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Synthesis of trifunctional ligands containing thiophosphoryl, pyridine and pyridine *N*-oxide donor groups

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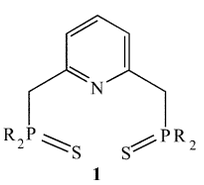
The trifunctional mixed donor ligands 2,6-$[R_2P(S)CH_2]_2C_5H_3N$ **1** (R = Ph **1a**, Tol **1b**, *n*-Bu, **1c**) and 2,6-$[R_2P(S)CH_2]_2C_5H_3NO$ **2** (R = Ph **2a**, Tol **2b**, *n*-Bu, **2c**) have been prepared and characterized by spectroscopic (MS, IR, NMR) techniques. The coordination chemistry of one derivative **1a** has been examined and the complex $\{[Ph_2P(S)CH_2]_2C_5H_3N\}Ni(NO_3)_2$ has been crystallized and characterized by single-crystal X-ray diffraction methods. The structure contains a six coordinate Ni(II) ion bonded to a tridentate ligand **1a** with Ni–N_{pyr} 2.110(3) Å and Ni–S 2.481(1) and 2.402(1) Å, a bidentate nitrate anion and a monodentate NO_3^- anion.

Introduction

The coordination chemistry of lanthanide, Ln(III), and actinide, An(III), ions in aqueous solutions, in many respects, is very similar.[1] Therefore, the logical design of ligands that might selectively coordinate with one of these ions or a small group of ions in a complex matrix represents a great challenge.[2] Both classes of ions are normally considered to be "hard" and they tend to bind relatively strongly to neutral and anionic ligands containing oxo-donor sites,[1,2] *e.g.* phosphine oxides and N-oxides. In this regard, we have prepared and studied a number of bifunctional and trifunctional ligands that contain phosphine oxide and pyridine *N*-oxide donor groups[3,4] and it is observed that the ligands with proper "backbone" designs strongly chelate with Ln(III), An(III) and An(IV) cations. Further, it appears that An(III) binding in the case of Am(III) is slightly favored over Eu(III) binding.[5,6] It has been previously suggested that "softer" donors (N and S) might more strongly favor coordination with An(III) ions over Ln(III) ions of similar size[7–13] and limited liquid–liquid extraction data support this proposal. As a result, our group has been attempting to prepare "softened" derivatives of the oxo ligands previously reported by us. This includes examples where the pyridine *N*-oxide group is replaced by a pyridine fragment and the phosphine oxide group is replaced by phosphine sulfide. Of course, this ligand softening opens up the possibility that these new ligands may coordinate effectively with main group or transition metal cations. In this regard, we report here the synthesis of two trifunctional ligand types, 2,6-$[R_2P(S)CH_2]_2C_5H_3N$ **1** (R = Ph **1a**, Tol **1b** and *n*-Bu **1c**) and 2,6-$[R_2P(S)CH_2]_2C_5H_3NO$ **2** (R = Ph **2a**, Tol **2b** and *n*-Bu **2c**), and the coordination chemistry of **1a** toward Ni(II).



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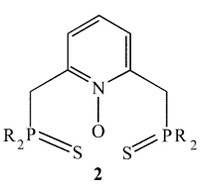

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Results and discussion

The oxophilicity of phosphorus somewhat limits the synthetic approaches that may be employed to successfully prepare the trifunctional phosphinomethylpyridine *P*,*P*′-disulfides, **1**, and phosphinomethylpyridine *N*-oxide *P*,*P*′-disulfides, **2**. Nonetheless, the chemistry outlined in Schemes 1 and 2 provides good to modest yields of the target compounds. Compound **1a** was most conveniently obtained by allowing 2,6-bis(chloromethyl)-pyridine to react with two equivalents of $KPPh_2$ in THF. The intermediate 2,6-bis[(diphenylphosphino)methyl]pyridine was treated, without isolation, with sulfur and the mixture, after standard workup, gave 2,6-bis[(diphenylphosphino)methyl]-pyridine *P*,*P*′-disulfide, **1a**, as a white solid in 89% yield. The compound shows modest solubility in $CHCl_3$, but little solubility in other common organic solvents. The compound also can be obtained from the combination of $Ph_2P(S)Li$ and 2,6-bis-(chloromethyl)pyridine, but the yield is significantly lower. Attempts to prepare the corresponding N-oxide derivative **2a** by peroxide oxidation of the pyridine nitrogen atom in **1a** led to replacement of the sulfur atoms on phosphorus by oxygen atoms with formation of 2,6-bis[(diphenylphosphino)methyl]-pyridine *N*,*P*,*P*′-trioxide. However, **2a** was obtained in 86% yield by combination of two equiv. of $KPPh_2$ with 2,6-bis(chloromethyl)pyridine *N*-oxide in THF followed by treatment, without isolation, of the bis-phosphine with sulfur. The 2,6-bis[(diphenylphosphino)methyl]pyridine *N*-oxide *P*,*P*′-disulfide was obtained as a white solid that is moderately soluble in $CHCl_3$ but insoluble in aliphatic and aromatic hydrocarbons. The success of this reaction may seem surprising since phosphines have been used to deoxygenate pyridine *N*-oxides.[14] However, room temperature deoxygenation reactions typically employ a highly electrophilic phosphine such as PCl_3 or PBr_3. More electron rich phosphines, *e.g.* Ph_3P, generally require forcing conditions to accomplish oxygen atom transfer. The electron rich diphenyl phosphide clearly prefers to undergo the chloride displacement chemistry.

