The Synthesis, *X*-Ray Crystal Structure, and Solution Characterization of a Bis(diphosphine)-bridged Dirhodium(I) Complex containing a Rh_2P_4 Six-membered Ring*

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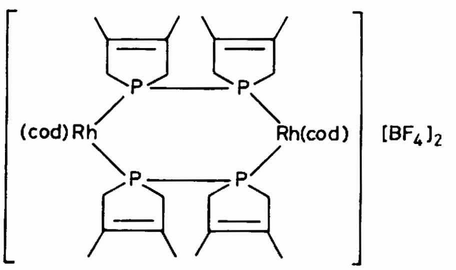
The preparation of $[\{Rh(cod)\}_2(\mu\text{-}L^1)_2][BF_4]_2$ (**1**) from $(\overline{CH_2CMe{=}CMeCH_2P})_2$ (L^1) and $[Rh(cod)_2]$-BF_4 (cod = cyclo-octa-1,5-diene) is described. The compound crystallizes in the monoclinic space group $P2_1/c$ (C^5_{2h}), with $a = 9.650(1)$, $b = 11.609(1)$, $c = 21.884(3)$ Å, $\beta = 117.07(1)°$, and $Z = 2$. The structure was refined to $R = 0.033$ for 3 434 reflections. The solid-state structure shows two diphosphine ligands L^1 bridging two rhodium(I) atoms to form a six-membered Rh_2P_4 ring in a chair conformation. Solution studies (^1H and ^{13}C-$\{^1H\}$ variable-temperature n.m.r. spectra) exhibit characteristics of a ring inversion equilibrium with $\Delta G^{\ddagger}_{271} = 14.0(0.2)$ kcal mol^{-1}. Computer simulation of the ^{31}P-$\{^1H\}$ n.m.r. spectrum is used to analyse the internuclear couplings of the AA′A″A‴XX′ pattern (A = ^{31}P, X = ^{103}Rh). The bridging diphosphine ligands exhibit a deshielding effect on the *trans* olefinic carbon atoms of cod in (**1**) which is in the range normally found for phosphine ligands.

There is currently a great deal of interest in binuclear transition-metal complexes containing bridging bis(phosphine) ligands of the type $R_2P(CH_2)_nPR_2$.[1] Diphosphine (H_2PPH_2) and the substituted diphosphines (R_2PPR_2), where $n = 0$, represent the shortest form of the potentially bridging bis(phosphine) ligands. Although chelation to a single metal centre has been proposed,[2] apparently steric constraints of the diphosphine and the resulting three-membered chelate ring strongly favour other modes of metal co-ordination. The diphosphines have been reported to function as monodentate ligands,[3,4] and as single[5–7] or double bridges between metal centres to form dimers and polymers.[4,6,8] The singly-bridged species may in some cases serve as precursors to phosphido-bridged complexes.[7,9,10]

Although it has been reported that tetraphenyldiphosphine reacts with $[\{Rh(CO)_2\}_2(\mu\text{-}Cl)_2]$ to form a monomeric complex which is unstable with respect to polymer formation,[10] in general little attention has been given to the reactions of diphosphines with rhodium(I) complexes. In this paper we describe the reaction of 2,2′,5,5′-tetrahydro-3,3′,4,4′-tetramethyl-1,1′-biphosphole (L^1), $(\overline{CH_2CMe{=}CMeCH_2P})_2$, with bis(cyclo-octa-1,5-diene)rhodium(I), $[Rh(cod)_2]^+$. Replacement of a chelating cod ligand favours substitution by two diphosphine ligands to form the dirhodium(I) complex (**1**) containing a six-membered ring. There is no evidence for polymer formation. Solution characterization of (**1**) in the form of variable-temperature multinuclear n.m.r. data is correlated with the solid-state structure determined by *X*-ray crystallography.

Experimental

General.—Proton, ^{13}C-$\{^1H\}$, and ^{31}P-$\{^1H\}$ n.m.r. spectra were obtained using a JEOL FX-90Q spectrometer operating at 89.56, 22.50, and 36.20 MHz, respectively, and equipped with a JEOL NM-VTS variable-temperature control. The ^{31}P-$\{^1H\}$ n.m.r. spectrum was also obtained using a Bruker WH-400 instrument operating at 162.00 MHz. The ^{31}P spectrum simulation was performed with the PANIC Version 810515.1 program using an IBM Aspect 2000 computer. Carbon, H, and P analyses were performed by MHW Laboratories, Phoenix, Arizona. The diphosphine ligand L^1 (ref. 11) and $[Rh(cod)_2]BF_4$[12] were prepared as reported in the literature. Solvents were dried and distilled under N_2 and solution transfers were made with syringes.



