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Synthesis, crystal structures, and solution dynamics of some mono(2,4-dimethylpentadienyl)ruthenium(II) complexes

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Abstract

The reaction of $[Ru(\eta^5\text{-}C_7H_{11})_2H]BF_4$ (1; $(\eta^5\text{-}C_7H_{11}) = \eta^5$-2,4-dimethylpentadienyl (DMP)) with 2-electron or cyclic 6-electron ligands gives the salts $[Ru(\eta^5\text{-}C_7H_{11})L_3]BF_4$ (L = CO, PMe_3, $P(OMe)_3$, CH_3CN; L_3 = 1,1,1-tris(diphenylphosphinomethyl)ethane) and $[Ru(\eta^5\text{-}C_7H_{11})(\eta^n\text{-ring})]BF_4$ ($(\eta^n\text{-ring}) = \eta^6$-cyclohepta-1,3,5-triene, η^6-cycloocta-1,3,5,7-tetraene, η^6-arene, η^5-thiophene). In the presence of a halide salt, 1 reacts with 4-electron diene ligands to give neutral $[Ru(\eta^5\text{-}C_7H_{11})(diene)X]$ complexes (X = I, Cl, and (diene) = η^4-buta-1,3-diene, η^4-2,3-dimethylbuta-1,3-diene, $\eta^2:\eta^2$-cycloocta-1,5-diene) and with 2-electron ligands to give neutral $[Ru(\eta^5\text{-}C_7H_{11})L_2X]$ complexes (X = I, Br, Cl and L = CO, $P(OMe)_3$, PMe_3; X = I and L_2 = bis(diphenylphosphino)ethane; X = Cl and L_2 = N,N,N′,N′-tetramethylethylenediamine). $[Ru(\eta^5\text{-}C_6H_7)(\eta^4\text{-}C_6H_8)I]$ is the product of the reaction of 1 with cyclohexa-1,3-diene and KI. The complexes $[Ru(\eta^5\text{-}C_7H_{11})(P(OMe)_3)_3]BF_4$ and $[Ru(\eta^5\text{-}C_7H_{11})L_2I]$ (L = CO, $P(OMe)_3$) have been crystallographically characterized. Complexes of the type $[Ru(\eta^5\text{-}C_7H_{11})L_3]^+$ and $[Ru(\eta^5\text{-}C_7H_{11})L_2X]$ exhibit dynamic behaviour in solution due to rotation of the DMP ligand with respect to the RuL_3 or RuL_2X groups, and activation energies for twelve of the complexes have been evaluated. Exchange of free and coordinated acetonitrile in solutions of $[Ru(\eta^5\text{-}C_7H_{11})(NCCH_3)_3]BF_4$ is non-stereospecific and associative in character.

Introduction

In view of the rich and varied chemistry of cyclopentadienyl- and pentamethylcyclopentadienyl-ruthenium(II) fragments [1,2], the availability of a general method of entry into acyclic mono(pentadienyl)-ruthenium(II) chemistry [3] is of interest. Relevant to this goal is our recent report of the synthesis of the complex $[Ru(\eta^5\text{-}C_7H_{11})_2H]BF_4$ (1) in a one-pot reaction from the ruthenium(IV) precursor $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(\mu\text{-}Cl)]_2$ ($C_{10}H_{16}$ = 2,7-dimethylocta-2,6-diene-1,8-diyl), $AgBF_4$, and 2,4-dimethylpenta-1,3-diene (C_7H_{12}) in deoxygenated ethanol [4]. It

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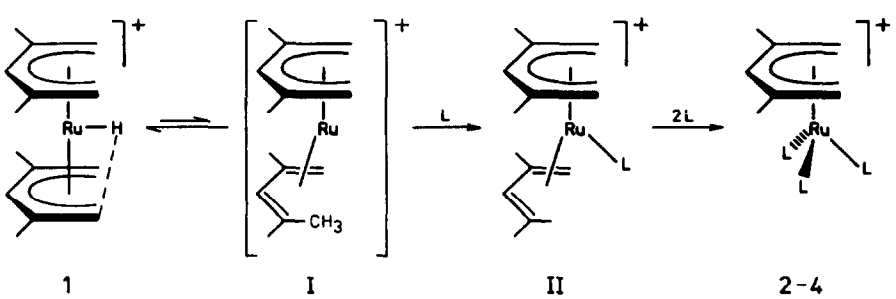
has since been shown that complex **1** can also be obtained by direct protonation of the open-ruthenocene $[Ru(\eta^5\text{-}C_7H_{11})_2]$ with HBF_4 [5]. The fluxional behaviour of complex **1** was studied by variable temperature ^1H- and ^{13}C-NMR spectroscopy [6], and it was established that in the ground state the hydrido ligand is involved in a three-centre Ru–H–C agostic interaction with a terminal methylene group carbon atom of one of the dimethylpentadienyl ligands. The nature of the fluxionality in complex **1**, however, is substantially different from that in related agostic pentadiene complexes of chromium or manganese [6–8]. Both we and Newbound *et al.* have independently noted that complex **1** is highly reactive toward 2-electron addition, *e.g.*, reacting readily with CO to give $[Ru(CO)(\eta^4\text{-}C_7H_{12})(\eta^5\text{-}C_7H_{11})]BF_4$, and that the resulting $\eta^4\text{-}C_7H_{12}$ ligand is substitutionally labile [9,10]. The high reactivity of **1** has been ascribed to its relatively facile transformation into the 16-electron unsaturated intermediate $[Ru(\eta^5\text{-}C_7H_{11})(\eta^4\text{-}C_7H_{12})]$ by rupture of the Ru–H component of the three-centre agostic interaction, i.e. in effect a Ru to C hydrogen transfer.

We now report details of the reactivity of **1** towards 2-, 4- and 6-electron ligands, further demonstrating the generality of this entry into mono(pentadienyl)-ruthenium chemistry. The fluxional behaviour of complexes of the type $[Ru(\eta^5\text{-}C_7H_{11})L_3]^+$ and $[Ru(\eta^5\text{-}C_7H_{11})L_2X]$ (L = 2-electron ligand, X = halide) is also analysed and described.

Results and discussion

Synthesis of cationic complexes

The reaction of **1** with an excess of the 2-electron ligands CO, PMe_3 or $P(OMe)_3$ in acetone at ambient temperature gives the salts $[Ru(\eta^5\text{-}C_7H_{11})L_3]BF_4$ (L = CO (**2**), PMe_3 (**3**), $P(OMe)_3$ (**4**)) in high yields. The first step (Scheme 1) is probably intramolecular hydrogen transfer to one 2,4-dimethylpentadienyl (DMP) ligand to form intermediate **I**. The electron poor **I** is subsequently stabilised by addition of a 2-electron ligand to give the intermediate **II**, which is isolable for L = CO or $P(OMe)_3$ [9,10]. Further ligand is then able to displace 1 molar equiv. of 2,4-dimethylpenta-1,3-diene (identified by GLC) to give **2–4**. In the solid state, salts **2–4** are all air stable, although in solution, **3** readily decomposes on exposure to oxygen.



1 I II 2-4

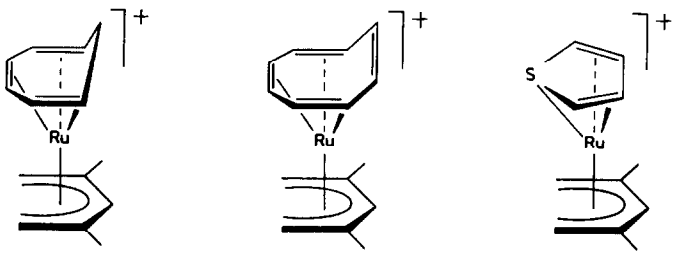
Scheme 1.

Dissolution of complex **1** in deoxygenated acetonitrile leads to rapid displacement of 1 molar equiv. of 2,4-dimethylpenta-1,3-diene and formation of the cation $[Ru(\eta^5\text{-}C_7H_{11})(NCMe)_3]^+$. The salt $[Ru(\eta^5\text{-}C_7H_{11})(NCMe)_3]BF_4$ (**5**) is readily isolated from the acetonitrile solution as colourless air-stable crystals by addition of diethyl ether. The coordinated acetonitrile ligands of **5** are substitutionally labile, and similar observations have previously been noted for the related cyclopentadienyl analogue $[Ru(\eta^5\text{-}C_5H_5)(NCMe)_3]BF_4$ [11]. Hence even in acetonitrile solution, **5** readily reacts with an excess of CO or $P(OMe)_3$ to give complexes **2** or **4**, respectively. Solvent exchange of the acetonitrile ligands in **5** is discussed in a later section of this article.

The reaction of **1** with 1,1,1-tris(diphenylphosphinomethyl)ethane ($CH_3C[CH_2PPh_2]_3$; TRIPHOS) in acetone at 273 K gives the yellow salt $[Ru(\eta^5\text{-}C_7H_{11})(TRIPHOS)]BF_4$ (**6**). The limiting low temperature ^1H, ^{13}C and ^{31}P NMR spectra for all of the complexes **2**–**6** (see Experimental) are consistent with an η^5-bound C_7H_{11} ligand coordinated in its usual U-shaped conformation, giving rise to an overall ground state piano-stool geometry of C_s symmetry [12]. The mirror plane lies perpendicular to the plane of the DMP ligand and contains the central C(3) atom, the ruthenium atom, and the unique L ligand situated under the open-face of the DMP ligand. The crystal structure of **4** (*vide infra*) indicates that this geometry is maintained in the solid state. It has also been found in $[Ru(\eta^5\text{-}C_5H_7)(PMe_3)_3]O_3SCF_3$ [3] and related complexes of Fe, Mn and Re [13–15].

Reactions of complex **1** with a range of cyclic polyolefins in excess in acetone solution at room temperature provide clean high yield routes to salts of formula $[Ru(\eta^5\text{-}C_7H_{11})(\eta^n\text{-ring})]BF_4$ (η^n-ring = η^6-cyclohepta-1,3,5-triene (C_7H_8) (**7**); η^6-cycloocta-1,3,5,7-tetraene (C_8H_8) (**8**); η^6-benzene (**9**); η^6-*para*-xylene (C_8H_{10}) (**10**); η^5-thiophene (C_4H_4S) (**11**)). The salts **7**–**11** are air-stable in the solid state and are soluble in chloroalkane solvents to form air-sensitive solutions. For the η^6-arene complexes **9** and **10**, it was not possible to stop the rapid parallel rotation of the arene ring relative to the DMP ligand on the 360 MHz ^1H NMR timescale, even at low temperatures. For example in the ^1H NMR spectrum of **10** at 190 K in CD_2Cl_2 solution, there is only one singlet from the two *p*-xylene methyl groups (6H) and one singlet from the four *p*-xylene ring protons (4H). The ^1H and ^{13}C NMR spectra of complexes **7**, **8** and **11** are also temperature invariant (200–320 K), and all imply the presence of a real or time-averaged element of symmetry in the cations. For these complexes, however, rapid rotation of the coordinated ring at low temperatures must be considered unlikely. Hence the observed spectra of **7**, **8** and **11** are consistent with static structures for these cations of overall C_s-symmetry. The unique feature of each ring ligand (*i.e.* the methylene group in **7**, the centre of the uncoordinated double bond in **8**, or the S atom in **11**) must therefore lie on the mirror plane. It cannot be decided from the spectroscopic data whether these features lie directly under the open-edge, or alternatively under the central C(3) atom of the U-shaped DMP ligand. The most probable structures for the cations of **7**, **8** and **11**, however, can be deduced if the preferred piano-stool conformation of ligands in complexes of the type $[Ru(\eta^5\text{-pentadienyl})L_3]^+$ is taken into account (see below and [3,13,14,15]). The proposed structures are shown in Scheme 2.

