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Complexes of sterically-hindered diaminophosphinothiolate ligands with Rh(I), Ni(II) and Pd(II)

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ABSTRACT

Two new sterically demanding diaminophosphinothiolate ligands (HL^1 and HL^2) have been prepared and the X-ray crystal structure of the Li salt of HL^2 has been determined. The complex $[Pd(L^1)_2]$ was fully characterized, but in contrast to other phosphinothiolates, complexes with the $M(L)_3$ stoichiometry could not be prepared. Reaction of LH^1 with Ni(II) led to cleavage of the arythiolate group and isolation of a thiolate bridged dimer, confirmed by an X-ray crystal structure. The Rh(I) complexes [Rh(nbd)L] (L = L^1, L^2) were characterized including an X-ray structure.

1. Introduction

There has been considerable interest in the coordination chemistry of multidentate ligands incorporating phosphorus donors in combination with thiolate, oxide or nitrogen donors. The combination of phosphorus with sulfur provides particularly versatile ligands capable of forming complexes with a wide variety of coordination modes. The most widely investigated class are probably the 2-phosphinoaryl thiolates which are readily available via the direct lithiation of arene thiolates and reaction with the appropriate phosphine halide [1,2]. Bidentate phosphinothiolates of the type $Ph_2PC_6H_4SH$-2 have been shown to be potent ligands, forming stable complexes with a wide range of metal and metalloid elements. The dominant structural motif for divalent and trivalent metal ions with the bidentate ligands are complexes of the types $[M(PS)_2]$ (M = Ni, Pd, Pt) [3–8] and $[M(PS)_3]$ (M = Re, Tc, Ru, Rh, Ir) [9–16]. The topic of phosphinothiolate chemistry in general was reviewed comprehensively in 2000 [17]. Since that time research has focused on phosphino alkylthiolates and there have been relatively few reports on the chemistry of the phosphinoarylthiolates. However, some investigations of the chemistry of the coordinated ligands have been made. In the case of M = Ru, the anionic Ru(II) complexes $[Ru(PS)_3]^-$ can be oxidized in two one electron steps to give complexes where the sulfur atoms have significant thiyl radical character [16]. This confers reactivity and the complexes can undergo reactions at the coordinated sulfur, such as C—S bond formation [16] and oxidation with atmospheric oxygen [18]. We here investigate if new complexes with coordinative unsaturation or novel structures could be generated by increasing the steric bulk of the ligand at phosphorus. In the past steric congestion has been introduced adjacent to sulfur using groups such as Me_3Si at the 6-position of the arene thiolate group [19]. However, this did not change the stoichiometry as complexes of the type $[Fe(PS)_3]$ were formed with both the simple PS ligand and the sterically hindered analog [19]. We were therefore interested to see if using very large sterically hindered phosphino substituents would have any impact on the nature of the complexes formed. We here report the synthesis and coordination chemistry of the new 2-diazaphospholiden-2-ylbenzenethiolate proligands of the type shown in Fig. 1.

2. Experimental

2.1. Materials and instrumentation

All reactions were carried out using standard Schlenk-line techniques under an atmosphere of anhydrous N_2. All ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian Mercury VX 300 spectrometer (^1H at 300 MHz, $^{13}C\{^1H\}$ at 75.5 MHz and $^{31}P\{^1H\}$ at 121.5 MHz) or a Varian Unity 500 MHz spectrometer (^1H at 499.9 MHz, $^{13}C\{^1H\}$ at 125.7 MHz and $^{31}P\{^1H\}$ at 202.4 MHz). ^1H and $^{13}C\{^1H\}$ NMR spectra were referenced internally to the residual solvent resonance or tetramethylsilane at zero ppm (for ^1H NMR) and $^{31}P\{^1H\}$ spectra were externally referenced to 85% H_3PO_4 at zero ppm. Chemical shift values are quoted in ppm and all coupling constants are quoted in Hertz (Hz). Signal multiplicities are designated by s = singlet, d = doublet, dd = doublet of doublets and m = multiplet, and the abbreviation br = broad.

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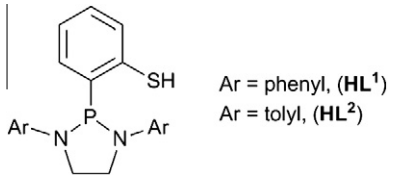


Fig. 1. Structures of 2-diarylphospholiden-2-yl benzenethiolate proligands.

Electrospray mass spectrometry was performed on a Micromass LCT Time of Flight Mass Spectrometer with a 'Z' Spray electrospray source. Probe Electron Impact and Field Ionisation mass spectrometry were performed on a Micromass GCT Time of Flight Mass Spectrometer, with a heated solid probe. FAB mass spectrometry was performed on a Fisons Autospec, using dithiothreitol and dithioerythritol or *m*-nitrobenzyl alcohol as the matrix. Infra red spectra were recorded on a Perkin Elmer Paragon 1000 FT-IR spectrometer and GRAMS Analyst software by Galactic Industries was used in conjunction with this. Abbreviations: w = weak, m = medium, s = strong intensity absorption, sh = sharp, and br = broad peak width. Elemental analyses were measured on an Elementor varioEL. All measurements were performed by the elemental analysis department of the Inorganic Chemistry Laboratory, University of Oxford. The ligand precursor lithium 2-lithiobenzenethiolate/TMEDA complex was prepared as a solution in hexane and is described in the literature [20].

2.2. Synthetic work

2.2.1. Preparation of 2-chloro-1,3-diphenyl-1,3,2-diazaphospholidine

2-Chloro-1,3-diphenyl-1,3,2-diazaphospholidine was prepared in a similar manner to the previously published 2-chloro-1,3-di(2,4,6-trimethylphenyl)-1,3,2-diazaphospholidine [21]. To a clear, orange/brown solution of *N,N′*-diphenylethylenediamine (1.27 g, 6 mmol) in CH_2Cl_2 (40 cm^3), anhydrous degassed triethylamine (16 cm^3, 115 mmol) was added. The solution was cooled to 0 °C, and phosphorus trichloride (0.52 cm^3, 6 mmol) added slowly over a period of 5 min giving a brown solution with small amounts of a white precipitate. The solution was stirred at 0 °C for 30 min, then at room temperature for a further 90 min and then all the volatile components were removed under vacuum. The orange/brown solid produced was extracted with thf (3 × 10 cm^3). The thf solutions were combined and evaporated to dryness *in vacuo* yielding a brown free-flowing solid (1.8 g, 5.9 mmol, 98% yield). *Anal.* Calc. for $C_{14}H_{14}N_2PCl$: C, 60.8; H, 5.1; N, 10.1; Cl, 12.8. Found: C, 60.8; H, 5.2; N, 10.1; Cl, 10.9%. ^1H NMR (d^8-Toluene): δ 7.11 (*pseudo* t, J_{H-H} = 8 Hz, 4H, *m*-Ph), 6.96 (m, 4H, *o*-Ph), 6.85 (t, $^3J_{H-H}$ = 7 Hz, 2H, *p*-Ph), 3.26 and 3.07 (two s, br, 4H, CH_2CH_2). $^{13}C\{^1H\}$ NMR (d^8-Toluene): δ 143.1 (d, $^2J_{C-P}$ = 15 Hz, *i*-Ph), 129.6 (s, *o*-Ph), 122.1 (s, *p*-Ph), 117.2 (s, br, *m*-Ph), 47.5 (d, $^2J_{C-P}$ = 10 Hz, CH_2). $^{31}P\{^1H\}$ NMR (d^8-Toluene): δ 137.4 (s). Mass spectrum (ES^+): *m/z* = 241.2 $[L-Cl]^+$. High Resolution MS (ES^+), found (calc): *m/z* = 241.0894 (241.0895), $[L-Cl]^+$. Selected IR/cm^{-1} (KBr disk): 3038 (m, $\nu_{C-H\ aromatic}$), 2893 (m, $\nu_{C-H\ aliphatic}$), 1599 (s, $\nu_{C=C}$).

