

Proc. Indian Acad. Sci. (Chem. Sci.), Vol. 115, Nos 5 & 6, October–December 2003, pp 741–749
© Indian Academy of Sciences

Rhodium(I) complexes of α -keto-stabilised 1,2-bis(diphenylphosphino)alkane mono ylides[†]

D SARAVANABHARATHI, T S VENKATAKRISHNAN, M NETHAJI
and S S KRISHNAMURTHY*

Department of Inorganic and Physical Chemistry, Indian Institute of Science,
Bangalore 560 012, India
e-mail: sskrish@ipc.iisc.ernet.in

Abstract. Rhodium(I) complexes of the hybrid ylide-phosphine ligands, $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2(\text{CHC}(\text{O})\text{C}_6\text{H}_5)$ ($n = 1$: dppm-yl, or 2: dppe-yl) have been synthesised from $[\text{Rh}(\text{mCl})(\text{COD})]_2$ (COD = 1,5-cyclooctadiene) and characterized by NMR spectroscopic and X-ray structural methods. The dppe-yl behaves as an ambidentate ligand; it functions as a monodentate P-donor ligand with a dangling ylidic carbon in the neutral chloro complex, $[(\text{COD})\text{Rh}(\text{Cl})(\text{dppe-yl})]$ (**1**), whereas replacement of the chloride by a non-coordinating counter anion results in the formation of the complexes, $[(\text{COD})\text{Rh}(\text{L-L}')^+]$ ($\text{L-L}' = \text{dppe-yl}$ (**2**) or dppm-yl (**3**)) respectively in which the ligands are bonded to the metal via the phosphorus and the ylidic carbon atoms. The 1,5-cyclooctadiene (COD), present in the Rh(I) precursor, remains intact in the products. The structures of **1**, **2** and **3** have been confirmed by X-ray crystallography.

Keywords. Rh(I) complexes; ylide-phosphine; ambidentate coordination; crystal structure; NMR.

1. Introduction

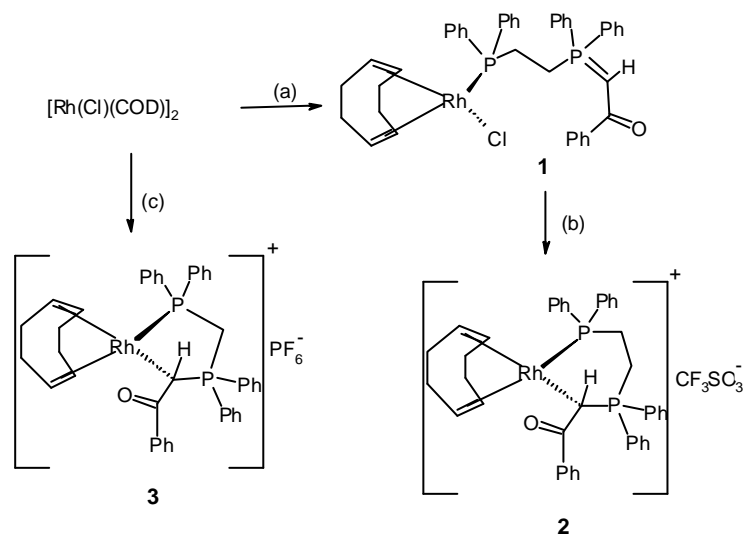
The coordination and organometallic chemistry of α -keto stabilised phosphorus ylides has been investigated extensively and their ambidenticity explained in terms of a delicate balance between electronic and steric factors.^{1,2} Heterofunctional ligands of the type $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2(\text{CHC}(\text{O})\text{R})$ ($n = 1$, or 2; $\text{R} = \text{Me}$, Ph or $-\text{OMe}$) containing both a phosphine and a keto stabilised phosphorus ylide moieties are also known and their transition metal complexes are mostly confined to palladium and to a lesser extent platinum.^{3,4} In this, paper we report the rhodium(I) complexes of the hybrid ylide-phosphine ligands, $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2(\text{CHC}(\text{O})\text{C}_6\text{H}_5)$ ($n = 1$; dppm-yl, or 2: dppe-yl). Most of the rhodium ylide complexes reported so far have been prepared by the oxidative addition of CH_2X_2 ($\text{X} = \text{halide}$) to $\text{Rh}(\text{I})\text{-PR}_3$ bonds;⁵ these reactions yield Rh(III) complexes of the type $[\text{L}_n\text{Rh}(\text{III})(\text{CH}_2\text{PR}_3)(\text{X})_2]^+$ ($\text{L}_n = \text{cyclopentadiene}/\text{PMe}_3$). Surprisingly, the coordination chemistry of Rh(I)-ylide complexes is not well studied. A rare Rh(I) complex $[\text{RhCl}(\text{PR}_3)(\text{R}_3\text{P}=\text{CHCOPh})]$ ($\text{R} = \text{CHMe}_2$) has been structurally characterised⁶ and recently a Rh(I) complex species $[\text{Rh}(\text{I})(\text{COD})(\text{BINAPCH}_2)]^+$ [COD = 1,5-cyclooctadiene, BINAP = 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl] containing BINAP mono ylide has been spectroscopically characterised.⁷

