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Synthesis and derivatization, structures and transition metal (Mo(0), Fe(II), Pd(II) and Pt(II)) complexes of phenylaminobis(diphosphonite), $PhN\{P(OC_6H_4OMe\text{-}o)_2\}_2$

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Abstract

The synthesis, derivatization and coordination behavior of a new aminobis(diphosphonite), $PhN\{P(OC_6H_4OMe\text{-}o)_2\}_2$ (**1**) is described. The ligand **1** reacts with H_2O_2, elemental sulfur or selenium to give the corresponding dichalcogenides $PhN\{P(E)(OC_6H_4OMe\text{-}o)_2\}_2$ (E = O, **2**; S, **3**; Se, **4**) in good yield. Reactions of **1** with $Mo(CO)_6$, $Pd(NCCH_3)_2Cl_2$ and $Pt(COD)Cl_2$ resulted in the formation of the chelate complexes, $Mo(CO)_4[PhN\{P(OC_6H_4OMe\text{-}o)_2\}_2]$ (**5**) and $MCl_2[PhN\{P(OC_6H_4OMe\text{-}o)_2\}_2]$ (M = Pd,**7**; M = Pt, **8**) whereas in the reaction of **1** with $[CpFe(CO)_2]_2$, one of the P–N bonds cleaves due to the metal assisted hydrolysis to give a mononuclear complex, $[CpFe(CO)\{P(O)(OC_6H_4OMe\text{-}o)_2\}\{PhN(H)(P(OC_6H_4OMe\text{-}o)_2)\}]$ (**6**). The molecular structures of **1**, **4**, **5** and **6** are determined by X-ray studies.

Keywords: Aminobis(diphosphonite); Dichalcogenides; Metal complexes; P–N bond cleavage; Crystal structures

1. Introduction

Recently we have reported the insertion of carbon fragments into phosphorus–nitrogen bonds and also the cleavage of phosphorus–nitrogen bonds in aminophosphines and aminobis(phosphines) [1,2]. The reactions of aminophosphines and aminobis(phosphines) with aldehydes either leads to the insertion of carbon fragments into the phosphorus–nitrogen bonds or results in the formation of α-hydroxy phosphates through phosphorus–nitrogen bond cleavage. Although, phosphorus–nitrogen bonds are moderately stable toward moisture, lithium and Grignard reagents, during the complexation reactions with transition metals, the P–N bonds are prone to the metal assisted cleavage to give unusual products with or without the aid of trace amounts of moisture or acid impurities [3,4]. Aminophosphines containing aryloxides are moderately stable towards hydrolysis. Further, the aminophosphines with pendant hemilabile groups would be more interesting as they can provide additional weak donor sites toward complex formation. Appropriate reagents can cleave these metal–ligand bonds if the metal undergoes oxidative addition, an important step in a variety of metal mediated organic transformations. As a part of our interest [5–9] and that of others [10–16] in designing aminophosphines and phosphorus based ligands for transition metal chemistry and catalytic applications, herein we report the synthesis, reactivity and Mo(0), Fe(II) and Pd(II) complexes of a new aminobis(diphosphonite), $PhN\{P(OC_6H_4OMe\text{-}o)_2\}_2$. The molecular structures of $PhN\{P(OC_6H_4OMe\text{-}o)_2\}_2$ (**1**), PhN

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{P(Se)-(OC_6H_4OMe-*o*)$_2$}$_2$ (**4**), Mo(CO)$_4$[PhN{P(OC_6H_4-OMe-*o*)$_2$}$_2$] (**5**) and the phosphorus–nitrogen bond cleavage product, [CpFe(CO){P(O)(OC_6H_4OMe-*o*)$_2$}-{PhN(H)-(P(OC_6H_4OMe-*o*)$_2$)}] (**6**) are also described.