The η^6-cyclooctatetraene ligand in **8** is static with respect to metal migration around the C_8 ring even at 353 K (CD_3NO_2 solution) on the 360 MHz ^1H NMR



7 8 11

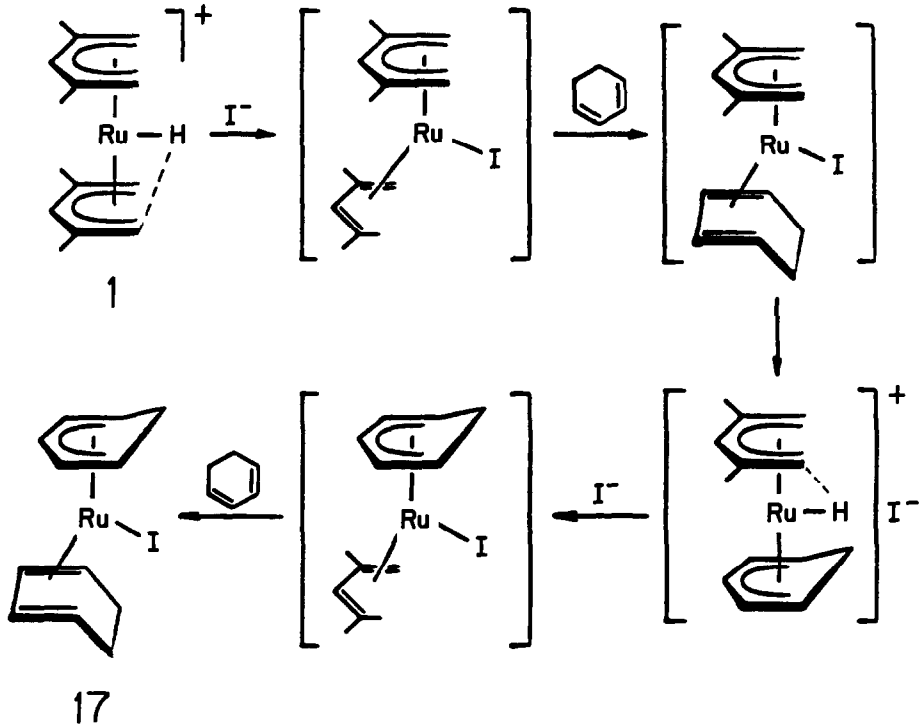
Scheme 2.

timescale. This parallels findings reported for the cyclopentadienyl analogue $[RuCp(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_8H_8)]PF_6$ which is also static at room temperature [16], but is in marked contrast to the complexes $[M(\eta^6\text{-}C_8H_8)(CO)_3]$ (M = Cr, Mo, W) where 1,3-shifts are facile [17,18]. Upon dissolution of **8** in acetonitrile solution, cyclooctatetraene is rapidly displaced and the cation $[Ru(\eta^5\text{-}C_7H_{11})(NCMe)_3]^+$ is cleanly formed.

Synthesis of neutral halo-complexes

The reaction of **1** with an excess of the dienes 1,3-butadiene (C_4H_6), 2,3-dimethylbutadiene (C_6H_{10}) or cycloocta-1,5-diene (C_8H_{12}) in the presence of a halide salt leads, on work-up, to the isolation of the neutral complexes $[Ru(\eta^5\text{-}C_7H_{11})(diene)X]$ (diene = $\eta^4\text{-}C_4H_6$, X = I (**12**) or Cl (**13**); $\eta^4\text{-}C_6H_{10}$, X = I (**14**) or Cl (**15**); 1,2,5,6-η-C_8H_{12}, X = I (**16**)) in high yields. The reactants are mixed at low temperature (195 K) and the choice of halide salt is dictated by solubility considerations: *e.g.*, KI in acetone; Et_4NCl in CH_2Cl_2. The reactions probably proceed via initial halide ion addition to give intermediates $[Ru(\eta^5\text{-}C_7H_{11})(\eta^4\text{-}C_7H_{12})X]$ (not isolated), with subsequent displacement of the sterically demanding 2,4-dimethylpenta-1,3-diene by the smaller diene. Of the complexes **12–16**, only **14** is air-stable in the solid state, and the chloro-complexes are generally less stable than the iodo-complexes. The ^1H and ^{13}C NMR spectra of **12–16** are temperature invariant (190–300 K) and show that the complexes must have C_s symmetry, the mirror plane passing through the central C(3) atom of the U-shaped $\eta^5\text{-}C_7H_{11}$ ligand, the ruthenium atom, and the halide ligand. Of the two possible conformers consistent with the NMR spectra, consideration of preferred ligand conformation in complexes of the type $[Ru(\eta^5\text{-pentadienyl})L_3]^+$ (*vide infra* and [3,13–15]) leads to the conclusion that the most likely structures for **12–16** are those with the halide ligand directly under the open edge of the DMP ligand. Complex **14** is inert towards an excess of cyclohexa-1,3-diene (100 molar equiv., 6 h at 343 K, toluene solvent), but the coordinated 2,3-dimethylbutadiene is readily displaced by CO (1 atm) giving $[Ru(\eta^5\text{-}C_7H_{11})(CO)_2I]$.

The reaction of **1** with an excess of cyclohexa-1,3-diene in the presence of KI in acetone takes a different course from the reactions with the other dienes. The expected product $[Ru(\eta^5\text{-}C_7H_{11})(\eta^4\text{-}C_6H_8)I]$, analogous to **12–16**, is not observed in this reaction. The reaction proceeds with liberation of 2 molar equiv. of 2,4-dimethylpenta-1,3-diene, and the observed final product, obtained in high yield (94%), is the yellow complex $[Ru(\eta^5\text{-}C_6H_7)(\eta^4\text{-}C_6H_8)I]$ (**17**). A plausible mecha-



1

17

Scheme 3.

nism for the formation of **17** in this reaction is outlined in Scheme 3 and involves formation of an intermediate species $[Ru(\eta^5\text{-}C_6H_7)(\eta^5\text{-}C_7H_{11})H]^+$, probably with an agostic structure analogous to **1**. The ^1H and ^{13}C NMR spectra of **17** are fully consistent with the proposed structure of C_s symmetry for **17** illustrated in the scheme. The coordinated diene in **17** is readily displaced by CO (1 atm) in acetone giving $[Ru(\eta^5\text{-}C_6H_7)(CO)_2I]$.

The reaction of **1** with CO (1 atm) in acetone at room temperature followed by addition of KI or Et_4NBr gives **2** as an observable intermediate, and leads to the neutral halo-complexes $[Ru(\eta^5\text{-}C_7H_{11})(CO)_2X]$ (X = I (**18**), Br (**19**)) as the final products. The best method found for preparing the corresponding chloro-complex $[Ru(\eta^5\text{-}C_7H_{11})(CO)_2Cl]$ (**20**) was the reaction of **18** with an excess of AgCl in acetone. Similarly reaction of **1** with free $P(OMe)_3$ or PMe_3 and the halide salts KI, LiBr or Et_4NCl gives the complexes $[Ru(\eta^5\text{-}C_7H_{11})(P(OMe)_3)_2X]$ (X = I (**21**), Br (**22**), Cl (**23**)) and $[Ru(\eta^5\text{-}C_7H_{11})(PMe_3)_2X]$ (X = I (**24**), Br (**25**), Cl (**26**)). Although the complexes **18–26** are fluxional in solution (*vide infra*), their limiting low temperature ^1H and ^{13}C NMR spectra all suggest unsymmetrical ground states of C_1 symmetry. Hence, the two 2-electron ligands are in inequivalent sites, with one of them occupying the unique site directly below the open edge of the DMP ligand. This geometry, which has also been observed in the related iron complex $[Fe(\eta^5\text{-}C_7H_{11})(CO)_2I]$ [19], has been confirmed in the solid state by single crystal X-ray diffraction studies of **18** and **21** (*vide infra*). The complexes **24–26** are thermally unstable in CH_2Cl_2 solution above 313 K (precluding a complete study

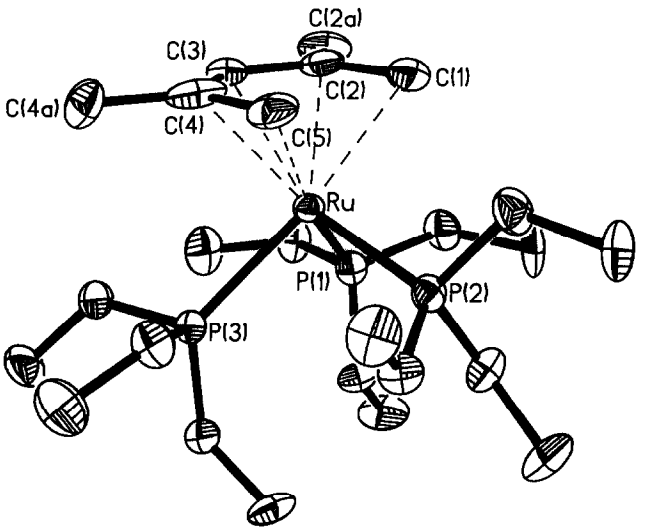


Fig 1. ORTEP drawing of complex 4; 50% displacement ellipsoids are shown. H atoms are omitted. Arbitrary numbering.

of their fluxional behaviour), but complexes **18–23** are more thermally robust, and are air-stable in the solid state and in solution.

The chloro-ligand in **26** is readily displaced by CO (1 atm) or by ^{t}BuNC in methanol solutions containing a molar equivalent of KPF_6, giving the complexes $[Ru(\eta^5\text{-}C_7H_{11})(PMe_3)_2L]PF_6$ (L = CO (**27**), ^{t}BuNC (**28**)). The ^1H and ^{13}C NMR spectra of both complexes show that the cations have unsymmetrical ground states of C_1 symmetry, implying that one of the PMe_3 ligands occupies the unique site directly below the open edge of the DMP ligand. A similar preference for a phosphine ligand to occupy the unique open-edge site was previously noted in the complexes $[Ru(\eta^5\text{-}C_7H_{11})(CO)_n(PEt_3)_{3-n}]BF_4$ ($n = 1$ and 2) [10]. Neither **27** nor **28** exhibit any fluxional behaviour up to 353 K in 1,1,2,2-tetrachloroethane-d_2 ($C_2D_2Cl_4$) solution. The complexes $[Ru(\eta^5\text{-}C_7H_{11})(Ph_2P(CH_2)_2PPh_2)I]$ (**29**) and $[Ru(\eta^5\text{-}C_7H_{11})(Me_2N(CH_2)_2NMe_2)Cl]$ (**30**) were also prepared in high yields by reaction of **1** with molar equivalents of bis(diphenylphosphino)ethane (DPPE) and KI in acetone or with N,N,N′,N′-tetramethylethylenediamine (TMEDA) and Et_4NCl in CH_2Cl_2. Their limiting low temperature ^1H and ^{13}C NMR spectra show that both **29** and **30** possess unsymmetrical C_1 ground states similar to **18–26**.

Crystal structures of 4, 18 and 21

The molecular structures of $[Ru(\eta^5\text{-}C_7H_{11})(P(OMe)_3)_3]BF_4$ (**4**), $[Ru(\eta^5\text{-}C_7H_{11})(CO)_2I]$ (**18**) and $[Ru(\eta^5\text{-}C_7H_{11})(P(OMe)_3)_2I]$ (**21**) were determined by single crystal X-ray diffraction studies (see Experimental) and are shown in Figs. 1–3. Relevant bond distances and angles are listed in Tables 1 and 2.

The cation in **4** has C_s symmetry, whereas the molecular symmetry in **18** and **21** is C_1, in agreement with the results of the NMR studies. The coordination polyhedron in **4**, **18** and **21** is best considered as a distorted octahedron. Three *fac*-related vertices are occupied by the atoms C(1), C(3) and C(5) of the U-shaped

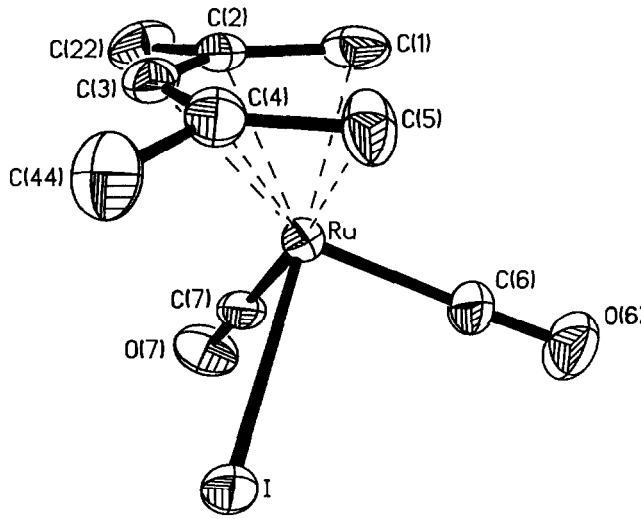


Fig. 2. ORTEP drawing of complex **18**; 50% displacement ellipsoids are shown. H atoms are omitted. Arbitrary numbering.

DMP ligand. The three remaining vertices are occupied by three P atoms in **4**, the halide and the C atoms of the carbonyls in **18**, and by the halide and two P atoms in **21**. A major distortion from ideality, in each of the three structures, is the pseudo-*trans* bond angle C(3)–Ru–E, where E is the donor atom of the 2-electron ligand in the unique site below the open edge of the DMP ligand. Values are C(3)–Ru–P(2) = 149.6(3)° in **4**, C(3)–Ru–C(6) = 154.2(4)° in **18**, and C(3)–Ru–P(1) = 147.9(6)° in **21**. These deviations from linearity are best viewed as an upward tilt

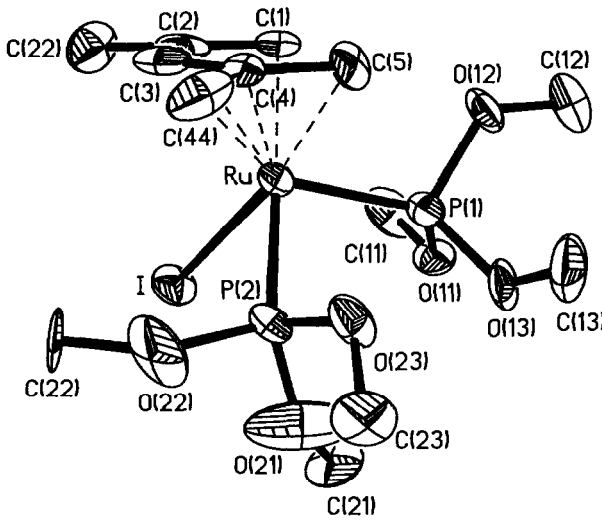


Fig. 3 ORTEP drawing of complex **21**; 50% displacement ellipsoids are shown. H atoms are omitted. Arbitrary numbering.

