177. Synthesis of Cationic 2,4-Dimethylpenta-2,4-dienylruthenium Complexes. Crystal Structure of Carbonyl(η^4-cyclohexa-1,3-diene)(η^5-2,4-dimethylpenta-2,4-dienyl)ruthenium Tetrafluoroborate

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The complex [Ru(η^5-C_7H_{11})$_2$H]BF_4 (C_7H_{11} = 2,4-dimethylpenta-2,4-dienyl) is highly reactive towards two- and six-electron ligands, *e.g.* giving with CO complex [RuCO(η^4-C_7H_{12})(η^5-C_7H_{11})]BF_4. The 2,4-dimethylpenta-1,3-diene ligand (C_7H_{12}) of the latter complex is readily displaced giving, *e.g.* with excess cyclohexa-1,3-diene (C_6H_8) complex [RuCO(η^4-C_6H_8)(η^5-C_7H_{11})]BF_4. These reactions provide a convenient entry into monopentadienylruthenium chemistry.

Introduction. – During the last decade, there has been increasing interest in metal complexes containing the acyclic pentadienyl ligand [1] [2]. This can be traced to the realisation that, compared to the ubiquitous cyclopentadienyl ligands, acyclic pentadienyl ligands offer greater chemical versatility since they can more readily adopt a variety of bonding modes (η^5, η^3, and η^1) [3] and, further, may be susceptible to internal migratory attack [4]. Relatively few pentadienylruthenium(II) complexes have been reported to date, *e.g.* the 'open ruthenocenes' bis(2,4-dimethylpenta-2,4-dienyl)ruthenium, bis(2,3,4-trimethylpenta-2,4-dienyl)ruthenium, and (cyclopentadienyl)(2,4-dimethylpenta-2,4-dienyl)ruthenium [5] [6] and a series of (pentadienyl)(tertiary phosphine)ruthenium complexes [7]. The synthetic route to the latter compounds starts with [$RuCl_2(PPh_3)_3$] and tributyl(pentadienyl)tin and cannot be adapted to the preparation of (diene)(pentadienyl)ruthenium complexes. We recently reported that treatment of [Ru(η^3:η^3-$C_{10}H_{16}$)Cl_2]$_2$ ($C_{10}H_{16}$ = 2,7-dimethylocta-2,6-diene-1,8-diyl) or [Ru(η^3:η^3-$C_{10}H_{16}$)Cl_2L] (L = $P(OMe)_3$ or *t*-BuNC) with $AgBF_4$ in EtOH effectively delivers Ru^{2+} or $[RuL]^{2+}$ ions, respectively, for *in situ* reactions with dienes [8]. The reaction between the above dimer, 2,4-dimethylpenta-1,3-diene (C_7H_{12}), and $AgBF_4$ in deoxygenated EtOH gave [Ru(η^5-C_7H_{11})$_2$H]BF_4 (**1**) in 65% yield. Complex **1** is highly reactive towards 2- and 6-electron ligands (*e.g.* MeCN, CO, arenes, thiophene). One mol-equiv. of 2,4-dimethylpenta-1,3-diene is formed, and these reactions thus provide a convenient entry into monopentadienylruthenium chemistry. The synthesis and structure of a (diene)(pentadienyl)ruthenium complex obtained by this route is now described.

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Results and Discussion. – The fluxional behaviour of complex **1** has previously been described, and it has been established that, in the ground state, the Ru-bound hydrido ligand is involved in a three-centre Ru-H-C interaction with a terminal methylene group C-atom of one of the 2,4-dimethylpentadienyl ligands [9]. The presence of an agostic interaction in **1** presumably promotes its reactivity toward 2-electron ligand addition, *e.g.* giving with CO complex $[RuCO(\eta^4\text{-}C_7H_{12})(\eta^5\text{-}C_7H_{11})]BF_4$ (**2**). The 2,4-dimethylpenta-1,3-diene ligand in **2** is readily displaced by other dienes. Thus, stirring a solution of **2** and excess cyclohexa-1,3-diene (C_6H_8) in acetone at room temperature gave $[RuCO(\eta^4\text{-}C_6H_8)(\eta^5\text{-}C_7H_{11})]BF_4$ (**3**).

