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Heterodifunctional Ligands Derived from Monooxidized Bis(phosphino)amines. Synthesis and Transition Metal (Molybdenum(0), Tungsten(0), Rhodium(I), Palladium(II), and Platinum(II)) Complexes of (Diphenylphosphino)(diphenylphosphinothioyl)- and (Diphenylphosphino)(diphenylphosphinoselenoyl)phenylamine, $Ph_2PN(Ph)P(E)Ph_2$ (E = S, Se). Crystal and Molecular Structure of the Pt(II) Complex $[\mathrm{Cl_2}\overline{\mathrm{PtPPh_2N(Ph)P(S}}\mathrm{)Ph_2}]\cdot\mathrm{H_2O}$

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Bis(diphenylphosphino)phenylamine can be selectively oxidized by S or Se in toluene or hexane solvents to the monooxidized thioyl or selenoyl products $Ph_2PN(Ph)PPh_2{=}E$, (E = S, Se). These compounds act as bidentate chelate ligands toward metal complexes forming $(CO)_4M(LL)$ (M = Mo, W), CO(Cl)Rh(LL), and $Cl_2M(LL)$, (M = Pt, Pd) where (LL) is the thioyl or selenoyl derivative of the aminobis(phosphine). IR and NMR data are given for all complexes. The carbonyl infrared stretching frequencies show that the chelates form with the phosphine *cis* to any CO which is present. The ^{31}P NMR of all complexes consists of two doublets except for the Rh complexes wherein the Rh spin also couples to phosphorus to produce two doublets of doublets. The $^2J_{PP}$ values range from 56 to 112 Hz. $^1J_{PSe}$ coupling provide valuable assistance for the assignment of the phosphorus resonances which range widely from 55 to 126 ppm for P^{III} and from 60 to 80 ppm for the P^V case. Assignment of P^{III} and P^V signals, which invert relative shift positions on occasion, is aided by the analysis of appropriate spin satellites arising from the substituents. It is concluded that coordination shifts for P^{III} are always positive, ranging from 22 ppm for Pt^{II} complexes to 70 ppm for Rh^I complexes. Coordination shifts for P^V centers are much smaller, e.g. 0–12 ppm, and in some cases the coordination shifts for the P^V centers are negative *versus* the free ligand. A crystal structure of the Pt complex $[\mathrm{Cl_2}\overline{\mathrm{PtPPh_2N(Ph)P(S}}\mathrm{)Ph_2}]\cdot\mathrm{H_2O}$ (at 25 °C, monoclinic $P2_1/c$ $a = 9.117(1)$ Å, $b = 18.783(3)$ Å, $c = 17.288(2)$ Å, $\beta = 92.16(1)°$, $V = 2959(1)$ Å^3, $Z = 4$) showed the chelate structure comprising a relatively strain-free five membered ring containing a trigonal planar N in the backbone. The short $P^V(1)$–N (1.674(7) Å) bond length is similar to a phosphazene bond length and indicative of multiple bond character. Although the complex could only be crystallized with 1 mol of H_2O, there was no evidence for unusual interaction of this water molecule with the complex. The P^{III}–N bond length (1.737(7) Å) is similar to the usual P^{III}–N distances. The geometry suggests significant delocalization from the nitrogen bridge into the backbone of the chelate.

Introduction

In the last two decades several bis(phosphino)amines of the type $R_2PN(R)PR_2$ have been prepared and their transition metal ligation chemistry explored.[2-20] As an extension of our interest[21-23] and the interest of others[24,25] in heterodifunctional hard/soft ligand systems of the general form $R_2PQPR_2{=}E$, we have sought to prepare systems of the type PNP(E) (E = O, S, Se and NR) from the P–N–P backbone. Herein we report the synthesis and characterization of the monooxidized (E = S, Se) aminophosphines and the complexes formed from these ligands with Mo(0), W(0), Rh(I), Pd(II), and Pt(II). The crystal structure of a Pt(II) complex with the sulfur-containing ligand is described.

Experimental Section

All preparative and spectroscopic measurements were carried out at the Unversity of Alberta. All experimental manipulations

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were performed under an atmosphere of dry argon using Schlenk techniques. Solvents were dried and distilled prior to use. $Ph_2PN(Ph)PPh_2$, (**1**)[26] *cis*-$[M(CO)_4(piperidine)_2]$ (M = Mo or W),[27] $PdCl_2(PhCN)_2$,[28] $PtCl_2(COD)$,[29] and $[Rh(CO)_2Cl]_2$[30] were prepared according to published procedures. ^{31}P NMR spectra were recorded on a Bruker WH-400 instrument operating at 161.97 MHz using 85% H_3PO_4 as the external standard. $CDCl_3$ and CD_2Cl_2 were used as both the solvent and the internal lock. Positive shifts lie downfield of the standard in all cases. Infrared spectra were recorded on a Nicolet 20SX FTIR spectrometer in CH_2Cl_2 solution. Microanalyses were performed by the Microanalytical Laboratory in the Department of Chemistry at the University of Alberta. Mass spectra were recorded on a Kratos MS9 instrument. Solution molecular weight measurements were performed in dibromomethane solution on a Mechrolab 301A vapor phase osmometer.

