3)C_6H_3S\}_2]$ have been previously prepared by nonelectrochemical methods and their structures described [15], the other compounds reported in this article have not been reported previously.

EXPERIMENTAL

All manipulations were carried out under an inert atmosphere of dry nitrogen. Cobalt and nickel (Aldrich Chemie) were used as plates (*ca.* 2 × 2 cm). Ligands were synthesised using slight modifications of the standard literature procedure [16].

Electrochemical synthesis

The electrochemical method used in the synthesis of the complexes was similar to that described by Tuck [17]. The foil anode was suspended from a platinum wire and the cathode was also a platinum wire. The ligand was dissolved in acetonitrile and about 10 mg of tetramethylammonium perchlorate was added to the solution. Applied voltages of 10–20 V allowed sufficient current flow for smooth dissolution of the metal. During electrolysis, nitrogen was bubbled through the solution to provide an inert atmosphere and to stir the solution phase. The cell can be summarised as $Pt_{(-)}/CH_3CN + RP\text{–}SH/M_{(+)}$, where RP–SH represents the ligand and M is either Co or Ni.

$[Co\{2\text{-}(PPh_2)C_6H_4S\}_3]$, ***1***. Electrochemical oxidation of a cobalt anode in a solution of 2-diphenylphosphinobenzenethiol, $2\text{-}(Ph_2P)C_6H_4SH$, (0.230 g, 0.782 mmol) in acetonitrile (50 cm^3), at 16 V and 10 mA for two h caused 21 mg of cobalt to be dissolved, $E_f = 0.48\ mol\ F^{-1}$. During the electrolysis hydrogen was evolved at the cathode and at the end of the electrolysis green crystalline needles appeared at the bottom of the vessel. The solid was filtered, washed with acetonitrile and ether and dried under vacuum, (0.20 g, 83%). Anal. Calc. for $C_{54}H_{42}CoP_3S_3$: C, 69.1; H, 4.5; S, 10.2. Found: C, 68.8; H, 4.6; S, 9.8% IR (KBr, cm^{-1}): 1571(m), 1482(m), 1433(s), 1416(m), 1241(s), 1091(m), 738(s), 692(s), 525(s). FAB (*m/z*): 939, $[Co(R\text{–}PS)_3]^+$; 645, $[Co(R\text{–}PS)_2]^+$; 294, $[RP\text{–}S]^+$. ^1H NMR ($CDCl_3$ ppm): δ 8.0–6.1 (m, 42 H). ^{31}P NMR ($CDCl_3$, ppm): δ 40.6, 38.8 and 37.0.

$[Ni\{2\text{-}(PPh_2)C_5H_4S\}_2]$, ***2***. A similar experiment (12 V, 10 mA, 2 h) with nickel as anode and 0.220 g (0.748 mmol) of $2\text{-}(Ph_2P)C_6H_4SH$ in 50 cm^3 of acetonitrile, dissolved 23 mg of nickel, $E_f = 0.52\ mol\ F^{-1}$. As the reaction proceeds, the solution colour changed from colourless to dark green. At the end of the electrolysis the green crystals deposited in the cell were recovered, washed with cool acetonitrile and diethyl ether, dried under vacuum and identified as **2** (0.17 g, 70%). Anal. Calc. for $C_{36}H_{28}NiP_2S_2$: C, 67.0; H, 4.3; S, 9.9. Found: C, 66.7; H, 4.3; S, 9.4%. IR (KBr, cm^{-1}): 1568(m), 1481(m), 1437(s), 1423(m), 1244(s), 1096(m), 740(s), 693(s), 530(s). FAB (*m/z*): 644, $[Ni(R\text{–}PS)_2]^+$; 352, $[Ni(R\text{–}PS)]^+$; 294, $[RP\text{–}S]^+$. ^1H ($CDCl_3$, ppm): δ 7.9–6.7(m, 28 H). ^{31}P NMR ($CDCl_3$, ppm): δ 54.0.

