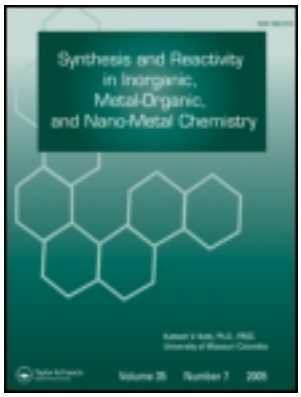

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Synthesis and Characterization of Monoaminophosphine, Bis(Amino)Phosphine Derivatives, and their Metal Complexes

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Synthesis and Characterizatıon of Monoaminophosphine, Bis(Amino)Phosphine Derivatives, and their Metal Complexes

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Functionalized monoaminophosphine of the type Ph_2PNR_2 (1 and 3) and bis(amino)phosphine of the type $PhP(NR_2)_2$ (2) have been synthesized by treating Ph_2PCl or $PhPCl_2$ with corresponding amines. Ligands react with aqueous hydrogen peroxide, elemental sulfur, or selenium to give the corresponding chalcogenides in good yield. The metal complexes of the aminophosphines have been obtained. All of the compounds were obtained in good yields and were characterized by IR, NMR, and microanalysis.

Keywords aminophosphines, complexation, oxidation, synthesis

INTRODUCTION

The coordination and organometallic chemistry of phosphorus bearing ligands possessing one (or more) P—N bond(s) has received some attention, especially of late.[1–7] Although they possess two potential donor atoms, their coordination compounds involve almost exclusively the metal–phosphorus bond.[8] The transition metal chemistry of aminophosphines is limited. This is partly due to the sensitivity of the P(III)/N bonds towards acid or base catalysed hydrolysis during complexation reactions.[2] Many aminophosphine ligands and their complexes have been investigated in a number of catalytic processes.[5,9–12] The presence of P-N bidentate ligands enables many different and important catalytic processes to occur, including asymmetric hydroboration, carbonylation of alkynes, Stille coupling, and asymmetric hydrogenation of highly substituted alkenes, to name a few.[10] Some aminophosphines and derivatives have also found application as anticancer drugs, herbicides, and antimicrobial agents, as well as neuroactive agents[9]

Herein, we describe the synthesis of new aminophosphine ligands and the corresponding aminophosphine chalcogenides of the general formula $Ph_2P(E)NR_2$ or $PhP(E)(NR_2)_2$ and their transition metal complexes. The compounds were fully characterized by IR, ^1H NMR, and ^{31}P NMR spectroscopic techniques, and by elemental analysis.

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EXPERIMENTAL

Reactions were routinely carried out using Schlenk-line techniques under pure dry nitrogen gas. Solvents were dried and distilled prior to use. $[Mo(CO)_4(bipy)]$ and $[Cr(CO)_4(bipy)]$ were prepared according to the literature procedures.[13] All other chemicals were reagent grade, available commercially, and used without further purification. Melting points were determined on a Electrothermal A 9100 and are uncorrected. $^{31}P\text{-}\{^1H\}$ and ^1H NMR spectra were taken on Bruker UltraShield-400 spectrophotometer. Infrared spectra were recorded on a Perkin Emler FT-IR System Spectrum BX as KBr pellets. Elemental analysis were performed in a CHNS-932 (LECO).

Preparation of $PPh_2N(CH_2C_6H_5)_2$ (1)

Triethylamine (1.8 mL, 13.05 mmol) and Ph_2PCl (2.4 mL, 13.05 mmol) were sequentially added with stirring to a solution of $NH(CH_2C_6H_5)_2$ (2.5 mL, 13.05 mmol) in THF (20 mL). The reaction mixture was stirred for 3 h and then filtered to remove $Et_3N.HCl$. The resulting solution was evaporated under reduced pressure and the product extracted with diethyl ether at –78°C. The solvent was removed under vacuum to give a white solid of the crude product, which was crystallized from CH_2Cl_2/diethyl ether mixture (2:1) at 0°C. Yield 3.75 g (75%). m.p.: 83–85°C. ^1H NMR ($CDCl_3$, δ, ppm): 7.01–8.02 (m, Ph, 20H), 4.10 (d, N-CH_2, 4H, $J_{P\text{-}H} = 8.2$ Hz). $^{31}P\text{-}\{^1H\}$ NMR ($CDCl_3$, δ, ppm): 66.5 (s). Selected IR (KBr, cm^{-1}): 861 (PN), 1438 (PPh). Elemental analysis: $C_{26}H_{24}PN$ (381.45 $gmol^{-1}$) Found (required): C, 81.74 (81.87); H, 6.15 (6.34); N, 3.52 (3.67).

Preparation of $PhP\{N(CH_2C_6H_5)_2\}_2$ (2)

A similar procedure to that described in 1 was used. Yield 6.0 g (65%). m.p.: 93–94°C. ^1H NMR ($CDCl_3$, δ, ppm): 7.27–7.65 (m, Ph, 25H), 4.05 (d, NCH_2, 8H, $J_{P\text{-}H} = 7.9$ Hz). $^{31}P\text{-}\{^1H\}$ NMR ($CDCl_3$, δ, ppm): 24.3 (s). Selected IR (KBr, cm^{-1}): 850 (PN), 1443 (PPh). Elemental analysis: $C_{34}H_{33}PN_2$

(500.61 $gmol^{-1}$) Found (required): C, 81.23 (81.57); H, 6.48 (6.64); N, 5.49 (5.60).