Preparations of (Diphenylphosphino)(diphenylphosphinothioyl)- and (Diphenylphosphino)(diphenylphosphinoselenoyl)phenylamines. (a) $Ph_2PN(Ph)P(S)Ph_2$ (2). A mixture of **1** (5.0 g, 10.8 mmol) and sulfur (0.35 g, 10.8 mmol) in *n*-hexane (50 mL) was heated under reflux condition for 6 h. The solution was then cooled to 25 °C. The analytically pure microcrystalline precipitate of **2** which formed was separated by filtration and dried under vacuum. The yield was quantitative. Mp: 142–144 °C. Anal. Calcd for $C_{30}H_{25}NP_2S$: C, 73.02; H, 5.07; N, 2.84. Found: C, 72.94; H, 5.14; N, 2.78. MS (EI *m/z*) = 493 (M^+).

(b) $Ph_2PN(Ph)P(Se)Ph_2$ (3). A mixture of **1** (2.5 g, 5.4 mmol) and selenium powder (0.43 g, 5.4 mmol) in a mixture of *n*-hexane (30 mL) and toluene (10 mL) was heated under reflux conditions for 6 h. The solution was then cooled to 25 °C and filtered to remove any undissolved material. The clear solution was cooled to 0 °C whereupon white crystalline, analytically pure **3** (yield 86%; mp 135–137 °C) was isolated. Anal. Calcd for $C_{30}H_{25}NP_2Se$: C, 66.66; H, 4.63; N, 2.59. Found: C, 66.50; H, 4.70, N, 2.59%. MS (EI, *m/z*) 540 (M^+).

Preparation of Complexes $M(CO)_4PPh_2N(Ph)P(E)Ph_2$ (4–7) (4, M = Mo, E = S; 5, M = Mo, E = Se; 6, M = W, E = S; 7, M = W, E = Se). A mixture of *cis*-$[M(CO)_4(piperidine)_2]$ (M = Mo or W) (0.3 mmol) and $Ph_2PN(Ph)P(E)Ph_2$ (0.3 mmol) in CH_2Cl_2 (20 mL) was heated under reflux for 3 h. The solution was then cooled to 25 °C and concentrated to 5 mL, and methanol (5 mL) for (**4**, **6**) *or n*-hexane (5 mL) for (**5**, **7**) was added. Keeping this solution at 0 °C gave crystalline products in 70–85% yield. **4**, $Mo(CO)_4PPh_2PN(Ph)P(S)Ph_2$: yellow crystals; yield 80%; mp 140 °C dec. Anal. Calcd for $C_{34}H_{25}NO_4P_2SMo$: C, 58.20; H, 3.56; N, 1.99. Found: C, 57.92; H, 3.52; N, 1.78. IR (CH_2Cl_2): ν_{CO} 2019, 1894 (br), 1859 cm^{-1}. **5**, $Mo(CO)_4PPh_2N(Ph)P(Se)Ph_2$: yellow crystals; yield 76%; mp 120 °C dec. Anal. Calcd for $C_{34}H_{25}NO_4P_2SeMo$: C, 54.54; H, 3.34; N, 1.87. Found: C, 54.30; H, 3.31; N, 1.82. IR (CH_2Cl_2): ν_{CO} 2017, 1912, 1884, 1847 cm^{-1}. **6**, $W(CO)_4PPh_2N(Ph)P(S)Ph_2$: yellow crystals; yield 74%; mp 172 °C dec. Anal. Calcd for $C_{34}H_{25}NO_4P_2SW$: C, 51.71; H, 3.16; N, 1.77. Found: C, 51.26; H, 3.10; N, 1.65. IR (CH_2Cl_2): ν_{CO} 2014, 1904, 1884, 1848 cm^{-1}. **7**, $W(CO)_4PPh_2N(Ph)P(Se)Ph_2$: yellow crystals, yield 86%, mp 162 °C dec. Anal. Calcd for $C_{34}H_{25}NO_4P_2SeW$: C, 48.80; H, 2.99; N, 1.67. Found: C, 47.97; H, 2.99; N, 1.62. IR (CH_2Cl_2): ν_{CO} 2012, 1885 (br), 1845 cm^{-1}.

Preparation of Complexes $RhCl(CO)PPh_2N(Ph)P(E)Ph_2$ (8; E = S, 9; E = Se). A solution of **2** or **3** (0.3 mmol) in dry CH_3CN (8 mL) was added to a solution of $[Rh(CO)_2Cl]_2$ (0.15 mmol) also in CH_3CN (10 mL). The reaction mixture, which was initially red, turned yellow during the course of this reaction. The reaction mixture was stirred at room temperature for 3 h. A microcrystalline product precipitated during the reaction. Removal of the solvent upon completion of the reaction by filtration and drying the resultant solid product under vacuum gave analytically pure products.

