DALTON

Mixed phosphito–phosphonato rhodium(I) complexes

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O,O'-3,3'-Di-*tert*-butyl-5,5'-dimethoxy-1,1'-biphenyl-2,2'-diyl phosphonate (HL) **I** was prepared by hydrolysis of (3,3'-di-*tert*-butyl-5,5'-dimethoxy-1,1'-biphenyl-2,2'-diyl)phosphorus chloride. Its tautomeric equilibrium with the corresponding phosphite form was completely shifted toward the phosphonate form. The reaction of **I** with the solvato complex $[Rh(C_8H_{12})(thf)_2]ClO_4$ (C_8H_{12} = cycloocta-1,5-diene, thf = tetrahydrofuran), in thf, in the molar ratio 2:1, afforded the rhodium(I) complex $[Rh(HL)L(C_8H_{12})]$ containing **I** co-ordinated both as a phosphonate and phosphite ligand. Carbon monoxide replaces the C_8H_{12} ligand of **1** to afford the corresponding dicarbonyl species **2**. The latter was better obtained by treating $[Rh(acac)(CO)_2]$ (acac = acetylacetonate) with **I**, in benzene solution, in the molar ratio 1:2. The $^{31}P-\{^1H\}$ NMR spectra indicate for **1** and **2** the existence either of a P–OH to P=O proton-exchange process faster than the NMR time-scale or of a symmetrical O $\cdots$ H $\cdots$ O bridge. The existence of a symmetrical O $\cdots$ H $\cdots$ O bridge was confirmed by treating **2** with $BF_3 \cdot Et_2O$. The acidic character of the hydrogen of the O $\cdots$ H $\cdots$ O framework was also confirmed treating **2** with NaOH. The reaction of the resulting anionic species with the solvato species $[Rh(C_8H_{12})(thf)_2]ClO_4$ afforded a binuclear dirhodium(I) zwitterionic compound $[Rh_2L_2(C_8H_{12})_2]$ containing bridging phosphonate ligands both bonded to a rhodium(I) centre through the phosphorus atoms and to the other one through the oxygen atoms. Attempts to crystallize **1** from a dilute diethyl ether–dichloromethane (4:1) solution also afforded the binuclear complex in low yield. Its crystal structure has been determined by single-crystal X-ray diffraction. Under catalytic hydroformylation conditions, the complexes lose the phosphorus-containing moieties to give the catalyst $[RhH(CO)_4]$.

Recently[1] we have obtained promising results in the enantioselective hydroformylation of olefins using as precatalysts cationic rhodium(I) complexes containing the new chiral bidentate P,N ligand 2-(3-phosphinoxy-3-menthyl)pyridine.

Also operating under rigorously anhydrous conditions, our attempts to obtain a P,N-chiral ligand in which the PPh_2 group was replaced by a phosphorus-bound 3,3'-*tert*-butyl-5,5'-dimethoxy-1,1'-biphenyl-2,2'-diyl group failed, and 3-(2-pyridyl)-3-menthol and compound **I** were obtained as hydrolysis products (Scheme 1). Probably the extensive hydrolysis was favoured by the large steric hindrance from the bulky *tert*-butyl substituents. Analogously, van Leeuwen and co-workers[2] were unable to synthesize tetra-4,4',6,6'-*tert*-butyl-substituted 2,2'-biphenyldiol diphosphite ligands based on chiral diols, monosubstituted diols being formed in the presence of a considerable amount of hydrolysed phosphorus chlorides.

We report here the synthesis of the phosphonate **I** starting from PCl_3 and 3,3'-*tert*-butyl-5,5'-dimethoxy-2,2'-biphenyldiol and its reactions with rhodium(I) substrates; the crystal structure of a binuclear dirhodium(I) zwitterionic compound, containing bridging phosphonate ligands bonded to one metal through the phosphorus atoms and to other through the oxygen atoms, is also reported. van Leeuwen and co-workers[3,4] observed that platinum–diphenylphosphine oxide systems catalyse the hydroformylation of hept-1-ene and, more significantly, hept-2-ene yielding products of high linearity. Besides, Alper and Sommovigo[5] developed a palladium-based catalyst, characterized as $[Pd(O_2PBu^t_2)\{PBu^t_2(OH)OPBu^t_2\}]$,[6] which catalyses selectively the hydrogenation of the double carbon–carbon bond of α,β-unsaturated carbonyl compounds.