Due to the modest solubilities of **1a** and **2a**, syntheses for derivatives with tolyl and *n*-butyl substituents were explored. Since the precursor phosphines Tol_2PH and Bu_2PH are expensive and/or less readily available from commercial suppliers, alternative synthetic routes for **1b**, **2b** (Tol) and **1c**, **2c** (Bu) were sought. The method selected here involved treatment of commercially available $(EtO)_2P(O)H$ with Lawesson's reagent which afforded $(EtO)_2P(S)H$ in 82% yield.[15,16] This reagent was treated with the appropriate organolithium reagent, TolLi or BuLi, and the resulting mixtures combined directly with 2,6-bis(chloromethyl)pyridine (0.5 equiv.) to give **1b** and **1c**, respectively, or 2,6-bis(chloromethyl)pyridine *N*-oxide (0.5 equiv.) to give **2b** and **2c**. In each case, ^{31}P NMR analysis of the crude reaction mixtures showed that the desired compounds were formed in >80% yield. Unfortunately, the crude **1b** and **2b** are sticky solids that proved difficult to rid of pesky impurities. The compounds were purified by repeated recrystallization from cold (−20 °C) acetone or $CHCl_3$–acetone mixtures, but with significant loss of material. Pure samples were recovered with 17 and 33% yields, respectively.[17]

The Bu derivatives **1c** and **2c** were prepared in similar fashions to **1b** and **2b** and the crude yields of orange oily products

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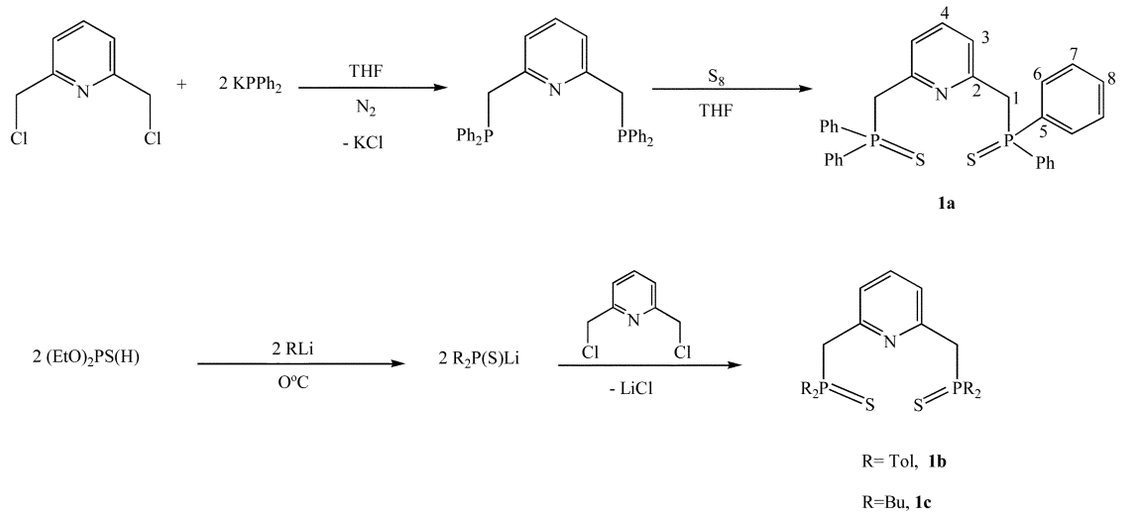
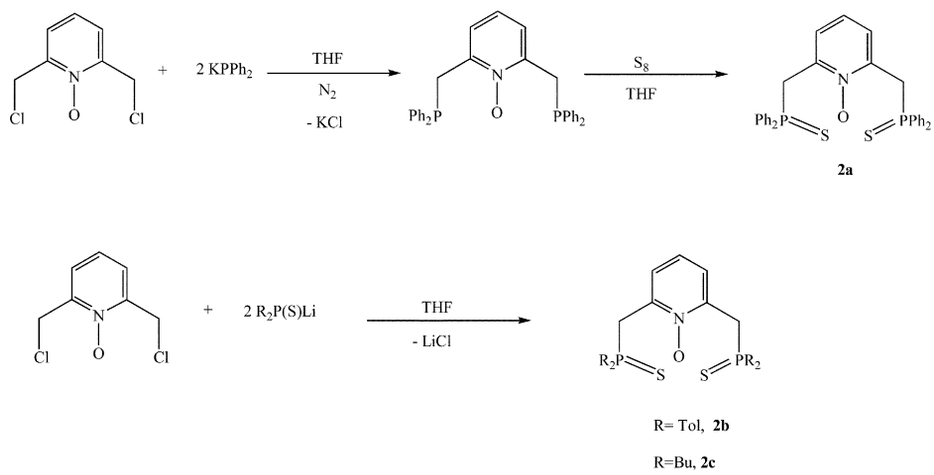