$[Co\{2\text{-}(Ph_2P)\text{-}6\text{-}(Me_3Si)C_6H_3S\}_3]$, ***3***. A solution of acetonitrile (50 cm^3) containing 2-diphenylphosphino-6-trimethylsilylbenzenethiol (0.307 g, 0.839 mmol) was electrolyzed at 10 mA during 1.5 h and 17 mg of cobalt metal were dissolved from the anode, $E_f = 0.51\ mol\ F^{-1}$. Dark blue crystals of **3**, suitable for X-ray studies, were obtained and the end of the reaction. They were recovered by filtration, washed with acetonitrile and dried (0.42 g, 88%) and identified by elemental analysis. Anal. Calc. for $C_{63}H_{66}CoP_3S_3Si_3$: C, 66.0; H, 5.7; S, 8,3. Found: C, 65.5; H, 5.9; S, 8.0% IR(KBr, cm^{-1}): 1554(m), 1483(m), 1434(m), 1355(s), 1245(m), 1086(m), 852(s), 746(s), 692(s), 530(s). FAB (*m/z*): 1153, $[Co(R\text{–}PS)_3]^+$; 789, $[Co(R\text{–}PS)_2]^+$; 365, $[RP\text{–}S]^+$. ^1H NMR ($CDCl_3$, ppm): δ 7.7–5.9 (m, 39H), 0.10(s, 9H), 0.30 (s, 9H), 0.50(s, 9H). ^{31}P NMR ($CDCl_3$, ppm): δ 45.0, 43.0 and 39.0.

$[Ni\{2\text{-}(Ph_2P)\text{-}6\text{-}(Me_3Si)C_6H_3S\}_2]$, ***4***. A similar experiment (6 V, 10 mA, 2.0 h) with 0.29 g (0.792 mmol) of the ligand $2\text{-}(Ph_2PO)\text{-}6\text{-}(Me_3Si)C_6H_3SH$ in 50 cm^3 of acetonitrile, dissolved 21 mg of nickel, $E_f = 0.48\ mol\ F^{-1}$. Green crystals, suitable for X-ray studies, were obtained directly from the cell. The solid was collected, washed with cool acetonitrile, diethyl ether and dried under vacuum (0.27 g, 86%). Anal. Calc. for $C_{42}H_{44}NiP_2S_2Si_2$: C, 63.9; H, 5.8; S, 8.1. Found: C, 63.7; H, 5.7; S, 7.8%. IR(KBr, cm^{-1}): 1555(m), 1482(m), 1433(m), 1359(s), 1243(m), 1098(m), 852(s), 746(m), 690(m), 540(s).). FAB (*m/z*): 789, $[Ni(R\text{–}PS)_2]^+$; 424, $[Ni(R\text{–}PS)]^+$; 365, $[RP\text{–}S]^+$. ^1H RMN ($CDCl_3$, ppm): δ 7.9–6.9(m, 26 H), 0.25(s, 18H). ^{31}P NMR($CDCl_3$, ppm): δ 52.5.

$[Co\{2\text{-}(Ph_2PO)\text{-}6\text{-}(Me_3Si)C_6H_3S\}_2]$, ***5*** *and* $[Co\{2\text{-}(Ph_2PO)\text{-}6\text{-}(Me_3Si)C_6H_3S\}_3]$, ***6***. The electrochemical oxidation of cobalt in a solution of $2\text{-}(Ph_2PO)\text{-}6\text{-}(Me_3Si)C_6H_3SH$ (0.428 g 1.12 mmol) in acetonitrile (60 ml) for 3 h at 10 V and 10 mA resulted in the loss of 32 mg of cobalt from the anode, $E_f = 0.50\ mol\ F^{-1}$. During the electrolysis a small amount of a red crystalline compound, **5**, was recovered in the cell as a minor product. This compound has been characterised as $[Co\{2\text{-}(Ph_2PO)\text{-}6\text{-}(Me_3Si)C_6H_3S\}_2]$. Anal. Calc. for $C_{42}H_{44}P_2O_2S_2Si_2Co$: C, 61.4; H, 5.4; S, 7.8. Found: C, 61.0; H, 5.3; S, 7.7%. Concentration of the solution yielded dark blue crystals (0.35 g, 76%) of **6**. (Anal. Calc. for $C_{63}H_{66}P_3O_3S_3Si_3Co$: C, 62.9; H, 5.5; S, 8.0. Found: C, 62.5; H, 5.4; S, 7.9%, IR(KBr, cm^{-1}): 1554(m), 1437(s), 1352(s), 1243(m), 1127(s), 1062(s), 852(s), 750(s), 691(m), 558(s). FAB (*m/z*): 1201, $[Co(R\text{–}PS)_3]^+$; 821, $[Co(R\text{–}PS)_2]^+$; 382, $[RP\text{–}S]^+$. ^1H NMR ($CDCl_3$, ppm): δ 8.0–6.5(m, 39H), 0.35(s, 27H). ^{31}P($CDCl_3$, ppm): δ 41.7 ppm.