(**1**)

Synthesis of Bis(η^4-*cyclo-octa*-1,5-*diene*)-μ-*bis*(2,2′,5,5′-*tetrahydro*-3,3′,4,4′-*tetramethyl*-1,1′-*biphosphole*)-*dirhodium*(I) *Tetrafluoroborate* (**1**).—A benzene (5 cm^3) solution of the diphosphine L^1 (0.22 g) was added dropwise with stirring under N_2 to CH_2Cl_2 (5 cm^3) containing $[Rh(cod)_2]BF_4$ (0.40 g, 1.0 mmol). Diethyl ether (4 cm^3) was added dropwise to initiate precipitation. The solution was cooled at 0 °C for 24 h, whereupon (**1**) was obtained as air-stable orange crystals [0.25 g, m.p. 180 °C (decomp.)] in 47% yield. The product was soluble in CH_2Cl_2, but only slightly soluble in $CHCl_3$ (Found: C, 45.75; H, 5.95; P, 11.85. Calc. for $C_{40}H_{64}B_2F_8P_4Rh_2$: C, 45.85; H, 6.10; P, 11.80%). Crystals suitable for *X*-ray structural analysis were obtained by slow recrystallization from CH_2Cl_2–Et_2O.

Crystal Data for $[\{Rh(cod)\}_2(\mu\text{-}L^1)_2][BF_4]_2$ (**1**).—C_{40}-$H_{64}B_2F_8P_4Rh_2$, $M = 1\,048.27$, monoclinic, $a = 9.650(1)$, $b = 11.609(1)$, $c = 21.884(3)$ Å, $\beta = 117.07(1)°$, $U = 2\,183.0$ Å^3, $Z = 2$, $D_c = 1.595$ g cm^{-3}, $F(000) = 1\,072$, Cu-K_α radiation, $\lambda = 1.5418$ Å, μ(Cu-K_α) = 82 cm^{-1}. Space group $P2_1/c$ (C^5_{2h}) uniquely defined by the systematic absences: 0*k*0

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* *Supplementary data available* (No. SUP 56568, 10 pp.): thermal parameters, H-atom co-ordinates, torsion angles, least-squares planes data. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx.

Non-S.I. units employed: cal = 4.184 J, G = 10^{-4} T.

Table 1. Non-hydrogen fractional atomic co-ordinates ($\times 10^4$), with estimated standard deviations in parentheses

Atom	x	y	z
Rh	333.5(3)	488.0(2)	1 122.3(1)
P(1)	−1 552.9(9)	1 026.6(8)	52.9(4)
C(2)	−2 692(4)	2 348(3)	−35(2)
C(3)	−4 352(4)	2 046(4)	−542(2)
C(4)	−4 639(4)	956(4)	−743(2)
C(5)	−3 290(4)	121(4)	−430(2)
C(6)	−5 487(5)	3 022(5)	−740(2)
C(7)	−6 182(5)	448(5)	−1 239(3)
P(1′)	−663.9(10)	1 251.6(7)	−717.3(4)
C(2′)	984(4)	2 265(3)	−300(2)
C(3′)	350(4)	3 430(3)	−604(2)
C(4′)	−1 105(4)	3 458(3)	−1 115(2)
C(5′)	−1 989(4)	2 342(3)	−1 323(2)
C(6′)	1 427(5)	4 441(4)	−328(3)
C(7′)	−1 966(6)	4 499(4)	−1 509(3)
C(1″)	804(5)	2 326(3)	1 461(2)
C(2″)	−213(5)	1 954(4)	1 675(2)
C(3″)	225(6)	1 642(5)	2 411(2)
C(4″)	634(6)	425(5)	2 583(2)
C(5″)	1 411(5)	−166(4)	2 204(2)
C(6″)	2 579(4)	273(4)	2 084(2)
C(7″)	3 376(6)	1 431(4)	2 320(3)
C(8″)	2 537(7)	2 432(4)	1 876(3)
B	5 677(6)	3 217(5)	1 350(3)
F(1)	4 719(5)	2 540(3)	836(2)
F(2)	6 417(5)	2 593(3)	1 930(2)
F(3)	6 762(4)	3 719(3)	1 187(2)
F(4)	4 904(4)	4 076(4)	1 476(2)

when $k \neq 2n$, $h0l$ when $l \neq 2n$. Sample dimensions: $0.16 \times 0.16 \times 0.34$ mm.

