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Stabilising Rh–P coordination by phosphanylalkylcyclopentadienyl ligands

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(Phosphanylalkyl/aryl)cyclopentadienyl complexes have been synthesised from lithiated 1,2,3,4-tetramethyl-5-(2-*P*,*P*-dialkyl/arylphosphinoethyl)cyclopentadiene and $[RhCl(CO)_2]_2$; the electron donating properties of these ligands have been compared and the P–Rh interaction is shown to be stable under methanol carbonylation reaction conditions.

Electron rich metal complexes have recently been shown to have a number of important uses in catalysis,[1] with considerable rate enhancements being observed in reactions such as methanol carbonylation, where nucleophilic attack of the metal centre on methyl iodide is the rate determining step.[2,3] In particular, we have recently shown that rhodium-PEt_3 complexes are more active than the industrially used catalyst, $[RhI_2(CO)_2]^-$,[3] although its lifetime is short because the PEt_3 ligand is lost as Et_3PO. We have also shown that a rhodium complex containing the electron donating pentamethylcyclopentadienyl (Cp*) ligand is highly active for the carbonylation of methyl acetate to acetic anhydride in the absence of added hydrogen.[4] A related cobalt complex containing two electron donating ligands, $[Cp^*Co(CO)PEt_3]$, has a higher intrinsic activity for methanol carbonylation than does $[RhI_2(CO)_2]^-$.[5] These observations of the beneficial effects of pentamethylcyclopentadienyl ligands and trialkylphosphines has led us to investigate the possibility of stabilising the coordination of both ligands using the chelate effect. To do this we now report the synthesis of a ligand in which a trialkylphosphine is attached to a pentamethylcyclopentadienyl ligand *via* a hydrocarbon bridge together with the properties of rhodium complexes of this and related ligands. Many ligands of this type have been reported,[6,7] but none that contain a permethylated cyclopentadienyl ring and ethyl groups on phosphorus. The chemical properties of the two groups are quite different and binding these onto a metal may lead to some interesting chemical reactivities.[8]

The lithiated ligand and some related ones that are already known,[7,10,11] were synthesised by reactions of the spirohydrocarbons shown in Fig. 1 with lithium diethyl/diphenyl phosphide in high yield. Tetramethyl-spiro-[2,4]-hepta-4,6-diene was synthesised *via* direct alkylation of lithium tetramethylcyclopentadienide with 1-bromo-2-chloroethane and subsequent reaction with butyl lithium.[7] †

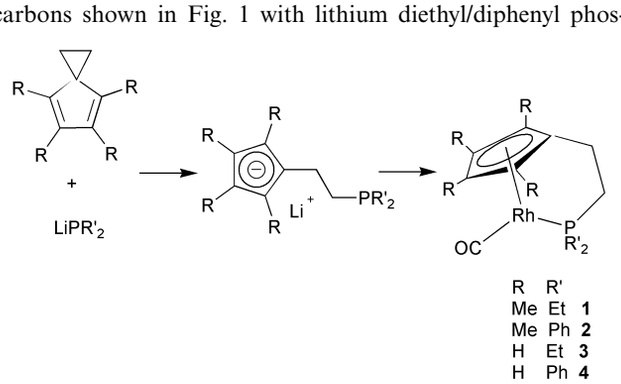

Fig. 1 Synthesis of chelating ligands and their rhodium complexes.