Table 1

Selected bond distances (Å) for **4**, **18** and **21**; standard deviation in parentheses

4			
Ru–C(1)	2.30(1)	Ru–P(3)	2.252(3)
Ru–C(2)	2.29(1)	C(1)–C(2)	1 46(2)
Ru–C(3)	2 29(1)	C(2)–C(2a)	1.53(2)
Ru–C(4)	2.27(1)	C(2)–C(3)	1.44(2)
Ru–C(5)	2.31(1)	C(3)–C(4)	1.45(2)
Ru–P(1)	2 265(3)	C(4)–C(4a)	1.55(2)
Ru–P(2)	2.261(3)	C(4)–C(5)	1.41(2)
18			
Ru–C(1)	2 19(1)	C(1)–C(2)	1.42(2)
Ru–C(2)	2.21(1)	C(2)–C(22)	1.52(2)
Ru–C(3)	2.23(1)	C(2)–C(3)	1.42(2)
Ru–C(4)	2.27(1)	C(3)–C(4)	1.42(2)
Ru–C(5)	2.27(1)	C(4)–C(44)	1.52(2)
Ru–C(6)	1 88(1)	C(4)–C(5)	1.40(2)
Ru–C(7)	1.89(1)	C(6)–O(6)	1.12(1)
Ru–I	2.729(1)	C(7)–O(7)	1.15(2)
21			
Ru–C(1)	2.31(2)	C(2)–C(3)	1.52(4)
Ru–C(2)	2.38(2)	C(3)–C(4)	1.41(3)
Ru–C(3)	2.27(2)	C(4)–C(44)	1.61(3)
Ru–C(4)	2.25(2)	C(4)–C(5)	1,47(3)
Ru–C(5)	2.17(2)	P(1)–O(11)	1.67(1)
Ru–P(1)	2.236(6)	P(1)–O(12)	1.60(2)
Ru–P(2)	2.229(7)	P(1)–O(13)	1.64(2)
Ru–I	2.775(2)	P(2)–O(21)	1.56(2)
C(1)–C(2)	1.50(3)	P(2)–O(22)	1.62(2)
C(2)–C(22)	1.51(3)	P(2)–O(23)	1.61(1)

of the ligand *trans* to C(3) towards the open edge of the DMP ligand, and their likely origins have previously been discussed [19]. In none of the structures, however, is there a statistically significant difference (*i.e.* $> 3\sigma$) between the Ru–E distance and the other Ru–L distance(s) in the same complex.

Overall bonding between the Ru atom and the DMP ligand is broadly comparable in the three structures. The five metal-coordinated C atoms are coplanar (mean deviations 0.004 Å in **4**; 0.03 Å in **18**; 0.02 Å in **21**) with mean Ru–C distances of 2.29 Å in **4**, 2.23 Å in **18** and 2.27 Å in **21**. The 2,4-substituted methyl groups are displaced from the plane of the DMP ligand towards the metal atom (mean deviations 0.07 Å in **4**; 0.20 Å in **18**; 0.14 Å in **21**). For the halo-complexes **18** and **21**, however, an asymmetric bonding of the η^5-DMP ligand is apparent when the Ru–C distances to the two terminal C atoms of the DMP ligand are compared: Ru–C(1) 2.19(1) Å *versus* Ru–C(5) 2.27(1) Å in **18**; Ru–C(1) 2.31(2) Å *versus* Ru–C(5) 2.17(2) Å in **21**. This asymmetry, also notable in the Ru–C(2) *versus* Ru–C(4) distances, can be rationalized by the observation that the shorter Ru–C distance in both complexes is to the C atom that is *trans* to the iodine atom, and that iodine exerts a much smaller *trans* weakening influence than the π-acceptor ligand (CO in **18**, $P(OMe)_3$ in **21**) *trans* to the more distantly bound

Table 2

Bond angles (°) for **4**, **18** and **21**; standard deviation in parentheses

4			
C(1)–Ru–C(3)	67.9(4)	C(3)–Ru–P(3)	104.8(3)
C(1)–Ru–C(5)	78.0(4)	C(5)–Ru–P(1)	171.0(3)
C(3)–Ru–C(5)	67.8(4)	C(5)–Ru–P(2)	86.9(3)
P(1)–Ru–P(2)	95.0(1)	C(5)–Ru–P(3)	95.8(3)
P(1)–Ru–P(3)	92.7(1)	C(1)–C(2)–C(3)	124(1)
P(2)–Ru–P(3)	94.1(1)	C(1)–C(2)–C(2a)	121(1)
C(1)–Ru–P(1)	93.2(3)	C(3)–C(2)–C(2a)	115(1)
C(1)–Ru–P(2)	91.1(3)	C(2)–C(3)–C(4)	123(1)
C(1)–Ru–P(3)	171.8(3)	C(3)–C(4)–C(5)	124(1)
C(3)–Ru–P(1)	107.4(3)	C(3)–C(4)–C(4a)	115(1)
C(3)–Ru–P(2)	149.6(3)	C(5)–C(4)–C(4a)	120(1)
18			
C(1)–Ru–C(3)	68.0(5)	C(6)–Ru–C(7)	93.6(3)
C(1)–Ru–C(5)	78.8(5)	C(6)–Ru–I	89.3(2)
C(1)–Ru–C(6)	92.4(4)	C(7)–Ru–I	83.2(2)
C(1)–Ru–C(7)	101.7(4)	C(1)–C(2)–C(3)	121(1)
C(1)–Ru–I	174.7(4)	C(1)–C(2)–C(22)	122(1)
C(3)–Ru–C(5)	67.4(4)	C(3)–C(2)–C(22)	117(1)
C(3)–Ru–C(6)	154.2(4)	C(2)–C(3)–C(4)	127(1)
C(3)–Ru–C(7)	106.4(4)	C(3)–C(4)–C(5)	124(1)
C(3)–Ru–I	108.8(3)	C(3)–C(4)–C(44)	115(1)
C(5)–Ru–C(6)	93.1(3)	C(5)–C(4)–C(44)	120(1)
C(5)–Ru–C(7)	173.2(4)	O(6)–C(6)–Ru	177(1)
C(5)–Ru–I	96 1(4)	O(7)–C(7)–Ru	176(1)
21			
C(1)–Ru–C(3)	69.5(8)	C(5)–Ru–P(2)	99.0(5)
C(1)–Ru–C(5)	81.6(7)	P(1)–Ru–I	97.7(2)
C(1)–Ru–I	92.2(5)	P(1)–Ru–P(2)	95.0(2)
C(1)–Ru–P(1)	87.7(6)	P(2)–Ru–I	87.0(2)
C(1)–Ru–P(2)	177.2(6)	C(1)–C(2)–C(3)	120(2)
C(3)–Ru–C(5)	69.2(8)	C(1)–C(2)–C(22)	119(2)
C(3)–Ru–I	105.2(6)	C(3)–C(2)–C(22)	120(2)
C(3)–Ru–P(1)	147.9(6)	C(2)–C(3)–C(4)	128(2)
C(3)–Ru–P(2)	108.2(7)	C(3)–C(4)–C(5)	123(2)
C(5)–Ru–I	172.8(5)	C(3)–C(4)–C(44)	114(2)
C(5)–Ru–P(1)	85.8(5)	C(5)–C(4)–C(44)	123(2)

carbon atom. No abnormally short inter- or intramolecular contacts were observed in the three structures.

Solution dynamics of $[Ru(\eta^5\text{-}C_7H_{11})L_3]BF_4$ and $[Ru(\eta^5\text{-}C_7H_{11})L_2X]$ complexes

Complexes **2–6** are categorized as $[Ru(\eta^5\text{-}C_7H_{11})L_3]^+$ complexes (L = 2-electron ligand), and their limiting low temperature ^1H, ^{13}C and ^{31}P NMR spectra confirm structures analogous to **4**, with the three L ligands occupying two equivalent sites and a third unique site. Complexes **18–26**, **29** and **30** are categorized as $[Ru(\eta^5\text{-}C_7H_{11})L_2X]$ complexes (L = 2-electron ligand, X = halide), and their limiting low temperature ^1H, ^{13}C and ^{31}P NMR spectra confirm structures analogous to **18** and **21** with the two L ligands occupying inequivalent sites. The two chemical

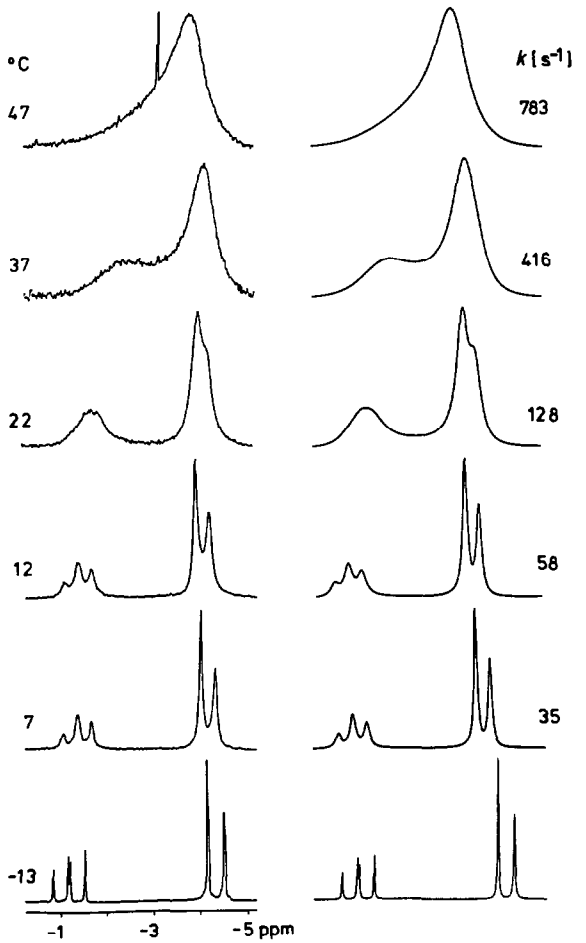


Fig. 4 Observed and simulated variable temperature $^{31}P\{^1H\}$ NMR spectra of $[Ru(\eta^5\text{-}C_7H_{11})(PMe_3)_3]BF_4$ (**3**) in $C_2D_2Cl_4$ solution.

environments for the L ligands in both types of complex can be rendered equivalent by relative rotation of the DMP ligand and RuL_3 or RuL_2X groups. For the complexes **3–6**, **18–23**, **29** and **30** we obtained sets of variable temperature ^1H and/or ^{31}P NMR spectra which reveal the effects of the various site exchanges, caused by the relative rotation, from the slow exchange limit through coalescence and into the fast exchange domain. Subsequently, Kubo–Sack line-shape analysis techniques [20] were used to evaluate the activation energies for the rotation in these complexes.

For **3**, taken as an example for $[Ru(\eta^5\text{-}C_7H_{11})L_3]^+$ complexes, the $^{31}P\{^1H\}$ NMR spectrum in $C_2D_2Cl_4$ is at the slow exchange limit below 260 K and consists of a six-line pattern typical of an AB_2 spin system. The variable temperature spectra (260–320 K) were simulated [21] using a 6×6 matrix for an exchanging AB_2 spin system, and the observed and calculated spectra are shown in Fig. 4. The free energy of activation, $\Delta G^{\ddagger}_{298}$, was then evaluated by linear regression of an Eyring plot [22].

