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Synthesis, structures and ligating properties of 2,6-bis(phosphino)thiophenol derivatives

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Abstract

New *t*-butyl-aryl thioethers where the aryl group is 2,6-bis(phosphino)phenyl have been synthesized. The syntheses were completed via sequential *ortho*-lithiations of *t*-butylphenylsulfide, followed by chlorophosphine ($ClPR_2$) quenches; symmetric (2,6-bis(diphenylphosphino)phenyl, (**4a**)) and unsymmetric (2-diisopropylphosphino-6-diphenylphosphino)phenyl, (**4b**) aryl groups were obtained. Treatment of **4a** with Li or Na naphthalenide yielded 2,6-bis(diphenylphosphino)thiophenol **5**. Reactions of **4a** or **5** with $NiCl_2 \cdot 6H_2O$ yielded nickel bis(phosphinothiophenolate) **6**. Compounds **4a**,**b**, **5** and **6** were characterized by ^1H and ^{31}P NMR, and by mass-spectrometry. In addition, **4a**, **5** and **6** were characterized by single crystal X-ray diffraction methods.

Keywords: *P*,*S*-Chelating ligands; Nickel *o*-phosphinotiophenolate; X-ray crystal structures

1. Introduction

Bimetallic transition metal complexes supported by binucleating μ-phenolate ligands (**1**, Fig. 1) have been extensively used as synthetic models for mimicking of biological processes occurring at the bimetallic sites of certain proteins [1–4]. The binucleating ability of such phenolates is rendered by the presence of two [O, N] chelating pockets, formed by flanking the Ph–O$^-$ unit by amine or imine functionalities connected through one- or two-bond "arms" to the 2- and 6-positions of the phenol ring (**1**, Fig. 1) [5]. Such a motif (**1**) often serves as a platform for more elaborate polydentate bicompartmental ligands, where the flanking nitrogens also serve as branching points for additional chelating "arms". One attractive feature of such bimetallic complexes is their ability to bind small molecules or ions at one or both of the metal centers of the binuclear core. For example, dicopper and diiron complexes supported by the ligands centered on the structural motif **1** have been used for modeling of dioxygen activation [6–8]. Structurally analogous bimetallic complexes where "soft" phosphorus/sulfur ligands (e.g., **2**, Fig. 1) are incorporated into the ligand design are less common [5]. While less directly relevant to modeling of biological functions, such ligating environments may provide access to bimetallic complexes where the lower oxidation states of the metal centers are stabilized. Thus, if the same overall geometry of the bimetallic complex is retained, a different preference for small molecule binding and activation may be anticipated. Bridging thiophenolates flanked by nitrogen donors (**2**, E = N, Fig. 1) have been successfully incorporated into the construction of various binucleating macrocyclic ligands [9,10]. To the best of our knowledge, only one binucleating ligand fitting the general structural motif **2** where the flanking ligating groups are phosphines, 2,6-bis(diphenyl-phosphinomethyl)benzenethiolate, has been reported [11]. (Structurally similar oxygen analogues, phenolates with

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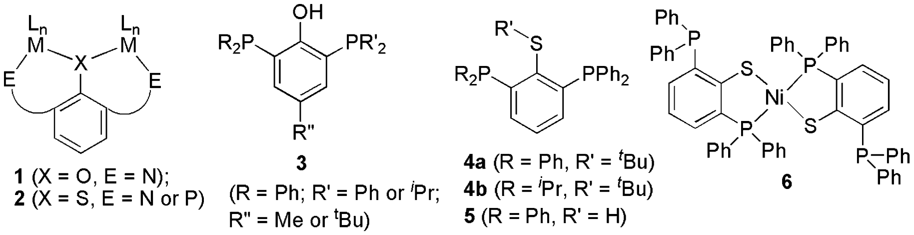


Fig. 1. Binucleating motifs built around bridging phenolate/thiophenolate ligands.

flanking phosphine arms, have been used as mononucleating “pincer” ligands [12–15]). Given into account the ubiquitous use of phosphine ligands in coordination chemistry, the limited use of phosphine-flanked phenolates and thiophenolates as binucleating motifs seems rather surprising. Recently we have reported on the syntheses of symmetric and unsymetric 2,6-bis(phosphino)phenols (**3**, Fig. 1), and on the usage of 2,6-bis(phosphino)phenol core for the construction of a bicompartmental ligand with soft ligating compartments flanking the bridging phenolate [16,17]. We also succeeded in developing the synthetic procedures for assembling analogous structural motifs starting with a thiophenol core, and herein we report on the synthesis of the 2,6-bis(phosphino)thiophenol derivatives **4a**,**b** and **5**, and on a nickel bis(phoshinothiophenolate) complex **6** (Fig. 1). Structural characterizations of **4a**, **5** and **6** are also reported.