8: yellow crystals; yield 72%; mp 186 °C dec. Anal. Calcd for $C_{31}H_{25}ClNOP_2RhS$: C, 56.40; H, 3.79; N, 2.12. Found: C, 56.21; H, 3.80; N, 2.10. IR (CH_2Cl_2): ν_{CO} 1979 cm^{-1}.

9: yellow crystals; yield 84%; mp 216 °C dec. Anal. Calcd for $C_{31}H_{25}NOP_2SeRhCl$: C, 52.65; H, 3.53; N, 1.98. Found: C, 52.66; H, 3.45; N, 2.1 IR (CH_2Cl_2): ν_{CO} 1981 cm^{-1}.

Preparation of Complexes $PdCl_2PPh_2N(Ph)P(E)Ph_2$ (10, E = S; 11, E = Se). A solution of **2** or **3** (0.3 mmol) in dry CH_2Cl_2 (10 mL) was added dropwise to a solution of $(PhCN)_2PdCl_2$ (0.3 mmol) in CH_2Cl_2 (10 mL). The reaction mixture was stirred at room temperature for 3 h. The solution was then concentrated to 8 mL, and 3 mL of *n*-hexane was added. Cooling this solution to 0 °C gave analytically pure samples of **10** or **11**.

10: orange red crystals; yield 70%; mp 200 °C dec. Anal. Calcd for $C_{30}H_{25}Cl_2NP_2PdS$: C, 53.69; H, 3.72; N, 2.08. Found: C, 53.52; H, 3.62; N, 2.07. **11**: orange crystals; yield 90%; mp 200 °C dec. Anal. Calcd for $C_{30}H_{25}NP_2SePdCl_2$: C, 50.18; H, 3.48; N, 1.95. Found: C, 50.30; H, 3.21; N, 1.92.

Preparation of Complexes $PtCl_2PPh_2N(Ph)P(E)Ph_2$ (12, E = S; 13, E = Se). A solution of (**2** or **3**) (0.3 mmol) in dry CH_2Cl_2 (8 mL) was added dropwise to a solution of $[(COD)PtCl_2]$ (0.3 mmol) also in CH_2Cl_2 (10 mL). The reaction mixture, which turned yellow during the course of this reaction, was stirred at room temperature for 2 h. The solution was concentrated to 6 mL, and then 2 mL of *n*-hexane was added. Cooling this solution to 0 °C gave a yellow microcrystalline product. This product did not recrystallize well from very dry CH_2Cl_2; however, excellent crystals (containing 1 mol of cocrystallized water) suitable for X-ray analysis were obtained from solvent which had not been well dried.

12: yellow crystals; yield 88%; mp 190 °C dec. Anal. Calcd for $C_{30}H_{25}NCl_2P_2PtS\cdot H_2O$: C, 46.33; H, 3.47; N, 1.80. Found: C, 46.57; H, 3.40; N, 1.72.

13: yellow crystals; yield 95%; mp 208 °C dec. Anal. Calcd for $C_{30}H_{25}NP_2SePtCl_2$: C, 44.66; H, 3.10; N, 1.74. Found: C, 44.27; H, 3.10; N, 1.68.

Crystal Structure Determination for 12, $[Cl_2PtP(Ph_2)N(Ph)P(S)Ph_2]\cdot H_2O$. A crystal (0.40 × 0.20 × 0.20 mm) of $[Cl_2PtP(Ph_2)N(Ph)P(S)Ph_2]\cdot H_2O$ was mounted on a Pyrex filament with epoxy resin. Unit cell dimensions were determined from 25 well-centered reflections ($9.7 < \theta < 14.0°$). Intensity data (6396 total reflections measured, 6003 unique, 4158 reflections with $F_o^2 > 3.00(F_o)^2$) were collected with an Enraf-Nonius CAD4 diffractometer at the University of Toledo using graphite-monochromated Mo Kα (λ = 0.710 73 Å) radiation by the (ω–2θ) scan technique. The data were corrected for Lorentz, polarization, and background effects. After removal of redundant and space group forbidden data, observed data (4158 reflections with $F_o^2 > 3.0\sigma(F_o)^2$) were used for solution refinement. Direct methods were used for solution.[31] Hydrogen atoms were calculated on idealized positions and included in the refinement as riding atoms with fixed isotropic thermal parameters. The final cycle of refinement minimizing the function $\sum w(|F_o| - |F_c|)^2$ (weight w is defined as $4F_o^2/\sigma^2(F_o)^2$) lead to the final agreement factors shown

