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Synthesis and crystal structure of $[Ni\{Ph_2PC(S)NPh\}_2]$ and $[Ni\{Ph_2P(Y)C(S)NPh\}_2]$ (Y = S or Se)

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The square-planar nickel(II) complexes $[Ni\{Ph_2PC(S)NPh\}_2]$ and $[Ni\{Ph_2P(Y)C(S)NPh\}_2]$ (Y = S or Se) have been prepared and characterised spectroscopically. Their structures have been confirmed by single-crystal X-ray diffraction methods. In $[Ni\{Ph_2PC(S)NPh\}_2]$ the Ni atom is chelated by the thioamide S atoms [2.188(2), 2.163(2) Å] and phosphine P atoms [2.171(2), 2.182(2) Å] which define a *trans*-S_2P_2 donor set. In $[Ni\{Ph_2P(S)C(S)NPh\}_2]$ the centrosymmetric structure features S,S chelating ligands with the Ni–S (thioamide) distance of 2.184(2) Å being equivalent to the Ni–S (sulfide) distance of 2.197(2) Å in the S_4 donor set. In $[Ni\{Ph_2P(Se)C(S)NPh\}_2]$ the Ni atom in the centrosymmetric structure exists in a square-planar S_2Se_2 donor set with Ni–S 2.202(3) Å and Ni–Se 2.344(1) Å.

Despite being known for sometime,[1-4] the co-ordination chemistry of ions with the general formulae $R_2P(Y)C(S)S^-$ and $R_2P(Y)C(S)NR'^-$ (Y = lone pair, O and S, R = R′ = alkyl or aryl) remains relatively unexplored, in particular when compared to the ubiquitous dithiocarbamates. A major focus of investigation has been on their complexes with Mo,[5-7] W[6-8] and Mn.[9,10] Points of interest include the diversity of co-ordination modes that may be adopted and the expansion of metal chalcogenide chemistry in general.[11] In the former context, it is noteworthy that in the dimolybdenum phosphine complex $[Mo_2\{Ph_2PC(S)NMe\}_4]$[5] both S,N (×2) and P,N (×2) co-ordination modes are found in one isomer and in the other a S,N (×4) mode is observed. This paper describes the characterisation of a series of neutral nickel complexes of the $Ph_2P(Y)C(S)NPh^-$ anion, including that of the novel Y = Se complex.

Experimental

Reagents and materials

All materials were of reagent grade or better used without further purification. Red selenium,[12] PPh_2H[13] and the compounds $Ph_2PC(S)N(H)Ph$,[3] $Ph_2P(S)C(S)N(H)Ph$[4] and $Ph_2P(Se)C(S)N(H)Ph$[14] were all prepared by published methods.

Instrumentation

Infrared spectra were recorded as KBr discs on a Perkin-Elmer 1720X FT spectrophotometer, proton (300.13 MHz) and ^{13}C (75.47 MHz) NMR spectra on a Bruker ACP-300 NMR spectrometer with $CDCl_3$ as the solvent and $SiMe_4$ as the internal reference in each case. Proton-decoupled ^{31}P NMR spectra were recorded as $CHCl_3$ solutions on a Bruker CXP-300 NMR spectrometer at 121.5 MHz with 85% H_3PO_4 in D_2O as the internal reference. Fast atom bombardment (FAB) mass spectra were recorded with the assistance of T. Blumenthal on a VG ZAB-2HF spectrometer (using 3-nitrobenzyl alcohol as matrix, exciting gas argon, FAB gun voltage 7 kV, current 1 mA and accelerating potential 8 kV).

Syntheses

$[Ni\{Ph_2PC(S)NPh\}_2]$. To a stirred ethanolic solution (30 cm^3) of $NiNO_3\cdot 6H_2O$ (200 mg, 0.69 mmol) was added 2.1 molar equivalents of solid $Ph_2PC(S)N(H)Ph$ (464 mg, 1.44 mmol). The solution was stirred for about 10 min until all the solid was dissolved then NEt_3 (2 cm^3) was added dropwise over 1 min. After 30 min of stirring a red precipitate appeared which was collected by vacuum filtration and washed with cold ethanol (10 cm^3) and diethyl ether (10 cm^3). Recrystallisation from chloroform solution afforded an orange-red crystalline product which was dried *in vacuo* over P_2O_5; yield 457 mg (95%), m.p. 150 °C (decomp.). NMR: ^1H, δ 7.11–8.03 (m); ^{13}C (PPh_2), δ 132.7 [$^1J(PC)$ 10.1, C_α], 133.3 [$^2J(PC)$ 6.2, C_β], 128.9 [$^3J(PC)$ 4.9 Hz, C_γ], 131.3 (C_δ); (NPh), 151.6 (C_α), 128.4 (C_β), C_γ and C_δ not observed, 173.4 (C_q).

