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ScienceDirect
Polyhedron 25 (2006) 3215–3221
POLYHEDRON
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Aminophosphines derived from morpholine and *N*-methylpiperazine: Synthesis, oxidation reactions and transition metal complexes

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Received 21 May 2006; accepted 26 May 2006
Available online 27 June 2006

Abstract

The synthesis, derivatization and coordination behavior of *N*-diphenylphosphinomorpholine (**1**) and *N*-diphenylphosphinopiperazine (**2**) is described. Ligands **1** and **2** react with elemental sulfur or selenium to give the corresponding chalcogenides in good yield. Reaction of **1** with paraformaldehyde leads to the insertion of methylene into P–N bond to give phosphine oxide, $Ph_2P(O)CH_2NC_4H_8O$ in quantitative yield. Treatment of **2** with $[Pd(COD)Cl_2]$ produces both the mononuclear $[PdCl_2\{(Ph_2PNC_4H_8O)\text{-}\kappa P\}_2]$ and the chloro-bridged dinuclear complex, $[(OC_4H_8NPh_2P)Pd\text{-}(\mu\text{-}Cl)Cl]_2$ whereas the similar reaction of **2** with $[Pt(COD)Cl_2]$ affords only the mononuclear complex $[PtCl_2\{(Ph_2PNC_4H_8O)\text{-}\kappa P\}_2]$. Interestingly, ligand **2** reacts with Mo(0), W(0), Ru(II), Pd(II), Pt(II) and Au(I) derivatives to furnish exclusively mononuclear complexes. The molecular structures of Ru(II) and Pd(II) dimer have been confirmed by X-ray studies.

Keywords: Aminophosphines; Insertion reaction; Sulfur and selenium derivatives; Palladium and platinum complexes; Ruthenium(II)

1. Introduction

There has been large interest in the use of hybrid ligands or hemi labile ligands having both hard and soft donor centers. These hemi labile ligands form weak metal–oxygen [1], metal–sulfur [2], or metal–nitrogen bonds [3], while phosphorus atom can strongly coordinate to the metal centers. The hard centers in these hemi labile ligands may behave as intramolecular solvent molecules stabilizing the empty coordination site and due to chelate effect these complexes are much more stable than simple solvent adducts. Such systems would be ideal for homogeneous catalysis, since the more labile donor center can readily dissociate from the metal, thus facilitating a vacant coordination site, which can produce an active intermediate in catalytic process.

In this context, tertiaryphosphines with amine functionalities have drawn considerable interest as ligands [4], and their platinum metal complexes [5], have shown excellent catalytic properties in a variety of organic transformations [6], including various polymerization reactions [7]. This is due to the multiple bonding nature of P–N bonds which can readily alter the electronic properties of phosphorus(III) center thus influencing its coordinating abilities and hence the catalytic properties. Further, the electronic properties vary with nitrogen substituents. Although phosphines containing morpholine and piperidine moieties have been prepared, derivatized [8], and employed in catalytic studies [9], the reports on coordination chemistry is scant. As a part of our continued interest in developing phosphine based ligand systems for transition metal chemistry [10], and catalytic applications [5a,11], we report in this paper some transition metal complexes of phosphines containing morpholine and *N*-methylpiperazine.

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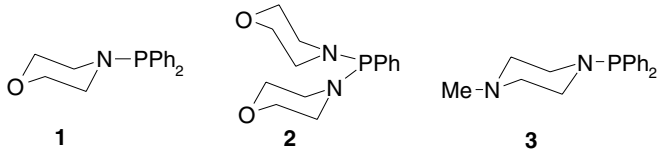
doi:10.1016/j.poly.2006.05.041

2. Results and discussion

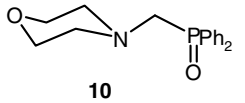
The reactions of two equivalents of morpholine or *N*-methylpiperazine with diphenylchlorophosphine in diethyl ether at room temperature afford the corresponding derivatives *N*-diphenylphosphinoamines $Ph_2PNC_4H_8O$ (**1**) and $Ph_2PNC_4H_8NMe$ (**2**) in good yield. Similarly, the reaction of four equivalents of morpholine with $PhPCl_2$ afforded bis(morpholino)phenylphosphine $PhP(NC_4H_8O)_2$ (**3**). Both the morpholine and *N*-methylpiperazine derivatives (**1**–**3**) react smoothly with elemental sulfur or selenium in toluene under reflux conditions to give the corresponding sulfide or selenide derivatives **4**–**9** as air stable solids. The preparation of some of these chalcogen derivatives have been reported previously but without all the details [12]

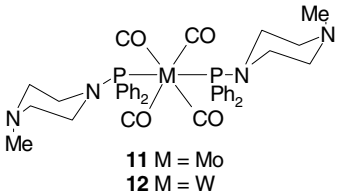


The $^{31}P\{^1H\}$ NMR spectra of compounds **1**–**3** show single resonances at 61.7, 63.3 and 95.8 ppm, respectively, whereas their chalcogenides **4**–**9** show single resonance in the range of 65–79 ppm. The mono-morpholine and *N*-methylpiperazine derivatives **7** and **8** show $^1J_{PSe}$ coupling around 760 Hz whereas the bis(morpholine) derivative **9** shows a $^1J_{PSe}$ coupling of 788 Hz. The ^1H NMR spectral data of **1**–**9** are consistent with the structures proposed. The structural composition of all compounds has been confirmed by elemental analysis.