Scheme 1



Scheme 2

were >80%. These compounds show significant solubility in chlorinated solvents, Et_2O, benzene, toluene, xylene and cyclohexane, but they are insoluble in hexane. The greater solubility complicated efforts to purify these compounds and analytically pure samples of **2c** were obtained only after column chromatography on silica gel. This led to significant loss of material: 8–40% isolated yields as faintly orange oils.

The new compounds was characterized by CHN analyses,[18] high or low resolution FAB-MS, IR and ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectroscopy. Compounds **1a**, **2a**, **2b** and **2c** gave satisfactory analytical data. The HRFAB mass spectra of **1a**, **1c** and **2a**–**c** display a (M + H$^+$) parent ion that is the most intense ion and the *m*/*z* values agree well with the calculated molecular weights. A low-resolution FAB MS was obtained for **1b**, and it showed an intense ion at the expected mass for (M + H$^+$). The infrared spectra of **2a**–**c** contain a band at 1230, 1238 and 1248 cm^{-1}, respectively, that may be tentatively assigned to ν_{NO}. These assignments are supported by the absence of a band in this region in **1a**–**c** and the appearance of similar absorptions for 2,6-bis[(phosphino)methyl]pyridine *N*,*P*,*P*′-trioxides, 1260–1240 cm^{-1}.[3,4] Assignment of observed absorptions to ν_{PS} are less certain; however, we propose the following assignments: **1a** 615 cm^{-1}; **1c** 731 cm^{-1}; **2a** 623 cm^{-1}; **2b** 656 cm^{-1}; **2c** 731 cm^{-1}. The $\nu_{P=S}$ bands for the alkyl phosphine sulfides appear at higher frequency as expected[19] and the $\nu_{P=S}$ bands for the aryl phosphine sulfides are comparable with data reported for 2-bis[(diphenylphosphino)methyl]-6-methylpyridine *P*,*P*′disulfide, 625 cm^{-1}, 2-[(diphenylphosphino)methyl]-6-methylpyridine *P* sulfide, 620 cm^{-1}, and 2-bis[(diphenylphosphino)methyl]pyridine *P*,*P*′-disulfide, 620 cm^{-1}.[20] The ^{31}P{^{1}H} NMR spectra of purified samples contain a single resonance in the region expected for thiophosphoryl compounds:[21] **1a** 42.4 ppm; **1b** 40.9 ppm; **1c** 49.6 ppm; **2a** 43.2 ppm; **2b** 40.2 ppm; **2c** 52.8 ppm. The ^{1}H and ^{13}C{^{1}H} spectra are consistent with the organic backbones present in the compounds.

The chelation properties of **1** and **2** toward selected metal ions is of interest and studies of the coordination chemistry with Ln(III) ions and Pu(III) are in progress. In addition, initial surveys of the liquid–liquid extraction performance of **1c** and **2c** are underway. Anticipating that derivatives of **1**, in particular, might also coordinate with and extract selected d- and p-block metals, the molecular coordination chemistry with Ni(II) has been examined. The 1 : 1 combination of **1a** with $Ni(NO_3)_2$ gave $Ni\{[Ph_2P(S)CH_2]_2C_5H_3N\}(NO_3)_2$ in analytically pure form. The complex forms green crystals that display an infrared spectrum with an absorption at 599 cm^{-1}. This is tentatively assigned to a coordinated P=S group with ν_{PS} 15 cm^{-1} lower in frequency than in **1a**. This is consistent with a P=S–Ni coordination interaction.