$[Ni\{2\text{-}(Ph_2PO)\text{-}6\text{-}(Me_3Si)C_6H_3S\}_2]$, *7*. Electrolysis of an acetonitrile solution (50 cm^3) containing $2\text{-}(Ph_2PO)\text{-}6\text{-}(Me_3Si)C_6H_3SH$ (0.214 g, 0.56 mmol) using

10 mA electric current for 1.5 h caused the dissolution of 16 mg of nickel ($E_f = 0.49$ mol F^{-1}). Concentration of the final solution produced green crystals (0.17 g, 74%) of **7**. Anal. Calc. for $C_{42}H_{44}P_2O_2S_2Si_2Ni$: C, 61.4; H, 5.4; S, 7.8. Found: C, 61.0; H, 5.3; S, 7.7%. IR(KBr, cm^{-1}): 1556(m), 1437(s), 1352(s), 1244(m), 1129(s), 1067(s), 854(s), 749(s), 692(m), 555(s).). FAB (*m*/*z*): 819, [Ni(R–PS)$_2$]$^+$; 439, [Ni(R–PS)]$^+$; 382, [RP–S]$^+$. ^{1}H NMR ($CDCl_3$, ppm): δ 8.6–6.4(m, 26H), 0.5 (s, 18H). ^{31}P($CDCl_3$, ppm): δ 58.2 ppm.

Instrumentation

Elemental analysis were performed on a Carlo-Erba EA microanalyser. IR spectra were recorded in KBr mulls on a Bruker IFS 66 V spectrophotometer. FAB mass spectra were recorded on a Kratos-MS-50T connected to a DS90 data system, using 3-nitrobenzyl alcohol (3-NBA) a matrix material. ^{1}H and ^{31}P NMR spectra were recorded on a Bruker AMX 300 MHz instrument, using in all cases $CDCl_3$ as solvent; ^{1}H NMR chemical shifts were determined against TMS as internal standard and ^{31}P NMR against 85% H_3PO_4. Solid-state electronic spectra were recorded on a Shimadzu UV 3101 PC.

X-ray crystallography

Compound **3** was studied on a Siemens Smart diffractometer, **4** on a CAD-4 system and **5** on a Rigaku AFC6S diffractometer. Data collection was carried out under ambient conditions, using graphite monocromated Mo Kα for all compounds. The crystal parameters and other experimental details of the data collection are summarized in Table 2. A complete description of the details of the crystallographic methods is given in Table 1. The structures were solved by direct methods and refined by a full matrix least squares procedure. Neutral atom scattering factors were taken from Cromer and Waber [18] and anomalous dispersion were taking from Cromer [19]. All calculation were performed using SHELXTL PLUS (PC version) [20] for **3** and **5** and using DECMicroVAX 3500 computer for **4**. No anomalies were encountered in the refinements of any of the structures. The crystal parameters and other experimental details of data collection and refinement are summarized in Table 1. Atomic positions, a full list of bond lengths, angles and other crystallographic data have been deposited as supplementary publication No. CCDC 102069–102071. Copies can be obtained through Cambridge crystallographic data centre, Union Road, Cambridge.

RESULTS AND DISCUSSION

The analytical data show that the electrochemical procedure described can be satisfactorily used, in good yield, for the synthesis of complexes of cobalt and nickel with phosphinothiol ligands and the method represents a simple alternative to other standard chemical procedures.

The nickel compounds have general formulae [Ni(RP–S)$_2$] where RP–S stands for the monoanion of the RP–SH ligand. The electrochemical efficiency value, E_f, defined as the amount of metal dissolved per Faraday of charge, was always close to 0.5 mol F^{-1}. This fact and the evolution of hydrogen at the cathode are compatible with the following reaction mechanisms

$$\text{cathode: } 2\,\mathrm{RP-SH} + 2e^- \rightarrow 2\,\mathrm{RP-S}^- + \mathrm{H}_2$$

$$\text{anode:} \mathrm{Ni} + 2\,\mathrm{RP-S}^- \rightarrow [\mathrm{Ni(RP-S)_2}] + 2e^-.$$

Values of E_f close to 0.5 mol F^{-1} were found in the synthesis of cobalt complexes and are indicative of a similar anodic oxidation mechanism. However, the ddformulation of these compounds is [Co(RP–S)$_3$]. This observation suggests an additional oxidation in solution of Co(II) to Co(III). This behaviour has been previously observed in the synthesis of other cobalt complexes via an electrochemical procedure [21]. When the ligand used was 2-(Ph_2PO)-6-($SiMe_3$) C_6H_3SH, in addition to the analogous Co(III) compound, a small amount of crystals of [Co{2-Ph_2P(O)-6-(Me_3Si)C_6H_3S}$_2$] could be isolated as a minor product.