2.2.2. Preparation of 2-chloro-1,3-di-p-tolyl-1,3,2-diazaphospholidine

To a clear, colorless solution of *N*-(2-(4-toluidino)ethyl)-4-methylbenzenamine [22,23] (1.44 g, 6 mmol) and triethylamine (16 cm^3, 0.11 mol) in CH_2Cl_2 (40 cm^3) cooled to 0 °C, phosphorus trichloride (0.52 cm^3, 0.82 g, 6 mmol) was added slowly from a syringe over a period of 3 min. The mixture was stirred at 0 °C for 30 min and then at room temperature for a further 90 min. The volatiles were removed under vacuum, and the resulting yellow solid was extracted with thf (3 × 15 cm^3). The thf solutions were then combined and evaporated to dryness *in vacuo* yielding an orange/brown solid (1.8 g, 5.9 mmol, 98%). *Anal.* Calc. for $C_{16}H_{18}N_2PCl$: C, 63.1; H, 6.0; N, 9.2; Cl, 11.6. Found: C, 63.0; H, 6.5; N, 8.9; Cl, 9.8%. ^1H NMR ($CDCl_3$): δ 7.07 (d, $^3J_{H-H}$ = 8 Hz, 4H, *m*-Ph), 6.98 (dd, $^3J_{H-H}$ = 8 Hz, $^4J_{H-P}$ = 2 Hz, 4H, *o*-Ph), 3.83 (d, $^3J_{H-P}$ = 5 Hz, 4H, CH_2), 2.24 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 140.1 (d, $^2J_{C-P}$ = 20 Hz, *i*-Ph), 131.8 (s, *p*-Ph), 130.1 (s, *m*-Ph), 117.2 (d, $^3J_{C-P}$ = = 14 Hz, *o*-Ph), 48.1 (d, $^2J_{C-P}$ = 10 Hz, CH_2N), 20.7 (s, CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 138.8 (s). Mass spectrum (ES^+): *m/z* = 269.1 $[L-Cl]^+$. High Resolution MS (ES^+), found (calc): *m/z* = 269.1211 (269.1208), $[L-Cl]^+$. Selected IR/cm^{-1} (KBr disk): 2919 (m, br, $\nu_{C-H\ stretch}$), 1573 (w, $\nu_{C=C\ aromatic}$), 780 (w, ν_{P-N}).

2.2.3. Preparation of lithium 2-(1,3-diphenyl-1,3,2-diazaphospholidin-2-yl)benzenethiolate, Li[$\mathbf{L^1}$]

To a suspension of lithium 2-lithio-benzenethiolate/TMEDA complex (1.65 g, 4.66 mmol) in hexane (20 cm^3) at 0 °C, a gently warmed, clear, orange/brown toluene solution (10 cm^3) of 2-chloro-1,3-diphenyl-1,3,2-diazaphospholidine (1.40 g, 5.05 mmol) was added drop-wise over a period of 3 min. The mixture was stirred at 0 °C for 5 min, at room temperature for 10 min, and then heated to 50 °C for a further 90 min. The solvent was then removed under vacuum and the brown solid triturated with hexane (20 cm^3). The solid produced was isolated by filtration, washed with toluene (2 × 10 cm^3), and hexane (10 cm^3) and dried *in vacuo* producing an off white solid (1.75 g, the yield is unknown due to the unknown composition of the solid produced). ^1H NMR ($CDCl_3$): δ 7.48 (dd, $^3J_{H-H}$ = 8 Hz, $^4J_{H-P}$ = 5 Hz, 1H, *CH*CS), 7.10–7.20 (m, 8H, *o*-Ph and *m*-Ph), 6.95 (*pseudo* t, $^3J_{H-H}$ = 7 Hz, 1H, *CH*CHCS), 6.90 (m, 1H, *CH*CP), 6.70–6.80 (m, 3H, p-Ph and *CH*CHCP), 3.85 (m, 2H, NH_{2a}), 3.57 (m, 2H, NH_{2b}), 2.20 (s, 6H, TMEDA-NCH_2), 1.92 (s, 18H, TMEDA-NCH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 155.7 (d, $^2J_{C-P}$ = 31 Hz, *C*S), 147.8 (d, $^2J_{C-P}$ = 17 Hz, *i*-Ph), 138.7 (d, $^1J_{C-P}$ = 14 Hz, *C*P), 135.7 (s, *C*HCP), 130.2 (d, $^3J_{C-P}$ = 7 Hz, *C*HCS), 129.5 (s, *C*HCHCP), 129.3 (s, *m*-Ph), 120.5 (s, *C*HCHCS), 119.6 (s, *p*-Ph), 116.4 (d, $^3J_{C-P}$ = 13 Hz, *o*-Ph), 57.0 (s, TMEDA-NCH_2), 46.9 (d, $^2J_{C-P}$ = 7 Hz, NCH_2), 46.1 (s, TMEDA-NCH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 89.5 (s, br). Mass spectrum (ES^+): *m/z* = 349.1 $[L-Li]^+$, 317.1 $[L-Li-S]^+$.

2.2.4. Preparation of lithium 2-(1,3-di-p-tolyl-1,3,2-diazaphospholidin-2-yl)benzenethiolate, Li[$\mathbf{L^2}$]

To a suspension of lithium 2-lithio-benzenethiolate/TMEDA complex (1.6 g, 4.6 mmol) in hexane (20 cm^3) at 0 °C, a lightly warmed, clear, orange/brown toluene solution (10 cm^3) of 2-chloro-1,3-di-*p*-tolyl-1,3,2-diazaphospholidine (1.50 g, 4.9 mmol) was added drop-wise over a period of 3 min. The mixture was stirred at 0 °C for 5 min, at room temperature for 10 min, and then heated to 50 °C for a further 90 min. The volatiles were removed under vacuum and the brown solid triturated with hexane (20 cm^3). The solid produced was isolated by filtration, washed with toluene (2 × 10 cm^3), and hexane (10 cm^3) and dried *in vacuo* producing an off-white solid (1.67 g, the yield is unknown due to the unknown composition of the solid produced). ^1H NMR ($CDCl_3$): δ 7.51 (dd, $^3J_{H-H}$ = 5 Hz, $^3J_{H-P}$ = 3 Hz, 1H, *CH*CS), 7.15–7.25 (d, $^3J_{H-H}$ = 8 Hz, 4H, *o*-Ph), 6.90–7.10 (m, 6H, *m*-Ph, *CH*CP and *CH*CHCS), 6.80 (t, $^3J_{H-H}$ = 15 Hz, 1H, *CH*CHCP), 3.92 (m, 2H, NCH_{2a}), 3.64 (m, 2H, NCH_{2b}), 2.20–2.30 (m, 10H, CCH_3 and TMEDA-NCH_2), 1.87 (s, 12H, TMEDA-NCH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 155.7 (d, $^2J_{C-P}$ = 31 Hz, *C*S), 145.4 (d, $^2J_{C-P}$ = 16 Hz, *i*-Ph), 138.7 (d, $^2J_{C-P}$ = 14 Hz, *C*P), 136.2 (s, *C*HCP), 130.2 (d, $^3J_{C-P}$ = 8 Hz, *C*HCS), 129.9 (s, *m*-Ph), 129.6 (s, *C*HCHCS), 129.5 (s, *p*-Ph), 120.5 (s, *C*HCHCP), 116.6 (d, $^3J_{C-P}$ = 13 Hz, *o*-Ph), 57.1 (s, TMEDA-NCH_2), 47.1 (d, $^2J_{C-P}$ = 6 Hz, NCH_2), 45.9 (s, TMEDA-NCH_3), 20.6 (s, CCH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 94.7 (s, br). Mass spectrum (ES^+): *m/z* = 377.1 $[L-Li]^+$.