The molecular structure of the complex was subsequently determined by single crystal X-ray diffraction methods. The complex crystallizes in the orthorhombic space group *Pbca* with eight molecules per unit cell with no solvent molecules or disordered atoms. A view of the molecule is shown in Fig. 1 and selected bond lengths are summarized in Table 1. There is one ligand **1a** in the complex and it acts as a tridentate chelate binding in a facial mode to the Ni(II) ion through the pyridine nitrogen atom and the two thiophosphoryl sulfur atoms. The

Table 1 Selected bond lengths (Å) Ni{[$Ph_2P(S)CH_2]_2C_5H_3N$}$(NO_3)_2$

Ni–S(1)	2.481(1)	Ni–O(1)	2.154(3)
Ni–S(2)	2.402(1)	Ni–O(2)	2.136(3)
Ni–N(1)	2.110(3)	Ni–O(4)	2.061(3)
P(1)–S(1)	1.980(2)	P(1)–C(6)	1.825(4)
P(2)–S(2)	1.981(2)	P(2)–C(7)	1.811(4)
C(1)–C(6)	1.501(5)	C(1)–N(1)	1.347(5)
C(5)–C(7)	1.507(5)	C(5)–N(1)	1.356(5)
N(2)–O(1)	1.276(4)	N(3)–O(4)	1.268(5)
N(2)–O(2)	1.271(4)	N(3)–O(5)	1.199(5)
N(2)–O(3)	1.208(4)	N(3)–O(6)	1.220(5)

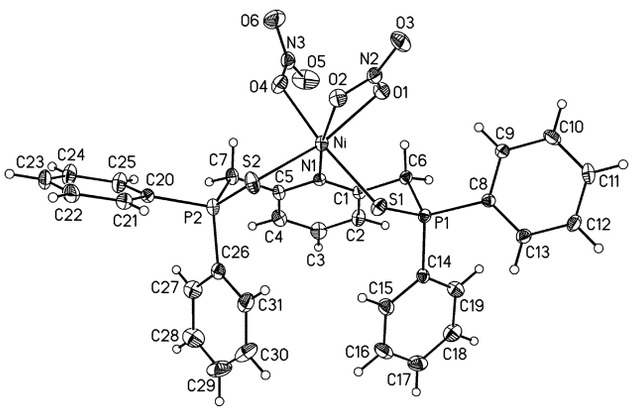


Fig. 1 Molecular structure and atom labeling scheme for Ni{[$Ph_2P(S)CH_2]_2C_5H_3N$}$(NO_3)_2$.

coordinate bond lengths involving **1a** are relatively dissimilar: Ni–S(1) 2.481(1) Å, Ni–S(2) 2.402(1) Å and Ni–N(1) 2.110(3) Å. The Ni–N(1) bond length is similar to Ni–N bond lengths (2.04–2.14 Å) found in a large number of complexes containing high-spin Ni(II).[22] It is interesting to compare the Ni–N(1) bond length to that in the complex $[Ph_2P(O)CH_2C_5H_4N]_2NiCl_2$ where the Ni–N bond length is 2.133(3) Å.[23] In the latter, $Ph_2P(O)CH_2C_5H_4N$ acts as a bidentate chelating ligand. In that complex the P(O)–Ni coordinate bond length is 2.053(2) Å which is, as expected, significantly shorter than the Ni–(S)P distances in Ni(**1a**)$(NO_3)_2$. The Ni–S bond lengths are similar to those found in a six-coordinate Ni(II) complex containing two neutral tridentate 2-pyridineformamide-*N*(4)-methylthiosemicarbazone ligands: Ni–S 2.420(2) and 2.416(2) Å.[24] The Ni–N distances, 2.099(6) and 2.117(6) Å, are also comparable to the distances in Ni(**1a**)$(NO_3)_2$. The remaining three coordination sites on the Ni(II) are occupied by oxygen atoms from one bidentate nitrate ion and one monodentate nitrate ion. The bidentate nitrate coordination is relatively symmetric with Ni–O(1) 2.154(3) Å and Ni–O(2) 2.136(2) Å. The second nitrate ion provides Ni–O(4) 2.061(3) Å and Ni ··· O(5) 3.183 Å. The former is clearly a bonding interaction while the latter is nonbonding. It is interesting to note that the short, monodentate interaction Ni–O(4) is approximately *trans*[O(4)–Ni–S(1) 168.5(1)°] to the longer Ni–S(1) interaction. Despite the range in Ni–S and Ni–N coordinate bond lengths the ligand–Ni docking footprint is very symmetric forming a nonbonded nearly equilateral triangle: N(1) ··· S(1) 3.348 Å, N(1) ··· S(2) 3.503 Å, S(1) ··· S(2) 3.394 Å; internal internal angles at N(1) 59.3°, S(1) 62.6°, S(2) 58.0°. This symmetry is distinct from the asymmetric footprints displayed by bis(phosphinomethyl)pyridine *N*,*P*,*P*′-trioxide ligands on Ln(III) and An(IV) ions[2,3,25,26] which typically form isosceles triangles with the nonbonding P=O ··· O=P edge showing a large variation depending upon the size of the metal ion. The two P=S bond lengths are identical, 1.980(2) Å, suggesting that the asymmetry in Ni–S distances does not impact the P=S donor groups in a significant fashion. Given the interesting bonding mode, further studies of related ligands with d-block and p-block metals will be undertaken, and findings described in the future.

