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Pentakis(methoxycarbonyl)cyclopentadiene chemistry

XII [*]. Some rhodium and iridium derivatives: X-ray crystal structures of $Rh(\eta^4\text{-}C_8H_{12})\{\eta^5\text{-}C_5(CO_2Me)_5\}$, $Rh(azb)_2\{C_5(CO_2Me)_5\}$, and $[M(CO)\{OC(OH)Me\}(PPh_3)_2][C_5(CO_2Me)_5]$ (M = Rh and Ir)

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Abstract

The reaction between $\{Rh(\mu\text{-}Cl)(\eta^4\text{-}C_8H_{12})\}_2$ and $Tl[C_5(CO_2Me)_5]$ gave $Rh(\eta^4\text{-}C_8H_{12})\{\eta^5\text{-}C_5(CO_2Me)_5\}$ (**3**), which with $PPh_2(CH_2)_2PPh_2$ (dppe) gave $[Rh(dppe)(\eta^4\text{-}C_8H_{12})][C_5(CO_2Me)_5]$. The complex $Rh(azb)_2\{C_5(CO_2Me)_5\}$ (**6**; azb $= C_6H_4N_2Ph$) was obtained from $\{Rh(\mu\text{-}Cl)(azb)_2\}_2$ and $Tl[C_5(CO_2Me)_5]$. Crystallographic characterisation of **3** and **6** showed that in the former, the $C_5(CO_2Me)_5$ group is attached via the ring carbons, whereas in **6**, the ligand chelates the metal via two ester CO groups. Reactions of $Tl[C_5(CO_2Me)_5]$ with $MCl(CO)(PPh_3)_2$ in MeCN gave $[M(NCMe)(CO)(PPh_3)_2][C_5(CO_2Me)_5]$ (**7**, M = Rh; **8**, M = Ir), in which the MeCN ligand is converted into (probably) acetic acid during recrystallisation, as shown by structural studies of the isomorphous Rh and Ir salts, **11** and **12**. The $[C_5(CO_2Me)_5]^-$ anion is hydrogen-bonded to this acetic acid ligand. Crystal data: **3**, triclinic, space group $P\bar{1}$, a 18.591(3), b 14.053(4), c 10.395(3) Å, α 75.15(2), β 72.13(2), γ 81.38(2)°, $Z = 4$; **6**, monoclinic, space group $P2_1/n$, a 23.897(5), b 9.900(1), c 15.828(3) Å, β 99.56(2)°, $Z = 4$; **11**, triclinic, space group $P\bar{1}$, a 21.695(7), b 13.669(7), c 9.319(3) Å, α 103.15(3), β 95.39(3), γ 98.20(3)°, $Z = 2$; **12**, triclinic, space group $P\bar{1}$, a 21.685(2), b 13.615(2), c 9.306(2) Å, α 103.34(2), β

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[*] Part XI: M.I. Bruce, P.A. Humphrey, J.K. Walton, B.W. Skelton and A.H. White, J. Organomet. Chem., 333 (1987) 393.

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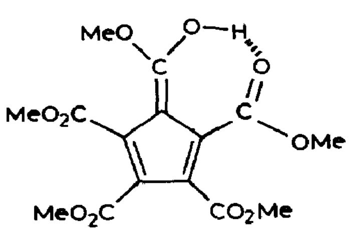
95.28(2), γ 98.31(1)°, $Z = 2$. For the four structure determinations, 6343, 5024, 3785 and 5462 observed data with $I \geqslant 3\sigma(I)$ were refined to R 0.043 (**3**), 0.042 (**6**), 0.064 (**11**) and 0.057 (**12**), respectively.

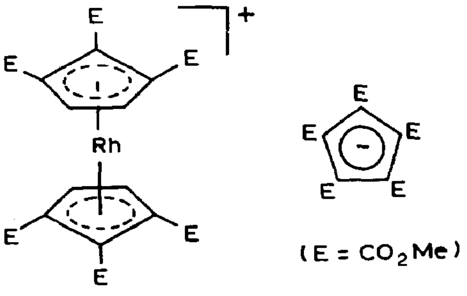
Introduction

In earlier papers of this series we described some of the compounds formed from 1,2,3,4,5-pentakis(methoxycarbonyl)cyclopentadiene (**1**) and metal derivatives. Compound **1** is a strong organic acid and readily displaces weaker acids from their metal salts [1,2]. The iron [2] and silver [3] salts were described before our work, but since 1981 we have reported the isolation and characterisation (in many cases including single crystal X-ray diffraction studies) of Group 1 (Li, Na, K, Rb, Cs) [4,5], Group 2 (Mg, Ca, Sr, Ba) [6], first-row transition metal (Cr, Mn, Fe, Co, Ni) [7,8], Group 11 (Cu, Ag, Au) [9,10,11], Group 12 (Zn, Cd) [6] and thallium(I) compounds [5]. A single manganese carbonyl complex has been reported [12]. Others have described related germanium [13] and tin [14] chemistry; a characteristic feature of the solution chemistry is the ready ionisation with formation of the stable $[C_5(CO_2Me)_5]^-$ anion. This species has been crystallographically characterised in the salts $[NMe_4][C_5(CO_2Me)_5]$ [15], $[SnBu_3(OH_2)_2][C_5(CO_2Me)_5]$ [14], $[Au(PPh_3)_2][C_5(CO_2Me)_5]$ [11], $[Ru(NCMe)(PPh_3)_2(\eta^5\text{-}C_5H_5)][C_5(CO_2Me)_5]$ [16], and $[Rh\{\eta^5\text{-}C_5H_2(CO_2Me)_3\}_2][C_5(CO_2Me)_5]$ [17].

The presence of the five strongly electron-withdrawing CO_2Me groups confers on the $C_5(CO_2Me)_5$ ligand properties which are in marked contrast to those of the well-known related hydrocarbon ligands C_5H_5 and C_5Me_5. In particular, first-row transition metals are reluctant to enter into M–C bonding, the $C_5(CO_2Me)_5$ ligand preferring to bond via the ester carbonyl oxygen atoms (with the exception of $Mn(CO)_3\{\eta^5\text{-}C_5(CO_2Me)_5\}$ [12]). While the formation of structural analogues of the first-row metallocenes may be precluded for steric reasons (model studies show that the five CO_2Me groups are not able to become coplanar with the C_5 ring, and hence interact with similar groups on the second η^5 ligand), electronic effects are undoubtedly also important with reduction in donor power of the ring A and E_1 orbitals being a major consideration [18]. In our studies so far we have found metal–ring carbon interactions in the compounds $Ag\{C_5(CO_2Me)_5\}(L)$ ($L = H_2O$



(**1**)



(**2**)

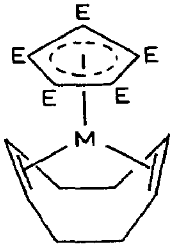
or PPh_3) [10], where there appears to be a weak interaction of two of the ring carbons with the metal, in $Au\{C_5(CO_2Me)_2\}(PPh_3)$ [11], in which one carbon interacts strongly, and the two adjacent carbons weakly, with the gold (as also found in $Au(C_5HPh_4)(PPh_3)$ [19], and for which a theoretical rationalisation has been supplied by Evans and Mingos [20]), and in the metallocene $Ru(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_5(CO_2Me)_5\}$ [21]. In the latter, the $C_5(CO_2Me)_5$ ligand is attached to the ruthenium in true η^5 mode, with Ru–C distances similar to those of the C_5H_5 ring. However, its reactions demonstrate the weaker bonding of the $C_5(CO_2Me)_5$ ligand, which is lost readily as the $[C_5(CO)_2Me)_5]^-$ anion in the presence of ligands such as acetonitrile, tertiary phosphines, etc.

Only in the case of rhodium have we been able to obtain a complex containing two $\eta^5\text{-}C_5$ ligands containing CO_2Me groups, namely $[Rh\{C_5H_2(CO_2Me)_3\}_2]$-$[C_5(CO_2Me)_5]$ (**2**), although it can be seen that loss of two of the CO_2Me groups from each of the η^5 rings has occurred [17]. This paper describes further chemistry of complexes containing $C_5(CO_2Me)_5$ ligands on rhodium or iridium, including an interesting change of bonding mode as the oxidation number of the metal changes.

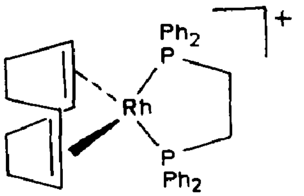
Results and discussion

In this paper we are concerned with the synthesis of rhodium and iridium complexes containing $C_5(CO_2Me)_5$ and related ligands. By analogy with the preparation of the hydrocarbon analogue, we treated $\{RhCl(\eta^4\text{-}C_8H_{12})\}_2$ with $Tl[C_5(CO_2Me)_5]$. An immediate reaction occurred, with precipitation of TlCl, and orange crystals of $Rh(\eta^4\text{-}C_8H_{12})\{\eta^5\text{-}C_5(CO_2Me)_5\}$ (**3**) were isolated from the solution in good yield. Characterisation of this complex was from elemental microanalyses, the IR spectrum, which contains the plethora of $\nu(CO)$ bands around 1700 and 1200 cm^{-1} characteristic of the $C_5(CO_2Me)_5$ ligand, and especially from the ^1H NMR spectrum, which contained only a single OMe resonance at δ 3.83 in addition to the usual CH and CH_2 resonances of the C_8H_{12} ligand. This result suggested that the C_5 ligand was symmetrically bonded to the rhodium, since **3** was shown not to dissociate in solution (conductivity). The analogous iridium complex **4** formed yellow crystals, with similar properties. The FAB mass spectrum of **3** contained the molecular ion as base peak, which showed loss of OMe and CO_2Me groups as the major fragmentation routes. The negative ion spectrum contained a weak ion $[Rh(C_8H_{12})\{C_5(CO_2Me)_4\}]^-$, but the major ion was found at m/z 355, corresponding to $[C_5(CO_2Me)_5]^-$.

The presence of the $\eta^5\text{-}C_5(CO_2Me)_5$ ligand was confirmed by a single-crystal X-ray diffraction study of **3**. Two independent pseudo-symmetrically related molecules comprise the asymmetric unit of the structure (Fig. 1); it can be seen that the structure is similar to that of $Rh(\eta^4\text{-}C_8H_{12})(\eta\text{-}C_5H_4CO_2Me)$ [22]. The Rh–C(cp) distances in the latter average 2.262 Å, while in **3**, they have lengthened to 2.28 Å; the C_8 ligand is coordinated in the usual chelating "tub" form, with a Rh–C(olefin) separation of 2.13 Å (cf. 2.11 Å in $Rh(C_8H_{12})(C_5H_4CO_2Me)$). Comparison with the only other $\eta^5\text{-}C_5(CO_2Me)_5$ ligand which has been structurally characterised, in $Ru(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_5(CO_2Me)_5\}$ [21], shows that metal–ring carbon distances to the C_5H_5 and $C_5(CO_2Me)_5$ ligands, respectively, are 2.181 and 2.173 Å (for Ru), and 2.262 and 2.28 Å (for Rh); while for the two ligands attached to the same metal, the



(3) M = Rh
(4) M = Ir



(5)

differences are small, the differences in the lengths of the bonds to the metals exceed the difference between the covalent radii of the metals.

