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A new diphosphinite derived from cyclohexane-1,4-diol: oxidation reactions, metal complexes, P–O bond cleavage and X-ray crystal structures of $Ph_2P(E)O(C_6H_{10})OP(E)Ph_2$ (E = S, Se)

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Abstract

The reaction of cyclohexane-1,4-diol with chlorodiphenylphosphine affords bis(phosphinite), $Ph_2PO(C_6H_{10})OPPh_2$ (**1**) in good yield. The bis(phosphinite) (**1**) reacts with H_2O_2, elemental sulfur or selenium to give the corresponding dichalcogenide; the structures of the disulfide (**3**) and diselenide (**4**) derivatives are confirmed by X-ray crystal structure analysis. The reaction of **1** with phosphoryl azide, $N_3P(O)(OPh)_2$ gives the phosphinimine derivative, $(PhO)_2(O)PN{=}PPh_2O(C_6H_{10})OPh_2P{=}NP(O)(OPh)_2$ (**5**) in quantitative yield. Treatment of the ligand **1** with $CpRu(PPh_3)_2Cl$ results in a bis(phosphinite) bridged dinuclear complex, $[CpRuCl(PPh_3)]_2(\mu\text{-}PPh_2O(C_6H_{10})OPPh_2)$ (**7**) whereas the reaction of **1** with Pd(II) and Pt(II) derivatives afford *cis*-chelate complexes, $[MCl_2\{Ph_2PO(C_6H_{10})OPPh_2\}]$ (M = Pd, **8**; Pt, **9**). The reaction of **1** with $Mo(CO)_6$ in the presence of $TMNO \cdot 2H_2O$ does not give the expected *cis*-$[Mo(CO)_4\{Ph_2PO(C_6H_{10})OPPh_2\}]$; instead a cubane-shaped tetranuclear molybdenum(V) complex, $[Mo_4O_4(\mu^3\text{-}O)_4\ (\mu\text{-}O_2PPh_2)_4]$ (**6**) was obtained due to water assisted cleavage of P–O bonds.

Keywords: Bis(phosphinite); Cyclohexane-1,4-diol; Disulfide and diselenide; Crystal structure

1. Introduction

Synthesis of new chelating bis(phosphines) to stabilize transition metals in low valent states is considered to be a most challenging task in view of their potential utility in a variety of metal-mediated organic transformations [1]. To date, a number of such systems with a variety of backbone frameworks have been synthesized and their transition metal chemistry has been explored [2], whereas similar studies on analogous bis(phosphinites) are less extensive, although some of them have proved to be efficient catalysts [3]. Also, the number of bis(phosphinites) having cyclic systems as bridging units are also limited [4]. As a part of our interest [5] in designing new ligand systems with different spacers to control the electronic attributes at the phosphorus centers and to explore their coordination chemistry, we report here the synthesis of a new bis(phosphinite), $Ph_2PO(C_6H_{10})OPPh_2$ (**1**) derived from 1,4-cyclohexanediol, and its chalcogen and imine derivatives and transition metal complexes. The disulfide and diselenide derivatives are structurally characterized.

2. Experimental

All manipulations were performed under an atmosphere of dry nitrogen or argon using standard Schlenk

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and vacuum line techniques. Solvents were dried and distilled by standard methods prior to use. The ^{1}H and ^{31}P NMR spectra were recorded on a VXR 300 S spectrometer operating at the appropriate frequencies using tetramethylsilane and 85% H_3PO_4 as internal and external references, respectively. Positive shifts lie downfield of the standard in all cases. Microanalyses were performed on a Carlo Erba Model 1112 elemental analyzer.

