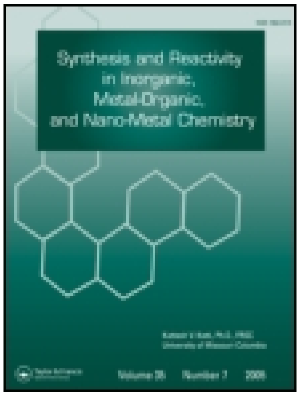

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Bis(amino)phosphines Derived From N-phenylpiperazine and N-ethylpiperazine: Synthesis, Oxidation Reactions, and Molybdenum Complexes

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Bis(amino)phosphines Derived From N-phenylpiperazine and N-ethylpiperazine: Synthesis, Oxidation Reactions, and Molybdenum Complexes

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Functionalized bis(amino)phosphines that are the type $PhP(NR_2)_2$ (1,2) have been synthesized by treating $PhPCl_2$ with N-phenylpiperazine or N-ethylpiperazine. Ligands react with aqueous hydrogen peroxide, elemental sulfur, or selenium to give the corresponding chalcogenides (3–8) in good yield. The molybdenum complexes of the bis(amino)phosphines (9,10) have been obtained. All of the compounds obtained in good yields and they were characterized by IR, NMR, microanalysis, and also quantum chemical calculations such as HOMO-LUMO energies, Mulliken charges, and dipole moment for compounds 1–8 and complex 9 were carried out by using B3LYP/6-31G(d,p), a version of the DFT method with standard Gaussian 09 software package program.

Keywords aminophosphines, oxidation, quantum chemical calculations, 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 toward acid or base catalyzed 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 bis(amino)phosphine ligands and the corresponding bis(amino)phosphine chalcogenides of the general formula $PhP(E)(NR_2)_2$ and their molybdenum complexes. The compounds were fully characterized by IR, ^{1}H NMR, and ^{31}P NMR spectroscopic techniques, and by elemental analysis. Quantum chemical calculations were carried out by using B3LYP/6–31G(d,p), a version of the DFT method that uses Becke's three parameter functional (B3) and includes a mixture of HF with DFT Exchange terms associated with the gradient corrected correlation functional of Lee, Yang, and Parr (LYP), in this paper.[13] The theoretical parameters were calculated in gas phase by using Gaussian 09 software package program.[14]

EXPERIMENTAL

Reactions were routinely carried out using Schlenk-line techniques under pure dry nitrogen gas. Solvents were dried and distilled prior to use. $[Mo(CO)_4(bipy)]$ was prepared according to the literature procedures.[15] All other chemicals were reagent grade, available commercially and used without further purification. Melting points were determined on an Electrothermal A 9100 and are uncorrected. ^{31}P-$\{^{1}H\}$ and ^{1}H NMR spectra were taken on Bruker UltraShield-400 spectrophotometer (Germany). Infrared spectra were recorded on a Perkin Elmer FT-IR System Spectrum BX (USA). Elemental analysis were performed in a CHNS-932 (LECO, USA).

Preparation of $PPh(NC_4H_8NC_6H_5)_2$ (1)

Triethylamine (2.3 mL, 16.59 mmol) and $PhPCl_2$ (1.1 mL, 8.11 mmol) were sequentially added with stirring to a solution of N-phenylpiperazine (2.5 mL, 16.37 mmol) in THF (20 mL). The reaction mixture was stirred for 6 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 2.87 g (82%). m.p.: 164–166°C.

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^{1}H NMR ($CDCl_3$, δ, ppm): 6.76.-7.30 (m, Ph, 15H), 3.25 (t, N-CH_2, 8H), 3.05 (t, N-CH_2, 8H). ^{31}P-{^{1}H} NMR ($CDCl_3$, δ, ppm): 22.3 (s). Selected IR (KBr, cm^{-1}): 917 (PN), 1438 (PPh). Elemental Analysis: $C_{26}H_{31}PN_4$ (430.52 gmol^{-1}) Found (Required): C, 72.34 (72.53); H, 7.11 (7.26); N, 12.88 (13.01).

Preparation of $PPh(NC_4H_8NC_2H_5)_2$ (2)

A similar procedure to that described in **1** was used. Yield 2.33 g (86%). m.p.: 197–198°C. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.20–7.82 (m, Ph, 5H), 2.81 (t, N-CH_2, 8H), 2.24 (q, N-CH_2, 12H), 0.96 (t, N-CH_2-$\underline{CH_3}$, 6H). ^{31}P-{^{1}H} NMR ($CDCl_3$, δ, ppm): 23.8 (s). Selected IR (KBr, cm^{-1}): 920 (PN), 1435 (PPh). Elemental Analysis: $C_{18}H_{31}PN_4$ (334.44 gmol^{-1}); Found (Required): C, 64.41 (64.64); H, 9.15 (9.34); N, 16.52 (16.75).

Preparation of $PhP(O)(NC_4H_8NC_6H_5)_2$ (3)

A THF solution (10 mL) of 1 (0.75 g, 1.74 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 3. Yield 0.43 g (55%). m.p.: 115–117°C. ^{1}H NMR ($CDCl_3$, δ, ppm): 6.76–7.77 (m, Ph, 15H), 3.50 (t, N-CH_2, 8H), 3.37 (t, N-CH_2, 8H). ^{31}P-{^{1}H} NMR ($CDCl_3$, δ, ppm): 8.4 (s). Selected IR (KBr, cm^{-1}): 917 (PN), 1438 (PPh), 1172 (P = O). Elemental Analysis: $C_{26}H_{31}PN_4O$ (446.52 gmol^{-1}); Found (Required): C, 69.76 (69.93); H, 6.75 (7.00); N, 12.36 (12.55).

Preparation of $PhP(O)(NC_4H_8NC_2H_5)_2$ (4)

A similar procedure to that described in **3** was used. Yield 0.38 g (61%). m.p.: 118–119°C. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.20–8.03 (m, Ph, 5H), 2.83 (t, N-CH_2, 8H), 2.32 (q, N-CH_2, 12H), 0.95 (t, N-CH_2-$\underline{CH_3}$, 6H). ^{31}P-{^{1}H} NMR ($CDCl_3$, δ, ppm): 15.8 (s). Selected IR (KBr, cm^{-1}): 931 (PN), 1438 (PPh), 1171 (P = O). Elemental Analysis: $C_{18}H_{31}PN_4O$ (350.44 gmol^{-1}); Found (Required): C, 61.52 (61.69); H, 8.75 (8.92); N, 15.76 (15.99).