Table 3

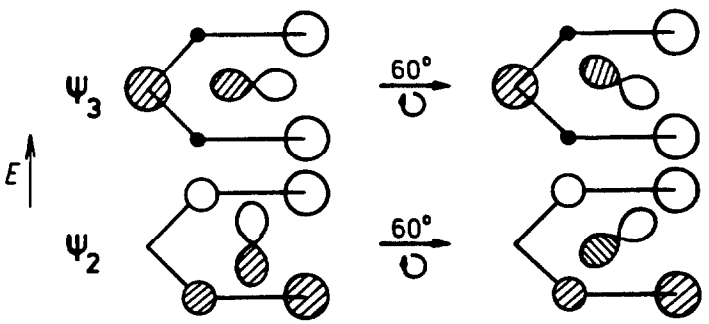
Free energy of activation for ligand rotation in $[Ru(\eta^5\text{-}C_7H_{11})L_3]^+$ and $[Ru(\eta^5\text{-}C_7H_{11})L_2X]$

Complex [a]	$\Delta G^{\ddagger}$ (kJ/mol) [b]
$[Ru(\eta^5\text{-}C_7H_{11})(PMe_3)_3]^+$ (3)	60.5 ± 0.4
$[Ru(\eta^5\text{-}C_7H_{11})(P(OMe)_3)_3]^+$ (4)	57.3 ± 0.4
$[Ru(\eta^5\text{-}C_7H_{11})(NCCH_3)_3]^+$ (5)	65.7 ± 0.4
$[Ru(\eta^5\text{-}C_7H_{11})(TRIPHOS)]^+$ (6)	53.5 ± 0.4
$[Ru(\eta^5\text{-}C_7H_{11})I(CO)_2]$ (18)	51.8 ± 0.5
$[Ru(\eta^5\text{-}C_7H_{11})Br(CO)_2]$ (19)	55.3 ± 0.4
$[Ru(\eta^5\text{-}C_7H_{11})Cl(CO)_2]$ (20)	62.0 ± 0.2
$[Ru(\eta^5\text{-}C_7H_{11})I(P(OMe)_3)_2]$ (21)	53.8 ± 0.4
$[Ru(\eta^5\text{-}C_7H_{11})Br(P(OMe)_3)_2]$ (22)	61.3 ± 0.3
$[Ru(\eta^5\text{-}C_7H_{11})Cl(P(OMe)_3)_2]$ (23)	66.8 ± 0.6
$[Ru(\eta^5\text{-}C_7H_{11})I(DPPE)]$ (29)	40.3 ± 0.5
$[Ru(\eta^5\text{-}C_7H_{11})Cl(TMEDA)]$ (30)	51.3 ± 0.4

[a] In $C_2D_2Cl_4$ for **3–5**, **20** and **23**; in CD_2Cl_2 for all others. [b] At 298 K.

For complexes of the type $[Ru(\eta^5\text{-}C_7H_{11})L_2X]$, the effects of the rotation are not limited to a time-averaging of the environments of the ligands L, since the seven environments for the protons of the DMP ligand in the C_1 symmetry static structures (H–C(3); *Z* and *E* protons on C(1) and C(5); Me groups on C(2) and C(4)) are also reduced, to only four, by time-averaging. Hence for the complexes **21–23**, two sets of rate constant *versus* temperature data were obtained for each complex: (i) by simulation of the observed collapse and coalescence of the ^1H NMR resonances from the two methyl groups and from the two *E* protons of the DMP ligand; (ii) by simulation of the observed collapse and coalescence of the ^1H NMR resonances from the $P(OMe)_3$ ligands. Linear regression of the Eyring plots gave two initial values of $\Delta G^{\ddagger}_{298}$ that were in excellent agreement (*e.g.*, for **21**, $\Delta G^{\ddagger}_{298} = 53.9 \pm 0.4$ and 53.8 ± 0.5 kJ mol^{-1} from the DMP and L site exchanges, respectively). A unique value of $\Delta G^{\ddagger}_{298}$ was then obtained by combining the two data sets on a single Eyring plot. For the carbonyl complexes **18–20**, $\Delta G^{\ddagger}_{298}$ values are derived uniquely from simulation of the ^1H NMR resonances of the DMP ligand as a function of temperature. As a quality indicator, the Eyring plots for the twelve complexes studied, all span the slow and fast exchange domains, with a mean of 8 points collected over a 50 K range (minimum figures 5 points over a 30 K range (complex **19**)). Temperatures within the NMR probe were precalibrated by the substitution technique using a digital thermometer [23]. The activation energies, $\Delta G^{\ddagger}_{298}$, for the relative rotations of the DMP and RuL_3 or RuL_2X groups are summarized in Table 3.

Perhaps surprisingly, the ranges of values spanned by the rotational barriers in the $[Ru(\eta^5\text{-}C_7H_{11})L_3]^+$ complexes (53–66 kJ mol^{-1}) and $[Ru(\eta^5\text{-}C_7H_{11})L_2X]$ complexes (generally 51–67 kJ mol^{-1}, although the barrier for **29** is considerably lower) are very similar. Indeed, the only clear trends that emerge from the results are for the two series of halo-complexes **18–20** and **21–23**. For these series, the rotational barrier increases along the sequence I < Br < Cl. The most significant orbital interactions in the ground and transition states are those between the sub-HOMO (Ψ_2) and the HOMO (Ψ_3) of the DMP^- fragment and the unoccupied *dp*-hybrid orbitals of $[RuL_3]^{2+}$ or $[RuL_2X]^+$ fragments (Scheme 4) [24,25].



Scheme 4.

A rotation of 60° will decrease the total fragment orbital overlap, particularly with Ψ_3. The energy separation of ground and transition states should therefore be directly related to the extent to which an electron density transfer from DMP to Ru is favoured. Hence, as is indeed observed, there is an increase in the rotational barrier as the electronegativity of the halide ligand, X, increases. The trend I < Br < Cl for the DMP complexes **18–20** and **21–23** is comparable to related observations previously made concerning the rotational barriers in [Fe(η^3-allyl)$(CO)_3$X] complexes [26,27].

Acetonitrile solvent exchange in [Ru(η^5-C_7H_{11})$(NCMe)_3$]BF_4 (5)

The kinetics of acetonitrile exchange between coordinated and free acetonitrile in **5** were investigated in CD_3CN/CD_3NO_2 solutions by using sampling techniques. The decrease in intensity of the coordinated CH_3CN resonances in the ^1H NMR spectra of **5** was monitored as a function of time in solutions of **5** (0.21 M) and CD_3CN (5.6 M) in CD_3CN/CD_3NO_2 solution at temperatures over the range 253–273 K. It was observed that the acetonitrile solvent exchanges were non-stereospecific, the 1:2 intensity ratio between the two coordinated CH_3CN resonances remaining constant throughout the experiments. The observed pseudo-first-order rate constants for acetonitrile solvent exchange at each temperature were evaluated using eq. (2) of ref. 28, and values were: 1.65×10^{-4} s^{-1} (253 K); 2.41×10^{-4} s^{-1} (258 K); 3.57×10^{-4} s^{-1} (263 K); 5.16×10^{-4} s^{-1} (268 K); 7.27×10^{-4} s^{-1} (273 K). Extrapolation of these results on an Eyring plot gave a pseudo-first-order rate constant, $k_{298} = (3.61 \pm 0.07) \times 10^{-3}$ s^{-1}, and activation parameters of $\Delta H^{\ddagger} = 40.6 \pm 0.4$ kJ mol^{-1} and $\Delta S^{\ddagger} = -155 \pm 1$ J mol^{-1} K^{-1}.

The relative rotation in **5** was shown in the previous section to occur at a rate of $k_{298} = (19.6 \pm 1.4\ s^{-1})$ (corresponding to $\Delta G^{\ddagger}_{298} = 65.7 \pm 0.4$ kJ mol^{-1}) and therefore clearly operates on a much shorter timescale than acetonitrile solvent exchange. Hence, stereospecific acetonitrile exchange in **5** is not possible. Furthermore, the low $\Delta H^{\ddagger}$ and large negative $\Delta S^{\ddagger}$ values for acetonitrile solvent exchange on **5** are suggestive of an associative type mechanism, and such a proposal would be consistent with an $\eta^5 \rightarrow \eta^3$ transformation being accessible for an acyclic pentadienyl ligand [12]. It is noteworthy that for solvent exchange on the related cyclopentadienyl analogue, [Ru(η^5-C_5H_5)$(NCMe)_3$]BF_4, a dissociative mechanism has been firmly established ($\Delta H^{\ddagger} = 86.5$ kJ mol^{-1}; $\Delta S^{\ddagger} = 59.6$ J mol^{-1} K^{-1}; $\Delta V^{\ddagger} = 11.1$ cm^3 mol^{-1}) [28].

Experimental

General comments

All reactions were carried out under nitrogen in deoxygenated solvents by standard Schlenk techniques. IR spectra (cm^{-1}) were recorded on a Perkin–Elmer 883 spectrophotometer, in $CHCl_3$ solution unless otherwise stated. NMR spectra were recorded on Bruker WH-360 (^1H, 360; ^{13}C, 90.55 MHz) and AC-200 (^1H, 200; ^{13}C, 50.32; ^{31}P, 80.9 MHz) FT spectrometers. Chemical shifts are reported in δ ppm downfield from $SiMe_4$ (^1H and ^{13}C) and from external 85% H_3PO_4 (^{31}P). Spin-spin coupling constants, J, are given in Hz. Microanalyses were carried out by Ilse Beetz, Kronach (Germany). The preparation of **1** has previously been described [4].

Tricarbonyl(η^5-2,4-dimethylpentadienyl)ruthenium tetrafluoroborate (2). A solution of **1** (0.17 g, 0.45 mmol) in acetone (30 mL) was stirred under CO (1 atm) at room temperature for 3 h. Filtration, evaporation to 10 mL, addition of Et_2O and cooling (250 K) gave colourless crystals of **2** (0.14 g, 84%); m.p. 224°C (dec.). IR (acetone): 2126, 2073 (CO). ^1H NMR (acetone-d_6, 298 K): 6.90 (t, $^4J(3,E) = 1.4$, 1H, H(3)); 3.86 (dd, $^2J(Z,E) = 3.7$, 2H, H(1E), H(5E)); 2.56 (s, 6H, 2 Me); 2.44 (d, 2H, H(1Z), H(5Z)). ^{13}C NMR (acetone-d_6, 298 K): 192.6, 187.1 (each s, relative intensity 1:2, CO); 130.1 (s); 97.8 (d, $J = 171$); 60.1 (t, $J = 163$); 26.9 (q, $J = 132$). Anal. Found: C, 32.64; H, 3.32. $C_{10}H_{11}BF_4O_3Ru$ (367.07) calc.: C, 32.72; H, 3.02%.

(η^5-2,4-Dimethylpentadienyl)tris(trimethylphosphine)ruthenium tetrafluoroborate (3); (η^5-2,4-dimethylpentadienyl)tris(trimethylphosphite)ruthenium tetrafluoroborate (4). The procedure was as for **2**, but by use of PMe_3 (4 molar equiv., addition at 273 K) or $P(OMe)_3$ (10 molar equiv.), respectively, under N_2 in place of CO. **3**: Colourless crystals (72%); m.p. 187°C (dec.). ^1H NMR (CD_2Cl_2, 200 K): 5.44 (s, 1H, H(3)); 2.21 (s, 2H, H(1E), H(5E)); 2.11 (s, 6H, 2 Me); 1.59, 1.31 (each d, $^2J(P,H) = 8.7$, 9H and 18H, PMe_3); 0.60 (s, 2H, H(1Z), H(5Z)). ^{13}C NMR (CD_2Cl_2, 200 K): 118.5 (s); 88.6 (d, $J = 161$, $J(C,P) = 8$); 52.1 (t, $J = 155$); 26.3 (q, $J = 127$); 24.2 (q, $J = 130$, $J(C,P) = 30$); 22.2 (q, $J = 128$). ^{31}P NMR (CD_2Cl_2, 200 K): −1.19 (t, $J(P,P) = 29.6$); −4.27 (d); relative intensity 1:2. Anal. Found: C, 37.05; H, 7.32; P, 17.87. $C_{16}H_{38}BF_4P_3Ru$ (511.28) calc.: C, 37.59; H, 7.49; P, 18.17%. **4**: Colourless crystals (84%); m.p. 163°. ^1H NMR (CD_2Cl_2, 200 K): 5.72 (s, 1H, H(3)); 3.67, 3.55 (each d, $^3J(P,H) = 11.2$, 9H and 18H, OMe); 2.70 (s, 2H, H(1E), H(5E)); 2.02 (s, 6H, 2 Me); 0.78 (s, 2H, H(1Z), H(5Z)). ^{13}C NMR ($CDCl_3$, 260 K): 121.4 (s); 90.0 (d, $J = 159$, $J(C,P) = 15$); 54.8 (t, $J = 155$); 53.8, 53.5 (each q, $J = 146$); 26.4 (q, $J = 128$). ^{31}P NMR (CD_2Cl_2, 200 K): 11.43 (d, $J(P,P) = 64.7$); −3.14 (t); relative intensity 2:1. Anal. Found: C, 30.22; H, 5.85; P, 13.86. $C_{16}H_{38}BF_4O_9P_3Ru$ (655.27) calc.: C, 29.33; H, 5.84; P, 14.18.

Trisacetonitrile(η^5-2,4-dimethylpentadienyl)ruthenium tetrafluoroborate (5). A solution of **1** (0.23 g, 0.61 mmol) in CH_3CN (25 mL) was stirred at room temperature for 8 h. Filtration, evaporation to 6 mL, addition of Et_2O and cooling (250 K) gave colourless crystals of **5** (0.21 g, 85%); m.p. 110°C (dec.). IR (Nujol): 2313, 2277 (CN). ^1H NMR ($CDCl_3$, 298 K): 5.24 (s, 1H, H(3)); 2.67, 2.42 (each s, 3H and 6H, MeCN); 1.99 (d, $J(Z,E) = 2.8$, 2H, H(1E), H(5E)); 1.86 (s, 6H, 2 Me); −0.18 (d, 2H, H(1Z), H(5Z)). ^{13}C NMR ($CDCl_3$, 298 K): 126.0, 121.6 (each s, relative intensity 1:2, CN); 103.6 (s); 83.0 (d, $J = 160$); 39.2 (t, $J = 156$); 25.3 (q, $J = 127$); 4.0, 3.3 (each q, relative intensity 1:2, H_3CCN, $J = 137$). Anal. Found: C,

38.49; H, 5.25; N, 10.16. $C_{13}H_{20}BF_4N_3Ru$ (406.19) calc.: C, 38.44; H, 4.96; N, 10.34%.