Structure of [Co{2-(Ph_2P)-6-(Me_3Si)C_6H_3S}$_3$], ***3***

Figure 1 shows the molecular structure of **3** together with the atom labelling scheme. Selected bond distances and angles are given in Table 2. The compound consists of discrete molecules with the metal coordinated to three monoanionic bidentate ligands, bonded to the cobalt through their phosphorus and sulfur atoms. The environment around the metal can be described as [CoP_3S_3] slightly distorted octahedral geometry; all the dihedral angles between the coordination planes defined by four donors atoms are close to 90°. Angles defined by two *trans* donor atoms and the metal atom are the range 167.67(7)–177.39(7)° and the angles determined by cobalt atom and two *cis* donor atoms are close to 90°, even those corresponding to five membered chelating rings exhibit values of 86.49(6), 88.37(6) and 81.72(6)°. These values are larger than those found in other trischelate metal complexes containing this ligand.

The arrangement of the three sulfur and phosphorous atoms in **3**, is such that the compound can be described as the *meridional* isomer. This is the disposition found in [Tc{2-(Ph_2P)C_6H_4S}$_3$], [Re{2-(Ph_2P)C_6H_4S}$_3$] [7] and [Ir{2-(Ph_2P)C_6H_4S}$_3$] [9]. ^{1}H and ^{31}P NMR data (*vide infra*) show that this arrangement is maintained in solution.

The Co–S bond distances are in the range 2.245(2)–2.335(2) Å, with the longer one corresponding to the

Table 1. Crystal data, data collection and structure refinement for compounds (**3**), (**4**) and (**5**)

	(**3**)	(**4**)	(**5**)
Crystal data			
Empirical formula	$C_{63}H_{66}CoP_3S_3Si_3$	$C_{42}H_{44}NiP_2S_2Si_2$	$C_{42}H_{44}CoO_2P_2S_2Si_2$
Formula weight	1155.45	789.72	821.94
Crystal size (mm)	0.15 × 0.12 × 0.10	0.17 × 0.15 × 0.10	40 × 0.40 × 0.40
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$	Cc
Unit cell dimensions (Å)	$a = 20.3177(12)$	13.262(3)	17.8803(2)
(Å)	$b = 12.5633(7)$	12.690(3)	16.7345(3)
(Å)	$c = 25.825(2)$	12.873(3)	29.1871(6)
(°)	$\beta = 109.578(1)$	108.96(3)	92.183(1)
Volume (Å^3)	6211.0(6)	2048.9(8)	8727.0(3)
Z	4	2	8
Dc (g/cm^3)	1.236	1.280	1.251
Absorption coefficient (mm^{-1})	0.549	0.740	0.650
$F(000)$	2424	828	3432
Data collection			
Radiation	Mo Kα(0.71073 Å)		
Temperature (K)	293(2)	293(2)	298(2)
θ range (°)	1.11–28.32	1.62–22.47	1.40–28.34
Limiting indices	$-27 < h < 14$	$-14 < h < 12$	$-23 < h < 23$
	$-16 < k < 16$	$-13 < k < 0$	$-22 < k < 22$
	$-33 < l < 34$	$0 < l < 13$	$-14 < l < 38$
Reflections collected	36811	2971	26385
Independent reflections	14523 (rint = 0.070)	790 (rint = 0.0168)	13663 (rint = 0.0381)
Solution and refinement			
System used	full-matrix least squares on F^2		
Data/restrains/parameters	14523/0/653	790/0/224	13661/2/919
R	0.1003	0.0345	0.0503
R_w	0.1553	0.0345	0.068
Goodness-of-fit on F^2	1.381	1.153	1.118
Largest difference peak (e Å^{-3})	1.755	0.220	0.258
Largest difference hole (e Å^{-3})	−0.339	−0.211	−0.264

cobalt–sulfur bond *trans* to a phosphorous atom, suggesting some *trans* influence of the phosphorus. This effect has been also observed in other complexes, such as [Ir(2-(Ph_2P)C_6H_4S)$_3$]. Nevertheless, the average value for the Co–S bond distances, 2.286(2) Å, is comparable to the value of 2.27 Å reported for Co–S bond distances in [Co(III)–S_6] octahedral complexes [22] or 2.297(4) Å in the octahedral cation [Co(SC_6H_5)$_2$(phen)$_2$]$^+$ [10]. The Co–P bond distances are also different, with longer bond distances associated with atoms *trans* to one another. This may be again due to the *trans* influence of two mutually *trans* positioned phosphine donor atoms. The average value, 2.278(2) Å, is in the range of other octahedral Co(III) complexes containing tertiary phosphine as donors [23] (and references cited therein).