*2.2.5. Preparation of [Rh(2-(1,3-diphenyl-1,3,2-diazaphospholidin-2-yl)benzenethiolate)(nbd)], **3***

To a dark red solution of $[Rh(nbd)_2]^+BF_4^-$ (0.25 g, 0.67 mmol) in CH_2Cl_2 (20 cm^3), the ligand lithium 2-(1,3-diphenyl-1,3,2-diazaphospholidin-2-yl)benzenethiolate Li[**L^1**] (0.32 g, 0.67 mmol) was added forming a dark orange/red solution immediately. The solution was stirred at room temperature for 1 h, during which time no change occurred. The volume was reduced to ca. 5 cm^3 and pentane (50 cm^3) added to precipitate. The solid produced was removed by filtration and the CH_2Cl_2/pentane solutions evaporated to dryness producing bright orange/red solid which was washed with pentane (2 × 4 cm^3) and dried *in vacuo* (0.26 g, 0.48 mmol, 71%). *Anal.* Calc. for $C_{27}H_{26}N_2PRhS$: C, 59.6; H, 4.8; N, 5.2. Found: C, 59.2; H, 5.2; N, 4.8%. ^{1}H NMR (CD_2Cl_2): δ 7.40–7.50 (m, 5H, *o*-Ph and C*H*CS), 7.25–7.3 (m, 4H, *m*-Ph), 7.00–7.15 (m, 2H, C*H*CHCP and C*H*CHCS), 6.92 (tt, $^3J_{H-H}$ = 7 Hz, $^4J_{H-H}$ = 1 Hz, 2H, *p*-Ph), 6.76 (tt, $^3J_{H-H}$ = 8 Hz, $^4J_{H-P}$ = 1 Hz, 1H, C*H*CP), 5.66 (m, 2H, C=C*H*), 4.05 (m, 2H, CH_2N), 3.85 (m, 2H, CH_2N), 3.70 (m, 2H, C*H*CH_2), 3.54 (m, 2H, C=C*H*), 1.52 (m, 2H, nbd-CH_2). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 155.4 (d, $^1J_{C-P}$ = 41 Hz, *C*—P), 143.4 (d, $^2J_{C-P}$ = 11 Hz, *i*-Ph), 139.3 (dd, $^2J_{C-P}$ = 41 Hz, $^2J_{C-Rh}$ = 10 Hz, *C*—S), 132.7 (s, *C*HCHCS), 130.0 (s, *C*HCHCP), 129.5 (s, *C*HCS), 129.1 (s, *m*-Ph), 122.4 (d, $^2J_{C-P}$ = 5 Hz, *C*HCP), 120.5 (s, *p*-Ph), 116.5 (d, $^3J_{C-P}$ = 9 Hz, *o*-Ph), 91.8 (dd, $^2J_{C-P}$ = 13 Hz, $^1J_{C-Rh}$ = 4 Hz, *C*=C), 67.7 (s, nbd-*C*H$_2$), 59.1 (m, *C*=*C*), 53.1 (d, $^3J_{C-P}$ = 8 Hz, *C*CH$_2$), 46.5 (s, *C*H$_2$CH$_2$). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 118.5 (d, $^1J_{P-Rh}$ = 224 Hz). Mass spectrum (ES$^+$): *m/z* = 545.1 [M+H]$^+$, 551.1 [M+Li]$^+$, 567.1 [M+Na]$^+$, 583.1 [M+K]$^+$.

*2.2.6. Preparation of [Rh(2-(1,3-di-p-tolyl-1,3,2-diazaphospholidin-2-yl)benzenethiolate)(nbd)], **4***

To a dark red solution of $[Rh(nbd)_2]^+BF_4^-$ (0.25 g, 0.67 mmol) in CH_2Cl_2 (20 cm^3), the ligand lithium 2-(1,3-di-*p*-tolyl-1,3,2-diazaphospholidin-2-yl)benzenethiolate Li[**L^2**] (0.335 g, 0.67 mmol) was added forming a dark orange/red solution immediately. The solution was stirred at room temperature for 1 h, during which time no change occurred. A small amount of solid was removed by filtration, and the resulting clear bright orange/red solution was evaporated to dryness producing bright orange/red solid which was washed with pentane (2 × 4 cm^3) and dried under vacuum (0.38 g, 0.66 mmol, 99%). *Anal.* Calc. for $C_{29}H_{30}N_2PRhS$: C, 60.8; H, 5.3; N, 4.9. Found: C, 60.4; H, 5.0; N, 5.0%. ^{1}H NMR (CD_2Cl_2): δ 7.35–7.45 (dd, $^3J_{H-H}$ = 8 Hz, $^4J_{H-P}$ = 4 Hz, 1H, C*H*CS), 7.34 (dd, $^3J_{H-H}$ = 8 Hz, $^4J_{H-P}$ = 1 Hz, 4H, *o*-Ph), 7.09 (d, $^3J_{H-H}$ = 8 Hz, 4H, *m*-Ph), 7.00–7.10 (m, 2H, C*H*CHCP and C*H*CHCS), 6.74 (tt, $^3J_{H-H}$ = 7 Hz, $^4J_{H-P}$ = 2 Hz, 1H, C*H*CP), 5.66 (m, 2H, C=C*H*), 4.00 (m, 2H, CH_2N), 3.80 (m, 2H, CH_2N), 3.72 (m, 2H, C*H*CH$_2$), 3.56 (m, 2H, C=C*H*), 2.28 (s, 6H, CH_3) 1.55 (m, 2H, nbd-CH_2). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 155.4 (d, $^1J_{C-P}$ = 33 Hz, *C*—P), 141.0 (d, $^2J_{C-P}$ = 11 Hz, *i*-Ph), 139.4 (dd, $^2J_{C-P}$ = 32 Hz, $^2J_{C-Rh}$ = 9 Hz, *C*—S), 132.8 (d, $^4J_{C-Rh}$ = 2 Hz *C*HCHCS), 129.6 (m, *m*-Ph, *C*HCHCP and *C*HCS), 122.3 (d, $^2J_{C-P}$ = 6 Hz, *C*HCP), 116.4 (d, $^3J_{C-P}$ = 8 Hz, *o*-Ph), 113.2 (s, *p*-Ph), 91.7 (dd, $^2J_{C-P}$ = 12 Hz, $^1J_{C-Rh}$ = 4 Hz, *C*=*C*), 67.6 (d, $^4J_{C-P}$ = 4 Hz, nbd-*C*H$_2$), 58.9 (d, $^2J_{C-P}$ = 10 Hz, *C*=*C*), 53.1 (obscured by solvent, *C*CH$_2$), 46.6 (s, *C*H$_2$CH$_2$), 20.4 (s, *C*H$_3$). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 115.1 (d, $^1J_{P-Rh}$ = 224 Hz). Mass spectrum (ES$^+$): *m/z* = 573.1 [M+H]$^+$, 579.1 [M+Li]$^+$, 595.2 [M+Na]$^+$, 611.1 [M+K]$^+$. High Resolution MS (ES$^+$), found (calc): *m/z* = 573.0988 (573.1001), [M]$^+$. Selected IR/cm^{-1} (KBr disk): 3035 (w, $\nu_{C-H\ aromatic}$), 2989, 2919, 2855 (w, $\nu_{C-H\ aliphatic}$), 1616 (w, $\nu_{C=C}$).

*2.2.7. Preparation of [Pd(2-(1,3-diphenyl-1,3,2-diazaphospholidin-2-yl)benzenethiolate)$_2$], **5***

To a clear dark brown solution of Na_2PdCl_4 (0.10 g, 0.33 mmol) in methanol (7 cm^3), lithium 2-(1,3-diphenyl-1,3,2-diazaphospholidin-2-yl)benzenethiolate Li[**L^1**] (0.35 g, ~0.73 mmol) was added forming an orange precipitate immediately. The solution was stirred at room temperature for 1 h, during which time no further change occurred. The solid was isolated by filtration, washed with methanol (3 cm^3) and diethyl ether (2 × 5 cm^3) and dried under vacuum (0.21 g, 0.26 mmol, 79%). *Anal.* Calc. for $C_{40}H_{36}N_4P_2PdS_2$: C, 59.7; H, 4.5; N, 7.0. Found: C, 59.9; H, 4.9; N, 6.6%. ^{1}H NMR (CD_2Cl_2): δ 6.50–7.60 (m, 28H, aromatics), 4.02 (m, 4H, CH_2N), 3.92 (m, 4H, CH_2N). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 141.2 (virtual t, $^2J_{C-P}$ = 10 Hz, *i*-Ph), 132.8 (s, *C*HCHCS), 129.7 (m, *C*HCHCP and *C*HCS), 129.1 (m, *m*-Ph), 122.7 (m, *C*HCP), 120.8 (s, *p*-Ph), 115.8 (virtual t, $^3J_{C-P}$ = 10 Hz, *o*-Ph), 46.2 (s, CH_2CH$_2$). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 116.7 (s), 104.8 (s). Mass spectrum (ES$^+$): *m/z* = 805.1 [M+H]$^+$, 811.1 [M+Li]$^+$, 827.1 [M+Na]$^+$. Selected IR/cm^{-1} (KBr disk): 3058 (w, $\nu_{C-H\ aromatic}$), 2868 (w, $\nu_{C-H\ aliphatic}$), 1597 (s, $\nu_{C=C}$).