The structure of the cation in **3** is shown in the *Figure*, where the numbering scheme is indicated. Selected bond lengths and angles are presented in *Tables 1* and *2*, respectively. The Ru-atom is coordinated by a planar η^5-2,4-dimethylpenta-2,4-dienyl ligand, a linear carbonyl ligand, and an η^4-cyclohexa-1,3-diene ligand. The latter is in the *exo*-orientation relative to the C_7H_{11} ligand and is markedly folded such that the angle between the C(1), C(2), C(3), C(4) and C(1), C(4), C(5), C(6) planes is 37.5(4)°. The structure of the analogous cyclopentadienyl complex $[RuCO(\eta^4\text{-}C_6H_8)(\eta^5\text{-}C_5H_5)]BF_4$ (**4**) has been determined [10] and shows a similar *exo*-orientation of the η^4-cyclohexa-1,3-diene ligand with a folding angle of 36.4°. A series of substituted tricarbonyliron complexes have a related interplanar angle varying from 36.3 to 39.9° [11]. The following comparisons of the structures of **3** and **4** highlight the different steric features of a 2,4-dimethylpentadienyl ligand and a cyclopentadienyl ligand: *i*) the angle between the normals to planes C(1), C(2), C(3), C(4) and C(7), C(8), C(9), C(10), C(11) is 165.7(4)° in **3**, compared with the corresponding angle of 159.6(6)° in **4**. The larger angle in **3** can be ascribed to the 2,4-dimethylpentadienyl ligand having a greater overall cone angle than the cyclopentadienyl ligand [12]; *ii*) atoms C(12) and C(13) deviate from the C(7), C(8), C(9), C(10), C(11) plane by 0.290(5) and 0.244(5) Å, respectively, towards the Ru-atom; *iii*) the C(carbonyl)–Ru–C(outer diene) angles in **3** are 84.5(1) and 87.8(1)°, compared with the corresponding angles in **4** of 81.6(2)°. The larger angles in **3**, although apparently incon-

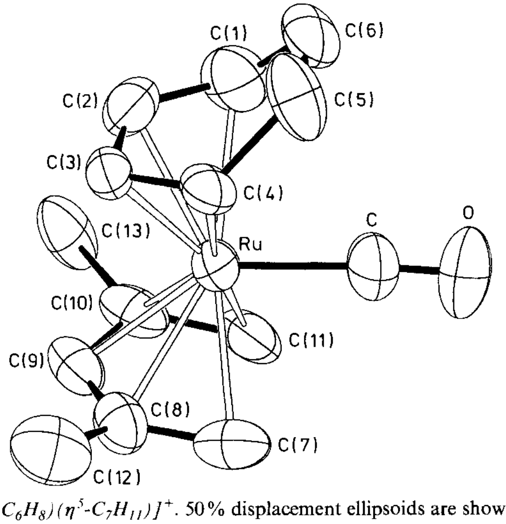

Figure. *Structure of* $[RuCO(\eta^4\text{-}C_6H_8)(\eta^5\text{-}C_7H_{11})]^+$. 50% displacement ellipsoids are shown. H-atoms are omitted. Arbitrary numbering.

Table 1. *Selected Bond Distances* [Å] *for* **3**. Standard deviation in parentheses.

Ru–C	1.911(3)	Ru–C(10)	2.212(4)	C(7)–C(8)	1.401(6)
Ru–C(1)	2.276(5)	Ru–C(11)	2.177(5)	C(8)–C(9)	1.354(6)
Ru–C(2)	2.159(5)	C(1)–C(2)	1.390(8)	C(8)–C(12)	1.528(6)
Ru–C(3)	2.194(4)	C(1)–C(6)	1.426(7)	C(9)–C(10)	1.483(6)
Ru–C(4)	2.267(4)	C(2)–C(3)	1.404(6)	C(10)–C(11)	1.444(7)
Ru–C(7)	2.274(4)	C(3)–C(4)	1.389(5)	C(10)–C(13)	1.483(6)
Ru–C(8)	2.232(4)	C(4)–C(5)	1.556(6)	C–O	1.126(4)
Ru–C(9)	2.224(2)	C(5)–C(6)	1.562(6)	B–F	1.342(3)

Table 2. *Selected Bond Angles* [°] *for* **3**. Standard deviation in parentheses.