Preparation of $PPh_2NHCH_2SO_3H$ (3)

A similar procedure to that described in 1 was used. Yield 2.1 g (71%). m.p.: 147°C. ^1H NMR ($CDCl_3$, δ, ppm): 6.90–8.01. (m, PPh, SO_3H, 11H), 5.41 (b, NH, 1H), 2.90 (d, $PNCH_2$, 2H, $J_{P\text{-}H}$ = 29 Hz). ^{31}P-$\{^1H\}$ NMR ($CDCl_3$, δ, ppm): 30.3 (s). Selected IR (KBr, cm^{-1}): 960 (PN), 1433 (PPh). Elemental analysis: $C_{13}H_{14}PNO_3S$ (295.29 $gmol^{-1}$) Found (required): C, 52.77 (52.88); H, 4.75 (4.78); N, 4.71 (4.74); S, 10.76 (10.86).

Preparation of $Ph_2P(O)N(CH_2C_6H_5)_2$ (4)

A THF solution (10 mL) of 1 (0.75 g, 1.96 mmol) and aqueous H_2O_2 (30% w/w, 0.2 mL) was stirred for 2 h at room temperature. The reaction mixture was concentrated to ca. 1–2 mL *in vacuo* and diethylether (20 mL) was added. The precipitate was filtered and dried in air to yield 4. Yield 0.33 g (42%). m.p.: 195–196°C. ^1H NMR ($CDCl_3$, δ, ppm): 7.12–8.07 (m, Ph, 20H), 4.11 (s, N-CH_2, 4H). ^{31}P-$\{^1H\}$ NMR ($CDCl_3$, δ, ppm): 31.4 (s). Selected IR (KBr, cm^{-1}): 897 (PN), 1438 (PPh), 1199 (P = O). Elemental analysis: $C_{26}H_{24}PNO$ (397.45 $gmol^{-1}$) Found (required): C, 78.21 (78.57); H, 5.95 (6.09); N, 3.66 (3.52).

Preparation of $Ph_2P(S)N(CH_2C_6H_5)_2$ (5)

Ligand 1 (0.71 g, 1.87 mmol) and S_8 (0.06 g, 1.87 mmol) were refluxed in toluene (20 mL) for 5 h. The reaction mixture was concentrated to ca. 1–2 mL *in vacuo* and diethylether (20 mL) was added. The precipitate was filtered and dried in air to yield 5. Yield 0.44 g (57%). m.p.: 90–91°C. ^1H NMR ($CDCl_3$, δ, ppm): 7.10–8.01 (m, Ph, 20H), 4.19 (d, N-CH_2, 4H, $J_{P\text{-}H}$ = 7.2 Hz). ^{31}P-$\{^1H\}$ NMR ($CDCl_3$, δ, ppm): 70.8 (s). Selected IR (KBr, cm^{-1}): 896 (PN), 633 (PS), 1437 (PPh). Elemental analysis: $C_{26}H_{24}PNS$ (413.51 $gmol^{-1}$) Found (required): C, 75.33 (75.52); H, 5.72 (5.85); N, 3.22 (3.39); S, 7.56 (7.75).

Preparation of $Ph_2P(Se)N(CH_2C_6H_5)_2$ (6)

Ligand 1 (0.50 g, 1.30 mmol) and grey Se (0.10 g, 1.30 mmol) were refluxed in toluene (20 mL) for 5 h. The reaction mixture was concentrated to ca. 1–2 mL *in vacuo* and diethylether (20 mL) was added. The precipitate was filtered and dried in air to yield 6. Yield 0.40 g (62%). m.p.: 84–86°C. ^1H NMR ($CDCl_3$, δ, ppm): 7.11–8.01 (m, Ph, 20H), 4.21 (d, N-CH_2, 4H, $J_{P\text{-}H}$ = 11.7 Hz). ^{31}P-$\{^1H\}$ NMR ($CDCl_3$, δ, ppm): 70.4 (s, J_{PSe} = 755 Hz). Selected IR (KBr, cm^{-1}): 896 (PN), 566 (PSe), 1436 (PPh). Elemental analysis: $C_{26}H_{24}PNSe$ (460.41 $gmol^{-1}$) Found (required): C, 67.63 (67.83); H, 5.14 (5.25); N, 2.86 (3.04).

Preparation of $PhP(O)\{N(CH_2C_6H_5)_2\}_2$ (7)

A similar procedure to that described in 4 was used. Yield 0.20 g (40%). m.p.: 117–120°C. ^1H NMR ($CDCl_3$, δ, ppm): 7.29–7.57 (m, Ph, 25H), 3.95 (s, N-CH_2, 8H). ^{31}P-$\{^1H\}$ NMR ($CDCl_3$, δ, ppm): 18.9 (s). Selected IR (KBr, cm^{-1}): 856 (PN), 1429 (PPh), 1209 (P=O). Elemental analysis: $C_{34}H_{33}PN_2O$ (516.61 $gmol^{-1}$) Found (required): C, 78.87 (79.05); H, 6.22 (6.44); N, 5.28 (5.42).