Structure of [Ni{2-(Ph_2P)-6-(Me_3Si)C_6H_3S}$_2$], *4*

The molecular structure of [Ni{2-(Ph_2P)-6-(Me_3Si)C_6H_3S}$_2$] is shown in Fig. 2, together with the atomic numbering scheme adopted. Selected bond distances and angles are given in Table 3. The structure shows the nickel atom, located at a crystallographic inversion centre and coordinated to two thiolato sulfur atoms and to two phosphorous atoms of two symmetry related moieties. The arrangement is strictly planar to within experimental accuracy, with the sulfur atoms in a *trans* disposition; bond angles between the adjacent atoms are very close to the theoretical 90° limit. The structure of this molecule is similar to that of [Ni{2-(Ph_2P)C_6H_4S}$_2$] which exhibits the same environment for the metal, but distinct from that of [Ni{2-(Ph_2PO)-6-($SiMe_3$)C_6H_3S}$_2$] which possesses planar S_2O_2 environment around the metal, in which the two thiolate sulfur atoms adopt a *cis* disposition [15]. The Ni–S bond distance, 2.151(3) Å, is similar to the value found in [Ni{2-(Ph_2P)C_6H_4S}$_2$], 2.180(1) Å and also in the range 2.149–2.179 Å described for Ni(II) square planar complexes with five ring chelating ligands and sulfur thiolate donor atoms [15]. In addition, the Ni–P bond distance, 2.172(3) Å, is marginally shorter than the value of 2.181(2) Å found

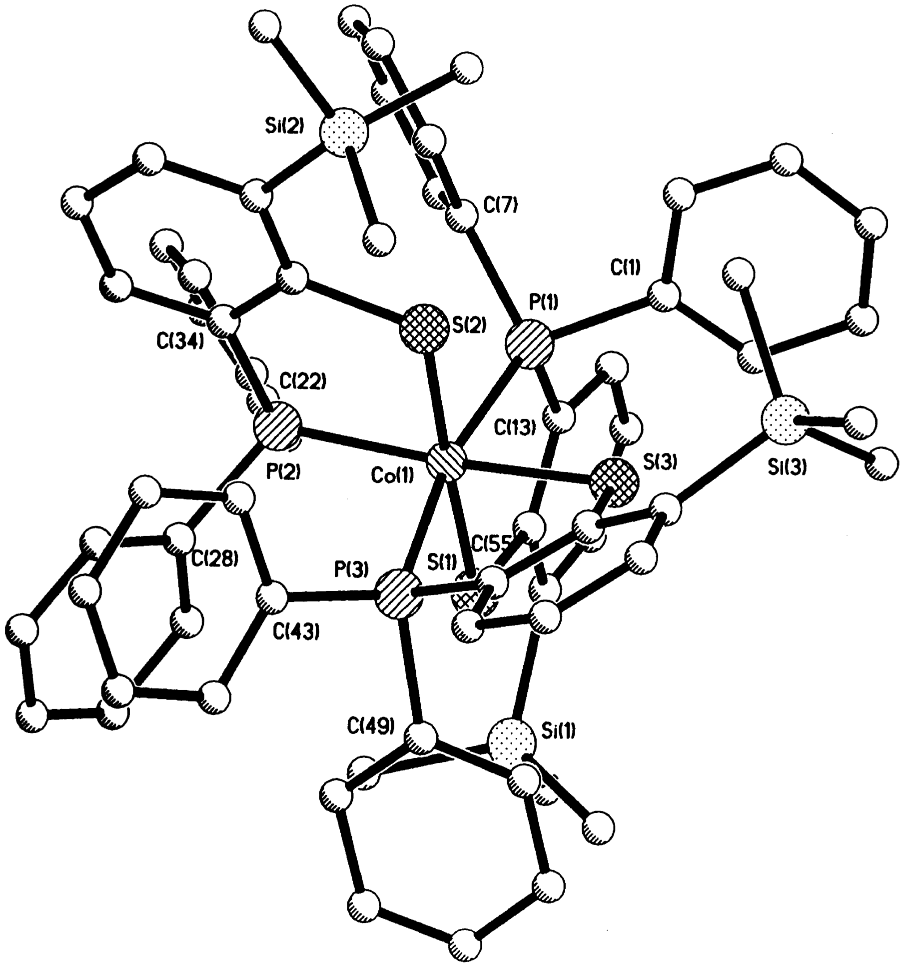

Fig. 1. The molecular structure of [Co{2-(Ph$_2$P)-6-(Me$_3$Si)C$_6$H$_3$S}$_3$].