C(1)–Ru–C(4)	71.4(2)	C(2)–C(1)–C(6)	120.1(4)	C(8)–C(9)–C(10)	127.6(3)
C(2)–Ru–C(3)	37.6(2)	C(1)–C(2)–C(3)	120.7(5)	C(9)–C(10)–C(11)	115.4(3)
C(7)–Ru–C(11)	79.1(2)	C(2)–C(3)–C(4)	112.8(4)	C(9)–C(10)–C(13)	115.9(3)
C(8)–Ru–C(10)	69.9(2)	C(3)–C(4)–C(5)	118.5(3)	C(11)–C(10)–C(13)	128.6(3)
C–Ru–C(1)	84.5(1)	C(4)–C(5)–C(6)	109.9(4)	F–B–F	109.5(2)
C–Ru–C(4)	87.8(1)	C(1)–C(6)–C(5)	112.7(4)		
C–Ru–C(7)	85.4(1)	C(7)–C(8)–C(12)	110.5(3)		
C–Ru–C(11)	82.3(1)	C(7)–C(8)–C(9)	128.5(4)		
Ru–C–O	176.3(4)	C(9)–C(8)–C(12)	120.1(4)		

sistent with the relative cone angles of the dienyl ligands, reflect the presence of an open edge in the acyclic pentadienyl ligand. The relative tilting of a ligand towards this open edge has previously been noted in piano-stool monopentadienyl complexes [13]. Steric hindrance between the Me groups of the 2,4-dimethylpentadienyl ligand and the H–C(inner) groups of the cyclohexa-1,3-diene ligand seems to be responsible for the absence of a mirror plane and the asymmetric C–C distances in **3**.

The reaction of **2** with dienes is not restricted to cyclohexa-1,3-diene, and may be extended to a range of 2- and 4-electron ligands, *e.g.* cyclohexa-1,4-diene, CO, $P(OMe)_3$, *t*-BuNC, $Ph_2PCH_2CH_2PPh_2$, and $Me_2NCH_2CH_2NME_2$ [14]. Therefore, both complexes **1** and **2** provide convenient entries into monopentadienylruthenium chemistry.

Experimental. – *General.* All reactions were carried out under N_2 in deoxygenated solvents using standard *Schlenk* techniques. IR spectra (cm^{-1}): in $CHCl_3$. ^1H-NMR spectra: at 360 MHz; δ in ppm rel. to TMS (= 0 ppm), J in Hz.

Carbonyl(η^4-2,4-dimethylpenta-1,3-diene)(η^5-2,4-dimethylpenta-2,4-dienyl)ruthenium Tetrafluoroborate (**2**). A soln. of **1** (0.91 g, 2.4 mmol) in CH_2Cl_2 (60 ml) was stirred under CO (1 atm) at r.t. for 1 h. Reduction to 10 ml and addition of Et_2O gave yellow crystals of $[RuCO(\eta^4\text{-}C_7H_{12})(\eta^5\text{-}C_7H_{11})]BF_4$ (**2**; 0.92 g, 94%) on cooling to −25°. M.p. 136° (dec.). IR: 2040 (CO). ^1H-NMR ($CDCl_3$): 6.37 (*d*, $^4J = 1.5$, 1H); 5.36 (*s*, 1H); 3.67 (*dd*, $^2J = 3.3$, $^4J = 1.5$, 1H); 3.10, 1.50 (each *d*, $^2J = 3.5$, 1H); 2.59, 2.40 (each *d*, $^2J = 3.3$, 1H); 2.39, 2.30, 2.02, 1.70, 1.46 (each *s*, 4 Me); 1.54 (*d*, $^2J = 3.3$, 1 H).