2.1. Preparation of $Ph_2PO(C_6H_{10})OPPh_2$ (1)

A solution of PPh_2Cl (1.23 g, 5.57 mmol) in dry toluene (20 ml) was added, with stirring, to a mixture of 1,4-cyclohexanediol (0.32 g, 2.73 mmol) and triethylamine (0.56 g, 5.57 mmol) in toluene (80 ml) at 0 °C. After completion of the addition, the reaction mixture was refluxed under nitrogen with stirring for 24 h. The solution was cooled to 25 °C and Et_3NHCl was filtered off. The filtrate was passed through activated silica gel and then passed through celite and the solvent was evaporated under reduced pressure to give a white residue. An analytically pure sample of **1** was obtained by recrystallizing in a 4:1 mixture of CH_2Cl_2–hexane. Yield: 78% (1.02 g), m.p. 120–122 °C. *Anal.* Calc. for $C_{30}H_{30}O_2P_2$: C, 74.37; H, 6.24. Found: C, 74.21; H, 6.18%. ^{1}H NMR ($CDCl_3$): δ 7.27–8.15 (20H, m, phenyl), 1.62–2.24 (10H, m, cyclohexyl). ^{31}P NMR (300 MHz, $CDCl_3$): δ 106.4 (s).

2.2. Preparation of $Ph_2(O)PO(C_6H_{10})OP(O)Ph_2$ (2)

To a solution of **1** (0.5 g, 1.03 mmol) in acetonitrile was added 1 ml of 10% H_2O_2 and the mixture was stirred for 20 min at 25 °C. On cooling the solution to 0 °C, analytically pure crystalline **2** was obtained in quantitative yield.

A dichloromethane solution **1** on exposure to air also results in the formation of the white crystalline product **2** in quantitative yield. M.p.: 160–162 °C (dec.). *Anal.* Calc. for $C_{30}H_{30}O_4P_2$: C, 69.76; H, 5.85. Found: C, 70.01; H, 5.87%. ^{1}H NMR ($CDCl_3$): δ 7.36–8.16 (20H, m, phenyl), 1.58–2.15 (10H, m, cyclohexyl). ^{31}P NMR (300 MHz, $CDCl_3$): δ 20.9 (s).

2.3. Preparation of $Ph_2(S)PO(C_6H_{10})OP(S)Ph_2$ (3)

A mixture of compound **1** (0.5 g, 1.03 mmol) and sulfur (0.066 g, 2.06 mmol) in toluene (50 ml) was refluxed under nitrogen with stirring for 6 h. The solution was cooled to 25 °C, concentrated to 5 ml under vacuum and 3 ml of hexane was added. Keeping this solution at 0 °C gave the analytically pure sample of **3** in 92% (0.52 g) yield. M.p.: 178–180 °C (dec.). *Anal.* Calc. for $C_{30}H_{30}O_2S_2P_2$: C, 65.67; H, 5.51; S, 11.69. Found: C, 65.47; H, 5.50; S, 11.32%. ^{1}H NMR ($CDCl_3$): δ 7.34–8.16 (20H, m, phenyl), 1.62–2.28 (10H, m, cyclohexyl). ^{31}P NMR (300 MHz, $CDCl_3$): δ 79.4 (s).

2.4. Preparation of $Ph_2(Se)PO(C_6H_{10})OP(Se)Ph_2$ (4)

A mixture of compound **1** (0.5 g, 1.03 mmol) and selenium powder (0.162 g, 2.06 mmol) in toluene (20 ml) was refluxed under nitrogen for 6 h. The solution was then cooled to 25 °C and passed through celite and the solvent was removed under reduced pressure to give a white residue. The analytically pure product of **4** was obtained by recrystallizing in a mixture of CH_2Cl_2–hexane (4:1) at 0 °C. Yield: 80% (0.53 g). M.p.: 254–256 °C. *Anal.* Calc. for $C_{30}H_{30}O_2Se_2P_2$: C, 56.08; H, 4.71. Found: C, 56.07; H, 4.56%. ^{1}H NMR ($CDCl_3$): δ 7.27–8.15 (20H, m, phenyl), 1.62–2.24 (10H, m, cyclohexyl). ^{31}P NMR (300 MHz, $CDCl_3$): δ 82.4 (s); $^{1}J_{PSe} = 794.6$ Hz.