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Table I. Phosphorus-31 NMR[a] Spectroscopic Data for Ligands (**1**–**3**) and Their Complexes

		chem shifts and shift diff, ppm				coupling const, Hz	
		$\delta(P^{III})$	$\Delta\delta(P^{III})^b$	$\delta(P^V)$	$\Delta\delta(P^V)^c$	$^2J_{PP}$	J_{PM}
$Ph_2PN(Ph)PPh_2$	**1**	68.6					
$Ph_2P(S)N(Ph)PPh_2$	**2**	54.5(d)		72.4(d)		104.6	
$Ph_2(Se)PN(Ph)PPh_2$	**3**	55.1(d)		72.1(d)		110.3	$^1J_{PSe} = 766.5$
$Ph_2(S)PN(Ph)(Ph)_2PMo(CO)_4$	**4**	115.3(d)	60.8	73.0(d)	0.6	100.4	
$Ph_2(Se)PN(Ph)(Ph)_2PMo(CO)_4$	**5**	120.3(d)	65.2	60.5(d)	−11.6	111.8	$^1J_{PSe} = 673.8$
$Ph_2(S)PN(Ph)(Ph)_2PW(CO)_4$	**6**	99.9(d)	45.4	73.6(d)	1.2	100.0	$^1J_{PW} = 258$, $^2J_{PW} = 8$
$Ph_2(Se)PN(Ph)(Ph)_2PW(CO)_4$	**7**	103.6(d)	48.5	60.1(d)	−12.0	111.8	$^1J_{PW} = 259$, $^1J_{PSe} = 660.9$
$Ph_2(S)PN(Ph)(Ph)_2PRh(CO)Cl$	**8**	122.8(dd)	68.3	76.0(dd)	3.6	71.3	$^1J_{RhP} = 158.7$, $^2J_{RhP} = 3.0$
$Ph_2(Se)PN(Ph)(Ph)_2PRh(CO)Cl$	**9**	126.8(dd)	71.7	64.7(dd)	−7.4	79.4	$^1J_{RhP} = 167.6$, $^1J_{PSe} = 601.5$, $^2J_{RhP} = 1.1$
$Ph_2(S)PN(Ph)(Ph)_2PPdCl_2$	**10**	106.2(d)	51.7	80.5(d)	8.1	56.7	
$Ph_2(Se)PN(Ph)(Ph)_2PPdCl_2$	**11**	111.2(d)	56.1	67.6(d)	−4.5	66.4	$^1J_{PSe} = 578.2$
$Ph_2(S)PN(Ph)(Ph)_2PPtCl_2$	**12**	76.6(d)	22.1	75.4(d)	3.0	53.0	$^1J_{PtP} = 3856.7$, $^2J_{PtP} = 88.2$
$Ph_2(Se)PN(Ph)(Ph)_2PPtCl_2$	**13**	80.8(d)	25.7	61.4(d)	−10.7	58.8	$^1J_{PtP} = 3918.2$, $^2J_{PSe} = 554.4$, $^2J_{PtP} = 93.3$

[a] All spectra in $CDCl_3$ or CD_2Cl_2; ppm vs 85% H_3PO_4; d = doublet; dd = doublet of doublets. [b] $\Delta\delta(P^{III}) = \delta(P^{III}(\text{complex})) - \delta(P^{III}(\text{free ligand}))$. [c] $\Delta\delta(P^V) = \delta(P^V(\text{complex})) - \delta(P^V(\text{free ligand}))$.

Table II. Crystal Data for $[Cl_2PtP(Ph)_2N(Ph)P(S)Ph_2 \cdot H_2O$ (**12**)

formula	$C_{30}H_{27}Cl_2PtNOP_2S$	$F(000)$	1520
fw	777.56	T, deg	298K
space group	monoclinic, $P2_1/c$	λ, Å	0.710 73 (graph monoch)
a, Å	9.117(1)	μ(Mo Kα), cm^{-1}	51.7
b, Å	18.783(3)	ρ_{calcd}, g cm^{-3}	1.75
c, Å	17.288(2)	no. of obsd reflcns	4158
β, deg	92.16(1)	max 2θ, deg	52
V, Å^3	2959(1)	R^a	0.044
Z	4	$R_w{}^b$	0.057

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

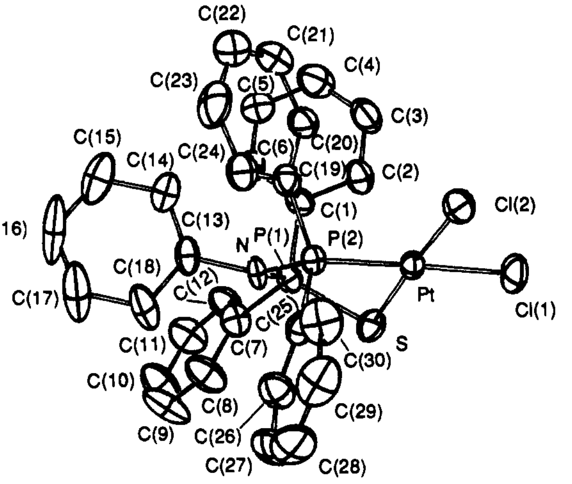

Figure 1. ORTEP[39] plot of a perspective view of $[Cl_2PtP(Ph)_2N(Ph)P(S)Ph_2 \cdot H_2O]$ showing the atom numbering scheme.

in Table II. Scattering factors for neutral atoms and the corrections for anomalous dispersions were taken from ref 32. All computations were carried out using the MolEN program set.[33] The structure of $[Cl_2PtPPh_2N(Ph)PPh_2(S)]$ is depicted in Figure 1 wherein the atom numbering scheme is given and an illustration of the central atom structure is given in Figure 2.