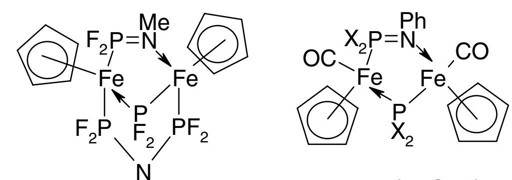
2. Results and discussion

The reaction of phenylaminobis(dichlorophosphine), PhN(PCl_2)$_2$ with guaiacol in a 1:4 ratio in the presence of triethylamine affords the aminobis(diphosphonite), PhN{P(OC_6H_4OMe-*o*)$_2$}$_2$ (**1**). Treatment of **1** with aqueous H_2O_2 (30% w/v) gives the dioxide derivative, PhN{P(O)(OC_6H_4OMe-*o*)$_2$}$_2$ (**2**) in quantitative yield. Aminobis(diphosphonite) **1** reacts smoothly with two equivalents of elemental sulfur or selenium powder in toluene under reflux conditions to give the corresponding disulfide, PhN{P(S)(OC_6H_4OMe-*o*)$_2$}$_2$ (**3**) or diselenide, PhN{P(Se)(OC_6H_4OMe-*o*)$_2$}$_2$ (**4**) in good yield.

The elucidation of the structures of ligand **1** and the chalcogen derivatives **2**, **3** and **4** are based on NMR (^{1}H and ^{31}P{^{1}H}) spectroscopic data and elemental analyses. The ^{31}P{^{1}H} NMRspectra of **1**–**4** exhibit single resonances at 131.9, −12.3, 58.3, 64.7 and −12.3 ppm, respectively. The diselenide derivative **4** shows a very large $^1J_{P\text{–}Se}$ coupling of 1004 Hz. Further, the molecular structures of **1** and **4** are confirmed by single crystal X-ray structure determinations.

The reaction of **1** with Mo(CO)$_6$ in presence of two equivalents of $Me_3NO \cdot 2H_2O$ in dichloromethane at room temperature affords the chelate complex, *cis*-[Mo(CO)$_4$-{PhN(P(OC_6H_4OMe-*o*)$_2$)$_2$-κP,κP}] (**5**) in good yield. The IR spectrum of **5** shows four bands in the carbonyl region in the range 1897–2035 cm^{-1} as expected for an {M(CO)$_4$} moiety of C_{2v} symmetry [17]. The ^{31}P NMR spectrum of **5** shows a single resonance at 147.8 ppm with a coordination shift of 15.9 ppm. The structure of **5** was further confirmed by a single crystal X-ray structure determination.

The reaction of ligand **1** with [CpFe(CO)$_2$]$_2$ in a 1:1 ratio in toluene under reflux conditions for 24 h afforded a mononuclear complex [CpFe(CO){P(O)(OC_6H_4O-Me*o*)$_2$}{PhN(H)(P(OC_6H_4OMe-*o*)$_2$)}] (**6**). During the complexation, one of the P–N bonds of the ligand undergoes moisture assisted hydrolysis to give two different fragments, PhN(H)P(OC_6H_4OMe-*o*)$_2$ and P(O)-(OC_6H_4OMe-*o*)$_2$. The aminophosphine acts as a σ-donor ligand whereas the P(O)(OC_6H_4OMe-*o*)$_2$ fragment forms a covalent bond with the metal center. Similar reactions of [CpFe(CO)$_2$]$_2$ with aminophosphines of the type PhN(PX_2)$_2$ (X = F [3], OPh [4]) led to the isolation of dinuclear complexes containing PX_2 and RN = PX_2 fragments bridging the two metal centers with or without metal–metal bonds as shown in structures **I** and **II**. The complex **6** exhibits a sharp band in its IR spectrum ($\nu_{C{=}O}$) at 1973 cm^{-1} indicating the presence of a terminal carbonyl group. The ^{1}H NMR spectrum exhibits phenyl, cyclopentadienyl and methoxy resonances at δ 6.49, 4.75 and 3.68 ppm, respectively. The ^{31}P NMR spectrum of **6** shows an AX spin system due to the presence of two types of phosphorus centers. The low field resonance at 171 ppm is assigned to the PhN(H)P(OC_6H_4OMe-*o*)$_2$ unit whereas the resonance due to P(O)(OC_6H_4OMe-*o*)$_2$ appears at 129 ppm. The $^2J_{P\text{–}Fe\text{–}P}$ coupling is 120.8 Hz. In the mass spectrum, the most intense fragment ion appears at *m*/*e* 812 [M$^+$ + 1] which is the expected molecular ion. Further, the structure of **6** was confirmed by a single crystal X-ray diffraction study.



