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Synthesis and derivatization, structures and transition metal chemistry of a new large bite bis(phosphinite) derived from bis(2-hydroxy-1-naphthyl)methane

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Bis(2-hydroxy-1-naphthyl)methane reacts with chlorodiphenylphosphine to afford the bis(phosphinite), $Ph_2P\{(-OC_{10}H_6)(\mu-CH_2)(C_{10}H_6O-)\}PPh_2$ (**1**) in good yield. The bis(phosphinite) **1** reacts with elemental sulfur or selenium to give the corresponding disulfide or diselenide; the structure of the selenium derivative, $Ph_2P(Se)\{(-OC_{10}H_6)(\mu-CH_2)(C_{10}H_6O-)\}P(Se)Ph_2$ (**3**) is confirmed by X-ray crystal structure analysis. Treatment of the ligand **1** with platinum metal derivatives results in the formation of ten-membered chelate complexes with the ligand showing an η^2-mode of coordination. The elucidation of the structures of the products is based on NMR (^1H and ^{31}P) spectroscopic data. Molecular structures of $[CpRuCl\{\eta^2-Ph_2P\{(-OC_{10}H_6)(\mu-CH_2)(C_{10}H_6O-)\}PPh_2-\kappa P,\kappa P\}]$ (**4**) and $[PtCl_2\{\eta^2-Ph_2P\{(-OC_{10}H_6)(\mu-CH_2)(C_{10}H_6O-)\}PPh_2-\kappa P,\kappa P\}]$ (**7**) are determined by single crystal X-ray studies.

Introduction

Many homogeneous catalysts used in industrial applications include phosphine ligands with bulky substituents. In these systems both steric and electronic effects are important with the bulk of the ligands imposing regioselectivity during the catalytic process.[1,2] Transition metal complexes containing bulky mono- and bis(phosphines) as catalysts in organic transformations are well documented.[3–8] Surprisingly, the utilization of analogous bis(phosphinite) ligands in such reactions is sparse although some of them are proved to be efficient catalysts.[5,9–13] As a part of our interest[14–19] in designing new phosphorus-based ligand systems, we describe in this paper the synthesis of a new bis(phosphinite), $Ph_2P\{(-OC_{10}H_6)(\mu-CH_2)(C_{10}H_6O-)\}PPh_2$ (**1**). Compound **1** reacts with chalcogens to give dichalcogenides; the molecular structure of the diselenide is confirmed by an X-ray crystal study. Some transition metal chemistry of **1** is also described with X-ray crystal structures of ruthenium and platinum complexes.

Results and discussion

The reaction of bis(2-hydroxy-1-naphthyl)methane with chlorodiphenylphosphine in the ratio 1 : 2 in THF in the presence of a catalytic amount of 4-dimethylaminopyridine affords the expected bis(naphthol) derivative, $Ph_2P\{(-OC_{10}H_6)(\mu-CH_2)(C_{10}H_6O-)\}PPh_2$ (**1**) in good yield. Stoichiometric reaction of the new bis(phosphinite) (**1**) with two molar equivalents of elemental sulfur or selenium powder in toluene under reflux conditions gives the corresponding disulfide, $Ph_2P(S)\{(-OC_{10}H_6)(\mu-CH_2)(C_{10}H_6O-)\}P(S)Ph_2$ (**2**) or diselenide, $Ph_2P(Se)\{(-OC_{10}H_6)(\mu-CH_2)(C_{10}H_6O-)\}P(Se)Ph_2$ (**3**) as shown in Scheme 1. The disulfide derivative **2** was formed very rapidly within 15 minutes at 60 °C whereas the formation of the diselenide derivative was slow and took nearly 8 h for the completion of the reaction. The progress of the reaction can be readily followed visually by the disappearance of sulfur in the case of **2** and the black colour of selenium in the case of **3**.

The elucidation of the structures of ligand **1** and the chalcogen derivatives **2** and **3** are based on NMR (^1H and $^{31}P\{^1H\}$) spectroscopic data and elemental analyses. The $^{31}P\{^1H\}$ NMR spectra of compounds **1**–**3** exhibit single resonances at 112.2, 82.6 and 86.0 ppm, respectively. The diselenide derivative **3** shows $^1J_{PSe}$ coupling of 827 Hz. The molecular structure of **3** is also confirmed by single crystal X-ray analysis.

A perspective view of the molecular structure of the compound **3** with the atomic numbering scheme is shown in the Fig. 1. Crystal data and the details of the structure determination are given in Table 4. Selected parameters are listed in Table 1.

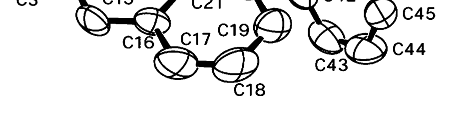

Fig. 1 Perspective view of compound **3** showing the atom numbering scheme. Thermal ellipsoids are drawn at the 50% probability level and hydrogen atoms are omitted for clarity.