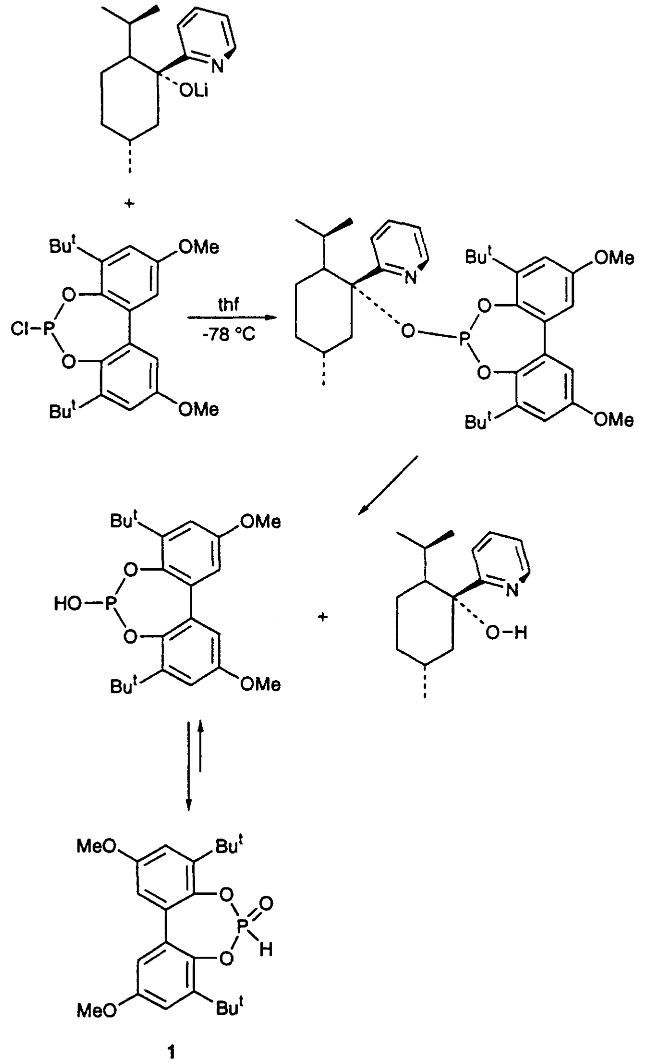
Experimental

Established methods were used to prepare the compounds $[\{Rh(C_8H_{12})(\mu\text{-}Cl)\}_2]$[7] and (3,3'-di-*tert*-butyl-5,5'-dimethoxy-1,1'-biphenyl-2,2'-diyl)phosphorus chloride.[8] All other reagents were obtained commercially and used as supplied. Solvents were dried by standard procedures. All experiments were performed under an atmosphere of purified nitrogen. Infrared spectra were recorded as Nujol mulls on KBr or CsI plates using a Perkin-Elmer FTIR 1720 spectrophotometer, ^1H and $^{31}P-\{^1H\}$ NMR spectra on a Bruker AMX R300 and ^{19}F NMR spectra on a Varian-Gemini 300 MHz spectrometer. The ^1H NMR spectra were referenced to internal tetramethylsilane, ^{19}F to $CFCl_3$ and $^{31}P-\{^1H\}$ to external 85% H_3PO_4; positive chemical shifts to higher frequency. Gas chromatographic analyses were run on a Carlo Erba HRGC 5160 Mega Series apparatus (split/splitless injector, MEGA OV1 25 m column, film thickness 2 μm, carrier gas He, flame ionization detector). Elemental analyses were performed by Redox s.n.c., Cologno Monzese, Milano.

Preparations

***O,O'*-3,3'-Di-*tert*-butyl-5,5'-dimethoxy-1,1'-biphenyl-2,2'-diyl phosphonate I.** This compound was obtained by hydrolysis of (3,3'-di-*tert*-butyl-5,5'-dimethoxy-1,1'-biphenyl-2,2'-diyl)phosphorus chloride (20 g, 24 mmol) in ethanol (100 cm^3). After evaporation of the solvent at reduced pressure, **I** was obtained as a white solid, almost quantitatively. Yield 9.23 g (95%) (Found: C, 65.4; H, 7.2. $C_{44}H_{57}O_{10}P_2$ requires C, 65.4; H, 7.1%). NMR ($CDCl_3$): ^1H, δ 1.55 [18 H, s, $C(CH_3)_3$], 3.40 (6 H, s, OCH_3) and 7.2 (1 H, d, PH, $^1J_{PH}$ 728.3); ^{31}P, δ 11.2 (d, J_{PH} 728.3 Hz).

Complex 1. A solution of compound **I** (0.486 g, 0.12 mmol) in tetrahydrofuran (thf) (10 cm^3) was added to a solution of $[Rh(C_8H_{12})(thf)_2]ClO_4$ (obtained by adding $AgClO_4$ (0.124 g, 0.6 mmol) to a solution of $[\{Rh(C_8H_{12})Cl\}_2]$ (0.150 g, 0.30 mmol) in thf and following filtration of the AgCl precipitate) in the same solvent (20 cm^3). The reaction mixture was left to stir for 20 h. The solution was filtered and the solvent evaporated at reduced pressure to a volume of 10 cm^3. Addition of hexane



Scheme 1

produced an orange solid which was separated and crystallized several times from dichloromethane–hexane to give the product **1**. Yield 0.385 g (63%) (Found: C, 59.55; H, 6.7. $C_{52}H_{69}O_{10}P_2Rh$ requires C, 61.3; H, 6.85%). NMR ($CDCl_3$): ^1H, δ 1.59 [36 H, s, $C(CH_3)_3$], 2.02 (8 H, br, C_8H_{12}), 3.78 (12 H, s, OCH_3), 5.18 (4 H, br, C_8H_{12}), 6.58 (4 H, d, C_6H_2, J_{HH} 2.8) and 6.97 (4 H, d, C_6H_2, J_{HH} 2.8 Hz); $^{31}P-\{^1H\}$, δ 119.9 (d, J_{RhP} 237.9 Hz).

Reaction of complex 1 with CO. Carbon monoxide was slowly bubbled into a CH_2Cl_2 (15 cm^3) solution of complex **1** (0.11 g, 0.108 mmol) for 30 min. During this time the solution turned from yellow-orange to yellow, while the IR spectrum showed the appearance of ν(CO) bands at 2097 and 2054 cm^{-1}. On adding hexane to the solution compound **2** was obtained as a yellow solid. This was filtered off, washed with hexane and dried. Yield 0.094 g (90%) (Found: C, 56.9; H, 5.95. $C_{46}H_{57}O_{12}P_2Rh$ requires C, 57.15; H, 5.95%). IR (KBr, CH_2Cl_2)/cm^{-1} 2105, 2071 [ν(C=O)]. NMR ($CDCl_3$): ^1H, δ 1.45 [36 H, s, $C(CH_3)_3$], 3.75 (12 H, s, OCH_3), 6.61 (4 H, d, C_6H_2, J_{HH} 2.8) and 6.99 (4 H, d, C_6H_2, J_{HH} 2.8 Hz); $^{31}P-\{^1H\}$, δ 116.7 (d, J_{RhP} 196.8 Hz).