I **II** (X=OPh)

Treatment of M(COD)Cl_2 (M = Pd, Pt) with 1:1 molar proportions of the ligand **1** in dichloromethane afford the chelate complexes **7** and **8** in good yield. The ^{31}P NMR spectra of **7** and **8** exhibit single resonances at 76.3 and 48.5 ppm ($^1J_{Pt\text{–}P}$ = 2948 Hz), respectively.

2.1. The crystal and molecular structures of 1, 4, 5 and 6

Perspective views of the molecular structures of compounds **1**, **4**, **5** and **6** with the atom numbering schemes are shown in Figs. 1–4, respectively. Crystal data and details of the structure determinations are given in Table 1 while selected bond lengths and interbond angles appear in Table 2.

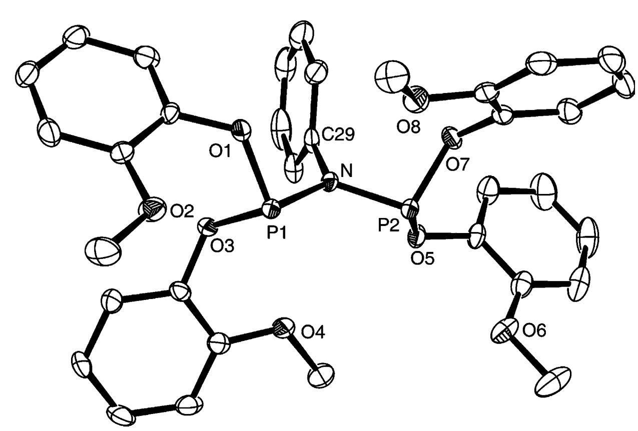


Fig. 1. Perspective view of compound PhN{P(OC_6H_4OMe-*o*)$_2$}$_2$ (**1**) showing the atom numbering scheme. Thermal ellipsoids are drawn at the 50% probability level and hydrogen atoms are omitted for clarity.

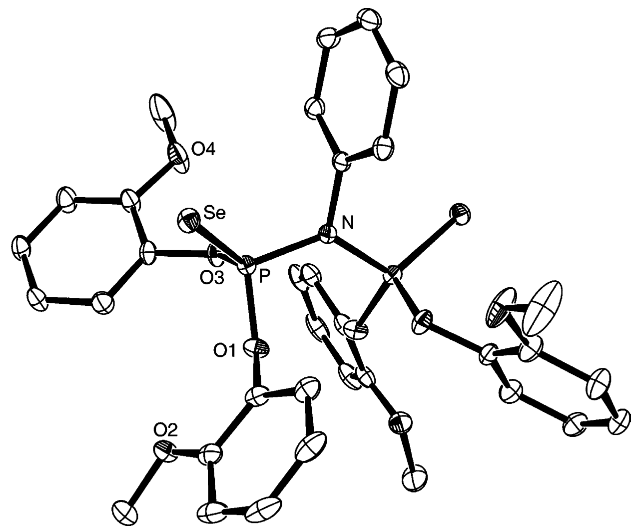


Fig. 2. Perspective view of compound PhN{P(Se)(OC$_6$H$_4$OMe-*o*)$_2$}$_2$ (**4**) showing the atom numbering scheme. Thermal ellipsoids are drawn at the 50% probability level and hydrogen atoms are omitted for clarity.