$[Ni\{Ph_2P(S)C(S)NPh\}_2]$. This was prepared in a similar manner as a dark green-brown solid which was recrystallised from a chloroform solution that had been layered with light petroleum (b.p. 40–60 °C); yield 65%, m.p. 134–136 °C. NMR: ^1H, δ 7.03–7.96 (m); ^{13}C (PPh_2), δ 127.8 [$^1J(PC)$ 60.6, C_α], 132.9–128.7 (C_β–C_δ); (NPh), 149.2 [$^3J(PC)$ 29.1, C_α], 128.6 (C_β), 121.3 (C_γ), 125.1 (C_δ), 176.2 [$^1J(PC)$ 109.3 Hz, C_q].

$[Ni\{Ph_2P(Se)C(S)NPh\}_2]$. This was prepared and recrystallised as described above for $[Ni\{Ph_2P(S)C(S)NPh\}_2]$; yield of brown crystals 75%, m.p. 135 °C (decomp.). NMR: ^1H, δ 7.05–7.93 (m); ^{13}C (PPh_2), δ 127.5 [$^1J(PC)$ 70.7, C_α], 133.0–128.6 (C_β–C_δ); (NPh), 149.2 [$^3J(PC)$ 28.1, C_α], 128.9 (C_β), 121.4 (C_γ), 125.1 (C_δ), 177.8 [$^1J(PC)$ 98.9 Hz, C_q].

Crystallography

Crystal data and refinement parameters for $[Ni\{Ph_2PC(S)NPh\}_2]$, $[Ni\{Ph_2P(S)C(S)NPh\}_2]$ and $[Ni\{Ph_2P(Se)C(S)NPh\}_2]$ are given in Table 1.

Intensity data were measured at 290 K on a Rigaku AFC6R diffractometer using Ni-filtered Cu-Kα radiation, λ 1.5418 Å, and the ω–2θ scan technique such that θ_{max} was 60.0°. The data sets were corrected for Lorentz and polarisation effects[15] and for absorption using an empirical procedure.[16] The structures were solved by direct methods[17] and each refined by a full-matrix least-squares procedure based on *F*.[15] The non-H atoms were refined anisotropically and H atoms were included in the models at their calculated positions (C–H 0.97 Å). The refinements were continued until convergence employing a weighting scheme of the form $w = 1/\sigma^2(F)$. Scattering factors for all atoms were as incorporated in the TEXSAN package[15] installed on an Iris Indigo workstation. The numbering schemes employed are shown in Figs. 1–3, which were drawn with ORTEP[18] using 25, 25 and 30% probability ellipsoids, respectively.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and its reference number 186/38.

Results and Discussion

The complexes $[Ni\{Ph_2PC(S)NPh\}_2]$ and $[Ni\{Ph_2P(Y)C(S)NPh\}_2]$ (Y = S or Se) were formed by the reaction of $Ni(NO_3)_2{\cdot}6H_2O$ and the respective phosphoryl compound in the presence of base in good to high yields. Similar products have been isolated with other $R_2P(Y)C(S)NR'$ compounds where R, R' = aryl and/or alkyl,[19] however only the R = R' = Ph derivatives are reported here. The preparation of the complexes was found to be most efficient with $Ni(NO_3)_2{\cdot}6H_2O$ and the use of hydroxide as the base often resulted in the isolation of $Ph_2P(Y)OH$ (Y = O, S or Se).[19] The $[Ni\{Ph_2PC(S)NPh\}_2]$ complex has been prepared previously from the reaction of $[Ni(PPh_3)(PPh_2H)]$ with PhNCS as well as electrochemically, albeit in lower yields.[20] The complexes are air-stable, soluble in chlorinated solvents, however prolonged standing of solutions of $[Ni\{Ph_2P(Se)C(S)NPh\}_2]$ invariably resulted in the deposition of elemental selenium. The complexes have been characterised spectroscopically (IR, NMR and FAB mass) as well as crystallographically.