2.2.8. Attempted synthesis of [Ni(2-(1,3-diphenyl-1,3,2-diazaphospholidin-2-yl)benzenethiolate)$_2$], preparation of $Ni_2\{SC_6H_4P(NPh)_2C_2H_4\}_2(SPh)_2$], 6

To a clear colorless solution of lithium 2-(1,3-diphenyl-1,3,2-diazaphospholidin-2-yl)benzenethiolate Li[**L^1**] (0.45 g, ~1.00 mmol) in methanol (10 cm^3), $[Ni(acac)_2]\cdot 4H_2O$ (0.124 g, 0.50 mmol was added forming a dark brown precipitate immediately. The solution was stirred at room temperature for 2 h, during which time no further change occurred. The volume of the solution was reduced to ca. 3 cm^3 *in vacuo*, the solid isolated by filtration, washed with diethyl ether (2 × 5 cm^3) and dried under vacuum (0.27 g, 0.36 mmol, 71%). ^{1}H NMR (CD_2Cl_2): δ 6.60–7.50 (m, 31H, aromatics), 4.24 (m, CH_2N), 4.20 (m, CH_2N), 4.02 (m, CH_2N), 3.92 (m, CH_2N). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 121.0 (s), 115.1 (s), 107.6 (s). Mass spectrum (ES$^+$): *m/z* = 757.1 [M+H]$^+$. Selected IR/cm^{-1} (KBr disk): 3058 (w, $\nu_{C-H\ aromatic}$), 2865 (w, $\nu_{C-H\ aliphatic}$), 1597 (s, $\nu_{C=C}$).

2.3. Crystallographic methods

X-ray crystal structures were determined by mounting a single crystal encased in perfluoropolyether oil on a glass fiber and then cooling rapidly to 150 K in a stream of cold N_2 using an Oxford Cryosystems CRYOSTREAM unit [24]. Diffraction data was subsequently measured at 150 K using an Enraf-Nonius KappaCCD diffractometer (graphite-monochromated Mo Kα radiation, λ = 0.71073 Å) over the range of $5.0 \leqslant \theta \leqslant 27.5°$. Intensity data were processed using the DENZO-SMN package [25]. The structures were solved using the direct-methods program SIR92 [26], which located all non-hydrogen atoms of the complexes. Subsequent full-matrix least-squares refinement on *F* was carried out using the CRYSTALS program suite [27]. Absorption correction was semi-empirical from equivalent reflections. Hydrogen atoms were positioned geometrically after each cycle of refinement. A 3-term Chebychev polynomial weighting scheme was applied. Crystal data and structure refinement parameters are included in Table 1.

2.4. Results and discussion

The lithium salts of the new ligands were prepared using a modification of the published route for 2-diaryphosphinothiolate ligands via the *ortho*-lithiation of thiophenol [20] and reaction with the appropriate 2-chloro-1,3-diaryl-1,3,2-diazaphospholidine [21] in a 2:1 toluene–hexane mixture. The lithium salts were isolated as air-sensitive white solids and incorporated 1.5 equivalents of TMEDA (*N,N,N′,N′*-tetramethylethylenediamine) which was present from the solution of lithium 2-lithiobenzenethiolate/TMEDA complex precursor used. For the salt with aryl = 4-tolyl (**L^2**), crystals suitable for an X-ray structure determination were obtained upon standing the mother liquor at room temperature overnight. An ORTEP representation of the structure is shown in Fig. 2 and selected bond lengths and angles displayed in Table 2.

Table 1
Summary of the crystallographic parameters for compounds Li[$\mathbf{L^2}$], **3**, **5** and **6**.

Crystal identification	Li[$\mathbf{L^2}$]	**3**	**5**	**6**
Chemical formula	$C_{62}H_{92}ClLi_3N_{10}P_2S_2$	$C_{27}H_{26}N_2PRhS$	$C_{42}H_{40}Cl_4N_4P_2PdS_2$	$C_{158}H_{142}Cl_4N_{12}Ni_6P_6S_{12}$
Formula weight	1159.84	544.46	975.10	3273.44
Crystal system	orthorhombic	monoclinic	triclinic	triclinic
Space group	*Aba*2	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a (Å)	27.4303(3)	9.5787(2)	9.5532(4)	10.8756(2)
b (Å)	22.1492(2)	14.1261(3)	9.6527(4)	15.7082(3)
c (Å)	11.0717(2)	18.0712(5)	11.2342(5)	24.2802(5)
α (°)	90	90	89.7843(18)	106.3675(10)
β (°)	90	105.0861(9)	80.4544(19)	93.7148(9)
γ (°)	90	90	89.4097(19)	109.4812(8)
Cell volume (Å^3)	6726.71(15)	2360.94(10)	1021.55(8)	3693.75(13)
Z	4	4	1	2
D_{calc} (Mg/m^3)	1.145	1.532	1.585	1.472
Absorption coefficient (mm^{-1})	0.210	0.898	0.934	1692
F(0 0 0)	2488	1112	496	1.113
Crystal size (mm)	0.10 × 0.24 × 0.36	0.08 × 0.24 × 0.24	0.08 × 0.28 × 0.32	0.14 × 0.18 × 0.18
Description of crystal	Pale-yellow tablet	Orange–red fragment	Orange-yellow plate	dark-brown fragment
Transmission coefficients (minimum, maximum)	0.93, 0.98	0.81, 0.93	0.74, 0.93	0.82, 0.86
Index ranges	$0 \leqslant h \leqslant 35$, $0 \leqslant k \leqslant 28$, $0 \leqslant l \leqslant 14$	$-12 \leqslant h \leqslant 12$, $0 \leqslant k \leqslant 18$, $0 \leqslant l \leqslant 23$	$-12 \leqslant h \leqslant 12$, $-12 \leqslant k \leqslant 12$, $0 \leqslant l \leqslant 14$	$-14 \leqslant h \leqslant 14$, $-20 \leqslant k \leqslant 20$, $-30 \leqslant l \leqslant 31$
Reflections measured	61 092	17 222	14 614	48 110
Unique reflections	7661	5564	4653	16 773
R_{int}	0.053	0.034	0.047	0.049
Observed reflections ($I > 3\sigma(I)$)	6248	4067	3226	10 163
Parameters refined	363	305	250	964
Goodness of fit	1.0822	1.1131	1.1138	1.0901
R	0.0365	0.0279	0.0340	0.0409
wR	0.0415	0.0304	0.0368	0.0488
Residual electron density (minimum, maximum) (e Å^{-3})	−0.30, 0.40	−0.61, 0.61	−0.54, 0.38	−0.42, 0.52

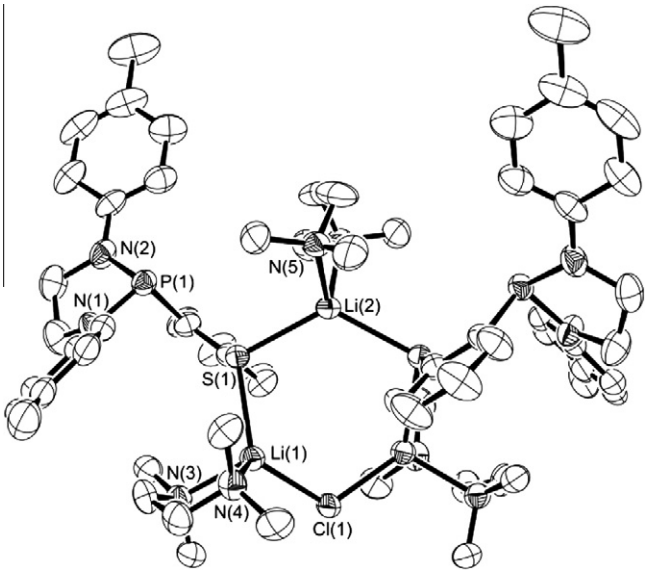


Fig. 2. ORTEP representation (50% probability ellipsoids) of the molecular structure of the LiCl/TMEDA adduct of the proligand Li[$\mathbf{L^2}$]. Hydrogen atoms have been omitted for clarity.

Table 2
Selected bond distances (Å) and angles (°) for Li[$\mathbf{L^2}$]·0.5LiCl·1.5TMEDA.