2. Experimental

2.1. General procedures

Manipulations requiring inert atmospheres were carried out by using Schlenk techniques or in a dry box under a N_2 atmosphere. Solvents were purified before use by distillation from Na–benzophenone ketyl (ether, THF, hexanes, benzene) or Na (pyridine) under a N_2 atmosphere. Commercially available chlorophosphines $ClPR_2$ were purified prior to use: $ClPPh_2$ was vacuum distilled, and Cl*Pi*Pr$_2$ was frozen, degassed and thawed under vacuum (repeated 3 times). *t*-Butylphenylsulfide and 2-(*t*-butylthio)phenyldiphenylphosphine were obtained via published synthetic methods [18,19]. Other reagents were obtained from commercial suppliers. ^1H and ^{31}P NMR spectra were recorded on a Varian INOVA spectrometer operating at 400 and 161 MHz, respectively. Spectra are referenced to tetramethysilane (^1H) and 85% H_3PO_4 (^{31}P) (external reference). Low resolution mass spectrometric measurements were performed on a Shimadzu QP5050A instrument; high resolution measurements were performed at the Mass Spectrometric Facility of Michigan State University (East Lansing, MI 48824-1319).

Cyclic voltammetry of **6** was performed using CHI420 electrochemical analyzer. Standard 3-electrode cell fitted to operate under air-tight conditions was used. Glassy carbon disk (3 mm), Ag/$AgNO_3$, and Pt wire and were used as working, reference, and counter electrodes, respectively. Measurements were performed in CH_2Cl_2 containing 0.1 M NBu_4PF_6 as supporting electrolyte, at 0.1 V/s scan rate.

2.2. Syntheses

2.2.1. (2,6-Bis(diphenylphosphino)phenyl)(t-butyl)sulfide (*4a*)

n-Butyl lithium (1.6 M in hexanes, 3.1 mL, 5.0 mmol) was slowly added to an ice-cold solution of 2-(*t*-butylthio)phenyldiphenylphosphine (1.75 g, 5.0 mmol) in hexanes (70 mL). *N*,*N*,*N*′,*N*′-Tetramethylenediamine (TMEDA) (0.94 mL, 6.8 mmol) was then slowly added (over 15 min). The reaction mixture was left to stir overnight and allowed to attain room temperature, leading to the formation of a pale-yellow suspension. The reaction vessel was ice-cooled, and a solution of chlorodiphenylphosphine (0.89 mL, 5.0 mmol) in hexanes (5 mL) was slowly added to the stirred suspension. The reaction mixture was stirred for 3 h and hydrolyzed with degassed 5% aqueous NaOH. The organic phase was separated, the aqueous phase was extracted with ether (20 mL), the extract was added to the original organic phase, and the combined organic phases were dried over $MgSO_4$. Slightly yellow crystals precipitated on standing at −28 °C for 3 days. Yield: 1.25 g (49%). Melting point: 158–160 °C. ^1H NMR (C_6D_6) δ: 7.05–6.65 (m, 23H) 1.41 (s, 9H). ^{31}P NMR (C_6D_6) δ: −6.4 (s). HRMS (FAB): Calc. for $C_{34}H_{33}P_2S$: 535.1778 (MH^+); found: 535.1776.

2.2.2. (2-Diisopropylphosphino-6-diphenylphosphino)phenyl(t-butyl)sulfide (*4b*)