Compound **3** crystallizes in the monoclinic crystal system in the extended conformation. The P=Se bond lengths (P(1)–Se(1), 2.0722(9) Å; P(2)–Se(2), 2.0699(9) Å) compare well with those found in $Ph_2P(Se)NHP(Se)Ph_2$ (P(1)–Se(1), 2.085(1); P(2)–Se(2), 2.101(1) Å).[20] The two selenium atoms are in an approximately *syn* disposition with the Se(1)–P(1) and Se(2)–P(2) vectors making an angle of 26.6° when projected down P(1) ··· P(2).

Here the P(1) and P(2) centers are distinctly pyramidal with sum of the angles 344.70(10) and 346.60(10)°, respectively. The average P–O distance of 1.618(2) Å is closer to the values (*ca.* 1.62 Å) typically found for P–O bond distances in phosphites.[1]

The complexation behavior of the phosphinoxy derivative **1** has been investigated by its reactions with platinum metal

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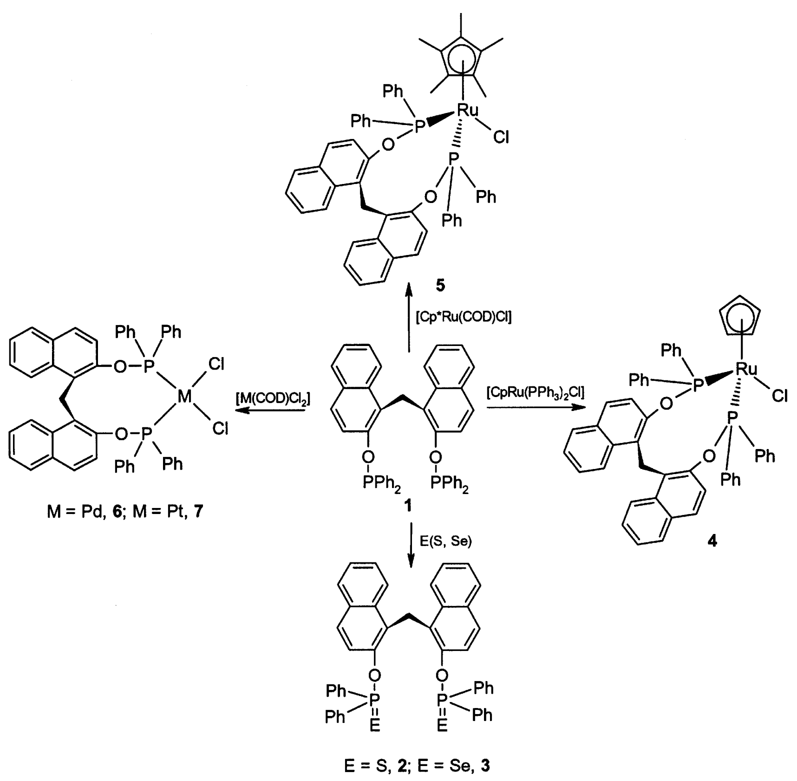

Scheme 1

Table 1 Selected bond distances (Å) and bond angles (°) for **3**

Se(1)–P(1)	2.072(9)	P(2)–C(40)	1.799(3)
Se(2)–P(2)	2.070(9)	O(1)–C(13)	1.393(4)
P(1)–O(1)	1.624(2)	O(2)–C(33)	1.400(4)
P(2)–O(2)	1.612(2)	C(13)–C(22)	1.377(4)
P(1)–C(1)	1.800(3)	C(22)–C(23)	1.517(4)
P(1)–C(7)	1.804(3)	C(23)–C(24)	1.521(3)
P(2)–C(34)	1.811(3)	C(24)–C(33)	1.371(4)
Se(1)–P(1)–O(1)	117.25(9)	P(1)–O(1)–C(13)	129.6(2)
Se(1)–P(1)–C(1)	115.58(11)	P(2)–O(2)–C(33)	129.2(2)
Se(1)–P(1)–C(7)	114.97(11)	O(1)–C(13)–C(22)	116.3(2)
O(1)–P(1)–C(1)	102.21(13)	C(13)–C(22)–C(21)	117.8(2)
O(1)–P(1)–C(7)	98.63(13)	C(13)–C(22)–C(23)	120.2(2)
C(1)–P(1)–C(7)	106.04(15)	C(21)–C(22)–C(23)	121.9(2)
Se(2)–P(2)–O(2)	116.70(9)	O(2)–C(33)–C(24)	116.3(3)
Se(2)–P(2)–C(34)	114.25(11)	C(22)–C(23)–C(24)	119.1(2)
Se(2)–P(2)–C(40)	115.65(11)	C(23)–C(24)–C(25)	122.2(2)
O(2)–P(2)–C(34)	104.23(13)	C(23)–C(24)–C(33)	120.3(3)
O(2)–P(2)–C(40)	97.50(13)	C(25)–C(24)–C(33)	117.2(2)
C(34)–P(2)–C(40)	106.59(15)		