Table 1 Properties of phosphanylethylcyclopentadienyl complexes of rhodium and the related cyclopentadienyl phosphine complexes

Compound	ν_{CO}/cm^{-1}	C–O/pm	Rh–P/pm
1	1924	116.3(8)	221.6(2)
2	1933	115.7(5)	223.06(10)
3	1938	117.1(6)	218.38(11)
4[10]	1947		
5[11]	1920		
6[11]	1947		
7[11]	1944		
8[12]	1953		

The ligands were then reacted with $[RhCl(CO)_2]_2$ to give the complexes **1**–**3** (Fig. 1) as air stable red solids, which were fully characterised analytically and spectroscopically and by X-ray structural determinations. These data are deposited, but for compound **1** the structure is shown in Fig. 2. ‡ They all show

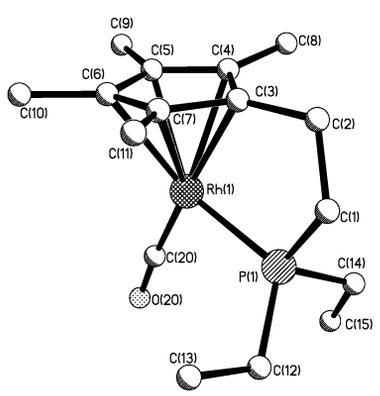

Fig. 2 X-Ray crystal structure and numbering scheme for compound **1**. Selected bond angles (°): Rh(1)–P(1)–C(1) 103.2(2), P(1)–C(1)–C(2) 112.6(3), C(1)–C(2)–C(3) 112.7(6), C(2)–C(3)–C(4) 126.1(6), C(2)–C(3)–C(7) 126.1(5), C(4)–C(3)–C(7) 107.8(4).

chelate binding of the ligands through the cyclopentadienyl ring and the phosphorus atom with little strain in the bridge and planarity at C(3). The IR stretching frequencies (Table 1) of these complexes were used as an indication of the electron donating properties of the ligands and are compared with those of the known complex **4**[10] and complexes in which the Cp ring is not attached to the phosphine, $[(C_5R_5)Rh(CO)(PR'_3)]$, (**5** R = Me, R′ = Et;[11] **6** R = Me, R′ = Ph;[11] **7** R = H, R′ = Et[11] and **8** R = H, R′ = Ph[12]). A low ν_{CO} indicates a high electron density on the metal centre because of increased back bonding into the π* orbitals of the CO.

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From comparison of **1** with **5**, it appears that there is similar electron density on the metal for the chelating ligand to that in the analogous complex containing Cp* and PEt_3 although comparison of **3** with **7** shows that the extra methylene substituent on the ring in **3** increases the electron density at rhodium. For the other pairs of complexes (**2** and **6**, **4** and **8**), the electron density on rhodium is enhanced by the presence of the chelate backbone because a phenyl group on phosphorus is replaced by the alkyl backbone chain. As expected, the compounds with R′ = Et (**1**, **3**, **5**, **7**) are significantly more electron rich then their analogues with R′ = Ph (**2**, **4**, **6**, **8**) and those with R = Me (**1**, **2**, **5**, **6**) are significantly more electron rich than if R = H (**3**, **4**, **7**, **8**), so that the most electron rich of the complexes containing the chelate ligands is **1** with R = Me and R′ = Et.

The C≡O bond lengths for complexes **1**–**3** are not significantly different. However, the Rh–P bond lengths are in the order **2** > **1** > **3**, suggesting that, at least for the PEt_2 complexes, the Rh–P bond has little π-back bonding component. Significant back binding should make Rh–P in **1** shorter than that in **3**.

Additional evidence for the large electron density on, and hence high nucleophilicity of, the rhodium centre for complex **1** comes from its reaction with MeI at room temperature to give $[Rh(Et_2PCH_2CH_2C_5Me_4)(C(O)Me)I]$, (**9**, ^{31}P δ 65.2 J_{RhP} = 165 Hz, Fig. 3) and with deuteriated methylene chloride at

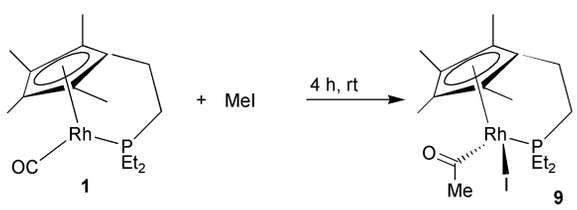

Fig. 3 Reaction of **1** with MeI.