About the C_5 ring, the dihedral angles of the carboxylate substituents are 79.9, 36.7, 42.7, 65.4, 11.0 (molecule A); 56.3, 47.7, 16.8, 90.0, 16.7° (molecule B), consistent with only approximate pseudo-symmetry. Nevertheless, certain features of the fine detail within the molecular core show parallel variations for the two molecules; vide e.g. the distances r in Table 2, where the distances Rh–C(ring) all agree within 2σ for any given carbon atom, but range over many times that value

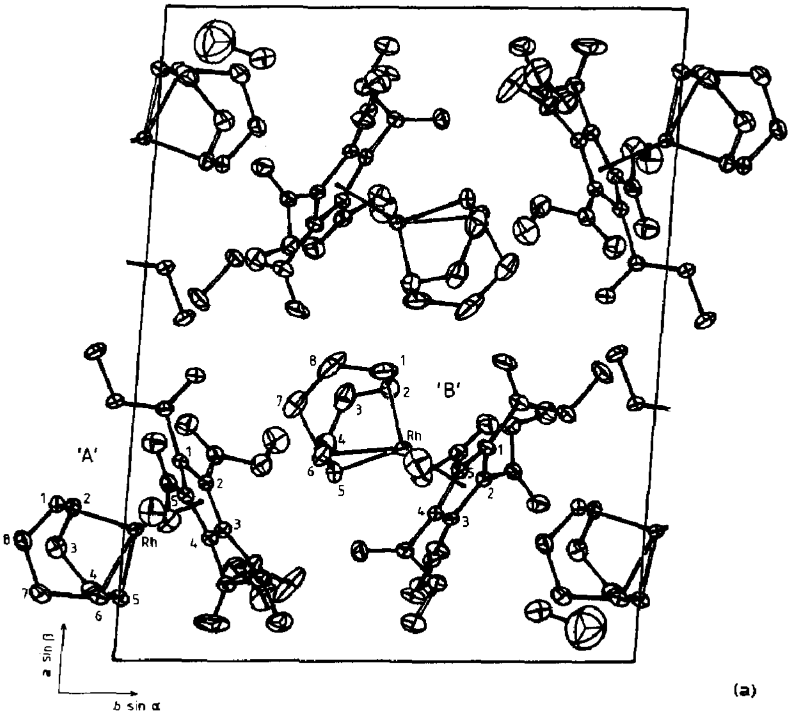


Fig. 1. (a) Unit cell contents of 3, projected down c. 20% thermal ellipsoids are shown for the non-hydrogen atoms, together with key atom labelling. Note the pseudo-symmetric disposition of the two independent molecules A, B; (b) Molecules A, B of 3, projected down the Rh–cp(centroid) line, and *quasi*-perpendicular to it.

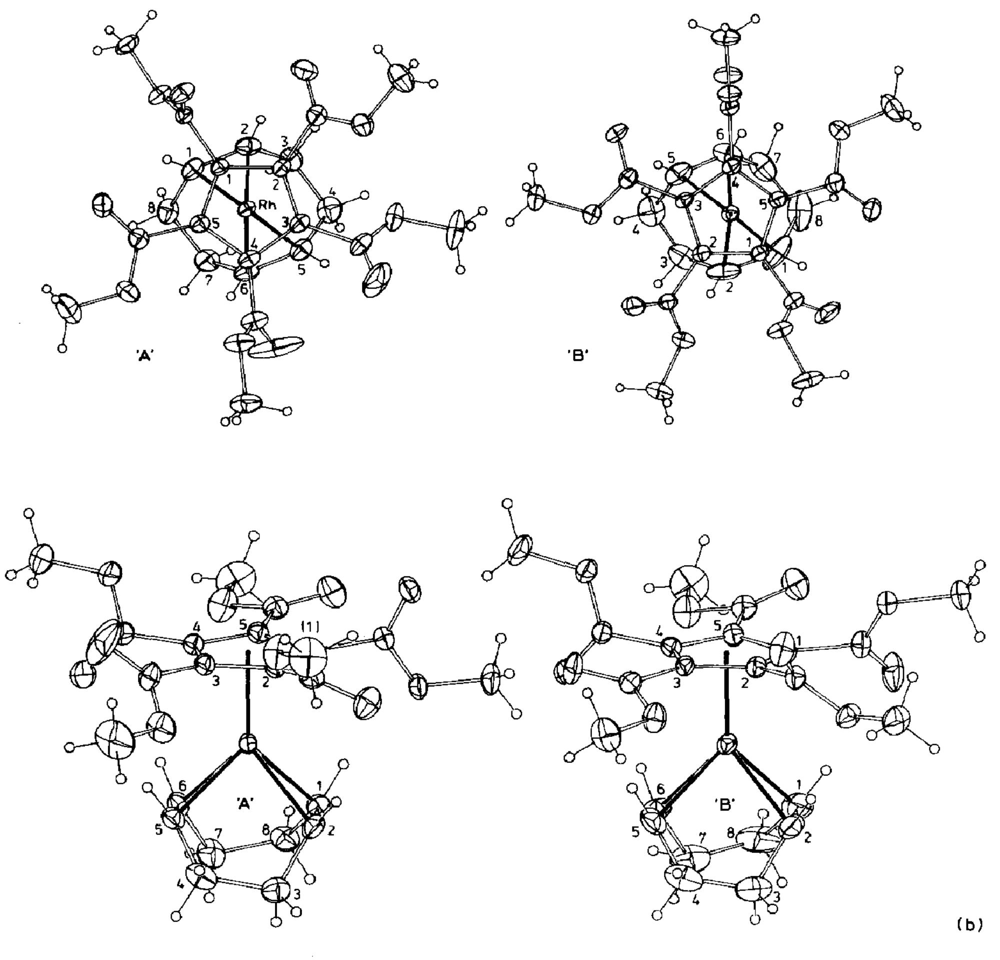
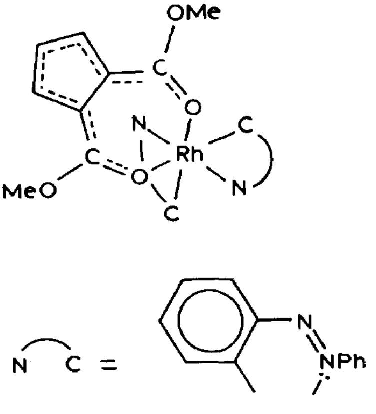


Fig. 1 (continued).

around the ring. Note also the low value of C(05)–Rh–C(centroid) relative to the three other counterpart values.

The reaction between **3** and the chelating bis-tertiary phosphine $PPh_2CH_2CH_2PPh_2$ (dppe) afforded an ionic product which proved to be the $[C_5(CO_2Me)_5]^-$ salt of the known [23] $[Rh(dppe)(C_8H_{12})]^+$ cation (**5**). In this complex, the OMe resonance of the anion was found at δ 3.63; conductivity measurements confirmed the 1/1 electrolyte formulation. In the FAB mass spectrum, the base peak corresponds to the cation $[Rh(C_8H_{12})(dppe)]^+$, which fragments to $[Rh(dppe)]^+$ (77%) and $[Rh(C_8H_{12})]^+$ (17%). A weak ion at *m/z* 856 can be assigned to $[Rh(dppe)\{C_5(CO_2Me)_5\}]^+$, while in the negative ion spectrum, the only peak of significant intensity is the expected *m/z* 355, $[C_5(CO_2Me)_5]^-$. This reaction demonstrates the relatively weak Rh–C_5 bond in **3**, and parallels similar observations on the ruthenium complex mentioned above [21].

The reaction between $\{RhCl(azb)_2\}_2$ (azb = $C_6H_4N{=}NPh$) [24] and $Tl[C_5(CO_2Me)_5]$ gave a red complex, characterised as the mononuclear complex $Rh(azb)_2\{C_5(CO_2Me)_5\}$ (**6**). The presence of the $C_5(CO_2Me)_5$ ligand was evident from the IR spectrum, but the ^1H NMR spectrum contained three OMe resonances, at δ 3.32, 3.69, and 3.75 ppm, with relative intensities 2/1/2. The complex resonances for the



(6)

azb ligands had a similar profile to those for other complexes containing this chelating ligand, so that a reasonable structure was one in which the $C_5(CO_2Me)_5$ ligand was bonded through two carbonyl oxygen atoms in the manner found in the solid state structures of first-row transition metal derivatives [7,8] but not preserved in solution.

The proposed formulation was confirmed by an X-ray study; Fig. 2 shows the structure. The C_5 ligand, chelating through the carbonyl oxygens of CO_2Me groups 1 and 2, is seen to have three different CO_2Me groups, in agreement with the ^1H NMR results. The data for the seven-membered chelate ring are similar to those found in earlier structural studies [7,8], the C(1)–C(2) distance being the longest of the five C–C separations in the C_5 ring (1.450(6) vs. 1.40(av.) Å), and C(*n*1)–O(*n*1) are correspondingly elongated also (Table 5). The two metallated aryl carbons are each *trans* to an oxygen of the $C_5(CO_2Me)_5$ ligand, with the coordinated nitrogen atoms mutually *trans*. While the $RhC_2N_2O_2$ molecular core has potential *2* symmetry, very substantial departures from this ideal are observed for the metal–ligand distances, presumably as a consequence of steric interaction between the ligand planes. The aromatic system of the azb chelate rings is strongly coupled with that of the metallated phenyl ring, and not at all with that of the pendant phenyl ring, in spite of its coplanarity; C(6)–N(7) are 1.39_5 Å(av.), while N(8)–C(9) are 1.44_1 Å(av.).

Two other complexes containing the $Rh(azb)_2$ moiety have been structurally studied, namely $Rh(OAc)(azb)_2$ [25] and $(azb)_2Rh(\mu\text{-}Cl)_2Rh(CO)_2$ [26]. In all three cases the two azb ligands are similar, with the metal-bonded nitrogen occupying mutually *trans* sites about the octahedrally coordinated rhodium.

Complexes **3** and **6** thus show an interesting difference in respect of the coordination of the $C_5(CO_2Me)_5$ ligand. In the former, a rhodium(I) complex, interaction of the metal with the ring carbons gives a complex containing a symmetrical η^5-bonded ligand, while in the rhodium(III) derivative there is a chelating O-bonded ligand. While these two complexes do not have any other ligands in common, it is useful to relate the bonding mode of the $C_5(CO_2Me)_5$ ligand to the nature of the metal centre, with the relatively electron-rich soft rhodium(I) bonding to the soft ring carbons in **3** and the more highly oxidised centre attaching to the hard oxygen donors in **6**.