The reaction of *N*-diphenylphosphinomorpholine **1** with paraformaldehyde in toluene under reflux conditions lead to methylene inserted product **10** in good yield. The methylene insertion reaction proceeds in accordance with our reports on similar aminophosphines [10e,13]. The ^{31}P NMR spectrum of **10** shows a singlet at 28.4 ppm. The ^1H NMR spectrum of compound **10** exhibits two types of resonances for the alkyl (NC_4H_8O and CH_2) protons apart from aryl protons. The NC_4H_8O protons appear at 3.80 ppm and CH_2 protons appear at 3.42 ppm. In the mass spectrum (MS), the most intense fragment ion appears at *m*/*e* 302 [$M^+ + 1$] which is the expected molecular ion.

The reactions of **2** with either $M(CO)_6$ or *cis*-$W(CO)_4(piperidine)_2$ under refluxing conditions produce the *trans*-tetracarbonyl complexes of the type *trans*-$[M(CO)_4(PPh_2NC_4H_8NMe)_2]$ (**11**, M = Mo; **12**, M = W). The ^{31}P NMR spectra of **11** and **12** exhibit single resonances at 106.2 and 80.8 ppm with tungsten complex showing tungsten satellites with a $^1J_{WP}$ coupling of 304.4 Hz which confirms the mutual *trans* dispositions of two phosphine ligands [10f]. Further confirmation for the *trans* geometry of complexes **11** and **12** comes from IR spectra which show single absorption for *ν*CO at 1888 and 1895 cm^{-1}, respectively, characteristic of complexes containing *trans*-$M(CO)_4$ moieties [14].





The ruthenium-arene dimer, $[(p\text{-cymene})RuCl_2]_2$ reacts with two equivalents of **2** in dichloromethane at room temperature to produce an orange-red complex $[(\eta^6\text{-}C_{10}H_{14})RuCl_2\{PPh_2NC_4H_8NMe\}]$ (**13**) in quantitative yield. The ^{31}P NMR spectrum of **13** shows a single resonance at 73.5 ppm with a coordination shift of 12 ppm. The mass spectrum of **13** exhibits parent ion peak (M + 1) at 591.3. The structure of complex **13** was further confirmed by single crystal X-ray diffraction study.

2.1. Structure of $[(\eta^6\text{-}C_{10}H_{14})RuCl_2\{PPh_2NC_4H_8NMe\}]$ (13)

Perspective view of the molecular structure of the compound **13** with the atomic numbering scheme is shown in Fig. 1 along with selected bond lengths and bond angles. The details of the structure determination are given in Table 1.

The coordination geometry around the ruthenium center in **13** can be best described as pseudo octahedral three-legged piano stool, typically of half-sandwich complexes. The P–N (1.680(2) Å) bond is shorter than the

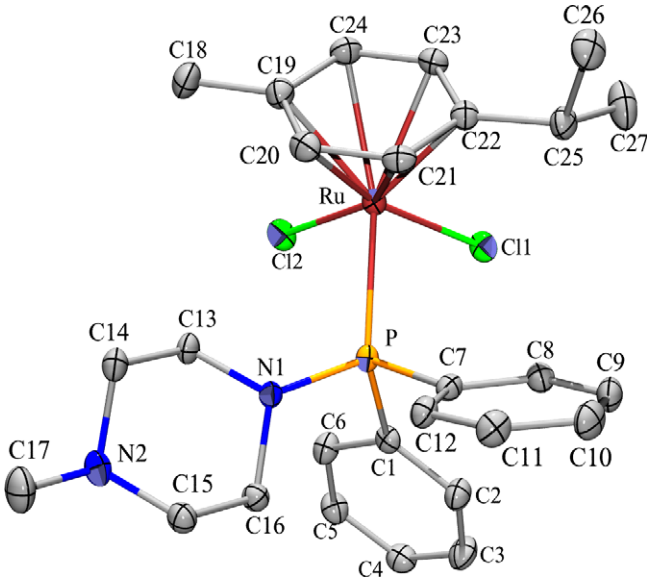


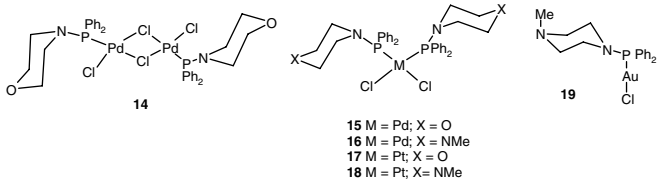
Fig. 1. Molecular structure of **13**. For clarity, solvent and all hydrogen atoms have been omitted. Thermal ellipsoids are drawn at 50% probability. Selected bond distances (Å): Ru–Cl(1), 2.4031(7); Ru–Cl(2), 2.4095(6); Ru–P, 2.3356(6); P–N(1), 1.680(2); N(1)–C(13), 1.471(3); N(2)–C(17), 1.448(3). Selected bond angles (°): Cl(1)–Ru–Cl(2), 86.83(2); Cl(1)–Ru–P, 84.78(2); Cl(1)–Ru–C(19), 150.28(6); Cl(2)–Ru–P, 87.25(2).