Carbonyl(η^4-cyclohexa-1,3-diene)(η^5-2,4-dimethylpenta-2,4-dienyl)ruthenium Tetrafluoroborate (**3**). A soln. of **2** (0.2 g, 0.49 mmol) and excess cyclohexa-1,3-diene (C_6H_8; 10.5 mmol) in acetone (20 ml) was stirred for 2 h at r.t. Addition of Et_2O and cooling to −25° gave yellow crystals of $[RuCO(\eta^4\text{-}C_6H_8)(\eta^5\text{-}C_7H_{11})]BF_4$ (**3**; 0.14 g, 73%). M.p. 146° (dec.). IR: 2053 (CO). ^1H-NMR ((D_6)acetone): 6.68 (*t*, $J = 1.2$, 1H); 5.75, 4.31 (each *m*, 2H); 3.92 (*dd*, $^2J = 2.4$, $^4J = 1.2$, 2H); 2.12 (*s*, 2 Me); 2.02, 1.77 (each *m*, $^2J = 11.5$, 2H); 1.80 (*d*, $^2J = 2.4$, 2H).

Crystal Data of **3**. $M = 391.18$, orthorhombic, space group $P2_1nb$ (I.T.C. No. 33), $a = 8.919(2)$, $b = 12.572(2)$, $c = 14.211(3)$ Å, $V = 1593.5(5)$ Å^3, $Z = 4$, $F(000) = 784$, $T = 295$ K, $D_c = 1.63$ g·cm^{-3}, graphite-monochromatized Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å), $\mu = 10.0$ cm^{-1}.

Data Collection and Refinement. A crystal of **3** with dimensions 0.42 × 0.38 × 0.28 mm was mounted on a *Syntex R3m/V* four-circle diffractometer. Cell parameters were determined and refined with constraints by 34 accurately centered reflections with $15° < 2\theta < 30°$. At r.t., 8652 intensities were recorded up to $2\theta = 55°$ by the θ–2θ scan method, 2° scan-range and a variable scan-speed from 2 to 8 °/min. Intensities were evaluated by the *Lehmann-Larsen* algorithm and their e.s.d.'s derived from counting statistics. No significant variation was observed on the intensity of 3 reference reflections periodically monitored. The systematic absences, $h\ 0\ l: h+l = 2n+1$ and $h\ k\ 0: k = 2n+1$, indicated the two possible space groups $P2_1nb$ or $Pmnb$. Chemical considerations based on crystal density and molecular symmetry prompted us to choose space group $P2_1nb$ (standard $Pna2_1$). This hypothesis was confirmed by the *Wilson*-plot statistics and successful refinement.

The intensities were corrected for *Lorentz* polarization. An extinction correction was included with final steps of refinement. Absorption effects were neglected. From 3525 unique reflections with *Laue* symmetry *mmm* ($R_{int} = 0.014$), 2649 were considered as observed for $I_{obs} > 3\sigma(I_{obs})$. Data reduction and structure solution were performed by the *Nicolet* SHELXTL-PLUS [15] package, and refinement by SHELX76 [16]. Atomic scattering factors and dispersion corrections were taken from [17]. The structure was solved from a 3-dimensional *Patterson* map and by successive difference-*Fourier* syntheses. The origin was fixed by the heavy atom at $x = ½$. The BF_4^- anion showed a disorder of the F-positions. Its geometry was fixed as a regular tetrahedron by constraining the B–F bond lengths and F–B–F angles to be equal; the corresponding two parameters were refined. The full-matrix least-squares refinement was carried out with anisotropic non-H-atoms. On the final difference-*Fourier* map, all H-atoms were located and included in the refinement with variable positions and a unique common isotropic displacement parameter. The refinement converged to $R = 0.027$ and $R_w = 0.032$ with a goodness-of-fit $S = 1.05$. The final weighting scheme was $1/[\sigma(F)^2+0.001\ F^2]$. On the last difference-*Fourier* synthesis, only one significant electron residual of *ca.* 0.9 $e \cdot Å^{-3}$ was located at 1.38 Å from the B-atom. Attempts to interpret this residual as an additional BF_4^- orientation failed. The geometrical calculations and drawings were performed by the PARST [18] program and *Nicolet* package, resp.

Supplementary Material. – Crystal data, 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. All data are deposited with the *Cambridge Crystallographic Data Centre.*

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