To a solution of 2-(*t*-butylthio)phenyldiphenylphosphine (4.82 g, 13.75 mmol) in hexane (130 mL), *n*-butyl lithium (8.6 mL, 1.6 M in hexanes, 13.75 mmol) and TMEDA (2.1 mL, 13.75 mmol) were added successively. The reaction mixture was stirred at room temperature overnight, resulting in the formation of a slightly yellow precipitate. The reaction vessel was then cooled to 0 °C, chlorodiisopropylphosphine (2.43 mL, 15.13 mmol) was added, and the reaction mixture was stirred overnight at ambient temperature. After filtration and removal of all volatiles under vacuo, the resulting solid was dissolved in pentane (100 mL) and placed at −20 °C. White crystalline solid **4b** deposited slowly (weeks). Yield: 1.62 g (25%), after accounting for the presence of ~5% of the starting material, 2-(*t*-butylthio)phenyldiphenylphosphine. ^{1}H NMR (C_6D_6): δ 7.34 (m, 4H); 7.07 (m, 6H); 7.04 (m, 1H); 6.97 (m, 1H); 6.87 (m, 1H); 1.88 (s (br), 2H); 1.64 (s, 9H); 1.12–0.94 (m (br), 12H). ^{31}P NMR (THF): δ 3.4 (d), −7.2 (d), $^4J_{PP} = 12$ Hz. HRMS (FAB): Calc. for $C_{28}H_{37}P_2S$: 467.2091 (MH^+); found: 467.2090.

2.2.3. 2,6-Bis(diphenylphosphino)benzenethiol (5)

To a cold (0 °C) lithium naphthalenide solution, generated from 0.037 g (5.3 mmol) of lithium and 0.574 g (4.5 mmol) of naphthalene in 30 mL of THF, was added a solution of **4a** (1.131 g, 2.11 mmol) in 20 mL of THF. The dark brown reaction mixture was stirred for 3 hours at 0 °C, and anhydrous HCl (2.5 mL, 2 M solution in ether) was added. A white precipitate (LiCl) was separated from the pale yellow solution via filtration. All volatiles were removed under vacuo (including naphthalene by sublimation), leaving behind **5** as a waxy pale yellow solid, which crystallized slowly upon standing. It was further purified by washing with heptane (20 mL). Yield: 0.973 g (96%). Melting point: 153–155 °C. ^{1}H NMR (C_6D_6): δ 7.31 (m, 8H), 7.01 (m, 12 H), 6.97 (dm, 2H, $^3J_{HH} = 8$ Hz); 6.65 (t, 1H, $^3J_{HH} = 8$ Hz), 5.34 (s (br), 1H). ^{31}P NMR (C_6D_6) δ: −11.6 (s). HRMS (FAB): Calc. for $C_{30}H_{25}P_2S$: 479.1152 (MH^+); found: 479.1154. Crystals suitable for X-ray analysis were obtained from a solution of **5** in benzene/Et_2O (~1:1) upon prolonged standing (weeks) at −28 °C.

2.2.4. Nickel bis(2,6-bis(diphenylphosphino)-benzenethiolate) (6)

A solution of **4a** (0.5 g, 1.0 mmol) in THF (15 mL) was added to $NiCl_2 \cdot 6H_2O$ (0.12 g, 0.5 mmol), and the resulting suspension was refluxed overnight. A bright green precipitate (**6**) formed which was isolated by filtration and dried under vacuo. Yield: 0.23 g (47%). ^{1}H NMR (C_5D_5N): δ 7.67–6.85 (m). ^{31}P NMR (C_5D_5N): δ 55.3 (s), −13.0 (s). The elemental analysis data were consistently low on carbon. HRMS (FAB): Calc. for $C_{60}H_{47}NiP_4S_2$ (MH^+): 1013.1423; found: 1013.1418. Crystals suitable for X-ray analysis were obtained by slow evaporation of the solution of **6** in pyridine/THF (~10/1).

2.3. X-ray crystallography

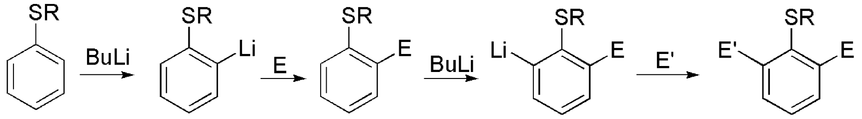
In all cases, the handling of the crystals and data collection was as described previously [20]. Data were first reduced and corrected for absorption using psi-scans [21] and then solved using the program SIR-04 [22], which afforded nearly complete solutions for the non-H atoms in all cases. These programs were utilized using the WinGX interface [23]. The models were then refined using SHELXL97 [24] first with isotropic and then anisotropic thermal parameters to convergence. The positions and isotropic thermal parameters of the different H-atoms were constrained according to the specifics arranged in the SHELXL97 program. Complex **4a** contained unequal disorder in the position of the tertiary butyl ligand, complex **5** was ordered and **6** contained disorder in the THF molecules of solvation. The disorder was accounted for with the SHELXL97 program using procedures detailed previously [25].