Complex 2. A benzene solution (10 cm^3) of compound **I** (0.251 g, 0.620 mmol) was added to a solution (20 cm^3) of [Rh(acac)$(CO)_2$] (0.08 g, 0.310 mmol) in the same solvent. The reaction mixture was left to stir for about 2 h. During this time the solution turned yellow. It was filtered and the solvent evaporated at reduced pressure to a volume of 10 cm^3; on adding hexane the product was obtained as a yellow solid. It was filtered off, washed with hexane and dried. Yield 0.255 g (85%) (Found: C, 57.2; H, 5.95. $C_{46}H_{57}O_{12}P_2Rh$ requires C, 57.15; H, 5.95%).

Complex 3. To a yellow solution containing complex **1** (0.154 g, 0.16 mmol) in CH_2Cl_2 (5 cm^3) was added $BF_3{\cdot}Et_2O$ (4 cm^3). The resultant solution was reduced to 1 cm^3 and diethyl ether (20 cm^3) added. The crude yellow solid was collected and recrystallized from CH_2Cl_2–Et_2O to give **3** as a yellow solid. Yield 0.049 g (30%) (Found: C, 54.5; H, 5.6. $C_{46}H_{56}BF_2O_{12}P_2Rh$ requires C, 54.5; H, 5.55%). IR (KBr, CH_2Cl_2)/cm^{-1} 2058, 2090 [ν(C=O)]. NMR ($CDCl_3$): ^{19}F, δ −138.5 (br s); $^{31}P-\{^1H\}$, δ 111.4 (d, J_{RhP} 198.7 Hz).

Complex 4. An aqueous NaOH solution (2 mol dm^{-3}, 0.073 cm^3, 0.147 mmol) was added, with stirring, to a solution of complex **1** (0.15 g, 0.147 mmol) in thf (20 cm^3). After 10 min a solution of $[Rh(C_8H_{12})(thf)_2]ClO_4$ {obtained by adding $AgClO_4$ (0.030 g, 0.147 mmol) to a solution of $[\{Rh(C_8H_{12})Cl\}_2]$ (0.036 g, 0.0735 mmol) in thf (15 cm^3) and filtration of AgCl} was added to the reaction mixture. After 10 min the orange solution was filtered and the volume reduced to *ca.* 10 cm^3; on adding hexane an orange product was obtained. This was filtered off, dissolved in CH_2Cl_2 and dried over Na_2SO_4. The solvent was evaporated under reduced pressure to 10 cm^3; on adding hexane the product **4** was obtained as an orange solid. Yield 0.176 g, 86% (Found: C, 58.55; H, 6.8. $C_{60}H_{80}O_{10}P_2Rh_2$ requires C, 58.65; H, 6.55%). NMR ($CDCl_3$): ^1H, δ 1.71 [36 H, s, $C(CH_3)_3$], 3.51 (4 H, br, C_8H_{12}), 3.78 (12 H, s, OCH_3), 4.7 (4 H, br, C_8H_{12}), 6.62 (4 H, d, C_6H_2, J_{HH} 2.8) and 6.96 (4 H, d, C_6H_2, J_{HH} 2.8 Hz); $^{31}P-\{^1H\}$, δ 113.5 (d, J_{RhP} 243.4 Hz).

Compound **4**·$2CH_2Cl_2$ was also obtained, in low yield, as orange crystals, on standing of a dilute diethyl ether–dichloromethane (4:1) solution of **1** for some days. Yield 32% (Found: C, 53.25; H, 6.1. $C_{62}H_{84}Cl_4O_{10}P_2Rh_2$ requires C, 53.2; H, 6.05%).

Catalytic runs

All catalytic runs were performed with a Berghoff stainless-steel autoclave (100 cm^3) equipped with gas and liquid inlets, a heating device, and magnetic stirring. The reactions were carried out in a Teflon vessel fitted to the internal wall of the autoclave, thus preventing undesirable effects due to the metal of the reactor. The autoclave was closed and degassed by three vacuum and nitrogen purge cycles. A solution of the starting complex and of the olefin (in a typical experiment 5 mmol of substrate and 0.01 mmol of complex), in benzene (10 cm^3), was introduced under nitrogen, and gases (H_2:CO 1:1) were admitted to the desired pressure. At the end of each catalytic run the autoclave was cooled in a cold water-bath and slowly vented. A sample of the homogeneous reaction mixture was then analysed by gas chromatography.

Crystallography

Orange crystals of complex **4**·$2CH_2Cl_2$ suitable for X-ray analysis were obtained from diethyl ether–dichloromethane (4:1) solution. Diffraction data were collected at room temperature on a Siemens *R*3*m*/*V* automatic four-circle diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å). Cell parameters were obtained from least-squares refinement of the setting angles of 32 reflections with $14 \leqslant 2\theta \leqslant 28°$. A summary of the crystallographic data and the structure refinement is reported in Table 1. 7495 Independent reflections were obtained from 11 488 measurements (R_{int} = 0.0266) collected up to 2θ = 55° by the variable-speed ω-scan method. The intensities of three standard reflections, monitored after every 97 measurements, decreased

Table 1 Crystallographic data for compound **4**·2CH$_2$Cl$_2$

Formula	$C_{62}H_{84}Cl_4O_{10}P_2Rh_2$
M	1398.85
Colour, crystal form	Orange, prismatic
Crystal size/mm	0.30 × 0.30 × 0.12
Crystal system	Monoclinic
Space group	$C2/c$ (no. 15)
a/Å	18.188(3)
b/Å	13.611(4)
c/Å	27.580(7)
β/°	108.14(2)
U/Å^3	6489(3)
Z	4
F(000)	2896
D_c/g cm^{-3}	1.432
μ(Mo-Kα)/mm^{-1}	0.777
Transmission factors	0.784–0.902
2θ Range/°	3–55
No. data collected/unique	11 488/7495
No. observed data [$F \geqslant 7\sigma(F)$], N_o	3166
No. variables, N_v/restraints	357/12
R (observed/all)	0.0420/0.0907
R' (observed/all), on F^2	0.1106/0.1343
Goodness of fit * (observed/all)	1.134/0.837
Maximum, minimum, $\Delta\rho$/e Å^{-3}	0.791/−0.631

* $[\Sigma w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$.