Crystallographic Measurements.—Preliminary unit-cell parameters and space-group information were obtained by photographic (oscillation, Weissenberg, and precession) methods. Intensity data for one quadrant of reciprocal space to $\theta = 67°$ were recorded initially on an Enraf–Nonius CAD-3 diffractometer (Cu-K_α radiation, incident-beam Ni filter; θ—2θ scans) and subsequently on an Enraf–Nonius CAD-4 unit (Cu-K_α radiation, incident-beam graphite monochromator; ω—2θ scans). From a total of 3 871 non-equivalent measurements, 2 869 [$I > 2.0\sigma(I)$] and 3 434 [$I > 3.0\sigma(I)$] reflections were retained from the CAD-3 and CAD-4 data sets, respectively, for the structure analysis and corrected for the appropriate Lorentz and polarization effects. Empirical absorption corrections, based on the φ dependence of the intensities of reflections at χ *ca.* 90°, were also applied to these data. Refined unit-cell parameters were derived by least-squares treatment of the CAD-4 diffractometer setting angles for 25 high order ($59.9 < \theta < 66.6°$) reflections widely separated in reciprocal space.

Structure Analysis.—With $Z = 2$ in space group $P2_1/c$, an ordered complex cation is constrained to possess a crystallographic centre of symmetry. The crystal structure was solved by the heavy-atom approach using the CAD-3 data. Approximate co-ordinates for the Rh atom were derived from a Patterson map, and those for the remaining non-hydrogen atoms were obtained from the Rh-phased ($R = 0.38$) F_o Fourier synthesis. Full-matrix least-squares adjustment of positional and anisotropic thermal parameters reduced R to 0.090, at which point a difference Fourier synthesis revealed significant positive regions at the majority of positions calculated for hydrogen atoms, but those on the methyl groups were not clearly defined. With the inclusion of contributions for all non-methyl hydrogen atoms in the structure-factor calculations, further least-squares iterations led to convergence at $R = 0.083$. At this stage, a second data set from the same crystal was recorded on a CAD-4 diffractometer. Refinement of non-hydrogen atom parameters reduced R to 0.040, and a difference Fourier synthesis then revealed quite clearly positions for all hydrogen atoms. Several further cycles of least-squares adjustment of non-hydrogen atom positional and anisotropic thermal parameters, with hydrogen atoms included at their idealized calculated positions, led to convergence at $R = 0.033$. Final non-hydrogen atom positional parameters are in Table 1.

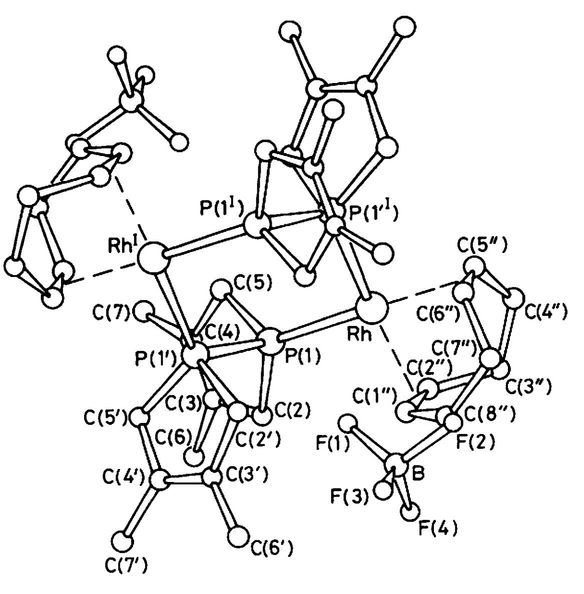

Figure 1. Molecular structure of $[\{Rh(cod)\}_2(\mu\text{-}L^1)_2][BF_4]_2$ (**1**). Roman numeral superscript I designates atoms related to the reference atoms by a crystallographic centre of symmetry

Neutral-atom scattering factors used in the structure-factor calculations and their anomalous dispersion corrections were taken from ref. 13. In the least-squares iterations, $\Sigma w\Delta^2$ [$w = 1/\sigma^2(|F_o|)$, $\Delta = ||F_o| - |F_c||$] was minimized.

Results and Discussion

The structure and solid-state conformation of the centrosymmetric complex $[\{Rh(cod)\}_2(\mu\text{-}L^1)_2][BF_4]_2$ (**1**), obtained from the reaction of L^1 with $[Rh(cod)_2]^+$, is shown in Figure 1. Interatomic distances and angles are given in Table 2. An important feature resulting from the complexation is the formation of a bimetallic, six-membered $\overline{RhPPRhPP}$ ring in a chair conformation.* That the carbon substituents on the phosphorus atoms assume true axial and equatorial character relative to the Rh_2P_4 ring is apparent from the projection along the P–P bond shown in Figure 2. There is no evidence for any BF_4^- interaction with the $[\{Rh(cod)\}_2(\mu\text{-}L^1)_2]^{2+}$ cation.