2.5. Preparation of $(PhO)_2(O)PN{=}PPh_2O(C_6H_{10})OPh_2P{=}NP(O)(OPh)_2$ (5)

A solution of $(PhO)_2(O)PN_3$ (0.18 g, 0.65 mmol) in CH_2Cl_2 (6 ml) was added dropwise to a solution of **1** (0.15 g, 0.31 mmol), also dissolved in CH_2Cl_2 (10 ml) at −78 °C. After the addition was complete the reaction mixture was slowly warmed to room temperature and stirred for 3 h. The solution was then concentrated to 8 ml, 2–3 ml of *n*-hexane was added, and the solution was cooled to 0 °C whereupon **5** precipitated as a analytically pure white crystalline solid. Yield: 93% (0.23 g). M.p.: 148–150 °C (dec.). *Anal.* Calc. for $C_{54}H_{50}N_2O_8P_4 \cdot 0.5CH_2Cl_2$: C, 64.09; H, 5.03; N, 2.74. Found: C, 63.93; H, 4.97; N, 2.63%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.78–7.72 (m, 40H, Ph), 1.82 (d, 8H, C_2H_4), 1.51 (m, 2H, CH); ^{31}P{^{31}H} NMR (300 MHz, $CDCl_3$): δ 20.8 (2P, d, $^{2}J_{PP} = 36$ Hz), −12.6 (2P, d). MS (FAB): 979 ($M^+ + 1$).

2.6. Preparation of $[Mo_4O_4(\mu^3\text{-}O)_4(\mu\text{-}Ph_2PO_2)_4]$ (6)

To a solution of **1** (0.16 g, 0.34 mmol) and $Mo(CO)_6$ (0.10 g, 0.33 mmol) in CH_2Cl_2 (10 ml) was added a solution of $Me_3NO \cdot 2H_2O$ (0.04 g, 0.36 mmol) in methanol, and the reaction mixture was stirred at room temperature for 18 h, filtered through celite and the solvent was evaporated under reduced pressure. The solid residue obtained was dissolved in a 1:1 diethylether/CH_2Cl_2 mixture. Cooling this solution to 0 °C gave **6** as red crystals. Yield: 85% (0.1 g). M.p.: 168–170 °C. *Anal.* Calc. for $C_{48}H_{40}O_{16}P_4Mo_4 \cdot CH_2Cl_2$: C, 40.16; H, 2.88. Found: C, 40.27; H, 2.79%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.26–7.87 (m, 40H, Ph), 5.30 (s, 2H, CH_2Cl_2); ^{31}P{^{1}H} NMR (300 MHz, $CDCl_3$): δ 44.2 (s).

2.7. Preparation of $[C_5H_5RuCl(PPh_3)]_2(PPh_2O(C_6H_{10})OPPh_2)$ (7)

To a solution of **1** (0.03 g, 0.07 mmol) in CH_2Cl_2 (10 ml) was added, dropwise, a solution of $CpRuCl(PPh_3)_2$ (0.05 g, 0.07 mmol) also in CH_2Cl_2 (10 ml) at room temperature. The mixture was stirred for 8 h before it was concentrated to 5 ml, and 3 ml of petroleum ether was added. Cooling this solution to 0 °C gave **7** as yellow crystals. Yield: 82% (0.08 g). M.p.: 178–182 °C. *Anal.* Calc. for $C_{76}H_{70}O_2P_4Ru_2Cl_2 \cdot CH_2Cl_2$: C, 61.76; H, 4.84. Found: C, 61.51; H, 4.77%. ^1H NMR (300 MHz, $CDCl_3$): δ 7.13–8.15 (m, 20H, Ph), 1.91 (d, 8H, C_2H_4), 1.31 (t, 2H, CH); $^{31}P\{^1H\}$ NMR (300 MHz, $CDCl_3$): δ 138.1 (2P, d, $^2J_{PP} = 58.6$ Hz), 43.3 (2P, d).