Table 1
Crystallographic data for complexes **14** and **13**

Formula	$C_{32}H_{36}Cl_4N_2O_2P_2Pd_2$	$C_{27}H_{35}Cl_2N_2PRu \cdot CH_2Cl_2$
M	897.2	675.44
Crystal size (mm)	$0.08 \times 0.09 \times 0.13$	$0.09 \times 0.12 \times 0.19$
Crystal system	monoclinic	triclinic
Space group	$C2_1/c$	$P\bar{1}$ (No. 2)
a (Å)	17.3015(9)	11.7680(10)
b (Å)	8.3673(4)	11.8570(10)
c (Å)	23.6400(1)	11.9230(10)
α (°)	90	67.78(1)
β (°)	95.91(1)	76.59(1)
γ (°)	90	72.59(1)
V (Å^3)	3404.1(3)	1456.3(2)
Z	4	2
D_{calc} (g cm^{-3})	1.751	1.540
μ (mm^{-1})	1.498	0.981
T (K)	293	100
$\theta_{min,max}$ (°)	1.7, 28.3	2.2, 28.4
Total number of reflections	14700	25781
Number of unique reflections	4106	7177
R_{int}	0.031	0.025
R	0.0373	0.0315
R'	0.0833	0.0747

normally accepted value for a single bond (1.77 Å), but it compares well with those found in a variety of phosphorus(III)–nitrogen compounds suggesting a degree of P–N multiple bonding. Similarly, the Ru–P bond distance is (2.336(1) Å) comparable with those observed in ruthenium complexes containing a variety of tertiary phosphines. The average Ru–Cl bond distance is 2.403(1) Å.

Treatment of $Pd(COD)Cl_2$ with one equivalent of ligand **1** in dichloromethane, afforded a chloro-bridged dinuclear complex, $[Pd_2Cl_2(\mu\text{-}Cl_2)\{Ph_2P(NC_4H_8O)\}_2]$ (**14**). The reaction of two equivalents of **1** with $Pd(COD)Cl_2$ in dichloromethane afforded mononuclear complex, *cis*-$[PdCl_2\{Ph_2PNC_4H_8O\}_2]$ (**15**) as a major product containing small quantities of dinuclear complex, **14** [15] which are separated by fractional crystallization. Surprisingly, $Pd(COD)Cl_2$ on treatment with **2** produced exclusively the *cis*-$[PdCl_2\{PPh_2NC_4H_8NMe\}_2]$ (**16**) as a major product irrespective of the stoichiometry of the reactants and the reaction conditions



In contrast, the reaction of either one or two equivalents of ligand **1** or **2** with $Pt(COD)Cl_2$ afforded only the mononuclear complexes, *cis*-$[PtCl_2\{Ph_2PNC_4H_8X\}_2]$ (**17**, X = O; **18**, X = NMe) in good yield. Further attempts to synthesize a dinuclear platinum complex analogues to the dipalladium complex **14** have been unsuccessful.

The $^{31}P\{^1H\}$ NMR spectra of **14** show a single resonance at 75.4 ppm. In the mass spectrum (MS) the expected molecular ion appears at m/e 862 [M − Cl]. The structure of **14** was confirmed by a single crystal X-ray diffraction study. The $^{31}P\{^1H\}$ NMR spectra of **15** and **16** exhibit single resonances at 67.3 and 68.5 ppm, respectively. The phosphorus-31 chemical shifts due to the corresponding platinum derivatives (**17** and **18**) are relatively shielded and appear at 50.7 and 50.2 ppm, respectively. Both the complexes show large $^1J_{PtP}$ coupling (**17**, 3968 Hz; **18**, 3965 Hz) which is characteristic of phosphines having mutually *cis*-dispositions [16].

The gold(I) complex, $[ClAu(PPh_2NC_4H_8NMe)]$ (**19**) was produced in the reaction between **2** and $AuCl(SMe_2)$ as colorless light sensitive solid soluble in most of the organic solvents. The ^{31}P NMR spectrum of **19** shows a single resonance at 77.9 ppm with a coordination shift of 16.5 ppm.

2.2. Structure of $[Pd_2Cl_2(\mu\text{-}Cl_2)\{Ph_2P(NC_4H_8O)\}_2]$ (**14**)

Perspective view of the molecular structure of the compound **14** with the atomic numbering scheme is shown in Fig. 2 along with selected bond lengths and bond angles. The Pd_2Cl_2 plane is perpendicular to morpholine rings. The Cl(1)–Pd–P angle is 93.35(3)° where as Cl(1_a)–Pd–Cl(2) angle is 89.61(3)° which clearly indicates some distortion at the metal center. The Cl(1)–Pd–P angle (93.35(3)°) appears to have increased from the squareplanar value of 90° to an extent limited by the development of phosphine–chloride interactions. The Pd–Cl(1) (2.32 Å) bond distance is slightly longer than Pd–Cl(2) (2.27 Å) bond distance. That there is only a single ^{31}P NMR resonance in solution suggests that the observed difference may result from packing (or) other solid state effects.