3. Results and discussion

3.1. Syntheses and spectroscopic characterizations

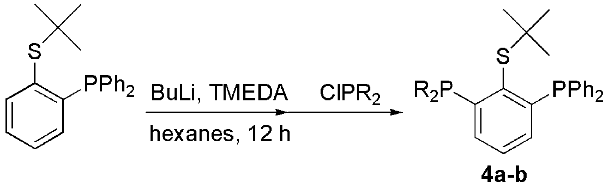
Various derivatives of *o*-(phosphino)thiophenols have been extensively used in the coordination chemistry of transition metals [26]. Simple *o*-phosphinothiophenols containing [P,S] chelating pockets typically function as mononucleating ligands towards metal centers. Since thiolate ligands are well known to bridge two or more metal centers [27], a suitably designed thiophenolate ligand where the sulfur center is an integral part for two adjacent chelating pockets may function as an attractive binucleating motif. Thus, bimetallic complexes based on thiophenolates where the sulfur is shared between two [N,S] chelating pockets are well known [28]. The flanking donor atoms in such ligands are separated from the parent thiophenol ring by =CH– or –CH_2– spacers, stemming from both positions *ortho* to sulfur. Analogous binucleating ligands where the flanking donor groups are phosphorus atoms have received only limited attention [11].

Thiophenolate ligands with two flanking donor groups attached *directly* to the thiophenol ring have not been reported yet. This is rather surprising as facile *ortho*-lithiations of the thiophenol ring allow for the introduction of donor groups at both *ortho* positions. Thus, sequential *ortho*-lithiations of thiophenol, followed by electrophile quench [29,30] (Eq. (1)) have been used for the syntheses of *o*-phosphinothiophenols and related polydentate ligands. In such ligands, the thiophenolate typically is flanked by a phosphine and a silyl (–SiR_3) groups, resulting in steric properties of the ligand which facilitate the formation of mononuclear complexes. Presently there are no reports of the synthesis of 2,6-bis(phosphino)thiophenols, although such compounds should be accessible via appropriate modifications of the sequence shown as Eq. (1).



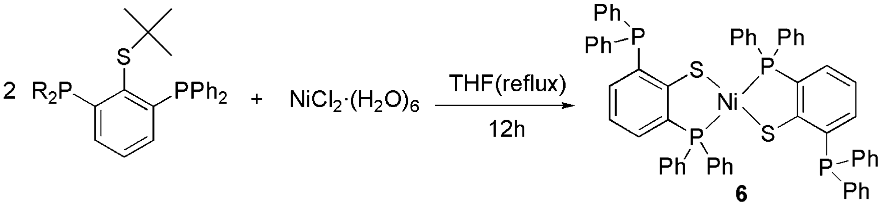
(1)

Prolonged exposure of 2-(*t*-butylthio)phenyldiphenylphosphine to BuLi in the presence of TMEDA (Eq. (2)) resulted in *ortho*-lithiation of the thiophenyl ring, in accordance with previously reported *o*-lithiations of some alkylaryl thioethers [19,31]. Quenching such reaction mixtures with chlorophosphines ClPR$_2$ produced *t*-butylaryl thioethers where the aryl group is symmetrically (R = Ph, **4a**) or unsymmetrically (R = *i*Pr, **4b**) substituted 2,6-bis(phosphino)thiophenol. Compound **4a** was isolated by simple crystallization from the reaction mixture. Compound **4b** was not obtained in pure form, as small quantities of the starting material, 2-(*t*-butylthio)phenyldiphenyl- phosphine (ca. 5%) were always present even after repeated crystallizations. Both **4a** and **4b** are white crystalline substances, which are quite stable in air (no oxidation was observed by ^{31}P NMR when benzene solutions of **4a**,**b** were exposed to air for 1 week). Spectroscopic (NMR) characterizations of **4a** (^{31}P NMR, δ −6.4, (s); H NMR, δ 1.41 (s, 9H)) correspond to C_s symmetry of the molecule, and analogous spectral features were observed for isostructural, symmetrically substituted 2,6-bis(phosphino)phenols [17]. Phosphorus centers in unsymmetrically substituted 2,6-bis(phosphino)thiophenol **4b** are weakly coupled ($^4J_{PP} = 12$ Hz), whereas such coupling was not resolved in analogous O-protected phenol derivatives [17]. Broad signals for the *i*Pr groups in the room temperature H NMR spectrum of **4b** (δ 1.88, s (br, 2H); 1.12–0.94, (m, (br, 12H))) suggest that rotation around the P–C bonds in the P*i*Pr$_2$ substituent is restricted. Similar ^{1}H NMR spectral patterns were observed in related compounds when the P*i*Pr$_2$ group is positioned *ortho* to a relatively bulky substituent [17,32].