2.8. Preparation of $[PdCl_2(Ph_2(O)PO(C_6H_{10})OP(O)Ph_2)]$ (8)

To a solution of $[Pd(NCCH_3)_2Cl_2]$ (0.04 g, 0.23 mmol) (generated in situ by refluxing $PdCl_2$ in CH_3CN for 4 h) in CH_3CN (8 ml) was added, dropwise, a solution of **1** (0.12 g, 0.25 mmol) also in CH_3CN (4 ml), and the reaction mixture was stirred at room temperature for 3 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 yellow crystals. Yield: 90.5% (0.25 g). M.p.: 174–176 °C. *Anal.* Calc. for $C_{30}H_{30}Cl_2O_2P_2Pd$: C, 54.4; H, 4.5. Found: C, 54.6; H, 4.5%. ^1H NMR (300 MHz, $CDCl_3$): δ 7.24–7.58 (m, 20H, Ph), 1.73 (d, 8H, C_2H_4), 1.33 (m, 2H, CH). $^{31}P\{^1H\}$ NMR (300 MHz, $CDCl_3$): δ 79.4 (s).

2.9. Preparation of $[PtCl_2(Ph_2(O)PO(C_6H_{10})OP(O)Ph_2)]$ (9)

To a solution of $[Pt(COD)Cl_2]$ (0.03 g, 0.08 mmol) in CH_2Cl_2 (5 ml), a solution of **1** (0.02 g, 0.08 mmol) also in CH_2Cl_2 (8 ml) was added dropwise and the reaction mixture was stirred at room temperature for 4 h. The solution was concentrated to 5 ml, and 2 ml of petroleum ether was added. Cooling this solution to 0 °C gave **9** as a white crystalline material. Yield: 98% (0.04 g). M.p.: 158–160 °C. *Anal.* Calc. for $C_{30}H_{30}Cl_2O_2P_2Pt$: C, 48.06; H, 4.03. Found: C, 47.92; H, 3.9%. ^1H NMR (300 MHz, $CDCl_3$): δ 7.26–7.64 (m, 20H, Ph), 1.75 (d, 8H, C_2H_4), 1.35 (m, 2H, CH); $^{31}P\{^1H\}$ NMR (300 MHz, $CDCl_3$): δ 76.04 (s), $^1J_{PPt} = 4132$ Hz.

2.10. Structure determination

Colorless crystals of **3** and **4**, crystallized from CH_2Cl_2 at 0 °C, were mounted on Pyrex filaments with epoxy resin. Unit cell dimensions were determined from 25 well-centered reflections. Intensity data were collected with a Nonium MACH3 diffractometer using graphite-monochromated Mo Kα (0.71073 Å) radiation. Periodic monitoring of check reflections showed stability of the intensity data. The structures were solved by direct methods [6] and refined using SHELXS-97 software [7]. The non-hydrogen atoms were geometrically fixed and allowed to refine using a riding model. Details of the data collections and refinements are summarized in Table 1.

Table 1
Crystallographic data for compounds **3** and **4**

Compound	3	4
Formula	$C_{30}H_{30}O_2P_2S_2$	$C_{30}H_{30}O_2P_2Se_2$
Molecular weight	548.60	642.40
Crystal size (mm)	0.4 × 0.25 × 0.20	0.2 × 0.17 × 0.12
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	9.201(7)	12.919(5)
b (Å)	13.141(4)	13.395(1)
c (Å)	12.429(4)	17.661(6)
α (°)	90	90
β (°)	110.51(7)	109.18(8)
γ (°)	90	90
V (Å^3)	1407.5(2)	2886.4(5)
Z	2	4
D_{calc} (g cm^{-3})	1.294	1.478
μ (mm^{-1})	0.329	2.698
T (K)	293(2)	293(2)
Total number of reflections	2124	3076
Number of unique reflections	2124	3076
R_{int}	0.0391	0.0606
R	0.0512	0.1254
R'	0.0984	