room temperature to give $[Rh(Et_2PCH_2CH_2C_5Me_4)(CO)Cl_2]$ (**10**, ^{31}P δ 76.3 J_{RhP} = 189 Hz). This reaction was carried out at room temperature in an NMR tube with CD_2Cl_2 that had been pretreated with $NaHCO_3$ to remove any HCl that may have been present. After 18 h the reaction had gone halfway to completion and after 48 h all of complex **1** had reacted. These products were characterised by ^1H NMR, ^{13}C NMR, ^{31}P NMR and X-Ray crystallography (deposited). We have previously reported that electron rich rhodium complexes can oxidatively add dihaloalkanes[13] and shown that the haloalkyl complexes formed react with CO to give dihalo complexes, probably with the elimination of ketene.[14]

In an attempt to discover whether the chelate stabilisation of the bonding of the phosphine and the Cp* ring is effective under methanol carbonylation conditions, complex **1** was used for methanol carbonylation in the presence of methyl iodide (Entry 1, Table 2). Zero order kinetics were obtained throughout the 4 h reaction at a rate approximately half that obtained using $[RhCl(CO)_2]_2$, which gives the Monsanto catalyst under the reaction conditions. A ^{31}P NMR spectrum of the final solution from reaction 4, Table 2, showed that most of the P atoms were coupled to rhodium (no oxidation had occurred, but ^{31}P resonances at δ 36.1 and 33.7 may indicate small amounts of quaternised phosphine (< 5%)§. Most of the rhodium precipitated from the final solution as pure $[Rh(Et_2PCH_2CH_2C_5Me_4)I_2]$ (**11**, ^{31}P δ 60.5, J_{RhP} = 147 Hz), which was crystallographically characterised.

An *in situ* ^{31}P NMR study carried out under similar conditions to those used for entry 1, Table 2, but using a higher concentration of rhodium and 180 °C, also showed that all the P was coordinated to Rh throughout the reaction. Three doublets (δ 71.1, J_{RhP} = 134 Hz, 64.6, J_{RhP} = 166 Hz and 61.0, J_{RhP} = 150 Hz) in a ratio 20 : 3 : 5 were the only resonances observed at the end of the reaction. The last two of these can be assigned to

Table 2 Carbonylation of methanol catalysed by rhodium complexes

Entry	Complex	Rate/mol (dm solution)$^{-3}$ h^{-1}
1	**1**[a]	0.4
2	**5**[a,b]	0.4
3	$[RhCl(CO)_2]_2$[a]	0.8
4	**1**[c]	11.4, 2[d]
5	**3**[e]	10.9, 0[f]

[a] [Rh] = 1.25 mmol dm^{-3}, [MeI] = 1.61 mol dm^{-3}, [MeOAc] = 2.52 mol dm^{-3}, [HOAc] = 10.5 mol dm^{-3}, [H_2O] = 5.55 mol dm^{-3}, solution volume = 10 cm^3, 150 °C, 27 bar. [b] PEt_3 (1.25 mmol dm^{-3}) added. [c] [Rh] = 0.11 mol dm^{-3}, [MeI] = 1.37 mol dm^{-3}, [MeOH] = 21 mol dm^{-3}, [H_2O] = 3.32 mol dm^{-3}, solution volume = 5.85 cm^3, 150 °C, 27 bar. [d] Rate drops after 30 min (20 bar consumed, 26% conversion). [e] As *c*, except [Rh] = 0.078 mol dm^{-3}. [f] Reaction stops after 13 min (5 bar consumed, 6.5% conversion).