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

Ru–Cl	2.424(3)	P(1)–O(1)	1.635(4)
Ru–P(1)	2.254(18)	P(2)–O(2)	1.645(5)
Ru–P(2)	2.254(2)	O(1)–C(13)	1.423(8)
Ru–C(46)	2.229(10)	O(2)–C(33)	1.385(11)
Ru–C(47)	2.223(8)	C(13)–C(22)	1.366(10)
Ru–C(48)	2.216(8)	C(22)–C(23)	1.520(9)
Ru–C(49)	2.212(11)	C(23)–C(24)	1.531(12)
Ru–C(50)	2.196(13)	C(24)–C(33)	1.368(10)
Cl–Ru–P(1)	95.39(8)	P(2)–O(2)–C(33)	128.7(4)
Cl–Ru–P(2)	89.53(8)	O(1)–C(13)–C(22)	114.9(5)
P(1)–Ru–P(2)	93.94(7)	O(2)–C(33)–C(24)	118.8(7)
Ru–P(1)–O(1)	113.84(16)	C(13)–C(22)–C(23)	121.1(6)
Ru–P(2)–O(2)	121.5(2)	C(22)–C(23)–C(24)	114.7(6)
P(1)–O(1)–C(13)	131.4(4)	C(23)–C(24)–C(33)	121.1(8)

organometallic derivatives containing one or two labile ligands (Scheme 1). The reaction of **1** with one equivalent of [CpRu(PPh$_3$)$_2$Cl] in toluene at refluxing temperature gives the monomeric complex [CpRuCl{η^2-Ph$_2$P{(–OC$_{10}$H$_6$)(μ-CH$_2$)(C$_{10}$H$_6$O–)}PPh$_2$-κP,κP}] (**4**) in which the bis(phosphinoxy) ligand shows chelating bidentate mode of coordination. Treatment of a solution of **1** in THF with an equimolar ratio of the Ru(II) derivative, [Cp*Ru(COD)Cl] afforded a similar ten-membered chelating complex [Cp*RuCl{η^2-Ph$_2$P{(–OC$_{10}$H$_6$)(μ-CH$_2$)(C$_{10}$H$_6$O–)}PPh$_2$-κP,κP}] (**5**) in 83% yield. The stoichiometric reactions of [M(COD)Cl$_2$] (M= Pd, Pt) with 1 : 1 molar proportions of **1** in CH$_2$Cl$_2$ at ambient temperature give the chelate complexes [MCl$_2${η^2-Ph$_2$P{(–OC$_{10}$H$_6$)(μ-CH$_2$)(C$_{10}$H$_6$O–)}PPh$_2$-κP,κP}] (M = Pd, **6**; Pt, **7**).

The chemical compositions of complexes **4**–**7** are established by elemental analyses and the proposed structures are consistent with their spectroscopic data. The ^{31}P{^{1}H} NMR spectra of **4** and **5** show single resonances at 153.5 and 154.0 ppm, respectively, with coordination shifts ($\Delta\delta$) of 41.3 and 42.0 ppm. The ^{31}P resonance due to the platinum complex **7** appears at 85.9 ppm ($\Delta\delta = -26.3$ Hz) with ^{195}Pt satellites. Phosphorus resonance in Pt(II) complexes are upfield of those for Ru(II) complexes of the same ligands. The large $^1J_{PtP}$ coupling of 4155 Hz is attributed to a *cis* configuration of the coordinated phosphorus centers.[14,21,22] Spectroscopic studies on complex **6** could not be carried out because of its poor solubility in most organic solvents. The molecular structures[23] of the complexes **4** and **7** are further confirmed by single crystal X-ray diffraction studies.

A perspective view of **4** with the numbering scheme is shown in Fig. 2(a) and the central core is shown in Fig. 2(b). The crystallographic data are given in Table 4. Selected bond lengths and bond angles are listed in Table 2. The complex adopts the well-known piano-stool structure that consists of an η^5-cyclopentadienyl ring, a chlorine atom and the two phosphorus centers. The average Ru–P bond distance of 2.254(10) Å is shorter than those observed in analogous complexes[24–28] containing organophosphines. This may be attributed to the better π-acceptor nature of the phosphite ligands compared to organophosphines. In addition, it may also be due to the steric factors and the size of the chelate ring in the complex; the M–P distances are sensitive to the bulkiness of the phosphine ligands.[29] The chlorine atom is bent towards the P(2) atom: Cl–Ru–P(1) 95.39(8)°, Cl–Ru–P(2) 89.53(8)°, to avoid steric interactions with one of the phenyl rings bound to P(1). The

Table 3 Selected bond distances (Å) and bond angles (°) for **7**

Pt–Cl(1)	2.346(3)	O(1)–C(13)	1.413(12)
Pt–Cl(2)	2.324(3)	O(2)–C(33)	1.408(12)
Pt–P(1)	2.229(3)	C(13)–C(22)	1.355(14)
Pt–P(2)	2.224(2)	C(22)–C(23)	1.537(14)
P(1)–O(1)	1.606(8)	C(23)–C(24)	1.521(13)
P(2)–O(2)	1.616(8)	C(24)–C(33)	1.380(14)
Cl(1)–Pt–Cl(2)	87.23(11)	O(1)–C(13)–C(22)	116.9(9)
Cl(1)–Pt–P(2)	178.30(10)	P(1)–O(1)–C(13)	123.8(7)
Cl(1)–Pt–P(2)	84.91(10)	P(2)–O(2)–C(33)	124.2(6)
Cl(2)–Pt–P(1)	92.58(10)	C(13)–C(22)–C(23)	120.4(9)
Cl(2)–Pt–P(2)	171.54(11)	C(22)–C(23)–C(24)	116.9(8)
P(1)–Pt–P(2)	95.37(9)	C(23)–C(24)–C(33)	119.8(9)
Pt–P(1)–O(1)	114.1(3)	O(2)–C(33)–C(24)	117.1(8)
Pt–P(2)–O(2)	111.9(3)		