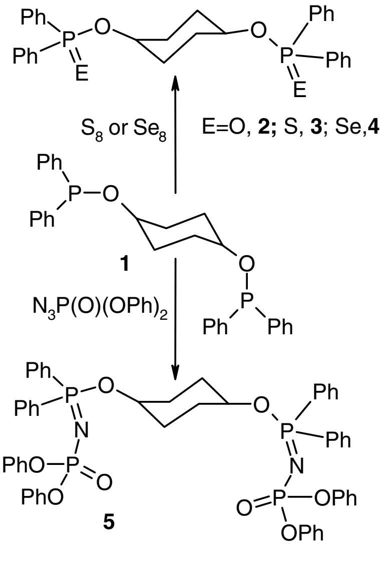
3. Results and discussion

The reaction of cyclohexane-1,4-diol with two equivalents of chlorodiphenylphosphine in the presence of triethylamine in toluene affords bis(phosphinite), $Ph_2PO(C_6H_{10})OPPh_2$ (**1**) in good yield. The $^{31}P\{^1H\}$ NMR spectrum of **1** shows a single resonance at 106.4 ppm indicating the symmetric nature of the molecule. Treatment of **1** with 10% H_2O_2 solution in CH_3CN affords the dioxide derivative **2** in quantitative yield. The diethyl ether or acetonitrile solution of **1** on exposure to air also gives the same dioxide after 2–3 days in quantitative yield. The ^{31}P NMR spectrum of **2** shows a singlet at 20.9 ppm, which is considerably deshielded when compared to the parent ligand **1** with a shift of 85.5 ppm. The reaction of **1** with two equivalents of sulfur or selenium in toluene under refluxing conditions affords the corresponding disulfide (**3**) and diselenide (**4**) in 70–80% yield. The disulfide can also be prepared by reacting the chlorodiphenylphosphinesulfide with cyclohexane-1,4-diol. Attempts to synthesize the monochalcogenides have been unsuccessful. The reaction of **1** with one mole of elemental sulfur or selenium did not give the expected monochalcogenide derivatives, instead dichalcogenides were obtained in low yields and half the original amount of bis(phosphinite) was left unreacted. The physical and analytical data for the compounds are summarized in Section 2 (see Scheme 1).

The ^{31}P NMR spectrum of **3** and **4** show single resonances at 79.4 and 82.4 ppm, respectively. The selenide derivative **4** shows a $^{1}J_{\mathrm{PSe}}$ coupling of 795 Hz, characteristic of tetracoordinated pentavalent phosphine selenides [4a,5e,8]. ^{1}H NMR spectra of all the compounds are consistent with the structural compositions. Further, the structures of $Ph_2P(S)OC_6H_{10}OP(S)PPh_2$ (**3**) and $Ph_2P(Se)OC_6H_{10}OP(Se)PPh_2$ (**4**) were confirmed by single crystal X-ray analysis.

The solid-state structures of disulfide, $Ph_2P(S)O(C_6H_{10})OP(S)PPh_2$ (**3**) and diselenide $Ph_2P(Se)O(C_6H_{10})OP(Se)PPh_2$ (**4**) were determined by single-crystal X-ray diffraction studies. The perspective views of the molecular structures of compounds **3** and **4** are shown in Figs. 1 and 2, respectively. Crystal data and details of the structure determinations are given in Table 1 while selected bond lengths and inter-bond angles appear in Table 2.

The phosphorus centers are in typical tetrahedral environments. The P=S bond length of 1.928(1) Å is shorter than those observed in amine derivatives, $Ph_2P(S)N(Ph)C_2H_4N(Ph)P(S)PPh_2$ (1.951(1) Å) [8b] and $Ph_2P(S)N(C_4H_8)NP(S)PPh_2$ [8c] (1.943(1) Å). Interestingly, the P=Se distance in **4** is 2.089(3) Å which is longer than those observed in aminophosphonite, $PhN\{P(Se)(OC_6H_4OMe\text{-}o)_2\}_2$ (2.058(6) Å) or bisphosphinite, $Ph_2P(Se)\{(\text{–}OC_{10}H_6)(\mu\text{-}CH_2)(C_{10}H_6O\text{–})\}P(Se)Ph_2$ (2.072(1) Å). However, the P=Se distance in **4** is quite comparable with those found in $Ph_2P(Se)NHP(Se)Ph_2$ (2.085(1) Å). The chalcogen



Scheme 1.