The P–P bond length at 2.227(1) Å is similar to the corresponding distance in a wide variety of P–P containing compounds, both free and co-ordinated to a transition metal.[14] For example, in diphosphine (P_2H_4) and the six-membered ring compound $(PPh)_6$, which also assumes a chair conformation, the P–P distances are 2.218(5)[15] and 2.237 Å,[16] respectively. For metal-co-ordinated diphosphine derivatives, the P–P bond length ranges from 2.231 Å in $[\{Fe(CO)_4\}_2(\mu\text{-}Me_2PPMe_2)]$[7] to 2.15 Å in polymeric $[\{CuBr(P_2Et_4)\}_\infty]$[8] which contains six-membered $\overline{CuPPCuPP}$ rings in chair conformations.

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* Endocyclic torsion angles: P(1′$^{\text{I}}$)–Rh–P(1)–P(1′) −66.0, Rh–P(1)–P(1′)–Rh$^{\text{I}}$ 78.1, P(1)–P(1′)–Rh$^{\text{I}}$–P(1$^{\text{I}}$) −63.7°.

Table 2. Interatomic distances (Å) and angles (°), with estimated standard deviations in parentheses[a,b]

(*a*) Distances			
(*i*) At the rhodium atom			
Rh–P(1)	2.303(1)	Rh ··· C(5″)	2.241(4)
Rh–P($1'^{I}$)	2.285(1)	Rh ··· C(6″)	2.244(3)
Rh ··· C(1″)	2.237(4)	Rh ··· M(1″—2″)	2.160(5)
Rh ··· C(2″)	2.284(5)	Rh ··· M(5″—6″)	2.136(4)
(*ii*) In L^1			
P(1)–C(2)	1.846(4)	P(1′)–C(2′)	1.851(4)
P(1)–C(5)	1.849(4)	P(1′)–C(5′)	1.858(3)
C(2)–C(3)	1.517(4)	C(2′)–C(3′)	1.508(5)
C(3)–C(4)	1.327(6)	C(3′)–C(4′)	1.339(4)
C(3)–C(6)	1.496(6)	C(3′)–C(6′)	1.500(5)
C(4)–C(5)	1.514(5)	C(4′)–C(5′)	1.503(5)
C(4)–C(7)	1.507(5)	C(4′)–C(7′)	1.497(5)
P(1)–P(1′)	2.227(1)		
(*iii*) In cod			
C(1″)–C(2″)	1.337(8)	C(4″)–C(5″)	1.512(8)
C(1″)–C(8″)	1.501(7)	C(5″)–C(6″)	1.367(7)
C(2″)–C(3″)	1.511(6)	C(6″)–C(7″)	1.518(6)
C(3″)–C(4″)	1.469(8)	C(7″)–C(8″)	1.495(7)
(*iv*) In BF$_4^-$			
B–F(1)	1.338(6)	B–F(3)	1.380(8)
B–F(2)	1.349(6)	B–F(4)	1.347(8)
(*b*) Angles			
(*i*) At the rhodium atom			
P(1)–Rh–P($1'^{I}$)	91.79(3)	P($1'^{I}$)–Rh–M(1″—2″)	173.7(1)
P(1)–Rh–M(1″—2″)	92.9(1)	P($1'^{I}$)–Rh–M(5″—6″)	91.5(1)
P(1)–Rh–M(5″—6″)	176.0(1)	M(1″—2″)–Rh–M(5″—6″)	84.0(2)
(*ii*) In L^1			
Rh–P(1)–P(1′)	113.72(4)	Rh^{I}–P(1′)–P(1)	111.07(4)
Rh–P(1)–C(2)	119.3(1)	Rh^{I}–P(1′)–C(2′)	120.9(1)
Rh–P(1)–C(5)	121.2(1)	Rh^{I}–P(1′)–C(5′)	119.9(1)
C(2)–P(1)–C(5)	94.1(2)	C(2′)–P(1′)–C(5′)	94.4(2)
C(2)–P(1)–P(1′)	103.9(1)	C(2′)–P(1′)–P(1)	104.0(2)
C(5)–P(1)–P(1′)	101.3(2)	C(5′)–P(1′)–P(1)	104.0(2)
P(1)–C(2)–C(3)	105.4(3)	P(1′)–C(2′)–C(3′)	105.5(2)
C(2)–C(3)–C(4)	117.0(3)	C(2′)–C(3′)–C(4′)	116.8(3)
C(2)–C(3)–C(6)	115.3(3)	C(2′)–C(3′)–C(6′)	117.1(3)
C(4)–C(3)–C(6)	127.7(3)	C(4′)–C(3′)–C(6′)	126.0(3)
C(3)–C(4)–C(5)	117.0(3)	C(3′)–C(4′)–C(5′)	117.8(3)
C(3)–C(4)–C(7)	126.9(4)	C(3′)–C(4′)–C(7′)	126.6(3)
C(5)–C(4)–C(7)	116.1(4)	C(5′)–C(4′)–C(7′)	115.6(3)
P(1)–C(5)–C(4)	105.3(3)	P(1′)–C(5′)–C(4′)	105.1(2)
(*iii*) In cod			
C(2″)–C(1″)–C(8″)	127.4(4)	C(4″)–C(5″)–C(6″)	126.5(4)
C(1″)–C(2″)–C(3″)	123.8(4)	C(5″)–C(6″)–C(7″)	126.8(5)
C(2″)–C(3″)–C(4″)	114.6(4)	C(6″)–C(7″)–C(8″)	115.3(3)
C(3″)–C(4″)–C(5″)	116.0(5)	C(1″)–C(8″)–C(7″)	117.0(5)
(*iv*) In BF$_4^-$			
F(1)–B–F(2)	110.1(5)	F(2)–B–F(3)	109.3(4)
F(1)–B–F(3)	110.2(5)	F(2)–B–F(4)	108.1(5)
F(1)–B–F(4)	111.8(4)	F(3)–B–F(4)	107.2(5)
(*c*) Cation ··· anion distances < 3.40 Å			
C(6″) ··· F(4^{II})	3.29	C(5″) ··· F(2^{II})	3.34
C(7′) ··· F(4^{IV})	3.31	C(2) ··· F(3^{III})	3.35
C(2″) ··· F(3^{III})	3.32	C(4″) ··· F(3^{II})	3.37
C(2′) ··· F(1)	3.33	C(8″) ··· F(4)	3.38
C(5) ··· F(1^{I})	3.33		