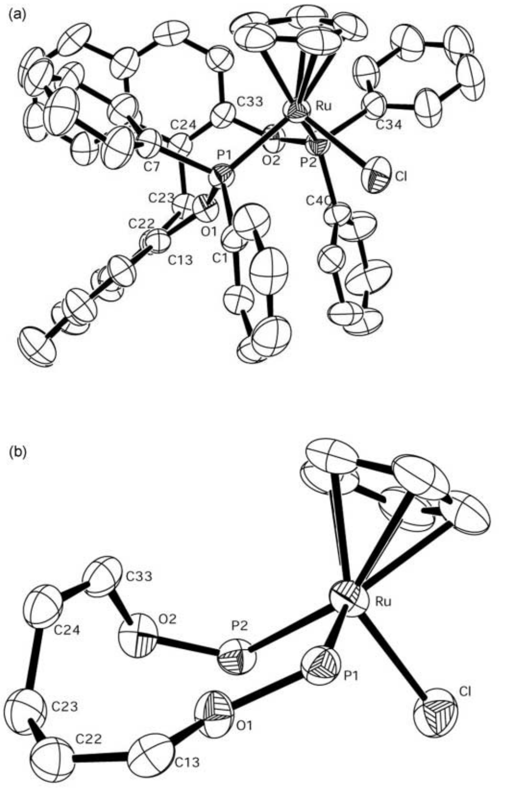

Fig. 2 (a) Perspective view of complex **4** showing the atom numbering scheme. Thermal ellipsoids are drawn at the 50% probability level and hydrogen atoms are omitted for clarity. (b) Plot of the central core of the complex **4**.

average P–O bond distance of 1.64(5) Å is in agreement with the typical value of P–O single bonds in other related phosphites.

A perspective view of molecule **7** with the numbering scheme is shown in Fig. 3(a) and the central core is shown in Fig. 3(b). Selected bond lengths and bond angles are listed in Table 3 and the crystallographic data are given in Table 4. The structure of the complex shows a typical square-planar environment around the metal center with the bis(phosphinoxy) ligand, and two chlorine atoms in a mutually *cis*-disposition. The average Pt–P distance is 2.226(3) Å. The Cl(2)–Pt–P(1) angle is 92.58(10)° whereas the Cl(1)–Pt–P(2) angle is 84.91(10)° which clearly indicates some distortion at the metal center. The P(1)–Pt–P(2) angle (95.37(9)°) appears to have increased from the square-planar value of 90° to an extent limited by the development of phosphine–chlorine interactions. The PtP_2Cl_2 plane is perpendicular to two of the four phenyl rings. The average Pt–Cl bond distance of 2.335(3) Å is comparable with that observed (2.33–2.35 Å) in analogous Pt–phosphine complexes.[30,31] It is interesting to note that the longer Pt–Cl distance is paired with the shorter Pt–P distance and *vice versa* but there is no obvious explanation. The average P–O bond distance of 1.611(8) Å is slightly shorter than the normally accepted P–O single bond distance of 1.62 Å.

Conclusion

The new bis(phosphinite) ligand prepared in high yield can be readily oxidized with chalcogens to give the corresponding dichalcogenides and chelate complexes with transition metal derivatives. The ruthenium complex adopts a well-known piano-stool structure whereas the structure of platinum complex shows a typical square-planar geometry. Diphosphines with large bite angles are useful in catalysis and further research in this direction is in progress.

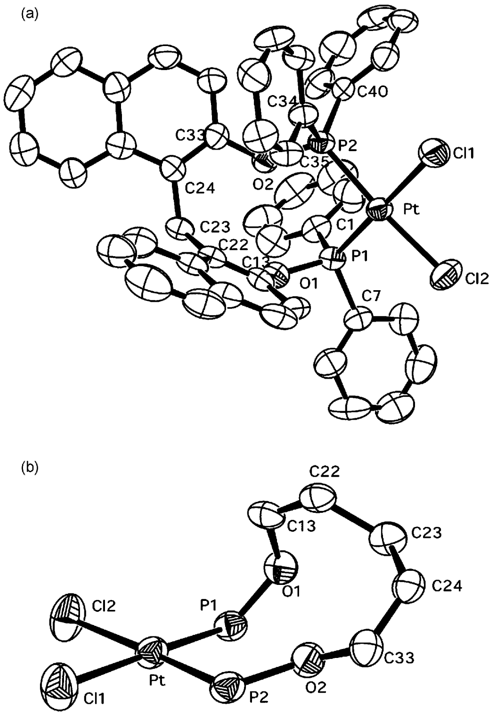

Fig. 3 (a) Perspective view of complex **7** showing the atom numbering scheme. Thermal ellipsoids are drawn at the 50% probability level and hydrogen atoms are omitted for clarity. (b) Plot of the central core of the complex **7**.