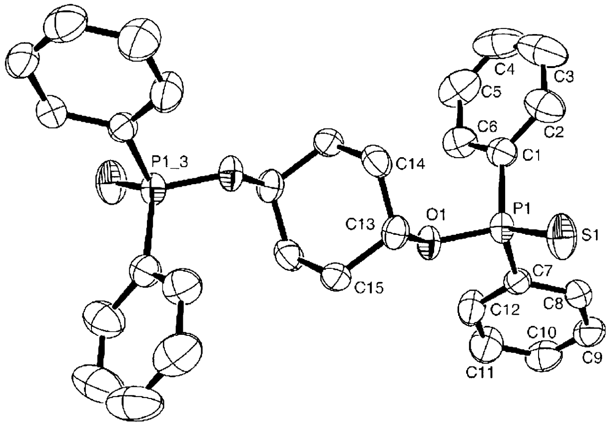


Fig. 1. Perspective view of **3** showing the atom numbering scheme. Hydrogen atoms are omitted for clarity.

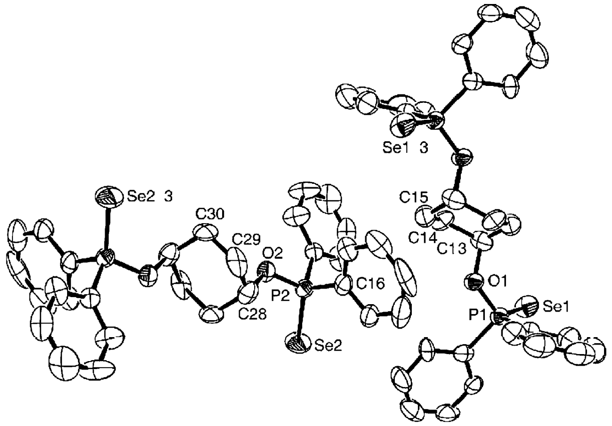
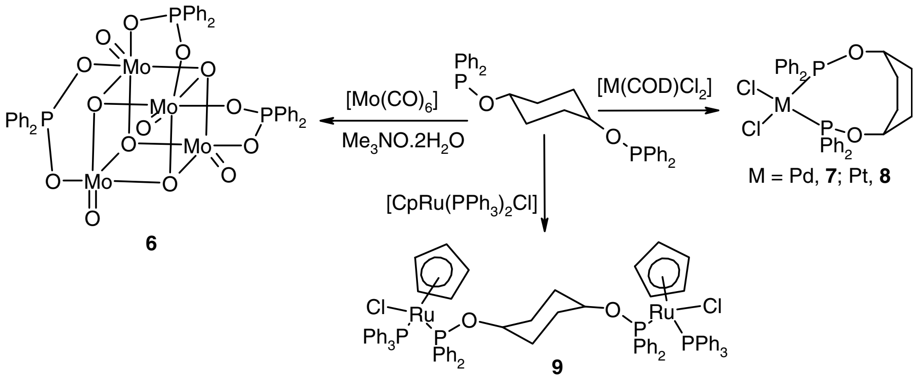


Fig. 2. Perspective view of **4** showing the atom numbering scheme. Hydrogen atoms are omitted for clarity.

Table 2
Selected bond distances (Å) and bond angles (°) in **3** and **4**

Compound	**3**	**4**
Bond lengths (Å)		
P(1)–O(1)	1.590(8)	1.596(3)
P(1)–C(7)	1.809(3)	1.809(1)
P(1)–C(1)	1.809(3)	1.799(1)
C(1)–C(2)	1.387(4)	1.371(5)
C(1)–C(6)	1.388(4)	1.387(15)
C(2)–C(3)	1.382(6)	1.382(18)
O(1)–C(13)	1.478(3)	1.504(1)
P(1)–E(1) (E = S or Se)	1.928(2)	2.089(3)
Bond angles (°)		
O(1)–P(1)–C(7)	100.57(14)	100.57(14)
O(1)–P(1)–C(1)	105.02(13)	105.02(13)
C(7)–P(1)–C(1)	105.13(13)	105.13(13)
O(1)–P(1)–S(1)	116.13(9)	116.13(9)
C(7)–P(1)–S(1)	113.39(13)	113.39(13)
C(1)–P(1)–S(1)	115.02(14)	115.02(14)
C(13)–O(1)–P(1)	122.64(17)	122.64(17)



Scheme 2.

atoms in both **3** and **4** are in an approximately *syn*-disposition. The P–O bond distances in **3** and **4** are 1.591(2) and 1.596(3) Å whereas the average P–C bond distances are 1.806(2) Å.