Table 2 Selected bonds (Å) and angles (°) for compound **4**·2CH$_2$Cl$_2$; X(1) and X(2) represent the centres of the C(1)=C(2) and C(5)=C(6) bonds, respectively. Primed atoms are related by the symmetry operator $-x + 1, y, -z + \frac{1}{2}$

Rh(1)–O(1)	2.077(3)	Rh(2)–P(1)	2.294(1)
Rh(1)–C(1)	2.088(5)	Rh(2)–C(5)	2.224(4)
Rh(1)–C(2)	2.082(5)	Rh(2)–C(6)	2.245(4)
Rh(1)–X(1)	1.967(6)	Rh(2)–X(2)	2.131(5)
C(1)–C(2)	1.384(8)	C(5)–C(6)	1.343(7)
C(2)–C(3)	1.516(8)	C(6)–C(7)	1.511(7)
C(3)–C(4)	1.447(9)	C(7)–C(8)	1.484(8)
C(4)–C(1′)	1.500(8)	C(8)–C(5′)	1.508(7)
O(1)–P(1)	1.504(3)	C(14)–C(20)	1.491(6)
P(1)–O(2)	1.635(3)	P(1)–O(3)	1.639(3)
O(2)–C(9)	1.408(5)	O(3)–C(21)	1.402(5)
C(10)–C(15)	1.531(6)	C(22)–C(26)	1.547(6)
C(15)–C(17)	1.518(7)	C(26)–C(28)	1.527(7)
C(15)–C(16)	1.542(8)	C(26)–C(27)	1.544(7)
C(15)–C(18)	1.537(6)	C(26)–C(29)	1.520(8)
C(12)–O(4)	1.374(5)	C(24)–O(5)	1.373(6)
O(4)–C(19)	1.413(6)	O(5)–C(30)	1.406(6)
O(1)–Rh(1)–X(1)	90.1(2)	P(1)–Rh(2)–X(2′)	93.74(1)
X(1)–Rh(1)–X(1′)	88.8(2)	X(2)–Rh(2)–X(2′)	84.7(2)
O(1)–Rh(1)–O(1′)	90.9(2)	P(1)–Rh(2)–P(1′)	87.96(6)
O(1)–Rh(1)–X(1′)	178.8(2)	P(1)–Rh(2)–X(2)	176.5(1)
C(2)–C(1)–C(4′)	123.6(6)	C(6)–C(5)–C(8′)	124.5(5)
C(1)–C(2)–C(3)	125.6(6)	C(5)–C(6)–C(7)	125.5(5)
C(4)–C(3)–C(2)	115.3(5)	C(8)–C(7)–C(6)	114.9(5)
C(3)–C(4)–C(1′)	114.8(5)	C(7)–C(8)–C(5′)	117.4(5)
C(12)–O(4)–C(19)	117.8(4)	C(24)–O(5)–C(30)	117.2(4)
P(1)–O(1)–Rh(1)	126.2(2)	O(1)–P(1)–Rh(2)	120.5(1)
O(2)–P(1)–Rh(2)	109.6(1)	O(3)–P(1)–Rh(2)	114.6(1)
C(9)–O(2)–P(1)	122.0(3)	C(21)–O(3)–P(1)	123.8(3)
O(1)–P(1)–O(2)	106.3(2)	O(1)–P(1)–O(3)	101.7(2)
O(2)–P(1)–O(3)	102.3(1)		

by almost 11% from their initial values. The reflection intensities were evaluated by a profile fitting among 2θ shells[9] and then corrected for Lorentz-polarization and decay effects. The Gaussian method was used for absorption correction by using experimental crystal shape determination. The systematic absences *hkl* with $h + k$ odd and *h*0*l* with *h* and *l* odd pointed out to the monoclinic space groups *C*2*c* and *Cc*. Statistical and density considerations suggested the centric packing with the molecule in special position, as confirmed by the following model.

The structure was solved by standard Patterson methods and subsequently completed by a combination of least-squares techniques and Fourier syntheses by using the SHELXTL PLUS system[10] (also used to perform data reduction). Then the refinement of the model was continued with SHELXL 93[11] by full-matrix least squares based on F^2 values. The difference syntheses revealed significant electron-density residuals which were interpreted as one co-crystallized dichloromethane molecule. This appeared quite disordered, as evidenced by the large displacement parameters and the surrounding electron residuals, and some weak restraints were adopted (both anisotropic chlorines were forced to approximate isotropic behaviour). Whereas several hydrogens were located on the final Δ*F* map, the H atoms were included in the refinement using the 'riding' model method with the C–H bond geometry depending on the parent carbon and with a unique common fixed isotropic displacement parameter (0.080 Å^2). The refinement, minimizing the function $\Sigma w(F_o^2 - F_c^2)^2$ and with all non-H atoms anisotropic except the dichloromethane carbon, converged to $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.0420$ and $R' = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}} = 0.1106$ for 3166 observed reflections [$F_o \geqslant 7\sigma(F_o)$] with the final weighting scheme $w^{-1} = \{\sigma^2(F_c^2) + [0.0228(F_o^2 + 2F_c^2)]^2\}$. In the last Fourier difference map the most significant density residuals (ranging from −0.631 up to 0.791 e Å^{-3}) were located around the disordered solvent molecule. Any attempt to interpret them as further CH$_2$Cl$_2$ orientations were unsuccessful. Neutral-atom scattering factors and anomalous dispersion corrections were from ref. 12.

Final geometrical calculations and drawings were carried out with the PARST program[13] and the XP utility of the Siemens package, respectively. All the research and statistical analysis on literature structures were performed by the Cambridge Structural Database (release 5.10).[14] Selected bond distances and angles are listed in Table 2. An ORTEP[15] view of the binuclear complex, with the corresponding atom-labelling scheme, is shown in Fig. 1, while Fig. 2 depicts the crystal packing.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/238.