$[Ni\{Ph_2PC(S)NPh\}_2]$

The infrared spectra of related compounds have shown that there are two regions of particular interest, *i.e.* 1400–1600 and around 1350 cm^{-1}, and these have been assigned as thioamide I (mainly due to C–N) and II (mainly C–S) bands, respectively.[4,21,22] For $[Ni\{Ph_2PC(S)NPh\}_2]$ there is a band at 1555 cm^{-1} which has been shifted to higher frequency compared with the free phosphine (*i.e.* 1528 cm^{-1}) indicating additional C–N double-bond character. The band at 1388 cm^{-1} of the free phosphine is no longer present, however a new band appears at 924 cm^{-1} which is ascribed to ν(C–S), consistent with similar absorptions found for related phosphinothioformamide complexes involved in four-membered chelate rings.[23,24] No evidence was found for ν(N–H). Similarly, δ(N–H) was absent in the ^1H NMR spectrum which showed the expected resonances. In the ^{13}C NMR spectrum a single resonance was observed at δ 173.4 [no *J*(P–C) observed] due to the quaternary carbon atom. This resonance has shifted significantly upfield compared with the free phosphine (*i.e.* δ 206.6). The other major difference between the free and co-ordinated phosphine is found in δ(C_α of NPh) which has shifted downfield to δ 151.6 from δ 138.7 for the free phosphine. The ^{31}P NMR spectrum showed one resonance only at δ −1.8 which has shifted significantly upfield from δ 19.2 for the free phosphine. In the FAB mass spectrum the $[M]^+$ ion was present at low abundance (7%) and the most abundant fragment was assigned to $[Ph_2PNiS_2]^+$ at *m/z* 307; the fragment $[Ni\{Ph_2PC(S)NPh\}]^+$ was observed at 12% abundance. The major non-Ni-containing fragments were assigned to $[Ph_2PC(S)NPh]^+$ (15%) and $[Ph_2PCNPh]^+$ (82%); there were no significant fragments at *m/z* greater than that of $[M]^+$. A full characterisation was afforded by a crystal structure analysis.

The molecular structure of $[Ni\{Ph_2PC(S)NPh\}_2]$ is shown in Fig. 1 and selected interatomic parameters are collected in Table 2. In contrast to a previous report of an incompletely refined structure,[20] the molecule is not situated about a crystallographic centre of inversion, however the Ni atom does exist in a *trans*-S_2P_2 donor set which defines a distorted square-

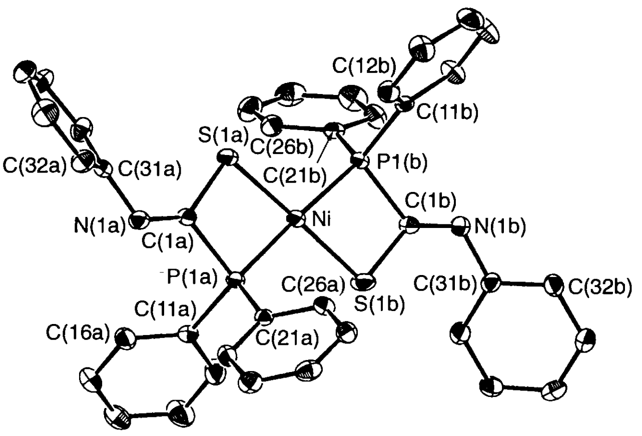

Fig. 1 Molecular structure and crystallographic numbering scheme for $[Ni\{Ph_2PC(S)NPh\}_2]$