Preparation of $PhP(S)\{N(CH_2C_6H_5)_2\}_2$ (8)

A similar procedure to that described in 5 was used. Yield 0.29 g (54%). m.p.: 113–114°C. ^1H NMR ($CDCl_3$, δ, ppm): 7.22–7.32 (m, Ph, 25H), 4.12 (d, N—CH_2, 8H, $J_{P\text{-}H}$ = 6.8 Hz). ^{31}P-$\{^1H\}$ NMR ($CDCl_3$, δ, ppm): 109.4 (s). Selected IR (KBr, cm^{-1}): 850 (PN), 665 (PS), 1442 (PPh). Elemental analysis: $C_{34}H_{33}PN_2S$ (532.68 $gmol^{-1}$) Found (required): C, 76.43 (76.66); H, 6.18 (6.24); N, 5.17 (5.26); S, 5.88 (6.02).

Preparation of $PhP(Se)\{N(CH_2C_6H_5)_2\}_2$ (9)

A similar procedure to that described in 6 was used. Yield 0.34 g (59%). m.p.: 103–105°C. ^1H NMR ($CDCl_3$, δ, ppm): 7.25–7.58 (m, Ph, 25H), 3.94 (d, N—CH_2, 8H, $J_{P\text{-}H}$ = 8.1 Hz). ^{31}P-$\{^1H\}$ NMR ($CDCl_3$, δ, ppm): 102.2 (s, J_{PSe} = 746 Hz). Selected IR (KBr, cm^{-1}): 851 (PN), 578 (PSe), 1443 (PPh). Elemental analysis: $C_{34}H_{33}PN_2Se$ (579.57 $gmol^{-1}$) Found (required): C, 70.23 (70.46); H, 5.55 (5.74); N, 4.66 (4.83).

Preparation of $Ph_2P(O)NHCH_2SO_3H$ (10)

A similar procedure to that described in 4 was used. Yield 0.29 g (55%). m.p.: 165–167°C. ^1H NMR (DMSO, δ, ppm): 7.21–7.82 (m, PPh, SO_3H, 11H), 4.29 (s, NH, 1H), 3.11 (s, $PNCH_2$, 2H). ^{31}P-$\{^1H\}$ NMR ($CDCl_3$, δ, ppm): 22.9 (s). Selected IR (KBr, cm^{-1}): 937 (PN), 1205 (P=O), 1438 (PPh). Elemental analysis: $C_{13}H_{14}PNO_4S$ (311.29 $gmol^{-1}$) Found (required): C, 50.06 (50.16); H, 4.47 (4.53); N, 4.56 (4.50); S, 10.35 (10.30).

Preparation of $Ph_2P(Se)NHCH_2SO_3H$ (11)

A similar procedure to that described in 6 was used. Yield 0.4 g (63%). m.p.: 191–192°C. ^1H NMR ($CDCl_3$, δ, ppm): 7.15–7.80 (m, PPh, SO_3H, 11H), 3.79 (s, NH, 1H), 2.37 (s, $PNCH_2$, 2H). ^{31}P-$\{^1H\}$ NMR ($CDCl_3$, δ, ppm): 61.4 (s, J_{PSe} = 747 Hz). Selected IR (KBr, cm^{-1}): 957 (PN), 567 (PSe), 1435 (PPh). Elemental analysis: $C_{13}H_{14}PSeNO_3S$ (374.25 $gmol^{-1}$) Found (required): C, 41.63 (41.72); H, 3.66 (3.77); N, 3.66 (3.74); S, 8.48 (8.57).

Preparation of cis-$[Mo(CO)_4(PPh_2N(CH_2C_6H_5)_2)_2]$ (12)

Ligand 1 (0.73 g, 1.92 mmol) and $[Mo(CO)_4(bipy)]$ (0.35 g, 0.96 mmol) were refluxed in 20 mL CH_2Cl_2 for 5 h. The solution was concentrated *in vacuo*, and the purple product was precipitated with diethylether (30 mL). The residue was washed with toluene (3×5 mL). Yield: 0.77 g (83%). m.p.: 139–141°C (decomp).^1H NMR ($CDCl_3$, δ, ppm): 7.00–7.96 (m. Ph, 40H), 4.05 (s, CH_2, 8H). ^{31}P-$\{^1H\}$ NMR ($CDCl_3$, δ, ppm): 102.4. Selected IR (KBr, cm^{-1}): 894 (PN), 1437 (PPh), 2011, 1910, 1871 and 1818 (CO). Elemental analysis: $C_{56}H_{48}P_2N_2O_4Mo$ (970.88 $gmol^{-1}$) Found (required): C, 69.13 (69.28); H, 4.78 (4.98); N, 2.57 (2.88).