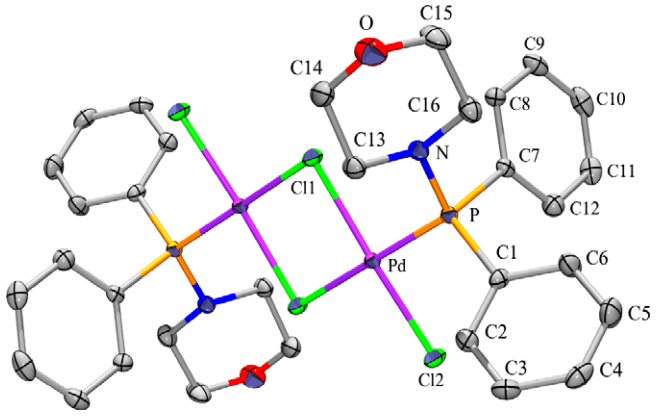


Fig. 2. Molecular structure of **14**. For clarity, solvent and all hydrogen atoms have been omitted. Thermal ellipsoids are drawn at 50% probability. Selected bond distances (Å): Pd–Cl(1), 2.325(8); Pd–Cl(2), 2.271(1); Pd–P, 2.215(1); Pd–Cl(1a), 2.437(1); P–N, 1.676(3); P–Cl, 1.808(3); P–C(7), 1.804(3). Selected bond angles (°): Cl(1)–Pd–Cl(2), 171.39(3); Cl(1)–Pd–P, 93.35(3); Cl(1)–Pd–C(11a), 86.80(3); Cl(2)–Pd–P, 89.73(5); Pd–P–N, 113.46(9).

3. Experimental

All experimental manipulations were carried out under an atmosphere of dry nitrogen or argon using Schlenk techniques. All the solvents were purified by conventional procedures and distilled prior to use. The metal precursors $[W(CO)_4(pip)_2]$ [17], $[(p\text{-cymene})RuCl_2]_2$ [18], $[AuCl(SMe_2)]$ [19], $[(COD)PdCl_2]$, $[(COD)PtCl_2]$ [20] are prepared according to the literature methods and $[Mo(CO)_6]$ was obtained from Aldrich chemicals.

The ^1H and ^{31}P NMR (δ in ppm) spectra were obtained on a VXR300S spectrometer operating at frequencies of 300 and 121 MHz, respectively. The spectra were recorded in $CDCl_3$ solutions with $CDCl_3$ as an internal lock; TMS and 85% H_3PO_4 were used as external standards for ^1H and $^{31}P\{^1H\}$ NMR, respectively. Positive shifts lie downfield of the standard in all cases. Melting points of all compounds were determined on Veego melting point apparatus and were uncorrected. Mass spectra were recorded on MASPEC (msco/9849) system. Microanalyses were carried out on a Carlo Erba model EA 1112 elemental analyzer.

3.1. Preparation of $Ph_2P(NC_4H_8O)$ (1)

A solution of HNC_4H_8O (1.73 g, 19.93 mmol) in dry diethyl ether (20 mL) was added drop wise to a chlorodiphenylphosphine (2 g, 9.06 mmol) also in diethyl ether (70 mL) at 0 °C with vigorous stirring. Then the solution was allowed to room temperature and stirring was continued for 24 h. The morpholine hydrochloride was removed by filtration. The solvent was removed under vacuum to give a white solid of the crude product, which was crystallized from dichloromethane/petroleum ether (b.p. 60–80 °C) (2:1). Yield: 89% (2.20 g); m.p. 84–85 °C. *Anal.* Calc. for $C_{16}H_{18}NOP$: C, 70.83; H, 6.68; N, 5.16. Found: C, 70.02; H, 6.32; N, 5.06%. ^1H NMR (300 MHz, $CDCl_3$): δ 7.23–7.59 (m, 10H, Ph), δ 3.71 (t, 4H, OC_2H_4), δ 3.07 (tt, 4H, NC_2H_4). $^{31}P\{^1H\}$ NMR (300 MHz, $CDCl_3$): δ 63.7 (s).

3.2. Preparation of $[Ph_2PNC_4H_8NMe]$ (2)

To an ice cooled solution of *N*-methylpiperazine (2.26 g, 22.5 mmol) in diethyl ether (50 mL), a solution of chlorodiphenylphosphine (2.48 g, 11.25 mmol) in diethyl ether (30 mL) was added dropwise over a period of 15 min with constant stirring. The reaction mixture was allowed to warm to room temperature and stirring was continued for 16 h. The piperazinehydrochloride was filtered off and the filtrate was dried under vacuum. The residue obtained was dissolved in 20 mL of acetonitrile and the solution was cooled to −25 °C for 10 h to give analytically pure product of **1** as colorless blocks. Yield: 70% (2.24 g); m.p. 58–60 °C. *Anal.* Calc. for $C_{17}H_{21}N_2P$: C, 71.81; H, 7.44; N, 9.85. Found: C, 71.31; H, 7.22; N, 9.91%. ^1H NMR (400 MHz, $CDCl_3$): δ 2.98 (s, 4H, CH_2), 2.38 (s, 4H, CH_2), 2.20 (s, 3H, *NMe*), 7.30–7.55 (m, 10H, *phenyl*). $^{31}P\{^1H\}$ NMR (400 MHz, $CDCl_3$): δ 61.3 (s).