Preparation of $PhP(S)(NC_4H_8NC_6H_5)_2$ (5)

Ligand 1 (1.06 g, 2.46 mmol) and S_8 (0.079 g, 2.46 mmol) were refluxed in toluene (20 mL) for 6 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 0.52 g (46%). m.p.: 182–184°C. ^{1}H NMR ($CDCl_3$, δ, ppm): 6.76–7.97 (m, Ph, 15H), 3.15 (t, N-CH_2, 8H), 3.09 (t, N-CH_2, 8H). ^{31}P-{^{1}H} NMR ($CDCl_3$, δ, ppm): 75.4 (s). Selected IR (KBr, cm^{-1}): 912 (PN), 639 (PS), 1438 (PPh). Elemental Analysis: $C_{26}H_{31}PN_4S$ (462.59 gmol^{-1}); Found (Required): C, 67.33 (67.51); H, 6.62 (6.75); N, 11.92 (12.11); S, 6.76 (6.93).

Preparation of $PhP(S)(NC_4H_8NC_2H_5)_2$ (6)

A similar procedure to that described in **5** was used. Yield 0.25 g (28%). m.p.: 175–177°C. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.26–8.02 (m, Ph, 5H), 2.9 (t, N-CH_2, 8H), 2.3 (q, N-CH_2, 12H), 0.95 (t, N-CH_2-$\underline{CH_3}$, 6H). ^{31}P-{^{1}H} NMR ($CDCl_3$, δ, ppm): 75.2 (s). Selected IR (KBr, cm^{-1}): 906 (PN), 632 (PS), 1437 (PPh). Elemental Analysis: $C_{18}H_{31}PN_4S$ (366.50 gmol^{-1}); Found (Required): C, 58.83 (58.99); H, 8.39 (8.52); N, 15.12 (15.29); S, 8.59 (8.75).

Preparation of $PhP(Se)(NC_4H_8NC_6H_5)_2$ (7)

Ligand **1** (1.06 g, 2.46 mmol) and grey Se (0.2 g, 2.53 mmol) were refluxed in toluene (20 mL) for 6 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 7. Yield 0.81 g (65%). m.p.: 157–158°C. ^{1}H NMR ($CDCl_3$, δ, ppm): 6.8–8.19 (m, Ph, 15H), 3.11 (m, N-CH_2, 16H). ^{31}P-{^{1}H} NMR ($CDCl_3$, δ, ppm): 78.2 (s, J_{PSe} = 812.5 Hz). Selected IR (KBr, cm^{-1}): 910 (PN), 538 (PSe), 1438 (PPh). Elemental Analysis: $C_{26}H_{31}PN_4Se$ (509.48 gmol^{-1}) Found (Required): C, 61.13 (61.29); H, 5.98 (6.13); N, 10.86 (11.00).

Preparation of $PhP(Se)(NC_4H_8NC_2H_5)_2$ (8)

A similar procedure to that described in **7** was used. Yield 0.8 g (78%). m.p.: 184–186°C. ^{1}H NMR ($CDCl_3$, δ, ppm): 7.26–8.02 (m, Ph, 5H), 2.92 (t, N-CH_2, 8H), 2.30 (q, N-CH_2, 12H), 0.95 (t, N-CH_2-$\underline{CH_3}$, 6H). ^{31}P-{^{1}H} NMR ($CDCl_3$, δ, ppm): 77.8 (s, J_{PSe} = 818.30 Hz). Selected IR (KBr, cm^{-1}): 906 (PN), 526 (PSe), 1437 (PPh). Elemental Analysis: $C_{18}H_{31}PN_4Se$ (413.40 gmol^{-1}); Found (Required): C, 52.13 (52.30); H, 7.34 (7.56); N, 13.36 (13.55).

Preparation of cis-$[Mo(CO)_4\{PPh(NC_4H_8NC_6H_5)_2\}_2]$ (9)

Ligand **1** (0.76 g, 1.76 mmol) and $[Mo(CO)_4(bipy)]$ (0.32 g, 0.88 mmol) were refluxed in 20 mL CH_2Cl_2 for 4.5 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: 0.32 g (34%). m.p.: 151–153°C (decomp). ^{1}H NMR ($CDCl_3$, δ, ppm): 7.0–7.8 (m. Ph, 30H), 3.35 (t, N-CH_2, 16H), 3.09 (t, N-CH_2, 16H). ^{31}P-{^{1}H} NMR ($CDCl_3$, δ, ppm): 102.4. Selected IR (KBr, cm^{-1}): 952 (PN), 1440 (PPh), 2008, 1913, 1864 and 1802 (CO). Elemental Analysis: $C_{56}H_{62}P_2N_8O_4Mo$ (1069.03 gmol^{-1}); Found (Required): C, 62.63 (62.92); H, 5.78 (5.85); N, 10.27 (10.48).

Preparation of cis-$[Mo(CO)_4\{PPh(NC_4H_8NC_2H_5)_2\}_2]$ (10)

A similar procedure to that described in **9** was used. Yield: 0.57 g (74%). m.p.: 137–139°C (decomp). ^{1}H NMR ($CDCl_3$, δ, ppm): 7.60–8.70 (m, Ph, 10H), 2.49 (t, N-CH_2, 16H), 2.34 (q, N-CH_2, 24H), 0.96 (t, N-CH_2-$\underline{CH_3}$, 12H). ^{31}P-{^{1}H} NMR ($CDCl_3$, δ, ppm): 119.7. Selected IR (KBr, cm^{-1}): 942 (PN), 1440 (PPh), 2008, 1896, 1866 and 1778 (CO). Elemental Analysis: $C_{40}H_{62}P_2N_8O_4Mo$ (876.86 gmol^{-1}); Found (Required): C, 54.13 (54.79); H, 6.98 (7.13); N, 12.57 (12.78).

RESULTS AND DISCUSSION

Synthesis and Structure Determination of the Compounds

Earlier works had shown that primary and secondary amines react with chlorophosphines in the presence of a tertiary amine base to form aminophosphines.[16,17] The reactions of N-ethylpiperazine or N-phenylpiperazine with dichlorophenylphosphine afford the corresponding derivatives bis(amino)phospine $PhP(NC_4H_8NC_6H_5)_2$ (1) and $PhP(NC_4H_8NC_2H_5)_2$ (**2**) in good yield. Synthesis of bis(amino)phosphine ligands **1** and **2** and their oxidation reactions are shown in Figure 1.