4a-b

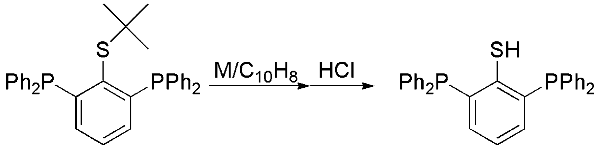
(2)



6

(4)

Reactions of **4a** with alkali metal (Li or Na) naphthalenides followed by acidification of the reaction media produced thiophenol **5** (Eq. (3)). A better selectivity for S–C(CH$_3$)$_3$ bond cleavage and higher yields of **5** (>95%) were observed when lithium was used. When sodium was used, the reaction mixtures were always contaminated with minor quantities of products containing P–H bonds ^{31}P NMR: δ −39.0 (d, $J_{PH} = 215$ Hz); −44.9 (d, $J_{PH} = 227$ Hz), resulting in a decreased yield of **5** (about 80%). The presence of such byproducts is consistent with previously reported P–C bond cleavage reactions observed upon subjection of selected phosphines to sodium naphthalenide [33]. Thiophenol **5** is a white, foamy substance, which was isolated in crystalline form. Oxidations at both phosphorus and sulfur can be expected for **5**, as related compounds containing *o*-(phosphino)thiophenol fragments have been reported to form oxidation products containing P=O and S–S fragments [34,35]. However, thiophenol **5** appears to be relatively stable to aerial oxidation, as no changes were observed in its ^{31}P NMR spectra when a benzene solution of **5** was exposed to air and monitored for 5 days. Interestingly, structural analogs of **5**, 2,6-bis(phosphino)phenols are extremely air sensitive [17].



5

(3)

Reactions of the new ligands with Ni(II) sources allowed for the initial assessment of their coordinating properties. Ligands containing mixed-donor [P,S] chelating pockets are well known to form mononuclear complexes of the general formula M[P,S]$_2$, particularly when reacted with Group 8 metal ions [26]. For example, nickel bis(phosphinothiophenolate) complexes are readily formed in reactions of *o*-(diphenylphosphino)thioanisole or related chelating phosphine–thioether ligands with nickel(II) halides, via facile dealkylations at sulfur [36,37]. Since compounds **4a**,**b** and **5** have two [P,S] chelating compartments, formation of binuclear complexes containing bridging thiolate moieties may be expected. However, only the mononuclear bis(phosphinothiophenolate) complex **6** was obtained in reactions of **4a** with NiCl$_2$ · 6H$_2$O (Eq. (4)). No formation of a bimetallic complex was detected when the reaction depicted in Eq. (4) was repeated using different ratios of the reagents (ligand/metal, 2:1, 1:1, and 1:2); **6** was always isolated as a major product. Complex **6** was also obtained when a THF solution of thiophenol **5** was subjected to NaOEt and followed by NiCl$_2$ · 6H$_2$O (2:1 ratio). Deep green **6** is soluble in THF, pyridine, and dichloromethane;

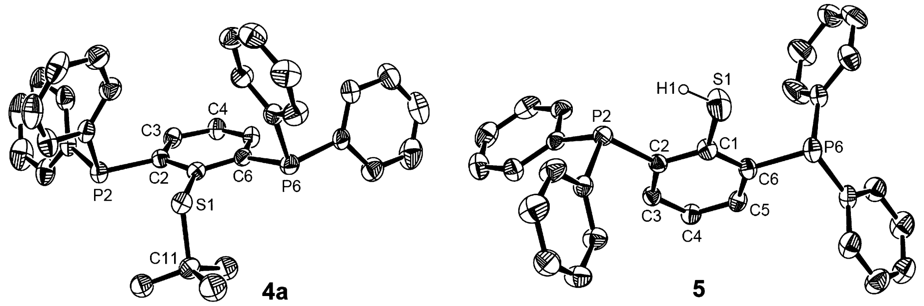


Fig. 2. Thermal ellipsoid (30%) plots of **4a** and **5**. One orientation of the disordered *t*-Bu group of **4a** is shown; cocrystallyzed benzene molecule is omitted in the plot for **5**.