Table 1 Crystallographic data

	$[Ni\{Ph_2PC(S)NPh\}_2]$	$[Ni\{Ph_2P(S)C(S)NPh\}_2]$	$[Ni\{Ph_2P(Se)C(S)NPh\}_2]$
Formula	$C_{38}H_{30}N_2NiP_2S_2$	$C_{38}H_{30}N_2NiP_2S_4$	$C_{38}H_{30}N_2NiP_2S_2Se_2$
M	699.4	763.6	857.4
Colour	Orange	Brown	Brown
Crystal size/mm	0.05 × 0.18 × 0.21	0.03 × 0.10 × 0.16	0.05 × 0.13 × 0.39
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/n$
a/Å	10.357(1)	12.160(4)	9.74(1)
b/Å	18.309(2)	8.909(2)	19.26(1)
c/Å	8.9393(8)	16.375(3)	10.39(2)
α/°	96.125(9)		
β/°	99.152(7)	91.15(2)	115.22(9)
γ/°	80.479(9)		
$U/Å^3$	1644.8(3)	1773.7(7)	1763(3)
Z	2	2	2
$D_c/g\ cm^{-3}$	1.412	1.430	1.614
F(000)	724	788	860
μ/cm^{-1}	31.90	40.79	53.53
Range of transmission factors	0.948–1.027	0.961–1.011	0.957–1.023
No. data collected	5202	2982	2893
No. unique data	4889	2833	2718
No. unique data with $I \geqslant 3.0\sigma(I)$	2903	1336	1701
R	0.039	0.049	0.053
R'	0.041	0.046	0.059
Residual density/e $Å^{-3}$	0.24	0.32	0.67

Table 2 Selected bond distances (Å) and angles (°) for [Ni{Ph$_2$PC(S)NPh}$_2$]

Ni–S(1a)	2.188(2)	Ni–S(1b)	2.163(2)
Ni–P(1a)	2.171(2)	Ni–P(1b)	2.182(2)
S(1a)–C(1a)	1.757(5)	S(1b)–C(1b)	1.763(5)
P(1a)–C(1a)	1.825(5)	P(1b)–C(1b)	1.829(5)
P(1a)–C(11a)	1.807(5)	P(1b)–C(11b)	1.810(5)
P(1a)–C(21a)	1.816(5)	P(1b)–C(21b)	1.813(5)
N(1a)–C(1a)	1.276(5)	N(1b)–C(1b)	1.265(5)
N(1a)–C(31a)	1.415(6)	N(1b)–C(31b)	1.441(6)
S(1a)–Ni–S(1b)	177.73(7)	P(1a)–Ni–P(1b)	177.62(7)
S(1a)–Ni–P(1a)	77.58(5)	S(1b)–Ni–P(1b)	77.40(6)
S(1a)–Ni–P(1b)	104.78(6)	S(1b)–Ni–P(1a)	100.24(6)
Ni–S(1a)–C(1a)	92.2(2)	Ni–S(1b)–C(1b)	93.3(2)
Ni–P(1a)–C(1a)	90.9(2)	Ni–P(1b)–C(1b)	90.9(2)
Ni–P(1a)–C(11a)	120.8(2)	Ni–P(1b)–C(11b)	119.7(2)
Ni–P(1a)–C(21a)	118.4(2)	Ni–P(1b)–C(21b)	118.0(2)
C(1a)–P(1a)–C(11a)	108.6(2)	C(1b)–P(1b)–C(11b)	110.0(2)
C(1a)–P(1a)–C(21a)	107.8(2)	C(1b)–P(1b)–C(21b)	105.3(2)
C(11a)–P(1a)–C(21a)	107.9(2)	C(11b)–P(1b)–C(21b)	109.9(2)
C(1a)–N(1a)–C(31a)	121.3(4)	C(1b)–N(1b)–C(31b)	121.2(4)
S(1a)–C(1a)–P(1a)	99.3(2)	S(1b)–C(1b)–P(1b)	98.3(2)
S(1a)–C(1a)–N(1a)	134.3(4)	S(1b)–C(1b)–N(1b)	132.5(4)
P(1a)–C(1a)–N(1a)	126.4(4)	P(1b)–C(1b)–N(1b)	129.3(4)