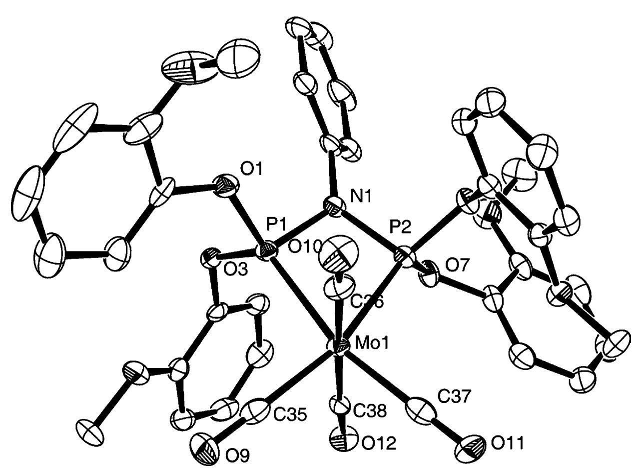


Fig. 3. Perspective view of compound [Mo(CO)$_4${PhN(P(OC$_6$H$_4$OMe-*o*)$_2$)$_2$-κP,κP}] (**5**) showing the atom numbering scheme. Thermal ellipsoids are drawn at the 50% probability level and hydrogen atoms are omitted for clarity.

The unit cell of **5** contains two independent molecules, one of which has crystallographically imposed C$_2$ symmetry, but the corresponding bond lengths and bond angles in the two molecules are not significantly different. The mean P–N bond distances in both **1** and **4** are comparable to those in molybdenum complex **5**. The P–N–P angle in the diselenide derivative **4** is larger [127.5(1)°] when compared to the same in the free ligand **1** [116.1(1)°] whereas in the molybdenum complex the P–N–P angle shrinks to 102.4(2)° due to the formation of a strained four-membered chelate ring. However, the sum of the angles around nitrogen in all these compounds is 359.9° which clearly indicates that the geometry around nitrogen is strictly planar; a characteristic feature of

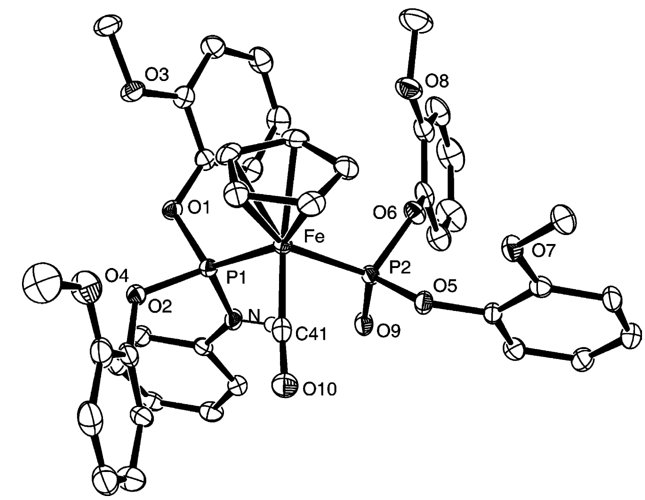


Fig. 4. Perspective view of [CpFe(CO){P(O)(OC$_6$H$_4$OMe-*o*)$_2$-κP}{PhN(H)-(P(OC$_6$H$_4$OMe-*o*)$_2$)-κP}] (**6**) showing the atom numbering scheme. Thermal ellipsoids are drawn at the 50% probability level and hydrogen atoms are omitted for clarity.

aminobis(phosphines) [5], their dichalcogenides [18,19], diimines [20,21] or metal complexes [22]. The non bonded P···P separation in complex **5** [2.631(2) Å] is shorter than that in free ligand **1** [2.868(2) Å] due to the chelation. The diselenide derivative **4**, which has crystallographically imposed C$_2$ symmetry, shows a much larger P···P separation of 3.027(2) Å. The P=Se distance of 2.058(6) Å in **4** is the shortest ever reported for either monophosphineselenides or bis(phosphineselenides). Interestingly, the compound **4** also shows the largest $^1J_{P-Se}$ coupling reported to date (1004 Hz). The shorter P=Se distance coupled with larger $^1J_{P-Se}$ value is an indication of a higher s-character [23] of the lone pair on phosphorus in free ligand **1** which is eventually donated to selenium. Our predictions are of course not absolute and further efforts to definitely unravel the uncertainties would be warranted. The molybdenum center in **5** is octahedral and the atoms of the MP$_2$N ring are essentially planar.