Experimental

The organic reagents were purchased from Aldrich Chemical Co. Organic solvents were obtained from VWR and dried by standard methods. The $Ni(NO_3)_2{\cdot}6H_2O$ was purchased from Fisher Scientific. Infrared spectra were recorded on a Mattson 2020 FTIR instrument and NMR spectra were obtained with Bruker FX-250 and JEOL GSX-400 spectrometers using Me_4Si (^1H, ^{13}C) and 85% H_3PO_4 (^{31}P) as shift standards. All downfield shifts from the standards are assigned as $+\delta$ and the ^1H and ^{13}C peak assignments are based upon assignments made previously for related ligands.[3,4] The mass spectra were obtained at the Midwest Center for Mass Spectrometry, University of Nebraska and elemental analyses were acquired from Galbraith Laboratories.

Ligand syntheses

2,6-Bis(chloromethyl)pyridine was prepared as described by Rezzonico and Grignon-Dubois.[27] **CAUTION:** Handling of this reagent and its solutions should be done in a well ventilated hood. Skin and eye contact must be carefully avoided since the compound is an aggressive irritant. The compound has a small vapor pressure at 23 °C and it can cause bronchial irritation as well. We find considerable variation in the intensity of irritation between individuals, so care should be exercised when preparing and handling this reagent.

2,6-Bis[(diphenylphosphino)methyl]pyridine *P*,*P*′-disulfide (1a). Under dry nitrogen, a red solution of $KPPh_2$[4] (40 mL, 0.5 M in THF, 20 mmol) was added dropwise (30 min) at 23 °C to a stirred solution of 2,6-bis(chloromethyl)pyridine (1.76 g, 10 mmol) in dry tetrahydrofuran (THF, 40 mL). The red color changed immediately and an orange, cloudy mixture formed. The mixture was stirred at 23 °C for an additional period (1 h) and then sulfur (0.7 g, 22 mmol) in benzene (40 mL) was added. This combination was stirred at 23 °C (1 h) and then poured into water (100 mL). The resulting mixture was extracted with $CHCl_3$ (2 × 100 mL), the organic and aqueous phases separated and the organic phase dried over Na_2SO_4. The $CHCl_3$ solution was decanted, vacuum evaporated and the solid residue was treated with acetone (50 mL). The suspension was stirred (1 h), the white solid collected by filtration, and rinsed with acetone (2 × 20 mL). The solid was vacuum dried overnight leaving a white solid **1a** (4.8 g, 89%). The solid was recrystallized from $CHCl_3$–acetone (2 : 1) resulting in a colorless crystalline solid, mp 217–218 °C. Soluble in $CHCl_3$ (7×10^{-2} M). Found: C, 68.75; H, 4.97; N, 2.53%. $C_{31}H_{27}NP_2S_2$ requires C, 69.07; H, 5.05; N, 2.60%. HRFAB-MS: *m*/*z* ($M + H^+$) 540.1115; $C_{31}H_{28}NP_2S_2$ requires 540.1138. NMR (23 °C, $CDCl_3$): $^{31}P\{^1H\}$ δ 42.4; ^1H δ 3.86 (d, J = 14.2 Hz, CH_2), 7.13 (d, *J* = 7.6 Hz), 7.37–7.47 (m); 7.76–7.84 (m); $^{13}C\{^1H\}$ δ 43.36 (d, *J* = 50.1 Hz, C_1), 123.54 (C_3), 128.32 (d, *J* = 12.4 Hz, C_7), 131.41 (C_8), 131.80 (d, *J* = 9.3 Hz, C_6), 132.52 (d, *J* = 81.5 Hz, C_5), 135.96 (C_4), 151.66 (d, *J* = 7.2 Hz, C_2). IR (KBr, cm^{-1}): 3047 (m), 2945 (m), 2893 (m), 1585 (m), 1481 (w), 1437 (s), 1396 (m), 1273 (w), 1101 (s), 995 (w), 823 (s), 744 (s), 704 (s), 692 (s), 615 (m), 505 (m), 476 (m).