[†]Dedicated to Professor C N R Rao on his 70th birthday

*For correspondence

2. Results and discussion

Diphosphines such as dppe [1,2-*bis*(diphenylphosphino)ethane], or BINAP react with $[\text{Rh}(\mu\text{Cl})(\text{COD})]_2$, by displacing the COD ligand to yield chloro-bridged dimers, in which the diphosphine ligands are chelated to the metal centres.^{8a,8b} On the other hand, reactions of $[\text{Rh}(\mu\text{Cl})(\text{COD})]_2$ with monodentate phosphorus ligands $[\text{PPh}_3, \text{P}(\text{OMe})_3, \text{P}(\text{OPh})_3]$, though resulting in the displacement of COD, yield monomeric $[\text{L}_3\text{RhCl}]$ and dimeric products $[\text{L}_2\text{RhCl}]_2$ depending upon the stoichiometry of the reactions.^{8c} Diphosphazanes of the type, $\text{X}_2\text{PN}(\text{R})\text{PX}_2$ ($\text{R} = \text{Me, Et, Ph}$ and $\text{X} = \text{F}$ or OPh) displace the COD ligand stepwise to give dimeric complexes in which the chloro bridges are retained.^{8d} Interestingly, the cyclodiphosphazanes $[\text{Bu}'\text{NP}(\text{X})]_2$ [$\text{X} = \text{Cl, F,}$ or OPh] split the chloro-bridge of the Rh(I) source without replacing the COD ligand and yield monomeric and dimeric products in which cyclodiphosphazanes function as monodentate or bridging bidentate ligands respectively.^{8e,8f} In the present study, we observe that dppe-monoylide (dppe-yl) reacts with the rhodium precursor $[\text{Rh}(\mu\text{Cl})(\text{COD})]_2$, to split the chloro-bridges and form a mononuclear complex, $[(\text{COD})\text{RhCl}(\text{dppe-yl})]$ (**1**), in which the ylide functions as a monodentate P-donor ligand. In contrast to the reaction of BINAP-monoylide with $[\text{Rh}(\mu\text{Cl})(\text{COD})]_2$,⁷ the 'C' coordination to Rh is not observed in complex **1**. Treatment of **1** with silver triflate yields complex **2** in which the ylide functions as a chelating ligand via phosphorus and ylidic carbon atoms. The anion replacement reaction proceeds with a characteristic colour change from yellow (complex **1**) to orange (complex **2**). Direct reaction of dppm-yl with $[\text{Rh}(\mu\text{Cl})(\text{COD})]_2$ yields a mixture of products, which decompose rapidly, whereas the anion replacement reaction proceeds in the same way as that observed for the reaction of dppe-yl to yield a chelate complex **3**. These reactions are shown in scheme 1.



(a) dppe-yl/ CHCl_3 ; (b) $\text{AgSO}_3\text{CF}_3/\text{CHCl}_3$; (c) dppm-yl/ $\text{NH}_4\text{PF}_6/\text{acetone}$

Scheme 1.