Table 1

Non-hydrogen atom coordinates, 3

Atom	Molecule A			Molecule B		
	x	*y*	*z*	*x*	*y*	*z*
Rh	0.20138(2)	0.02212(2)	0.37271(4)	0.32800(2)	0.52319(3)	0.84066(4)
$C_5(CO_2Me)_5$ ligand						
C(1)	0.3063(3)	0.0968(3)	0.2362(5)	0.3299(3)	0.6830(4)	0.7243(5)
C(11)	0.3874(3)	0.0580(3)	0.1976(5)	0.3993(3)	0.7374(4)	0.6602(6)
O(11)	0.4378(2)	0.1117(3)	0.1421(4)	0.4608(3)	0.7036(4)	0.6088(6)
O(12)	0.3975(2)	−0.0383(2)	0.2355(4)	0.3822(2)	0.8309(3)	0.6709(4)
C(12)	0.4740(3)	−0.0819(5)	0.2062(7)	0.4454(4)	0.8926(5)	0.6205(9)
C(2)	0.2743(3)	0.1486(3)	0.3455(5)	0.2816(3)	0.6814(3)	0.8623(5)
C(21)	0.3172(3)	0.1626(4)	0.4371(5)	0.2934(3)	0.7374(4)	0.9571(5)
O(21)	0.3632(3)	0.1030(3)	0.4767(5)	0.2443(2)	0.7913(3)	1.0138(5)
O(22)	0.3011(3)	0.2511(3)	0.4631(5)	0.3635(2)	0.7271(3)	0.9626(4)
C(22)	0.3395(5)	0.2760(7)	0.5501(9)	0.3839(4)	0.7913(5)	1.0334(7)
C(3)	0.2019(3)	0.1892(3)	0.3371(5)	0.2198(3)	0.6255(3)	0.8830(5)
C(31)	0.1483(4)	0.2509(4)	0.4286(6)	0.1569(3)	0.5961(4)	1.0102(5)
O(31)	0.1163(5)	0.3235(5)	0.3870(7)	0.1008(2)	0.5646(3)	1.0107(4)
O(32)	0.1434(3)	0.2170(3)	0.5574(4)	0.1719(2)	0.6057(3)	1.1239(4)
C(32)	0.0991(6)	0.2764(7)	0.6528(9)	0.1131(4)	0.5820(6)	1.2515(6)
C(4)	0.1887(3)	0.1659(3)	0.2202(5)	0.2289(3)	0.5949(3)	0.7571(5)
C(41)	0.1174(3)	0.2034(4)	0.1799(6)	0.1712(3)	0.5429(3)	0.7330(5)
O(41)	0.0579(3)	0.1821(6)	0.2492(8)	0.1692(2)	0.4555(3)	0.7541(5)
O(42)	0.1266(2)	0.2676(3)	0.0677(4)	0.1213(2)	0.6088(3)	0.6871(4)
C(42)	0.0589(4)	0.3109(6)	0.0261(8)	0.0594(4)	0.5705(6)	0.6631(8)
C(5)	0.2548(3)	0.1129(3)	0.1536(5)	0.2946(3)	0.6328(3)	0.6587(5)
C(51)	0.2729(3)	0.0767(4)	0.0257(5)	0.3218(3)	0.6294(4)	0.5107(6)
O(51)	0.3345(3)	0.0446(3)	−0.0287(4)	0.3659(3)	0.6810(3)	0.4221(4)
O(52)	0.2138(3)	0.0830(3)	−0.0216(5)	0.2873(3)	0.5613(3)	0.4861(4)
C(52)	0.2282(6)	0.0504(7)	−0.1490(8)	0.3064(6)	0.5531(7)	0.3451(8)
C_8H_{12} ligand						
C(01)	0.2393(3)	−0.1310(3)	0.3981(6)	0.4554(4)	0.4737(7)	0.7933(9)
C(02)	0.2353(3)	−0.0999(4)	0.5166(6)	0.4196(4)	0.4876(5)	0.9290(9)
C(03)	0.1729(4)	−0.1265(5)	0.6520(6)	0.4060(5)	0.4015(5)	1.0558(8)
C(04)	0.1049(4)	−0.0505(5)	0.6630(7)	0.3300(6)	0.3723(6)	1.1034(8)
C(05)	0.0955(3)	0.0018(4)	0.5260(6)	0.2913(4)	0.3925(4)	0.9938(8)
C(06)	0.0962(3)	−0.0386(4)	0.4185(6)	0.3179(4)	0.3674(4)	0.8743(8)
C(07)	0.1016(4)	−0.1505(5)	0.4330(7)	0.3943(5)	0.3069(5)	0.8364(8)
C(08)	0.1824(4)	−0.1907(4)	0.3832(6)	0.4551(6)	0.3722(7)	0.7541(9)
Solvent						
C	0.0789(5)	0.8077(7)	0.1029(13)			
O	0.0532(9)	0.9019(10)	0.0756(15)			

Reactions between $Tl[C_5(CO_2Me)_5]$ and $MCl(CO)(PPh_3)_2$ (M = Rh or Ir) also proceed readily in polar solvents, such as acetonitrile, but the only products we have been able to isolate are the $[C_5(CO_2Me)_5]^-$ salts of the acetonitrile cations $[M(CO)(NCMe)(PPh_3)_2]^+$. These were characterised by the usual methods, and have properties consistent with the illustrated structures, **7** and **8**. The IR spectra contain bands at ca. 2300 and 2010 cm^{-1}, assigned to $\nu(CN)$ and $\nu(CO)$, respectively, and complex absorptions between 1650–1750 from the ester CO groups. The

Table 2

Rhodium atom environments, 3; *r* is the rhodium–ligand atom distance (Å). Other entries in the matrix are the angles subtended at the rhodium by the relevant atom at the head of the row and column. C(0) is the centroid of each C_5 ring. The two values in each entry are for molecules A, B

	r	C(0)	C(01)	C(02)	C(05)	C(06)
C(1)	2.252(4); 2.261(5)	32.4(−); 32.4(−)	102.9(2); 102.5(3)	107.6(2); 108.9(2)	158.6(2); 160.3(2)	156.1(2); 156.5(3)
C(2)	2.304(5); 2.302(5)	31.7(−); 32.0(−)	125.6(2); 124.2(3)	106.9(2); 106.4(2)	122.5(2); 124.5(2)	152.9(2); 153.5(2)
C(3)	2.282(5); 2.285(4)	31.9(−); 32.0(−)	161.1(2); 160.2(3)	133.8(2); 132.8(2)	99.0(2); 100.1(2)	118.3(2); 118.6(2)
C(4)	2.258(4); 2.268(5)	32.3(−); 32.1(−)	145.9(2); 146.8(3)	167.2(2); 167.1(2)	107.5(2); 107.6(2)	102.9(2); 103.7(2)
C(5)	2.303(4); 2.297(5)	32.0(−); 31.9(−)	112.7(2); 113.5(3)	137.3(2); 139.4(2)	141.4(2); 140.4(3)	120.1(2); 120.5(3)
C(01)	2.137(5); 2.134(7)	134.4(−); 134.2(−)	−	38.0(2); 38.4(4)	95.8(2); 95.1(3)	80.5(2); 81.0(3)
C(02)	2.124(5); 2.113(9)	135.0(−); 135.4(−)		−	81.0(2); 79.7(3)	89.7(2); 88.4(2)
C(05)	2.123(5); 2.140(6)	129.7(−); 130.6(−)			−	37.8(3); 35.4(3)
C(06)	2.121(6); 2.155(6)	135.2(−); 135.8(−)				−
C(0)	1.93_2; 1.93_4	−				

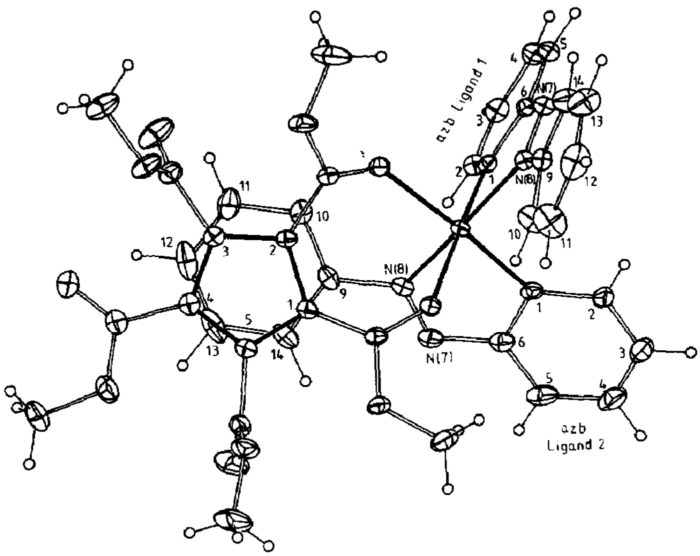
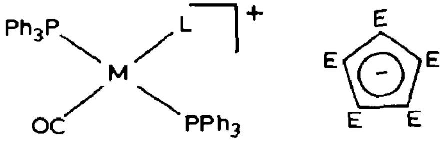
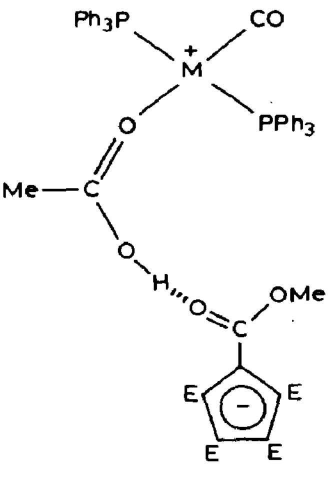


Fig. 2. A molecule of **6**.

${}^1H$ NMR spectra contain the expected resonances at δ 1.2 (MeCN), 3.6 (CO_2Me) and 7.4 (PPh_3) ppm. The FAB mass spectra contain weak ions corresponding to $[M(NCMe)(CO)(PPh_3)_2]^+$ and $[M(CO)(PPh_3)_2]^+$, while the base peak is [M-



(**7**) M = Rh , L = NCMe
(**8**) M = Ir , L = NCMe
(**9**) M = Rh , L = bqH
(**10**) M = Rh , L = phen



(**11**) M = Rh
(**12**) M = Ir

$(PPh_3)_2]^+$. Other fragment ions are detailed in the Experimental section. Finally, elemental analyses were consistent with values calculated for the formulations given, and conductivity measurements showed that the complexes were 1/1 electrolytes. These cations were described earlier [27], and undergo ready exchange of the acetonitrile for other nitrogen donors; the preparation of the benzoquinoline (**9**) and 1,10-phenanthroline (**10**) cations [28], both isolated with $[C_5(CO_2Me)_5]^-$ counter-ions, is described in the Experimental section. These results further illustrate the utility of the stable $[C_5(CO_2Me)_5]^-$ anion in the isolation of cationic species, but we have not yet been able to induce either complex to undergo loss of MeCN or CO to give species containing a covalently bonded $C_5(CO_2Me)_5$ ligand.

Crystals of the supposed salts of the acetonitrile cations were subjected to crystallographic studies, but in both cases, the structures revealed a unit cell composed of $[M(X)(CO)(PPh_3)_2]^+$ cations and $[C_5(CO_2Me)_5]^-$ anions (**11** and **12**). As shown in Fig. 3, the ligand X refined as a four-atom, branched chain fragment, and was not consistent with the presence of acetonitrile (a linear three-atom ligand). The most satisfactory refinement was in terms of a monodentate acetato or acetamide group (Rh–O 2.123(9), Ir–O 2.074(10) Å]. The remainder of the cationic geometry is square planar, with mutually *trans* PPh_3 ligands [Rh–P 2.327(3), 2.323(3); Ir–P 2.317(3), 2.318 Å] and CO *trans* to X [Rh–CO 1.814(10), Ir–CO 1.740(14) Å], and does not call for further comment.