(η^5-2,4-Dimethylpentadienyl)tris(diphenylphosphinomethyl)ethaneruthenium tetrafluoroborate (6). A solution of **1** (0.18 g, 0.47 mmol) in acetone (20 mL) was added to a solution of tris(diphenylphosphinomethyl)ethane (0.32 g, 0.51 mmol) in acetone (10 mL) at 273 K. The mixture was allowed to warm to room temperature and stirring continued for 5 h. Filtration, partial evaporation, addition of Et_2O and cooling (250 K) gave yellow crystals of **6** (0.35 g, 81%); m.p. 266°C (dec.). ^1H NMR (CD_2Cl_2, 200 K): 7.01 (m, 30H, TRIPHOS); 6.02 (s, 1H, H(3)); 2.86, 2.44 (each d, $J(CH_2,P) = 8.7$, 2H and 4H, TRIPHOS); 2.18 (s, 2H, H(1*E*), H(5*E*)); 1.98 (s, 2H, H(1*Z*), H(5*Z*)); 1.74 (s, 6H, 2 Me); 1.55 (d, $J(CH_3,P) = 3.0$, 3H, TRIPHOS). ^{13}C NMR (CD_2Cl_2, 200 K): 141.9–128.1 (Ph); 119.5 (s); 87.8 (d, $J = 161$); 57.9 (t, $J = 156$); 39.1, 37.1 (each t, relative intensity 1:2, $J = 137$, TRIPHOS); 31.3 (q, $J = 126$, TRIPHOS); 25.9 (q, $J = 128$). ^{31}P NMR (CD_2Cl_2, 200 K): 24.52 (d, $J(P,P) = 32.7$); 18.56 (t); relative intensity 2:1. Anal. Found: C, 62.96; H, 5.77. P, 9.93. $C_{48}H_{50}BF_4P_3Ru$ (907.73) calc.: C, 63.51; H, 5.55; P, 10.24%.

(η^6-Cyclohepta-1,3,5-triene)(η^5-2,4-dimethylpentadienyl)ruthenium tetrafluoroborate (7). A solution of **1** (0.14 g, 0.37 mmol) and cyclohepta-1,3,5-triene (0.38 mL, 3.69 mmol) in acetone (20 mL) was stirred at room temperature for 1 h. Filtration, partial evaporation, addition of Et_2O and cooling (250 K) gave colourless crystals of **7** (0.13 g, 94%); m.p. 253° (dec.). ^1H NMR (acetone-d_6, 298 K): 6.44 (m, $J(2',3') = J(4',5') = 7.3$, $J(1',3') = J(4',6') = 0.6$, $J(2',4') = J(3',5') = 2.2$, 2H, H(3'), H(4')); 6.07 (s, 1H, H(3)); 5.90 (m, 2H, H(2'), H(5')); 4.17 (ddd, $J(1',2') = J(5',6') = 7.3$, 2H, H(1'), H(6')); 3.98 (d, $J(Z,E) = 3.0$, 2H, H(1*E*), H(5*E*)); 3.26, 1.78 (each dt, $J(7's,6') = 8.5$, $J(7'gem) = 13.5$, $J(7'a,6') = 3.9$, 2H, H(7'*s*), H(7'*a*)); 2.03 (s, 6H, 2 Me); 1.47 (d, 2H, H(1*Z*), H(5*Z*)). ^{13}C NMR (acetone-d_6, 298 K): 112.2 (s); 100.6, 99.1 (each d, $J = 166$); 98.3 (d, $J = 184$); 55.4 (t, $J = 165$); 45.5 (d, $J = 171$); 24.5 (q, $J = 128$); 23.8 (t, $J = 134$). Anal. Found: C, 44.99; H, 5.22. $C_{14}H_{19}BF_4Ru$ (375.18) calc.: C, 44.82; H, 5.10%.

(η^6-cycloocta-1,3,5,7-tetraene)(η^5-2,4-dimethylpentadienyl)ruthenium tetrafluoroborate (8). A solution of **1** (0.13 g, 0.34 mmol) and cyclo-octa-1,3,5,7-tetraene (0.5 mL, 4.4 mmol) in acetone (25 mL) was stirred at room temperature for 1 h. Solvent evaporation gave a residue, which on recrystallization from $CHCl_3/Et_2O$ gave yellow needles of **8** (0.10 g, 72%); m.p. 180° (dec.). ^1H NMR ($CDCl_3$, 298 K): 6.39 (dd, 2H, H(3'), H(4')); 6.23 (m, $J(2',3') = 4.5$, $J(2',4') = 2.1$, $J(1',2') = 8.5$, 2H, H(2'), H(5')); 6.18 (s, 1H, H(3)); 5.35 (dd, $J(1',8') = 2.2$, 2H, H(1'), H(6')); 5.16 (d, 2H, H(7'), H(8')); 3.95 (d, $J(Z,E) = 3.2$, 2H, H(1*E*), H(5*E*)); 2.05 (s, 6H, 2 Me); 1.60 (d, 2H, H(1*Z*), H(5*Z*)). ^{13}C NMR ($CDCl_3$, 298 K): 133.5 (d, $J = 163$); 113.9 (s); 106.1 (d, $J = 168$); 100.5 (d, $J = 171$, DMP); 98.8 (d, $J = 170$); 88.4 (d, $J = 162$); 59.1 (t, $J = 162$); 24.1 (q, $J = 129$). Anal. Found: C, 46.59; H, 4.98. $C_{15}H_{19}BF_4Ru$ (387.19) calc.: C, 46.53; H, 4.95%.

(η^6-Benzene)(η^5-2,4-dimethylpentadienyl)ruthenium tetrafluoroborate (9); (η^5-2,4-dimethylpentadienyl)(η^6-p-xylene)ruthenium tetrafluoroborate (10); (η^5-2,4-dimethylpentadienyl)(η^5-thiophene)ruthenium tetrafluoroborate (11). The procedure was as for **8**, but with cyclo-octatetraene replaced by benzene (50 molar equiv., 6 h at room temperature, CH_2Cl_2 solvent), by *p*-xylene (60 molar equiv., 2 h at room temperature, acetone solvent), or by thiophene (60 molar equiv., 24 h at room temperature, CH_2Cl_2 solvent), respectively. **9**: Yellow microcrystals, recrystallized

from CH_2Cl_2/Et_2O (74%); m.p. 245°C (dec.). ^1H NMR (CD_2Cl_2, 298 K): 6.27 (s, 1H, H(3)); 6.14 (s, 6H, C_6H_6); 3.72 (d, $J(Z,E) = 3.0$, 2H, H(1*E*), H(5*E*)); 2.13 (s, 6H, 2 Me); 1.02 (d, 2H, H(1*Z*), H(5*Z*)). ^{13}C NMR (CD_2Cl_2, 298 K): 106.1 (s); 97.7 (d, $J = 165$); 91.6 (d, $J = 161$, C_6H_6); 51.5 (t, $J = 162$); 25.6 (q, $J = 126$). Anal. Found: C, 43.11; H, 4.80. $C_{13}H_{17}BF_4Ru$ (361.15) calc.: C, 43.23; H, 4.74%. **10**: Cream coloured microcrystals, recrystallized from $CHCl_3/Et_2O$ (80%); m.p. 249°C (dec.). ^1H NMR ($CDCl_3$, 298 K): 6.14 (s, 1H, H(3)); 6.04 (s, 4H, *p*-xylene); 3.37 (d, $J(Z,E) = 3.0$, 2H, H(1*E*), H(5*E*)); 2.27, 2.09 (each s, 12H, 4Me); 1.03 (d, 2H, H(1*Z*), H(5*Z*)). ^{13}C NMR (CD_2Cl_2, 198 K): 106.8, 105.2 (each s); 96.6 (d, $J = 166$); 91.5 (d, $J = 175$, *p*-xylene); 52.3 (t, $J = 160$); 24.9, 18.7 (each q, $J = 129$). Anal. Found: C, 46.19; H, 5.44. $C_{15}H_{21}BF_4Ru$ (389.21) calc.: C, 46.29; H, 5.44%. **11**: Yellow microcrystals, recrystallized from CH_2Cl_2/Et_2O (81%); m.p. 182°C (dec.). ^1H NMR (CD_2Cl_2, 298 K): 6.21 (m, 2H, H(3′), H(4′)); 5.99 (s, 1H, H(3)); 5.84 (m, 2H, H(2′), H(5′)); 3.78 (d, $J(Z,E) = 2.8$, 2H, H(1*E*), H(5*E*)); 2.11 (s, 6H, 2 Me); 1.41 (d, 2H, H(1*Z*), H(5*Z*)). ^{13}C NMR (CD_2Cl_2, 298 K): 108.0 (s); 97.1 (d, $J = 170$); 94.9, 80.9 (each d, $J = 186$ and 201, respectively, C_4H_4S); 53.4 (t, $J = 160$); 26.3 (q, $J = 134$). Anal. Found: C, 36.08; H, 4.18; S, 8.85. $C_{11}H_{15}BF_4SRu$ (364.18) calc.: C, 35.98; H, 4.12; S, 8.73%.

(η^4-1,3-Butadiene)(η^5-2,4-dimethylpentadienyl)iodoruthenium (12). A solution of **1** (0.18 g, 0.47 mmol) in acetone (20 mL) was slowly added to a mixture of an excess buta-1,3-diene (approx. 3 mL) and KI (0.12 g, 0.7 mmol) in acetone (25 mL) at 195 K. The mixture was stirred at 195 K for 1 h and then allowed to warm to room temperature and stirring was continued for 2 h. Solvent evaporation gave a residue, which was extracted with toluene (80 mL). Filtration, partial evaporation and cooling (250 K) gave yellow crystals of **12** which were washed with pentane, and dried *in vacuo* (0.14 g, 78%); m.p. 215°C (dec.). ^1H NMR (CD_2Cl_2, 298 K): 5.25 (t, 1H, H(3)); 4.61 (m, $^3J(1'Z,2') = 13.8$, $^4J(1'Z,3') = 4.5$, $^3J(1'E,2') = 5.3$, $^4J(1'E,3') = 2.5$, 2H, H(2′), H(3′)); 3.78 (dd, $J(E,3) = 1.5$, $J(Z,E) = 3.0$, 2H, H(1*E*), H(5*E*)); 2.61 (dd, 2H, H(1′*E*), H(4′*E*)); 1.82 (s, 6H, 2 Me); 1.68 (d, 2H, H(1*Z*), H(5*Z*)); 1.55 (dd, 2H, H(1′*Z*), H(4′*Z*)). ^{13}C NMR (CD_2Cl_2, 298 K): 105.8 (s); 92.0, 90.6 (each d, $J = 161$ and 164); 62.4, 50.7 (each t, $J = 162$); 24.3 (q, $J = 128$). Anal. Found: C, 35.30; H, 4.73. $C_{11}H_{17}IRu$ (377.23) calc.: C, 35.02; H, 4.54%.

(η^4-1,3-Butadiene)chloro(η^5-2,4-dimethylpentadienyl)ruthenium (13). The procedure was as for **12**, but with use of Et_4NCl (2 molar equiv., 1 h at 195 K, 3 h at room temperature) in place of KI. The residue after evaporation was extracted with THF. **13**: Yellow crystals (81%); m.p. 157°C (dec.). ^1H NMR (CD_2Cl_2, 298 K): 4.87 (m, $^3J(1'Z,2') = 13.0$, $^4J(1'Z,3') = 5.0$, $^3J(1'E,2') = 6.0$, $^4J(1'E,3') = 2.0$, 2H, H(2′), H(3′)); 4.67 (s, 1H, H(3)); 3.82 (d, $J(Z,E) = 2.7$, 2H, H(1*E*), H(5*E*)); 3.03 (dd, 2H, H(1′*E*), H(4′*E*)); 1.96 (d, 2H, H(1*Z*), H(5*Z*)); 1.76 (s, 6H, 2 Me); 1.39 (dd, 2H, H(1′*Z*), H(4′*Z*)). ^{13}C NMR (CD_2Cl_2, 298 K): 109.5 (s); 94.4 (d, $J = 166$); 88.9 (d, $J = 163$); 67.7, 58.4 (each t, $J = 160$–162); 24.7 (q, $J = 128$). Anal. Found: C, 45.92; H, 6.05. $C_{11}H_{17}ClRu$ (285.78) calc.: C, 46.23; H, 6.00%.