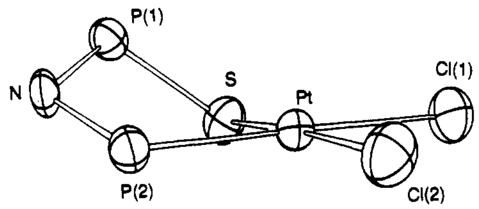

Figure 2. Plot of the central core of the complex $[Cl_2PtP(Ph)_2N(Ph)P(S)Ph_2 \cdot H_2O]$.

Table III. Positional Parameters of Important Framework[a] Atoms, Thermal Parameters and Estimated Standard Deviations for $[Cl_2PtP(Ph)_2N(Ph)P(S)Ph_2 \cdot H_2O]^b$ (**12**)

atom	x	y	z	B,[c] Å^2
Pt	0.11155(3)	0.23173(2)	0.60666(2)	2.292(6)
Cl(1)	0.3062(3)	0.2869(1)	0.5435(2)	4.07(5)
Cl(2)	0.2405(3)	0.1259(1)	0.6123(1)	3.56(5)
S	−0.0211(3)	0.3359(1)	0.5940(1)	3.11(5)
P(1)	−0.1144(2)	0.3291(1)	0.6967(1)	2.47(4)
P(2)	−0.0727(2)	0.1802(1)	0.6629(1)	2.32(4)
O[d]	−0.6549(8)	0.5175(4)	0.5043(4)	4.8(2)
N	−0.1806(7)	0.2461(4)	0.7024(4)	2.4(1)
C(1)	0.0127(9)	0.3466(5)	0.7768(5)	2.7(2)
C(7)	−0.265(1)	0.3885(5)	0.7034(5)	3.3(2)
C(13)	−0.2892(9)	0.2252(4)	0.7588(5)	3.0(2)
C(19)	−0.1904(9)	0.1340(5)	0.5931(5)	2.8(2)
C(25)	−0.0317(9)	0.1228(5)	0.7441(5)	2.7(2)

[a] The *ipso* phenyl carbons are given but all other phenyl carbons and hydrogen atoms are omitted. [b] Full details for all atoms are given in supplementary material. [c] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3) * [a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$. [d] Of water molecule.

The crystal data, experimental conditions for data collection, and details of structure and refinements are given in Table II. Selected atomic coordinates are listed in Table III. Selected bond lengths and angles are given in Table IV. Full details are given in the supplementary material.

Results and Discussion

We found the most efficient and clean synthesis of the sulfide (**1**) and selenide (**2**) to be the direct stoichiometric reaction of bis(diphenylphosphino)phenylamine with an equimolar amount of elemental sulfur or selenium powder in hexane, in toluene, or in a mixture of toluene and hexane (1:2), respectively (eq 1). The

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Table IV. Selected Bond Distances and Bond Angles for $[\overline{Cl_2PtPPh_2N(Ph)P(S)}Ph_2]\cdot H_2O$

	Distances (Å)[a]		
Pt–Cl(1)	2.358(3)	P(1)–C(1)	1.802(9)
Pt–Cl(2)	2.309(2)	P(1)–C(7)	1.777(9)
Pt–S	2.306(2)	P(2)–N	1.737(7)
Pt–P(2)	2.197(2)	P(2)–C(19)	1.807(9)
S–P(1)	2.003(3)	P(2)–C(25)	1.800(9)
P(1)–N	1.674(7)	N–C(13)	1.47(1)
	Angles (deg)[a]		
Cl(1)–Pt–Cl(2)	90.37(9)	N–P(1)–C(7)	107.4(4)
Cl(1)–Pt–S	89.12(9)	C(1)–P(1)–C(7)	108.2(4)
Cl(1)–Pt–P(2)	178.66(8)	Pt–P(2)–N	108.3(2)
Cl(2)–Pt–S	176.77(8)	Pt–P(2)–C(19)	111.2(3)
Cl(2)–Pt–P(2)	89.96(8)	Pt–P(2)–C(25)	118.0(3)
S–Pt–P(2)	90.49(8)	N–P(2)–C(19)	105.9(4)
Pt–S–P(1)	95.7(1)	N–P(2)–C(25)	103.0(4)
S–P(1)–N	106.1(3)	C(19)–P(2)–C(25)	109.5(4)
S–P(1)–C(1)	112.8(3)	P(1)–N–P(2)	115.4(4)
S–P(1)–C(7)	111.9(3)	P(1)–N–C(13)	122.8(6)
N–P(1)–C(1)	110.4	P(2)–N–C(13)	118.4(5)

[a] Numbers in parentheses beside values indicate standard deviations in the least significant digits.