Experimental

All experimental manipulations were carried out under an atmosphere of dry nitrogen or argon using Schlenk techniques. Solvents were dried and distilled prior to use by conventional methods. PPh_2Cl, elemental sulfur and selenium powder were used as purchased. Bis(2-hydroxy-1-naphthyl)methane,[32] $[CpRu(PPh_3)_2Cl]$,[33] $[Cp^*Ru(COD)Cl_2]$,[34] $[M(COD)Cl_2]$ (M = Pd,[35] Pt[36]) were prepared by the cited procedures. The ^1H and $^{31}P\{^1H\}$ NMR (δ in ppm) spectra were obtained on a VXR 300S 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. Microanalyses were carried out on a Carlo Erba Model 1106 elemental analyzer.

Synthesis of $Ph_2P\{(-OC_{10}H_6)(\mu\text{-}CH_2)(C_{10}H_6O-)\}PPh_2$ (1)

A solution of PPh_2Cl (4.63 g, 20 mmol) in diethyl ether/THF (1: 2, 30 mL) was added dropwise to a mixture of bis(2-

Table 4 Crystallographic data for **3**, **4** and **7**

	3	**4**	**7**
Empirical formula	$C_{45}H_{34}O_2P_2Se_2$	$C_{50}H_{39}ClO_2P_2Ru\cdot CH_2Cl_2\cdot 0.5H_2O$	$C_{45}H_{34}Cl_2O_2P_2Pt\cdot CH_2Cl_2\cdot H_2O$
Formula weight	826.58	964.25	1037.68
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$C2/c$ (no. 15)	$C2/c$ (no. 15)	$P2_1/c$ (no. 14)
a/Å	44.656(3)	41.312(2)	15.357(3)
b/Å	11.1275(9)	12.8234(17)	11.005(2)
c/Å	15.5265(18)	22.770(2)	26.594(4)
β/°	99.753(8)	122.897(8)	106.300(10)
V/Å^3	7603.8(12)	10128.4(18)	4314(1)
Z	8	8	4
D_c/g cm^{-3}	1.444	1.265	1.598
F(000)	3344	3944	2056
μ(Mo-Kα)/cm^{-1}	2.067	0.568	3.6
Crystal size/mm	0.23 × 0.40 × 0.40	0.26 × 0.40 × 0.40	0.30 × 0.40 × 0.43
T/K	293	293	293
λ(Mo-Kα)/Å	0.71073	0.71073	0.71073
$\theta_{\text{min–max}}$/°	1.9–25.1	1.7–25.1	1.6–25.1
Total no. reflections	6871	9164	7934
No. unique reflections	6778	9030	7630
Observed data	4413	5018	5065
R_{int}	0.023	0.051	0.138
R	0.0353	0.0619	0.0605
R_w	0.1078	0.2354	0.1858

hydroxy-1-naphthyl)methane (3.0 g, 10 mmol), a catalytic amount of 4-dimethylaminopyridine (0.015 g) and triethylamine (2.02 g, 20.1 mmol) also in THF (50 mL) at 0 °C with vigorous stirring. Then the solution was allowed to warm to room temperature and stirring was continued for 20 h. The triethylamine hydrochloride was removed by filtration. The solvent was removed under vacuum to give a white solid of the crude product, which was recrystallized from dichloromethane/petroleum ether (2 : 1, bp range for petroleum ether: 60–80 °C). Yield: 94% (6.3 g). Mp 182–184 °C. Anal. Calc. for $C_{45}H_{34}O_2P_2$: C, 80.82; H, 5.12. Found: C, 80.71; H, 5.03%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.27 (d, 2H, Ar), 7.65–7.71 (m, 4H, Ar), 7.61 (d, 2H, Ar), 7.47–7.51 (m, 2H, Ar), 7.34–7.41 (m, 20H, $OPPh_2$), 7.19 (t, 2H, Ar), 4.89 (s, 2H, Ar–CH_2–Ar). ^{31}P{^{1}H} NMR (300 MHz, $CDCl_3$): δ 112.2 (s).

Synthesis of $Ph_2P(S)\{(-OC_{10}H_6)(\mu\text{-}CH_2)(C_{10}H_6O-)\}P(S)Ph_2$ (2)

A mixture of the bis(phosphine) **1** (0.14 g, 0.021 mmol) and sulfur (0.014 g, 0.043 mmol) in toluene (10 mL) was heated to 80 °C for 5 min to give a clear solution. Solvent was removed under reduced pressure to give a pale white residue. The residue was dissolved in CH_2Cl_2 (1.5 mL), layered with 1 mL of petroleum ether (bp 60–80 °C) and kept at room temperature to give X-ray quality colorless crystals of **2**. Yield: 97% (0.15 g). Mp 214–216 °C. Anal. Calc. for $C_{45}H_{34}O_2P_2S_2$: C, 73.76; H, 4.68. Found: C, 73.69; H, 4.61%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.09 (d, 2H, Ar), 8.01 (d, 2H, Ar), 7.97 (d, 2H, Ar), 7.65 (d, 2H, Ar), 7.39–7.52 (m, 20H, $OPPh_2$), 7.29 (t, 2H, Ar), 7.23 (t, 2H, Ar), 4.78 (s, 2H, Ar–CH_2–Ar). ^{31}P{^{1}H} NMR (300 MHz, $CDCl_3$): δ 82.6 (s).