Results and Discussion

The phosphonate compound **I** was obtained as a white solid by hydrolysis of (3,3′-di-*tert*-butyl-5,5′-dimethoxy-1,1′-biphenyl-2,2′-diyl)phosphorus chloride; the latter compound was prepared, following a literature method,[8] by treating lithium 3,3′-*tert*-butyl-5,5′-dimethoxy-2,2′-biphenyldiolate with PCl$_3$ in the presence of 1-methylpyrrolidin-2-one. The ^{1}H NMR spectrum of **I**, in CDCl$_3$ solution, shows resonances at δ 1.55 and 3.40, as singlets, due to the Bu^t and OMe groups respectively, and, significantly, a doublet at δ 7.20 (J_{PH} 728.3 Hz) due to P–H; in accord, the ^{1}H-coupled ^{31}P NMR spectrum, in CDCl$_3$ solution, exhibits a doublet at δ 11.2 ($^1J_{PH}$ 728.3 Hz). The absence of other detectable peaks in the NMR spectra indicates that the expected[16,17] tautomeric equilibrium between **I** and the corresponding phosphite form is shifted far towards the phosphonate. A complete shift of the tautomeric equilibrium to the more stable[16,17] phosphonate was considered to occur in analogous systems. The presence of a phosphite form in tautomeric equilibrium with phosphonate was considered in spite of the lack of NMR evidence to explain fundamental reactions.[17b,c]

The reaction of compound **I** with the solvato complex

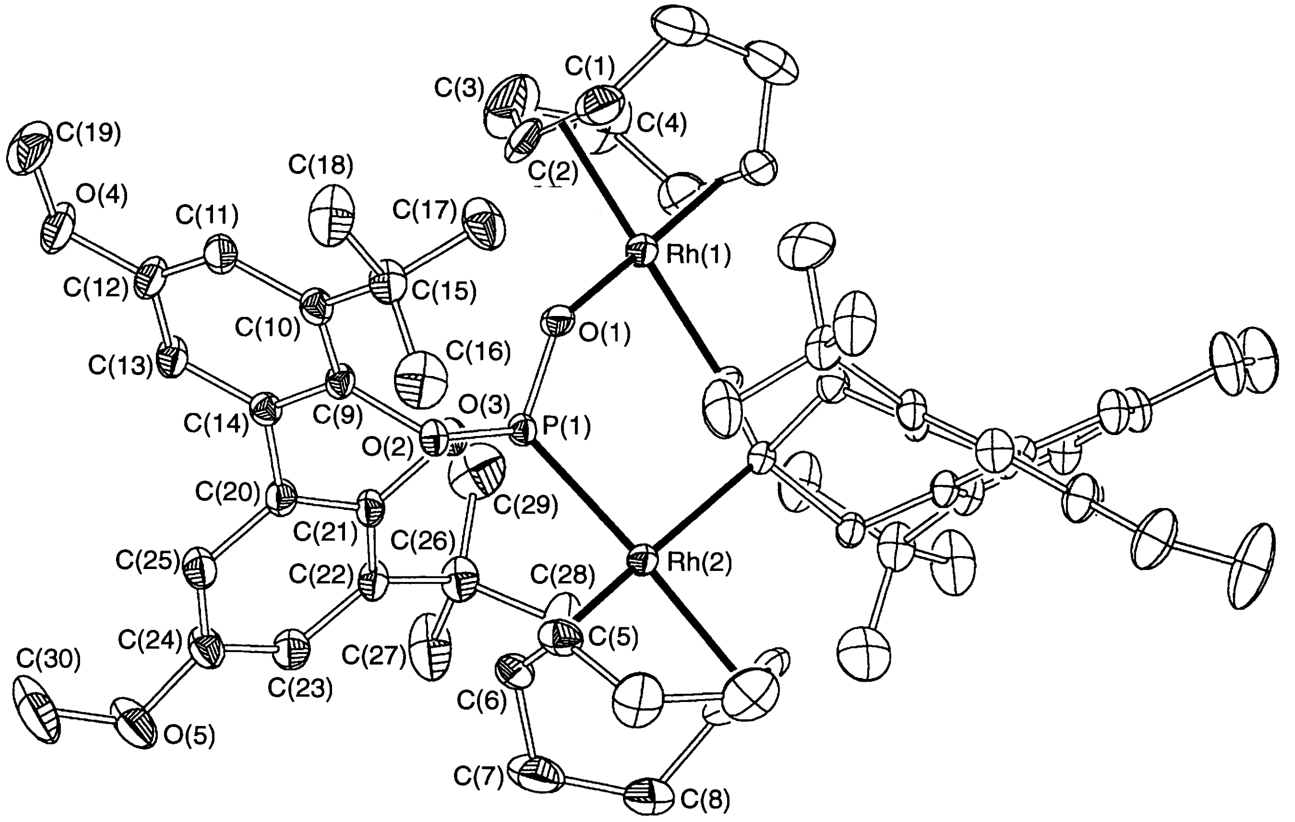


Fig. 1 View of the whole molecule $4 \cdot 2CH_2Cl_2$ lying on the crystallographic glide *c* through the two metal centres. The numbering scheme is shown for the asymmetric unit only. Thermal ellipsoids are drawn at 25% probability. Hydrogen atoms and the two cocrystallized CH_2Cl_2 molecules are omitted for clarity