The structure of compounds **1** and **2** were confirmed by spectroscopic analysis. The ^{31}P-$\{^1H\}$ NMR spectra of the bis(amino)phosphines show singlets at 22.3 ppm for **1** and 23.8 ppm for **2**. The absence of a signal at 160.2 ppm indicates that no unreacted $PPhCl_2$ remained.[18] The ^{31}P NMR and ^1H NMR spectra are consistent with the proposed structure. In the IR spectra of the ligands, the υ(PN) vibration is tentatively assigned to a very strong absorption at 917 cm^{-1} for **1** and 920 cm^{-1} for **2**, respectively.[19,20] The υ(PPh) bands are observed in 1438 cm^{-1} for **1** and 1435 cm^{-1} for **2**, respectively.[21]

Oxidation of **1**, **2** aqueous hydrogen peroxide, elemental sulfur and selenium formed to the corresponding oxides (**3** and **4**), sulfides (**5** and **6**), and selenides (**7** and **8**), respectively. Oxidation of **1**, **2** 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, because elemental sulfur and selenium are weaker oxidizing agents than hydrogen peroxide, especially toward phosphorus atoms with bulky phenyl groups. As is typical of $P(V) = E$ compounds, ^{31}P chemical shifts of compounds **3–8** occurred in the δ 8.4–78.2 ppm range, and the chemical shift region is quite consistent with the literature for analogous derivatives.[22–26] As indicated in the literature, coupling constants of $^1J_{PSe}$ 812.5 –818.3 Hz are often seen for E=Se.[26] The ^1H NMR spectra are consistent with the proposed structure.

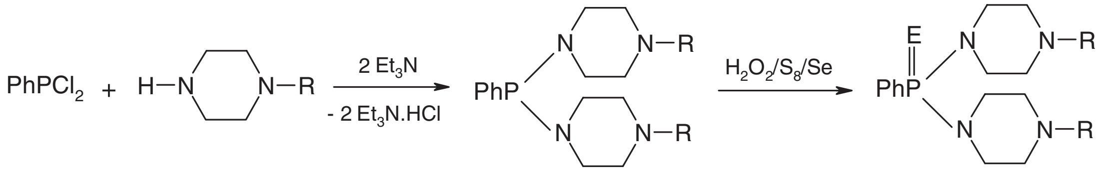
In the IR spectra of **3–8**, the υ(PN) vibration is observed at 917 cm^{-1} (**3**), 931 cm^{-1} (**4**), 912 cm^{-1} (**5**), 906 cm^{-1} (**6**), 910 cm^{-1} (**7**), and 906 cm^{-1} (**8**). The ν(PPh) bands are observed in range of 1437–1438 cm^{-1}. In the IR spectra of the compounds, while the $\upsilon P = O$ vibrations are observed in very narrow range, the υP-N vibrations are observed in relatively wide range, suggesting that P(III)-N bonds are quite sensitive to the substituents attached to them. The IR spectra of **3** and **4** show υP=O vibration at 1172 for **3** and 1171 cm^{-1} for **4**. υ(P=S) vibration is observed at 639 cm^{-1} for **5** and 632 cm^{-1} for **7**, and υ(P=Se) vibration at 533 for **7** and 526 cm^{-1} for **8**, respectively.

Vibrational analyses have been reported for some important functional groups. The computed vibrational wavenumbers for some important functional groups (raw values) with together experimental values are collected in Table 1.

The υ(PN) bands of compounds **1–8** have been calculated in the region 893–909 cm^{-1} with B3LYP/6–31G(d,p) and 961–971 cm^{-1} with RHF/LANL2DZ method. The ν(PPh) bands have been calculated in the region 1475–1478 cm^{-1} for B3LYP/6–31G(d,p) and 1475–1477 cm^{-1} for RHF/LANL2DZ method. The υP=O bands have been calculated at 1203 cm^{-1} for **3** and 1226 cm^{-1} for **4** with B3LYP method and 1233 cm^{-1} for **3** and **4** with RHF/LANL2DZ method, respectively. The υ(P=S) vibrations have been assigned at 727 cm^{-1} and 726 cm^{-1} with B3LYP method, and 743 cm^{-1} and 737 cm^{-1} for RHF/LANL2DZ method while the υ(P=Se) bands have been calculated at 596 cm^{-1} and 556 cm^{-1} for B3LYP method, and 598 cm^{-1} and 564 cm^{-1} for RHF/LANL2DZ method, respectively. Theoretical harmonic frequencies as seen from Table 1 typically overestimate observed fundamentals due to the neglect of mechanical anharmonicity, electron correlation. and basis set effects. The correlation coefficient between theoretical and experimental values was found 0.9888 for B3LYP and 0.9919 for RHF/LANL2DZ method, respectively.

The structures of the oxidized derivatives (**3** and **4**), sulfides (**5** and **6**), and selenides (**7** and **8**) were further confirmed by using microanalysis, and found to be in good agreement with the theoretical values.

The molybdenum carbonyl derivatives, cis-$[Mo(CO)_4(L)_2]$ (L=$PPh(NC_4H_8NC_6H_5)_2$, 9; L=$PPh(NC_4H_8NC_2H_5)_2$, **10**) were obtained by the displacement of bipyridine from the $[Mo(CO)_4(bipy)]$. The molybdenum carbonyl derivatives are shown in Figure 2.



1-2

1; R= C_6H_5
2; R= C_2H_5

3-8

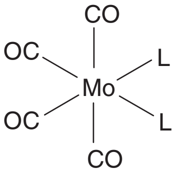
3; E=O, R= C_6H_5, 4; E= O, R= C_2H_5
5; E=S, R= C_6H_5, 6; E= S, R= C_2H_5
7; E=Se, R= C_6H_5, 8; E= Se, R= C_2H_5

FIG. 1. Synthesis of bis(amino)phosphine ligands **1** and **2** and their oxidation reactions.

TABLE 1
Some experimental and theoretical (B3LYP/631G(d,p) and RHF/LANL2DZ) vibrational data (in cm^{-1}) for aminophosphine derivatives

Compound		υ		
		B3LYP 6–31G(d,p)	RHF LANL2DZ(d,p)	Experimental
$PPh(NC_4H_8NC_6H_5)_2$ (1)	PN	896	969	917
	PPh	1475	1475	1438
$PPh(NC_4H_8NC_2H_5)_2$ (2)	PN	897	968	920
	PPh	1475	1475	1435
$PhP(O)(NC_4H_8NC_6H_5)_2$ (3)	PN	907	971	917
	PPh	1478	1477	1438
	PO	1203	1233	1172
$PhP(O)(NC_4H_8NC_2H_5)_2$ (4)	PN	893	970	931
	PPh	1477	1477	1438
	PO	1226	1233	1171
$PhP(S)(NC_4H_8NC_6H_5)_2$ (5)	PN	900	965	912
	PPh	1476	1477	1438
	PS	727	743	639
$PhP(S)(NC_4H_8NC_2H_5)_2$ (6)	PN	907	965	906
	PPh	1477	1476	1437
	PS	726	737	632
$PhP(Se)(NC_4H_8NC_6H_5)_2$ (7)	PN	904	961	910
	PPh	1477	1477	1438
	PSe	596	598	533
$PhP(Se)(NC_4H_8NC_2H_5)_2$ (8)	PN	909	963	906
	PPh	1477	1477	1437
	PSe	556	564	526