Preparation of cis-[Mo(CO)$_4$(PhP{N(CH$_2$C$_6$H$_5$)$_2$}$_2$)$_2$] (13)

A similar procedure to that described in 12 was used. Yield: 0.45 g (75%). m.p.: 150–151°C (decomp).^{1}H NMR (DMSO, δ, ppm): 7.40–7.98 (m, Ph, 50H), 4.13 (s, CH_2, 16H). ^{31}P-{^{1}H} NMR ($CDCl_3$, δ, ppm): 73.7. Selected IR (KBr, cm^{-1}): 858 (PN), 1440 (PPh), 2009, 1865 and 1813 (CO). Elemental analysis: $C_{72}H_{66}P_2N_2O_4Mo$ (1209.21 gmol^{-1}) Found (required): C, 71.33 (71.51); H, 5.38 (5.50); N, 4.37 (4.63).

Preparation of cis-[Cr(CO)$_4$(PhP{N(CH$_2$C$_6$H$_5$)$_2$}$_2$)$_2$] (14)

A similar procedure to that described in 12 was used. Yield: 0.38 g (65%). m.p.: 147–149°C (decomp). ^{1}H NMR ($CDCl_3$, δ, ppm): 7.32–8.11 (m, Ph, 50H), 3.66 (s, CH_2, 16H). ^{31}P-{^{1}H} NMR ($CDCl_3$, δ, ppm): 102.2. Selected IR (KBr, cm^{-1}): 885 (PN), 1440 (PPh), 2002, 1871 and 1813 (CO). Elemental analysis: $C_{72}H_{66}P_2N_4O_4Cr$ (1165.26 gmol^{-1}) Found (required): C, 73.98 (74.21); H, 5.58 (5.71); N, 4.57 (4.81).

Preparation of [Cu(Ph$_2$PN(CH$_2$C$_6$H$_5$)$_2$)$_2$Cl$_2$] (15)

Ligand 1 (0.45 g, 1.20 mmol) and $CuCl_2.2H_2O$ (0.10 g, 0.59 mmol) and were refluxed in 20 mL THF for 3 h. The solution was concentrated *in vacuo*, and the green product was precipitated with diethylether (30 mL). Yield: 0.38 g (70%). m.p.: 272–274°C (decomp). ^{1}H NMR ($CDCl_3$, δ, ppm): 7.21–7.74 (m, Ph, 40H), 4.06 (s, CH_2, 8H). ^{31}P-{^{1}H} NMR ($CDCl_3$, δ, ppm): 80.8. Selected IR (KBr, cm^{-1}): 894 (PN), 1437 (PPh). Elemental analysis: $CuC_{52}H_{48}P_2N_2Cl_2$ (897.35 gmol^{-1}) Found (required): C, 69.43 (69.60); H, 5.18 (5.39); N, 2.99 (3.12).

Preparation of [Cu{(CH$_3$COO)$_2$(PhP{N(CH$_2$C$_6$H$_5$)$_2$}$_2$)$_2$}] (16)

Ligand 2 (0.50 g, 1.0 mmol) and $Cu(CH_3COO)_2H_2O$ (0.10 g, 0.50 mmol) were refluxed in 20 mL CH_2Cl_2 for 4 h. The solution was concentrated *in vacuo*, and the green product was precipitated with diethylether (30 mL). Yield: 0.40 g (68%). m.p.: 253–254°C (decomp).^{1}H NMR ($CDCl_3$, δ, ppm): 6.91–7.56 (m, Ph, 50H), 3.57 (s, CH_2, 16H), 2.22 (s, CH_3COO, 6H). ^{31}P-{^{1}H} NMR ($CDCl_3$, δ, ppm): 80.8. Selected IR (KBr, cm^{-1}): 850 (PN), 1443 (PPh). Elemental analysis: $CuC_{72}H_{72}P_2N_4O_4$ (1182.86 gmol^{-1}) Found (required): C, 72.93 (73.11); H, 5.98 (6.13); N, 4.44 (4.74).

Preparation of [Ni(PPh$_2$NHCH$_2$SO$_3$H)$_2$Cl$_2$] (17)

A mixture of $NiCl_2.6H_2O$ (0.13 g, 0.88 mmol) and $PPh_2NHCH_2SO_3H$ (0.50 g, 1.7 mmol) in THF (10 ml) was stirred at r.t. for 1 h. The solution was evaporated under reduced pressure and the orange product was precipitated with diethylether (20 mL). Yield: 0.44 g (72%). m.p.: 178–180°C (decomp). ^{1}H NMR ($CDCl_3$, δ, ppm): 6.91–8.56 (m, Ph, SO_3H, 22H), 3.45 (b, NH, 2H), 2.83 (s, $PNCH_2$, 4H). ^{31}P-{^{1}H} NMR ($CDCl_3$, δ, ppm): 47.2. Selected IR (KBr, cm^{-1}): 943 (PN), 1436 (PPh). Elemental analysis: $NiC_{26}H_{28}P_2N_2O_6S_2Cl_2$ (720.19 gmol^{-1}) Found (required): C, 43.21 (43.36); H, 4.18 (3.92); N, 3.98 (3.89); S, 8.82 (8.90).