Li(1)—Cl(1)	2.259(3)	S(1)—C(1)	1.843(2)
Li(1)—S(1)	2.474(3)	P(1)—C(6)	1.7209(19)
Li(2)—S(1)	2.483(2)	P(1)—N(2)	1.7402(17)
S(1)—C(1)	1.7575(19)		
S(1)—Li(2)—S(1)	123.45(17)	N(1)—P(1)—N(2)	118.40(8)
Li(1)—S(1)—Li(2)	108.77(11)	N(1)—P(1)—C(6)	120.79(8)
S(1)—Li(2)—Cl(1)	125.36(13)	N(1)—P(1)—N(2)	91.88(10)
Li(1)—P(1)—N(2)	114.82(16)		

The six-membered assembly of three Li^+ ions, one Cl^- ion and two of the sulfur atoms of the 1,3,2-diazaphospholidin-2-ylbenzenethiolate unit is located on a crystallographic twofold axis of symmetry. The Li_3ClS_2 ring is appreciably non-planar, with the sulfur atoms displaced by 0.67 Å from the plane of the lithium and chloride ions. The P—N bond lengths of 1.7209(19) and 1.7402(17) Å are at the upper range of values expected for a P—N single bond [28]. The five-membered 1,3,2-diazaphospholidine ring has similar geometry to the previously published platinum-1,3,2-diazaphospholidine complex [29], and the bond angles around the phosphorus atom are similar to the literature values [29]. The P(1)—C(6) bond length at 1.843(2) Å is consistent with the value of 1.8251(15) Å for the cyclic lithium salt, [{$(Me_3Si)_2CH$}P(C_6H_4-2-S){Li(tmeda)}]{Li(tmeda)}, synthesized by Clegg and co-workers [30]. This indicates that the long P—Cl bond observed in the solid state structure of compounds similar to the ligand precursor is a result of the bonding between phosphorus and chlorine atoms and not as a result of the presence of the 1,3,2-diazaphospholidine ring.

The ^{1}H NMR spectrum for Li[$\mathbf{L^2}$]·0.5LiCl·1.5TMEDA in $CDCl_3$ shows the presence of 1.5 equivalents of TMEDA for each PS unit in accord with the stoichiometry of the X-ray structure. However, the fact that the TMEDA protons are observed as two sharp singlets in the ^{1}H NMR spectrum and the carbons as two sharp singlets in the ^{13}C suggests that the TMEDA molecules are magnetically equivalent. This indicates that it is unlikely that the solid state structure is preserved in the solution state or that there is a rapid fluxional process. All of the other ^{1}H NMR resonances for $\mathbf{L^1}$ and $\mathbf{L^2}$ are consistent with the observed solid state structure shown in Fig. 2. The ^{31}P NMR spectrum for Li[$\mathbf{L^2}$]·0.5LiCl·1.5TMEDA shows a broad singlet at 94.7 ppm (cf. 89.5 ppm for $\mathbf{L^1}$) which is in the same region as the previously published compound 1,2,3-triphenyl-1,3,2-diazaphospholidine (83.2 ppm) [31]. The broad nature of the ^{31}P NMR peak could be due to the fluxional coordination/dissociation of the lithium and TMEDA in solution and the

inherent fluxionality of the five-membered diazaphospholidine ring. Attempts to remove the LiCl by recrystallization were not successful and only uncharacterizable solids were obtained which did not react cleanly with the precursor complexes. The initial solid obtained from the ligand synthesis was therefore reacted without further purification. Previously, especially with the extremely versatile 2-(diphenylphosphino)benzenethiolate ligand (DPPTH), the bidentate phosphinothiolate ligands readily and cleanly formed complexes with a range of transition metals. However, the ligands H**L**^{1} and H**L**^{2} (or their lithium salts), when reacted with any of the ruthenium, tungsten or rhenium precursors used successfully for DPPTH, formed intractable mixtures that could not be characterized. This suggests that in contrast to all other aromatic phosphinothiolates investigated the octahedral complexes [M(PS)$_3$] are not accessible with these very large phosphine substituents. We therefore turned our attention to metals that formed square planar complexes with [M(PS)$_2$] stoichiometries (Scheme 1).

2.4.1. Synthesis and structural behavior of [Rh(L^1)(nbd)]BF$_4$ (3) and [Rh(L^2)(nbd)]BF$_4$ (**4**)

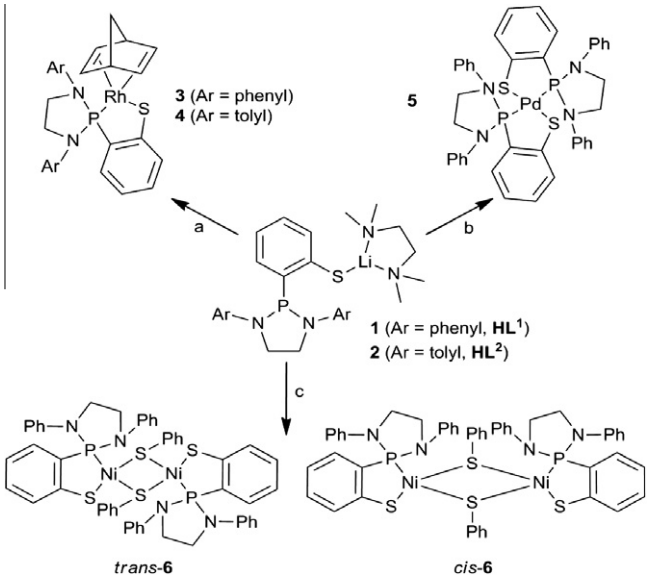
The reaction of approximately one equivalent of the ligand lithium 2-(1,3-diphenyl-1,3,2-diazaphospholidin-2-yl)benzenethiolate **L**^{1} or **L**^{2} with [Rh(nbd)$_2$)]$^+$BF$_4^-$ (nbd = norbornadiene) in CH_2Cl_2 at room temperature produced a bright red solution almost immediately. After the volume was reduced to ca. 5 cm^3, pentane was added producing a small amount of an orange precipitate. This solid was removed by filtration and the resulting clear bright red solution evaporated to dryness. The red colored solid produced was washed with pentane and dried under vacuum, giving **3** and **4** as orange/red microcrystalline solids in 71% and 99% yields, respectively. The elemental analysis was consistent with the formulation [Rh(**L**^{1})(nbd)]. The positive electrospray mass spectrum for **3** shows a series of peaks with the most intense peaks at *m/z* = 545.1, 551.1, 567.1 and 583.1 which correspond to [M+H]$^+$, [M+Li]$^+$, [M+Na]$^+$ and [M+K]$^+$, respectively. The ^{1}H NMR spectrum of **3** shows that the complex formed contains one anionic diazaphospholidin-2-yl-benzenethiolate ligand and one nbd ligand as expected. As observed for the free ligand, the four C*H*$_2$N protons appear as two complex multiplets. One is due to the protons on one side of the five-membered P—N—C—C—N ring facing the nbd ligand and the other mulitplet due to the two protons on the other side being directed towards the aryl ring. They appear as complex multiplets due to couplings to the geminal and vicinal protons and phosphorus. The asymmetric P,S-donor set results in the C=C*H* protons at opposite ends of the nbd ligand being inequivalent as the two carbon atoms to which they are attached are *trans* to different donor atoms. This results in the nbd protons appearing as four multiplets (eight protons). Finally, the 14 aromatic protons are observed between 6.76 and 7.50 ppm as expected. The ^{13}C NMR showed the expected 10 resonances all of which have been assigned and are consistent with the structure. Upon recrystallization of **3** by layering a CH_2Cl_2 solution with pentane, an orange–red polycrystalline aggregate was produced. This was cut to give a plate-like fragment which was used for X-ray structure determination. An ORTEP representation of the structure is shown in Fig. 3 and selected bond lengths and angles are presented in Table 3.

The X-ray crystal structure shows that the P—N bond lengths are indicative of single bonds at 1.705(2) and 1.696(2) Å for P(1)—N(1) and P(1)—N(2), respectively. The Rh—S—C—C—P chelate ring is essentially planar with the sum of the internal angles at 539.86° (cf. 540° for a planar pentagon). The Rh(1)—P(1) bond length of 2.2066(6) Å is similar to the published values for the known compounds [Rh(cod)(S,P-SC$_2$B$_{10}$H$_{10}$PPh$_2$)], A at 2.2615(9) Å, and [{Rh(S,P-μ-SC$_2$B$_{10}$H$_{10}$PPh$_2$)(CO)}$_2$], B at 2.224(3) Å [32]. Similarly, the Rh(1)—S(1) bond length of 2.3071(7) Å is comparable to those reported for A and B at 2.295(1) and 2.349(3) Å, respectively [32].

As anticipated, the analytical and spectroscopic data for **4** were similar to the closely related complex **3**. Unfortunately, we were unable to grow crystals of **4** suitable for X-ray crystallographic analysis. There was no evidence for a complex of the type [Rh(PS)$_2$]$^-$ even with the use of an excess of the lithium salt of the ligand.