Table 2. Selected bond lengths (Å) and angles (°) for [Co{2-(Ph$_2$P)-6-(Me$_3$Si}C$_6$H$_3$S}$_3$] **3**

Co(1)–S(2)	2.245(2)	Co(1)–P(2)	2.260(2)
Co(1)–P(1)	2.271(2)	Co(1)–S(1)	2.277(2)
Co(1)–P(3)	2.302(2)	Co(1)–S(3)	2.335(2)
S(1)–C(2)	1.757(6)	S(2)–C(23)	1.765(6)
S(3)–C(44)	1.762(6)	P(1)–C(13)	1.832(6)
P(1)–C(7)	1.843(6)	P(1)–C(1)	1.804(6)
P(2)–C(34)	1.843(6)	P(2)–C(28)	1.842(6)
P(2)–C(22)	1.820(6)	P(3)–C(55)	1.839(6)
P(3)–C(49)	1.827(6)	P(3)–C(43)	1.817(6)

S(2)–Co(1)–P(2)	88.37(6)	S(2)–Co(1)–P(1)	91.17(6)
P(2)–Co(1)–P(1)	95.68(6)	S(2)–Co(1)–S(1)	177.39(6)
P(2)–Co(1)–S(1)	93.00(6)	P(1)–Co(1)–S(1)	86.49(6)
S(2)–Co(1)–P(3)	91.35(6)	P(2)–Co(1)–P(3)	96.45(6)
P(1)–Co(1)–P(3)	167.67(7)	S(1)–Co(1)–P(3)	90.70(6)
S(2)–Co(1)–S(3)	83.43(6)	P(2)–Co(1)–S(3)	171.54(7)
P(1)–Co(1)–S(3)	86.58(6)	S(1)–Co(1)–S(3)	95.27(6)
P(3)–Co(1)–S(3)	81.72(6)		

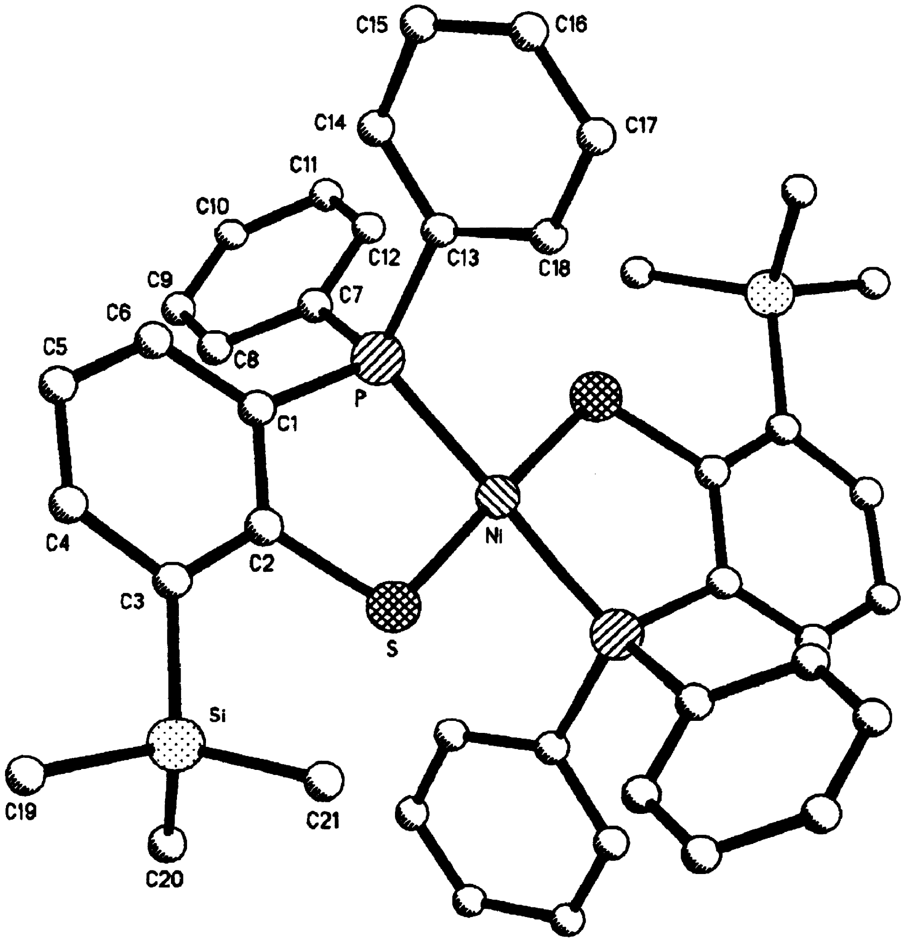

Fig. 2. The molecular structure of $[Ni\{2\text{-}(Ph_2P)\text{-}6\text{-}(Me_3Si)C_6H_3S\}_2]$.

in the mentioned complex. These structural considerations reveal that the introduction of a trialkylsilyl group to the ligand has a negligible influence on the structural parameters of the compound.