The formation of the iron complex **6** is an example of a aminobis(phosphine) undergoing moisture-assisted hydrolysis during complexation to give the protonated aminophosphine and phosphineoxide fragments which bind the metal center through a coordinate and a covalent bond, respectively. Analogous reactions of RN(PX$_2$)$_2$ (R = Me, X = F; R = Ph, X = OPh) with [CpFe(CO)$_2$]$_2$ resulted in the formation of binuclear complexes bridged by P–N cleavage fragments without the oxidation of phosphorus centers to give [CpFe{μ–PF$_2$}{μ-F$_2$PN(Me)PF$_2$}{μ-MeN=PF$_2$}FeCp] (**I**), [Cp-(OC)Fe{μ–P(OPh$_2$)}{μ-(PhO)$_2$P=N(Ph)-κP,κN}FeCp] (**II**), respectively. The P(1)–N distance [1.643(2) Å] in **6** is slightly shorter than that in compounds **1**, **4** and **5** which clearly indicates an enhancement of π-bonding in the P–N unit as a result of there being only one

Table 1
Crystallographic data for compounds **1**, **4**, **5** and **6**

	1	**4**	**5**	**6**
Formula	$C_{34}H_{33}NO_8P_2$	$C_{34}H_{33}NO_8P_2Se_2$	$C_{38}H_{33}MoNO_{12}P_2$	$C_{40}H_{39}FeNO_{10}P_2$
M	645.55	803.47	853.53	811.51
Crystal size (mm)	0.19 × 0.17 × 0.11	0.14 × 0.16 × 0.23	0.07 × 0.09 × 0.14	0.16 × 0.14 × 0.23
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_12_12_1$	*C*2/c	*C*2/c	$P\bar{1}$
a (Å)	10.2756(8)	20.264(3)	49.352 (2)	8.564 (2)
b (Å)	10.8282(3)	9.715(1)	11.865(2)	10.284(2)
c (Å)	29.013(5)	19.131(3)	19.647(5)	22.518(5)
α (°)	90	90	90	79.629(3)
β (°)	90	115.431(2)	103.272(2)	80.091(3)
γ (°)	90	90	90	71.344(3)
V (Å^3)	3228.1(4)	3401.2(9)	11197(3)	1834.3(7)
Z	4	4	12	2
D_c (g cm^{-3})	1.328	1.569	1.519	1.469
μ (mm^{-1})	0.187	2.32	0.502	0.56
T (K)	100(2)	100(2)	100(2)	100(2)
Total no. reflections	7972	14689	34065	15829
No. unique reflections	5691	4103	8055	8064
R_{int}	0.0475	0.0208	0.0719	0.0231
R	0.0556	0.0263	0.0459	0.0459
R'	0.065	0.0696	0.1107	0.1215
Goodness of fit	1.095	1.057	1.011	1.037

phosphorus center to interact with the nitrogen lone pair. The iron center is in a tetrahedral environment with a typical piano stool arrangement. The Fe–P(1) and Fe–P(2) distances are 2.158(1) and 2.191(1) Å while the Fe–C (carbonyl) and P=O distances are 2.095(3) and 1.495(2) Å, respectively. The mean Fe–C distance (cyclopentadienyl carbons) is 1.759(3) Å.

3. Conclusion

The aminobis(diphosphinite) (**1**) readily reacts with chalcogens and transition metal precursors to give appropriate derivatives in good yield. The diselenide derivative **4**, has the largest phosphorus–selenium coupling ($^1J_{P–Se}$ = 1004 Hz) and the shortest P–Se bond distance of 2.058(6) Å reported to date. This is an indication of the higher s-character of the lone pair on phosphorus in free ligand **1**. Thus, the ligand **1** can be used as a very effective π-acceptor ligand to stabilize low-valent metals. The reaction of **1** with $[CpFe(CO)_2]_2$ leads to cleavage of one of the P–N bonds to give a mononuclear Fe(II) complex **6**. Surprisingly all reports on metal-mediated P–N bond cleavage of aminobis(phosphines) have been reported with the same iron derivative, $[CpFe(CO)_2]_2$. We recently reported the moisture-assisted P–N bond cleavage of aminophosphine, $Ph_2N(H)PPh_2$ with a Pd(II) derivative to give an hydrogen bonded dinuclear complex, $Pd(\mu\text{-}Cl)_2(Ph_2POHOPPh_2)_2$ [8]. Further research on the behavior of P–N bonds under various reaction conditions is in progress in our laboratory.