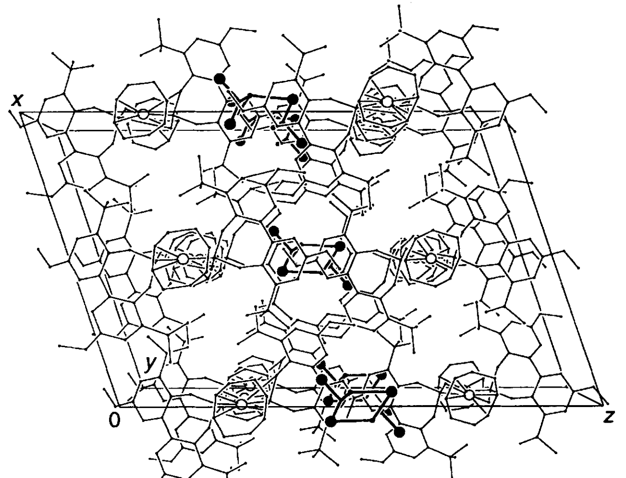


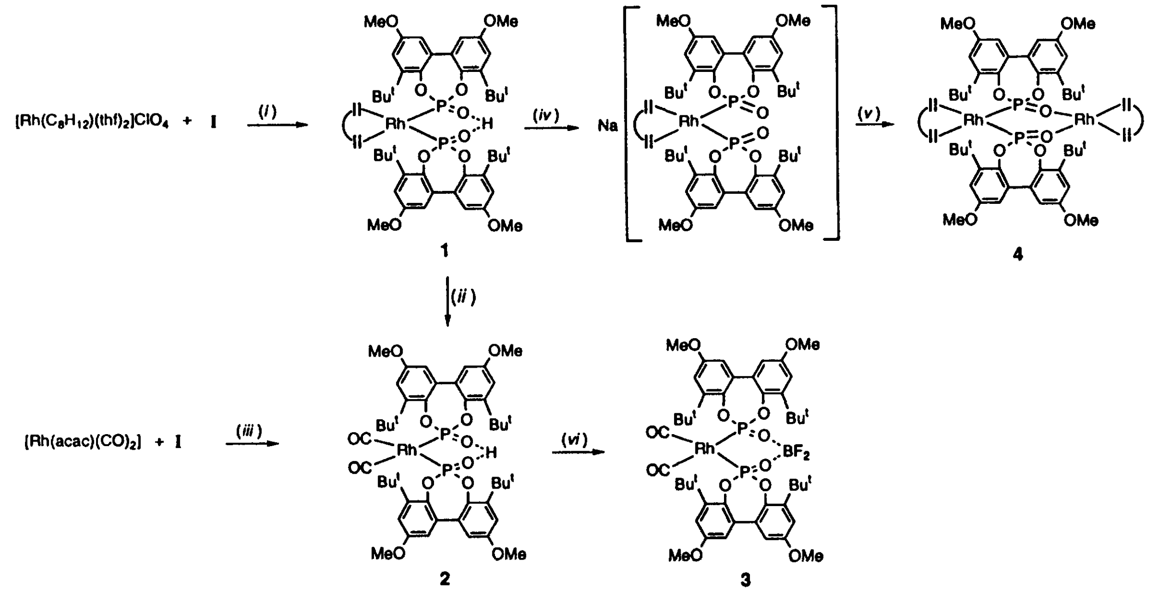
Fig. 2 Perspective view along the *b* axis of the crystal packing that points out the dichloromethane dimers surrounding the complex molecules. The rhodium atoms are denoted by empty circles

$[Rh(C_8H_{12})(thf)_2]ClO_4$ (C_8H_{12} = cycloocta-1,5-diene), in thf, in 2:1 molar ratio afforded a yellow-orange product which can be formulated, on the basis of analytical and spectroscopic data, as **1** (Scheme 2). In accordance, the $^{31}P-\{^1H\}$ NMR spectrum in $CDCl_3$ solution, exhibits a doublet centred at δ 119.9 (J_{RhP} 237.9 Hz) and the ^1H NMR, in the same solvent, shows resonances at δ 1.59 (Bu^t groups) and 3.78 (OCH_3 groups) and peaks due to the presence of the C_8H_{12} at δ 3.7 and 5.18. If **I** was not sufficiently pure, owing to the presence of hydrolysis by-products, **1** was obtained together with a minor product (6:1 ratio) which shows a doublet centred at δ 118.1 (J_{RhP} 268.1 Hz).

When carbon monoxide was bubbled into a dichloromethane solution of the crude product containing **1**, the colour changed from yellow-orange to yellow while in the IR spectrum, in CH_2Cl_2, ν(CO) bands occurred at 2097 and 2054 cm^{-1}, indicating the replacement of C_8H_{12} by CO; the $^{31}P-\{^1H\}$ NMR spectrum, in the same solvent, exhibits a doublet at δ 116.7 (J_{RhP} 196.8 Hz) besides the disappearance of the doublet at δ 119.9. The carbonyl compound **2** was better obtained by treating $[Rh(acac)(CO)_2]$ (acac = acetylacetonate) with **I**, in the molar ratio 1:2, in benzene solution. The formulation was supported by analytical and spectroscopic data, particularly the $^{31}P-\{^1H\}$ NMR spectrum. The single signal in the $^{31}P-\{^1H\}$ NMR spectrum originates from either a fast P–OH to P=O proton exchange which interchanges the two phosphorus atoms faster than the NMR time-scale, or the existence of a symmetrical bridge O···H···O.

The formation of complex **2** by treating $[Rh(acac)(CO)_2]$ with **I** very likely occurs by reductive elimination of acetylacetone from the rhodium(III) species, resulting from oxidative addition of the P–H bond of **I** across the rhodium(I) centre, and subsequent co-ordination of another ligand molecule formally a phosphite. Elimination of acetylacetone from rhodium(III)-hydride intermediate species is a frequent process and occurs in homogeneous catalysis using $[Rh(acac)(CO)_2]$. This proposal is also supported by the work of Powell *et al.*[18] They monitored the reaction between (*R*,*S*)-$Ph(O)HP(CH_2)_2PH(O)Ph$ and $[Pt(PPh_3)_4]$, in CD_2Cl_2 solution, by $^{31}P-\{^1H\}$ and ^1H NMR spectra and found evidence for the presence of the six-co-ordinate platinum(IV) intermediate species *syn*-$[PtH_2\{(R,S)\text{-}Ph(O)P(CH_2)_2P(OH)Ph\}_2]$ formed by oxidative addition of a P–H bond to platinum(0); the dihydride intermediate is converted into *syn*-$[Pt\{(R,S)\text{-}Ph(O)P(CH_2)_2P(OH)Ph\}_2]$ by reductive elimination of H_2.