2.4.2. Synthesis and structural behavior of [Pd(L^1)$_2$] (**5**)

The addition of approximately two equivalents of the ligand lithium 2-(1,3-diphenyl-1,3,2-diazaphospholidin-2-yl)benzenethiolate (from HL^1) to Na$_2$PdCl$_4$ in methanol at room temperature produced an orange precipitate almost immediately. The solution was stirred at room temperature for 1 h, during which time no further change occurred. The solid was isolated by filtration, washed with methanol and ether and dried under vacuum. The product was obtained as an orange solid in good yield (79%). The elemental analysis of the sample was in good agreement with the values expected for the proposed structure. The IR spectrum showed peaks at 3058, 2868 and 1597 cm^{-1} assigned to ν_{C-H}(aromatic), ν_{C-H}(aliphatic) and $\nu_{C=C}$, respectively. Finally, as seen for complexes **3** and **4**, the positive electrospray mass spectrum showed a series of peaks with the most intense peaks at *m/z* = 805.1,



Scheme 1. Reagents/conditions: (a) [Rh(nbd)$_2$]BF$_4$, CH_2Cl_2, rt (b) Na$_2$PdCl$_4$, MeOH, rt (c) Ni(acac)$_2$·4H$_2$O, MeOH, rt.

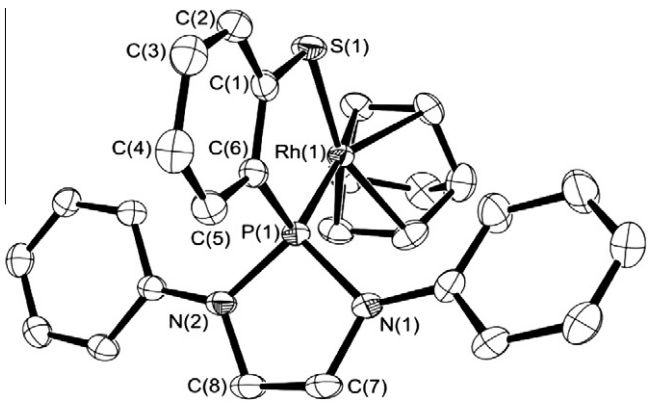


Fig. 3. ORTEP representation (50% probability ellipsoids) of the X-ray crystal structure of [Rh(L^1)(nbd)] **3** with hydrogen atoms omitted for clarity.

Table 3
Selected bond distances (Å) and angles (°) for **3**.

Rh(1)—S(1)	2.3071(7)	S(1)—C(1)	1.770(3)
Rh(1)—P(1)	2.2066(6)	P(1)—C(6)	1.808(3)
P(1)—N(1)	1.705(2)	P(1)—N(2)	1.696(2)
N(1)—C(7)	1.462(3)	N(2)—C(8)	1.467(3)
S(1)—Rh(1)—P(2)	87.49(2)	Rh(1)—P(1)—N(1)	118.40(8)
Rh(1)—S(1)—C(1)	105.50(9)	Rh(1)—P(1)—N(2)	120.79(8)
Rh(1)—P(1)—C(6)	109.41(8)	N(1)—P(1)—N(2)	91.88(10)

811.1 and 827.1 which correspond to $[M+H]^+$, $[M+Li]^+$ and $[M+Na]^+$. The ^{31}P NMR spectrum of **5** in CD_2Cl_2 showed two distinct phosphorus environments. The two peaks were both singlets and were observed at 116.7 and 104.8 ppm in a 1:3 ratio (from the integrated intensity). These two peaks have been tentatively assigned to the *cis* and *trans* isomers of the product. Due to the steric requirements of the ligand, it is expected that the major product is the *trans* isomer. The two isomers would be expected to have significantly different ^{31}P chemical shifts as the *cis* isomer has the two phosphorus atoms bound *trans* to an anionic sulfur atom, and the *trans* isomer has the two phosphorus atoms bound *trans* to each other. The alternative possibility, of an unbound phosphorus is unlikely as the chemical shift in the ^{31}P NMR spectrum would be closer to the free ligand (ca. 90 ppm) not the observed signal at 116.7 ppm.

The ^1H NMR of the solid was, as expected, relatively complex, with the aromatic region appearing as a large multiplet. The distinctive resonances corresponding to the CH_2N protons appeared as broad multiplets at 4.02 and 3.92 ppm, with the ratio of the integrated intensity of these peaks approximately 1:7 relative to the aromatic region as anticipated. The complex is not particularly soluble, thus obtaining a good quality ^{13}C spectrum was difficult. The problem was compounded by both the fact that three of the expected 11 peaks are due to quaternary carbons, and also that any carbon coupled to phosphorus is expected to appear as a virtual multiplet due to the presence of two phosphorus atoms coordinated to the palladium center. For these reasons it was not possible to resolve the quaternary carbon peaks from the baseline. Seven peaks were identified and assigned to the *C*H carbons of the aromatic rings, and a further peak at 46.2 ppm to the CH_2N carbon atoms. The ^{13}C spectrum only appears to show the presence of one species, although its possible that the second product has a coincidental ^{13}C spectrum, or that the peaks are so weak that they cannot be distinguished from the baseline. Recrystallization of **5** by layering a CH_2Cl_2 solution with pentane produced orange-yellow plates suitable for a X-ray structure analysis (Fig. 4 with selected bond lengths/angles are presented in Table 4).

As expected for a d^8 transition metal complex, complex **5** adopts a square planar geometry and the steric constraints of the ligand do not prevent the coordination of two PS ligands in a *trans* configuration. In fact, the palladium ion lies on a crystallographic center of inversion, which implies that the coordination geometry of the metal is planar. Furthermore, the two five-membered Pd—P—C—C—S chelate rings are essentially planar with the sum of the internal angles at 539.71° (cf. 540° for a planar pentagon). The X-ray crystal structure also shows P—N bond lengths indicative of single bonds at 1.695(3) and 1.688(3) Å for P(1)—N(1) and P(1)—N(2) respectively, in close agreement to the values obtained for Li[**L²**]·0.5LiCl·1.5TMEDA. The Pd(1)—P(1) bond length of 2.2852(7) Å is similar to the published values for the known compounds [Pd{1-(diphenylphosphino)butane-2-thiolato}$_2$] at 2.297 Å (average) and [Pd{1-(diphenylphosphino-3-benzyloxy)-propane-2-thiolato}$_2$] at 2.281 Å (average) [5,8]. Despite the apparent observation of two isomers in solution by ^{31}P NMR, the crystals isolated were only of the *trans* form.

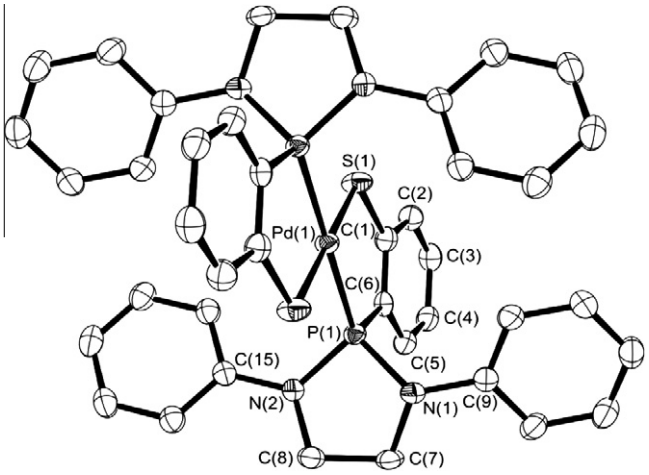


Fig. 4. ORTEP view (50% probability ellipsoids) of the X-ray crystal structure of [Pd(L^1)$_2$] **5** with hydrogen atoms and solvent omitted for clarity.

Table 4
Selected bond distances (Å) and angles (°) for [Pd(L^1)$_2$] **5**.

Pd(1)—S(1)	2.3072(8)	S(1)—C(1)	1.764(3)
Pd(1)—P(1)	2.2852(7)	P(1)—C(6)	1.802(3)
P(1)—N(1)	1.695(3)	P(1)—N(2)	1.688(3)
N(1)—C(7)	1.474(4)	N(2)—C(8)	1.477(4)
C(7)—C(8)	1.512(4)	C(1)—C(6)	1.396(4)
S(1)—Pd(1)—P(2)	87.84(3)	S(1)—C(1)—C(6)	123.2(2)
Pd(1)—S(1)—C(1)	104.73(10)	C(1)—C(6)—P(1)	117.0(2)
Pd(1)—P(1)—C(6)	106.94(10)	N(1)—P(1)—N(2)	92.52(12)
Pd(1)—P(1)—N(1)	121.78(9)	Pd(1)—P(1)—N(2)	118.09(9)

Interestingly, measurements of the unit-cell parameters of the crystals as a function of temperature showed a marked discontinuity indicative of a phase change. This appeared to be reversible, but exhibited a considerable degree of hysteresis. The two phases are structurally similar, but the high-temperature phase contained disorder of the solvent of crystallization and of the phenyl ring, C(15)—C(20).