The reaction of **1** with $Mo(CO)_6$ in the presence of $Me_3NO \cdot 2H_2O$ in THF resulted in the formation of a cubane shaped tetramolybdenum(V)oxo complex (**6**), containing four bridging $Ph_2PO_2^-$ units instead of the expected tetracarbonylmolybdenum(0) complex, $[Mo(CO)_4(Ph_2POC_6H_{10}OPPh_2)]$ as shown in Scheme 2. It is presumed that during the reaction, the P–O bonds of the ligand **1** undergo hydrolytic cleavage to give Ph_2POH moieties which are readily oxidized to give $Ph_2P(O)OH$. Thus, $Ph_2PO_2^-$ generated in situ readily oxidize Mo to its higher oxidation state and lead to the formation of the unexpected complex **6**. A similar reaction of $Mo(CO)_6$ with *N*,*N′*-bis(diphenylphosphino)-2,6-diaminopyridine, $Ph_2PNH(NC_5H_5)NHPPh_2$ led to the isolation of $[Mo(CO)_3\{Ph_2PNH(NC_5H_5)NHPPh_2\text{-}\kappa P,\kappa P,\kappa N\}]$ which on further aerial oxidation in tetramethylbenzene at 180 °C resulted in P–N bond rupture and formation of $[Mo_4\{(\mu^3\text{-}O)_4(\mu\text{-}Ph_2PO_2)_4\}_4]$. The $^{31}P\{^1H\}$ NMR of **6** shows a single resonance at 42 ppm. The structure of **6** was further confirmed by a single X-ray structure determination. The reaction of ligand **1** with $CpRuCl(PPh_3)_2$ in a 1:1 ratio in dichloromethane at room temperature for 48 h afforded diruthenium complex, $[CpRuCl(PPh_3)]_2(\mu\text{-}PPh_2O(C_6H_{10})OPPh_2)$ (**7**) with the ligand **1** acting as a bridging bidentate ligand as shown in Scheme 2. The $^{31}P\{^1H\}$ NMR spectrum of **7** shows two doublets at 44 and 138.1 ppm which are assigned, respectively, to PPh_3 and phosphinite centers. The $^2J_{PP}$ is 58.6 Hz. Treatment of $M(COD)Cl_2$ (M = Pd, Pt) with 1:1 molar proportions of the ligand **1** in dichloromethane afford the chelate complexes **8** and **9** in good yield. The $^{31}P\{^1H\}$ NMR spectra of **8** and **9** exhibit single resonances at 79.0 and 76.0 ppm ($^1J_{Pt\text{–}P} = 4137$ Hz), respectively. The chemical compositions of complexes **6**–**9** are established by element analyses and the proposed structures are consistent with their spectroscopic data.

4. Conclusions

Although, to date, several bisphosphinites are known, the number of bis(phosphinites) having cyclic systems as bridging units are limited. The cyclohexyl group in ligand **1** offers more flexibility for its coordination behavior as demonstrated in the case of Pd(II), Pt(II) and Ru(II) complexes. Interestingly, the reaction of **1** with $Mo(CO)_6$ in the presence of $TMNO \cdot 2H_2O$ gave a cubane-shaped tetramolybdenum(IV) complex containing four bridging $Ph_2PO_2^-$ units, through P–O bond cleavage. This method can be conveniently explored with various other metals to get unexpected but interesting metal oxide clusters which might find application in materials, heterogeneous catalysis and also in heterogenised homogeneous catalysis. The disulfide and diselenide derivatives may also find application in making silver and gold monolayers. Work in this direction is in progress in our laboratory.

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Appendix A. Supplementary data

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 201430 (**3**) and 251517 (**4**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ (fax: +44 1223 336 033; deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2004.12.009.

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