Previously[18–20] it has been shown that mixed phosphinous acid–phosphinito complexes readily react with electrophiles



Scheme 2 (*i*) thf, room temperature (r.t.); (*ii*) p_{CO} 1 atm (*ca.* 10^5 Pa), in CH_2Cl_2; (*iii*) benzene, r.t.; (*iv*) NaOH; (*v*) $[Rh(C_8H_{12})(thf)_2]ClO_4$ in thf; (*vi*) $BF_3{\cdot}Et_2O$

such as BF_3 and $SiCl_2Me_2$ to give complexes containing the macrocyclic-type structure $M(PR_2OEOR_2P)$ (E = BF_2 or $SiMe_2$; R generally Ph). The addition of an excess of $BF_3{\cdot}Et_2O$ to a CH_2Cl_2 solution of **2** afforded to **3**; the occurrence of this reaction further supports the presence in **2** of the fragment $\geqslant P{\cdots}O\cdots H\cdots O{\cdots}P\leqslant$. The $^{31}P\text{-}\{^1H\}$ NMR spectrum of **3** exhibits a single resonance at δ 111.4 (J_{RhP} 198.7 Hz) consistent with two equivalent phosphorus atoms, while a broad resonance at δ −138.5 is observed in the ^{19}F NMR spectrum.

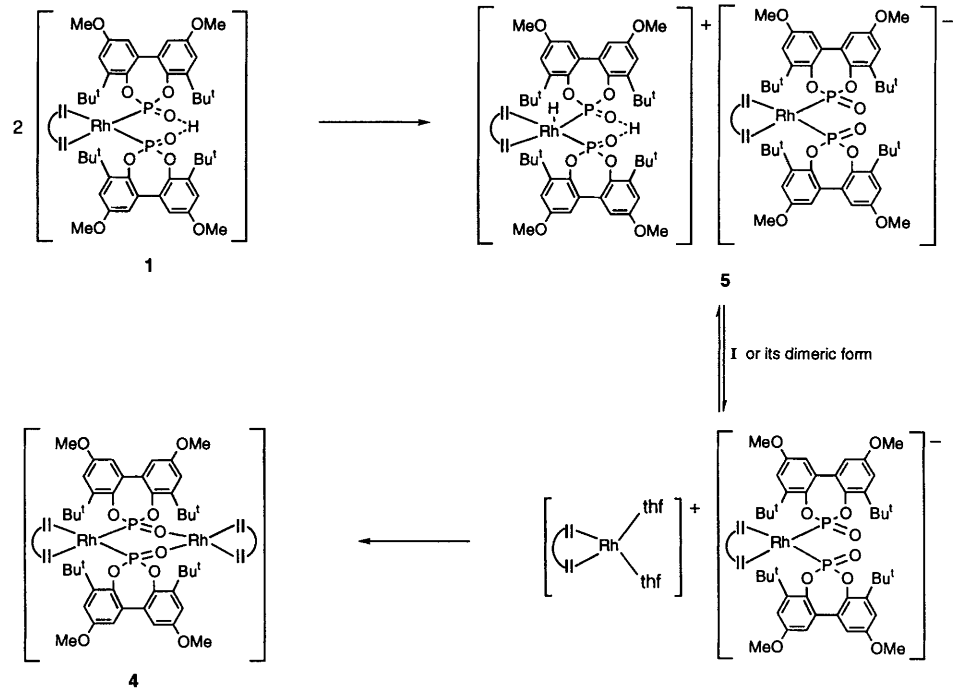
Reaction of the sodium salt of complex **1** with $[Rh(C_8H_{12})(thf)_2]ClO_4$ afforded **4** as an orange compound. This was characterized by elemental analyses, NMR spectroscopic data and X-ray diffractometry. It can be considered as a zwitterionic compound; in fact two $Rh(C_8H_{12})$ moieties are held together by two $\geqslant$P(O) bridging groups which are both bonded to one rhodium(I) centre through the phosphorus atoms and to the other through the oxygen atoms. In accordance, in the $^{31}P\text{-}\{^1H\}$ NMR spectrum, in $CDCl_3$ solution, only a doublet centred at δ 113.5 (J_{RhP} 243.4 Hz) was evidenced; in the ^1H NMR spectrum, in the same solvent, resonances at δ 1.71 (Bu^t groups) and 3.78 (OCH_3 groups) and peaks due to the presence of the C_8H_{12} at δ 3.51 and 4.7 are present, in correct integration ratio.

Unexpectedly, attempts to crystallize **1** from dilute diethyl ether–dichloromethane (4 : 1) solution led to the isolation in low yield of $\mathbf{4}{\cdot}2CH_2Cl_2$, as orange crystals. The formation of **4** from **1**, can be explained by considering that the O-bonded acidic hydrogen gives to **1** the character of a monoprotic acid.[21] In **1** the rhodium(I) is a basic centre; it can oxidatively add a proton by an intermolecular process to give a rhodium(I)–rhodium(III) ionic intermediate **5** (see Scheme 3). Reductive elimination of **I**, or of its dimeric form,[18] from **5** produces, probably in equilibrium, the species $[Rh(C_8H_{12})(thf)_2]^+$ which affords **4** by reacting with the anion derived from **1**. We have shown that **4** was not formed from the reaction of **1** with the solvato species $[Rh(C_8H_{12})(thf)_2]ClO_4$ eventually present, as minor product, together with **1**.