The molybdenum carbonyl derivatives, cis-[$Mo(CO)_4(L)_2$] (**9**, **10**) were characterized by IR, NMR, and elemental analysis. Ligands bearing both amine and tertiary phosphine donors should behave as monodentate ligand (via P or N) or bidentate ligand (via P and N). The P-N bond in aminophosphines is essentially a single bond, so the lone pairs on nitrogen and phosphorus are available for donor bonding toward 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-{^{1}H} NMR spectra, **9** and **10** exhibit singlets that show the expected low-field shifts relative to the uncoordinated ligands [**9**: 102.4 ppm ($\Delta\delta = 80.1$ ppm) and **10**: 119.7 ppm ($\Delta\delta = 95.9$ ppm).[19] The ^{31}P–{^{1}H} NMR chemical shifts of **9** and **10** are also within the expected range for structurally similar complexes.[20] The phosphorus chemical shifts for the complexes indicate P–Mo interaction. In the IR spectra of the molybdenum carbonyl complexes, the υ(PN) vibration is tentatively assigned to a very strong absorption at 952 cm^{-1} for **9** and 942 cm^{-1} for **10**, respectively, which is shifted to higher wavenumbers for 9 ($\Delta\upsilon$ = 35 cm^{-1}) and 10 ($\Delta\upsilon$ = 22 cm^{-1}) compared with their free ligands.[19,20] The ν(PPh) bands are observed in 1440 cm^{-1} for **9** and **10**. The infrared spectra of the complexes [$Mo(CO)_4L_2$] exhibit four intense υ(CO) absorptions, in the carbonyl region (2008–1778 cm^{-1}), characteristic of the presence of cis-[$Mo(CO)_4$] with C_{2v} symmetry.[5,27–30] 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.[31] The position of υCO for the molybdenum complexes **9** and **10**



9-10

9) L=$PhP(NC_2H_4NC_6H_5)_2$

10) L=$PhP(NC_2H_4NC_2H_5)_2$

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

is shown in Table 2. It was found that in the molybdenum complex **9** and **10** have similar υCO stretching frequency, indicating that **1** and **2** have electronic properties.

Theoretical Calculations

Quantum chemical calculations on compounds **1–9** were performed with full geometrical optimizations by using standard Gaussian 09 software package.[14] Geometrical optimization were carried out with two different methods: *ab initio* methods at the Hartree-Fock (HF) level, and density functional theory (DFT) with the B3LYP change-correlation corrected functional by using 6–31G(d,p) basis sets.

TABLE 2
Comparison of υCO of $[M(CO)^4L^2]$

Complex	υCO cm^{-1}
cis- $[Mo(CO)_4\{PPh(NC_4H_8NC_6H_5)_2\}_2]$ (9)	2008, 1913, 1864, 1802
cis- $[Mo(CO)_4\{PPh(NC_4H_8NC_2H_5)_2\}_2]$ (10)	2008, 1896, 1866, 1778

The molecular structure of compounds **1–8** and their atom numbering calculated by B3LYP/6–31(d,p) level are shown in Figure 3.

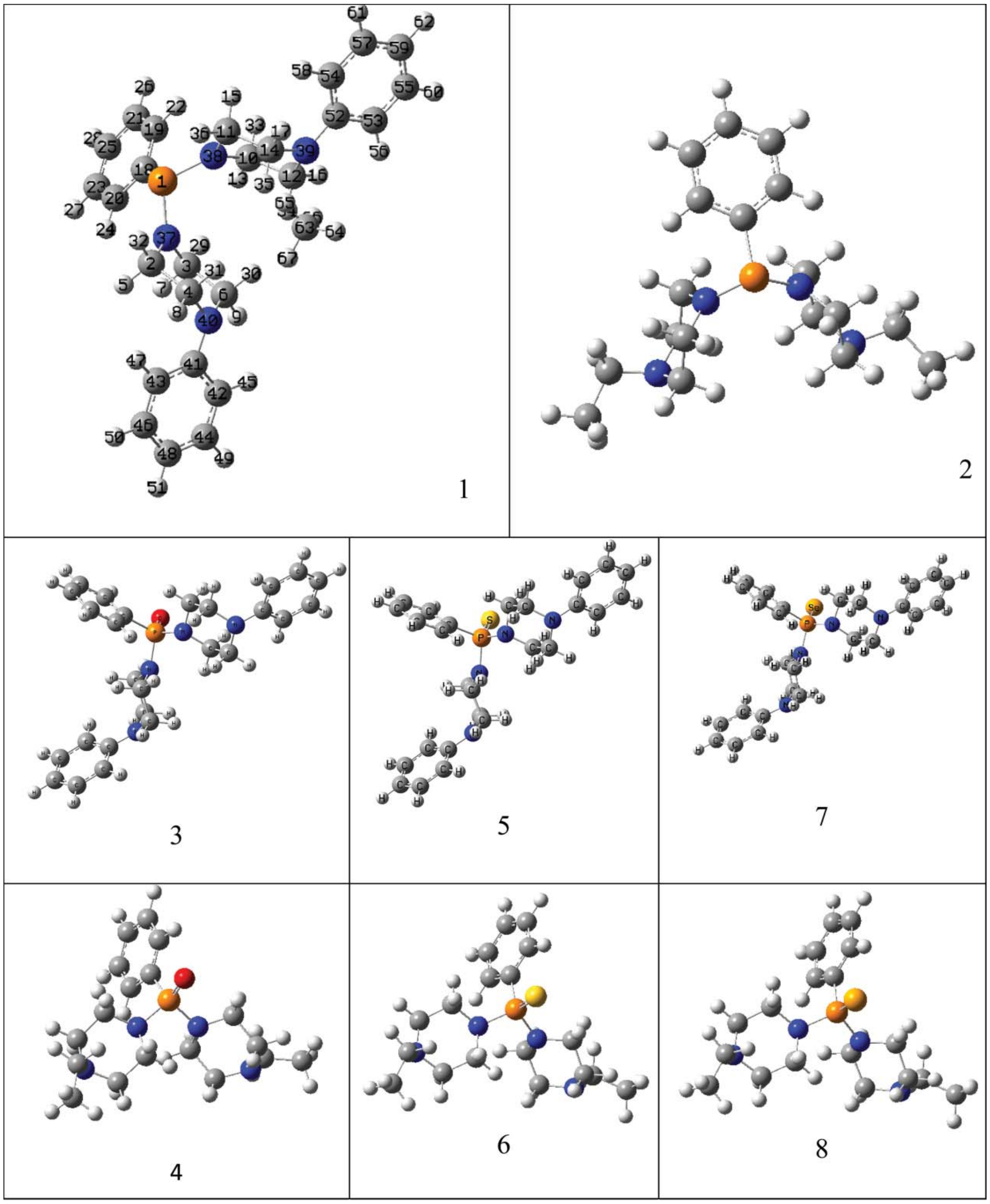


FIG. 3. Optimized structures of compounds **1–8** (color figure available online).