[a] Roman numeral superscripts refer to the following transformations of the co-ordinates in Table 1: I $-x, -y, -z$; II $1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$; III $-1 + x, y, z$; IV $-x, 1 - y, -z$. [b] M(1″—2″) and M(5″—6″) are the mid-points of the C(1″)–C(2″) and C(5″)–C(6″) bonds, respectively.

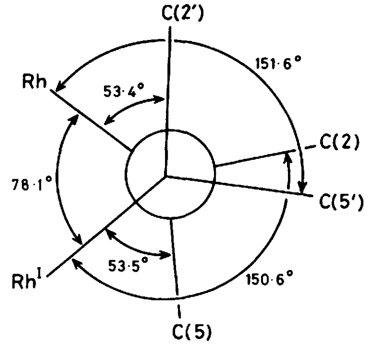

Figure 2. Projection view along the P(1)–P(1′) bond displaying the axial and equatorial positions assumed by the C(2) and C(5) substituents of L^1. Torsion angles obtained from data deposited in Supplementary Publication No. SUP 56568

Bond lengths and angles in the phosphole rings are close to those found previously in a Ni^{II} 2,5-dihydro-1-benzylphosphole complex.[17] In the present case, however, the phosphorus atom displacements from the least-squares planes through the phosphole ring carbon atoms not only differ significantly (0.209 and 0.115 Å to the opposite sides of the planes from their bonded Rh atoms) but also are much smaller than those encountered in the Ni^{II} complex (0.388 and 0.382 Å).

The Rh–P and Rh–C bond lengths lie in the normal range expected for rhodium(I)–bis(phosphine)–diene complexes.[18] Endocyclic torsion angles in the cod ring are related by an approximate C_2 symmetry axis [mean symmetry-related angles: C(8″)–C(1″)–C(2″)–C(3″) 3, C(1″)–C(2″)–C(3″)–C(4″) −87, C(2″)–C(3″)–C(4″)–C(5″) 29, C(3″)–C(4″)–C(5″)–C(6″) 45°] and the ring has a flexible twist-boat form. The Rh atom lies close (0.019 Å) to the least-squares plane through the mid-points [M(1″—2″) and M(5″—6″)] of the co-ordinated C=C bonds and the bonded phosphorus atoms [P(1) and P($1'^{I}$)], and thus the geometry of its inner co-ordination sphere is square planar; the small displacements of the centres defining the plane (0.059—0.070 Å) indicate that there is only a very slight distortion towards a tetrahedral arrangement. The dihedral angles between the P(1)–P($1'^{I}$)–M(1″—2″)–M(5″—6″) plane and those through the cod C–C=C–C moieties, at 85.2 and 88.1°, demonstrate that the C=C bonds lie approximately perpendicular to the co-ordination plane, but the Rh atom lies *ca.* 11° from each of the perpendiculars to the C–C=C–C groups thereby yielding a M(1″—2″)–Rh–M(5″—6″) bite angle of 84.0° [*vs.* 91.8° for the P(1)–Rh–P($1'^{I}$) angle].