planar geometry. The major distortions from the ideal geometry can be traced to the restricted bite angles of the S,P chelating ligands [*i.e.* 77.58(5) and 77.40(6)°, for ligands a and b respectively]. The four-membered rings formed are essentially planar as seen in the Ni–P(1)–C(1)–S(1) torsion angles of 0.4(2) and −3.3(2)°, respectively. There are no significant differences between comparable geometric parameters in the two ligands. It is notable that the C(1)–S(1) and C(1)–N(1) bond distances in the complex have elongated and contracted, respectively, compared with the equivalent values found for the parent Ph$_2$PC(S)N(H)Ph [1.650(3) and 1.334(3) Å, respectively[25]]. These variations indicate that the ligand co-ordinates essentially as a thiolate with significant double-bond character in the C(1)–N(1) bond. It is also noteworthy that the P(1)–C(1) bond has decreased by *ca.* 0.035 Å in the complex, from 1.862(3) Å in the free phosphine. Other noteworthy changes in the parameters upon co-ordination are found in the angles about the C(1) atom, *i.e.* S(1)–C(1)–P(1), S(1)–C(1)–N(1) and P(1)–C(1)–N(1) which have contracted, expanded and expanded, respectively by 15, 4 and 10°, reflecting the strain at the C(1) atom upon the formation of the $\overline{\text{NiSCP}}$ four-membered ring. The above observations, coupled with the planarity of the ligands {the S(1)–C(1)–N(1)–C(31) and P(1)–C(1)–N(1)–C(31) torsion angles are −177.0(4) [−177.5(4) for ligand b] and 6.4(8)° [2.6(8)°], respectively}, indicate the delocalisation of π-electron density over the ligand atoms. In the lattice there are no significant intermolecular contacts with the closest non-hydrogen contact of 3.430(8) Å occurring between atoms C(24a) and C(26a′) atoms (symmetry operation: $-1-x, 1-y, -z$).

[Ni{Ph$_2$P(S)C(S)NPh}$_2$]

The [Ni{Ph$_2$P(S)C(S)NPh}$_2$] complex may be thought of as the product of the insertion of S into the Ni–P bonds of [Ni{Ph$_2$PC(S)NPh}$_2$], however experience with related systems showed that this was not a useful method of preparation.[19] Three absorption bands of interest in the IR spectrum at 1524, 948 and 605 cm^{-1} were assigned to ν(thioamide I), ν(thioamide II) and ν(P=S), respectively; ν(N–H) was absent. Compared with the free phosphine, the ν(thioamide I) band has moved 19 cm^{-1} to higher frequency and ν(P=S) 35 cm^{-1} to lower frequency, indicating increased and reduced bond orders, respectively. Similar shifts have been reported in the related systems where S,S chelation occurs.[26–28] The ^{1}H NMR spectrum was as expected and in the ^{13}C NMR spectrum the significant changes compared with the free phosphine were found in the position of (*i*) the quaternary C$_q$ resonance which had moved upfield to δ 176.2 [^1J(PC) 109.3 Hz] (*cf.* δ 206.6) and (*ii*) the C$_\alpha$(PPh) resonance which had moved downfield to δ 149.2 (*cf.* δ 138.7). A single resonance was observed in the ^{31}P NMR spectrum at δ 50.0 (*cf.* 47.4 for the free phosphine). In the FAB mass spectrum [M]$^+$ was present only in 4% abundance, the most abundant peak being assigned to [Ph$_2$PNiS$_3$]$^+$; the [Ph$_2$P(S)C(S)N(H)Ph]$^+$ fragment was present at 54% intensity. The spectroscopic results indicate a S,S co-ordination mode and this was confirmed by an X-ray analysis.

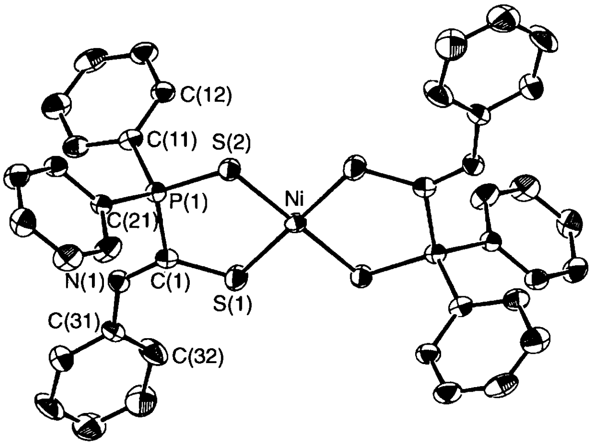

Fig. 2 Molecular structure and crystallographic numbering scheme for [Ni{Ph$_2$P(S)C(S)NPh}$_2$]

The molecular structure of [Ni{Ph$_2$P(S)C(S)NPh}$_2$] is shown in Fig. 2 and selected interatomic parameters are given in Table 3. The molecule is centrosymmetric with the Ni atom located at a site of symmetry and existing in a distorted square-planar geometry. The Ni atom is chelated *via* the thiophosphinoyl and thioamide S atoms forming essentially equivalent Ni–S(1) and Ni–S(2) separations of 2.184(2) and 2.197(2) Å, respectively. This mode of co-ordination results in the formation of a $\overline{\text{NiSPCS}}$ five-membered ring which is almost planar; the values of the Ni–S(1)–C(1)–P(1) and Ni–S(2)–P(1)–C(1) torsion angles are 13.0(3) and 6.8(4)°, respectively. The S(1)–Ni–S(2) chelate angle of 83.53(8)° is greater than that of *ca.* 77.5° found in the structure of