Preparation of [Co(PPh$_2$NHCH$_2$SO$_3$H)$_2$Cl$_2$] (18)

$CoCl_2.2H_2O$ (0.14 g, 0.84 mmol) and $PPh_2NHCH_2SO_3H$ (0.5 g, 1.69 mmol) were refluxed in 20 mL THF for 5 h. The solvent was removed under vacuum to give a blue solid of the crude product, which was crystallized from dichloromethane/diethylether (2:1). Yield: 0.42 g (69%). m.p.: 227–228°C (decomp). ^{1}H NMR ($CDCl_3$, δ, ppm): 7.10–7.70 (m, Ph, SO_3H, 22H), 4.52 (b, NH, 2H), 2.66 (s, $PNCH_2$, 4H). ^{31}P-{^{1}H} NMR ($CDCl_3$, δ, ppm): 45.8. Selected IR (KBr, cm^{-1}): 945 (PN), 1438 (PPh). Elemental analysis: $CoC_{26}H_{28}P_2N_2O_6S_2Cl_2$ (720.43 gmol^{-1}) Found (required): C, 43.03 (43.35); H, 3.88 (3.92); N, 3.78 (3.89); S, 8.98 (8.90).

RESULTS AND DISCUSSION

Earlier works had shown that primary and secondary amines react with chlorophosphines in the presence of a tertiary amine base to form aminophosphines.[14] Ligands 1–3 can be prepared from corresponding commercially available amine and dichlorophenylphosphine or chlorodiphenylphosphine according to the literature.[15] Synthesis of mono- and bis(amino)phosphine ligands (1–3) and their oxidation reactions are shown in Figure 1.

The structure of the compounds (**1**–**3**) was confirmed by spectroscopic analysis. The spectroscopic data for synthesized compounds is shown in Table 1. The ^{31}P-{^{1}H} NMR spectra of the aminophosphines and the bis(amino)phosphine show singlets at 66.5 ppm for **1**, 24.3 ppm for **2**, and 30.3 ppm for 3.[16–19] The absence of a signal at 81.5 or 160.2 ppm indicates that no unreacted PPh_2Cl or $PPhCl_2$ remained.[20] The ^{31}P NMR spectra are consistent with the proposed structure. The chemical shifts in the ^{31}P-{^{1}H} NMR spectra are in accordance with the electronic properties of the substituents on nitrogen and phosphorus.[16–19]

Among the routes used to prepare aminophosphines, the most frequently used method involves aminolysis of a phosphine chloride. The reaction of phosphine chloride and the primary amine usually provides the target compound, $RNHPR_2$, in high yield.[18] The reactions of some primary amine derivatives with Ph_2PCl in the presence of triethylamine have been thoroughly studied, and different substances were obtained, depending on the relative ratio of the reagents, the electron-withdrawing groups, and their positions on the aromatic ring and solvents such as diethyl ether and dichloromethane.[19] Aminophosphines (Ph_2PNHR) are found as the main products, and when the reaction conditions changed, diphosphinoamines ($RN(PPh_2)_2$) or iminodiphosphines ($RN = PPh_2PPh_2$) are also formed as the major products.[19] The substituents at the amine backbone can also play an important role in determining the outcome of the products.[21]

We investigated the aminolysis reaction of aminomethanesulfonic acid with Ph_2PCl in the presence of Et_3N in thf. The ^{31}P-{^{1}H} NMR spectrum of product 3 shows that the compound displays the characteristic signal of aminophosphine at

TABLE 1
The spectroscopic data for synthesized compounds

Compound	δ P	$\Delta\delta$	υ PN	υ PPh	υ P=O	υ P=S	υ P=Se
$PPh_2N(CH_2C_6H_5)_2$	66.5	–	861	1438			
$PhP\{N(CH_2C_6H_5)_2\}_2$	24.3	–	850	1443			
$PPh_2NHCH_2SO_3H$	30.3	–	960	1433			
$Ph_2P(O)N(CH_2C_6H_5)_2$	31.4	–	897	1438	1199		
$Ph_2P(S)N(CH_2C_6H_5)_2$	70.8	–	896	1437		633	
$Ph_2P(Se)N(CH_2C_6H_5)_2$	70.4	–	896	1436			566
$PhP(O)\{N(CH_2C_6H_5)_2\}_2$	18.9	–	856	1429	1209		
$PhP(S)\{N(CH_2C_6H_5)_2\}_2$	109.4	–	850	1442		665	
$PhP(Se)\{N(CH_2C_6H_5)_2\}_2$	102.2	–	851	1443			578
$Ph_2P(O)NHCH_2SO_3H$	22.9	–	937	1438	1205		
$Ph_2P(Se)NHCH_2SO_3H$	61.4	–	957	1435			567
cis-$[Mo(CO)_4(PPh_2N(CH_2C_6H_5)_2)_2]$	102.4	35.9	894	1437			
$[Cu(Ph_2PN(CH_2C_6H_5)_2)_2Cl_2]$	80.8	14.3	894	1437			
cis-$[Mo(CO)_4(PhP\{N(CH_2C_6H_5)_2\}_2)_2]$	73.7	49.4	858	1440			
cis-$[Cr(CO)_4(PhP\{N(CH_2C_6H_5)_2\}_2)_2]$	102.2	77.9	885	1440			
$[Cu\{(CH_3COO)_2(PhP\{N(CH_2C_6H_5)_2\}_2)_2\}]$	80.8	56.5	850	1443			
$[Ni(PPh_2NHCH_2SO_3H)_2Cl_2]$	47.2	16.9	943	1436			
$[Co(PPh_2NHCH_2SO_3H)_2Cl_2]$	45.8	15.5	945	1438			