Synthesis of $Ph_2P(Se)\{(-OC_{10}H_6)(\mu\text{-}CH_2)(C_{10}H_6O-)\}P(Se)Ph_2$ (3)

A mixture of the bis(phosphine) **1** (0.14 g, 0.021 mmol) and selenium powder (0.034 g, 0.043 mmol) in toluene (10 mL) was heated under reflux for 8 h. The solution was then cooled to room temperature and filtered to remove any undissolved material. 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 (bp 60–80 °C) and kept at room temperature to afford colorless crystals of **3** suitable for X-ray analysis. Yield: 96% (0.17 g). Mp 208–210 °C. Anal. Calc. for $C_{45}H_{34}O_2P_2Se_2$: C, 65.39; H, 4.15. Found: C, 65.27; H, 4.09%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.12 (d, 2H, Ar), 8.03 (d, 2H, Ar), 8.00 (d, 2H, Ar), 7.62 (d, 2H, Ar), 7.41–7.54 (m, 20H, $OPPh_2$), 7.25 (t, 2H, Ar), 7.20 (t, 2H, Ar), 4.81 (s, 2H, Ar–CH_2–Ar). ^{31}P{^{1}H} NMR (300 MHz, $CDCl_3$): δ 86.0 (s), $^1J_{\text{PSe}} = 827$ Hz.

Synthesis of $[CpRuCl\{\eta^2\text{-}Ph_2P\{(-OC_{10}H_6)(\mu\text{-}CH_2)(C_{10}H_6O-)\}\text{-}PPh_2\text{-}\kappa P,\kappa P\}]$ (4)

A mixture of $[CpRu(PPh_3)_2Cl]$ (0.038 g, 0.05 mmol) and the bis(phosphine) **1** (0.035 g, 0.05 mmol) in toluene (10 mL) was heated under reflux for 18 h. The orange–yellow solution was then cooled to room temperature. Solvent was removed under reduced pressure and the residue was extracted with cold diethyl ether to remove PPh_3. The remaining residue was recrystallized from CH_2Cl_2/diethyl ether (1 : 1) solution to afford orange yellow crystalline **4**. Yield: 86% (0.039 g). Mp 250 °C (decomp.). Anal. Calc. for $C_{50}H_{39}ClO_2P_2Ru\cdot CH_2Cl_2\cdot 0.5H_2O$: C, 63.52; H, 4.39. Found: C, 63.28; H, 4.33%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.10 (br s, 2H, Ar), 7.75 (d, 2H, Ar), 7.68 (br s, 2H, Ar), 7.24–7.42 (m, 20H, $OPPh_2$), 7.16 (br s, 2H, Ar), 6.98 (br s, 2H, Ar), 6.86 (br s, 2H, Ar), 4.86 (ABq, 2H, Ar–CH_2–Ar, $^2J_{\text{HH}} = 15.1$ Hz), 4.31 (s, 5H, Cp). ^{31}P{^{1}H} NMR (300 MHz, $CDCl_3$): δ 153.5 (s).

Synthesis of $[Cp^*RuCl\{\eta^2\text{-}Ph_2P\{(-OC_{10}H_6)(\mu\text{-}CH_2)(C_{10}H_6O-)\}\text{-}PPh_2\text{-}\kappa P,\kappa P\}]$ (5)

A solution of the bis(phosphine) **1** (0.05 g, 0.07 mmol) in THF (5 mL) was added dropwise to a solution of $[Cp^*Ru(COD)Cl]$ (0.025 g, 0.066 mmol) also in THF (5 mL). The reaction mixture was stirred at room temperature for 12 h. Solvent was removed completely under reduced pressure and the product was extracted with petroleum ether (bp 60–80 °C, 10 mL). The solution was concentrated to 3 mL, which upon cooling to 0 °C gave analytically pure sample of **5**. Yield: 83% (0.051 g). Mp 238–240 °C (melts with decomposition). Anal. Calc. for $C_{55}H_{49}ClO_2P_2Ru$: C, 70.23; H, 5.25. Found: C, 70.05; H, 5.19%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.88 (br s, 2H, Ar), 7.65 (br s, 2H, Ar), 7.54 (br s, 2H, Ar), 7.40 (t, 2H, Ar), 7.16–7.35 (m, 20H, $OPPh_2$), 7.11 (t, 2H, Ar), 6.38 (d, 2H, Ar), 4.61 (ABq, 2H, Ar–CH_2–Ar, $^2J_{\text{HH}} = 14.8$ Hz), 1.16 (s, 15H, Cp*). ^{31}P{^{1}H} NMR (300 MHz, $CDCl_3$): δ 155.0 (s).