(η^4-2,3-Dimethyl-1,3-butadiene)(η^5-2,4-dimethylpentadienyl)iodoruthenium (14). A solution of **1** (0.22 g, 0.58 mmol) in acetone (20 mL) was slowly added to a mixture of 2,3-dimethylbuta-1,3-diene (1.1 mL, 11.6 mmol) and KI (0.10 g, 0.60 mmol) in acetone (5 mL) at 195 K. The mixture was stirred at 195 K for 1 h and then allowed to warm to room temperature, and stirring was continued for 3 h.

The yellow precipitate was filtered off, washed with cold acetone, and recrystallized from toluene/pentane at 250 K to give yellow crystals of **14** (0.22 g, 94%); m.p. 172°C (dec.). ^{1}H NMR (CD_2Cl_2, 298 K): 4.86 (t, $J(1E,3) = 0.9$, 1H, H(3)); 3.80 (dd, $J(Z,E) = 3.2$, 2H, H(1*E*), H(5*E*)); 2.64 (d, $J(1'Z,E) = 2.1$, 2H, H(1'*E*), H(4'*E*)); 1.89, 1.83 (each s, 12H, 4 Me); 1.72 (d, 2H, H(1*Z*), H(5*Z*)); 1.67 (d, 2H, H(1'*Z*), H(4'*Z*)). ^{13}C NMR (CD_2Cl_2, 298 K): 105.5, 99.9 (each s); 92.7 (d, $J = 161$); 59.8 (t, $J = 163$); 51.9 (t, $J = 168$); 22.5, 19.6 (each q, $J = 128$). Anal. Found: C, 38.42; H, 5.10. $C_{13}H_{21}IRu$ (405.29) calc.: C, 38.53; H, 5.22%.

Chloro(η^4-2,3-dimethyl-1,3-butadiene)(η^5-2,4-dimethylpentadienyl)ruthenium (15). A solution of **1** (0.31 g, 0.82 mmol) in CH_2Cl_2 (20 mL) was slowly added to a mixture of 2,3-dimethylbuta-1,3-diene (1.8 mL, 15.9 mmol) and Et_4NCl (0.25 g, 1.5 mmol) in CH_2Cl_2 (30 mL) at 195 K. The mixture was stirred at 195 K for 1 h and then allowed to warm to room temperature and stirring was continued for 4 h. Filtration, partial evaporation and cooling (250 K) gave yellow crystals of **15**, which were washed with pentane and dried *in vacuo* (0.16 g, 62%); m.p. 146°C (dec.). ^{1}H NMR (CD_2Cl_2, 298 K): 4.36 (s, 1H, H(3)); 3.88 (d, $J(Z,E) = 2.7$, 2H, H(1*E*), H(5*E*)); 3.08 (d, $J(1'Z,E) = 1.7$, 2H, H(1'*E*), H(4'*E*)); 2.01 (d, 2H, H(1*Z*), H(5*Z*)); 1.84, 1.80 (each s, 12H, 4 Me); 1.38 (d, 2H, H(1'*Z*), H(4'*Z*)). ^{13}C NMR (CD_2Cl_2, 298 K): 110.8, 105.1 (each s); 90.6 (d, $J = 161$); 67.2 (t, $J = 163$); 61.3 (t, $J = 159$); 23.8, 21.3 (each q, $J = 128$). Anal. Found: C, 49.24; H, 6.88. $C_{13}H_{21}ClRu$ (313.83) calc.: C, 49.75; H, 6.74%.

(η^2:η^2-Cycloocta-1,5-diene)(η^5-2,4-dimethylpentadienyl)iodoruthenium (16). A solution of **1** (0.14 g, 0.37 mmol) in acetone (14 mL) was slowly added to a mixture of cyclo-octa-1,5-diene (0.90 ml, 7.3 mmol) and KI (0.08 g, 0.48 mmol) in acetone (5 mL) at 195 K. The resulting mixture was stirred at 195 K for 1 h and then allowed to warm to room temperature and stirring was continued for 1 h. Evaporation of the solvent gave a residue which was extracted with toluene (60 mL). Partial evaporation and cooling gave orange crystals of **16** (0.09 g, 57%); m.p. 168°C (dec.). ^{1}H NMR (CD_2Cl_2, 200 K): 5.76 (t, $J(E,3) = 1.0$, 1H, H(3)); 3.91, 3.56 (each m, $^3J(CH,CH_2) = 8.8$ and 9.8, 4H, COD); 2.90 (dd, $J(Z,E) = 3.6$, 2H, H(1*E*), H(5*E*)); 2.82, 2.33, 2.06 (each m, 2H, 2H, 4H, CH_2); 2.00 (s, 6H, 2 Me); 1.69 (d, 2H, H(1*Z*), H(5*Z*)). ^{13}C NMR (CD_2Cl_2, 200 K): 113.5 (s); 85.9, 84.3 (each d, $J = 155$); 81.7 (d, $J = 159$); 58.7 (t, $J = 161$); 30.8, 30.1 (each t, $J = 127$–129); 23.5 (q, $J = 128$). Anal. Found: C, 41.85; H, 5.31. $C_{15}H_{23}IRu$ (431.32) calc.: C, 41.77; H, 5.37%.

(η^4-Cyclohexa-1,3-diene)(η^5-cyclohexadienyl)iodoruthenium (17). A solution of **1** (0.25 g, 0.66 mmol) in acetone (20 mL) was slowly added to a mixture of cyclohexa-1,3-diene (1.2 mL, 12.6 mmol) and KI (0.12 g, 0.73 mmol) in acetone (5 mL) at 195 K. The mixture was stirred at 195 K for 1 h and then allowed to warm to room temperature and stirring was continued for 4 h. The yellow precipitate of **17** was collected by filtration, washed with cold acetone and dried *in vacuo* (0.24 g, 94%); m.p. 161°C (dec.). ^{1}H NMR (CD_2Cl_2, 200 K): 5.15 (t, $J(3,2) = 4.9$, 1H, H(3)); 4.99 (dd, $J(1,2) = 7.3$, 2H, H(2), H(4)); 4.67 (m, $^3J(2',1') = 5.2$, 2H, H(2'), H(3')); 4.05 (dd, 2H, H(1), H(5)); 3.62 (dt, $J(6s,1) = 5.4$, $J(6gem) = 14.2$, 1H, H(6*s*)); 3.36 (m, $^4J(1',3') = 2.4$, 2H, H(1'), H(4')); 3.21 (d, 1H, H(6*a*)); 2.02 (d, $J(5'gem) = 10.7$, 2H, H(6'*a*), H(5'*a*)); 1.64 (d, 2H, H(6'*s*), H(5'*s*)). ^{13}C NMR (CD_2Cl_2, 200 K): 91.8, 88.1 (each d, $J = 171$); 77.0 (d, $J = 168$); 66.9 (d, $J = 171$); 63.1 (d, $J = 160$); 29.8 (t, $J = 134$); 24.1 (t, $J = 130$). Anal. Found: C, 36.92; H, 3.69. $C_{12}H_{15}IRu$ (387.23) calc.: C, 37.22; H, 3.90%.

Dicarbonyl(η^5-2,4-dimethylpentadienyl)iodoruthenium (18). A solution of **1** (0.20 g, 0.53 mmol) in acetone (40 mL) was stirred under CO (1 atm) at room temperature for 2 h. KI (0.13 g, 0.79 mmol) was then added and stirring continued for 3 h. The solvent was evaporated and the residue was extracted with pentane (80 mL). Filtration, partial evaporation and cooling (195 K) gave orange crystals of **18** (0.17 g, 85%); m.p. 113°C. IR: 2055, 2007 (CO). ^{1}H NMR (acetone-d_6, 200 K): 6.33 (s, 1H, H(3)); 3.13, 2.84 (each d, $J(Z,E) = 2.5$ and 2.6, 2H, H(1E), H(5E)); 2.55, 2.27 (each s, 6H, 2 Me); 2.09, 1.52 (each d, 2H, H(1Z), H(5Z)). ^{13}C NMR (CD_2Cl_2, 200 K): 197.1, 191.6 (each s, CO); 128.9, 113.0 (each s); 92.8 (d, $J = 167$); 56.6, 48.5 (each t, $J = 161$); 28.6, 26.1 (each q, $J = 129$). Anal. Found: C, 28.72; H, 2.91. $C_9H_{11}IO_2Ru$ (379.16) calc.: C, 28.51; H, 2.92%.

Bromodicarbonyl(η^5-2,4-dimethylpentadienyl)ruthenium (19). Initial carbonylation of **1** (0.18 g, 0.47 mmol) was as for **18**, followed by addition of Et_4NBr (0.15 g, 0.71 mmol) in CH_2Cl_2 (10 mL) and stirring for 3 h. The residue after evaporation was extracted with Et_2O (70 mL), and partial evaporation, addition of pentane and cooling (195 K) gave orange crystals of **19** (0.13 g, 83%); m.p. 162°C (dec.). IR: 2058, 2011 (CO). ^{1}H NMR (CD_2Cl_2, 200 K): 6.11 (s, 1H, H(3)); 2.95, 2.59 (each d, $J(Z,E) = 3.2$ and 3.0, 2H, H(1E), H(5E)); 2.22, 2.20 (each s, 6H, 2 Me); 1.56, 0.87 (each d, 2H, H(1Z), H(5Z)). ^{13}C NMR (CD_2Cl_2, 200 K): 198.0, 193.2 (each s, CO); 131.4, 113.6 (each s); 94.9 (d, $J = 170$); 58.6, 46.4 (each t, $J = 161$); 27.2, 27.2 (2q, $J = 129$). Anal. Found: C, 32.77; H, 3.52. $C_9H_{11}BrO_2Ru$ (332.17) calc.: C, 32.54; H, 3.34%.

Dicarbonylchloro(η^5-2,4-dimethylpentadienyl)ruthenium (20). To a solution of **18** (0.20 g, 0.53 mmol) in acetone (20 mL), AgCl (0.38 g, 2.65 mmol) was added and the mixture stirred at room temperature for 72 h. Filtration and evaporation of the solvent gave a residue which was extracted with toluene (15 mL). Partial evaporation, addition of pentane, and cooling (250 K) gave yellow crystals of **20** (0.11 g, 72%); m.p. 141°C (dec.). IR: 2060, 2014 (CO). ^{1}H NMR (CD_2Cl_2, 200 K): 6.16 (s, 1H, H(3)); 2.95, 2.44 (each d, $J(Z,E) = 2.0$ and 3.1, 2H, H(1E), H(5E)); 2.20, 2.01 (each s, 6H, 2 Me); 1.48, 0.80 (each d, 2H, H(1Z), H(5Z)). ^{13}C NMR (CD_2Cl_2, 200 K): 198.2, 193.6 (each s, CO); 132.3, 113.4 (each s); 95.5 (d, $J = 165$); 59.1, 45.0 (each t, $J = 161$); 27.3, 26.1 (each q, $J = 129$). Anal. Found: C, 38.06; H, 3.64. $C_9H_{11}ClO_2Ru$ (287.71) calc.: C, 37.57; H, 3.85%.

(η^5-2,4-dimethylpentadienyl)iodobis(trimethylphosphite)ruthenium (21). A solution of **1** (0.12 g, 0.32 mmol) in acetone (15 mL) was slowly added to a mixture of KI (0.08 g, 0.47 mmol) and $P(OMe)_3$ (0.11 mL, 1.0 mmol) in acetone (10 mL) at 195 K. The mixture was stirred at 195 K for 1 h, then allowed to warm to room temperature and stirring was continued for 4 h. Evaporation of the solvent gave a residue which was extracted with pentane (50 mL). Filtration, partial evaporation and cooling (195 K) gave orange crystals of **21** (0.16 g, 88%); m.p. 215°C. ^{1}H NMR (CD_2Cl_2, 200 K): 5.75 (s, 1H, H(3)); 3.64, 3.51 (each d, $^3J(H,P) = 11.2$ and 11.1, 18H, OMe); 2.90, 1.89 (each s, 2H, H(1E), H(5E)); 2.34, 1.89 (each s, 6H, 2 Me); 0.73, −0.30 (each s, 2H, H(1Z), H(5Z)). ^{13}C NMR (CD_2Cl_2, 200 K): 118.7, 105.0 (each s); 90.6 (d, $J = 159$); 52.3 (t, $J = 156$); 51.4, 51.4 (2q, $J = 146$, OMe); 39.1 (t, $J = 159$); 29.1, 23.8 (each q, $J = 128$). Anal. Found: C, 27.83; H, 5.36; P, 10.60. $C_{13}H_{29}IO_6PRu$ (571.29) calc.: C, 27.33; H, 5.12; P, 10.84%.