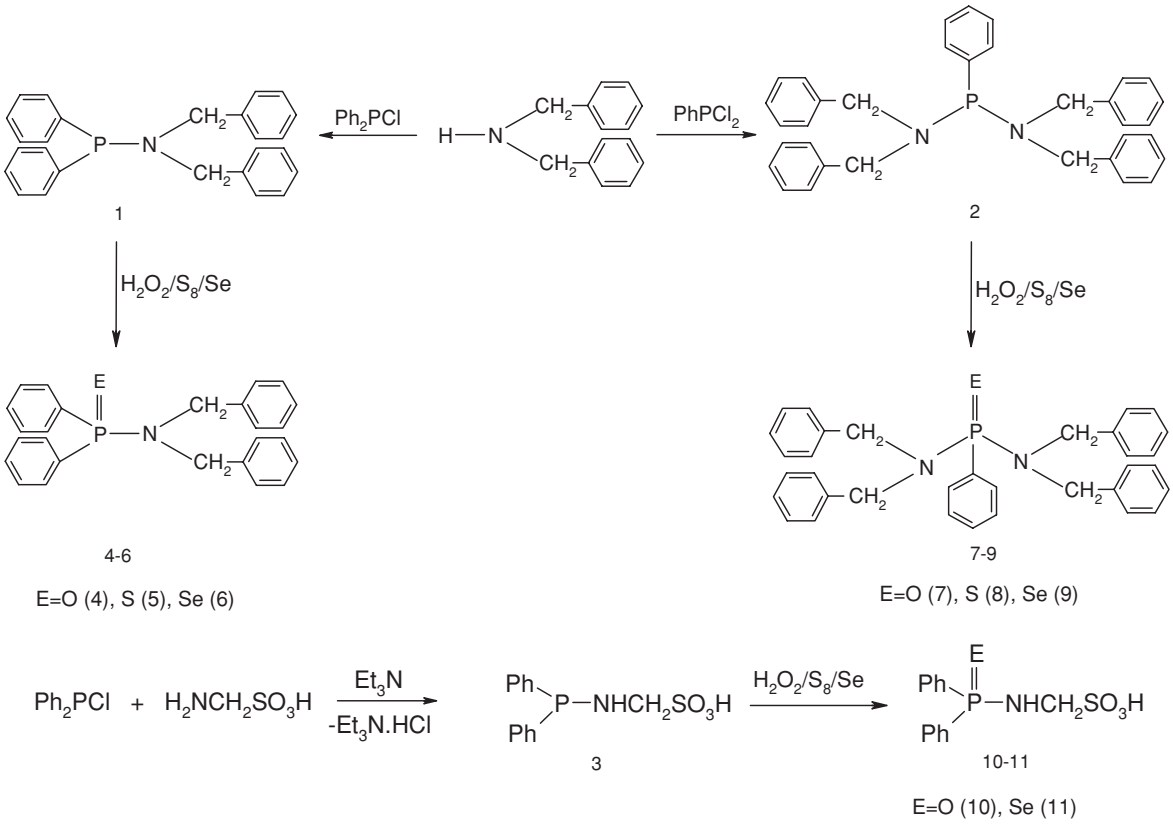


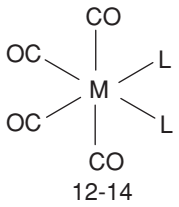
FIG. 1. Synthesis of mono- and bis(amino)phosphine ligands (**1–3**) and their oxidation reactions.

30.3 ppm, and the result is in agreement with the earlier studies.[19] In general, aminodiphenylphosphines $RNHPPh_2$ give rise to singlet resonances between 25 and 35 ppm. Diphosphinoamines ($R\text{-}N(PPh_2)_2$) also exhibit a singlet resonance, but at higher frequency, typically around 64–70 ppm.[19] There was no evidence for the formation of iminobiphosphine, producing two sets of doublets at $\sim +10$ to ~ -20 ppm.[22] The 1H NMR spectra are consistent with the proposed structure. In the IR spectra (KBr) of the ligands, the υ(PN) vibration is tentatively assigned to a very strong absorption at 861 cm^{-1} for **1**, 850 cm^{-1} for **2**, and 960 cm^{-1} for **3**, respectively [16,21]. The υ(PPh) bands are observed in 1438 cm^{-1} for **1**, 1443 cm^{-1} for 2, and 1433 cm^{-1} for 3, respectively.[23]