2,6-Bis[(diphenylphosphino)methyl]pyridine *N*-oxide *P*,*P*′-disulfide (2a). Under dry nitrogen a red solution of $KPPh_2$ (15 mL, 0.5 M in THF, 7.5 mmol) was added dropwise (5 min) at 23 °C to a stirred THF (15 mL) solution of 2,6-bis(chloromethyl)pyridine *N*-oxide[28] (0.72 g, 3.75 mmol). The red color was discharged immediately producing an orange, cloudy mixture. Stirring was continued at 23 °C (1 h). Sulfur (0.264 g, 8.2 mmol) in THF (15 mL) was added, stirred (1 h) and the THF removed by vacuum evaporation. The remaining residue was poured into a mixture of aqueous $NaHCO_3$ (50 mL sat. solution + 50 mL water). This mixture was extracted with

$CHCl_3$ (2 × 150 mL) and the combined $CHCl_3$ fractions dried over Na_2SO_4. The $CHCl_3$ solution was decanted, evaporated to dryness and the residue treated with acetone (30 mL). This suspension was stirred (1 h) at 23 °C and the white solid collected by filtration and washed with acetone (2 × 10 mL). The solid was dried *in vacuo* (12 h) and was obtained as a white solid **2a** (1.8 g, 86%). The solid was recrystallized from $CHCl_3$/acetone (2:1), and colorless crystals were obtained, mp 239–240 °C (decomp.). Soluble in $CHCl_3$ (1×10^{-2} M). Found: C, 66.31; H, 4.73; N, 2.50%. $C_{31}H_{27}NOP_2S_2$ requires C, 67.01; H, 4.90; N, 2.52%. HRFAB-MS: *m*/*z* ($M + H^+$) 556.1083; $C_{31}H_{28}NOP_2S_2$ requires 556.108. NMR (23 °C, $CDCl_3$): $^{31}P\{^1H\}$ δ 43.2; ^1H δ 4.30 (d, J = 14.0 Hz, CH_2), 7.02 (t, J = 6.0 Hz), 7.39–7.47 (m), 7.66 (d, J = 7.4 Hz), 7.85–7.93 (m); $^{13}C\{^1H\}$ δ 34.86 (d, J = 53.0 Hz, C_1), 123.56 (t, J = 2.8 Hz, C_4), 126.08 (t, J = 3.7 Hz, C_3), 128.49 (d, J = 12.4 Hz, C_7), 131.35 (d, J = 10.5 Hz, C_6), 131.69 (d, J = 2.7 Hz, C_8), 132.16 (d, J = 72.6 Hz, C_5), 143.46 (d, J = 7.3 Hz, C_2). IR (KBr, cm^{-1}): 3049 (m), 2966 (m), 2885 (m), 1564 (w), 1481 (m), 1435 (m), 1410 (m), 1386 (m), 1265 (w), 1230 (s), 1103 (s), 1026 (w), 950 (w), 854 (s), 800 (s), 752 (s), 698 (s), 623 (m), 499 (m).

2,6-Bis[(ditolylphosphino)methyl]pyridine *P*,*P*′-disulfide (1b). Under dry nitrogen, tolyllithium[29] (2.6 g, 26.5 mmol) in Et_2O (50 mL) was added with stirring to diethylthiophosphite[15,16] (1.36 g, 8.84 mmol) in Et_2O (30 mL) at 0 °C. The mixture was warmed to room temperature and stirred (2 h). A white suspension formed and this solution was combined with 2,6-bis-(chloromethyl)pyridine (0.72 g, 4.09 mmol) in THF (20 mL) at 23 °C. After stirring (2 h), a clear, light orange colored solution was obtained. The mixture was evaporated and the residue treated with aqueous saturated NH_4Cl solution (50 mL). This mixture was then extracted with Et_2O–CH_2Cl_2 solution (1 : 1) (2 × 50 mL) and the recovered organic phase was dried over Na_2SO_4. The solvent was evaporated leaving a sticky white solid **1b** that was recrystallized from acetone or $CHCl_3$–acetone (0.4 g, 17%). Soluble in $CHCl_3$. LRFAB-MS: *m*/*z* ($M + H^+$) 596; $C_{35}H_{36}NOP_2S_2$ requires 596. NMR (23 °C, $CDCl_3$):$^{31}P\{^1H\}$ δ 40.9.