Bromo(η^5-2,4-dimethylpentadienyl)bis(trimethylphosphite)ruthenium (22); chloro (η^5-2,4-dimethylpentadienyl)bis(trimethylphosphite)ruthenium (23). The procedure

was as for **21**, but with use of LiBr (2 molar equiv., acetone as solvent) or Et_4NCl (2 molar equiv., CH_2Cl_2 as solvent) in place of KI, respectively. **22**: Orange crystals (53%); m.p. 153°C (dec.). ^1H NMR (CD_2Cl_2, 200 K): 5.82 (s, 1H, H(3)); 3.67, 3.51 (each d, $^3J(H,P) = 11.8$ and 11.2, 18H, OMe); 2.87, 1.67 (each s, 2H, H(1*E*), H(5*E*)); 2.00, 1.89 (each s, 6H, 2 Me); 0.56, −0.44 (each s, 2H, H(1*Z*), H(5*Z*)). ^{13}C NMR (CD_2Cl_2, 200 K): 120.8, 105.1 (each s); 92.6 (d, $J = 168$, $J(C,P) = 17.9$); 52.6 (t, $J = 156$); 52.0, 52.0 (2q, $J = 146$, OMe); 36.9 (t, $J = 157$); 27.1, 25.1 (2q, $J = 129$). ^{31}P NMR (CD_2Cl_2, 200 K): 41.0, 27.7 (each d, $J(P,P) = 76.8$). Anal. Found: C, 29.62; H, 5.37; P, 12.08. $C_{13}H_{29}BrO_6P_2Ru$ (524.30) calc.: C, 29.78; H, 5.58; P, 11.82%. **23**: Yellow crystals (75%); m.p. 173°C (dec.). ^1H NMR (CD_2Cl_2, 270 K): 5.83 (d, $J(3,P) = 4.2$, 1H, H(3)); 3.75, 3.63 (each d, $^3J(H,P) = 11.2$, 18H, OMe); 2.83, 1.58 (each s, 2H, H(1*E*), H(5*E*)); 1.95, 1.89 (each s, 6H, 2 Me); 0.62, −0.31 (each s, 2H, H(1*Z*), H(5*Z*)). ^{13}C NMR ($CDCl_3$, 270 K): 122.2, 104.7 (each s); 92.8 (d, $J = 168$, $J(C,P) = 17.9$); 56.5 (t, $J = 156$, $J(C,P) = 34.4$); 52.5, 52.1 (2q, $J = 146$, OMe); 36.2 (t, $J = 156$); 25.6, 25.3 (2q, $J = 124$). Anal. Found: C, 32.89; H, 6.35; P, 12.03. $C_{13}H_{29}ClO_6P_2Ru$ (479.84) calc.: C, 32.54; H, 6.09; P, 12.91%.

*(η^5-2,4-Dimethylpentadienyl)iodobis(trimethylphosphine)ruthenium (**24**); bromo (η^5-2,4-dimethylpentadienyl)bis(trimethylphosphine)ruthenium (**25**); chloro(η^5-2,4-dimethylpentadienyl)bis(trimethylphosphine)ruthenium (**26**).* The procedure was as for **21**, but with PMe_3 (2.5 molar, equiv.) in place of $P(OMe)_3$, and KI, LiBr and Et_4NCl (1.5 molar equiv.) as halide source. Solvents for the reactions were acetone (for **24** and **25**) and CH_2Cl_2 (for **26**). **24**: Orange crystals (70%); m.p. 141°C (dec.). ^1H NMR (CD_2Cl_2, 240 K): 5.45 (s, 1H, H(3)); 2.51, 1.24 (each s, 2H, H(1*E*), H(5*E*)); 2.29, 1.98 (each d, $J(Me,P) = 2.4$ and 1.0, 6H, 2 Me); 1.69, 1.40 (each d, $^2J(Me,P) = 8.0$, 18H, PMe_3); 0.20, −0.45 (each s, 2H, H(1*Z*), H(5*Z*)). ^{13}C NMR (CD_2Cl_2, 240 K): 115.1, 99.7 (each s); 89.1 (d, $J = 160$, $J(C,P) = 11.5$); 53.6, 37.6 (each t, $J = 155$); 30.3 (q, $J = 122$); 25.4 (q, $J = 130$); 23.3, 22.8 (2q, $J = 129$, PMe_3). Anal. Found: C, 32.68; H, 6.36; P, 13.08. $C_{13}H_{29}IP_2Ru$ (475.30); calc.: C, 32.85; H, 6.15; P, 13.03%. **25**: Orange crystals (64%); m.p. 133°C (dec.). ^1H NMR (CD_2Cl_2, 200 K): 5.47 (s, 1H, H(3)); 2.42, 1.06 (each s, 2H, H(1*E*), H(5*E*)); 1.98, 1.95 (each s, 6H, 2 Me); 1.63, 1.29 (each d, $^2J(Me,P) = 8.00$, 18H, PMe_3); −0.03, −0.60 (each s, 2H, H(1*Z*), H(5*Z*)). ^{13}C NMR (CD_2Cl_2, 200 K): 116.4, 98.7 (each s); 90.6 (d, $J = 159$, $J(C,P) = 12.0$); 53.6 (t, $J = 155$, $J(C,P) = 23.7$); 35.2 (t, $J = 152$, $J(C,P) = 5.6$); 27.4, 26.1 (each q, $J = 127$); 22.1 (q, $J = 129$, $J(C,P) = 29.0$, PMe_3); 19.3 (q, $J = 130$, $J(C,P) = 26.1$, PMe_3). Anal. Found: C, 36.28; H, 6.81; P, 14.47. $C_{13}H_{29}BrP_2Ru$ (428.30) calc.: C, 36.46; H, 6.82; P, 14.46%. **26**: Yellow crystals (82%); m.p. 144°C (dec.). ^1H NMR ($CDCl_3$, 270 K): 5.55 (s, 1H, H(3)); 2.42, 1.08 (each d, $J(Z,E) = 2.9$, 2H, H(1*E*), H(5*E*)); 2.00 (d, $J(Me,P) = 2.4$, 3H, Me); 1.91 (s, 3H, Me); 1.69, 1.32 (each d, $^2J(Me,P) = 8.4$, 18H, PMe_3); −0.08, −0.52 (each d, 2H, H(1*Z*), H(5*Z*)). ^{13}C NMR ($CDCl_3$, 270 K): 117.7, 98.3 (each s); 91.7 (d, $J = 158$, $J(C,P) = 13.0$); 54.0 (t, $J = 152$, $J(C,P) = 27.0$); 34.6 (t, $J = 153$); 26.7 (q, $J = 126$); 26.0 (q, $J = 129$); 22.0 (q, $J = 129$, $J(C,P) = 29.0$, PMe_3); 19.3 (q, $J = 135$, $J(C,P) = 25.0$, PMe_3). Anal. Found: C, 40.90; H, 7.43; P, 15.88. $C_{13}H_{29}ClP_2Ru$ (383.85) calc.: C, 40.68; H, 7.61; P, 16.14%.

*Carbonyl(η^5-2,4-dimethylpentadienyl)bis(trimethylphosphine)ruthenium hexafluorophosphate (**27**).* A solution of **26** (0.24 g, 0.62 mmol) and KPF_6 (0.14 g, 0.75 mmol) in methanol (35 mL) was refluxed under CO (1 atm) for 4 h. Solvent evaporation gave a residue which was extracted with CH_2Cl_2 (25 mL). Filtration,

partial evaporation, addition of Et_2O and cooling (250 K) gave colourless microcrystals of **27** (0.25 g, 77%); m.p. 269°C (dec.). IR: 1982 (CO). ^1H NMR (CD_2Cl_2, 298 K): 5.85 (s, 1H, H(3)); 3.09, 2.50 (d, $J(E,P) = 4.4$, 1H and m, $J(E,Z) = 3.9$, 1H, H(1*E*), H(5*E*)); 2.27, 2.22 (d, $J(Me,P) = 2.2$, 3H and s, 3H, 2 Me); 1.81, 1.50 (each d, $^2J(Me,P) = 9.6$ and 9.2, 18H, PMe_3); 1.14, 0.84 (each m, $J(Z,P) = 10.4$, 4.9, 4.8 and 2.0, 2H, H(1*Z*), H(5*Z*)). ^{13}C NMR (CD_2Cl_2, 298 K): 197.6 (s, CO); 126.8, 118.0 (each s); 92.3 (d, $J = 162$, $J(C,P) = 7.6$); 59.6 (t, $J = 177$, $J(C,P) = 20.0$); 54.7 (t, $J = 154$); 27.8, 27.2 (each q, $J = 128$); 23.0 (q, $J = 127$, $J(C,P) = 33.2$, PMe_3); 20.2 (q, $J = 133$, $J(C,P) = 30.6$, PMe_3). Anal. Found: C, 32.34; H, 5.73; P, 17.68. $C_{14}H_{29}F_6OP_3Ru$ (521.37) calc.: C, 32.25; H, 5.61; P, 17.82%.

(tert-Butylisonitrile)(η⁵-2,4-dimethylpentadienyl)bis(trimethylphosphine)ruthenium hexafluorophosphate (28). A solution of **26** (0.26 g, 0.68 mmol) in methanol (20 mL) was slowly added to a solution of KPF_6 (0.15 g, 0.81 mmol) and ^{t}BuNC (0.1 mL, 0.8 mmol) in methanol (5 mL) at 273 K. The solution was allowed to warm to room temperature and stirring was continued for 15 h. Work-up as for **27** gave colourless microcrystals of **28** (0.29 g, 74%); m.p. 267°C (dec.). IR: 2122 (CN). ^1H NMR (CD_2Cl_2, 298 K): 5.56 (s, 1H, H(3)); 2.65, 2.20 (d, $J(E,Z) = 3.8$, 1H and m, $J(E,P) = 4.2$, 1H, H(1*E*), H(5*E*)); 2.15, 2.04 (each d, $J(Me,P) = 2.5$, $J(Me,P) = 1.0$, 6H, 2 Me); 1.70, 1.37 (each d, $^2J(Me,P) = 9.3$ and 8.5, 18H, PMe_3); 1.43 (s, 9H, ^{t}Bu); 0.69, 0.36 (each m, $J(Z,P) = 10.0$, 4.5, 4.6 and 2.4, 2H, H(1*Z*), H(5*Z*)). ^{13}C NMR (CD_2Cl_2, 298 K): 151.5 (s, Ru*C*N); 118.7, 115.2 (each s); 90.3 (d, $J = 168$, $J(C,P) = 9.2$); 58.4 (s, RuCN*C*); 55.8, 50.7 (each t, $J = 156$); 31.1 (q, $J = 129$, ^{t}Bu); 27.7, 27.3 (each q, $J = 124$ and 128); 23.2 (q, $J = 129$, $J(C,P) = 32.4$, PMe_3); 20.5 (q, $J = 129$, $J(C,P) = 28.8$, PMe_3). Anal. Found: C, 37.71; H, 6.65; N, 2.26; P, 15.86. $C_{18}H_{38}F_6NP_3Ru$ (576.49) calc.: C, 37.50; H, 6.64; N, 2.43; P, 16.12%.

(η⁵-2,4-Dimethylpentadienyl)bis(diphenylphosphino)ethaneiodoruthenium (29). A solution of **1** (0.17 g, 0.45 mmol) in acetone (15 mL) was slowly added to a mixture of KI (0.15 g, 0.90 mmol) and DPPE (0.27 g, 0.68 mmol) in acetone (10 mL) at 195 K. The mixture was stirred for 1 h at 195 K then allowed to warm to room temperature and stirring was continued for 5 h. Solvent evaporation gave a residue which was extracted with toluene (40 mL). Filtration, partial evaporation, addition of pentane and cooling (250 K) gave orange crystals of **29** (0.32 g, 99%); m.p. 175°C. ^1H NMR ($CD_2Cl_2/CHFCl_2$, 170 K): 7.92–7.14 (m, 20H, DPPE); 6.05 (s, 1H, H(3)); 3.35, 0.66 (each s, 2H, H(1*E*), H(5*E*)); 3.08, 2.90 (each m, 4H, DPPE); 2.63, 0.99 (each s, 6H, 2 Me); 1.54, −0.55 (2s, 2H, H(1*Z*), H(5*Z*)). ^{13}C NMR (CD_2Cl_2, 298 K): 139.5–127.1 (Ph); 109.9 (s); 90.2 (d, $J = 162$); 49.2 (t, $J = 160$); 29.3 (t, DPPE, $J = 130$); 26.9 (q, $J = 128$) [^{13}C in fast exchange domain]. ^{31}P NMR ($CD_2Cl_2/CHFCl_2$, 140 K): 90.2, 85.6 (s). Anal. Found: C, 55.50; H, 5.12; P, 8.76. $C_{33}H_{35}IP_2Ru$ (721.57) calc.: C, 54.93; H, 4.89; P, 8.58%.