Oxidation of **1–3** aqueous hydrogen peroxide or elemental sulfur or selenium gave the corresponding oxides (4, 7, and 10), sulfıdes (5 and 8), and selenides (6, 9, and 11), respectively (Scheme 1). Oxidation of **1–3** using aqueous H_2O_2 was very rapid even at ambient temperature. However, the reaction with elemental sulfur or selenium had to be carried out at elevated temperatures as expected because elemental sulfur and selenium are weaker oxidizing agents than hydrogen peroxide, especially towards phosphorus atoms with bulky phenyl groups. Compound **3** does not react even at elevated temperature with elemental sulfur. As is typical of P(V) = E compounds, ^{31}P chemical shifts of compounds **4–11** occured in the δ 18.9–109.4 ppm range, and the chemical shift region is quite consistent with the literature for analogous derivatives.[21,24–26] As indicated in the literature, coupling constants of $^1J_{PSe}$ 746–755 Hz are often seen for E = Se.[24] The ^1H NMR spectra are consistent with the proposed structure. In the IR spectra of **4–11**, the υ(PN) vibration is observed at 897 cm^{-1} (**4**), 896 cm^{-1} (**5**), 896 cm^{-1} (**6**), 856 cm^{-1} (**7**), 850 cm^{-1} (**8**), 851 cm^{-1} (**9**), 937 cm^{-1} (**10**), and 957 cm^{-1} (**11**).[16,21] The υ(PPh) bands are observed in region of 1429–1443 cm^{-1}. The IR spectra of **4**, **7**, and **10** show $\upsilon P = O$ vibration at 1199 for **4**, 1209 cm^{-1} for **7**, and 1205 cm^{-1} for **10**, respectively.[25] In the IR spectra of the compounds, while the υP=O vibration is observed in very narrow range, the υP-N vibration is observed in relatively wide range, suggesting that P(III)-N bonds are quite sensitive to the substituents attached to them. The structures of the oxidized derivatives (**4**,**7**,**10**), sulfıdes (**5** and **8**), and selenides (**6**,**9**,**11**) were further confirmed by using microanalysis, and found to be in good agreement with the theoretical values.

The metal carbonyl derivatives, cis-$[M(CO)_4(L)_2]$ (M = Mo, L = $Ph_2PN(CH_2Ph)_2$, **12**; M = Mo, L = $PhP(N(CH_2Ph)_2)_2$, **13**; M = Cr, L = $PhP(N(CH_2Ph)_2)_2$, **14**) were obtained by the displacement of bipyridine from the $[M(CO)_4(bipy)]$. Compound **3** does not react even at elevated temperature. The metal carbonyl derivatives are shown in Figure 2.

The metal carbonyl derivatives, cis-$[M(CO)_4(L)_2]$ (**12–14**) were characterized by IR, NMR, and elemental analysis. Ligands bearing both amine and tertiary phosphine donors can behave as monodentate ligand (via P or N) or bidentate ligand (via P and N). The P—N bond in aminophosphines is essentially



12 (L=$PPh_2N(CH_2Ph)_2$), M=Mo)
13 (L=$PPh(N(CH_2Ph)_2)_2$), M=Mo)
14 (L=$PPh(N(CH_2Ph)_2)_2$), M=Cr)

FIG. 2. Proposed structures of *cis*-$[M(CO)_4(L)_2]$ complexes.

a single bond, so the lone pairs on nitrogen and phosphorus are available for donor bonding towards metal atoms. However, no examples have been synthesized where both P and N have acted as donor atoms. It is only P that acts as the donor atom. The phosphorus chemical shift for complexes indicates P-M interaction due to the low coordination shift value of complexes ($\Delta\delta$). In the $^{31}P\text{-}\{^1H\}$ NMR spectra, **12**, **13**, and **14** exhibit singlets that show the expected low-fıeld shifts relative to the uncoordinated ligands [**12**: 102.4 ppm ($\Delta\delta$ = 35.9 ppm), **13**: 73.7 ppm ($\Delta\delta$ = 49.4 ppm), **14**: 102.2 ppm ($\Delta\delta$ = 77.9 ppm)].[16] The phosphorus chemical shifts for the complexes indicate P–M interaction. The coordination chemical shift value decreases considerably from chromium to molybdenum, as expected.[2,27] In the IR spectra of the metal carbonyl complexes, the υ(PN) vibration is tentatively assigned to a very strong absorption at 894 cm^{-1} for **12**, 858 cm^{-1} for **13**, and 885 cm^{-1} for **14**, respectively, which is shifted to higher wavenumbers for **12** ($\Delta\upsilon$ = 33 cm^{-1}), **13** ($\Delta\upsilon$ = 8 cm^{-1}), and **14** ($\Delta\upsilon$ = 35 cm^{-1}) compared with their free ligands.[28] The υ(PPh) bands are observed in 1437 cm^{-1} for **12**, 1440 cm^{-1} for **13** and **14**, respectively. The infrared spectra of the complexes $[M(CO)_4L_2]$ exhibit three or four intense ν(CO) absorptions, in the carbonyl region (1813–2011 cm^{-1}), characteristic of the presence of cis -$[M(CO)_4]$ with C_{2v} symmetry.[5,18,27,29,30] The generation of $[Mo(CO)_4L]$ complexes may be used to as a rapid "spot test" for the donor properties of new ligands. This attribute has been recognized for many years, and an extensive literature exists for these complexes, allowing ready comparison with a variety of other phosphorus (III) ligands. The value υCO has been used to evaluate the ligand electronic properties, and it has been found that for π-acceptor ligands, υCO is at higherwave number than for σ-donor ligands. A shift to lower frequency indicates a stronger donation of electron density from ligand to metal to carbonyl ligand and thereby indicates a stronger σ-donor ability for the P–N ligands.[31] The position of υCO for the molybdenum complexes (**12** and **13**) is shown in Table 2. It was found that in the molybdenum complex **13**, the CO stretching frequency (2009 cm^{-1}) is lower than in the molybdenum complex **12** (2011 cm^{-1}). Hence the ligand 2 is stronger σ-donor and more electron rich than the ligand 1. The chromium complex **14**, the CO stretching frequency (2002 cm^{-1}) is lower than in the molybdenum complex **13** (2009 cm^{-1}) as expected.[2]