2.1 Spectroscopic characterisation

The ^{31}P NMR spectrum of complex **1** exhibits a doublet of doublets at 29 ppm, which is assigned to the coordinated 'PPh₂' group and a doublet at 17 ppm for the dangling 'P=CHR' group. The chemical shift of the latter is very close to that observed for the ylidic phosphorus in the free ligand. Complex **2** exhibits broad spectral features. A doublet at 25 ppm and a broad singlet at 28 ppm can be assigned to the coordinated 'PPh₂' and 'P=CHR' groups respectively. The ^{31}P NMR spectrum of complex **3** closely resembles that of **2**, but the peaks are relatively sharper. A doublet of doublets at 29 ppm and a doublet at 37 ppm confirm the coordination of 'PPh₂' and 'P=CHR' groups respectively. As reported earlier,^{3,4} the downfield shift of the ylidic phosphorus signifies 'C-coordination' of the ylidic moiety.

The ^1H NMR spectra of these complexes are rather broad at room temperature. In all these complexes, the $-\text{CH}_2-$ signals of the COD ligand appear in the range 1.87–2.11 ppm. The broadness of the signals at room temperature is presumably the result of fluxional behaviour which is commonly encountered in several cationic Rh(I) complexes of the type $[\text{Rh}(\text{COD})(\text{P-X})]^+$ (P-X = chelating ligand).⁹ The fluxional behaviour usually involves the exchange between the $-\text{C}=\text{C}-$ group of the COD ligand. Selected NMR data are given in table 1.

2.2 Molecular structures

The structures of complexes **1–3** have been established by single crystal X-ray analysis. The molecular structure of complex **1** is shown in figure 1 and relevant bond lengths and angles are given in table 2. The Rh(I) atom is located in a distorted square planar environment with 'P' and 'Cl' atoms having a *cis* orientation. The remaining positions are occupied by the COD ligand. The coordination environment around Rh(I) closely resembles that found in $[\text{Rh}(\text{Cl})(\text{COD})\{\text{Ph}_2\text{PN}(\text{H})\text{P}(\text{O})\text{Ph}_2\}]$.¹⁰ As expected, the metric parameters are also in the same range. The ylidic moiety shows no interaction with Rh(I).

The structure of complex **2** is shown in figure 2. The ligand coordinates to the metal via 'P' and ylidic 'C' atoms to form a six-membered chelate. The Rh-C and Rh-P distances are in the usual range (table 2). The structure of complex **3** (figure 3) is very similar to that of complex **2**, in terms of the coordination mode of the ligand and the geometry around the metal centre. However, the bite angle of the chelate and the P...P

Table 1. Selected NMR values of complexes **1–3**.^a

Complex	^{31}P				$^1\text{H}^e$
	PPh ₂ (d_k) in ppm	Δd^d	P=CH (d_k) in ppm	Δd^d	
1	29.0 <i>dd</i> (150) ^b and (53) ^c	41.5	17.0 (48) ^c	0	1.92–2.12, <i>m</i>
2	25.0 <i>d</i> (143) ^b	37.5	28.0 <i>br s</i>	11	1.86 <i>br s</i> , 2.01 <i>br s</i>
3	29.0 <i>dd</i> (140) ^b and (45) ^c	56.0	37.0 (43) ^c	23	1.94 <i>br s</i> , 2.19 <i>br s</i>

Abbreviations: *d*, doublet; *dd*, doublet of doublets; *br s*, broad singlet; *m*, multiplet; ^arecorded in CDCl₃ at 293 K; ^{b,c}Rh-P and P-P coupling constants respectively in Hz; ^d $[\Delta d = d(\text{complex}) - d(\text{free ligand})]$; the (d_k) of dppe-yl and dppm-yl are –12.5 and –27.0 respectively; (d_k) of dppe-yl and dppm-yl are 17.0 and 14.0 respectively; ^e $-\text{CH}_2-$ protons of COD; P(CH₂) and ylidic C–H protons overlap with the olefinic protons of COD