The anionic fragment was satisfactorily modelled on the basis of a regular pentagonal $C_5(CO_2Me)_5$ group, as found previously in $[NMe_4][C_5(CO_2Me)_5]$ [15] and $[Rh\{\eta^5\text{-}C_5H_2(CO_2Me)_3\}_2][C_5(CO_2Me)_5]$ [17], with the planes of the CO_2Me groups taking up a random orientation relative to the C_5 ring plane; only $CO_2Me(1)$ is close to coplanar with the ring (Table 8).

However, interpretation of the structure in terms of $[M\{OC(O)Me\}(CO)(PPh_3)_2]^+$ cations and $[C_5(CO_2Me)_5]^-$ anions obviously violates the usual electron-counting rules applied to these systems; the diamagnetic (NMR) nature of these salts precludes their being derivatives of rhodium(II) or iridium(II). Inspection of the unit-cell contents (Fig. 3) shows that the closest contact is O(21)...O(101) (x, $y-1$, z) (2.86 Å), and that O(51) and O(102) are only 3.09 Å apart; the associated geometry is consistent with the possibility of a hydrogen bond between the two groups. The structure can thus be viewed as an aggregate of neutral $M\{OC(O)Me\}(CO)(PPh_3)_2$ and $HC_5(CO_2Me)_5$ molecules, joined by the hydrogen bond, or as a salt of the acetic acid cation $[M\{OC(OH)Me\}(CO)(PPh_3)_2]^+$ and $[C_5(CO_2Me)_5]^-$ anion (**11**, M = Rh; **12**, M = Ir). We incline to the latter view, based on the well-known stability of the anionic species, and the expected relative basicities of coordinated acetate and free $[C_5(CO_2Me)_5]^-$ anions; the determined geometry is unhelpful in this respect as the CO_2Me substituent libration is generally very high.

The acetic acid may be formed by hydration of acetonitrile, catalysed by the metal complex or strong acid; we have also considered the possibility that the ligand is acetamide. Attempted syntheses of these salts from $[M(NCMe)(CO)(PPh_3)_2]$-$[C_5(CO_2Me)_5]$ and the ligand were unsuccessful. The converse approach, the reaction between $HC_5(CO_2Me)_5$ and $Rh(OAc)(CO)(PPh_3)_2$ in a non-coordinating solvent (benzene), immediately gave a yellow powder which analysed for $Rh\{C_5(CO_2Me)_5\}(CO)(PPh_3)_2$ (**13**). We have been unable to obtain a suitable crystalline sample of this compound, as it is insoluble in all but coordinating

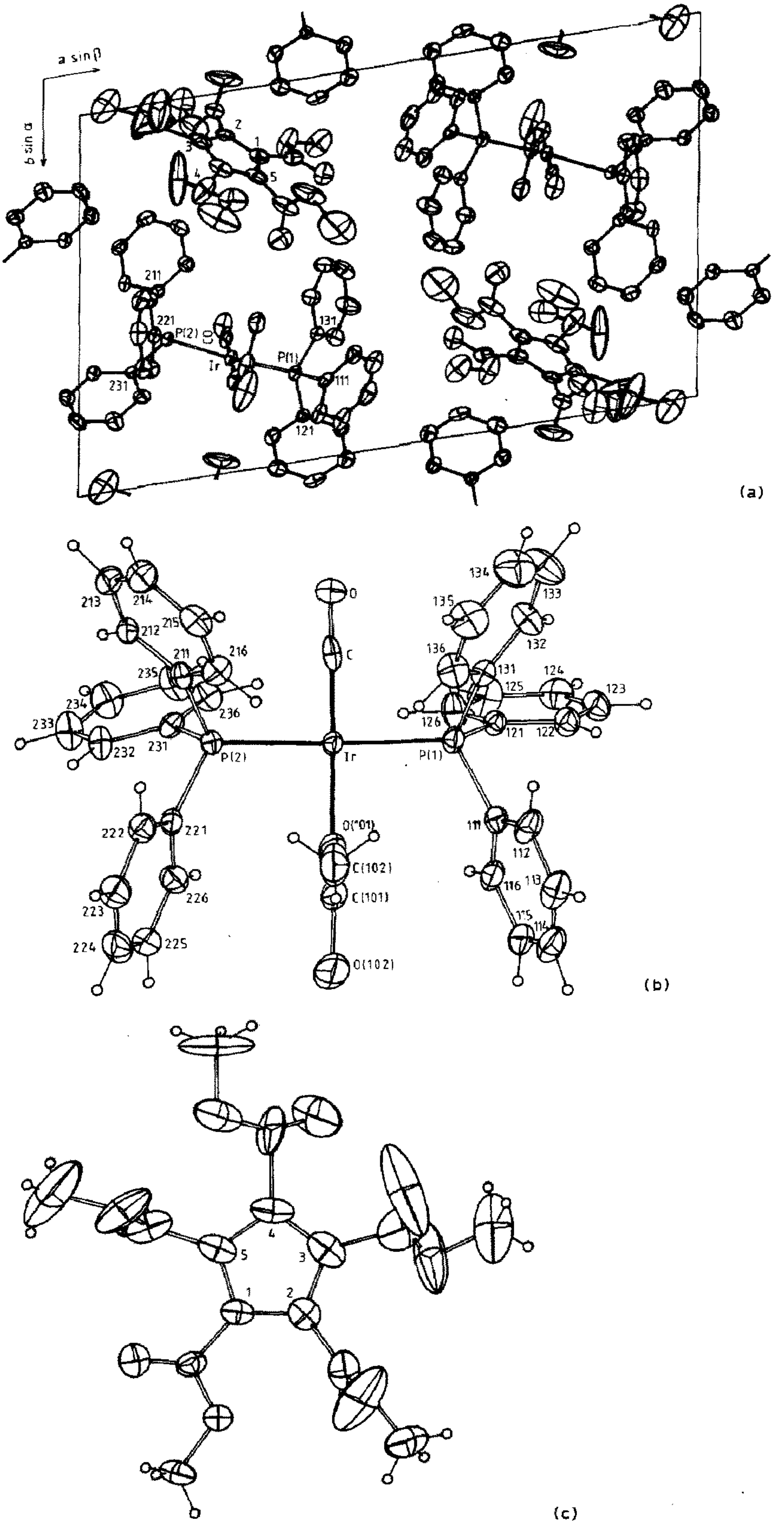
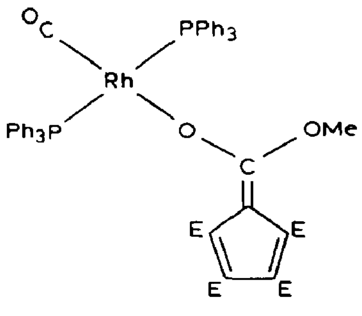


Fig. 3. (a) Unit cell contents of **12**, projected down *c*. (b) A single cation of **12**, projected normal to the iridium coordination plane. (c) The cpp anion of **12**, projected normal to the C_5 plane.



(13)

solvents; from the latter, only the salts $[Rh(S)(CO)(PPh_3)_2][C_5(CO_2Me)_5]$ (S = solvent) could be obtained. The FAB mass spectrum shows only $[Rh(CO)(PPh_3)_2]^+$ or $[C_5(CO_2Me)_5]^-$ and associated fragment ions, possibly because the matrix (3-nitrobenzyl alcohol) is sufficiently polar to coordinate to the rhodium. We suggest that this complex has the illustrated square planar structure, with an O-bonded $C_5(CO_2Me)_5$ group. An alternative structure containing a covalent chelating, O-bonded $C_5(CO_2Me)_5$ group, with five-coordinate rhodium(I), cannot be ruled out.

Conclusions

We have shown that discrete complexes containing the $C_5(CO_2Me)_5$ ligand coordinated to rhodium or iridium can be obtained by halogen exchange with $Tl[C_5(CO_2Me)_5]$ in the case of $\{MCl(C_8H_{12})\}_2$ (M = Rh or Ir) and $\{RhCl(azb)_2\}_2$. Spectroscopic and X-ray crystallographic characterisation showed the $C_5(CO_2Me)_5$ ligand to be η^5, C-bonded in the metal(I) complexes and η^2, O-bonded in the rhodium(III) complex; the latter is the first discrete molecular complex to be obtained that retains the coordinated ligand in solution. Ready displacement of the η^5-$C_5(CO_2Me)_5$ ligand by other ligands such as tertiary phosphines affords cationic complexes as their $[C_5(CO_2Me)_5]^-$ salts, exemplified by $[Rh(dppe)(cod)][C_5(CO_2Me)_5]$. Similar salts of $[M(CO)(NCMe)(PPh_3)_2]^+$ cations were obtained from reactions between $MCl(CO)(PPh_3)_2$ and $Tl[C_5(CO_2Me)_5]$ in acetonitrile. The complex $Rh\{C_5(CO_2Me)_5\}(CO)(PPh_3)_2$, obtained from $Rh\{OC(O)Me\}(CO)(PPh_3)_2$ and $HC_5(CO_2Me)_5$ in benzene, dissolves only in coordinating solvents to form $[Rh(solvent)(CO)(PPh_3)_2][C_5(CO_2Me)_5]$. Finally, crystallographic studies have led to the postulated existence of $[M\{OC(OH)Me\}(CO)(PPh_3)_2][C_5(CO_2Me)_5]$, in which coordinated acetic acid, or possibly acetamide, is hydrogen-bonded to the anion.

Experimental

General conditions. All reactions were carried out under nitrogen; no special precautions were taken to exclude air during work-up, since most complexes proved to be stable in air as solids, and for short times in solution. Solvents were dried and distilled before use.

Instruments. Perkin–Elmer 683 double-beam spectrometer, NaCl optics (IR); Bruker WP80 spectrometer (^{1}H NMR at 80 MHz, ^{13}C NMR at 20.1 MHz).

FAB mass spectra were obtained on a VG ZAB 2HF instrument equipped with a FAB source. Argon was used as the exciting gas, with source pressures typically 10^{-6} mbar; the FAB gun voltage was 7.5 kV, current 1 mA. The ion accelerating potential was 8 kV. The matrix was 6/1 dithiothreitol/dithioerythritol. The complexes were made up as ca. 0.5 *M* solutions in acetone or dichloromethane; a drop was added to a drop of matrix and the mixture was applied to the FAB probe tip.

Starting materials. $HC_5(CO_2Me)_5$ and $Tl[C_5(CO_2Me)_5]$ were made as previously described [5]. The complexes $\{RhCl(cod)\}_2$ [29], $\{IrCl(cod)\}_2$ [30] cod = η^4-C_8H_{12}, $\{RhCl(azb)_2\}_2$ [24], $RhCl(CO)(PPh_3)_2$ [31], and $IrCl(CO)(PPh_3)_2$ [32] were prepared by published methods.