When a THF solution of $CuCl_2.2H_2O$ is treated with a THF solution of $Ph_2PN(CH_2C_6H_5)_2$, the com-

TABLE 2
Comparison of υCO of $[M(CO)_4L_2]$

Complexes	υCO cm^{-1}
cis-$[Mo(CO)_4(PPh_2N(CH_2C_6H_5)_2)_2]$	2011, 1910, 1871, 1818
cis-$[Mo(CO)_4(PhP\{N(CH_2C_6H_5)_2\}_2)_2]$	2009, 1865, 1813
cis-$[Cr(CO)_4(PhP\{N(CH_2C_6H_5)_2\}_2)_2]$	2002, 1871, 1813

plex $[CuCl_2(Ph_2PN(CH_2C_6H_5)_2)_2]$ (**15**) is obtained. The reaction of $PhP\{N(CH_2C_6H_5)_2\}_2$ with $Cu(OAc)_2.H_2O$ gave $[Cu(CH_3COO)_2(PhP\{N(CH_2C_6H_5)_2\}_2)_2]$ (**16**). The products (**15**, **16**) were characterized by IR, NMR and elemental analysis. The $^{31}P-\{^1H\}$ NMR chemical shifts of **15** and **16** are also within the expected range, 80.8, for structurally similar complexes.[23] The phosphorus resonances of complexes **15** and **16** show a coordination shift to higher frequencies by ca. 14.3 and 56.5 ppm, respectively, compared to those of the free ligands. The phosphorus chemical shifts for the complexes indicate P–Cu interaction. In the IR spectra (KBr) of the complexes, the υ(PN) vibration in **15** and **16** is tentatively assigned to strong absorptions at 894 cm^{-1} (**15**) and 850 cm^{-1} (**16**), which is shifted to higher wavenumbers for **15** ($\Delta\upsilon = 33$ cm^{-1}). The υ(PN) vibration in **16** show no shift with respect to that of free ligand. The υ(PPh) bands are observed in 1437 cm^{-1} for **15** and 1443 cm^{-1} for **16**, respectively.

The reactions of $Ph_2PNHCH_2SO_3H$ with $NiCl_2.6H_2O$ and $CoCl_2.2H_2O$ gave $[Ni(PPh_2NHCH_2SO_3H)_2Cl_2]$ (**17**) and $[Co(PPh_2NHCH_2SO_3H)_2Cl_2]$ (**18**), respectively. The products (**17, 18**) were characterized by IR, NMR, and elemental analysis. The complexes **17** and **18** exhibit singlets that show the expected low-field shifts relative to the uncoordinated ligands [**17**: 47.2 ppm ($\Delta\delta = 16.9$ ppm), **18**: 45.8 ppm ($\Delta\delta = 15.5$ ppm)].[32] The phosphorus chemical shifts for the complexes indicate P–M interaction. In the IR spectra of the complexes, the υ(PN) vibration in **17** and **18** is tentatively assigned to strong absorptions at 943 cm^{-1} (**17**) and 945 cm^{-1} (**18**), which is shifted to higher wavenumbers for **17** ($\Delta\upsilon = 17$ cm^1) and **18** ($\Delta\upsilon = 15$ cm^1) compared with their free ligands. The υ(PPh) bands are observed in 1436 cm^{-1} for **17** and 1438 cm^{-1} for **18**, respectively.

CONCLUSIONS

In conclusion, the new monoaminophosphines and bis(amino)phosphine and their oxides, sulfides, selenides, and transition metal complexes have been prepared. The compounds were characterized. Although aminophosphines possess two potential donor atoms, their coordination compounds involve the metal–phosphorus bond. The coordination through phosphorus is attributed to the low basicity of the amine nitrogen because of the P–N π interaction between the phosphorus d_π and nitrogen p_π orbitals.

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