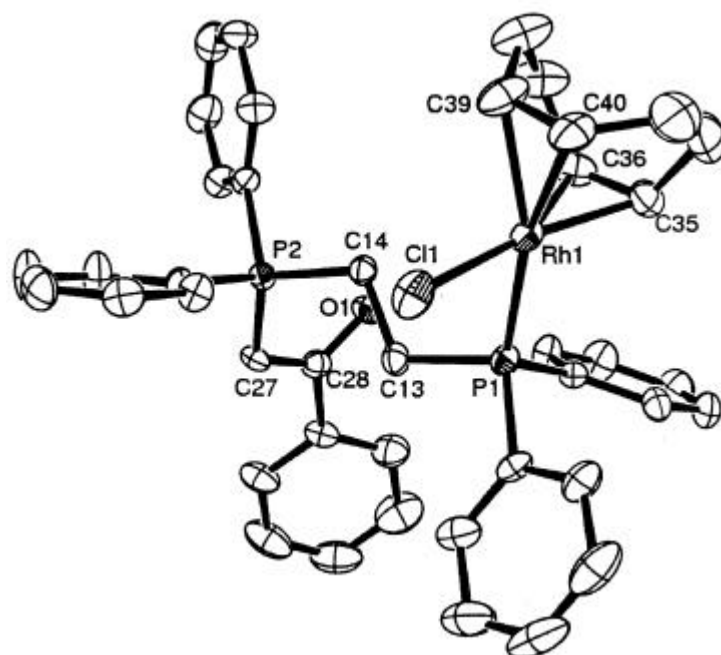


Figure 1. Molecular structure of $[\text{RhCl}(\text{C}_8\text{H}_{12})\{\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2(\text{CHO})\text{C}_6\text{H}_5\}]$ (**1**) with ellipsoids at the 30% probability level. (Hydrogen atoms are not shown.)

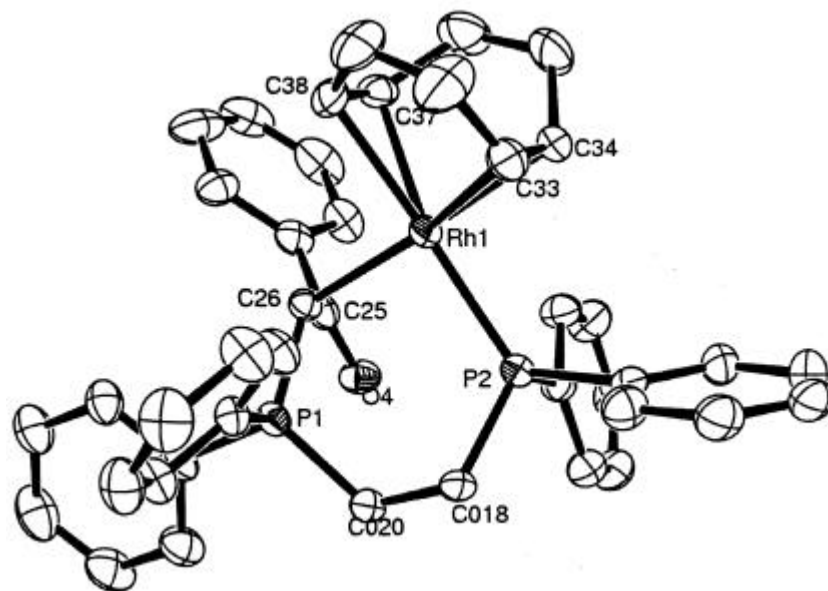


Figure 2. Molecular structure of $[\text{Rh}(\text{C}_8\text{H}_{12})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2(\text{CHO})\text{C}_6\text{H}_5)] \text{CF}_3\text{SO}_3$ (**2**) with ellipsoids at the 30% probability level. (Hydrogen atoms and the counter anion are not shown.)

non-bonded distances are lower than those for **2** owing to the reduced chelate ring size. (The P-P non-bonded distances in **2** and **3** are 3.48 and 2.92 Å respectively.)

As expected, the higher trans influence of phosphorus lengthens the corresponding Rh–C (COD) bonds, located trans to it compared to those trans to the chloride or carbon atoms, as evident from the observed bond lengths (table 2).

Considering the structural features of the ylidic moiety, one observes that the P–C (ylide) distance 1.715(7) Å in complex **1** is much shorter than the reported values¹¹ for C- or O-coordinated phosphorus-ylide complexes which lie in the range, 1.744(7) Å–1.806(10) Å. Furthermore, the C–O (keto) distances, 1.219(6) Å, and 1.226(3) Å observed in complexes **2** and **3** respectively are comparable to those of other ‘C-coordinated’ ylidic complexes [1.198(4) Å–1.229(8) Å] and are shorter than the C–O distances of the ‘O-coordinated’ ylidic complexes (1.27 Å), as would be expected from the enhanced contribution of the canonical structure C to the resonance hybrid (scheme 2).