Structure of $[Co\{2\text{-}(Ph_2PO)\text{-}6\text{-}(Me_3S)C_6H_3S\}_2]$, **5**

The crystal structure of **5** shows the presence of two independent but structurally similar, molecules in the

Table 3. Selected bond lengths (Å) and angles (°) for $[Ni\{2\text{-}(Ph_2P)\text{-}6\text{-}(Me_3Si)C_6H_3S\}_2]$. **4**

Ni–S	2.151(3)	Ni–S†1	2.151(3)
Ni–P†1	2.172(3)	Ni–P	2.172(3)
S–C(2)	1.770(11)	P–C(1)	1.792(11)
P–C(7)	1.809(10)	P–C(13)	1.832(11)
S–Ni–S†1	180.0	S–Ni–P†1	90.96(12)
S†1–Ni–P†1	89.04(12)	S–Ni–P	89.04(12)
S†1–Ni–P	90.9(12)	P†1–Ni–P	180.0
C(2)–S–Ni	109.2(4)	C(1)–P–Ni	107.8(4)
C(2)–C(1)–P	116.9(9)	C(2)–S–Ni	109.2(4)
C(1)–C(2)–S	117.0(9)		

Symmetry transformations used to generate equivalent atoms: $^{\dagger}1\ -x+1, -y+1, -z+1$.

asymmetric unit. The structure of one, with the atom labelling is given in Fig. 3. Selected bond distances and angles with the estimated standard deviations are given in Table 4. The compound consists of discrete molecules, with the cobalt atom tetracoordinated to two thiolate sulfur atoms and two oxygen atoms of two ligands, such that the environment around the central atom can be described as $[CoO_2S_2]$ distorted tetrahedral, with bond angles, 99.46(9) and 98.80(10)°, significantly distorted with respect to the tetrahedral value.

The average values for the Co–S bond lengths for both molecules, 2.2838(14) Å, are normal and similar to that in Co(II) complexes with the same geometry and coordination number. Thus, these values are comparable to those found for the tetrahedral anion $[Co(SC_6H_5)_4]^{2-}$, average value 2.328 Å [24, 25], or in $[Co(SC_{10}H_{13})_3CH_3CN]^{-}$, average value 2.28 Å [26]. Similarly, the Co–O bond distances, average 1.974 Å, are in the range for those found in tetrahedral complexes containing triphenylphosfineoxide as ligand, for instance 1.971 Å (average value) in $[CoCl_2(OPMe_3)_2]$ [27] and 1.928 Å (average value) in $[CoCl_2\{OP(CH_2Ph)_3\}_2]$ [28].

Bond distances and angles in the coordinated ligand are similar to those found for the free ligand [29]. Thus the average value for the P–O bond distance in the complex, 1.518(3) Å, is slightly higher than the 1.493(3) Å value found in the free ligand. This lengthening can be attributed to the weakening of the P=O bond, by coordination to the metal.

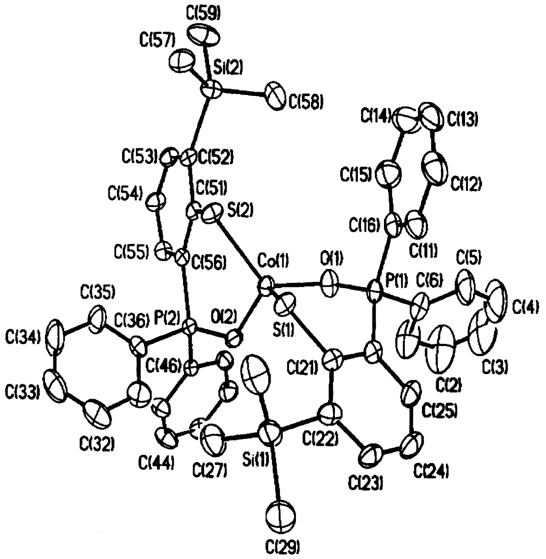

Fig. 3. The molecular structure of $[Co\{2\text{-}(Ph_2PO)\text{-}6\text{-}(Me_3Si)C_6H_3S\}_2]$.