Chloro(η⁵-2,4-dimethylpentadienyl)(N,N,N′,N′-tetramethylethylenediamine)-ruthenium (30). A solution of **1** (0.33 g, 0.87 mmol) in CH_2Cl_2 (20 mL) was slowly added to a mixture of Et_4NCl (0.19 g, 1.13 mmol) and TMEDA (0.17 mL, 1.13 mmol) in CH_2Cl_2 (10 mL). The mixture was stirred for 1 h at 195 K, allowed to warm to room temperature and stirring was continued for 5 h. Solvent evaporation gave a residue which was extracted with pentane (50 mL). Filtration, partial evaporation and cooling (195 K) gave orange crystals of **30** (0.27 g, 89%); m.p. 104°C (dec.). ^1H NMR (CD_2Cl_2, 230 K): 4.84 (s, 1H, H(3)); 3.50, 2.95, 2.65, 2.40 (each s, 12H, TMEDA); 3.08, 1.70 (each m, 4H, TMEDA); 2.01, 1.36 (s, 1H and d,

Table 4

Summary of crystal data and structure solution for complexes **4**, **18** and **21**

	4	**18**	**21**
Formula	$C_{16}H_{38}BF_4O_9P_3Ru$	$C_9H_{11}IO_2Ru$	$C_{13}H_{29}IO_6P_2Ru$
Mol. wt. (amu)	667.3	377.14	569.3
Crystal class	Triclinic	Monoclinic	Tetragonal
Space group	$P\bar{1}$	$P2_1/n$	$I4_1cd$
Cell dimensions (293 K)			
a (Å)	9.167(4)	8.053(1)	32.036(8)
b (Å)	10.679(4)	16.727(2)	32.036(8)
c (Å)	14.238(6)	8.584(1)	8.089(2)
α (deg)	91.46(3)	90	90
β (deg)	103 54(3)	90.69(1)	90
γ (deg)	91.06(3)	90	90
V (Å^3)	1354(1)	1156.2(3)	8302(3)
Z	2	4	16
D_{calc} (g cm^{-3})	1.64	2.17	1.82
μ (cm^{-1})	8.1	39.4	23.9
$F(000)$	684	704	4480
Scan speed (deg min^{-1})	4–15	4–15	8–24
2θ limits (deg)	3–56	3–50	3–45
$\sin(\theta/\lambda)_{max}$	0.66	0.595	0.54
No. of unique reflections	6259	2049	1487
No. with $I > 3\sigma(I)$	3100	1478	1112
R_{int}, reflections	0.022, 388	0.032, 587	0 055, 1483
Variables refined	282	118	209
$R(F)$	0.076	0.048	0.049
$R(W)$	0.073	0.047	0.037
$R(F^2)$	0.116	0.10	0.064
GoF(F)	2 3	3.2	2.6
GoF(I)	2 4	3.5	4.1
Extreme res. in diff. map (e Å^{-3})	+2.5, −1.2	+0.8, −2.2	+0.7, −0.8

$J(Z,E) = 3.1$, 1H, H(1E), H(5E)); 1.91, 1.76 (each s, 6H, 2 Me); −0.54, −1.33 (s, 1H and d, 1H, H(1Z), H(5Z)). ^{13}C NMR (CD_2Cl_2, 230 K): 98.2, 94.3 (each s); 77.9 (d, $J = 164$); 62.1 (t, $J = 151$); 61.3, 60.7 (each t, $J = 134$); 55.9 (t, $J = 148$); 51.4, 44.6, 40.1, 33.7, 25.5, 24.0 (each q, $J = 129$–132). Anal Found: C, 45.03; H, 7.96; N, 7.81. $C_{13}H_{27}ClN_2Ru$ (347.90) calc.: C, 44.88; H, 7.82; 8.05%.

X-Ray diffraction studies

The crystal structures of **4**, **18** and **21** were determined by use of a Syntex $P2_1$ four-cycle diffractometer and graphite monochromatized Mo-K_α ($\lambda = 0.71069$ Å) radiation at 293 K. Pertinent crystallographic data and structural quality indicators are summarized in Table 4.

Data reduction and structure solution were performed using the programs X-RAY 76 [29] and SHELX-76 [30]. Scan type 2θ–ω with collection in the octants $+h$, $\pm k$, $\pm l$ for all crystals. Atomic scattering factors and dispersion corrections were taken from published tables [31]. The structures were solved via the Patterson method and by successive Fourier difference mapping. Full-matrix least squares refinement based on F^2 was used with anisotropic thermal parameters for all

Table 5

Final positional parameters for complex **4**

Atom	*x*	*y*	*z*
Ru	0.2236(1)	0.21720(9)	0.32849(6)
P1	0.0957(3)	0.3964(3)	0.3300(2)
P2	0.3011(3)	0.2601(3)	0.1930(2)
P3	0.0173(3)	0.1081(2)	0.2486(2)
O11	0.0025(8)	0.4184(6)	0.4107(5)
O12	−0.0202(8)	0.4257(6)	0.2325(5)
O13	0.1916(8)	0.5243(6)	0.3597(5)
O21	0.2676(8)	0.1648(6)	0.1025(5)
O22	0.4780(7)	0.2791(7)	0.2189(5)
O23	0.2319(8)	0.3806(6)	0.1399(5)
O31	−0 1150(7)	0.1647(6)	0.1686(5)
O32	0.0622(8)	−0.0140(6)	0.1970(5)
O33	−0.0831(8)	0.0596(6)	0.3178(5)
C11	−0.104(1)	0.324(1)	0.4277(9)
C12	−0.113(1)	0 539(1)	0.2265(9)
C13	0.280(1)	0.584(1)	0.3033(9)
C21	0.349(1)	0.048(1)	0.1009(8)
C22	0.560(1)	0.320(1)	0.1462(9)
C23	0.230(2)	0.413(1)	0.0388(8)
C31	−0.098(1)	0.209(1)	0.0754(7)
C32	−0.039(2)	−0.115(1)	0.150(1)
C33	−0.241(1)	0.025(1)	0.2913(9)
C1	0.441(1)	0.304(1)	0.4237(8)
C2	0.342(1)	0.266(1)	0.4857(8)
C2A	0.300(1)	0.360(1)	0.5575(8)
C3	0.274(1)	0.143(1)	0.4819(7)
C4	0.294(1)	0.044(1)	0.4150(8)
C4A	0.204(1)	−0.079(1)	0.4204(8)
C5	0.382(1)	0.050(1)	0.3458(8)
B	0.5021(8)	0.2544(7)	0.8485(5)
F1	0.497(1)	0.2015(9)	0.7659(7)
F2	0.635(2)	0.272(1)	0.8925(9)
F3	0.436(2)	0.362(1)	0.8363(9)
F4	0.431(1)	0.180(1)	0.9001(7)

Table 6

Final positional parameters for complex **18**

Atom	*x*	*y*	*z*
Ru	0.0188(1)	0.16675(5)	0.30370(9)
I	−0.0688(1)	0.17352(5)	0.60957(8)
C1	0.067(2)	0.1564(8)	0.054(1)
C2	0.100(2)	0.0808(7)	0.124(1)
C22	0.271(2)	0.0428(8)	0.120(1)
C3	−0 022(2)	0.0423(7)	0 217(1)
C4	−0.180(2)	0.0733(7)	0.257(1)
C44	−0.275(2)	0.0232(9)	0.374(2)
C5	−0.242(2)	0.1476(7)	0.208(2)
C6	0.001(2)	0.2791(7)	0.297(1)
O6	−0.009(1)	0.3458(5)	0.286(1)
C7	0.238(2)	0.1714(6)	0.384(1)
O7	0.368(1)	0.1711(6)	0.438(1)

Table 7

Final positional parameters for complex **21**

Atom	*x*	*y*	*z*
Ru	0.10556(5)	0.13293(5)	0.2811(2)
I	0.10345(5)	0.17584(5)	−0.0168(2)
P1	0.1694(2)	0.1527(2)	0.3610(9)
O11	0.1950(4)	0.1905(4)	0.263(2)
C11	0.1770(7)	0.2311(5)	0.245(4)
O12	0.1682(4)	0.1690(4)	0.547(2)
C12	0.2049(6)	0.1881(7)	0.633(3)
O13	0.2095(5)	0.1210(4)	0.358(2)
C13	0.2158(7)	0.0890(7)	0.462(4)
P2	0.1275(2)	0.0778(2)	0.1374(9)
O21	0.1605(8)	0.0806(5)	−0.005(2)
C21	0.1940(8)	0.1052(8)	−0.048(3)
O22	0.0939(6)	0.0512(5)	0.031(2)
C22	0.0591(7)	0.0655(8)	−0.066(3)
O23	0.1441(4)	0.0396(4)	0.249(2)
C23	0.1593(6)	0.0014(7)	0.185(2)
C5	0.1006(6)	0.1041(6)	0.524(2)
C4	0.0626(7)	0.0929(8)	0.433(3)
C4A	0.0480(7)	0.0452(6)	0.405(3)
C3	0.0377(6)	0.1224(8)	0.350(3)
C2	0.0429(7)	0.1694(8)	0.343(3)
C2A	0.0158(5)	0.1953(6)	0.229(3)
C1	0.0797(7)	0.1896(7)	0.425(3)

non-H atoms. The final positions of the non-H atoms of **4**, **18** and **21** are given in Tables 5, 6 and 7, respectively.

Supplementary material. Crystal data, the data collection procedure, fractional coordinates of atoms, anisotropic displacement parameters, bond lengths and angles, selected weighted least-squares planes, and observed and calculated structure factors are available from R.R. upon request. Supplementary data will be deposited at the Cambridge Crystallographic Data Centre.

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References

1 M.O. Albers, D.J. Robinson and E. Singleton, Coord. Chem. Rev., 79 (1987) 1.
2 P.J. Fagan, W.S Mahoney, J.C. Calabrese and I D. Williams, Organometallics, 9 (1990), 1843 and refs. therein.
3 J.R. Bleeke and D.J. Raucher, Organometallics, 7 (1988) 2328.
4 D.N. Cox and R. Roulet, J. Chem. Soc., Chem. Commun , (1988) 951.
5 R Gleiter, I. Hyla-Kryspin, M.L. Ziegler, G. Sergeson, J.C. Green, L. Stahl and R.D. Ernst, Organometallics, 8 (1989) 298
6 D.N Cox and R. Roulet, J. Chem. Soc., Chem. Commun., (1989) 175.
7 G. Michael, J. Kaub and C.G. Kreiter, Angew. Chem., Int. Ed Engl., 24 (1985) 502.
8 J.R. Bleeke, J.J. Kotyk, D.A. Moore and D J. Rauscher, J. Am. Chem. Soc., 109 (1987) 417.
9 T. Lumini, D.N. Cox, R. Roulet, G Chapuis and F. Nicolo, Helv. Chim. Acta, 73 (1990) 1931.

10 T.D. Newbound, L. Stahl, M.L. Ziegler and R.D. Ernst, Organometallics, 9 (1990) 2962.
11 T.P. Gill and K.R. Mann, Organometallics, 1 (1982) 485.
12 R.D. Ernst, Chem. Rev., 88 (1988) 1255.
13 J.R. Bleeke, M.K. Hays and R. Wittenbrink, Organometallics, 7 (1988) 1417.
14 J.R. Bleeke, G.G Stanley and J.J. Kotyk, Organometallics, 5 (1986) 1642.
15 J.R. Bleeke and D.A. Moore, Inorg. Chem., 25 (1986) 3522.
16 M.O. Albers, D.J. Robinson, A. Shaver and E Singleton, Organometallics, 5 (1986) 2199.
17 B.E. Mann, J. Chem. Soc., Chem. Commun., (1977) 626.
18 J.A. Gibson and B.E. Mann, J. Chem. Soc., Dalton Trans., (1979) 1021.
19 H. Ma, P. Weber, M.L. Ziegler and R.D. Ernst, Organometallics, 6 (1987) 854.
20 C.S. Johnson and C.G. Moreland, J. Chem. Ed., 50 (1973) 477.
21 EXCHANGE, Program library, Computing Center, University of Lausanne, (1988).
22 EYRING-FIT, ANASPEC (ITERAT), Program library, Computing Center, University of Lausanne, (1988).
23 C. Ammann, P. Meier and A.E. Merbach, J. Magn. Reson., 46 (1982) 319.
24 T.A. Albright, P. Hofmann and R. Hoffmann, J. Am. Chem. Soc., 99 (1977) 7546.
25 T.A. Albright, Acc. Chem. Res., 15 (1982) 149.
26 J.W Faller and M.A. Adams, J. Organomet. Chem., 170 (1979) 71
27 A.N. Nesmeyanov, Y.A. Ustyneyuk, R I. Kristskaya and G.A. Shchembelov, J. Organomet. Chem., 14 (1968) 395.
28 W. Luginbuhl, P. Zbinden, P.A. Pittet, T. Armbruster, H.B Bürgi, A.E. Merbach and A. Ludi, Inorg Chem., 30 (1991) 2350.
29 J.M. Stewart, F.A. Kundell and J.C. Baldwin, X-RAY 76, Technical Report Tr-192, Computer Science Center, University of Maryland, College Park, MD, 1976 (locally modified by D. Schwarzenbach).
30 G.M. Sheldrick, SHELX-76, System of Computer Programs, University of Cambridge, UK, 1976.
31 International Tables of Crystallography, Vol. IV, Kynoch Press, Birmingham, 1974.