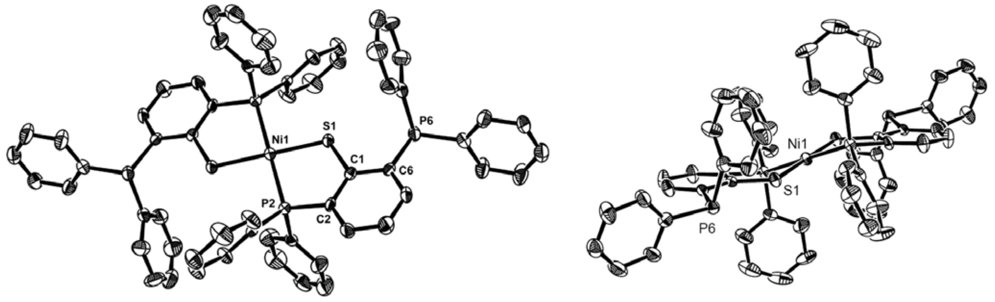


Fig. 3. Thermal ellipsoid (30%) plots of compound **6**.

Table 1
Summary of crystallographic data for **4a**, **5** and **6**

Compound	**4a**	**5** · C_6H_6	**6** · 2 THF
Formula	$C_{34}H_{32}P_2S$	$C_{36}H_{30}P_2S$	$C_{68}H_{62}NiO_2P_4S_2$
Formula weight	534.6	556.6	1157.88
Space group	$P\bar{1}$	$P21/n$	$P\bar{1}$
a (Å)	9.523(1)	10.187(1)	9.806(2)
b (Å)	12.370(3)	9.672(2)	11.817(3)
c (Å)	12.940(3)	31.27(1)	14.765(4)
α (°)	93.09(2)	90	81.45(2)
β (°)	100.54(2)	97.65(2)	73.13(2)
γ (°)	93.56(2)	90	67.73(2)
V (Å^3)	1492.4(5)	3053.6(12)	1513.7(6)
Z	2	4	2
ρ_{calc} (g/cm^3)	1.19	1.211	1.27
μ (MoKα mm^{-1})	0.236	0.234	0.539
T (K)	293(2)	293(2)	293(2)
λ (Å)	0.71069	0.71073	0.71073
θ Range (°)	1.60–22.47	2.04–22.47	1.44–22.47
Measured/independent reflections	3887/2384	3957/2942	3851/2035
Final R indices $[I > 2\sigma(I)]$[a,b]	$R_1 = 0.047$, $wR_2 = 0.097$[c]	$R_1 = 0.038$, $wR_2 = 0.093$[d]	$R_1 = 0.058$, $wR_2 = 0.096$[e]
R indices (all data)	$R_1 = 0.120$, $wR_2 = 0.117$	$R_1 = 0.068$, $wR_2 = 0.105$	$R_1 = 0.183$, $wR_2 = 0.122$
Largest difference peak and hole	0.295, −0.176	0.258, −0.212	0.299, −0.31
Goodness-of-fit on F^2	1.029	1.03	1.003

[a] $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$.

[b] $wR_2 = [\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]]^{1/2}$.

[c] $w = 1/[^2(F_o^2) + (0.0402P)^2 + 0.7299P]$ where $P = (F_o^2 + 2(F_c)^2)/3$.

[d] $w = 1/[^2(F_o^2) + (0.0477P)^2 + 1.2231P]$.

[e] $w = 1/[^2(F_o^2) + (0.0387P)^2 + 0.1973P]$.

it decomposes in acetonitrile. The ^{31}P NMR chemical shift value for nickel-coordinated phosphorus centers in **6** (δ 55.3, s) closely resembles those observed for other nickel bis(2-diphenylphosphinothiophenolates) (δ 56.1 [36], 52.6 [38]). The shift value for the uncoordinated phosphine in **6** (δ −13.0) is close to that for the free ligand **5** (δ −11.6).