$$Ph_2PN(Ph)PPh_2 + E \xrightarrow{\Delta} Ph_2PN(Ph)P(E)Ph_2$$

$$E = S \text{ or } Se \qquad (1)$$

progress of the reaction can be readily followed visually by the disappearance of sulfur in the case of **1** and the black color of Se in the case of **2**. Keat has reported[34] a few compounds of the type, $Y_2PN(R)'PY_2(E)$ obtained by using more complex routes shown in the reaction sequences (2) and (3) generally using preoxidized ($P(E)Y_2X$) reagents in the second step (eq 3). Our direct, one-step, method however (eq 1) gave us almost quantitative yields of the monooxidized bis(diphenylphosphino)phenylamines. Surprisingly, the reaction of bis(diphenylphosphino)phenylamine with elemental sulfur proceeded smoothly in hexane, a medium in which both of the reactants appear to be highly insoluble. The microcrystalline product (**2**) formed during the course of the reaction is also insoluble in hexane. The product was free of unreacted starting material or doubly oxidized product. In contrast, the same reaction proceeded rather slowly in toluene solvent, the product was always contaminated with the doubly oxidized product, $Ph_2P(E)N(Ph)P(E)Ph_2$, (~10%) and 10–15% of the starting material was not consumed. The bis(phosphino)amine reacted cleanly with selenium in a mixture of toluene and hexane (1:2) to give the monooxidized Se derivative (**3**) in almost quantitative yield.

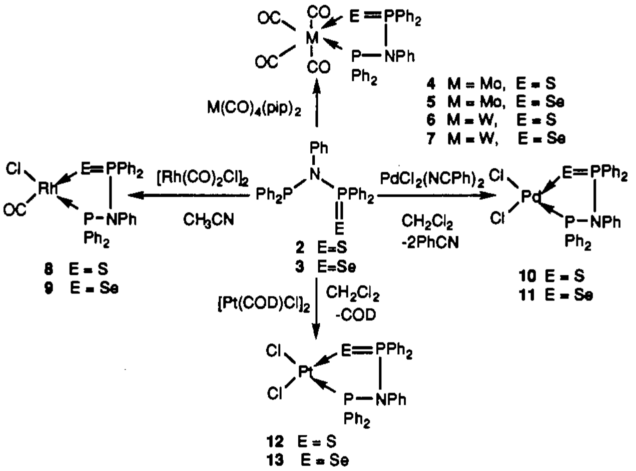
$$Me_3SiN(H)R + BuLi \rightarrow Me_3SiN(R)Li \xrightarrow{Ph_2PCl} Me_3SiN(R)PPh_2 \qquad (2)$$

$$Me_3SiN(R)PPh_2 + XCl \rightarrow XN(R)PPh_2 + Me_3SiCl$$

$$X = PCl_2,\ PPh_2,\ P(O)Cl_2 \text{ or } P(S)Ph_2 \qquad (3)$$

The ^{31}P NMR spectrum of **2** shows two sharp doublets at 54.5 ppm and 72.4 ppm, respectively, for P^{III} and P^V centers with a $^2J_{P^{III}P^V}$ value of 104.6 Hz. The ^{31}P NMR spectrum of **3** also shows two sharp doublets at 55.1 and 72.1 ppm with a $^2J_{P^{III}P^V}$ coupling of 110.3 Hz with the latter (P^V center) also showing $^1J_{PSe}$ coupling of 766.5 Hz. The large values of $^2J_{PP'}$ observed for these compounds are a characteristic feature of these $P^{III}NP^V$ backbone structures.

Scheme I



Reactions of 2 and 3 with Mo(0) and W(0) Derivatives: The new heterodifunctional compounds **2** and **3** act as chelating ligands with low-valent metal centers. For example, molybdenum and tungsten carbonyl derivatives reacted cleanly with **2** and **3** to give **4–7** in good yields (Scheme I). Ligands **2** and **3** are not sufficiently basic to displace CO directly from the group 6 metal carbonyls; labile substituents such as piperidine are required so that these soft base ligands will complex to the metal center. The complexes **4–7** are air-stable, crystalline solids which are monomeric in solution.

The infrared spectra of the complexes **4–7** exhibit four characteristic[35] ν_{CO} absorptions in the range 2020–1840 cm^{-1}, lying slightly toward the lower end of the CO frequency range compared to those for the bis(phosphino)amine ligands.[9,18,20] We attribute this to the fact that there is only one strong π-acceptor (P^{III}) coordinating center in the heterodifunctional chelate.

The ^{31}P NMR data for the complexes are given in Table I. Complexes **4–7** exhibit two sharp doublets as a result of the presence of two dissimilar phosphorus centers. In all cases the P^{III} center shows considerable deshielding upon coordination, with coordination shifts in the range 45–65 ppm. The P^V centers shift about 12 ppm upfield relative to the ligand resonance in the case of complexes of the sulfur-containing ligand and remain almost unchanged in the case of complexes of the selenium-containing ligand. There is also no significant change in the $^2J_{P^{III}P^V}$ values upon coordination, however, the $^1J_{PSe}$ satellite couplings for complexes **5** and **7** decrease by 100 Hz relative to the uncoordinated ligand, which could be due to a decreased P=Se double bond character arising from formation of the coordinate link. The tungsten complexes **5** and **7** exhibit $^1J_{PW}$ couplings of 258 and 259 Hz, respectively, with the former also showing a $^2J_{PW}$ value of 8.0 Hz.