Preparation of M(cod){$C_5(CO_2Me)_5$}

(i) M = Rh. Addition of $\{RhCl(cod)\}_2$ (119 mg, 0.24 mmol) to a stirred solution of $Tl[C_5(CO_2Me)_5]$ (271 mg, 0.48 mmol) in MeCN (20 ml) resulted in immediate separation of TlCl from a yellow solution. After 3 h stirring, the TlCl was filtered off, and washed with MeCN (2 ml). The combined filtrates were evaporated to dryness. Crystallisation of the residue (MeOH, −30 °C) afforded orange crystals of $Rh(cod)\{C_5(CO_2Me)_5\}$ (**3**) (213 mg, 78%), m.p. 124–126 °C. Found: C, 48.71; H, 4.98. $C_{23}H_{27}O_{10}Rh$ calcd. C, 48.78; H, 4.81%. IR (nujol): ν(C=O) at 1770(sh), 1764(sh), 1750(sh), 1742s, 1736s, 1727s, 1718s, 1715(sh), 1705(sh), 1678(sh); other bands at 1448s, 1420m, 1412m, 1408(sh), 1390s, 1331m, 1308m, 1304(sh), 1255s, 1228s(br), 1180s, 1075m, 1065m, 1000s, 990s, 980m, 807m, 674(sh), 636m cm^{-1}. ^{1}H NMR: δ ($CDCl_3$) 4.43 (s, 4H, CH), 3.83 (s, 15H, OCH_3), 2.33–1.94 (m, 8H, CH_2). FAB MS: 566, $[Rh(C_8H_{12})\{C_5(CO_2Me)_5\}]^+ \equiv M^+$, 100; 535, $[M - OMe]^+$, 60; 505, $[M - CO_2Me - 2H]^+$, 9; 447, $[M - 2CO_2Me - H]^+$, 28; negative ion: 507, $[M - CO_2Me]^-$, 8; 355, $[C_5(CO_2Me)_5]^-$, 100. Conductivity (acetone): 10.7 ohm^{-1} cm^2 mol^{-1}.

(ii) M = Ir. A similar procedure starting from $\{IrCl(cod)\}_2$ (92 mg, 0.14 mmol) and $Tl[C_5(CO_2Me)_5]$ (152 mg, 0.27 mmol) in acetonitrile (15 ml) afforded yellow crystals of $Ir(cod)\{C_5(CO_2Me)_5\}$ (**4**) (128 mg, 72%) m.p. 110–112 °C. Found: C, 42.08; H, 4.16. $C_{23}H_{27}O_{10}Ir$ calcd. C, 42.13; H, 4.15%. IR (nujol): ν(C=O) 1750(sh), 1745s, 1741(sh), 1730s, 1718s, 1709(sh), 1700(sh); other bands at 1410m, 1298(sh), 1263(sh), 1256(sh), 1225vs(br), 1180s, 1170(sh), 1155(sh), 1075m, 998s, 987s, 846(sh), 809m, 632m cm^{-1}. ^{1}H NMR: δ ($CDCl_3$) 4.33 (s, 4H, CH), 3.82 (s, 15H, OCH_3), 2.22–1.92 (m, 8H, CH_2).

Reaction of Rh(cod){$C_5(CO_2Me)_5$} with dppe

When dppe (133 mg, 0.33 mmol) was added to a stirred solution of $Rh(cod)\{C_5(CO_2Me)_5\}$ (187 mg, 0.33 mmol) in methanol (15 ml) the solution immediately changed from yellow to orange. The mixture was refluxed for approximately 18 h and then since TLC showed the reaction to be complete, evaporated to dryness (rotary evaporator). Crystallisation (MeOH) gave orange-red crystals of $[Rh(cod)(dppe)][C_5(CO_2Me)_5]$ (**5**) (233 mg, 73%) m.p. 156–158 °C. Found: C, 60.33; H, 5.43; $C_{49}H_{51}O_{10}P_2Rh$ calcd. C, 61.00; H, 5.33%. IR (nujol): ν(C=O) 1742m, 1732(sh), 1718s, 1706s, 1700s, 1697s, 1690(sh), 1677(sh), 1655m, 1642m; other bands at 1495m, 1490(sh), 1480m, 1437s, 1424m, 1418m, 1265s, 1197s, 1190s, 1175s, 1170s, 1105s, 1065s, 1020m, 709m, 699s, 680m, 677(sh), 645m cm^{-1}. ^1H NMR: δ ($CDCl_3$) 7.50 (s, 20H, Ph), 4.88 (s, 4H, CH), 3.63 (s, 15H, OCH_3), 2.31–2.01 (m, 12H, CH_2). FAB MS: 856, $[Rh(dppe)\{C_5(CO_2Me)_5\}]^+$, ~ 1; 609, $[Rh(C_8H_{12})(dppe)]^+$, 100; 501, $[Rh(dppe)]^+$, 77; 211, $[Rh(C_8H_{12})]^+$, 17; negative ion: 355, $[C_5(CO_2Me)_5]^-$, 100. Conductivity (acetone): 75.5 ohm^{-1} cm^2 mol^{-1}.

Preparation of $Rh(azb)_2\{C_5(CO_2Me)_5\}$. A mixture of $\{RhCl(azb)_2\}_2$ (150 mg, 0.15 mmol) and $Tl[C_5(CO_2Me)_5]$ (167 mg, 0.30 mmol) in MeCN (15 ml) was refluxed for approximately 18 h to give a red-brown solution over an off-white precipitate. The precipitate (TlCl) was filtered off and washed with MeCN (2 ml). The combined filtrates were evaporated to dryness (rotary evaporator). Purification by preparative TLC (silica gel; 1/1 acetone/light petroleum) gave the major product (in a fraction of R_f 0.37), which was crystallised ($MeOH/Et_2O$) to give red crystals of $Rh(azb)_2\{C_5(CO_2Me)_5\}$ (**6**) (78 mg, 32%), m.p. 209–210 °C (dec) Found C, 56.29; H, 4.19; N, 6.60. $C_{39}H_{33}N_4O_{10}Rh$ calcd. C, 57.08; H, 4.05; N, 6.83%. IR (nujol): ν(C=O) 1750(sh), 1746(sh), 1742s, 1732s, 1711m, 1707s, 1700s, 1670m, 1660s, 1655(sh), 1649vs, 1645vs, 1640(sh), 1629s, 1625(sh), 1618m; other bands at 1595s, 1590(sh), 1582s, 1578s, 1560m, 1558m, 1495m, 1490m, 1420m, 1410m, 1362m, 1322m, 1310s, 1260s, 1242m, 1235m, 1220(sh), 1212s, 1208s, 1200s, 1178s, 1168s, 1160s, 1082m, 1065m, 1045m, 1011m, 772s, 760m, 728m, 718m, 685m, 655m cm^{-1}. ^1H NMR: δ ($CDCl_3$) 8.3-7.0 (m, 18H, Ph); 3.75 (s, 6H, OMe); 3.69 (s, 3H, OMe); 3.32 (s, 6H, OMe).

Reactions between $Tl[C_5(CO_2Me)_5]$ *and* $MCl(CO)(PPh_3)_2$

(i) $M = Rh$. Addition of $RhCl(CO)(PPh_3)_2$ (365 mg, 0.53 mmol) to a stirred solution of $Tl[C_5(CO_2Me)_5]$ (296 mg, 0.53 mmol) in acetonitrile (35 ml) caused immediate separation of a white precipitate. After 1 h this was filtered off and washed with MeCN (5 ml). Evaporation of the combined filtrates, dissolution of the residue in hot MeOH (3 ml), and cooling the filtered solution gave yellow crystals of $[Rh(CO)(NCMe)(PPh_3)_2][C_5(CO_2Me)_5]$ (**7**) (418 mg, 75%), m.p. 170–172 °C. Found: C, 61.78; H, 4.59; N, 1.33. $C_{54}H_{48}NO_{11}P_2Rh$ calcd. C, 61.66; H, 4.60; N, 1.33%. IR (CH_2Cl_2): ν(CO) 2020 cm^{-1}; IR (nujol): ν(CN) 2302w; ν(CO) 2016s, 1970w; ν(C=O) 1741m, 1738s, 1725s, 1718s, 1714(sh), 1708(sh), 1702(sh), 1696s, 1691s, 1687(sh), 1680(sh), 1668(sh), 1655(sh); other bands at 1495(sh), 1490m, 1482m, 1478m, 1441s, 1439s, 1275(sh), 1272m, 1209s, 1202s, 1185s, 1180s, 1173s, 1165s, 1155s, 1135(sh), 1100s, 1080(sh), 1075m, 1065m, 710m, 705(sh), 696s, 690m cm^{-1}. ^1H NMR: δ ($CDCl_3$) 7.38 (m, 30H, Ph), 3.58 (s, 15H, OMe), 1.20 (s, 3H, MeCN). FAB MS; 696, $[Rh(NCMe)(CO)(PPh_3)_2]^+ \equiv M$, 2; 655, $[M - MeCN]^+$, 54; 627, $[Rh(PPh_3)_2]^+$, 100; 550, $[Rh(PPh_2(PPh_3)]^+$, 11; 393, $[Rh(CO)(PPh_3)]^+$, 4; 288, $[Rh(PPh_2)]^+$, 33. Conductivity (acetone): 86.7 ohm^{-1} cm^2 mol^{-1}.

(ii) $M = Ir$. A similar reaction between $Tl[C_5(CO_2Me)_5]$ (212 mg, 0.38 mmol) and $IrCl(CO)(PPh_3)_2$ (296 mg, 0.38 mmol) in MeCN (25 ml) afforded yellow crystals of $[Ir(CO)(NCMe)(PPh_3)_2][C_5(CO_2Me)_5]$ (**8**) (365 mg, 84%), m.p. 175–176 °C (dec.). Found: C, 56.65; H, 4.24; N, 1.25. $C_{54}H_{48}IrNO_{11}P_2$ calcd. C, 56.84; H, 4.24; N, 1.23%. IR (CH_2Cl_2): ν(CO) 2006 cm^{-1}; IR (nujol): ν(CN) 2300w; ν(CO) 2000vs, 1955w; ν(C=O) 1747m, 1742(sh), 1740s, 1727(sh), 1723vs, 1719vs, 1715vs, 1705s, 1695s, 1690vs, 1687s, 1680(sh), 1675s, 1670(sh), 1665(sh), 1652m, 1645m, 1640(sh); other bands at 1495m, 1485s, 1480s, 1435vs, 1417m, 1398m, 1394m, 1269s, 1207(sh), 1202vs, 1197s, 1185s, 1180s, 1170s, 1160s, 1152(sh),

1098s, 1071m, 1061m, 1013m, 999m, 750m, 710m, 701m, 692s, 685m cm^{-1}. ^{1}H NMR: δ ($CDCl_3$) 7.43 (m, 30H, Ph), 3.62 (s, 15H, OMe), 1.25 (s, 3H, MeCN). FAB MS: 786, $[Ir(NCMe)(CO)(PPh_3)_2]^+ \equiv M^+$, 12; 745, $[M - MeCN]^+$, 100; 715, $[Ir(PPh_3)_2 - 2H]^+$, 69; 483, $[Ir(CO)(PPh_3)]^+$, 25; 453, $[Ir(PPh_3) - 2H]^+$, 25; 375, $[Ir(PPh_2) - 3H]^+$, 50. Conductivity (acetone): 79.7, (MeCN) 94.7 ohm^{-1} cm^2 mol^{-1}.