4. 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. Phenylaminobis(dichlorophosphine) was prepared according to the literature [24]. The ^{1}H 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 ^{1}H 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.

4.1. Preparation of $PhN\{P(OC_6H_4OMe\text{-}o)_2\}_2$ (1)

A mixture of guaiacol, HOC_6H_4OMe-*o* (4.36 g, 35.15 mmol) and triethylamine (3.55 g, 35.15 mmol) in diethylether (40 ml) was added dropwise to a solution of *N*,*N*′-bis(dichlorophosphino)aniline (2.596 g, 8.78 mmol) also in diethylether (140 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 triethylamine hydrochloride was removed by filtration. The solvent was removed under reduced pressure to give a white residue, which was crystallized from

Table 2
Selected bond distances and bond angles for **1**, **4**, **5** and **6**

Bond lengths (Å)		Bond angles (°)	
Compound ***1***			
P1–N	1.696(2)	P1–N–P2	116.07(12)
P2–N	1.865(2)	P1–N–C29	122.46(16)
P1–O1	1.651(2)	P2–N–C29	121.47(16)
P1–O3	1.651(2)	O1–P1–N	97.20(10)
P2–O5	1.657(2)	O3–P1–N	100.68(10)
P2–O7	1.882(2)	O5–P2–N	96.19(10)
N–C29	1.445(3)	O7–P2–N	100.85(10)
Compound ***4***			
P–N	1.687(1)	P–N–C15	116.25(6)
Se–P	2.058(6)	P–N–P_a	127.51(12)
N–C15	1.460(3)	P_a–N–C15	116.25(6)
P–O1	1.589(3)	Se–P–N	116.18(6)
P–O3	1.588(1)	O1–P–N	104.41(8)
		O3–P–N	99.31(5)
Compound ***5***[a]			
Mo1–P1	2.434(1)	P1–N1–P2	102.4(2)
Mo1–P2	2.460(1)	P2–N1–C29	130.0(3)
P1–N1	1.686(4)	P1–N1–C29	127.5(3)
P1–O3	1.626(3)	P1–Mo1–P2	65.02(4)
P1–O1	1.605(3)	P1–Mo1–C35	98.51(14)
P2–N1	1.688(4)	P1–Mo1–C36	88.31(15)
P2–O7	1.610(3)	P1–Mo1–C37	165.83(15)
P2–O5	1.618(3)	P1–Mo1–C38	95.32(13)
N1–C29	1.454(6)	P2–Mo1–C35	162.39(13)
Mean Mo–C		P2–Mo1–C36	95.34(15)
Mean C–O(carbonyl)		P2–Mo1–C37	101.46(15)
		P2–Mo1–C38	86.84(13)
Compound ***6***			
Fe–P1	2.158(1)	P1–N–C16	132.18(16)
Fe–P2	2.191(1)	P1–N–H1N	111.45
P1–N	1.643(2)	C16–N–H1N	115.72
P1–O1	1.628(2)	Fe–P1–N	114.00(7)
P1–O2	1.625(2)	Fe–P2–O9	121.62(7)
P2–O5	1.638(2)	P1–Fe–P2	98.46(3)
P2–O6	1.645(2)	P1–Fe–C41	92.15(8)
P2–O9	1.495(2)	P2–Fe–C41	86.46(9)
N–C16	1.411(3)		
Fe–C41	1.759(3)		
O10–C41	1.136(3)		
Mean Fe–C(Cp)	2.095(3)		

[a] Values are given for molecule I only; these do not vary significantly for molecule II.

dichloromethane/*n*-hexane. Yield: 84% (4.78 g); m.p. 100–102 °C. Anal. Calc. for $C_{34}H_{33}NO_8P_2$: C, 63.25; H, 5.15; N, 2.17. Found: C, 63.40; H, 5.22; N, 2.14%. ^{1}H NMR (300MHz, $CDCl_3$): δ 6.74–7.59 (m, 21H, Ph), δ 3.62 (s, 12H, OMe); $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 131.9 (s).