2,6-Bis[(ditolylphosphino)methyl]pyridine *N*-oxide *P*,*P*′-disulfide (2b). A solution of *p*-tolyllithium[29] (2.6 g, 26.5 mmol) in diethyl ether (50 mL) was added dropwise (1 h) with stirring at 0 °C to a solution of diethylthiophosphite[15,16] (1.36 g, 8.84 mmol) in diethyl ether (30 mL). The mixture was warmed to 23 °C and stirred (2 h). To this mixture a solution of 2,6-bis-(chloromethyl)pyridine *N*-oxide[27] (0.78 g, 4.43 mmol) in THF (40 mL) was added and stirred (2 h). The solvent was then vacuum evaporated and the residue treated with saturated aqueous NH_4Cl (50 mL). This mixture was extracted with CH_2Cl_2 (2 × 50 mL), the organic phase collected, dried over Na_2SO_4 and the solvent removed by vacuum evaporation. The remaining residue was washed with cold acetone (2 × 25 mL) and a white solid was recovered (2.4 g). Further recrystallization from acetone gave pure samples of **2b** (0.80 g, 33%), mp 198–199 °C. Soluble in $CHCl_3$ (2×10^{-2} M). Found: C, 67.53; H, 5.63; N, 2.23%. $C_{35}H_{35}NOP_2S_2$ requires C, 68.72; H, 5.77; N, 2.29%. HRFAB-MS: *m*/*z* ($M + H^+$) 612.1708; $C_{35}H_{36}NOP_2S_2$ requires 612.171. NMR (23 °C, $CDCl_3$): $^{31}P\{^1H\}$ δ 40.2; ^1H δ 2.34 (12 H, CH_3), 4.28 (d, J = 14.0 Hz, 4H, CH_2), 6.94 (t, J = 8.0 Hz, 1H), 7.16–7.21 (m, 8H), 7.66 (d, J = 8.04 Hz, 2H), 7.72–7.81 (m, 8H); $^{13}C\{^1H\}$ δ 21.32 (C_9), 34.61 (d, J = 53.6 Hz, C_1), 123.39 (C_4), 125.79 (C_3), 128.93 (d, J = 84.3 Hz, C_5), 129.10 (d, J = 12.9 Hz, C_7), 131.16 (d, J = 11.1, C_6), 141.97 (d, J = 2.5 Hz, C_2), 143.49 (C_8). IR (KBr, cm^{-1}): 3047 (m), 3021 (m), 2961 (m) 2901 (m), 2866 (m), 1597 (m), 1560 (w), 1489 (m), 1447 (m), 1400 (s), 1238 (s), 1186 (m), 1101 (s), 1035 (m), 995 (w), 854 (m), 810 (s), 752 (m), 713 (m), 656 (s), 586 (m), 509 (s), 434 (m).

2,6-Bis[(dibutylphosphino)methyl]pyridine *P*,*P*′-disulfide (1c). A solution of *n*-butyllithium (20.6 mL, 1.6 M in hexane, 33 mmol) was added with stirring (1 h) at 0 °C to a solution of diethylthiophosphite (1.7 g, 11 mmol) in cyclohexane (40 mL). The mixture was warmed to 23 °C, stirred for an additional hour and a solution of 2,6-bis(chloromethyl)pyridine (0.88 g, 5.45 mmol) in cyclohexane (30 mL) was added. This mixture was stirred (4 h) then poured into sat. aqueous NH_4Cl solution (50 mL) which was then extracted with diethyl ether–CH_2Cl_2 (1 : 1) solution (2 × 40 mL). The combined organic phase was dried over Na_2SO_4 and evaporated to dryness leaving an orange oil **1c** (2.4 g). This was further purified by chromatography on silica gel using MeOH–$CHCl_3$ as the eluent (0.18 g, 7.8%). Soluble in $CHCl_3$, Et_2O, cyclohexane C_6H_6, toluene, xylene. HRFAB-MS: *m*/*z* ($M + H^+$) 460.2382; $C_{23}H_{44}NP_2S_2$ requires 460.2390. NMR (23 °C, $CDCl_3$): $^{31}P\{^1H\}$ δ 49.6; ^1H δ 0.93 (t, J = 7.2 Hz, 12 H, CH_3), 1.37–1.89 (m, 24 H, CH_2), 3.42 (d, J = 14.1 Hz, 4 H, CH_2), 7.25 (m, 2H), 7.64 (t, J = 7.7 Hz, 1 H); $^{13}C\{^1H\}$ δ 13.52 (C_8), 23.75 (d, J = 16.0 Hz, C_7), 24.17 (d, J = 3.5 Hz, C_6), 30.27 (d, J = 50.8 Hz, C_5), 41.57 (d, J = 43.1 Hz, C_1) 122.97 (C_3), 136.79 (C_4), 152.92 (d, J = 9.6 Hz, C_2). IR (KBr, cm^{-1}): 2957 (s), 2931 (s), 2868 (s), 1585 (m), 1452 (s), 1402 (m), 1276 (m), 1221 (m), 1089 (m), 1053 (w), 906 (s), 831 (m), 783 (m), 731 (s), 441 (w).