*2.4.3. Synthesis and structural behavior of cis- and trans-[Ni$_2${SC$_6$H$_4$-P(NPh)$_2$C$_2$H$_4$}$_2$(SPh)$_2$] (**6**)*

In contrast to the reactions discussed above, the addition of half an equivalent of [Ni(acac)$_2$]·4H$_2$O to a solution of the ligand lithium 2-(1,3-diphenyl-1,3,2-diazaphospholidin-2-yl)benzenethiolate (Li[**L¹**]) in methanol at room temperature did not immediately produce a pure compound. Although the ES(+) MS spectrum of the product showed exclusively the ion at m/z = 757.1 corresponding to [Ni(**L¹**)$_2$+H$^+$], the NMR solution spectra were complex and could not be assigned. It appeared that the initial solid formed is a mixture containing at least some neutral *bis*(ligand) Ni(II) complex. Recrystallization of the crude solid above by layering a CH_2Cl_2 solution with pentane produced a dark brown polycrystalline aggregate. This was cut to give a fragment which was suitable for X-ray structure analysis. The X-ray crystal structure found that the structure was not in fact monometallic but incorporated two Ni**L¹** units bridged by two thiophenolates. An assembly of this complex with both ligands on the same side (designated *cis*) or on opposing sides (designated *trans*) was noted from the crystal structure and explained the complex nature of the NMR spectra. The asymmetric unit of the crystal contains a molecule of the *trans* isomer (Fig. 5) of the dimeric complex located on a crystallographic center of inversion, together with a molecule of the *cis* isomer (Fig. 6) located on a site with no crystallographic symmetry, and

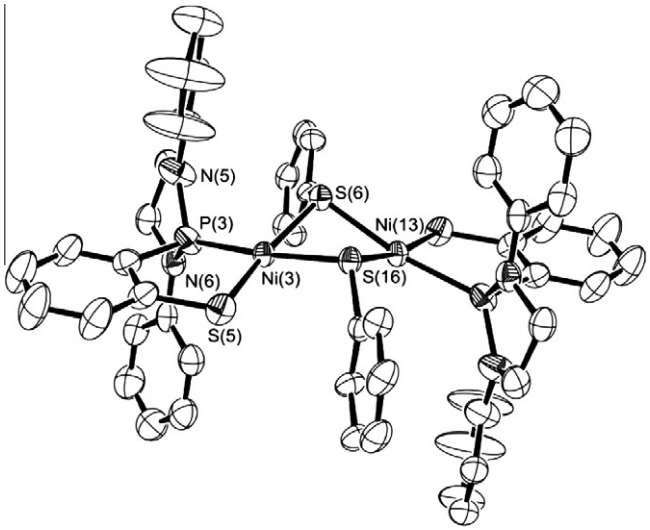


Fig. 5. ORTEP view (50% probability ellipsoids) of the X-ray crystal structure of '*trans*'-$[Ni_2\{SC_6H_4P(NPh)_2C_2H_4\}_2(SPh)_2]$ **6** with hydrogen atoms and solvent omitted for clarity.

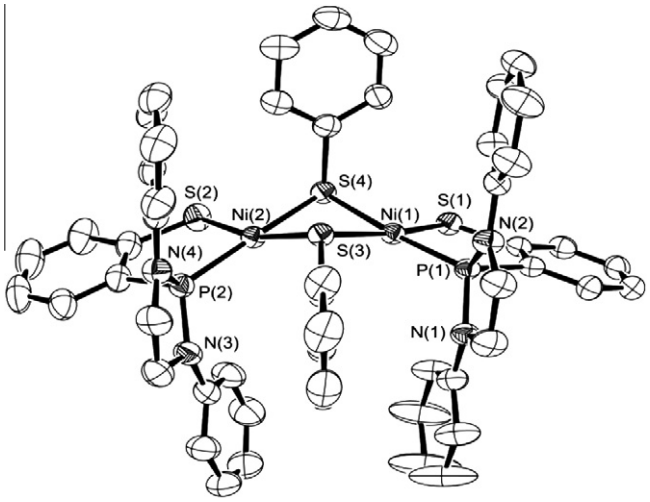


Fig. 6. ORTEP view (50% probability ellipsoids) of the X-ray crystal structure of '*cis*'-$[Ni_2\{SC_6H_4P(NPh)_2C_2H_4\}_2(SPh)_2]$ **6** with hydrogen atoms and solvent omitted for clarity.

a molecule of CH_2Cl_2 (see Table 5 for selected geometric parameters).

The NiS_2Ni units of both the *cis* and *trans* isomers are nonplanar with two possible geometries for the $Ni(SPh)_2Ni$ unit. The bridging S atoms lie further still from this plane and both S-phenyl groups occupy 'equatorial' positions in both of the two possible $Ni(SPh)_2Ni$ positions for the *trans* isomer. In contrast, in the *cis* isomer one of the S-phenyl groups occupies an axial position. The presence of the bridging thiophenolate groups indicates that partial decomposition of the ligands through P—C bond cleavage has occurred. This degradation of the ligand may be due to the presence of water of crystallization in the $[Ni(acac)_2]\cdot 4H_2O$ starting material, although reactions of P—N ligands catalyzed by nickel have been reported [33]. For example, the reaction of $Ph_2PN(Li)Ph$ with $[NiCl_2(PPh_3)_2]$ produced the dimer $[\{Ni(N,N\text{-}PhNPPh_2NPh)(Ph_2P)\}_2]$, which was characterized by X-ray crystallography [33]. We conclude that in this instance the P—N bonds are cleaved during recrystallization, followed by hydrolytic loss of P to give thiophenol, but the details of the mechanism are unknown.

Table 5
Selected bond distances (Å) and angles (°) for **6**.

trans		*cis*	
Ni(1)—S(1)	2.1660(9)	Ni(3)—S(5)	2.1004(12)
Ni(1)—P(1)	2.1414(8)	Ni(3)—P(3)	2.0864(12)
Ni(1)—S(3)	2.2042(9)	Ni(3)—S(6)	2.1979(17)
Ni(1)—S(4)	2.2520(8)	Ni(3)—S(16)	2.2369(16)
Ni(2)—S(2)	2.1659(9)	Ni(13)—S(5)[a]	2.2391(12)
Ni(2)—P(2)	2.1572(9)	Ni(13)—P(3)[a]	2.2550(12)
Ni(2)—S(3)	2.2037(8)	Ni(13)—S(16)	2.2026(17)
Ni(2)—S(4)	2.2540(9)	Ni(13)—S(6)	2.2374(17)
Ni(1)···Ni(2)	3.1284(11)	Ni(3)···Ni(13)	3.1337(5)
S(1)—Ni(1)—P(1)	89.88(3)	S(5)—Ni(3)—P(3)	93.69(5)
S(1)—Ni(1)—S(3)	169.82(3)	S(5)—Ni(3)—S(6)	168.00(6)
P(1)—Ni(1)—S(3)	100.03(3)	P(3)—Ni(3)—S(6)	97.56(6)
S(1)—Ni(1)—S(4)	87.17(3)	S(5)—Ni(3)—S(16)	89.42(5)
P(1)—Ni(1)—S(4)	175.11(3)	P(3)—Ni(3)—S(16)	174.53(7)
S(3)—Ni(1)—S(4)	82.78(3)	S(6)—Ni(3)—S(16)	79.04(6)
S(2)—Ni(2)—P(2)	90.02(4)	S(5)[a]—Ni(13)—P(3)[a]	85.62(4)
S(2)—Ni(2)—S(3)	164.52(4)	S(5)[a]—Ni(13)—S(16)	169.79(7)
P(2)—Ni(2)—S(3)	101.51(3)	P(3)[a]—Ni(13)—S(16)	100.18(6)
S(2)—Ni(2)—S(4)	86.38(3)	S(5)[a]—Ni(13)—S(6)	93.88(5)
P(2)—Ni(2)—S(4)	174.68(4)	P(3)[a]—Ni(13)—S(6)	170.00(7)
S(3)—Ni(2)—S(4)	82.75(3)	S(6)—Ni(13)—S(16)	78.93(6)
Ni(1)—S(3)—Ni(2)	90.62(3)	Ni(3)—S(6)—Ni(13)	89.17(6)
Ni(1)—S(6)—Ni(2)	88.13(3)	Ni(13)—S(16)—Ni(3)	89.60(6)
^Between NiS_2 planes	48.0	^Between NiS_2 planes	40.8
^Between Ni_2S planes	52.4	^Between Ni_2S planes	43.2

[a] Related to asymmetric unit by inversion, symmetry operator $-x, -y, 1-z$.