$[Rh(Et_2PCH_2CH_2C_5Me_4)(C(O)Me)I]$ and $[Rh(Et_2PCH_2CH_2C_5Me_4)I_2]$, respectively, whilst the remaining one (δ 71.1, J_{RhP} = 134 Hz) is from an unidentified complex. For this complex, the coupling to rhodium confirms that the PEt_2 unit is still bound, whilst the chemical shift indicates that the chelate is still in tact. If the $-C_5Me_4$ moiety were no longer bound, a chemical shift of *ca.* 20–30 ppm would be expected.[3]

Complex **5** also gave a rate similar to that obtained using complex **1**, but in this case ^{31}P NMR studies showed almost complete conversion of Et_3P to Et_3PO (δ 82.0) even at 90 °C (there was a small doublet at δ 26.2, J_{RhP} = 103 Hz, accounting for about 10% of the P atoms). Interestingly, a similar reaction using complex **3** was much less successful than that with **1**, with the reaction halting after 6.5% conversion. This suggests that the methyl groups on the Cp ring are essential for catalyst stability.

We conclude that binding of both Cp^* and PEt_3 to rhodium can be sufficiently stabilised by chelation that complexes containing $[Et_2PCH_2CH_2C_5Me_4]^-$ are stable under the aggressive conditions used for methanol carbonylation.

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Notes and references

† Synthesis: There is some controversy in the literature about the exact regioselectivity of the reaction with 1-bromo-2-chloroethane,[7,9] but we find that the method described by van Beek and Gruter gives the desired spirohydrocarbon in 50% yield.[7]

Compound **1**. $LiPEt_2$ (1.15 g, 12.0 mmol) was stirred with 4,5,6,7-tetramethyl-spiro-[2,4]-hepta-2,4-diene (2.0 g, 13.5 mmol) in THF (50 cm^3) at room temperature for 3 d. The THF was removed *in vacuo* and the residue washed with light petroleum (bp 40–60 °C, 2 × 50 cm^3) to leave a white solid ($LiC_5Me_4CH_2CH_2PEt_2$, 2.55 g, 87%). THF (10 cm^3) containing this white solid (0.18 g, 0.72 mmol) was added dropwise to THF (50 cm^3) containing $[RhCl(CO)_2]_2$ (0.11 g, 0.28 mmol). The colour changed immediately from pale yellow to dark red and the solution was refluxed for 8 h. The solvent was removed *in vacuo* and light petroleum (50 cm^3) added. After filtration, of a white solid, the red solution was concentrated to half volume and cooled to −78 °C to yield red crystals (0.12 g, 58%). Compounds **2** and **3** were similarly prepared but using $LiPPh_2$ and spiro-[2,4]-hepta-2,4-diene respectively.

Compound **9**. **1** (0.1 g, 0.27 mmol) in THF (15 cm^3) was strirred with MeI (2 cm^3, 32.1 mmol) at room temperature for 4 h. The solvent was removed *in vacuo* and the red solid recrystallised from light petroleum (25 cm^3). Yield 0.1 g, 75%.

Compound **10**. **1** (0.05 g, 0.14 mmol) was stirred at room temperature for 24 h in CD_2Cl_2 (5 cm^3), which had previously been treated with Na_2CO_3. After evaporation to dryness, the product was recrystallised from benzene to give bright orange crystals (0.05 g, 87%).

Compound **11**. **1** (0.23 g,0.61 mmol) was dissolved in methanol (4 cm^3) and charged into a mechanically stirred autoclave, which had previously been flushed with CO. Water (0.35 cm^3) was added, the reactor pressurised to 25 bar and the temperature raised to 150 °C. After 15 min, methanol (1 cm^3) containing MeI (0.5 cm^3) was injected from a substrate injector and the pressure adjusted to 27 bar. CO was

then fed into the reactor from a ballast vessel through a mass flow controller, which maintained the pressure within the reactor at 27 bar. The pressure in the ballast vessel was monitored every 5 s. After 2 h, the reactor was cooled and vented. The red crystals which separated from the deep red solution were collected and identified as **11**. Catalytic reactions were carried out as described above, but using the conditions described in Table 2, with rates being calculated from the pressure drop within the ballast vessel.