In agreement with the earlier reports,¹¹ the coordinating ylidic carbon atoms in complexes **2** and **3** exhibit a hybridisation change from sp^2 to sp^3 as reflected in the observed bond angles (table 2).

Table 2. Selected bond distances and angles of complexes **1–3**.

Complex	Bond distances (Å)	Bond angles (deg)
1	Rh(1)–P(1) 2.295(2)	C(36)–Rh(1)–C(40) 94.8(4)
	Rh(1)–Cl(1) 2.368(2)	C(35)–Rh(1)–C(39) 90.7(4)
	Rh(1)–C(36) 2.103(8)	C(36)–Rh(1)–P(1) 92.9(2)
	Rh(1)–C(35) 2.111(8)	C(40)–Rh(1)–Cl(1) 91.3(3)
	Rh(1)–C(40) 2.219(8)*	C(39)–Rh(1)–Cl(1) 91.6(3)
	Rh(1)–C(39) 2.224(8)*	P(1)–Rh(1)–Cl(1) 86.33(8)
2	Rh(1)–P(2) 2.281(2)	C(33)–Rh(1)–C(37) 91.8(2)
	Rh(1)–C(26) 2.202(5)	C(26)–Rh(1)–C(37) 91.6(2)
	Rh(1)–C(33) 2.136(5)	C(34)–Rh(1)–C(38) 89.9(2)
	Rh(1)–C(34) 2.164(6)	C(26)–Rh(1)–C(38) 89.5(2)
	Rh(1)–C(37) 2.227(6)*	C(34)–Rh(1)–P(2) 90.51(17)
	Rh(1)–C(38) 2.266(6)*	C(26)–Rh(1)–P(2) 92.53(14)
		P(1)–C(26)–Rh(1) 116.1(2)
		C(25)–C(26)–P(1) 109.4(4)
	C(25)–C(26)–Rh(1) 110.4(4)	
3	Rh(1)–P(1) 2.2784(17)	C(37)–Rh(1)–C(41) 95.7(3)
	Rh(1)–C(26) 2.190(6)	C(26)–Rh(1)–C(41) 95.3(2)
	Rh(1)–C(37) 2.148(8)	C(38)–Rh(1)–C(34) 88.3(3)
	Rh(1)–C(38) 2.188(7)	C(26)–Rh(1)–C(34) 92.4(3)
	Rh(1)–C(41) 2.210(6)*	C(38)–Rh(1)–P(1) 91.2(2)
	Rh(1)–C(34) 2.251(7)*	C(26)–Rh(1)–P(1) 88.44(16)
		C(27)–C(26)–P(2) 112.8(4)
		C(27)–C(26)–Rh(1) 96.9(4)
	P(2)–C(26)–Rh(1) 110.1(3)	

*Carbon atoms *trans* to the Rh–P bond (see text)

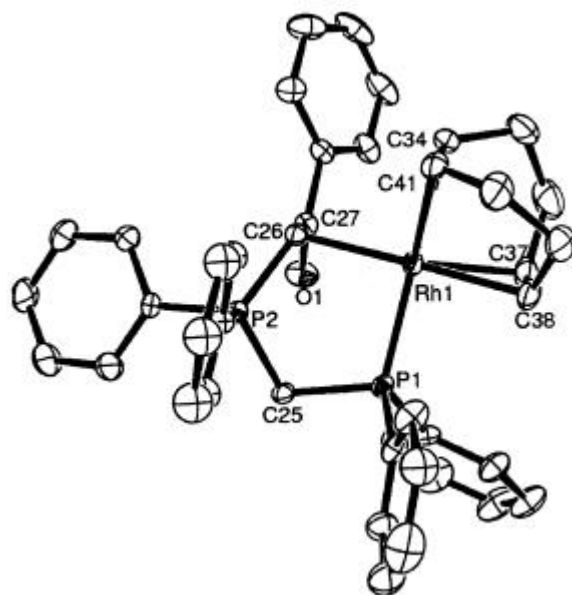
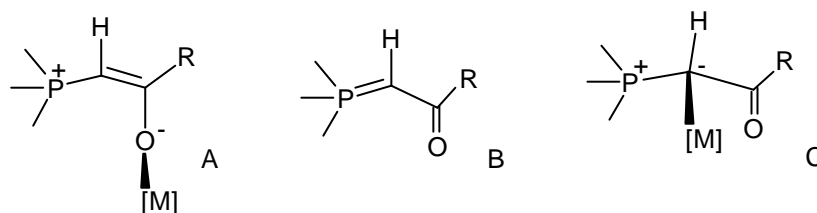