Proton and ^{13}C n.m.r. spectra of (**1**) were obtained at room temperature and −27 °C (Table 3). Upon cooling to −27 °C most of the resonances are resolved into pairs of signals. Although the six-membered ring adopts the usual chair shape in the solid state (Figure 1), the n.m.r. spectral changes with temperature are consistent with a rapid ring inversion process (*a*) $\rightleftharpoons$ (*b*) at room temperature which is frozen out at −27 °C. This inversion causes phosphorus substituents to exchange between axial and equatorial positions as shown below.

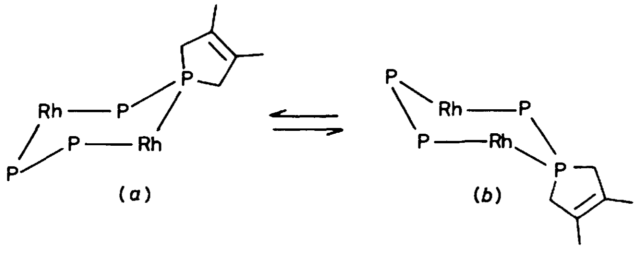

Table 3. Proton and ^{13}C n.m.r. peak assignments for $[\{Rh(cod)\}_2(\mu\text{-}L^1)_2][BF_4]_2$ (**1**)

	$\delta(^1H)$/p.p.m.		$\delta(^{13}C)$/p.p.m.	
	25 °C	−27 °C	24 °C	−27 °C
(*a*) cod				
$-CH_2-$	2.45	2.44	36	33, 41
$-CH-$	5.10	5.01, 5.14	101	98, 104
(*b*) L^1				
$-CH_3$	1.71	1.69, 1.73	15.9	15.9
$-CH_2-$	2.99	3.17	31.1	31.0, 31.3
$-C-$	—	—	131.2	130.0, 130.4

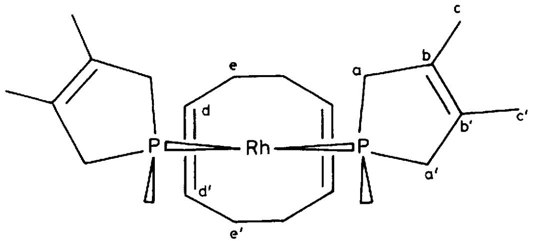

Figure 3. View of the Rh co-ordination shell from the perspective of the ligating atoms