Table 3 Selected bond distances (Å) and angles (°) for $[Ni\{Ph_2P(Y)C(S)NPh\}_2]$ (Y = S or Se)

	Y = S	Y = Se
Ni–S(1)	2.184(2)	2.202(3)
Ni–Y(2)	2.197(2)	2.344(1)
S(1)–C(1)	1.706(7)	1.751(8)
Y(2)–P(1)	2.001(3)	2.145(3)
P(1)–C(1)	1.836(7)	1.821(8)
P(1)–C(11)	1.820(7)	1.794(7)
P(1)–C(21)	1.794(7)	1.811(9)
N(1)–C(1)	1.290(8)	1.260(9)
N(1)–C(31)	1.414(9)	1.42(1)
S(1)–Ni–Y(2)	83.53(8)	83.8(1)
S(1)–Ni–Y(2′)	96.47(8)	96.2(1)
Ni–S(1)–C(1)	111.8(3)	112.2(3)
Ni–Y(2)–P(1)	105.4(1)	97.1(1)
Y(2)–P(1)–C(1)	108.9(2)	108.1(3)
Y(2)–P(1)–C(11)	112.7(3)	112.9(3)
Y(2)–P(1)–C(21)	110.2(3)	113.5(3)
C(1)–P(1)–C(11)	106.7(3)	109.7(4)
C(1)–P(1)–C(21)	108.5(3)	105.5(4)
C(11)–P(1)–C(21)	109.6(3)	107.0(4)
C(1)–N(1)–C(31)	124.9(6)	125.2(7)
S(1)–C(1)–P(1)	115.8(4)	113.9(5)
S(1)–C(1)–N(1)	132.6(6)	132.2(6)
P(1)–C(1)–N(1)	111.6(5)	113.9(6)

$[Ni\{Ph_2PC(S)NPh\}_2]$, reflecting the reduced steric strain owing to the inclusion of the additional atom, *i.e.* S(2), into the chelate ring. As expected, the P(1)–S(2) and S(1)–C(1) distances of 2.001(3) and 1.706(7) Å, respectively have been elongated significantly in the complex compared with the free phosphine,[29] *i.e.* 1.951(2) and 1.633(4) Å, respectively. Concomitantly, the P(1)–C(1) and C(1)–N(1) distances have decreased to 1.836(7) and 1.290(8) Å, respectively compared with 1.855(5) and 1.338(5) Å in the free phosphine. The torsion angles of −167.9(3)° for S(2)–P(1)–C(1)–S(1) and 9.4(6)° for S(2)–P(1)–C(1)–N(1) indicate that significant delocalisation of π-electron density over the ligand is unlikely. The closest non-hydrogen contact in the lattice of 3.47(2) Å occurs between two symmetry-related C(32) atoms (symmetry operation: $-x$, $1-y$, $-z$). There have been two other crystal-structure determinations containing the $[Ph_2P(S)C(S)NPh]^-$ anion, namely $[Mn(CO)_4\{Ph_2P(S)C(S)NPh\}]$ in which S,S chelation is found[10] and $[Mo(CO)_2(\eta^5\text{-}C_5H_5)\{Ph_2P(S)C(S)NPh\}]$[7] in which chelation is afforded by the thioamide S and N atoms with the S(2) atom not participating in co-ordination to the Mo atom, emphasising the varied co-ordination potential of these ligands.