Reactions of 2 and 3 with Rh(I), Pd(II), and Pt(II) Metal Centers. Ligands **2** and **3** readily react with $[Rh(CO)_2Cl]_2$ in CH_3CN at 25 °C to give chelates **8** and **9** respectively (Scheme I). The infrared spectra of the products **8** and **9** show ν_{CO} absorptions at 1978 and 1981 cm^{-1}, respectively, which is consistent with the *cis* phosphine structures proposed for these complexes. Further evidence comes from the $^{31}P\{^1H\}$ NMR spectroscopic data. The $^{31}P\{^1H\}$ NMR spectrum of complex **8** shows a doublet of doublets for the P^{III} center with a $^1J_{RhP}$ value of 158.7 Hz. The P^V center also appears as a doublet of doublets with $^2J_{RhP}$ coupling of 3.0 Hz. The $^2J_{PP}$ coupling is 71.3 Hz. In the case of complex **9**, the P^V center also shows a $^1J_{PSe}$ coupling value of 601.5 Hz and a small $^2J_{PRh}$ coupling of 1.1 Hz.

Reactions of **2** and **3** with $Cl_2Pd(PhCN)_2$ and $Pt(COD)Cl_2$ in CH_2Cl_2 at 25 °C give chelate complexes **10–13** in good yields.

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The X-ray structure of one of these complexes, **12**, shows that the complex is monomeric. The $^{31}P\{^1H\}$ NMR spectra of complexes **10–13** exhibit two characteristic doublet resonance patterns due to the P^{III} and P^{V} centers respectively with $^2J_{PP}$ couplings ranging from 61 to 80 Hz. Platinum complexes **12** and **13** also exhibit very large $^1J_{PPt}$ couplings of 3857 and 3918 Hz clearly indicative of P coordination to Pt. The $^2J_{PtP}$ values are 140 and 93 Hz respectively. The complexes **11** and **13** also show $^1J_{PSe}$ couplings of 578.2 and 554.4 Hz respectively, substantially smaller than the values found for the free ligand and characteristic of directly bound Se. These satellites serve to clearly identify the oxidized phosphorus center.

^{31}P NMR Spectroscopic Trends. Phosphorus-31 NMR data are given in Table I. The assignment of chemical shifts to P^{III} and P^{V} centers in these P^{III}–N–P^{V}-bridged bis(phosphines) is not always straightforward. In the case of **3**, however the low-field doublet at 72.1 ppm clearly shows selenium-77 satellites, thus identifying this signal as that arising from the P^{V} center in spite of the rather low-field resonance. By analogy, the even lower field signal (δ 72.4 ppm) in **2** is also assigned to the P^{V} center. In contrast Bulloch *et al.*[36] assigned the lowest field shifts in all cases to the P^{III} center in the analogous compounds, $Cl_2PN(Me)P(O)Cl_2$, $Cl_2PN(Me)P(S)Cl_2$, $Ph_2PN(Me)P(S)Ph_2$, $Ph_2PN(Et)P(S)Ph_2$, which is the reverse of our assignment. However, Bulloch *et al.* did not have access to the selenium analogs which guide our ^{31}P NMR assignments. Our assignments are of course not absolute for all cases and further efforts to definitively unravel the uncertainties would be warranted. It is also worth noting that the relatively large $^2J_{PP}$ coupling constant values are characteristic features of the bisphosphines containing $P^{III}NP^{V}$ backbones.

Chemical shifts of the P^{III} centers in molybdenum and tungsten complexes **4–7** are substantially shifted to low field compared to those of the free ligands. These large P^{III} coordination shifts indicate substantial deshielding of P^{III}, probably due to the chelate ring stabilizing effect,[37] and are in agreement with previous studies of a variety of metal complexes of symmetric bis(phosphine) donors.[20] The coordination shifts at the P^{V}–chalcogenyl phosphorus are generally very small; the smallest coordination shift values of 0.6 and 1.2 ppm are shown for the Mo and W complexes respectively of **2**. Larger coordination shifts of 11.6 and 12.0 ppm are observed for Mo and W complexes of **3**. It should be noted that the coordination of the chalcogen atom in these bis(phosphine)–monochalcogenides to form a five-membered chelate ring does not confer any extraordinary chelate ring effect for the chalcogenyl bearing phosphorus as compared to the trivalent phosphorus directly bound to the metal center. Also the $^2J_{PP}$ values were not greatly affected. In the case of Rh, Pd, and Pt chelates, the same shift trends are again observed, but the $^2J_{PP}$ couplings are considerably decreased compared to the free ligands. Similar trends are observed for the $^1J_{PSe}$ couplings of the complexes within the selenium-containing ligands, which decreases steadily from Mo to Pt. However, understanding the chelate ring effect on the chemical shifts of the phosphorus atom which is not coordinated to metal and rationalizing the magnitude of $^2J_{PP}$ values is a complex matter which cannot be resolved with the data available. With the formation of the chelate another coupling pathway linking the phosphorus atoms becomes available and we are undoubtedly observing a combination of ^2J and ^3J values. The former are large and probably positive[4] and are expected to dominate the longer range coupling which is most certainly smaller. The through-metal coupling interactions are undoubtedly strongly dependent on the nature of the metal and so we would expect to observe large variations of J_{PP}. Further complications are however introduced with the removal of conformational averaging within the ligand upon complex formation[38] so the ligand coupling values cannot be directly transferred to the complexes. The large values of J_{PP} demonstrated by these complexes suggest that they could be useful vehicles for further study of the influences of the different contributions to coupling constant variation in metal chelates.