‡ All data were collected on a Bruker SMART CCD diffractometer at 293(2) K using monochromated radiation [μ(Mo-Kα) = 24.58 cm^{-1}, λ = 0.71073 Å]. The Co, I, P and O atoms were refined anisotropically, the C atoms isotropically (any exceptions are noted). Structures were solved by direct methods and expanded using Fourier techniques.

Crystal data for **1**, [$C_{16}H_{26}$OPRh]: M_r = 368.25, monoclinic, space group $P2_1/c$, a = 7.2206(6), b = 16.6210(13), c = 14.3525(12) Å, β = 102.160(2)°, U = 1683.8(2) Å^3, Z = 4, F(000) = 760, 0.1 × 0.03 × 0.03 mm, 7070 reflections collected, 2382 observed, R_1 = 0.0440, wR_2 = 0.0838. CCDC reference number 197744.

For **2**, [$C_{24}H_{26}$OPRh]: M_r = 464.33, monoclinic, space group $P2_1/n$, a = 8.8431(9), b = 24.718(3), c = 9.8846(10) Å, β = 101.548(2)°, U = 2116.9(4) Å^3, Z = 4, F(000) = 952, 0.1 × 0.1 × 0.03 mm, 10327 reflections collected, 2989 observed. R_1 = 0.0297, wR_2 = 0.0632. CCDC reference number 197742.

For **3**, [$C_{12}H_{18}$OPRh]: M_r = 312.14, orthorhombic, space group $Pna2(1)$, a = 12.3029(4), b = 9.5500(3), c = 11.1065(4) Å, U = 1304.93(8) Å^3, Z = 4, F(000) = 632, 0.08 × 0.08 × 0.1 mm, 5187 reflections collected, 1841 observed, R_1 = 0.0229, wR_2 = 0.0562. CCDC reference number 197743.

For **9**, [$C_{17}H_{29}$IOPRh], M_r = 510.18, monoclinic, space group $P2_1/c$, a = 8.0159(2), b = 17.77960(10), c = 13.6522(3) Å, β = 94.2430(10) °, U = 1940.37(7) Å^3, Z = 4, F(000) = 1008, 0.2 × 0.2 × 0.03 mm, 7999 reflections collected, 2694 observed. C(21), C(22) and O(1) were refined as a rigid body as this proved the best way to overcome the slight disorder in the structure, R_1 = 0.0520, wR_2 = 0.1336. CCDC reference number 197739.

For **10**, [$C_{16.5}H_{27.5}Cl_2$PRh], M_r = 430.67, orthorhombic, space group $Pbcn$, a = 30.6515(13), b = 8.6919(4), c = 28.3619(7) Å, U = 7556.2(5) Å^3, Z = 16, F(000) = 3528, 0.1 × 0.1 × 0.03 mm, 31133 reflections collected, 5421 observed, R_1 = 0.0766, wR_2 = 0.1568. CCDC reference number 197740.

For **11**, [$C_{15}H_{26}I_2$PRh], M_r = 594.04, monoclinic, space group Cc, a = 12.1284(13), b = 13.5763(15), c = 11.9212(13) Å, β = 92.718(8)°, U = 1960.7(4) Å^3, Z = 4, F(000) = 1128, 0.18 × 0.1 × 0.1 mm, 4132 reflections collected, 2662 observed, R_1 = 0.0316, wR_2 = 0.0842. CCDC reference number 197741. See http://www.rsc.org/suppdata/dt/b2/b211287f/ for crystallographic data in CIF or other electronic format.

§ Doublets were observed at δ 76.5 (J_{RhP} = 117.1 Hz), 63.9 (J_{RhP} = 145.3 Hz) and 36.3 (J_{RhP} = 68 Hz) and broad singlets at δ 59 and 62 Hz). The phosphine oxide is expected to resonate near δ 70 and the quaternised phosphine near δ 40.[3]

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