Spectroscopic studies

The IR spectra of the ligands exhibit a band in the 2400–2550 cm^{-1} range attributed to ν(S–H). This band is absent in the spectra of the complexes, indicating that the ligand is in the anionic thiolate form in all complexes. The complexes also show bands in the 1500–1580 cm^{-1} region, characteristic of aromatic ring vibrations, as well as bands in the 1100–1000 cm^{-1} region attributable to ν(P–C). The trimethylsilyl derivatives show in addition a very strong band around 840–850 cm^{-1} assignable to the n(Si–C) mode. Compounds **5**, **6** and **7** show a very strong band at 1130 cm^{-1} characteristic of ν(P–O).

The FAB mass spectra of all compounds show the molecular ion with appropriate isotope distributions. In many cases, ions formed by loss of one ligand from the initial complex are also observed, as well as a peak attributed to the free ligand.

The magnetic moments of the Co(III) complexes show that these complexes are diamagnetic, as

Table 4. Selected bond lengths (Å) and angles (°) for $[Co\{2\text{-}(Ph_2PO)\text{-}6\text{-}(Me_3Si)C_6H_3S\}_2]$. **5**

Co(1)–O(1)	1.978(4)	Co(1)–O(2)	1.961(3)
Co(2)–O(3)	1.975(3)	Co(2)–O(4)	1.983(3)
Co(1)–S(1)	2.2826(14)	Co(1)–S(2)	2.2720(14)
Co(2)–S(3)	2.2761(14)	Co(2)–S(4)	2.3045(14)
S(1)–C(21)	1.772(5)	S(2)–C(51)	1.768(4)
S(3)–C(61)	1.775(4)	S(4)–C(111)	1.771(5)
P(1)–O(1)	1.516(3)	P(2)–O(2)	1.520(3)
P(3)–O(3)	1.521(3)	P(4)–O(4)	1.517(3)
O(2)–Co(1)–O(1)	103.3(2)	O(2)–Co(1)–S(2)	99.74(9)
O(1)–Co(1)–S(2)	126.38(1)	O(2)–Co(1)–S(1)	124.67(1)
O(1)–Co(1)–S(1)	99.19(10)	S(2)–Co(1)–S(1)	106.15(5)
O(3)–Co(2)–O(4)	108.5(2)	O(3)–Co(2)–S(3)	99.13(10)
O(4)–Co(2)–S(3)	124.18(1)	O(3)–Co(2)–S(4)	120.39(1)
O(4)–Co(2)–S(4)	98.47(10)	S(3)–Co(2)–S(4)	107.89(5)

expected for low spin d^6 octahedral complexes. The solid state electronic spectra of these complexes show two bands near 16,000 and 25,000 cm^{-1}. The first band is due to $^1T_{1g} \leftarrow {}^1A_{1g}$ transition and the second to $^1T_{2g} \leftarrow {}^1A_{1g}$ transition [30]. The nickel complexes are also diamagnetic, compatible with the square planar coordination around the metal. The solid-state electronic spectra of these complexes show two bands at *ca.* 16,000–17,000 and 22,000–24,000 cm^{-1}, which can be attributed to the $^1B_{1g} \leftarrow {}^1A_{1g}$ and $^1E_{1g} \leftarrow {}^1A_{1g}$ transitions, characteristic of nickel compounds in a square-planar environment [30].

The diamagnetic nature of these complexes (except compound **5**) allowed their study by in solution. In no instance do the ^1H NMR spectra show the thiol -SH signal of the free ligand around 4.1 ppm, proving that the ligand is in the monoanionic form in all complexes. The spectra also show multiplets over 8.0–6.5 ppm characteristic of the phenyl groups. The ^1H of $[Co\{2\text{-}(Ph_2P)\text{-}6\text{-}(Me_3Si)C_6H_3S\}_3]$ shows the presence of three nonequivalent trimethylsilyl groups, at 0.10, 0.30 and 0.50 ppm, indicating that the *meridional* conformation of the ligands found in the solid state is maintained in solution. This is corroborated by the presence of three signals in the ^{31}P NMR spectra at 39, 43 and 45 ppm corresponding to the nonequivalent phosphorus in the *meridional* conformation. By contrast, the ^1H NMR of $[Co\{2\text{-}(Ph_2PO)\text{-}6\text{-}(Me_3Si)C_6H_3S\}_3]$ shows only a singlet at 0.35 ppm, attributable to the $-SiMe_3$ groups, indicating that the ligands in this complex are equivalent and therefore that the compound has a *facial* arrangement of the ligands in solution. The ^{31}P NMR of this compound shows only one signal at 41.6 ppm, as expected for this ligand arrangement.

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