Figure 3. Molecular structure of $[\text{Rh}(\text{C}_8\text{H}_{12})(\text{Ph}_2\text{PCH}_2\text{PPh}_2(\text{CHO})\text{C}_6\text{H}_5)]\text{PF}_6$ (**3**) with ellipsoids at the 30% probability level. (Hydrogen atoms and the counter anion are not shown.)



Scheme 2.

3. Summary

The present study demonstrates that both neutral and cationic Rh(I) complexes containing *bis*(diphenylphosphino)alkane mono ylides and COD can be readily prepared. This offers an opportunity to explore the displacement reactions of COD by stronger chelating chiral bidentate phosphine ligands to generate a range of Rh(I) complexes, which would be useful for asymmetric catalysis.

4. Experimental

The solvents, chloroform, diethyl ether, petroleum ether (60–80°C) were dried and distilled by conventional methods and deoxygenated before use. The rhodium precursor

$[\text{Rh}(\text{COD})_2]$ was prepared as reported in the literature.¹² The NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer.

4.1. Synthesis of ligands

The ligands were prepared by a slight modification of the procedure reported in the literature.^{3b} Typically, diphosphines (2.5 mmol) were treated with bromoacetophenone (2.5 mmol) in chloroform at room temperature. Addition of 50 ml of diethyl ether caused the precipitation of phosphonium salts. The resulting phosphonium salts were treated with triethyl amine (2.5 ml) in toluene (75 ml). The triethyl amine hydrobromide was filtered off. Concentration of the toluene layer to 5 ml and subsequent addition of petroleum ether (50 ml) results in the precipitation of ligands as free-flowing white solids (75% yield). They were further purified by crystallisation from toluene/petroleum ether (1:5 v/v).

4.2. Synthesis of $[\text{RhCl}(\text{C}_8\text{H}_{12})\{\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2(\text{CHC}(\text{O})\text{C}_6\text{H}_5)\}]$ (**1**)

A solution of $[\text{Rh}(\text{COD})_2]$ (10 mg, 0.02 mmol) and dppe-yl (20 mg, 0.04 mmol) in 5 ml of CHCl_3 was stirred for 2 h. Addition of 30 ml of petroleum ether caused the precipitation of complex **1** as a yellow powder in quantitative yield. The product was air-dried. Suitable crystals for X-ray diffraction studies were obtained by the slow diffusion of petroleum ether into a chloroform solution of **1**. Analysis: Calcd for $\text{C}_{42}\text{H}_{42}\text{ClP}_2\text{ORh}\cdot\text{CHCl}_3$: C, 58.5; H, 4.9%. Found: C, 59.0; H, 5.1%.

4.3. Synthesis of $[\text{Rh}(\text{C}_8\text{H}_{12})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2(\text{CHC}(\text{O})\text{C}_6\text{H}_5))]\text{CF}_3\text{SO}_3$ (**2**)

Silver triflate (6 mg, 0.02 mmol) was added to a solution of complex **1** (20 mg, 0.02 mmol) in 3 ml of CHCl_3 . The reaction mixture was stirred for 2.5 h. The resulting orange solution was separated from silver chloride and layered with 10 ml of petroleum ether to obtain single crystals of complex **2** in 70% yield. Analysis: Calcd for $\text{C}_{43}\text{H}_{42}\text{F}_3\text{SP}_2\text{O}_4\text{Rh}\cdot\text{CHCl}_3$: C, 53.1; H, 4.3%. Found: C, 54.0; H, 4.4%.

4.4. Synthesis of $[\text{Rh}(\text{C}_8\text{H}_{12})(\text{Ph}_2\text{PCH}_2\text{PPh}_2(\text{CHC}(\text{O})\text{C}_6\text{H}_5))]\text{PF}_6$ (**3**)

The procedure is essentially same as that for **2**. A solution of $[\text{Rh}(\text{COD})_2]$ (5 mg, 0.01 mmol), dppm-yl (10 mg, 0.02 mmol), and NH_4PF_6 (5 mg, 0.03 mmol) in acetone (3 ml) was stirred for 0.5 h. The resulting orange solution was layered with petroleum ether to obtain the orange coloured single crystals of **3** (40% yield).