Synthesis of $[PdCl_2\{\eta^2\text{-}Ph_2P\{(-OC_{10}H_6)(\mu\text{-}CH_2)(C_{10}H_6O-)\}\text{-}PPh_2\text{-}\kappa P,\kappa P\}]$ (6)

A solution of the bis(phosphine) **1** (0.13 g, 0.194 mmol) in

CH_2Cl_2 (5 mL) was added dropwise to a solution of $[Pd(COD)Cl_2]$ (0.055 g, 0.194 mmol) also in CH_2Cl_2 (3 mL) and the reaction mixture was stirred at room temperature for 16 h. The solution was concentrated to 3 mL, and 1 mL of petroleum ether (bp 60–80 °C) was added. Cooling this solution to 0 °C gave yellow crystalline, analytically pure sample of **6**. Yield: 85% (0.14 g). Mp 270 °C (decomp.). Anal. Calc. for $C_{45}H_{34}Cl_2O_2P_2Pd$: C, 63.88; H, 4.05. Found: C, 63.75; H, 3.93%.

Synthesis of $[PtCl_2\{\eta^2\text{-}Ph_2P\{(\text{–}OC_{10}H_6)(\mu\text{-}CH_2)(C_{10}H_6O\text{–})\}\text{-}PPh_2\text{-}\kappa P,\kappa P\}]$ (7)

A solution of the bis(phosphine) **1** (0.1 g, 0.15 mmol) in CH_2Cl_2 (5 mL) was added dropwise to a solution of $[Pt(COD)Cl_2]$ (0.056 g, 0.15 mmol) also in CH_2Cl_2 (3 mL). The reaction mixture, which turned light yellow during the reaction, was stirred at room temperature for 12 h. The solution was concentrated to 3 mL, and 1 mL of petroleum ether (bp 60–80 °C) was added to it. Cooling this solution to 0 °C afforded the product **7** as colorless crystals suitable for X-ray analysis. Yield: 90% (0.126 g). Mp 145 °C (decomp.). Anal. Calc. for $C_{45}H_{34}Cl_2O_2P_2Pt\cdot CH_2Cl_2\cdot H_2O$: C, 53.70; H, 3.72. Found: C, 53.51; H, 3.66%. ^1H NMR (300 MHz, $CDCl_3$): δ 7.94 (br s, 2H, Ar), 7.68 (d, 2H, Ar), 7.52 (br s, 2H, Ar), 7.44 (t, 2H, Ar), 7.28–7.40 (m, 20H, $OPPh_2$), 7.14 (br s, 2H, Ar), 6.54 (d, 2H, Ar), 4.76 (ABq, 2H, Ar–CH_2–Ar, $^2J_{HH}$ = 15.2 Hz). $^{31}P\{^1H\}$ NMR (300 MHz, $CDCl_3$): δ 85.9 (s), $^1J_{PPt}$ = 4145 Hz.

X-Ray crystal structure

Crystals of compounds **3**, **4** and **7**, suitable for X-ray crystal analyses were obtained from slow evaporation of CH_2Cl_2 solutions, layered with petroleum ether (bp 60–80 °C), at room temperature. The crystals were coated with an epoxy resin and mounted on Pyrex filaments on a Enraf-Nonius CAD-4 diffractometer. General procedures for crystal orientation, unit cell determination, refinement and collection of intensity data have been published.[37] Intensity data were collected at room temperature using graphite-monochromated Mo-Kα (λ = 0.71073 Å) radiation with a Enraf-Nonius CAD-4 diffractometer. Intensities were corrected for Lorentz–polarisation effects (XCAD4)[38] and for absorption. The structures were solved by direct methods (SHELXS-97). Refinements were done by full-matrix least squares based on F^2 using the SHELXTL-PLUS[39] program package. Details of the data collections and refinements specific to these compounds are summarized in Table 4. In ruthenium compound **4** there is an ordered CH_2Cl_2 molecule at 50% occupancy (Cl1s–C1s–Cl2s) and a second one disordered over two sites having Cl3 in common (Cl3s–C4sa–Cl4a and Cl3s–C4sb–Cl4b). The hydrogen atoms on these carbon atoms were not included because of the disorder. Besides this, there are two isolated areas of electron density that were modeled by solvent water (with ~25% occupancy). Although hydrogen atoms were not identified clearly, O1s is 2.84 and 3.07 Å, respectively, from the alternate disordered locations for O2s (at $1.5-x$, $1.5-y$, $2-z$ and x, $y-1$, z), both of which seem reasonable distances for hydrogen bonding. In the platinum complex **7** there is a CH_2Cl_2 molecule at full occupancy and a water molecule (O3). Hydrogen atoms attached to O3 could not be reliably located, however, O3 is 2.64 Å from O3 at ($2-x$, $-y$, $2-z$) which is a reasonable separation for two waters H-bonded together.

CCDC reference numbers 190092–190094.

See http://www.rsc.org/suppdata/dt/b2/b206994f/ for crystallographic data in CIF or other electronic format.

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References and notes

1 C. A. McAuliffe, in *Comprehensive Coordination Chemistry*, eds. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon Press, New York, 1987, vol. 2, pp. 989–1066.

2 C. A. McAuliffe and A. G. Mackie, in *Encyclopedia of Inorganic Chemistry*, ed. R. B. King, John Wiley and Sons, New York, 1994, vol. 6, pp. 2989–3010.