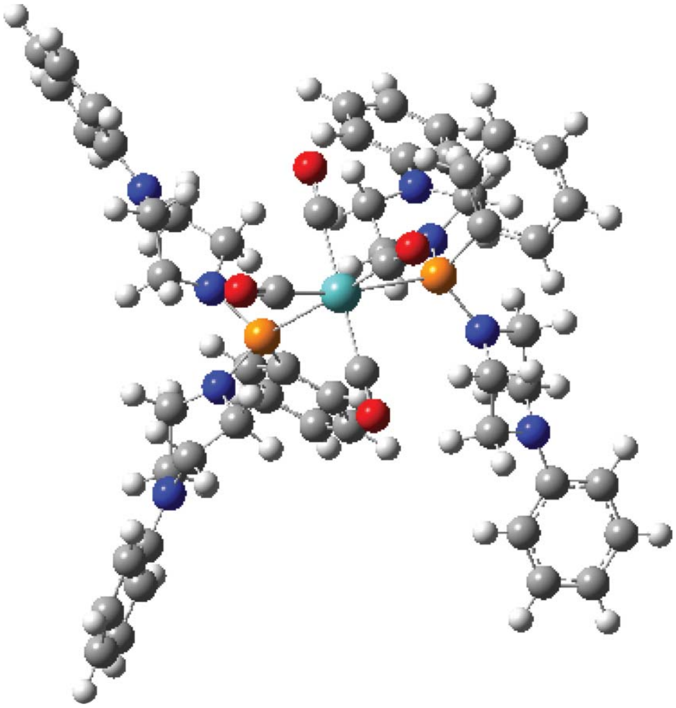


FIG. 4. Optimized structure of molybdenum complex **9** (color figure available online).

The molecular structure of complex **9** calculated by RHF/LANL2DZ is shown in Figure 4.

Optimized molecular structural parameters by B3LYP methods with 6–31G(d,p) basis set for compounds under study and their electronic parameters are summarized in Tables 3 and 4. The P1–N37 bond lengths for compounds **1**, **3**, **5**, **7**, **2**, **4**, **6**, and **8** are 1.748 Å, 1.720 Å, 1.735 Å, 1.740 Å, 1.748Å, 1.721 Å, 1.737 Å, and 1.741 Å, respectively, in the calculations carried out with RHF/LANL2DZ method and 1.721 Å, 1.700 Å, 1,713 Å, 1,717 Å, 1,720 Å, 1,698 Å, 1,711 Å, and 1,714 Å, respectively, in the calculatons carried out with B3LYP/6–31G(d,p) method. P-N bond lengths in aminophosphine chalcogenides are shorter than P-N bond length in the aminophosphine. When we move from Se to O, the P–N bond length is shortened. With an increase in the electronegativity of the chalcogen atom, enhanced electron transfer from nitrogen to chalcogen atom occurs, thus the P–N bond length reduces further.[32] The P1–C18 bond lengths for compounds **1**, **3**, **5**, **7**, **2**, **4**, **6**, and **8** are 1.878 Å, 1.843 Å, 1.854 Å, 1.858 Å, 1.879Å, 1.844 Å, 1.855 Å, and 1.858 Å, respectively, on the calculations carried out by using RHF/LANL2DZ, so the shortest P1-C18 bond lengths are obtained in aminophosphine oxides (**3** and **4**). P-O, P-S, P-Se bond lengths for **3–8** are calculated as 1.583 Å for **3**, 2.111 Å for **5**, 2.275 Å for **7**, 1.584 Å for **4**, 2.113 Å for **6**, and 2.277 Å for **8**, respectively, for RHF/LANL2DZ method. In morpholino series of compounds, P-O bond length for $(OC_4H_8N)_3PO$ and P-Se bond length for $(OC_4H_8N)_3PSe$ are 1.486 Å and 2.106 Å, respectively.[32] As seen in Table 5, when ligand **1** coordinated to the molybdenum atom, P-N bond length is shortened from 1.748 to 1.739 and P-C bond length changing is not important, and Mo-P length is found as 2.898 Å.

As seen in Table 3, the angle of N38P1N37 for compounds **1**, **3**, **5**, **7** are 112.5°, 101.7°, 101.1°, and 101.4°; C18P1N38 100.6°, 109.4°, 108.2°, and 108.5°; C18P1N37 100.6°, 104.0°, 102.9°, and 103.4°. When aminophosphine **1** coordinated to molybdenum, the angle of N38P1N37 changed from 112.5° to 104.4°. The P37-Mo-P38 bond angle is 104.4° that is larger than the ideal angle of 90° and Mo-C bond angle (C belongs to CO group) is 88.2° and C-Mo-P is 84.2°, and both are slightly smaller than the ideal angle of 90°. The molybdenum atom is coordinated with two phosphorus atoms of the aminophosphine ligands and four carbonyl groups in a slightly distorted octahedrally.

The energies of HOMO and LUMO for compounds **1–8** were calculated using B3LYP/6–31G(d,p) method (Figure 5). High values of E_{HOMO} indicates a tendency of the molecule to donate electrons to appropriate acceptor molecules, as electron donating ability of a molecule is related with E_{HOMO}. The energies of HOMO and LUMO for aminophosphines are higher than the energies of HOMO and LUMO for aminophosphine chalcogenides. When we move from O to Se, the energies of HOMO and LUMO decreases.

Molecular orbital calculations were carried out to calculate the molecular orbital coefficients of the HOMO and the LUMO levels for compounds **1–8** to explain the coordination of them on the metal. The HOMO electronic density distribution for compounds **1–8**, are plotted in Figu–re 6.