Reactions of $[Rh(CO)(NCMe)(PPh_3)_2][C_5(CO_2Me)_5]$

(i) With benzo[h]quinoline. Benzo[*h*]quinoline (19 mg, 0.11 mmol) was added to a solution of $[Rh(CO)(NCMe)(PPh_3)_2][C_5(CO_2Me)_5]$ (87 mg, 0.083 mmol) in $CHCl_3$ (5 ml). The mixture was stirred at room temperature for 1 h, then the solvent was removed and the residue crystallised ($CHCl_3/Et_2O$) to give pale yellow crystals of $[Rh(CO)(bqH)(PPh_3)_2][C_5(CO_2Me)_5]$ (**9**) (79 mg, 80%), m.p. 170 °C (dec.). Found: C, 64.94; H, 4.51; N, 1.20. $C_{65}H_{54}NO_{11}P_2Rh$ calcd. C, 65.61; H, 4.57; N, 1.18%. IR ($CHCl_2$): ν(CO) 2006s cm^{-1}; IR (nujol): ν(CO) 2008vs, 1965w; ν(C=O) 1740(sh), 1725s, 1722(sh), 1711s, 1707s, 1702(sh), 1695s, 1690s, 1688(sh), 1675s; other bands at 1495(sh), 1482s, 1438s, 1425(sh), 1403(sh), 1397m, 1282m, 1275(sh), 1205vs(br), 1179(sh), 1175s, 1145(sh), 1097m, 1072(sh), 1065m, 1052(sh), 1011m, 760(sh), 754s, 747(sh), 741m, 709m, 695s, 622m cm^{-1}. ^{1}H NMR: δ ($CDCl_3$) 7.90–6.65 (m, 39H, Ph + bq), 3.60 (s, 15H, OMe). FAB MS: 834, $[Rh(CO)(bqH)(PPh_3)_2]^+ \equiv M^+$, 13; 655 $[M - bqH]^+$, 42; 627, $[Rh(PPh_3)_2]^+$, 100; 550, $[Rh(PPh_2)(PPh_3)]^+$, 16; 544, $[Rh(bqH)(PPh_3)]^+$, 17; 393, $[Rh(CO)(PPh_3)]^+$, 7; 288, $[Rh(PPh_2)]^+$, 72. Conductivity (acetone): 87.9 ohm^{-1} cm^2 mol^{-1}.

(ii) With 1,10-phenanthroline. A similar procedure was carried out with 1,10-phenanthroline (24 mg, 0.13 mmol) and $[Rh(CO)(NCMe)(PPh_3)_2][C_5(CO_2Me)_5]$ (129 mg, 0.12 mmol) in $CHCl_3$ (12 ml). There was an immediate colour change from yellow to orange-yellow. After 18 h, evaporation and crystallisation of the residue ($CHCl_3/Et_2O$) gave pale orange crystals of $[Rh(CO)(phen)(PPh_3)_2][C_5(CO_2Me)_5] \cdot CHCl_3$ (**10**) (96 mg, 61%), m.p. 173 °C (dec.). Found: C, 59.08; H, 4.13; N, 2.14. $C_{64}H_{53}N_2O_{11}P_2Rh.\ CHCl_3$ calcd. C, 59.58; H, 4.15; N, 2.13%. IR (CH_2Cl_2): ν(CO) 1947s cm^{-1}; IR (nujol): ν(CO) 1931vs, 1885w; ν(C=O) 1745(sh), 1739(sh), 1728s, 1721(sh), 1705m, 1701(sh), 1698m, 1693m, 1691(sh), 1685(sh), 1681m, 1678m; other bands at 1482m, 1441m, 1438m, 1429(sh), 1421m, 1212s, 1178m, 1167(sh), 1095m, 755m, 748m, 708m, 698m cm^{-1}. ^{1}H NMR: δ ($CDCl_3$) 8.98–7.17 (m, 38H, Ph + phen), 7.27 (s, 1H, $CHCl_3$), 3.72 (s, 15H, OMe). FAB MS: 573, $[Rh(CO)(phen)(PPh_3)_2]^+$, 100; 545, $[Rh(phen)(PPh_3)]^+$, 33; 283, $[Rh(phen)]^+$, 69; 154, ?, 53. Conductivity (acetone): 103 ohm^{-1} cm^2 mol^{-1}.

Reactions between $HC_5(CO_2Me)_5$ *and* $Rh\{OC(O)Me\}(CO)(PPh_3)_2$

(i) In benzene. $HC_5(CO_2Me)_5$ (56 mg, 0.157 mmol) was added to a stirred solution of $Rh\{OC(O)Me\}(CO)(PPh_3)_2$ (112 mg, 0.157 mmol) in benzene (20 ml), whereupon a pale yellow precipitate formed immediately. After 30 min stirring the solid was collected, washed with light petroleum, and dried, to give $Rh\{C_5(CO_2Me)_5\}(CO)(PPh_3)_2$ (123 mg, 78%), m.p. 180–182 °C after darkening at 116–118 °C. Found: C, 61.54; H, 4.60; N, < 0.05. $C_{52}H_{45}O_{11}P_2Rh$ calcd. C, 61.79; H, 4.49; N, 0.0%. IR (Nujol): ν(CO) 1970s, 1925w; ν(C=O) 1745(sh), 1740(sh), 1735s, 1727m, 1715s, 1708s, 1701m, 1698s, 1693s, 1682, 1675s, 1671(sh), 1667(sh), 1653w; other bands at 1442s, 1438s, 1295m, 1282m, 1278m, 1198s, 1175s, 1170s, 1167(sh), 1096s, 1000m, 979m, 940(sh), 760m, 746m, 721m, 706m, 692s cm^{-1}. FAB

Table 3. Non-hydrogen atom coordinates, **6**

Atom	*x*	*y*	*z*
Rh	0.07456(1)	0.20428(3)	0.23241(2)
$C_5(CO_2Me)_5$ ligand			
C(1)	0.1416(2)	0.2948(4)	0.4624(2)
C(11)	0.0893(2)	0.3437(4)	0.4159(3)
O(11)	0.0583(1)	0.2917(3)	0.3554(2)
O(12)	0.0741(1)	0.4634(3)	0.4459(2)
C(12)	0.0254(2)	0.5299(6)	0.3983(4)
C(2)	0.1676(2)	0.1645(4)	0.4530(2)
C(21)	0.1494(2)	0.0551(4)	0.3934(3)
O(21)	0.1258(1)	0.0607(2)	0.3187(2)
O(22)	0.1630(2)	−0.0647(3)	0.4291(2)
C(22)	0.1567(4)	−0.1804(6)	0.3731(4)
C(3)	0.2165(2)	0.1567(4)	0.5145(2)
C(31)	0.2561(2)	0.0405(5)	0.5297(3)
O(31)	0.2870(2)	0.0009(4)	0.4835(2)
O(32)	0.2536(1)	−0.0154(3)	0.6057(2)
C(32)	0.2900(3)	−0.1300(6)	0.6297(4)
C(4)	0.2223(2)	0.2788(4)	0.5613(2)
C(41)	0.2723(2)	0.3142(5)	0.6234(3)
O(41)	0.3169(1)	0.2554(4)	0.6347(3)
O(42)	0.2643(1)	0.4274(4)	0.6660(2)
C(42)	0.3113(2)	0.4808(6)	0.7244(3)
C(5)	0.1760(2)	0.3607(4)	0.5302(2)
C(51)	0.1674(2)	0.4991(4)	0.5634(3)
O(51)	0.1841(2)	0.6003(3)	0.5358(3)
O(52)	0.1393(1)	0.4941(3)	0.6296(2)
C(52)	0.1336(3)	0.6197(8)	0.6728(5)
Azb ligands			
C(101)	0.0890(2)	0.1351(4)	0.1221(2)
C(102)	0.1220(2)	0.1876(4)	0.0644(3)
C(103)	0.1269(2)	0.1160(5)	−0.0095(3)
C(104)	0.1000(2)	−0.0061(5)	−0.0288(3)
C(105)	0.0665(2)	−0.0591(4)	0.0255(3)
C(106)	0.0611(2)	0.0133(4)	0.0997(2)
N(107)	0.0251(1)	−0.0387(3)	0.1530(2)
N(108)	0.0210(1)	0.0383(3)	0.2156(2)
C(109)	−0.0157(2)	−0.0143(4)	0.2718(3)
C(110)	−0.0309(2)	0.0703(5)	0.3322(3)
C(111)	−0.0665(3)	0.0231(7)	0.3874(4)
C(112)	−0.0857(2)	−0.1090(7)	0.3795(4)
C(113)	−0.0711(2)	−0.1906(5)	0.3185(4)
C(114)	−0.0359(2)	−0.1448(5)	0.2638(4)
C(201)	0.0253(2)	0.3404(4)	0.1685(2)
C(202)	−0.0324(2)	0.3370(5)	0.1340(3)
C(203)	−0.0591(2)	0.4503(6)	0.0960(3)
C(204)	−0.0303(3)	0.5709(6)	0.0920(4)
C(205)	0.0261(3)	0.5792(5)	0.1272(3)
C(206)	0.0536(2)	0.4638(4)	0.1646(3)
N(207)	0.1108(2)	0.4716(4)	0.2009(2)
N(208)	0.1289(1)	0.3588(3)	0.2326(2)
C(209)	0.1867(2)	0.3532(5)	0.2752(3)
C(210)	0.2179(2)	0.2381(5)	0.2672(3)
C(211)	0.2720(2)	0.2291(6)	0.3140(3)
C(212)	0.2936(2)	0.3311(7)	0.3681(3)
C(213)	0.2619(2)	0.4450(6)	0.3760(4)
C(214)	0.2082(2)	0.4584(5)	0.3290(3)

Table 4

Rhodium environment, **6**; *r* is the metal–ligand environment (Å), other entries are the angles subtended at the metal by the relevant atoms at the head of the associated row and column.

Atom	*r*	O(21)	C(101)	N(108)	C(201)	N(208)
O(11)	2.222(3)	82.4(1)	177.5(1)	103.2(1)	90.4(1)	84.8(1)
O(21)	2.197(3)		99.5(1)	80.5(1)	172.7(1)	101.5(1)
C(101)	1.959(4)			78.7(1)	87.7(2)	93.3(1)
N(108)	2.073(3)				100.0(1)	172.0(1)
C(201)	1.957(4)					79.0(1)
N(208)	2.006(3)					

MS: (positive ion) 655, $[Rh(CO)(PPh_3)_2]^+$, 17; 627, $[Rh(PPh_3)_2]^+$, 32; 550, $[Rh(PPh_2)(PPh_3)]^+$, 7; 393, $[Rh(CO)(PPh_3)]^+$, 4; 278, $[OPPh_3]^+$; (negative ion) 355, $[C_5(CO_2Me)_5]^-$, 100; 340, $[355 - Me]^-$, 3; 309, $[355 - Me - OMe]^-$, 5; 251, $[355 - CO_2Me - C_2H_6O]^+$, 3.