3 D. E. C. Corbridge, *Phosphorus: An Outline of its Chemistry, Biochemistry and Technology*, Elsevier, New York, 1995.

4 L. H. Pignolet, *Homogeneous catalysis with Metal Phosphine Complexes*, Plenum, New York, 1983.

5 G. D. Cuny and S. L. Buchwald, *J. Am. Chem. Soc.*, 1993, **115**, 2066.

6 P. W. N. M. van Leeuwen, *Organometallics*, 1997, **16**, 3027.

7 T. J. Kwok and D. J. Wink, *Organometallics*, 1993, **12**, 1954.

8 D. J. Darensbourg, *Inorg. Chem.*, 1994, **33**, 200.

9 O. Huttenloch, J. Spieler and H. Waldmann, *Chem. Eur. J.*, 2000, **6**, 671.

10 E. K. V. den Beuken, W. G. J. de Lange, P. W. N. M. van Leeuwen, N. Veldman, A. L. Spek and B. L. Feringa, *J. Chem. Soc., Dalton Trans.*, 1996, **17**, 3561.

11 Z. Csok, G. Szalontai, G. Czira and L. Kollar, *J. Organomet. Chem.*, 1998, **475**, 23.

12 P. G. Pringle, *J. Chem. Soc., Chem. Commun.*, 1991, 1292.

13 M. J. Baker and P. G. Pringle, *J. Chem. Soc., Chem. Commun.*, 1991, 803.

14 M. S. Balakrishna, R. M. Abhyankar and J. T. Mague, *J. Chem. Soc., Dalton Trans.*, 1999, 1407.

15 M. S. Balakrishna, R. Panda and J. T. Mague, *Inorg. Chem.*, 2001, **40**, 5620.

16 M. S. Balakrishna, R. Panda, D. C. Smith jr., A. Klaman and S. P. Nolan, *J. Organomet. Chem.*, 2000, **599**, 159.

17 M. S. Balakrishna, R. M. Abhyankar and M. G. Walawalker, *Tetrahedron. Lett.*, 2001, **42**, 2733.

18 M. S. Balakrishna, S. Teipel, A. A. Pinkerton and R. G. Cavell, *Inorg. Chem.*, 2001, **40**, 1802.

19 M. S. Balakrishna and M. G. Walawalker, *J. Organomet. Chem*, 2001, **628**, 76.

20 P. Bhattacharyya, J. Novosad, J. Phillips, A. M. Z. Slawin, D. Williams and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 1995, 1607.

21 M. S. Balakrishna, R. Klein, S. Uhlenbrock, A. A. Pinkerton and R. G. Cavell, *Inorg. Chem.*, 1993, **32**, 5676.

22 M. S. Balakrishna, B. D. Santarsiero and R. G. Cavell, *Inorg. Chem.*, 1994, **33**, 3079.

23 The complexes **4** and **7** did not crystallize well from very dry solvents. However, when air was bubbled for a few seconds through a dichloromethane/hexane (1 : 1) solution of the complex followed by cooling to 0 °C, X-ray quality crystals were obtained containing both dichloromethane and water of solvation.

24 W. H. Pearson, J. E. Shade, J. E. Brown and T. E. Bitterwolf, *Acta Crystallogr., Sect. C*, 1996, **52**, 1106.

25 I. d. l. Rios, M. J. Tenorio, J. Padilla, M. C. Puerta and P. Valerga, *Organometallics*, 1996, **15**, 4565.

26 M. P. Brown, R. Burns, D. Das, P. A. Dolby, M. M. Harding, R. W. Jones, E. J. Robinson and A. K. Smith, *J. Chem. Soc., Dalton Trans.*, 1991, 351.

27 W. Baratta, A. D. Zotto, E. Herdtweck, S. Vuano and P. Rigo, *J. Organomet. Chem.*, 2001, **617/618**, 511.

28 F. Morandini, G. Consiglio, B. Straub, G. Ciani and A. Sironi, *J. Chem. Soc., Dalton Trans.*, 1983, 2293.

29 C. A. Tolman, *Chem. Rev.*, 1977, **77**, 313.

30 G. K. Anderson, H. C. Clark, J. A. Davies, G. H. Ferguson and M. Parvez, *J. Crystallogr. Spectrosc. Res.*, 1982, **12**, 449.

31 D. H. Farraar and G. H. Ferguson, *J. Crystallogr. Spectrosc. Res.*, 1982, **12**, 465.

32 O. Manasse, *Ber. Dtsch. Chem. Ges.*, 1894, **27**, 2409.

33 M. I. Bruce, C. Hameister, A. G. Swincer and R. C. Wallis, *Inorg. Synth.*, 1982, **21**, 79.

34 P. J. Fagan, W. S. Maloney, J. C. Calabrese and I. D. Williams, *Organometallics*, 1990, 1843.

35 D. Drew and J. R. Doyle, *Inorg. Synth.*, 1972, **13**, 52.

36 D. Drew and J. R. Doyle, *Inorg. Synth.*, 1972, **13**, 48.

37 J. T. Mague and C. L. Lloyd, *Organometallics*, 1988, **7**, 983.

38 K. Harms and S. Wocadlo, CAD-4 Files, Program to Extract Intensity Data from Enraf-Nonius, Delft, 1987.

39 Bruker AXS, SHELXTL-PLUS, Version 5.1, Madison, WI, 1997.