In contrast, ligand **4b** does not afford bis(phosphinothiophenolate) complexes analogous to **6** upon exposure to nickel(II) halides. Instead, such reactions produced a poorly soluble, and as-yet uncharacterized, NMR-silent orange powder.

Both metal-based and sulfur-based electrochemical oxidations have been reported for Ni[P,S]$_2$ complexes. Metal-based (Ni(II)/Ni(III)) oxidation (0.67 V versus Ag/Ag$^+$) is reversible [36], while thiolate–thiyl conversion proceeds irreversibly at lover potential (0.26 V) [39]. Investigation of **6** by cyclic voltammetry displayed an irreversible oxidation peak at around 0.38 V (versus Ag/AgNO$_3$). We have assigned it to oxidation at sulfur, based on comparisons to similar thiolate–thiyl conversions reported for related Ni[P,S]$_2$ complex [39].

Table 2
Selected bond lengths and angles for compounds **4a**, **5** and **6**

Bond lengths (Å) and angles (°)	4a	5	6
C1–S1	1.780(4)	1.775(3)	1.752(6)
C2–P2	1.853(4)	1.840(2)	1.801(6)
C6–P6	1.850(4)	1.845(3)	1.823(6)
S1–C11	1.880(4)		
S1–Ni1			2.1628(17)
P2–Ni1			2.1633(17)
S1–C1–C2	119.1(3)	120.02(19)	120.7(5)
S1–C1–C6	120.1(3)	118.9(2)	119.4(5)
C1–S1–C11	105.38(18)		
C1–C2–P2	118.7(3)	120.04(19)	112.2(5)
C1–C6–P6	118.6(3)	119.75(19)	117.7(5)
S1–Ni1–P2			87.57(6)
C1–S1–Ni1			106.1(2)
C2–P2–Ni1			107.2(2)

*3.1.1. Structural characterizations of **4a**, **5**, and **6***

Compounds **4a**, **5** and **6** were characterized by single crystal X-ray diffraction methods. Their molecular structures are depicted in Figs. 2 and 3, crystallographic data are summarized in Table 1, and bond lengths and angles are listed in Table 2.

Single crystals of thioether **4a** suitable for X-ray analysis were obtained by crystallization directly from the reaction mixture. ORTEP-3 drawing of **4a** is shown in Fig. 2. The molecule adopts a conformation where the PPh$_2$ and *tert*-butylthio substituents are rotated around the bonds connecting the heteroatoms to the central phenyl ring to minimize the steric interactions among the *t*Bu group and the phenyl rings. Atom P6 is displaced from the plane of the central phenyl ring (torsion angle S1–C1–C6–P6 is 7.33°) whereas atoms P2 and S1 are essentially in that plane. Single crystals of thiophenol **5** were obtained by low temperature (−28 °C) crystallization from a benzene/Et$_2$O (~1:1) solution. The compound crystallizes with one molecule of benzene per thiophenol in the lattice. The bond distances and angles in **4a** and **5** (Table 2) are unremarkable.

Thiophenolate **6** was crystallized from a pyridine/THF (~9:1) solution. The complex crystallizes with two molecules of THF in the lattice. The metal center is in a square-planar geometry, with thiolate and phosphine donors from the two opposing [P,S] ligands located in a *trans* arrangement (Fig. 3). Analogous geometries have been reported for other divalent nickel Ni[P,S]$_2$ compounds [36,38–40]. Nickel–sulfur and nickel–phosphorus distances in **6** are within the range of analogous distances (2.15–2.18 Å) reported for other structurally characterized Ni[P,S]$_2$ complexes [36,38,40]. Thiolate and PPh$_2$ groups (both nickel-coordinated and free) in **6** are displaced into the opposite sides of the plane of the central phenyl ring (torsion angles S1–C1–C2–P2 and S1–C1–C6–P6 are