4.2. Preparation of PhN{P(O)(OC₆H₄OMe-o)₂}₂ (2)

Aqueous 30% H_2O_2 (0.3 g, 7.92 mmol) in acetone (5 ml) was added to aminobis(diphosphonite) **1** (0.6 g, 0.9 mmol) also in acetone (10 ml) and the mixture was stirred for 4 h. The solvent was removed under reduced pressure to give a white solid, which was crystallized from a 1:1 mixture of dichloromethane/diethyl ether. Yield: 68% (0.22 g); m.p. 170–172 °C. Anal. Calc. for $C_{34}H_{33}NO_{10}P_2$: C, 60.26; H, 4.90; N, 2.07. Found: C, 59.94; H, 4.84; N, 1.94%. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ −12.6 (s).

4.3. Preparation of PhN(P(S)(OC₆H₄OMe-o)₂)₂ (3)

A mixture of aminobis(diphosphonite) **1** (0.6 g, 0.9 mmol) and sulfur (0.06 g, 0.9 mmol) in toluene (30 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 (1.5 ml), layered with 1 ml of *n*-hexane and kept at room temperature to give colorless crystals of **3**. Yield: 86% (0.57 g); m.p.: 240 °C (decomp.). Anal. Calc. for $C_{34}H_{33}NO_8P_2S_2$: C, 57.53; H, 4.69; N, 1.97; S, 9.04. Found: C, 57.22; H, 4.63; N, 1.83; S, 8.78%. ^{1}H NMR (300MHz, $CDCl_3$): δ 6.78–7.72 (m, 21H, Ph), δ 3.64 (s, 12H, OMe); $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 58.3 (s).

4.4. Preparation of PhN{P(Se)(OC₆H₄OMe-o)₂}₂ (4)

A mixture of compound **1** (0.6 g, 0.9 mmol) and selenium powder (0.49 g, 1.8 mmol) in toluene (30 ml) was heated under reflux for 10 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 *n*-hexane and kept at room temperature to afford colorless crystals of **4**. Yield: 72% (0.57 g); m.p.: 254–256 °C. Anal. Calc. for $C_{34}H_{33}NO_8P_2Se_2$: C, 50.82; H, 4.14; N, 1.74. Found: C, 50.56; H, 4.13; N, 1.79%. ^{1}H NMR (300MHz, $CDCl_3$): δ 6.85–7.45 (m, 21H, Ph), δ 3.67 (s, 12H, OMe); $^{31}P^1H$ NMR (121 MHz, $CDCl_3$): δ 64.7 (s), $^1J_{P-Se}$ = 1004 Hz

4.5. Preparation of [Mo(CO)₄{PhN(P(OC₆H₄OMe-o)₂)₂}] (5)

To a mixture of **1** (0.23 g, 0.35 mmol) and $Mo(CO)_6$ (0.1 g; 0.37 mmol) in dichloromethane (10 ml) was added $Me_3NO \cdot 2H_2O$ (0.087 g, 0.78 mmol) in methanol (10 ml) and the mixture was stirred at room temperature for 18 h. The solution was concentrated to 3 ml and 1 ml of *n*-hexane was added. Cooling this solution to 0 °C gave **5** as yellow crystals. Yield: 72% (0.22 g); m.p.: 168–170 °C. Anal. Calc. for $C_{38}H_{33}NO_{12}P_2Mo$: C, 53.7; H, 3.8; N, 1.64. Found: C, 52.12; H, 3.7; N, 2.1%. IR($\nu_{C\equiv O}$): 2035, 1931, 1897 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.82–8.21 (m, 21H, Ph), δ 3.79 (s, 12H, OMe); $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 147.8 (s).