(ii) In acetonitrile. A solution of $HC_5(CO_2Me)_5$ (47 mg, 0.132 mmol) and $Rh\{OC(O)Me\}(CO)(PPh_3)_2$ (94 mg, 0.132 mmol) in MeCN (15 ml) was stirred at room temperature for 6 h. Evaporation of the solvent gave a yellow solid, which was recrystallised (MeOH, −30 °C) to give yellow crystals of $[Rh(CO)(NCMe)(PPh_3)_2]$ $[C_5(CO_2Me)_5]$ (73 mg, 53%), identical (m.p., IR, NMR) with the salt **7** prepared as described above.

Crystallography

Unique data sets were measured on crystals mounted in capillaries within the limit $2\theta_{max}$ 50 ° at ~ 295 K using Syntex $P2_1$ and Enraf–Nonius CAD-4 four circle

Table 5

$C_5(CO_2Me)_5$ geometry, **6**

Ring atom, *n*	1	2	3	4	5
Distances (Å)					
C(*n*)–C(*n* + 1)	1.450(6)	1.394(5)	1.413(6)	1.394(6)	1.399(5)
C(*n*)–C(*n*1)	1.426(5)	1.454(5)	1.483(6)	1.459(5)	1.494(6)
C(*n*1)–O(*n*1)	1.223(5)	1.224(5)	1.189(6)	1.200(6)	1.188(6)
C(*n*1)–O(*n*2)	1.348(5)	1.331(5)	1.334(6)	1.338(6)	1.337(6)
O(*n*2)–C(*n*2)	1.437(6)	1.441(7)	1.441(7)	1.433(6)	1.436(8)
Angles (degrees)					
C(*n* − 1)–C(*n*)–C(*n* + 1)	106.7(3)	107.5(3)	108.4(3)	108.0(3)	109.3(3)
C(*n* − 1)–C(*n*)–(C*n*1)	126.1(4)	130.0(3)	126.5(4)	123.8(4)	123.7(3)
C(*n* + 1)–C(*n*)–C(*n*1)	127.1(3)	122.5(4)	125.1(3)	127.8(4)	126.9(3)
C(*n*)–C(*n*1)–O(*n*1)	128.8(4)	129.3(4)	126.9(4)	126.3(4)	124.8(4)
C(*n*)–C(*n*1)–O(*n*2)	112.4(3)	111.3(3)	110.3(4)	111.7(4)	111.0(4)
O(*n*1)–C(*n*1)–O(*n*2)	118.8(4)	119.4(4)	122.9(4)	122.0(4)	124.2(4)
C(*n*1)–O(*n*2)–C(*n*2)	117.4(4)	117.0(4)	116.7(4)	118.1(4)	116.1(4)
C(*n*1)–O(*n*1)–Rh	132.8(3)	138.6(3)			
Carboxylate/C_5 ring dihedral					
θ (degrees)	4.9	34.3	67.4	14.5	87.1

Table 6

Azb geometries, **6**; The two values in each entry are for ligand $n = 1, 2$.

Atoms	Parameter	
Distance (Å)		
C(*n*01)–C(*n*02)	1.401(6)	1.395(6)
C(*n*01)–C(*n*06)	1.395(5)	1.404(6)
C(*n*02)–C(*n*03)	1.389(6)	1.379(7)
C(*n*03)–C(*n*04)	1.380(7)	1.385(8)
C(*n*04)–C(*n*05)	1.372(7)	1.372(8)
C(*n*05)–C(*n*06)	1.401(6)	1.400(7)
C(*n*06)–N(*n*07)	1.398(5)	1.393(6)
N(*n*07)–N(*n*08)	1.266(5)	1.270(5)
N(*n*08)–C(*n*09)	1.447(5)	1.435(5)
C(*n*09)–C(*n*10)	1.365(7)	1.379(6)
C(*n*09)–C(*n*14)	1.378(7)	1.389(6)
C(*n*10)–C(*n*11)	1.397(9)	1.382(6)
C(*n*11)–C*n*12)	1.384(10)	1.369(8)
C(*n*12)–C(*n*13)	1.349(9)	1.375(9)
C(*n*13)–C(*n*14)	1.380(9)	1.378(7)
Angles (degrees)		
Rh–C(*n*01)–C(*n*02)	130.8(3)	131.0(3)
Rh–C(*n*01)–C(*n*06)	112.4(3)	111.6(3)
C(*n*02)–C(*n*01)–C(*n*06)	116.9(4)	117.2(4)
C(*n*01)–C(*n*02)–C(*n*03)	119.7(4)	120.4(4)
C(*n*02)–C(*n*03)–C(*n*04)	122.1(4)	121.1(5)
C(*n*03)–C(*n*04)–C(*n*05)	119.7(4)	119.7(5)
C(*n*04)–C(*n*05)–C(*n*06)	118.3(4)	118.9(5)
C(*n*01)–C(*n*06)–C(*n*05)	123.3(4)	122.2(4)
C(*n*01)–C(*n*06)–N(*n*07)	118.8(3)	118.5(4)
C(*n*05)–C(*n*06)–N(*n*07)	118.0(3)	119.3(4)
C(*n*06)–N(*n*07)–N(*n*08)	112.7(3)	111.1(3)
N(*n*07)–N(*n*08)–C(*n*09)	113.5(3)	117.3(3)
N(*n*07)–N(*n*08)–Rh	116.8(3)	119.5(3)
C(*n*09)–N(*n*08)–Rh	129.1(2)	122.9(3)
N(*n*08)–C(*n*09)–C(*n*10)	118.0(4)	118.8(4)
N(*n*08)–C(*n*09)–C(*n*14)	121.3(4)	119.3(4)
C(*n*10)–C(*n*09)–C(*n*14)	120.7(5)	121.7(4)
C(*n*09)–C(*n*10)–C(*n*11)	119.5(5)	118.5(4)
C(*n*10)–C(*n*11)–C(*n*12)	119.1(6)	120.6(5)
C(*n*11)–C(*n*12)–C(*n*13)	120.7(6)	120.4(5)
C(*n*12)–C(*n*13)–C(*n*14)	120.6(5)	120.5(5)
C(*n*09)–C(*n*14)–C(*n*13)	119.4(5)	118.4(5)

diffractometers in conventional $2\theta/\theta$ scan mode (monochromatic Mo-K_α radiation; λ 0.7106$_9$ Å). N_o independent reflections were obtained, N_o with $I \geqslant 3\sigma(I)$ being considered 'observed' and used in the large block least squares refinements after solution of the structures by the heavy atom method and Gaussian absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{\text{iso}})_{\text{H}}$ were included at estimated values. Residuals at convergence are conventional R, R'. Neutral atom complex scattering factors were used [33]; computation used the XTAL program system [34] implemented by S.R. Hall on a

Table 7

Non-hydrogen atom coordinates, **11** and **12**

Atom	M = Rh			M = Ir		
	x	y	z	x	y	z
M	0.24653(4)	0.70060(7)	0.72962(9)	0.24635(2)	0.69949(4)	0.73222(5)
C	0.2380(4)	0.6464(7)	0.8888(10)	0.2382(5)	0.6476(9)	0.8852(13)
O	0.2337(3)	0.6106(6)	0.9886(7)	0.2333(5)	0.6090(8)	0.9890(10)
P(1)	0.3507(1)	0.7665(2)	0.8287(3)	0.3503(1)	0.7658(2)	0.8288(3)
C(111)	0.4014(4)	0.7999(7)	0.6949(9)	0.4006(5)	0.7983(8)	0.6938(11)
C(112)	0.4447(5)	0.7450(8)	0.6408(11)	0.4447(6)	0.7428(10)	0.6375(14)
C(113)	0.4791(5)	0.7695(9)	0.5306(12)	0.4774(6)	0.7718(12)	0.5304(15)
C(114)	0.4687(5)	0.8499(9)	0.4799(11)	0.4678(7)	0.8512(13)	0.4769(15)
C(115)	0.4252(5)	0.9076(9)	0.5292(12)	0.4257(7)	0.9079(12)	0.5298(16)
C(116)	0.3907(4)	0.8846(8)	0.6424(11)	0.3902(6)	0.8835(10)	0.6431(13)
C(121)	0.3634(4)	0.8828(6)	0.9767(9)	0.3638(5)	0.8815(8)	0.9771(10)
C(122)	0.4231(4)	0.9320(7)	1.0397(10)	0.4245(6)	0.9303(9)	1.0394(12)
C(123)	0.4322(5)	1.0184(8)	1.1536(11)	0.4333(6)	1.0159(10)	1.1562(13)
C(124)	0.3807(5)	1.0577(8)	1.2054(11)	0.3834(7)	1.0562(9)	1.2070(14)
C(125)	0.3225(5)	1.0095(8)	1.1424(12)	0.3234(7)	1.0109(11)	1.1447(17)
C(126)	0.3131(4)	0.9222(7)	1.0273(11)	0.3140(6)	0.9232(10)	1.0285(14)
C(131)	0.3848(4)	0.6739(7)	0.9053(10)	0.3850(5)	0.6728(8)	0.9041(12)
C(132)	0.4151(5)	0.6907(8)	1.0486(11)	0.4141(7)	0.6897(11)	1.0488(14)
C(133)	0.4349(6)	0.6116(9)	1.0990(13)	0.4348(9)	0.6127(13)	1.1002(18)
C(134)	0.4258(6)	0.5149(9)	1.0121(15)	0.4261(9)	0.5175(13)	1.0088(20)
C(135)	0.3961(6)	0.4974(8)	0.8700(14)	0.3964(8)	0.4965(11)	0.0661(19)
C(136)	0.3756(5)	0.5751(8)	0.8196(12)	0.3752(7)	0.5738(10)	0.8166(16)
P(2)	0.1434(1)	0.6253(2)	0.6359(3)	0.1433(1)	0.6242(2)	0.6384(3)
C(211)	0.1270(4)	0.4963(6)	0.6635(9)	0.1272(5)	0.4946(8)	0.6662(11)
C(212)	0.0735(4)	0.4592(7)	0.7143(9)	0.0732(5)	0.4578(9)	0.7201(12)
C(213)	0.0660(4)	0.3608(8)	0.7354(11)	0.0654(6)	0.3599(9)	0.7411(15)
C(214)	0.1106(5)	0.3006(7)	0.7031(12)	0.1087(7)	0.2987(9)	0.7049(16)
C(215)	0.1638(5)	0.3368(7)	0.6505(11)	0.1626(7)	0.3365(10)	0.6541(14)
C(216)	0.1722(4)	0.4354(7)	0.6322(10)	0.1726(6)	0.4347(10)	0.6353(14)
C(221)	0.1215(4)	0.6110(7)	0.4376(9)	0.1223(5)	0.6094(9)	0.4396(12)
C(222)	0.1138(5)	0.5174(8)	0.3342(10)	0.1138(6)	0.5152(9)	0.3374(13)
C(223)	0.0997(5)	0.5123(9)	0.1824(11)	0.1009(7)	0.5100(11)	0.1865(14)
C(224)	0.0947(5)	0.5994(10)	0.1380(11)	0.0965(7)	0.5949(13)	0.1386(14)
C(225)	0.1025(5)	0.6910(8)	0.2358(11)	0.1051(6)	0.6896(11)	0.2376(15)
C(226)	0.1159(4)	0.6969(7)	0.3873(10)	0.1182(6)	0.6973(9)	0.3895(13)
C(231)	0.0862(4)	0.6943(6)	0.7209(9)	0.0870(5)	0.6931(8)	0.7241(12)
C(232)	0.0241(4)	0.6790(7)	0.6559(10)	0.0239(5)	0.6804(9)	0.0567(14)
C(233)	−0.0184(5)	0.7342(8)	0.7196(12)	−0.0192(6)	0.7333(10)	0.7202(15)
C(234)	−0.0017(5)	0.8030(8)	0.8533(12)	−0.0022(6)	0.8003(11)	0.8565(15)
C(235)	0.0587(5)	0.8196(8)	0.9218(11)	0.0577(7)	0.8159(11)	0.9250(14)
C(236)	0.1026(5)	0.7653(7)	0.8561(10)	0.1026(6)	0.7626(9)	0.8589(13)
O(101)	0.2556(3)	0.7621(6)	0.5415(8)	0.2549(4)	0.7584(7)	0.5470(10)
C(101)	0.2701(6)	0.7409(11)	0.4024(15)	0.2711(6)	0.7286(14)	0.4241(14)
O(102)	0.2686(6)	0.8048(12)	0.3024(10)	0.2704(7)	0.7925(16)	0.3096(13)
C(102)	0.2893(7)	0.6209(14)	0.3853(18)	0.2878(8)	0.6181(14)	0.3950(24)
$C_5(CO_2Me)_5$ anion						
C(1)	0.2896(5)	0.1838(7)	0.5398(11)	0.2900(7)	0.1817(9)	0.5420(13)
C(11)	0.3445(6)	0.2031(8)	0.6502(13)	0.3452(7)	0.2011(10)	0.6518(14)
O(11)	0.3931(4)	0.2588(6)	0.6551(10)	0.3942(5)	0.2567(9)	0.6543(13)
O(12)	0.3362(4)	0.1578(8)	0.7546(11)	0.3360(6)	0.1590(11)	0.7585(14)
C(12)	0.3876(7)	0.1736(12)	0.8748(16)	0.3860(11)	0.1752(17)	0.8300(22)
C(2)	0.2346(5)	0.1123(7)	0.5223(11)	0.2346(7)	0.1121(9)	0.5244(15)