The Crystal and Molecular Structure of 12, [$Cl_2PtP(Ph)_2N(Ph)P(S)Ph_2 \cdot H_2O$]. The structure of platinum complex **12** was determined from a single crystal X-ray diffraction study. A perspective view of the molecule showing the numbering scheme is shown in Figure 1[39] and the central core is shown in Figure 2. Selected bond lengths and bond angles are listed in Table IV. The complex did not crystallize well from very dry solvents but curiously the complex did crystallize with one molecule of H_2O from undried solvent. The incorporated water does not however appear to be involved in any particularly strong interaction with any part of the complex.

The structure of the complex shows a monomeric chelated metal complex with a typical square planar metal environment in which the unsymmetric bis(phosphino)amine ligand, $PPh_2N(Ph)Ph_2P{=}S$ (**1**) acts as a bidentate ligand coordinating via the phosphorus(III) and sulfur centers to form a five-membered chelate ring. The chlorine atoms are *cis*-disposed as required by the geometry of the bidentate ligand. The Pt atom itself shows the greatest deviation (–0.04 Å) from the square plane of Cl(1), Cl(2), Pt, P(2), and S. The remaining ligand atoms (P(1) and N) are significantly displaced from the plane (–1.18 and –0.61 Å, respectively) as illustrated in Figure 2.

It is interesting to compare the structural features of **12** with the palladium complex of symmetric bis(diphenylphosphino)-ethylamine, [$Cl_2PdP(Ph)_2N(Et)PPh_2$] (**14**).[40] The Pt–P(2) distance, 2.197(2) Å, in the relatively strain-free five-membered chelate of **12** is significantly shorter than that observed in the four-membered PdP_2N ring (2.22, 2.23 Å) of **14**. The considerable strain in the PdP_2N ring of **14** was also reflected in the P–Pd–P bond angle of 71.4(3)° which is considerably reduced from the 90° expected for a square–planar configuration. The five-membered ring in our platinum complex, **12**, shows, in contrast, a P–Pt–S angle of 90.49(8)° as expected for a typical square planar complex. The bond angle at nitrogen (P^{III}–N–P^{V}) is 115.4(4)° which indicates a trigonal-planar geometry around nitrogen in a relatively strain-free PtSPNP ring. In contrast the P^{III}–N–P^{V} angle in **14** (97.7(1)°) is considerably smaller than either tetrahedral or trigonal angles and again indicates high strain in the PdPNP ring. The Pt–Cl(1) bond distance (2.358(3) Å) in **12** which is *trans* to the Pt–P(2) bond is comparable to typical Pt–Cl bond distances (2.33–2.35 Å) in Pt phosphine complexes,[41,42] but the Pt–Cl(2) bond distance *trans* to the Pt–S bond is much shorter (2.309(2) Å). This difference is in keeping with the apparently greater *trans* influence of phosphorus *vs* sulfur.[43,44]

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The P(2)–N bond distance of 1.737(7) Å in **12** is close to the normally accepted P–N single bond value of 1.77 Å,[45] but the $P^V(1)$–N bond distance of 1.674(7) Å is closer to the values (*ca.* 1.6 Å) typically found for the P–N bond lengths in cyclic phosphazenes[46] and is clearly suggestive of more multiple character in this P^V–N bond than might be expected, considering that the nitrogen is nominally an amine type. However this nitrogen is in reality almost planar and it is clear that the P^V center has accepted much of the lone pair electron density from the backbone N. The P(1)–S and Pt–S bond distances are 2.003(3) and 2.306(2) Å, respectively, and are not unusual.

Conclusion

The bis(phosphino)amines with PNP backbones can be readily oxidized at one phosphorus to form a series of P, E (E = S, Se) heterodifunctional ligands which have extensive coordination chemistry. These heterodifunctional ligands provide a soft P^{III} center in combination with a relatively harder chalcogenyl center (S or Se). NMR chemical shifts of the P(III) and P(V) centers are readily assigned through the assistance of Se coupling satellites with the surprising conclusion that the formal P(V) centers may often lie to low field of the P(III) centers. The range of coordination shifts of the P^V centers also can be negative as well as the usually observed positive sense.

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Supplementary Material Available: Table S1, listing non-hydrogen positional parameters and isotropic thermal parameters for all atoms along with the estimated standard deviations, Table S2, giving calculated hydrogen atom positional parameters, Table S3, giving all bond distances in Å, Table S4, giving all bond angles in deg, Table S5, giving general displacement parameter (*U*) expressions for all non-hydrogen atoms, and Table S6, giving least-squares planes (7 pages). Ordering information is given on any current masthead page.

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