Phosphines are considered a soft, strong σ-donor, but a relatively weak π-acceptor ligand in organometallic chemistry. However, the donor–acceptor properties are found to alter depending on the nature of substituents on the phosphorus.[19] In molecular orbital theory (e.g., Hartree-Fock theory or Huckel theory), Pearson emphasized that the hardness is given Eq. 1.[33]

$$\eta = \left(\frac{E_{LUMO} - E_{HOMO}}{2}\right) \qquad [1]$$

Softness (S), which is the reciprocal of hardness, is a property of molecules that measures the extent of chemical reactivity. Softness value calculated with Eq. 2 for compounds **1**, **3**, **5**, **7**, **2**, **4**, **6**, and **8** are 12,09, 12.48, 12.81, 12.86, 11.62, 11.48, 11.74, and 11.90, respectively. the softness of the molecule increases with the increase in the atomic size: O < S < Se.

$$s = \left(\frac{1}{\eta}\right) \qquad [2]$$

Figure 7 provides Mulliken charge values of some atoms for different aminophosphine derivatives that illustrates the

TABLE 3
Selected bond length calculated with RHF and B3LYP method for compounds **1, 3, 5, 7**

	1		**3**		**5**		**7**	
Bond length (Å)	B3LYP 6-31G(d,p)	RHF lanl2dz	B3LYP 6-31G(d,p)	RHF lanl2dz	B3LYP 6-31G(d,p)	RHF lanl2dz	B3LYP 6-31G(d,p)	RHF lanl2dz
P1-N37	1,721	1.748	1,700	1.720	1,713	1.735	1,717	1.740
P1-N38	1,721	1.748	1,699	1.715	1,709	1.725	1,707	1.728
P1-C18	1,852	1.878	1,827	1.843	1,839	1.854	1,837	1.858
C18-C19	1,404	1.400	1,405	1.398	1,406	1.400	1,405	1.400
C18-C20	1,404	1.397	1,400	1.396	1,402	1.395	1,402	1.395
N37-C3	1,467	1.467	1,475	1.475	1,475	1.474	1,475	1.474
N37-C2	1,465	1.465	1,468	1.468	1,474	1.473	1,472	1.474
N40-C47	1,406	1.421	1,407	1.422	1,408	1.422	1,408	1.422
N38-C11	1,467	1.467	1,479	1.476	1,481	1.478	1,484	1.478
N38-C10	1,465	1.464	1,477	1.476	1,480	1.478	1,483	1.479
N39-C41	1,406	1.422	1,408	1.422	1,410	1.422	1,410	1.422
P1-E63			1,497	1.583	1,969	2.111	2,106	2.275
Bond angle (°)								
N37-P1-N38	112,5	108.6	101,7	102.2	101,1	102.7	101,4	102.4
N38-P1-C18	100,6	100.8	109,4	110.3	108,2	108.4	108,5	108.0
N37-P1-C18	100,6	102.2	104	105.2	102,9	103.8	103,4	103.4
E63-P1-C18			110,6	110.1	112,6	112.7	112,6	113.4
E63-P1-N38			119,2	117.3	117,3	115.2	116,6	114.9
E63-P1-N37			111,3	110.1	113,5	113.0	113,3	113.6

TABLE 4
Selected bond length calculated with RHF and B3LYP method for compounds **2, 4, 6,** and **8**

	2		**4**		**6**		**8**	
Bond length (Å)	B3LYP 6-31G(d,p)	RHF lanl2dz	B3LYP 6-31G(d,p)	RHF lanl2dz	B3LYP 6-31G(d,p)	RHF lanl2dz	B3LYP 6-31G(d,p)	RHF lanl2dz
P1-N37	1,720	1.748	1,698	1.721	1,711	1.737	1,714	1.741
P1-N38	1,720	1.748	1,696	1.715	1,706	1.726	1,704	1.729
P1-C18	1,853	1.879	1,828	1.844	1,840	1.855	1,838	1.858
C18-C19	1,405	1.399	1,405	1.398	1,406	1.399	1,405	1.400
C18-C20	1,405	1.399	1,403	1.396	1,402	1.395	1,402	1.395
N37-C3	1,467	1.469	1,479	1.481	1,481	1.483	1,484	1.483
N37-C2	1,467	1.473	1,480	1.481	1,482	1.482	1,485	1.482
N40-C47	1,468	1.470	1,169	1.471	1,469	1.472	1,469	1.472
N38-C11	1,467	1.473	1,475	1.479	1,475	1.478	1,475	1.478
N38-C10	1,467	1.469	1,469	1.472	1,475	1.477	1,473	1.478
N39-C41	1,468	1.470	1,468	1.471	1,468	1.471	1,468	1.471
P1- E63			1,497	1.584	1,971	2.113	2,109	2.277
Bond angle (°)								
N37-P1-N38	112,7	109.5	101,9	103.8	101,2	103.0	101,6	102.7
N38-P1-C18	100,5	101.5	109,2	110.1	108,2	108.2	108,5	107.8
N37-P1-C18	100,5	101.5	100,9	105.2	102,9	103.9	103,4	103.4
E63-P1-C18			11,1	110.1	113,3	112.8	113,1	113.4
E63-P1-N38			110,9	110.4	112,8	112.9	112,6	113.6
E63-P1-N37			119,2	117.0	117,3	115.1	116,5	114.8

TABLE 5
Selected bond length calculated with RHF method for molybdenum complex **9**

Bond length (Å)	RHF lanl2dz		RHF lanl2dz	Bond angle (°)	RHF lanl2dz
P1-N37	1.739	N40-C41	4.423	N37-P1-N38	104.4
P1-N38	1.739	Mo1-C3	2.004	N38-P1-C18	99.7
P1-C18	1.879	C3-O7	1.558	N37-P1-C18	104
C18-C19	1.400	Mo1-C2	2.026	PMoP	104.2
C18-C20	1.395	C2-O6	1.153		
N38-C11	1.479	Mo1-C5	2.074		
N38-C10	1.470	C5-O9	1.150		
N39-C52	1.397	Mo-P1	2.898		
N37-C2	1.667	Mo1-P11	2.831		
N37-C3	1.467		$Mo(CO)_6$		
Mo1-C4	2.077		2.105		
C4-O8	1.150		1.143		

effect of varying groups on the phosphorus centre and the Mulliken charge for aminophosphine derivatives calculated by using B3LYP/6–31G(d,p) and RHF(LANL2DZ) methods. The electronic distribution of compounds are very sensitive to changes atoms coordinated to phosphorus. The Mulliken charges on phosphorus atom for compounds **1**, **3**, **5**, and **7**, are 0.612 ē, 1.116 ē, 0.827 ē, and 0.963 ē, respectively. The Mulliken charge of N37 atom bonded to phosphorus atom (Figure 7) is –0.560 ē for compound **1**, –0.599 ē for compound **3**, –0.588 ē for compound **5**, and –0.590 ē for compound **7**. The Mulliken charge on C18 atom bonded to phosphorus atom (Figure 7) is –0,142 ē for compound **1**, –0.153 ē for compound **3**, –0,123 ē for compound **5**, and –0135 ē for compound **7**. The Mulliken charges calculated with RHF/LANL2DZ on phosphorus atom are 1.203 for free ligand and 1.366 for molybdenum complex **9** (Figure 7). The Mulliken charge on N37, C2, C3, N38, C20, and N39 atoms are more negative than those of free ligand.