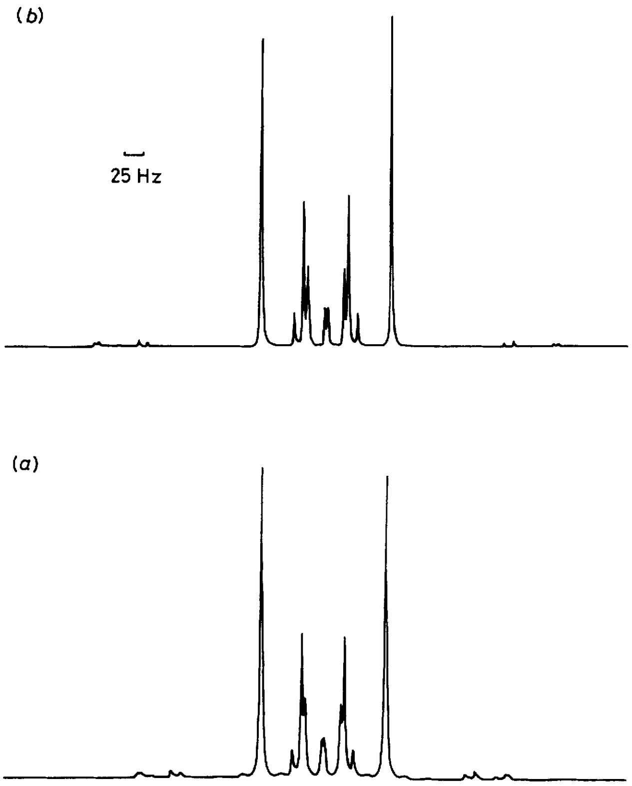

Figure 4. $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of $[\{Rh(cod)\}_2(\mu\text{-}L^1)_2][BF_4]_2$ (**1**) obtained in CD_2Cl_2 (*a*) and a computer simulated spectrum (*b*) produced using the following coupling constants (Hz): $^1J_{PP} = +212$, $^1J_{RhP} = -145$, $^2J_{PRhP} = -25$, $^2J_{RhPP} = 0$, $^3J_{PRhPP} = +42$, and $^3J_{RhPPRh} = 0$

Figure 3 illustrates the lack of symmetry with respect to the Rh co-ordination plane for a single conformation of the six-membered ring. This is a result of the substituents of the dihydrophosphole ring being in different chemical environments (*i.e.* axial and equatorial sites). Therefore, while resonances from primed and non-primed (Figure 3) atomic positions are identical at room temperature due to equivalence afforded by rapid ring inversion, non-equivalent resonances are observed when a single conformation is frozen out at −27 °C (Table 3).

Variable-temperature spectra were obtained for the cod olefinic protons to obtain a coalescence temperature (T_c) of $-2(\pm 2)$ °C. A free energy of activation $\Delta G^{\ddagger}_{271}$ of $14.0(\pm 0.2)$ kcal mol^{-1} was calculated using the olefinic proton signal separation at the limit of no exchange [$\Delta\nu = 12.1(0.3)$ Hz at −55 °C]. This activation barrier is not exceptional for highly substituted six-membered ring systems. $\Delta G^{\ddagger}_{285}$ for ring inversion of 3,3,6,6-tetramethyl-1,2-dioxane[19] is 14.5 kcal mol^{-1} ($\Delta\nu = 11.6$ Hz) and $\Delta G^{\ddagger}_{271}$ for a similar process in 3,3,6,6-tetramethyl-1,2-dithiane[19] is 13.6 kcal mol^{-1} ($\Delta\nu = 13.9$ Hz).

The ^{31}P n.m.r. spectrum of (**1**) presented in Figure 4 is centred at 18.7 p.p.m. downfield from external H_3PO_4 and represents a co-ordination shift ($\Delta\delta$) for the diphosphine of +61.3 p.p.m.[11] The complex pattern of resonance arises from magnetic non-equivalence of the ^{31}P and ^{103}Rh nuclei which results in a AA′A″A‴XX′ (A = ^{31}P, X = ^{103}Rh) spin system. The spectrum is independent of temperature (25 to −90 °C) and field strength (21 and 58 kG). This is consistent with a ring inversion process as discussed above since the chemical environment and relative orientations of coupled nuclei within the six-membered ring skeletons are not significantly changed.

Interpretation of the ^{31}P part of the spectrum is aided by computer simulation (Figure 4) which makes use of the internuclear coupling parameters listed in the figure legend. The magnitudes of $^1J_{RhP}$ and $^2J_{PRhP}$ in (**1**) are comparable to those in similar $[Rh(cod)(PR_3)_2]^+$ complexes. Thus $^1J_{RhP}$ in $[Rh(cod)(PPh_3)_2]^+$ is 146.5 Hz and $^1J_{RhPPh_3}$, $^1J_{RhPBu_3}$, and $^2J_{PRhP}$ in $[Rh(cod)(PPh_3)(PBu^n{}_3)]^+$ are 149, 137, and 29 Hz respectively.[20] The relative signs of the coupling constants for (**1**) are specific to the simulation, while the assignment of absolute signs is made by comparison to the literature which reports $^1J_{RhP}$ and $^2J_{PRhP}$ to be negative[21] and $^1J_{PP}$ to be either positive or negative.[22] Much of the complexity of the ^{31}P spectrum arises from non-zero values of the parameter $^nJ_{PP}$ (n = 1, 2, or 3), whereas the spectra of related compounds (six-membered ring structures of PNbPPNbP,[4] PCPPCP,[23] PSiPPSiP,[24] PNPPNP,[25] and PVPPVP[6a]) exhibit singlets.