4.6. Preparation of [CpFe(CO){P(O)(OC$_6$H$_4$OMe-o)$_2$}{PhN(H)P(OC$_6$H$_4$OMe-o)$_2$}] (6)

A mixture of compound **1** (0.185 g, 0.28 mmol) and $[CpFe(CO)_2]_2$ (0.1 g, 0.28 mmol) in toluene (10 ml) was heated under reflux for 24 h to give a dark brown solution. The solvent was removed under reduced pressure to give a dark brown residue. The residue was dissolved in CH_2Cl_2 (1.5 ml), layered with 1 ml of *n*-hexane and kept at room temperature to give crystals of **6**. Yield: 61% (0.16 g); m.p.: 144–146 °C. Anal. Calc. for $C_{34}H_{33}NO_8P_2S_2$ C, 58.32; H, 2.92; N, 0.68. Found: C, 58.56; H, 4.59; N, 1.48%. ^{1}H NMR (300MHz, $CDCl_3$): δ 6.49–7.58 (m, 21H, Ph), δ 4.75 (s, 5H, Cp), 3.68 (s, 12H, OMe); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ 171(2P, d) and 129(2P, d, $^2J_{PP}$ 120.8 Hz). MS (FAB): 812 (M^+ + 1).

4.7. Preparation of [PdCl$_2${PhN(P(OC$_6$H$_4$OMe-o)$_2$)$_2$}] (7)

A solution of **1** (0.14 g, 0.22 mmol) in CH_3CN (4 ml) was added dropwise to a solution of in situ generated $Pd(CH_3CN)_2Cl_2$ (0.04 g, 0.22 mmol) also in CH_3CN (8 ml) and the reaction mixture was stirred at room temperature for 3 h. The solution was concentrated to 3 ml and 1 ml of *n*-hexane was added. Cooling this solution to 0 °C gave **7** as yellow crystals. Yield: 81% (0.15 g); m.p.: 120–122 °C. Anal. Calc. for $C_{34}H_{33}Cl_2NO_8P_2Pd$: C, 49.1; H, 3.9; N, 1.2. Found: C, 48.81; H, 4.33; N, 1.64%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.75–7.54 (m, 21H, Ph), δ 3.66 (s, 12H, OMe); ^{31}P{^{1}H}046 NMR (121 MHz, $CDCl_3$): δ 76.3 (s).

4.8. [PtCl$_2${PhN(P(OC$_6$H$_4$OMe-o)$_2$)$_2$}] (8)

A solution of **1** (0.052 g, 0.8018 mmol) in CH_3CN (5 mL) was added dropwise to a solution of [Pt(COD)Cl$_2$] (0.03 g, 0.8018 mmol) also in CH_3CN (4 mL) and the reaction mixture was stirred at room temperature for 3–4 h. The solution was then concentrated to 2 mL and 1 mL of petroleum ether (b.p. 60–80 °C) was added. Cooling this solution to 0 °C gave **8** as white crystalline material. Yield: 95% (0.07 g); m.p.: 158–160 °C. Anal. Calc. for $C_{34}H_{33}Cl_2NO_8P_2Pt$: C, 44.79; H, 3.64; N, 1.53. Found: C, 44.98; H, 3.38; N, 1.52%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.77–7.60 (m, 21H, Ph), δ 3.67 (s, 12H, OMe); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ 48.46 (s), $^1J_{P-Pt}$ = 2948 Hz.

5. X-ray crystallography

Crystals of compounds **1**, **4**, **5** and **6** 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 φ = 0, 120° and 240° and graphite-monochromated Mo Kα radiation (λ = 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 ⟨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 except for that attached to nitrogen in **6** which was placed in the location 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. In **5**, the crystallographic C_2 symmetry imposed on the molecule built on Mo(2) results in disorder of the methoxyphenyl group built on C(46). 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.

6. Supplementary material

Full details of data collection and structure refinement have been deposited with the Cambridge Crystallography Data Centre, CCDC nos. 244091, 244092, 244093 and 244094 for compounds **1**, **4**, **5** and **6**, respectively. 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).

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