2,6-Bis[(dibutylphosphino)methyl]pyridine *N*-oxide *P*,*P*′-disulfide (2c). *n*-Butyllithium (20.6 mL, 1.6 M in hexane, 33 mmol) was added with stirring at 0 °C to a solution of diethylthiophosphite (1.7 g, 11 mmol) in cyclohexane (40 mL). The mixture was warmed to 23 °C, stirred (1 h) and then added to a solution of 2,6-bis(chloromethyl)pyridine *N*-oxide (0.96 g, 5.45 mmol) in THF (20 mL) at 23 °C. This mixture was stirred (2 h), poured into saturated aqueous NH_4Cl (100 mL) and then treated with CH_2Cl_2 (2 × 50 mL). The organic phase was separated, dried over Na_2SO_4, and solvent removed *in vacuo*. An orange oil (**2c**) (2.8 g) was collected and further purified by column chromatography (silica gel, MeOH–$CHCl_3$ 1 : 1 eluant) (0.9 g, 37.8%). Soluble in $CHCl_3$, Et_2O, C_6H_6, toluene, xylene. Found: C, 57.66; H, 9.46; N, 2.74%; $C_{23}H_{43}NOP_2S_2$ requires C, 58.08; H, 9.11; N, 2.94%. HRFAB-MS: *m*/*z* ($M + H^+$) 476.2341; $C_{23}H_{44}NOP_2S_2$ requires 476.2340. NMR (23 °C, $CDCl_3$): $^{31}P\{^1H\}$ δ 52.8. ^1H δ 0.93 (t, J = 7.2 Hz, 12 H, CH_3), 1.40–2.04 (m, 24 H, CH_2), 3.72 (d, J = 13.4 Hz, 4H, CH_2), 7.21 (t, 1 H), 7.47 (m, 2 H); $^{13}C\{^1H\}$ δ 13.49 (C_8), 23.71 (d, J = 16.4 Hz, C_7), 24.39 (d, J = 3.8 Hz, C_6), 31.79 (d, J = 49.9 Hz, C_5), 34.10 (d, J = 44.5 Hz, C_1), 124.04 (s, C_4), 126.66 (C_3), 143.80 (d, J = 10.7 Hz, C_2).

Preparation of complex

A solution of $Ni(NO_3)_2 \cdot 6H_2O$ (29.1 mg, 0.1 mmol) in acetone (10 mL) was combined with a solution of **1a** (54 mg, 0.1 mmol) in $CHCl_3$ (10 mL) and stirred (5 min). The mixture was filtered and the solvent allowed to slowly evaporate. The resulting crystals were suitable for crystallographic analysis. IR (KBr, cm^{-1}): 3061 (w), 2985 (w), 2924 (w), 1606 (w), 1574 (w), 1481 (s), 1444 (s), 1294 (s), 1103 (m), 1020 (m), 1030 (m), 945 (w), 852 (m), 746 (m), 694 (s), 599 (s), 489 (m).

X-Ray diffraction analysis

A single crystal (0.3 × 0.3 × 0.18 mm) was mounted on a glass fiber and data were collected on a Siemens R3m/V diffractometer equipped with a graphite monochromator and using Mo-Kα radiation (λ = 0.71073 Å). *Crystal data*: $C_{31}H_{27}N_3NiO_6P_2S_2$, M = 722.33, orthorhombic, space group *Pbca*, a = 15.431(2), b = 18.055(3), c = 22.931(4) Å, V = 6388.7(17) $Å^3$, Z = 8, μ = 0.887 mm^{-1}, T = 20 °C, 11 094 reflections collected, 5623 independent reflections (R_{int} = 0.0632) which were used in all calculations. The final refinement indices were $R1$ = 0.0508, $wR2$ = 0.1044 [$I > 2\sigma(I)$], $R1$ (all data) = 0.1026. All calculations were performed with XSCANS[30] Version 2.10 and the absorption correction used XPREP[31]

Version 5.03. The structure was solved by direct methods (SHELXL-97).[32] The refinement was well behaved and all non-hydrogen atoms were refined anisotropically. The H-atoms were allowed to vary in position with $U_{iso} = 1.25U_{equiv}$ of the parent atom.

CCDC reference number 215637.

See http://www.rsc.org/suppdata/dt/b3/b309336k/ for crystallographic data in CIF or other electronic format.

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