3.3. Preparation of $PhP(NC_4H_8O)_2$ (3)

A solution of HNC_4H_8O (1.73 g, 19.93 mmol) in dry diethyl ether (20 mL) was added drop wise to chlorodiphenylphosphine (2 g, 9.06 mmol) also in diethyl ether (70 mL) at 0 °C with vigorous stirring. Then the solution was allowed to warm to room temperature and stirring was continued for 24 h. The morpholine hydrochloride was removed by filtration. The solvent was removed under vacuum to give a white solid of the crude product, which was crystallized from dichloromethane/petroleum ether (2:1). Yield: 91.0% (2.95 g); m.p. 98–100 °C. *Anal.* Calc. for $C_{14}H_{21}N_2O_2P$: C, 59.98; H, 7.51; N, 9.94. Found: C, 59.02; H, 7.24; N, 9.27%. $^{31}P\{^1H\}$ NMR (300 MHz, $CDCl_3$): δ 95.8 (s).

3.4. Preparation of $Ph_2P(S)(NC_4H_8O)$ (4)

A mixture of compound **1** (0.5 g, 1.8 mmol) and sulfur (0.06 g, 1.8 mmol) in toluene (10 mL) was heated under reflux for 12 h to give a clear solution. Solvent was removed under reduced pressure to give a white residue. The residue was dissolved in CH_2Cl_2 (5 mL), layered with 1 mL of petroleum ether and kept at room temperature to give colorless crystals of **3**. Yield: 90% (0.49 g); m.p. 116–118 °C (decomp.). *Anal.* Calc. for $C_{16}H_{18}NOPS$: C, 63.32; H, 5.98; N, 4.61; S, 10.57. Found: C, 63.61; H, 5.99; N, 4.92; S, 8.74%. $^{31}P\{^1H\}$ NMR (300 MHz, $CDCl_3$): δ 65.9 (s).

3.5. Synthesis of $[P(S)Ph_2NC_4H_8NMe]$ (5)

As for **4**, using $Ph_2PNC_4H_8NMe$ (0.19 mg, 67.5 mmol) and elemental sulfur (0.022 mg, 67.6 mmol). Yield: 95% (0.202 g); m.p. 106–108 °C. *Anal.* Calc. for $C_{17}H_{21}N_2PS$: C, 64.53; H, 6.69; N, 8.85; S, 10.13. Found: C, 63.92; H, 6.45; N, 8.31; S, 9.6%. ^1H NMR (400 MHz, $CDCl_3$): δ 2.98 (s, 4H, CH_2), 2.38 (s, 4H, CH_2), 2.2 (s, 3H, *NMe*), 8.1 (m, 5H, *phenyl*), 7.25 (m, 5H, *phenyl*). $^{31}P\{^1H\}$ NMR (400 MHz, $CDCl_3$): δ 65.8 (s).

3.6. Preparation of $PhP(S)(NC_4H_8O)_2$ (6)

As for **4**, using $PhP(NC_4H_8O)_2$ (1 g, 3.56 mmol) and selenium powder (0.15 g, 3.56 mmol). Yield: 92% (1 g); m.p. 120–122 °C. *Anal.* Calc. for $C_{14}H_{21}N_2O_2PS$: C, 53.83; H, 6.77; N, 8.99; S, 10.26. Found: C, 53.70; H, 6.68; N, 9.18; S, 8.85%. $^{31}P\{^1H\}$ NMR (300 MHz, $CDCl_3$): δ 74.8 (s).

3.7. Preparation of $Ph_2P(Se)(NC_4H_8O)$ (7)

A mixture of **1** (1 g, 3.68 mmol) and selenium powder (0.29 g, 3.68 mmol) in toluene (25 mL) was heated under reflux for 12 h. The solution was then cooled to 25 °C and filtered to remove any undissolved selenium. The solvent was removed under reduced pressure to give a sticky residue. The residue was dissolved in 3 mL of CH_2Cl_2, layered with 1 mL of petroleum ether and kept at room temperature to afford crystals of **5**. Yield: 92% (0.12 g); m.p.

120–122 °C. *Anal.* Calc. for $C_{16}H_{18}NOPSe$: C, 54.86; H, 5.17; N, 3.99. Found: C, 55.3; H, 5.2; N, 4.4%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.12–7.2.1 (m, 21H, Ph), δ 3.77 (tt, 4H, OC_2H_4), δ 2.82 (tt, 4H, NC_2H_4). $^{31}P\{^1H\}$ NMR (300 MHz, $CDCl_3$): δ 66.9 (s), $^1J_{PSe} = 760$ Hz.