Table 7 (continued)

Atom	M = Rh			M = Ir		
	x	*y*	*z*	*x*	*y*	*z*
$C_5(CO_2Me)_5$ anion						
C(21)	0.2174(6)	0.0420(8)	0.6222(17)	0.2185(8)	0.0445(11)	0.6213(23)
O(21)	0.2269(7)	−0.0358(8)	0.6057(20)	0.2322(11)	−0.0348(11)	0.6143(29)
O(22)	0.1875(5)	0.0814(7)	0.7244(11)	0.1852(7)	0.0784(10)	0.7220(15)
C(22)	0.1674(9)	0.0152(15)	0.8212(22)	0.1650(12)	0.0160(23)	0.8206(31)
C(3)	0.1958(5)	0.1229(8)	0.3887(12)	0.1967(8)	0.1191(10)	0.3948(17)
C(31)	0.1306(9)	0.0616(9)	0.3484(17)	0.1231(15)	0.0611(12)	0.3405(22)
O(31)	0.1300(6)	0.0291(12)	0.1976(18)	0.1297(9)	0.0235(23)	0.2076(33)
O(32)	0.1011(6)	0.0293(12)	0.3987(14)	0.1055(9)	0.0297(20)	0.4052(18)
C(32)	0.0394(8)	−0.0146(14)	0.3313(21)	0.0418(14)	−0.0156(24)	0.3332(31)
C(4)	0.2296(6)	0.1968(9)	0.3376(12)	0.2286(8)	0.1966(12)	0.3403(14)
C(41)	0.1906(8)	0.2563(9)	0.1970(14)	0.2010(9)	0.2487(15)	0.2022(19)
O(41)	0.1619(6)	0.2004(16)	0.1561(15)	0.1590(7)	0.2070(24)	0.1601(22)
O(42)	0.2526(5)	0.2895(7)	0.1594(10)	0.2493(8)	0.2867(11)	0.1628(15)
C(42)	0.2263(11)	0.3262(15)	0.0312(10)	0.2269(17)	0.3268(23)	0.0361(21)
C(5)	0.2866(5)	0.2369(8)	0.4240(11)	0.2864(7)	0.2330(10)	0.4273(14)
C(51)	0.3335(6)	0.3268(9)	0.4177(12)	0.3337(9)	0.3252(13)	0.4204(18)
O(51)	0.3238(5)	0.4129(8)	0.4669(11)	0.3253(6)	0.4092(10)	0.4736(13)
O(52)	0.3775(6)	0.3122(8)	0.3364(13)	0.3703(9)	0.3032(11)	0.3314(19)
C(52)	0.4113(19)	0.4347(26)	0.3690(43)	0.4169(20)	0.4036(31)	0.3436(61)

Perkin–Elmer 3240 computer. Pertinent results are presented in the Tables and Figures; the latter show the non-hydrogen atom numbering schemes.

Specific details. **3**: Rh(cod){$C_5(CO_2Me)_5$}. 0.5MeOH≡$C_{23.5}H_{29}O_{10.5}$Rh, M = 582.4, Triclinic, space group $P\bar{1}$ (C_i^1, No 2), a 18.591(3), b 14.053(4), c 10.395(3) Å, α 75.15(2), β 72.13(2), γ 81.38(2)°, U 2491 Å^3, D_c ($Z = 4$) 1.55 g cm^{-3}. $F(000)$ =

Table 8

Metal atom environments, **11** and **12**; the two values in each entry are for M = Rh, Ir respectively

Atoms	Parameters
Distances (Å)	
M–C	1.814(10), 1.740(14)
M–P(1)	2.327(3), 2.317(3)
M–P(2)	2.323(3), 2.318(3)
M–O(101)	2.123(9), 2.074(10)
C–O	1.150(13), 1.21(2)
Angles (degrees)	
C–M–P(1)	88.6(3), 89.1(4)
C–M–P(2)	88.4(3), 88.6(4)
C–M–O(101)	179.1(3), 178.8(4)
P(1)–M–P(2)	176.3(1), 176.7(1)
P(1)–M–O(101)	92.0(2), 91.9(3)
P(2)–M–O(101)	90.8(2), 90.4(3)
M–C–O	178.4(9), 178.0(10)

Dihedral angles between cpp C_5 plane and C(n,n1)O(n1,2) plane, n = 1–5(°):
Rh: 17.4, 89.3, 39.6, 16.7, 86.7; Ir: 17.1, 84.2, 40.1, 15.3, 89.5.

1196. μ_{Mo} 7.0 cm^{-1}. Specimen: 0.18 × 0.50 × 0.32 mm (capillary). $A^{\star}_{min,max} = 1.13$, 1.31. $N = 8525$, $N_0 = 6343$. $R = 0.043$, $R' = 0.059$, $n_w = 7$.

Abnormal features. The asymmetric unit of the structure contains two independent complete molecules which differ only in the orientation of the ring substituents relative to the molecular core. The disposition of the molecules within the cell is pseudo-symmetric and the numbering schemes are parallel.

6: $Rh(azb)_2\{C_5(CO_2Me)_5\} \equiv C_{39}H_{33}N_4O_{10}Rh$, $M = 820.6$, Monoclinic, space group $P2_1/n$ (variant of C^5_{2h}, No 14), a 23.897(5), b 9.900(1), c 15.828(3) Å, β 99.56(2)°, U 3693 $Å^3$, D_c ($Z = 4$) 1.48 g cm^{-3}. $F(000) = 1680$. Monochromatic Mo-K_α radiation, γ 0.7106_9 Å, μ_{Mo} 5.0 cm^{-1}. Specimen: 0.42 × 0.23 × 0.30 mm. $A^{\star}_{min,max}$ (gaussian correction) = 1.10, 1.14. $N = 6469$, $N_0 = 5024$. $R = 0.042$, $R' = 0.049$, $n_w = 5$.

11: $[Rh\{OC(OH)Me\}(CO)(PPh_3)_2][C_5(CO_2Me)_5] \equiv C_{54}H_{48}O_{13}P_2Rh$, $M = 1069.8$, Triclinic, space group $P\bar{1}$, a 21.695(7), b 13.669(7), c 9.319(3) Å, α 103.15(3), β 95.39(3), γ 98.20(3)°, U 2640(2) $Å^3$. D_c ($Z = 2$) 1.35 g cm^{-3}. $F(000) = 1102$. μ_{Mo} 4.2 cm^{-1}. Specimen: 0.22 × 0.30 × 0.25 mm. $A^{\star}_{min,max} = 1.08$, 1.13. $N = 8172$, $N_0 = 3785$. $R = 0.064$, $R' = 0.054$, $n = 3.5$.

12: $[Ir\{OC(OH)Me\}(CO)(PPh_3)_2][C_5(CO_2Me)_5] \equiv C_{54}H_{48}IrO_{13}P_2$, $M = 1159$, Triclinic, space group $P\bar{1}$, a 21.685(2), b 13.615(2), c 9.306(2) Å, α 103.34(2), β 95.28(2), γ 98.31(1)°, U 2623(1) $Å^3$, D_c ($Z = 2$) 1.47 g cm^{-3}. $F(000) = 1166$. μ_{Mo} 25.9 cm^{-1}. Specimen: 0.12 × 0.12 × 0.40 mm. $A^{\star}_{min,max} = 1.30, 1.38$. $N = 9207$, $N_0 = 5462$. $R = 0.057$, $R' = 0.062$, $n = 0.3$.

The two crystals are isomorphous and the data of comparable precision, the more extensive data for the iridium derivative compensating for the heavier atom. The thermal motions on the central atoms of the two structures are very closely comparable, but towards the ligand peripheries in particular they become very high, rather more so for the iridium derivative, with adverse consequences for the reliability of the associated geometrical parameters in these regions. This is unfortunate; the square planar metal environment in the two structures implies the I valence state, in turn implying that one of the anionic residues must be protonated; from the geometries it is not at all clear which. Protonation might be expected to result in the usual type of hydrogen-bonded contacts; the shortest O...O interspecies distance is O(21)...O(101) (x, $y - 1$, z) at 2.86 Å in both structures, rather long for such an interaction and from the point of view of the coordinated O(101) perhaps rather unlikely as M–O(101)–C(101) in the two structures is quite obtuse (142.9(8), 135.4(11)°) and O(21) has very high thermal motion.

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