The large thermal parameters of some of the *N*-phenyl carbon atoms of both isomers suggest that there may be unresolved disorder of these groups. Attempts to model this did not lead to any improvement in the agreement with the X-ray data and were abandoned. An attempt was also made to refine the structure in the space group P_1 but this failed to reach convergence and the disorder was still clearly apparent, suggesting the original assignment of symmetry to be correct. The *cis* isomer and solvent do not exhibit any resolvable disorder. Geometric restraints were applied to the disordered phenyl groups: the C—C bond lengths were restrained to 1.39(2) Å and the C—C—C angles to 120(2)°. Similarity restraints were applied to the thermal parameters of directly-bonded pairs of disordered carbon atoms. In both metal sites, the nickel, phosphorus and bridging sulfur atoms are all approximately coplanar in a square planar coordination geometry. For the Ni(1) site of the *cis* complex the S atom of the PS-ligand approximately lies on the same plane. However, for the Ni(2) site, this atom lies 0.48 Å away from the $NiP(S_{bridge})_2$ plane. The geometry of the 1,3,2-diazaphospholidine ligand in these complexes is very similar to that seen in the X-ray crystal structures of **3** and **5**. The average $Ni—S_{diazaphospholidine}$ bond length of 2.168 Å is similar to the literature values for $[Ni(Ph_2PCH_2CH_2S)_2]$ [34] (2.174(1) Å) and $[Ni(Me_2PCH_2CH_2S)_2]$ [3,35] (2.177(1) Å). The average Ni—P bond length is also in good agreement with these known compounds at 2.160 Å (mean; cf. 2.186(1) Å [34] ($[Ni(Ph_2PCH_2CH_2S)_2]$) and 2.166(1) Å [3] ($[Ni(Me_2PCH_2CH_2S)_2]$)).

3. Conclusions

Two sterically demanding PS-ligands have been prepared and reacted with several transition metal precursor complexes. The resultant complexes were characterized in the solid and solution states. It appears that increasing bulk at phosphorus prevented formation of octahedral $M(PS)_3$ type complexes, but square planar complexes of the type $M(PS)_2$ and $LM(PS)$ were isolated and characterized. Attempts to prepare nickel(II) complexes led to P—C bond cleavage and formation of thiophenolate bridged complexes.

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Appendix A. Supplementary data

CCDC 767739, 767740, 767741 and 767742 contain the supplementary crystallographic data for Li[**L²**], **3**, **5** and **6**. This 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.

References

[1] E. Block, V. Eswarakrishnan, M. Gernon, G. Oforiokai, C. Saha, K. Tang, J. Zubieta, J. Am. Chem. Soc. 111 (1989) 658.
[2] E. Block, G. Oforiokai, J. Zubieta, J. Am. Chem. Soc. 111 (1989) 2327.
[3] M. Kita, T. Yamamoto, K. Kashiwabara, J. Fujita, Bull. Chem. Soc. Jpn. 65 (1992) 2272.
[4] J.R. Dilworth, A.J. Hutson, J. Zubieta, Q. Chen, Transition Met. Chem. (London) 19 (1994) 61.
[5] N. Brugat, J. Duran, A. Polo, J. Real, A. Alvarez-Larena, J.F. Piniella, Tetrahedron: Asymmetry 13 (2002) 569.
[6] D. Morales-Morales, R. Redon, Y.F. Zheng, J.R. Dilworth, Inorg. Chim. Acta 328 (2002) 39.
[7] J. Duran, N. Brugat, A. Polo, C. Segura, J. Real, X. Fontrodona, J. Benet-Buchholz, Organometallics 22 (2003) 3432.
[8] A. Dervisi, R.L. Jenkins, K.M.A. Malik, M.B. Hursthouse, S. Coles, Dalton Trans. (2003) 1133.
[9] E. Block, H. Kang, G. Oforiokai, J. Zubieta, Inorg. Chim. Acta 156 (1989) 27.
[10] E. Block, H.Y. Kang, G. Oforiokai, J. Zubieta, Inorg. Chim. Acta 166 (1989) 155.
[11] J.R. Dilworth, J. Hu, J.R. Miller, D.L. Hughes, J.A. Zubieta, Q. Chen, J. Chem. Soc., Dalton Trans. (1995) 3153.
[12] J.R. Dilworth, J.R. Miller, N. Wheatley, M.J. Baker, J.G. Sunley, J. Chem. Soc., Chem. Commun. (1995) 1579.
[13] J.R. Dilworth, A.J. Hutson, J.S. Lewis, J.R. Miller, Y.F. Zheng, Q. Chen, J. Zubieta, J. Chem. Soc., Dalton Trans. (1996) 1093.
[14] J.R. Dilworth, Y.F. Zheng, D.V. Griffiths, J. Chem. Soc., Dalton Trans. (1999) 1877.
[15] J.R. Dilworth, D. Morales, Y.F. Zheng, J. Chem. Soc., Dalton Trans. (2000) 3007.
[16] C.A. Grapperhaus, S. Poturovic, M.S. Mashuta, Inorg. Chem. 44 (2005) 8185.
[17] J.R. Dilworth, N. Wheatley, Coord. Chem. Rev. 199 (2000) 89.
[18] J.R. Dilworth, Y.F. Zheng, S.F. Lu, Q.J. Wu, Transition Met. Chem. (London) 17 (1992) 364.
[19] P. Perez-Lourido, J. Romero, J.A. Garcia-Vazquez, J. Castro, A. Sousa, L. Cooper, J.R. Dilworth, R.L. Richards, Y.F. Zheng, J.A. Zubieta, Inorg. Chim. Acta 356 (2003) 193.
[20] G.D. Figuly, C.K. Loop, J.C. Martin, J. Am. Chem. Soc. 111 (1989) 654.
[21] M.B. Abrams, B.L. Scott, R.T. Baker, Organometallics 19 (2000) 4944.
[22] A.R. Katritzky, W. Fan, C. Fu, J. Org. Chem. 55 (1990) 3209.
[23] W.-W. Tian, J.-Y. Xu, Z.-Q. Feng, S.-L. Dong, J.-T. Wang, Acta Crystallogr., Sect. E: Struct. Rep. E64 (2008) o135.
[24] J. Cosier, A.M. Glazer, J. Appl. Crystallogr. 19 (1986) 105.
[25] Z. Otwinowski, W. Minor, Macromol. Crystallogr., Part A 276 (1997) 307.
[26] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, J. Appl. Crystallogr. 27 (1994) 1045.
[27] P.W. Betteridge, J.R. Cooper, R.I. Cooper, K. Prout, D.J. Watkin, J. Appl. Crystallogr. 36 (2003) 1487.
[28] M.T. Ashby, Z. Li, Inorg. Chem. 31 (1992) 1321.
[29] I.C.F. Vasconcelos, G.K. Anderson, N.P. Rath, C.D. Spilling, Tetrahedron: Asymmetry 9 (1998) 927.
[30] S. Blair, K. Izod, R.W. Harrington, W. Clegg, Organometallics 22 (2003) 302.
[31] M.K. Das, J.J. Zuckerman, Inorg. Chem. 10 (1971) 1028.
[32] M. Gerisch, J.R. Krumper, R.G. Bergman, T.D. Tilley, J. Am. Chem. Soc. 123 (2001) 5818.
[33] D. Fenske, B. Maczek, K. Maczek, Z. Anorg. Allg. Chem. 623 (1997) 1113.
[34] Y.M. Hsiao, S.S. Chojnacki, P. Hinton, J.H. Reibenspies, M.Y. Darensbourg, Organometallics 12 (1993) 870.
[35] R.E. Marsh, M. Kapon, S.Z. Hu, F.H. Herbstein, Acta Crystallogr., Sect. B: Struct. Sci. 58 (2002) 62.