3.8. Preparation of *[P(Se)Ph$_2$NC$_4$H$_8$NMe] (**8**)*

As for **7** using $Ph_2PNC_4H_8NMe$ (0.230 g, 80.9 mmol) and grey selenium (0.064 g, 80.9 mmol). Yield: 90% (261 mg); m.p. 114–116 °C. *Anal.* Calc. for $C_{17}H_{21}N_2PSe$: C, 56.20; H, 5.83; N, 7.71. Found: C, 56.37; H, 5.46; N, 7.29%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.9 (s, 4H, *CH*$_2$), 2.5 (s, 4H, *CH*$_2$), 2.3 (s, 3H, *NMe*), 8.2 (m, 5H, *phenyl*), 7.5 (m, 5H, *phenyl*). $^{31}P\{^1H\}$ NMR (400 MHz, $CDCl_3$): δ 66.28 (s), $^1J_{PSe} = 758.4$ Hz.

3.9. Preparation of *PhP(Se)(NC$_4$H$_8$O)$_2$ (**9**)*

As for **7** using $PhP(NC_4H_8O)_2$ (1 g, 3.68 mmol) and selenium powder (0.29 g, 3.68 mmol). Yield: 78% (1 g); m.p. 120–122 °C. *Anal.* Calc. for $C_{14}H_{21}N_2O_2PSe$: C, 46.86; H, 5.58; N, 7.79. Found: C, 46.8; H, 5.34; N, 8.04%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.98–7.26 (m, 5H, Ph), δ 3.66 (tt, 4H, OC_2H_4), δ 3.07 (tt, 4H, NC_2H_4). $^{31}P\{^1H\}$ NMR (300 MHz, $CDCl_3$): δ 78.2 (s), $^1J_{PSe} = 788$ Hz.

3.10. Preparation of *Ph$_2$(O)PCH$_2$NC$_4$H$_8$O (**10**)*

A mixture of **1** (0.2 g, 0.73 mmol) and paraformaldehyde (0.02 g, 0.81 mmol) in toluene (6 mL) was heated at 100 °C with stirring for 12 h. The solution was then cooled to 25 °C and filtered to remove any undissolved impurities. The compound was crystallized from CH_2Cl_2–*n*-hexane (4:1). Yield: 81% (0.18 g); m.p. 136–138 °C. *Anal.* Calc. for $C_{17}H_{20}N0_2P$: C, 67.76; H, 6.69; N, 4.64. Found: C, 66.78; H, 6.79; N, 4.62%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.85–7.26 (m, 10H, Ph), δ 3.72 (t, 4H, OC_2H_4), δ 3.42 (d, 2H, CH_2, $^2J_{PH} = 6$ Hz), δ 2.85 (s, 4H, NC_2H_4). $^{31}P\{^1H\}$ NMR (300 MHz, $CDCl_3$): δ 28.4 (s). MS (FAB): 302 ($M^+ + 1$).

3.11. Preparation of *trans-[Mo(CO)$_4${(Ph$_2$PNC$_4$H$_8$NMe)-κP}$_2$] (**11**)*

A mixture of **2** (0.044 g, 0.153 mmol) and $[Mo(CO)_6]$ (20.22 mg, 0.076 mmol) in toluene (15 mL) was heated at 90 °C for 10 h. The yellow solution obtained was cooled to room temperature and passed through a column containing celite and the solvent was removed under *vacuo*. The pale yellow micro crystalline residue obtained was washed twice with diethyl ether (3 mL) to afford analytically pure product of **11**. Yield: 70% (41 mg); m.p. 186–188 °C (dec). *Anal.* Calc. for $C_{38}H_{42}O_4N_4P_2Mo$: C, 58.77; H, 5.45; N, 7.21. Found: C, 57.69; H, 5.42; N, 6.38%. FT IR (KBr disc) cm^{-1}: ν_{CO} at 1888 s. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.2 (s, 4H, *CH*$_2$), 2.4 (s, 4H, *CH*$_2$), 2.2 (s, 3H, *NMe*), 7.4 (m, 5H, *phenyl*), 7.1 (m, 5H, *phenyl*). $^{31}P\{^1H\}$ NMR (400 MHz, $CDCl_3$): δ 106.2 (s).

3.12. Preparation of *trans-[W(CO)$_4${(Ph$_2$PNC$_4$H$_8$NMe)-κP}$_2$] (**12**)*

As for **11** using $[Ph_2PNC_4H_8NMe]$ (0.053 mg, 188 mmol) and $[W(CO)_4(pip)_2]$ (0.044 g, 94 μmol). Yield: 68% (0.055 g); m.p. 178–180 °C (dec). *Anal.* Calc. for $C_{38}H_{42}O_4N_4P_2W$: C, 52.79; H, 4.89; N, 6.48. Found: C, 53.23; H, 5.09; N, 6.65%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.82 (s, 4H, *CH*$_2$), 2.43 (s, 4H, *CH*$_2$), 2.10 (s, 3H, *NMe*), 7.61–7.24 (m, 10H, *phenyl*). IR (KBr disc) cm^{-1}: ν_{CO} at 1890 s. $^{31}P\{^1H\}$ NMR (300 MHz, $CDCl_3$): δ 80.8 (s), $^1J_{PW} = 304.4$ Hz.