$[Ni\{Ph_2P(Se)C(S)NPh\}_2]$

The IR spectrum for $[Ni\{Ph_2P(Se)C(S)NPh\}_2]$ was similar to that of the Y = S analogue with the thioamide I and II bands occurring at 1523 and 944 cm^{-1}, respectively. The ν(P=Se) band at 529 cm^{-1} was shifted by 20 cm^{-1} to lower frequency compared with the free phosphine. The expected resonances were observed in the ^{1}H NMR spectrum and in the ^{13}C NMR spectrum the resonance of C_q had shifted upfield to δ 177.8 (*cf.* δ 186.3 for the free phosphine) with ^1J(PC) of 98.9 Hz, again resembling the results for the Y = S analogue. A single resonance at δ 41.3 with Se satellites [^1J(PSe) 549 Hz] was observed in the ^{31}P NMR spectrum (*cf.* δ 45.3, 722 Hz). In the FAB mass spectrum the $[M]^+$ ion was not observed and the most abundant ion was assigned to $[Ph_2PNiS_2]^+$; $[Ph_2P(Se)C(S)N(H)Ph]^+$ was present in 14% abundance. The molecular structure was determined unambiguously by X-ray methods.

The molecular structure of centrosymmetric $[Ni\{Ph_2P(Se)C(S)NPh\}_2]$ is shown in Fig. 3 and selected geometric parameters

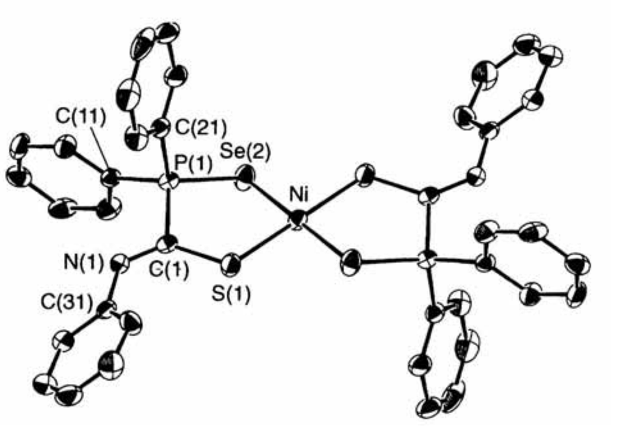

Fig. 3 Molecular structure and crystallographic numbering scheme for $[Ni\{Ph_2P(Se)C(S)NPh\}_2]$

are collected in Table 3. The Ni atom exists in a distorted square-planar geometry with a S_2Se_2 donor set. The Ni–S(1) distance of 2.202(3) Å is as expected and the Ni–Se(2) distance of 2.344(1) Å is comparable to 2.330(2) Å in $[NBu_4][Ni\{SSeC{=}C(CN)_2\}_2]$[30] which also features a *trans*-S_2Se_2 donor set. The Ni–S distance in the latter structure is longer at 2.292(3) Å than that in $[Ni\{Ph_2P(Se)C(S)NPh\}_2]$, this may be attributed to the presence of a sterically strained four-membered ring compared *cf.* 1.875(8) Å]. The NiSCPSe chelate ring is buckled signifi- which the chelate angle is 83.8(1)°. This analysis completes the series of $[Ni\{Ph_2P(Y)C(S)NPh\}_2]$ structures and shows that the magnitude of the Ni–S (thioamide) distance increases in the order Y = lone pair < S < Se. The P(1)–Se(2) distance in $[Ni\{Ph_2P(Se)C(S)NPh\}_2]$ of 2.145(3) Å is longer than that in the free phosphine[14] [2.106(3) Å] and other systematic variations, as observed above for the Y = S structure, are also found. Hence, the S(1)–C(1) distance in $[Ni\{Ph_2P(Se)C(S)NPh\}_2]$ has elongated [1.751(8) *cf.* 1.629(9) Å], C(1)–N(1) has contracted [1.260(9) *cf.* 1.31(1) Å] and P(1)–C(1) has contracted [1.821(8) with the five-membered NiSCPSe ring in the present case, for cantly, the mean deviation of the atoms from their least-squares plane being 0.193 Å. Similarly, the central chromophore of the ligand is far from planar as evidenced by the S(1)–C(1)–P(1)–Se(2) and Se(2)–P(1)–C(1)–N(1) torsion angles of 33.0(5) and −148.0(6)°, respectively. That the structure is molecular is seen in the closest distance between non-hydrogen atoms in the lattice of 3.29(2) Å which occurs between centrosymmetrically related C(23) atoms.

This study shows that deprotonated $Ph_2PC(S)N(H)Ph$ and $Ph_2P(Y)C(S)N(H)Ph$ (Y = S or Se), can form stable chelate complexes with Ni and, in particular, that $Ph_2P(Se)C(S)N(H)Ph$ offers the opportunity to access novel M–Se systems.

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