4.5. X-ray crystallography

Intensity data were obtained from a Bruker SMART APEX CCD diffractometer equipped with a fine focus 1.75 kW sealed tube Mo-K α X-ray source. The SMART software was used for data acquisition and the SAINT software for data reduction. Absorption corrections were made on the intensity data. The structure was solved using SIR-92 (level-4) and refined using SHELX-97. All non-hydrogen atoms were refined isotropically. The crystal data and details pertaining to data collection, structure solution and refinement are given in table 3.

Table 3. Brief summary of the crystal structure determination.

	Complex 1	Complex 2	Complex 3
Empirical formula	C ₄₂ H ₄₂ ClOP ₂ Rh ₂ CHCl ₃	C ₄₃ H ₄₂ F ₃ O ₄ P ₂ Rh S ₂ CHCl ₃	C ₄₁ H ₄₀ F ₆ OP ₃ Rh ₃ CHCl ₃
Formula weight	882.42	996.04	858.55
Crystal system, space group	Triclinic, <i>P</i> -1	Orthorhombic, <i>Pna</i> 21	Monoclinic, <i>P</i> 2 ₁ / <i>c</i>
Unit cell dimensions	<i>a</i> = 9.332(5) Å, a = 97.512(14)° <i>b</i> = 12.710(7) Å, b = 92.054(12)° <i>c</i> = 17.608(10) Å, g = 100.489(12)°	<i>a</i> = 19.750(14) Å <i>b</i> = 9.749(7) Å <i>c</i> = 22.484(16) Å	<i>a</i> = 10.2036 Å <i>b</i> = 20.636(3) Å, b = 96.902(3)° <i>c</i> = 18.360(3) Å
Volume	2032(2) Å ³	4329(5) Å ³	3837.9(9) Å ³
Z, Calculated density	2, 1.442 g/cm ³	4, 1.528 g/cm ³	4, 1.486 g/cm ³
Absorption coefficient	0.795 mm ⁻¹	0.757 mm ⁻¹	0.631 mm ⁻¹
<i>F</i> (000)	904	2032	1752
Theta range for data collection	1.65 to 28.15°	1.81 to 28.10°	1.49 to 28.00°
Limiting indices	-12 ≤ <i>h</i> ≤ 12, -16 ≤ <i>k</i> ≤ 16, -23 ≤ <i>l</i> ≤ 23	-26 ≤ <i>h</i> ≤ 23, -12 ≤ <i>k</i> ≤ 12, -29 ≤ <i>l</i> ≤ 29	-13 ≤ <i>h</i> ≤ 13, -27 ≤ <i>k</i> ≤ 26, -23 ≤ <i>l</i> ≤ 23
Reflections collected/unique	24162/9543 [R(int) = 0.0809]	35304/10185 [R(int) = 0.0493]	33283/9048 [R(int) = 0.0941]
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	9543/0/461	10185/1/523	9048/0/434
Goodness-of-fit on <i>F</i> ²	0.952	0.939	0.722
Final <i>R</i> indices [<i>I</i> > 2 sigma (<i>I</i>)]	<i>R</i> 1 = 0.0901, <i>wR</i> 2 = 0.1987	<i>R</i> 1 = 0.0508, <i>wR</i> 2 = 0.1301	<i>R</i> 1 = 0.0690, <i>wR</i> 2 = 0.1796
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1642, <i>wR</i> 2 = 0.2406	<i>R</i> 1 = 0.0737, <i>wR</i> 2 = 0.1432	<i>R</i> 1 = 0.1429, <i>wR</i> 2 = 0.2408
Largest diff. peak and hole	0.822 and -0.655 eÅ ⁻³	0.925 and -0.394 eÅ ⁻³	0.971 and -0.562 eÅ ⁻³

4.6 Supporting information

Crystallographic data for complexes **1–3** have been deposited with the Cambridge Crystallographic Data Centre with the following CCDC Nos: 217874 (complex **1**), 217875 (complex **2**), 217876 (complex **3**).