3.13. Preparation of *[Ru(η^6-C$_{10}$H$_{14}$)Cl$_2${(PPh$_2$NC$_4$H$_8$-NMe)-κP}] (**13**)*

A solution of [(*p*-cymene)$RuCl_2]_2$ (0.033 mg, 54.5 μmol) in dichloromethane (5 mL) was added dropwise to a solution of **2** (0.031 mg, 109 μmol) in the same solvent (5 mL) at room temperature. After the completion of the addition, the reaction mixture was stirred for 4 h and the solvent was removed under reduced pressure. The residue obtained was washed with diethyl ether to give analytically pure product of **13** as red micro crystalline solid. Yield: 85% (55 mg); m.p. 168–170 °C (dec). *Anal.* Calc. for $C_{27}H_{35}N_2PRuCl_2$: C, 54.91; H, 5.97; N, 4.74. Found: C, 54.63; H, 5.74; N, 4.07. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70–7.43 (m, 10H, *phenyl*), 5.15 (d, $J_{HH} = 6.4$ Hz, 2H, *Cymene phenyl*), 4.95 (d, $J_{HH} = 6.4$ Hz, 2H, *Cymene phenyl*), 3.1 (s, 3H, *NMe*), 2.75 (septet, 1H, *CH*), 2.5 (s, 4H, *CH*$_2$) 2.4 (s, 4H, *CH*$_2$), 1.95 (s, 3H, *CH*$_3$). $^{31}P\{^1H\}$ NMR (300 MHz, $CDCl_3$): δ 73.5 (s).

3.14. Preparation of *[Pd$_2$(μ-Cl)$_2$Cl$_2${(Ph$_2$PNC$_4$H$_8$O)-κP}$_2$] (**14**)*

To a mixture of $Pd(COD)Cl_2$ (0.05 g, 0.17 mmol) and compound **1** (0.05 g, 0.17 mmol) a CH_2Cl_2 solution (8 mL) was added and the resultant reaction mixture was stirred at room temperature for 48 h. The solution was concentrated to 3 mL and 1 mL of petroleum ether was added. Cooling this solution to 0 °C gave **8** as red crystals. Yield: 77% (0.06 g); m.p. 160–162 °C. *Anal.* Calc. for $C_{32}H_{36}Cl_4N_2O_2P_2Pd_2$: C, 42.83; H, 4.04; N, 3.12. Found: C, 42.6; H, 3.7; N, 3.5%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.26–8.05 (m, 10H, Ph), δ 3.68 (t, 4H, OC_2H_4), δ 3.13 (tt, 4H, NC_2H_4). $^{31}P\{^1H\}$ NMR (300 MHz, $CDCl_3$): δ 75.4 (s). MS (FAB): 862 (M − Cl).

3.15. Preparation of *cis-[PdCl$_2${(PPh$_2$NC$_4$H$_8$O)-κP}$_2$] (**15**)*

To a mixture of $Pd(COD)Cl_2$ (0.05 g, 0.17 mmol) and compound **1** (0.11 g, 0.35 mmol) a CH_2Cl_2 solution

(8 mL) was added and the resultant reaction mixture was stirred at room temperature for 48 h. The solution was concentrated to 3 mL and 1 mL of petroleum ether was added. Cooling this solution to 0 °C gave **9** as red crystalline material. Further cooling the remaining solution gave **9** as yellow crystals. Yield: 61% (0.08 g); m.p. 180–185 °C. *Anal.* Calc. for $C_{32}H_{36}Cl_2N_2O_2P_2Pd$: C, 53.38; H, 5.04; N, 3.91. Found: C, 52.82; H, 5.36; N, 3.72%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.71–7.27 (m, 10H, Ph), δ 3.64 (t, 4H, OC_2H_4), δ 3.01 (tt, 4H, NC_2H_4). $^{31}P\{^1H\}$ NMR (300 MHz, $CDCl_3$): δ 67.3 (s).

3.16. Preparation of cis-[$PdCl_2\{(PPh_2NC_4H_8NMe)$-κP$\}_2$] (16)

As for **15**, using [Pd(COD)Cl_2] (25 mg, 88 μmol) and **2** (50 mg, 175 μmol). Yield: 95% (62 mg); m.p. 150–152 °C (dec). *Anal.* Calc. for $C_{34}H_{42}Cl_2N_4P_2Pd$: C, 54.74; H, 5.67; N, 7.51. Found: C, 53.68; H, 5.38; N, 7.32%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.1 (s, 4H, CH_2), 2.5 (s, 4H, CH_2), 2.2 (s, 3H, CH_2), 7.71–7.42 (m, 10H, *phenyl*). $^{31}P\{^1H\}$ NMR (400 MHz, $CDCl_3$): δ 68.5 (s).