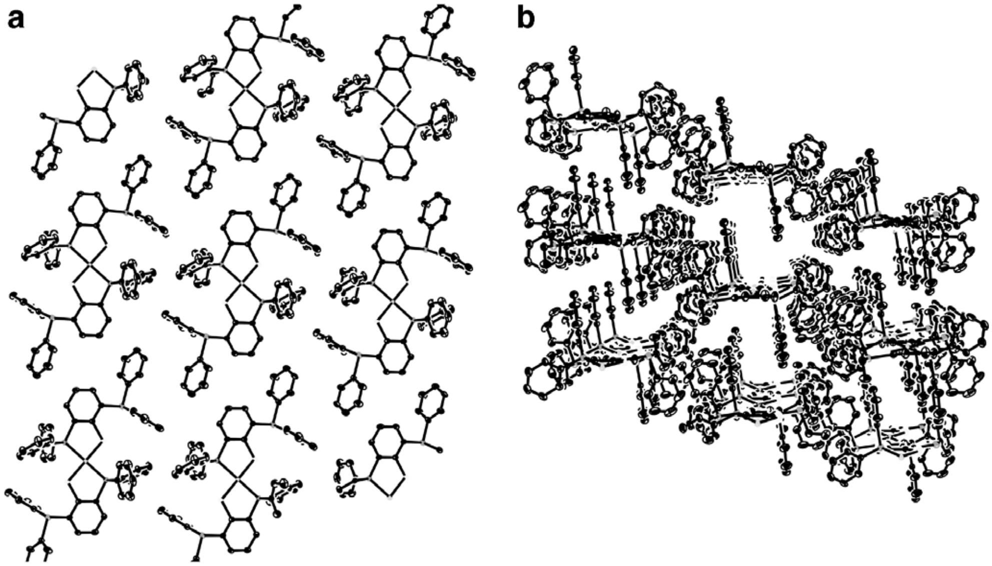


Fig. 4. Packing of **6** in the crystalline lattice (grey spheres represent nickel, sulfur, and phosphorus).

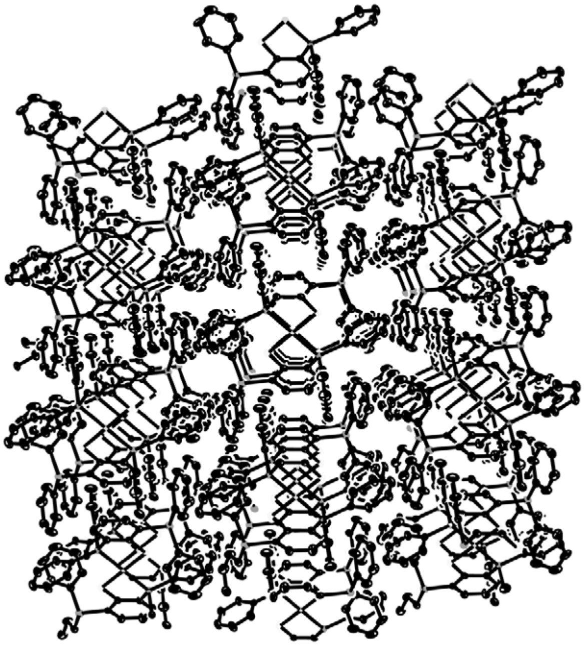


Fig. 5. Orientation of molecules of **6** along Ni–Ni vectors.

10.01° and 9.67°, respectively), resulting in displacing the nickel center from the plane of the central phenyl ring by 0.401 Å. A similar displacement (0.478 Å) is present in one of the two previously reported structures of nickel bis((*o*-diphenyplhosphino)thiophenolate) [40], whereas in another structure[36] and in the structure of [Ni{2-(Ph_2P)-6-(Me_3Si)(C_6H_3S)}$_2$] [38] such displacement is much smaller. The reasons behind these structural differences are not clear.

The structural regularities observed for packing of **6** in the crystalline lattice deserve special attention. Thus in the solid state molecules of **6** arrange in rows, shown vertically in Fig. 4a. The rows, in turn, pack together in the interlocking ladder pattern (Fig. 4b). This alignment is observed if a unit cell is arranged such that the vector defined by the C to BC points of the unit cell is situated in front of and is collinear with the vector from points A to AB (i.e., lattice vector [1, 0, −1]). The channels and cavities formed by such packing (Fig. 4b) are occupied by the THF molecules (not shown). The molecules of **6** are also aligned in the direction of the *a*-axis of the unit cell so that infinite rows along the Ni···Ni vector are formed (Fig. 5). Such an alignment is most likely an effect of the packing forces, as the intermolecular Ni–Ni distance of 9.806 Å excludes the possibility of metallophilic interactions.

4. Supplementary material

CCDC 652959, 652960 and 652961 contain the supplementary crystallographic data for **4a**, **5** and **6**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

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