Dipole moment for compounds **1**, **3**, **5**, and **7** are given in Table 6. The dipole moment of compound **1** is 1.10 D and for aminophosphine chalcogenides **3**, **5**, and **7** are 3.24 D, 4.07 D, and 3.96 D. Dipole moment of aminophosphine is less than those of aminophosphine chalco–genides.

The P1-C18 NBO composition is 0.585 P1 $(sp^{4.44}d^{0.07})$ + 0.811 $C18(sp^{2.43})$. So, there are 34.26% localization on P1 and

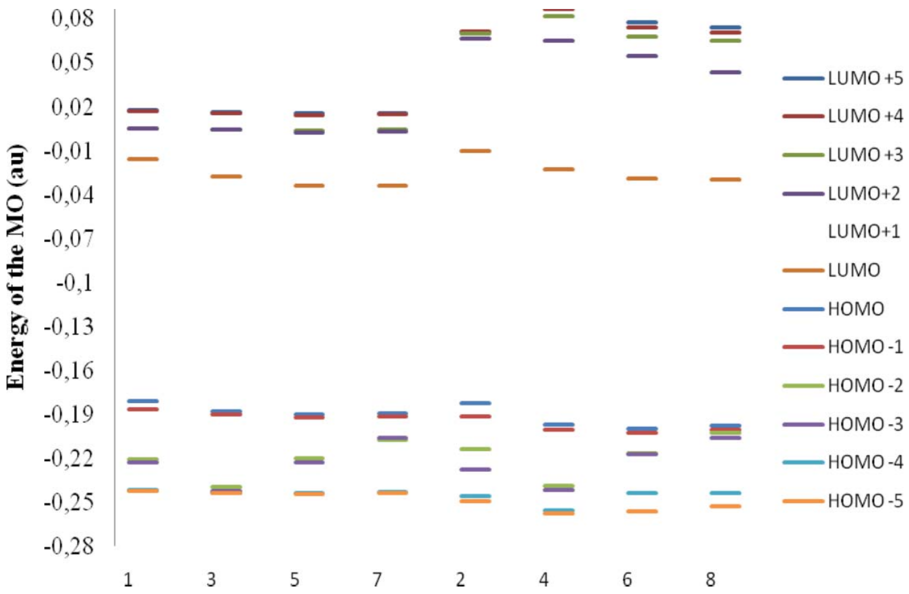


FIG. 5. HOMO, HOMO-1, HOMO-2, HOMO-3, HOMO-4, HOMO-5, LUMO, LUMO + 1, LUMO + 2, LUMO + 3, LUMO + 4, LUMO + 5 (au) energy values for compounds **1–8** (color figure available online).

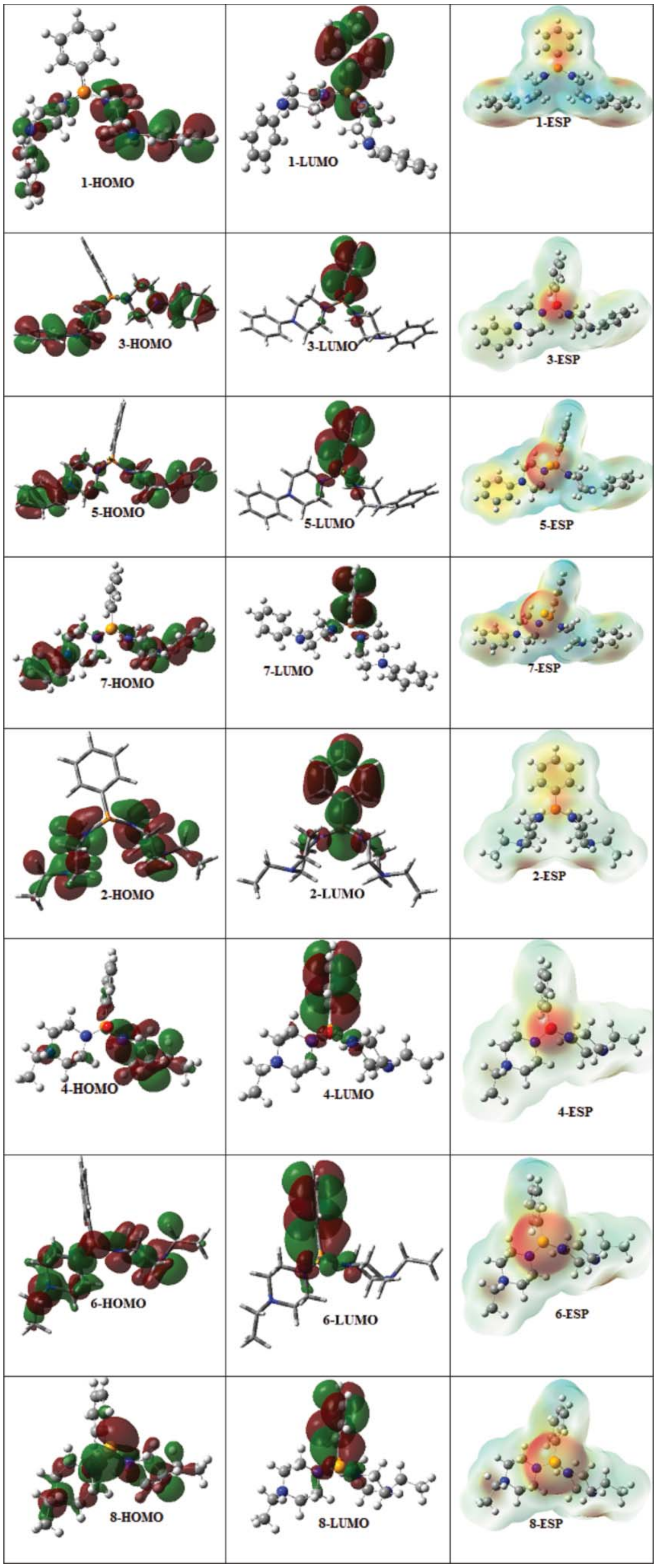
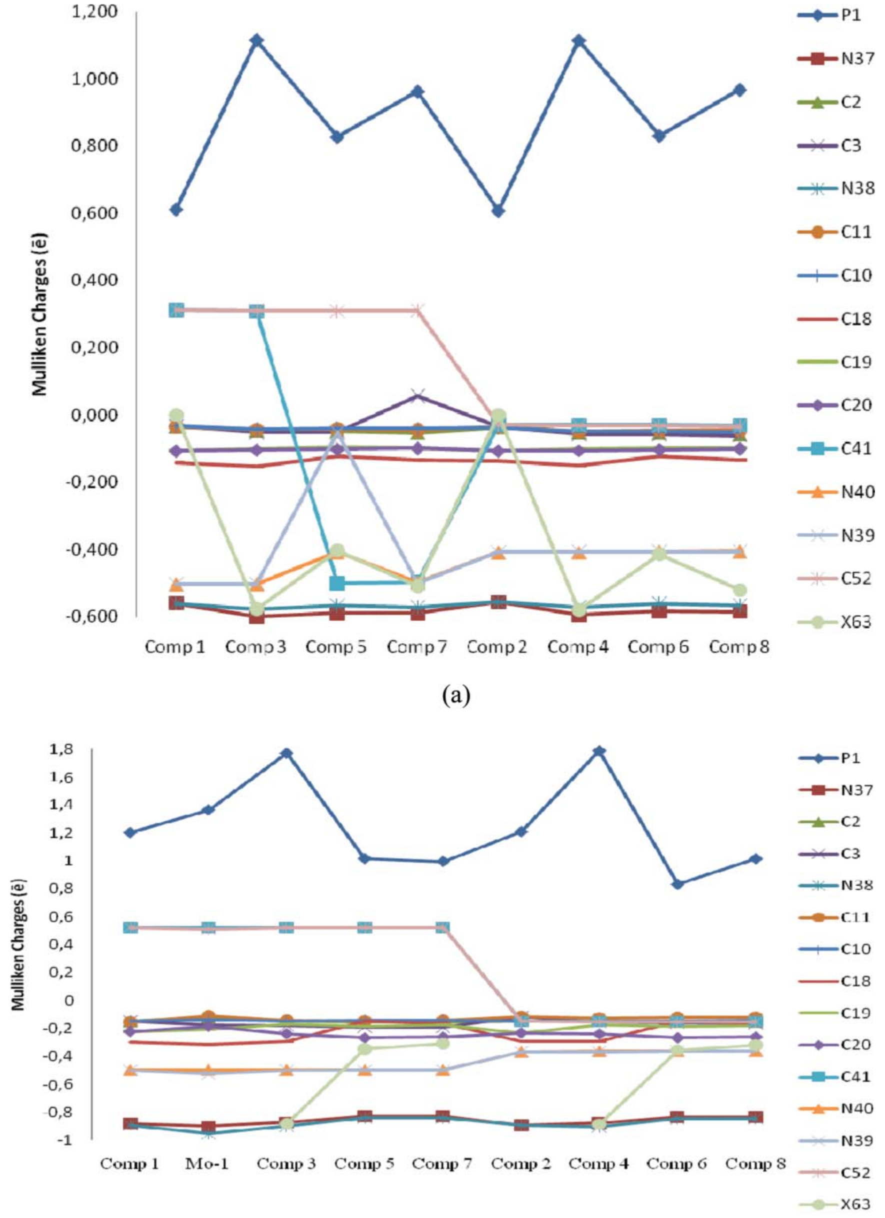