3.17. Preparation of cis-[$PtCl_2\{(Ph_2PNC_4H_8O)$-κP$\}_2$] (17)

To a solution of [Pt(COD)Cl_2] (0.03 g, 0.08 mmol) in CH_2Cl_2 (4 mL) was added a solution of **1** (0.04 g, 0.16 mmol) also in CH_2Cl_2 (5 mL) and the reaction mixture was stirred at room temperature for 48 h. The solution was concentrated to 2 mL and 1 mL of petroleum ether was added. Cooling this solution to 0 °C gave **10** as white crystalline material. Yield: 92% (0.06 g); m.p. 216–218 °C. *Anal.* Calc. for $C_{32}H_{36}Cl_2N_2O_2P_2Pt \cdot 0.5CH_2Cl_2$: C, 45.86; H, 4.38; N, 3.29. Found: C, 45.71; H, 4.30; N, 3.46%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.89–6.91 (m, 10H, Ph), δ 3.53 (t, 4H, OC_2H_4), δ 3.22 (t, 4H, NC_2H_4). $^{31}P\{^1H\}$ NMR (300 MHz, $CDCl_3$): δ 50.7 (s), $^1J_{PPt} = 3968$ Hz. MS (FAB): 772 (M − Cl).

3.18. Preparation of cis-[$PtCl_2\{(Ph_2PNC_4H_8NMe)$-κP$\}_2$] (18)

As for **17**, using [Pt(COD)Cl_2] (0.02 g, 53 μmol) and **2** (0.03 g, 106 μmol). Yield: 95% (43 mg); m.p. 164–166 °C (dec). *Anal.* Calc. for $C_{34}H_{42}Cl_2N_4P_2Pt$: C, 48.93; H, 5.07; N, 6.71. Found: C, 48.26; H, 5.09; N, 6.17%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.2 (s, 4H, CH_2), 2.4 (s, 4H, CH_2), 2.2 (s, 3H, CH_2), 7.43–7.16 (m, 10H, *phenyl*). $^{31}P\{^1H\}$ NMR (400 MHz, $CDCl_3$): δ 50.2 (s), $^1J_{PPt} = 3965$ Hz.

3.19. Preparation of [$AuCl\{(PPh_2NC_4H_8NMe)$-κP$\}$] (19)

A solution of [ClAu(SMe_2)] (0.026 g, 88.8 μmol) in dichloromethane (10 mL) was added dropwise to a solution of **2** (0.030 g, 88.8 μmol) also in dichloromethane (8 mL) at room temperature and the reaction mixture was stirred for 4 h. The solvent was removed under reduced pressure and the residue was washed with diethyl ether to give analytically pure product of **19** as white micro crystalline solid. Yield: 96% (41 mg); m.p. 150–152 °C (dec). *Anal.* Calc. for $C_{17}H_{21}N_2PAuCl$: C, 39.51; H, 4.09; N, 5.42. Found: C, 38.96; H, 3.85; N, 4.92%. ^{1}H NMR (400 MHz, $CDCl_3$): 3.24 (s, 4H, CH_2), 2.43 (s, 4H, CH_2), 2.21 (s, 3H, *NMe*), 7.71–7.50 (m, 10H, *phenyl*). $^{31}P\{^1H\}$ NMR (400 MHz, $CDCl_3$): δ 77.9 (s).

4. X-ray crystallography

Crystals of compounds **13** and **14** suitable for X-ray crystal analysis were mounted on Cryoloops™ with Paratone oil and placed in the cold nitrogen stream of the Bruker Kryoflex™ attachment of the Bruker APEX CCD diffractometer. Full spheres of data were collected using 606 scans in ω (0.3° per scan) at 0°, 120° and 240° and graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The raw data were reduced to F^2 values at a resolution of 0.75 Å using the SAINT+ software (SAINT+, V. 6.35A, Bruker-AXS, Madison, WI, 2002) and global refinements of unit cell parameters using 5000–9000 reflections chosen from the full sets of data were performed. Multiple measurements of equivalent reflections provided the basis for empirical absorption corrections as well as corrections for any crystal deterioration during the data collection (SADABS, V. 2.05, Bruker-AXS, Madison, WI, 2000). The structures were solved by direct methods (SHELX-97) and refined by full-matrix least-squares based on F^2 using the SHELXTL-PLUS program package (SHELXTL-PLUS, V. 6.10, Bruker-AXS, Madison, WI, 2000). Hydrogen atoms were placed in calculated positions provided by a difference map. All were included as riding contributions (C–H = 0.95–0.98 Å) with isotropic displacement parameters 1.2–1.5 times those of the attached carbon atoms. Two orientations were deduced from difference maps and were constrained to be regular hexagons in the final refinement. Other details of the data collections and refinements specific to these compounds are summarized in Table 1.

Acknowledgements

We thank the Department of Science and Technology (DST), New Delhi, for financial support of the work done at the Indian Institution of Technology, Bombay. J.T.M. acknowledges the support of the Louisiana Board of Regents through the Louisiana Educational Quality Support Fund (Grant: LEQSF (2002-2003)-ENH-TR-67) for purchase of the Bruker APEX diffractometer and Tulane University, New Orleans, LA, USA for the support of the Crystallography Laboratory. We thank the regional Sophisticated Center (RSIC), IIT Bombay for recording NMR spectra.

Appendix A. Supplementary material

Full details of data collection and structure refinement for compounds **8** and **14** have been deposited with the Cambridge Crystallography Data Centre, CCDC Nos. 606036 and 265737. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www://http.ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2006.05.041.

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