The data in Table 4 may be used to compare the co-ordination bonding of the diphosphine L^1 used in this study with other phosphine ligands. These data illustrate that olefinic ^{13}C chemical shifts of co-ordinated cod in $[Rh(cod)L_cL_t]^{n+}$ complexes are sensitive to the nature of the *cis* and *trans* ligands (L_c and L_t). This is as expected assuming the validity of the Dewar–Chatt–Duncanson bonding model[26,27] for rhodium–olefin co-ordination. The compounds are arranged in order of increased shielding of the olefinic carbon atoms of co-ordinated cod. Ligands which compete for the π symmetry electron density on rhodium (*e.g.* phosphines) deshield the co-ordinated olefin. Data in Table 4 illustrate that the cod olefinic ^{13}C chemical shift may be used as a probe for the electronic characteristics of the ligands L_c and L_t and that the *trans* ligand has the largest influence. The cod chemical shift for (**1**) suggests that diphosphine L^1 behaves in the normal fashion expected for tertiary phosphines, and has the most deshielding influence of the bis(tertiary phosphine) complexes listed.

Table 4. Cyclo-octa-1,5-diene olefinic ^{13}C chemical shifts for a series of rhodium complexes $[Rh(cod)L_cL_t]^{n+}$

Compound	L_t[a]	L_c[b]	$\delta(^{13}C)$/p.p.m.	Ref.
$[Rh(cod)_2]BF_4$	$>C{=}C<$	$>C{=}C<$	108.0	20
$[Rh(cod)(PPh_3)Cl]$	PPh_3	Cl	105.1	20
$[\{Rh(cod)\}_2(\mu\text{-}L^1)_2][BF_4]_2$	L^1	L^1	101	This work
$[Rh(cod)(dppb)]BF_4$[c]	PPh_2R	PPh_2R	100.1	20
$[Rh(cod)(PPh_3)_2]BF_4$	PPh_3	PPh_3	99.0	20
$[Rh(cod)(PBu^n{}_3)_2]BF_4$	$PBu^n{}_3$	$PBu^n{}_3$	94.7	20
$[Rh(cod)(dt)]PF_6$[d]	$S<$	$S<$	89.6	*e*
$[Rh(cod)(NCCH_3)_2]BF_4$	$NCCH_3$	$NCCH_3$	83.5	20
$[\{Rh(cod)\}_2(\mu\text{-}pz)_2]$[f]	$\mu\text{-}N_2C_3H_3$	$\mu\text{-}N_2C_3H_3$	81.3	*g*
$[Rh(cod)(C_5Cl_5)]$	C_5Cl_5		80.4	*h*
$[\{Rh(cod)\}_2(\mu\text{-}Cl)_2]$	μ-Cl	μ-Cl	78.6	*i*
$[Rh(cod)(CH_2PBu^t{}_2)]$	$-CH_2PBu^t{}_2$	$-CH_2PBu^t{}_2$	78.5	*j*
$[Rh(cod)(hfacac)]$[k]	$O{=}C<$	$O{=}C<$	78.2	*l*
$[Rh(cod)(acac)]$[m]	$O{=}C<$	$O{=}C<$	75.9	*l*
$[\{Rh(cod)\}_2(\mu\text{-}Me)_2]$	μ-Me	μ-Me	75.3	*n*
$[Rh(cod)(PPh_3)Cl]$	Cl	PPh_3	70.1	20
$[Rh(cod)(C_5H_5)]$	C_5H_5		62.3	*l*

[a] Ligand or part thereof *trans* to the co-ordinated olefin whose ^{13}C chemical shift is listed. [b] Ligand or part thereof *cis* to the co-ordinated olefin whose ^{13}C chemical shift is listed. [c] dppb = 1,4-Bis(diphenylphosphino)butane. [d] dt = 1,4-Dithiane. [e] M. J. H. Russell, C. White, A. Yates, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1978, 849. [f] pz = Pyrazolate. [g] J. Elguero, M. Esteban, M. F. Grenier-Lonstalot, L. A. Oro, and M. T. Pinillos, *J. Chim. Phys. Phys.-Chim. Biol.*, 1984, **81**, 251. [h] K. J. Reimer and A. Shaver, *Inorg. Chem.*, 1975, **14**, 2707. [i] R. Bonnaire and N. Platzer, *J. Organomet. Chem.*, 1976, **104**, 107. [j] H. Schmidbaur, G. Blaschke, H. J. Füller, and H. P. Scherm, *J. Organomet. Chem.*, 1978, **160**, 41. [k] hfacac = Hexafluoroacetylacetonate. [l] G. M. Bodner, B. N. Storhoff, D. Doddrell, and L. J. Todd, *Chem. Commun.*, 1970, 1530. [m] acac = Acetylacetonate. [n] G. F. Schmidt, E. L. Muetterties, M. A. Beno, and J. M. Williams, *Proc. Natl. Acad. Sci. U.S.A.*, 1981, **78**, 1318.

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