Structure of complex $4{\cdot}2CH_2Cl_2$

Crystals were formed by co-crystallization of the binuclear complex and dichloromethane in the ratio 1 : 2. The two molecular species do not interact and the presence of the solvent might be related to the crystal packing. One hydrogen of each CH_2Cl_2 interacts with a chlorine of the centrosymmetric molecule [H(OA)···Cl(2′) 2.77(3), C···Cl(2′) 3.61(2) Å, C–H(OA)···Cl(2′) 146(1)°, symmetry relation 1 − *x*, 1 − *y*, −*z*] forming a 'dimer' solvent species on the plane *c* which undergoes Van der Waals interactions with surrounding complex molecules. The binuclear complex is placed on a crystallographic glide *c* passing through the metal atoms and only half the molecule is independent. It consists of two $Rh(C_8H_{12})$ units bridged by two phosphite phosphonate ligands in head-to-head mode. Both ligands are connected *via* the phosphorus to Rh(2) and *via* the terminal oxygen to Rh(1) in such a way that the central bulk of the molecule is constituted by the six-membered ring Rh(1)O(1)P(1)Rh(2)P(1′)O(1′) crossing the glide plane. By analogy with the treatment of cyclohexane conformations, the puckering coordinates[22] *Q* = 0.71(1) and φ = 90.0(1)° denote the 'half chair' arrangement adopted by the bimetallic ring as expected from the imposed crystallographic symmetry. The 'boat'-shaped C_8H_{12} acts as a chelating ligand to the metal, considering each centres of a double bond as one co-ordinating site. Therefore both the rhodium atoms are four-co-ordinated and show perfect square-planar geometry [reciprocal dihedral angle 24.13(1)°] in respect of which the corresponding C_8H_{12} mean plane is perfectly orthogonal [both dihedral angles 90(3)°]. For each rhodium atom the two distances from the double-bond centres of C_8H_{12} (X_{cod}) and from the co-ordinating site of two $\geqslant$P(O) bridges are equivalent by symmetry. The Rh(1)–X_{cod} distance is significantly shorter than Rh(2)–X_{cod} [1.967(6) *vs.* 2.131(5) Å, respectively] mainly due to the *trans* effect of the phosphorus ligand with respect to the oxygen atom. A search for square-planar $Rh(C_8H_{12})$ compounds in the Cambridge Structural Database (CSD),[13] revealed that the average Rh–X_{cod} distance falls in the range 1.96–2.00 Å for cod *trans* to oxygen atoms while it is 2.09–2.18 Å when opposite to phosphorus atoms. The elongation of the Rh–C_8H_{12} bonds causes a decrease in the X_{cod}–Rh–X_{cod} angle [the corresponding CSD mean values are 88.7(7) and 84.9(8)°, respectively], in agreement with our co-ordination angle of 88.8(2)° for Rh(1) and 84.7(2)° for Rh(2).

Few examples of tris(2,2′-biphenyl) diphosphite structures have been reported; some are either co-ordinated *via* the phosphorus atom to Ru[24] or Pt.[23a] One case of a 2,2′-biphenyl phosphite ligand[25] has been reported which is P-co-ordinated to one rhodium while the third oxygen (not linked to the biphenyl fragment) is bonded to a phenyl group. Compound **4** is the first example of this ligand acting as bidentate with the P atom co-ordinated to a rhodium and the third oxygen to another



Scheme 3

metal centre. The ··· P–O ··· bite of the bridge is large enough to allow an intermetallic separation which avoids interaction between the two rhodium atoms [Rh ··· Rh 4.430(2) Å]. The coordination distance Rh(2)–P(1) 2.294(1) Å is larger than the mean value 2.155(1) Å in analogue[25] (where it is *trans* to an oxygen) but in agreement with the average bond length of 2.30(4) Å reported for *trans*-C_8H_{12} four-co-ordination, shorter than the usual Rh–P distance of 2.37 Å. The *trans* effect of C_8H_{12} determines the Rh(1)–O(1) bond length of 2.077(3) Å which is longer than usual Rh–O distances but very close to the mean value 2.08(2) Å found in the above-mentioned CSD search. The geometry of the 2,2′-biphenyl phosphite is the same as that of the reported monodentate ligand and similar to the analogous fragment of tris(2,2′-biphenyl) diphosphite structures. The significant difference between the P(1)=O(1) double bond [1.504(3) Å] with respect to the other two P–O distances [mean 1.637(4) Å] is in good agreement with the corresponding bond lengths found in $[Pd\{(\mu\text{-}Cl)[\mu\text{-}PO(OMe)_2]Rh(cod)\}_2]$.[26] However the 3,3′-di-*tert*-butyl-5,5′-dimethoxy-1,1′-biphenyl-2,2′-diyl moiety is constituted by two equivalent substituted phenyl rings that are not conjugated, as evidenced by the C(14)–C(20) single-bond length of 1.491(6) Å and by the torsion angle C(9)–C(14)–C(20)–C(21) of −53.1(6)°. The CSD search for comparable ligands evidenced that the size of the angle O–P–O is proportional to the biphenyl torsion angle (correlation coefficient = 0.753, with values in the range 93–103 *vs.* 36–52°, respectively) and then to the decrease in delocalization.

Catalysis

We demonstrated the ability of complexes **1**, **2** and **4** to act as catalyst precursors for the hydroformylation of styrene and 2-vinylnaphthalene. The systems formed by **1**, **2**, **4** or by $[Rh(C_8H_{12})(acac)]$ and **I** in different ratios show the same catalytic activity as $[Rh(C_8H_{12})(acac)]$ under the same conditions of CO–H_2 pressure, temperature and olefin concentration. The lack of any influence of **I** on the activity of the catalytic system indicates that in the hydroformylation, also using mild conditions, loss of co-ordinated **I**, with formation of $[RhH(CO)_4]$, occurs. On the other hand, $[RhH(CO)_4]$ is the catalytic species formed when using $[Rh(C_8H_{12})(acac)]$ as precatalyst in hydroformylation reactions of olefins.[27]

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