FIG. 6. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) and ESP of the molecules **1–8** (color figure available online).



(a)

(b)

FIG. 7. Mulliken Charges of molecules **1–8** calculated with (a) B3LYP/6-31G(d,p) and (b) RHF/LANL2DZ (color figure available online).

TABLE 6
Dipole moment calculated with B3LYP/6–31G(d,p) for molecules **1, 3, 5,** and **7**

Compound	Dipole moment (debye)	
	B3LYP 6-31G(d,p)	RHF lanl2dz
1	1.0996	0.6727
3	3.2440	4.8029
5	4.0694	5.2021
7	3.9634	5.0889

65.74% localization on C18 for P1-C18 bond, and 23.78%, localization on P1 and 76.22% localization on N37 and N38 for P1-N37 bond and P1-N38 bond. This describes a polar P-C and P-N bonds. Percent localization on P1 of P1-C18 for aminophosphine chalcogenides is slightly more than those for aminophosphine. As seen Table 7, P = E (O, S, Se) NBO composition bond in aminophosphine chalcogenides are (0.4945. $sp^{2.45}d^{0.05}$) P1 + (0.8692. $sp^{1.71}d^{0.01}$) O63, (0.6942. $sp^{2.40}d^{0.04}$) P1+ (0.7198. $sp^{4.49}d^{0.02}$) S63, and (0.7246. $sp^{2.52}d^{0.02}$) P1+ (0.6892. $sp^{5.94}d^{0.06}$) Se63, so there are 24.45%, 48.19%, and 52.50% localization on P1.

TABLE 7
P-C, P-N, and P-E (E = O, S, Se) NBO compositions calculated with B3LYP/6–31G(d,p) for molecules **1, 3, 5**, and **7**

Compound	
1	$(0.585.\ sp^{4.44}d^{0.07})P1 + (0.811.\ sp^{2.43})\ C18$
	$(0.4877.\ sp^{5.42}d^{0.11})\ P1 + (0.8730.\ sp^{1.90})\ N37$
	$(0.4877.\ sp^{5.42}d^{0.11})\ P1+ (0.8730.\ sp^{1.90})\ N38$
3	$(0.5826.\ sp^{2.89}d^{0.06})\ P1+ (0.8128.\ sp^{2.45})\ C18$
	$(0.4990.\ sp^{3.16}d^{0.09})\ P1+ (0.8666.\ sp^{2.39})\ N37$
	$(0.4975.\ sp^{3.29}d^{0.09})\ P1+ (0.8675.\ sp^{2.30})\ N38$
	$(0.4945.\ sp^{2.45}d^{0.05})\ P1 + (0.8692.\ sp^{1.71}d^{0.01})\ O63$
5	$(0.6031.\ sp^{2.96}d^{0.05})\ P1+ (0.7977.\ sp^{2.46})\ C18$
	$(0.5167.\ sp^{3.24}d^{0.07})\ P1+ (0.8562.\ sp^{2.53})\ N37$
	$(0.5134.\ sp^{3.32}d^{0.07})\ P1 + (0.8581.\ sp^{2.29})\ N38$
	$(0.6942.\ sp^{2.40}d^{0.04})\ P1+ (0.7198.\ sp^{4.49}d^{0.02})\ S63$
7	$(0.6052.\ sp^{2.90}d^{0.04})\ P1 + (0.7961.\ sp^{2.46})\ C18$
	$(0.5200.\ sp^{3.21}d^{0.07})\ P1+ (0.8542.\ sp^{2.66})\ N37$
	$(0.5144.\ sp^{3.26}d^{0.07})\ P1 + (0.8576.\ sp^{2.26})\ N38$
	$(0.7246.\ sp^{2.52}d^{0.02})\ P1+ (0.6892.\ sp^{5.94}d^{0.06})\ Se63$

CONCLUSIONS

In conclusion, the new bis(amino)phosphine and their oxides, sulfides, selenides, and molybdenum 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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