Acknowledgements

We wish to thank the Department of Science and Technology, New Delhi for financial support and for the data collection using the CCD X-ray diffractometer facility, Indian Institute of Science, Bangalore, set up under IRHPA program.

References

1. (a) Belluco U, Michelin R A, Mozzon M, Bertani R, Facchin G, Zanotto L and Pandolfo L 1998 *J. Organomet. Chem.* **557** 37; (b) Navarro R and Urriolabeitia E P 1999 *J. Chem. Soc., Dalton Trans.* 4111; (c) Kaska W C 1983 *Coord. Chem. Rev.* **48** 1; (d) Schmidbaur H 1983 *Angew. Chem., Int. Ed. Engl.* **22** 907
2. (a) Falvello L R, Fernandez S, Navarro R, Rueda A and Urriolabeitia E P 1998 *Inorg. Chem.* **37** 6007; (b) Falvello L R, Fernandez S, Navarro R, Rueda A and Urriolabeitia E P 1998 *Organometallics* **17** 5887
3. (a) Falvello L R, Fernandez S, Navarro R and Urriolabeitia E P 2000 *Inorg. Chem.* **39** 2957; (b) Uson R, Fornies J, Navarro R and Ortega A M 1987 *J. Organomet. Chem.* **334** 389; (c) Oosawa Y, Urabe H, Saito T and Sasaki Y 1976 *J. Organomet. Chem.* **122** 113; (d) Falvello L R, Fernandez S, Navarro R and Urriolabeitia E P 1997 *New. J. Chem.* **21** 909; (e) Lin I J B, Shy H C, Liu C W, Liu L-K and Yeh S-K 1990 *J. Chem. Soc., Dalton Trans.* 2509
4. (a) Uson R, Laguna A, Laguna M and Lazaro I 1987 *Organometallics* **6** 2326; (b) Gimeno M-C, Jones P G, Laguna A and Villacampa M-D 1995 *J. Chem. Soc., Dalton Trans.* 805
5. (a) Werner H, Schippel O, Wolf J and Schulz M 1991 *J. Organomet. Chem.* **417** 149; (b) Steinmetz M and Werner H 1989 *J. Organomet. Chem.* **369** 309; (c) Werner H, Hofmann L, Paul W and Schubert U 1988 *Organometallics* 1106; (d) Werner H, Hofmann L, Feser R and Paul W 1985 *J. Organomet. Chem.* **281** 317
6. Werner H, Mahr N, Frenking G and Jonas V 1995 *Organometallics* 619
7. Viau L, Lepetit C, Commenges G and Chauvin R 2001 *Organometallics* **20** 808
8. (a) Bunten K A, Farrar D H, Poe A J and Lough A 2002 *Organometallics* **21** 3344; (b) Fairlie D P and Bosnich B 1988 *Organometallics* 936; (c) Jardine F H and Sheridan P S 1987 in *Comprehensive coordination chemistry* (eds) G Wilkinson, R D Gillard and J A McCleverty (Oxford: Pergamon) vol 4, p. 901; (d) Balakrishna M S and Krishnamurthy S S 1995 *Inorg. Chim. Acta* **230** 245; (e) Balakrishna M S and Krishnamurthy S S 1992 *J. Organomet. Chem.* **424** 243; (f) Burckett J C T R, Laurent St, Hitchcock P B and Nixon J F 1983 *J. Organomet. Chem.* **249** 243
9. Valentini M, Selvakumar K, Worle M and Pregosin P S 1999 *J. Organomet. Chem.* **587** 244
10. Slawin A M Z, Smith M B and Woolins J D 1996 *J. Chem. Soc., Dalton Trans.* 1283
11. Falvello L R, Fernandez S, Navarro R, Pascual I and Urriolabeitia E P 1997 *J. Chem. Soc., Dalton Trans.* 763
12. Giordano G, Crabtree R H, Heintz R M, Forster D and Morris D E 1979 *Inorg. Syn.* **19** 218
13. (a) Altomare A, Cascarano G, Giacovazzo C and Guagliardi A 1993 *J. Appl. Crystallogr.* **26** 343 (Programs for Crystal Structure Analysis (Release 97-2)); (b) Sheldrick G M 1998 SHELX-97, Institut für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany