*Journal of Organometallic Chemistry*, 438 (1992) 195–207
Elsevier Sequoia S.A., Lausanne
JOM 22758

# Hydrogen migration to acyclic pentadienyl ligands: the reactions of ($\eta^5$-2,4-dimethylpentadienyl)($\eta^4$-2,4-dimethylpenta-1,3-diene)(L)ruthenium(II) tetrafluoroborates (L = $^t$BuNC, CO, P(OMe)$_3$) with dienes

David N. Cox [a,b], Tito Lumini [a] and Raymond Roulet [a]

[a] *Institut de Chimie Minérale et Analytique de l'Université, 3 Place du Château, CH-1005, Lausanne (Switzerland)*
[b] *School of Physics and Materials, Lancaster University, Lancaster, LA1 4YA (UK)*

(Received January 21, 1992)

**Abstract**

Diene-for-diene substitutions occur on reaction of the title complexes [Ru($\eta^5$-$C_7H_{11}$)($\eta^4$-$C_7H_{12}$)L]$BF_4$ (L = $^t$BuNC (**2**), CO (**3**), P(OMe)$_3$ (**4**)) with an excess of butadiene 2,3-dimethylbutadiene, cyclohexa-1,3-diene or cycloocta-1,5-diene giving complexes of the type [Ru($\eta^5$-$C_7H_{11}$)(diene)L]$BF_4$ (**5–16**). Apparent pentadienyl-for-pentadienyl substitutions occur on reaction of **2** with the cyclopentadienes $C_5H_6$ or $C_5Me_5H$ giving [Ru($\eta^5$-$C_5R_5$)($\eta^4$-$C_7H_{12}$)(CN$^t$Bu)]$BF_4$ (R = H (**17**), Me (**18**)), on reaction of **2** or **3** with cyclohexa-1,4-diene to give [Ru($\eta^5$-$C_6H_7$)($\eta^4$-$C_7H_{12}$)L]$BF_4$ (L = $^t$BuNC (**19**), CO (**20**)), and on reaction of **2**, **3** or **4** with cycloocta-1,3-diene to give [Ru($\eta^5$-$C_8H_{11}$)($\eta^4$-$C_7H_{12}$)L]$BF_4$ (L = $^t$BuNC (**21**), CO (**22**), P(OMe)$_3$ (**23**)). The ($\eta^4$-$C_7H_{12}$) ligand is readily displaced from **19** and **20** by an excess of a cyclohexadiene (1,3- or 1,4-) to give [Ru($\eta^5$-$C_6H_7$)($\eta^4$-$C_6H_8$)L]$BF_4$ (L = $^t$BuNC (**24**), CO (**25**)) and from **21** by an excess of cycloocta-1,5-diene giving [Ru($\eta^5$-$C_8H_{11}$)($\eta^2$ : $\eta^2$-$C_8H_{12}$)(CN$^t$Bu)]$BF_4$ (**26**). All the apparent pentadienyl-for-pentadienyl substitutions are suggested to occur via initial displacement of the ($\eta^4$-$C_7H_{12}$) ligand from **2–4**, with subsequent C–H activation and inter-ligand hydrogen migration from the incoming diene to the ($\eta^5$-$C_7H_{11}$) ligand leading to the observed products.

## Introduction

A major reason for the sustained interest in acyclic pentadienyl complexes of the transition metals in recent years has been the realisation that $\eta^5 \leftrightarrow \eta^3 \leftrightarrow \eta^1$ interconversions are more facile for such complexes than for related cyclopentadienyl complexes [1]. The relevance of this to possible enhanced catalytic activity for acyclic pentadienyl complexes has been emphasized [2].

Correspondence to: Dr. D.N. Cox or Prof. R. Roulet.

We have previously reported the synthesis of the complex $[Ru(\eta^5\text{-}C_7H_{11})_2H]BF_4$ (**1**, $C_7H_{11}$ = 2,4-dimethylpentadienyl) obtained in a one-pot reaction from the ruthenium(IV) precursor $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl(\mu\text{-}Cl)]_2$, $AgBF_4$ and 2,4-dimethylpentadiene in ethanol [3]. Complex **1** can also be obtained by direct protonation of the open-ruthenocene $[Ru(\eta^5\text{-}C_7H_{11})_2]$ with $HBF_4$ [4]. Complex **1**, which is highly reactive towards two-electron ligand addition, has an agostic ground state, and its dynamic behaviour in solution [5] is substantially different from that of related agostic pentadiene complexes of Cr or Mn [6,7]. It has been demonstrated that the reactivity of **1** can be exploited to provide a convenient synthetic entry into mono(2,4-dimethylpentadienyl)ruthenium(II) chemistry [8–10]. We report here on the reactions of the mono-ligand adducts of **1**, $[Ru(\eta^5\text{-}C_7H_{11})(\eta^4\text{-}C_7H_{12})L]BF_4$ (L = $^t$BuNC (**2**), CO (**3**), $P(OMe)_3$ (**4**)), with a range of free dienes. Some of these reactions involve novel $(\eta^5\text{-}C_7H_{11}) \rightarrow (\eta^4\text{-}C_7H_{12})$ transformations, and hence provide a further illustration of the chemical differences between acyclic pentadienyl complexes and their cyclopentadienyl analogues.

## Results and discussion

*Synthesis of $[Ru(\eta^5\text{-}C_7H_{11})(\eta^4\text{-}C_7H_{12})L]BF_4$ complexes*

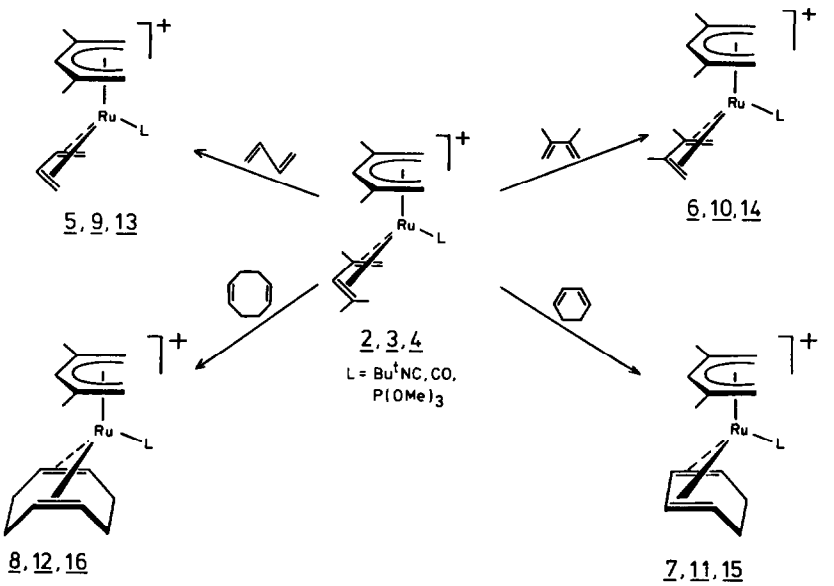
Treatment of $[Ru(\eta^5\text{-}C_7H_{11})_2H]BF_4$ (**1**) with $^t$BuNC, CO or $P(OMe)_3$ in dichloromethane at room temperature results in rapid ligand addition and formation of the complexes **2**, **3** or **4**, respectively, as shown in eq. 1.

$$[Ru(\eta^5\text{-}C_7H_{11})_2H]BF_4 + L \longrightarrow [Ru(\eta^5\text{-}C_7H_{11})(\eta^4\text{-}C_7H_{12})L]BF_4 \qquad (1)$$

(L = $^t$BuNC (**2**), CO (**3**), $P(OMe)_3$ (**4**))

The reactions probably proceed via an initial rupture of the Ru–H component of the three-centre Ru–H–C interaction in **1** to give the sixteen-electron intermediate, $[Ru(\eta^5\text{-}C_7H_{11})(\eta^4\text{-}C_7H_{12})]^+$, which subsequently coordinates the two-electron ligand. The sixteen-electron intermediate has previously been shown to be involved in fluxional processes of **1** that are rapid in solution at room temperature [5]. The reactions of eq. 1 are quantitative, and isolated yields of **2**, **3** and **4** exceed 85%. Dichloromethane is an ideal solvent for these reactions; acetone is unsuitable as its higher coordinating abilities have been shown to facilitate further reaction of **2**–**4** to give the complexes $[Ru(\eta^5\text{-}C_7H_{11})L_3]BF_4$ [9,10].

An alternative synthesis of **2** and **4**, which does not require **1** as a precursor, involves the room temperature reaction of the 2,7-dimethyloctadienediyl complexes $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2L]$ (L = $^t$BuNC, $P(OMe)_3$) [11] directly with $AgBF_4$ (2 mol. equiv.) and an excess of 2,4-dimethylpenta-1,3-diene in ethanol. This is our preferred synthesis for **2** and **4**, giving overall yields based on commercial $RuCl_3 \cdot nH_2O$ of *ca.* 50%, and providing a further illustration of a useful synthetic methodology that we have outlined elsewhere [3]. The structure of complex **3** has previously been reported. The $(\eta^5\text{-}C_7H_{11})$ ligand takes up its usual U-conformation, the CO resides under the open-edge of the pentadienyl ligand, and the diene is in the *exo*-orientation [9]. Similar structures for **2** and **4** are anticipated. The ease of reaction of complexes **2**–**4** with dienes in acetone solution follows the sequence **3** > **2** ≈ **4**; hence for the reactions described below, those involving **3**



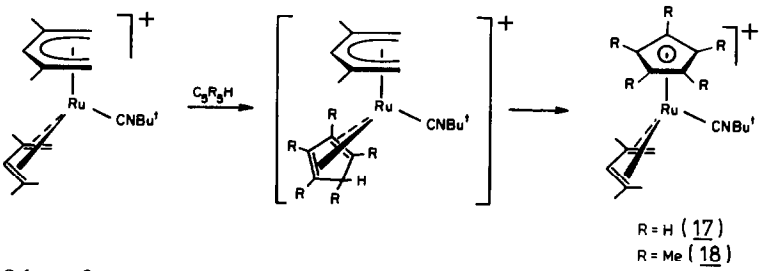

Scheme 1.

were carried out at room temperature and those involving **2** and **4** were under reflux.

*Diene-for-diene substitution reactions*

Reaction of the complexes **2, 3** or **4** with an excess of the free dienes butadiene, 2,3-dimethylbutadiene, cyclohexa-1,3-diene, or cycloocta-1,5-diene, in acetone solution results in formation of the complexes $[Ru(\eta^5\text{-}C_7H_{11})(diene)L]BF_4$ (L = $^t$BuNC, diene = $\eta^4$-$C_4H_6$ (**5**), $\eta^4$-$C_6H_{10}$ (**6**), $\eta^4$-$C_6H_8$ (**7**), $\eta^2:\eta^2$-$C_8H_{12}$ (**8**); L = CO, diene = $\eta^4$-$C_4H_6$ (**9**), $\eta^4$-$C_6H_{10}$ (**10**), $\eta^4$-$C_6H_8$ (**11**), $\eta^2:\eta^2$-$C_8H_{12}$ (**12**); L = $P(OMe)_3$, diene = $\eta^4$-$C_4H_6$ (**13**), $\eta^4$-$C_6H_{10}$ (**14**), $\eta^4$-$C_6H_8$ (**15**), $\eta^2:\eta^2$-$C_8H_{12}$ (**16**), as shown in Scheme 1. In these reactions the bulky $\eta^4$-bound 2,4-dimethylpenta-1,3-diene ligand is displaced from complexes **2–4** by the incoming diene to give complexes **5–16** in isolated yields of 60–90%. We have previously described the crystal structure of complex **11** [8]. The cation of **11** has an approximate, non-crystallographic, $C_s$ symmetry with the ($\eta^5$-$C_7H_{11}$) ligand in a U-conformation, the carbonyl resides in the site directly under the open-edge of the pentadienyl ligand, and the diene is in the *exo*-orientation. On the basis of their solution $^1H$ and $^{13}C$ NMR spectra all the cations in **5–16** possess an element of symmetry, and we propose the $C_s$ symmetry structures, similar to that of **11**, shown in Scheme 1.

Related cationic complexes of the type $[M(\eta^5\text{-dienyl})(\eta^4\text{-diene})CO]BF_4$ are known for M = Fe [12] and Ru [13], as are the neutral complexes $[Ru(\eta^5\text{-dienyl})(\eta^4\text{-diene})X]$ (X = halide, ($\eta^5$-dienyl) = cyclopentadienyl [14], pentamethylcyclopentadienyl [15], 2,4-dimethylpentadienyl [10]). Diene-for-diene substitution reactions, also, have previously been observed for both ruthenium(II) [14] and ruthenium(0) [16], although they have generally involved displacement of cycloocta-1,5-diene.



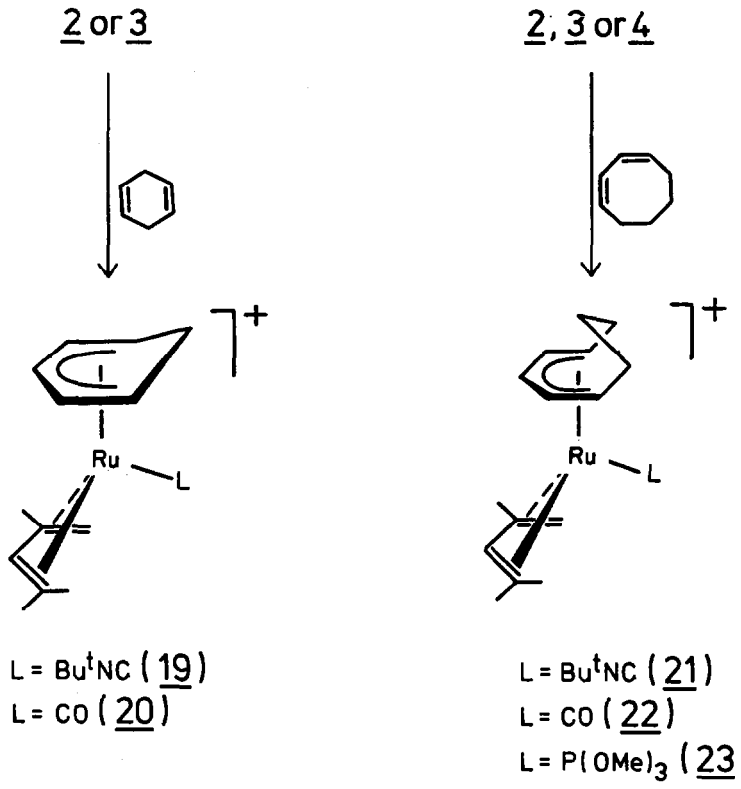

Scheme 2.

*Apparent pentadienyl-for-pentadienyl substitution reactions*

The reactions of **2** with a small excess (1.5 mol. equiv.) of either freshly distilled cyclopentadiene ($C_5H_6$) or 1,2,3,4,5-pentamethylcyclopentadiene ($C_5Me_5H$) in acetone solution give the complexes $[Ru(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_7H_{12})(CN^tBu)]BF_4$ (**17**) and $[Ru(\eta^5\text{-}C_5Me_5)(\eta^4\text{-}C_7H_{12})(CN^tBu)]BF_4$ (**18**) in yields of 75 and 80%, respectively. Hence in both reactions an apparent substitution of an acyclic pentadienyl ligand for a cyclic pentadienyl ligand has occurred. We suggest that these reactions proceed via an initial diene-for-diene substitution followed by an inter-ligand hydrogen transfer, as shown in Scheme 2. Although the proposed intermediates $[Ru(\eta^5\text{-}C_7H_{11})(\eta^4\text{-}C_5R_5H)(CN^tBu)]BF_4$ in this scheme were not observed, we have previously reported the isolation of the related complex $[Ru(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_5H_6)(CN^tBu)]BF_4$ containing an $\eta^4$-cyclopentadiene ligand [3].

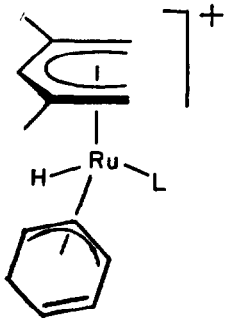
Additional examples of apparent pentadienyl-for-pentadienyl substitutions are observed on reaction of complexes **2** or **3** with cyclohexa-1,4-diene. Hence treatment of **2** or **3** with a small excess of cyclohexa-1,4-diene (1-2 mol. equiv.) in acetone solution gives the $\eta^5$-cyclohexadienyl complexes $[Ru(\eta^5\text{-}C_6H_7)(\eta^4\text{-}C_7H_{12})L]BF_4$ (L = $^t$BuNC (**19**), CO (**20**)) in isolated yields of *ca.* 80% (Scheme 3). In contrast to the reactions involving **2** and **3**, however, **4** reacts with a small excess of cyclohexa-1,4-diene (2 mol. equiv.) in acetone to give only $[Ru(\eta^5\text{-}C_7H_{11})(\eta^4\text{-}C_6H_8)(P(OMe)_3)]BF_4$ (**15**), isolated in 53% yield. Furthermore, analysis of the $^1H$ NMR spectrum of the entire crude product from the reaction of **4** and cyclohexa-1,4-diene showed no trace of an $\eta^5$-cyclohexadienyl complex analogous to **19** or **20**. We suggest that the reactions of **2**–**4** with cyclohexa-1,4-diene probably all follow a common initial pathway involving displacement of the $\eta^4$-bound 2,4-dimethylpentadiene ligand from **2**–**4** and initial $\eta^2$-coordination of cyclohexa-1,4-diene. Subsequent oxidative-addition of an allylic C–H bond [17] of the $\eta^2$-cyclohexa-1,4-diene ligand is then suggested to produce intermediates of the form $[Ru(\eta^5\text{-}C_7H_{11})(\eta^3\text{-}C_6H_7)LH]BF_4$ (**A**; L = $^t$BuNC, CO or $P(OMe)_3$). From intermediates **A** to final products, the least motion pathways consistent with our observations are: For L = $^t$BuNC or CO, the final products **19** or **20**, respectively, are formed by selective migration of the hydride ligand exclusively to either C(1) or C(5) of the 2,4-dimethylpentadienyl ligand. For L = $P(OMe)_3$, the final product **15** is formed by selective migration of the hydride ligand exclusively to either C(1) or C(5) of the cyclohexadienyl ligand.

The factors controlling the selectivities of the hydride migrations in the intermediates **A** are not understood, and further speculation is unwarranted given that




Scheme 3.

additional intermediates may be involved in the conversion of **A** into final products. For example, an $\eta^5 \leftrightarrow \eta^3$ interchange of the hapticities of the two dienyl ligands of **A** may occur, or the terminal hydride forms may be converted into related agostic intermediates.




(A)

The reactions of complexes **2**, **3** and **4** with a small excess of cycloocta-1,3-diene (1–2 mol. equiv.) in acetone solution all provide further examples of apparent pentadienyl-for-pentadienyl substitution reactions, giving the complexes $[Ru(\eta^5\text{-}C_8H_{11})(\eta^4\text{-}C_7H_{12})L]BF_4$ (L = $^t$BuNC (**21**), CO (**22**), $P(OMe)_3$ (**23**)) in isolated yields of *ca.* 70% (Scheme 3). A notable feature common to the solution $^1$H NMR spectra of complexes **21–23** is the presence of a high-field resonance (*ca.* 0.0–0.5 ppm) appearing as a quartet of triplets. This signal, which has been recognised previously as a characteristic feature of an $\eta^5$-cyclooctadienyl ligand [18], is assigned to the *endo*-hydrogen on C(7) ($^2J(HH) \approx 14$, $^3J(HH) \approx 14$, 14, 3 and 3 Hz). We suggest that these reactions, which are clearly related to those involving cyclohexa-1,4-diene, all occur through intermediates of the type $[Ru(\eta^5\text{-}C_7H_{11})(\eta^3\text{-}C_8H_{11})LH]BF_4$ (**B**; L = $^t$BuNC, CO or $P(OMe)_3$), formed from **2–4** by displacement of the $\eta^4$-2,4-dimethylpentadiene ligand, $\eta^2$-coordination of cycloocta-1,3-diene, and oxidative-addition of an allylic C–H bond. The observed final products, **21–23**, imply that all the intermediates **B** effectively undergo selective migration of the hydride ligand exclusively to either C(1) or C(5) of the 2,4-dimethylpentadienyl ligand.

The reactions of complexes **2–4** with dienes have provided selective syntheses of five pairs of isomeric complexes: $[Ru(\eta^5\text{-}C_7H_{11})(\eta^4\text{-}C_6H_8)L]BF_4$ and $[Ru(\eta^5\text{-}C_6H_7)(\eta^4\text{-}C_7H_{12})L]BF_4$ (L = $^t$BuNC, **7** and **19**; L = CO, **11** and **20**, respectively); $[Ru(\eta^5\text{-}C_7H_{11})(\eta^2\text{:}\eta^2\text{-}C_8H_{12})L]BF_4$ and $[Ru(\eta^5\text{-}C_8H_{11})(\eta^4\text{-}C_7H_{12})L]BF_4$ (L = $^t$BuNC, **8** and **21**; L = CO, **12** and **22**; L = $P(OMe)_3$, **16** and **23**, respectively). Even with prolonged reactions in acetone solution, none of these complexes undergoes any rearrangement into its isomeric partner. There is clearly a substantial kinetic barrier preventing their interconversion, and the relative thermodynamic stabilities within the isomeric pairs remain unknown.

For the $\eta^5$-cyclodienyl complexes **17–23**, selected reactions with dienes were investigated, and the results confirm that the $\eta^4$-coordinated 2,4-dimethylpentadiene ligand in these complexes is substitutionally labile. Hence reaction of complexes **19** or **20** with excess of either cyclohexa-1,3-diene or cyclohexa-1,4-diene gives the complexes $[Ru(\eta^5\text{-}C_6H_7)(\eta^4\text{-}C_6H_8)L]BF_4$ (L = $^t$BuNC (**24**), CO (**25**)), containing an $\eta^4$-bound cyclohexa-1,3-diene ligand. Similarly, reaction of **21** with excess cycloocta-1,5-diene gives $[Ru(\eta^5\text{-}C_8H_{11})(\eta^2\text{:}\eta^2\text{-}C_8H_{12})(CN^tBu)]BF_4$ (**26**), although **21** does not react with excess cycloocta-1,3-diene in acetone solution. Of these complexes, only **25** has been reported previously [13b]; its synthesis from **20**, however, is the first not requiring a precursor accessible only through metal vapour techniques.

## Experimental

### *General comments*

All reactions were carried out under nitrogen in dried and 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. Microanalyses were carried out by Ilse Beetz, Kronach, Germany. NMR spectra were recorded at room temperature in $CDCl_3$ solution, unless otherwise stated, on Bruker WH-360 ($^1$H, 360; $^{13}$C, 90.55 MHz) or AC-200 ($^1$H, 200; $^{13}$C, 50.32 MHz) FT spectrometers. Chemical shifts are reported in $\delta$ ppm downfield from $SiMe_4$.

Spin–spin coupling constants, $J$, are given in Hz. The hydrogen atom labelling scheme used in the $^1$H NMR assignments features a prime (′) to indicate a proton of the $\eta^4$-bound diene ligand. The absence of a prime indicates a proton of the $\eta^5$-bound dienyl ligand. The specific carbon atom to which the proton is attached is indicated using the IUPAC approved numbering scheme for the carbon skeleton of each ligand.

*Synthesis of complexes*

Syntheses and characterisation data for **1**, **3** and **11** have been described previously [3,8,10].

*(t-Butylisocyanide)(η⁴-2,4-dimethylpenta-1,3-diene)(η⁵-2,4-dimethylpentadienyl) ruthenium tetrafluoroborate (2).* To a solution of **1** (0.27 g, 0.71 mmol) in $CH_2Cl_2$ (30 ml) was added $^t$BuNC (0.10 ml, 0.88 mmol) and the mixture was stirred for 2 h at room temperature. Filtration, partial evaporation of the solution, addition of $Et_2O$ and cooling (250 K) gave pale yellow crystals of **2**, which were washed with $Et_2O$ and dried *in vacuo* (0.29 g, 88%). M.p. 155°C (dec.). IR: 2172 cm$^{-1}$ (CN). $^1$H NMR: 5.80 (s, 1H, H3); 4.94 (s, 1H, H3′); 3.48, 2.86 (each d, $^2J$ = 3.0, 3.8 Hz, 2H, H1*E*, H5*E*); 2.23 (d, $^2J$ = 3.4 Hz, 1H, H1′*E*); 2.21, 2.15 (each s, 6H, 2Me); 1.89 (s, 4H, Me′ and H1′*Z*); 1.69 (s, 9H, $^t$Bu); 1.51, 1.18 (each s, 6H, 2Me′); 1.35, 1.21 (each d, 2H, H1*Z*, H5*Z*). $^{13}$C NMR: 150.1 (s, Ru*C*N); 113.3, 113.1, 106.8 (3s); 99.5 (d, $J$ = 162 Hz); 91.0 (d, $J$ = 164 Hz); 89.2 (s); 59.7 (s, RuCN*C*); 58.2 (t, $J$ = 160 Hz); 53.4 (t, $J$ = 162 Hz); 48.1 (t, $J$ = 159 Hz); 30.8 (q, $J$ = 127 Hz, $^t$Bu); 28.7, 25.4, 24.6, 23.0, 22.1 (5q, $J$ = 123–128 Hz). Anal. Found: C, 49.64; H, 6.98; N, 3.27. $C_{19}H_{32}BF_4NRu$ calc.: C, 49.36; H, 6.98; N, 3.03%.

*(η⁴-2,4-Dimethylpenta-1,3-diene)(η⁵-2,4-dimethylpentadienyl)(trimethylphosphite)ruthenium tetrafluoroborate (4).* This was made as described for **2** but with $P(OMe)_3$ in place of $^t$BuNC. **1** (0.25 g, 0.66 mmol) and $P(OMe)_3$ (0.47 ml, 4.0 mmol) gave yellow crystals of **4** (0.33 g, 99%). M.p. 113°C (dec.). $^1$H NMR: 5.95 (s, 1H, H3); 4.86 (s, 1H, H3′); 4.02 (d, $J$(PH) = 11.2 Hz, 9H, OMe); 3.59, 2.89 (each d, $^2J$ = 3.9, 3.4 Hz, 2H, H1*E*, H5*E*); 2.33 (d, $^2J$ = 2.9 Hz, 1H, H1′*E*); 2.20, 2.17 (each s, 6H, 2Me); 1.85 (s, 3H, Me′); 1.70 (dd, $J$(PH) = 14.1 Hz, 1H, H1′*Z*); 1.37 (s, 3H, Me′); 0.97 (d, $J$(PH) = 3.0 Hz, 3H, Me′); 0.83, 0.69 (each dd, $J$(PH) = 7.7, 6.7 Hz, 2H, H1*Z*, H5*Z*). $^{13}$C NMR: 112.0, 111.1, 107.5 (3s); 100.9 (dd, $J$ = 158, $J$(PC) = 10.3 Hz); 89.6 (d, $J$ = 164 Hz); 86.3 (s); 57.4 (t, $J$ = 158 Hz); 55.3 (q, $J$ = 147 Hz, OMe); 54.5 (t, $J$ = 147 Hz); 47.7 (t, $J$ = 165 Hz); 27.8, 25.5, 24.4, 21.9, 21.6 (5q, $J$ = 126–129 Hz). Anal. Found: C, 40.45; H, 6.39; P, 5.87. $C_{17}H_{32}BF_4O_3PRu$ calc.: C, 40.57; H, 6.41; P, 6.15%.

*Alternative syntheses of 2 and 4.* The complex $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2(CN^tBu)]$ (0.34 g, 0.87 mmol) [11] was added to a solution of $AgBF_4$ (0.38 g, 1.95 mmol) and 2,4-dimethylpenta-1,3-diene (3.0 ml, 23 mmol) in ethanol (30 ml) and the mixture was stirred at room temperature for 3 h. AgCl was then removed by filtration through a bed of Celite (1 cm). Partial evaporation of the solution and cooling (250 K) gave yellow crystals of **2** (0.30 g, 75%), Similarly, $[Ru(\eta^3:\eta^3\text{-}C_{10}H_{16})Cl_2(P(OMe)_3)]$ (0.42 g, 0.97 mmol)] [11], $AgBF_4$ (0.40 g, 2.05 mmol) and 2,4-dimethylpenta-1,3-diene (3.0 ml, 23 mmol) in ethanol (30 ml) gave yellow crystals of **4** (0.42 g, 86%).

*(η⁴-Butadiene)(t-butylisocyanide)(η⁵-2,4-dimethylpentadienyl)ruthenium tetrafluoroborate (5).* Butadiene was bubbled through a solution of **2** (0.19 g, 0.41 mmol)

in acetone (40 ml) at reflux for 1 h. Filtration, partial solvent evaporation, addition of $Et_2O$ and cooling (250 K) gave colourless crystals of **5**. Washed with $Et_2O$ and dried *in vacuo* (0.12 g, 71%). M.p. 186°C (dec.). IR: 2181 $cm^{-1}$ (CN). $^1H$ NMR: 6.28 (s, 1H, H3); 5.45 (m, $^3J = 13.0$, 5.0, $^4J = 4.0$, 2.0 Hz, 2H, H2′, H3′); 3.46 (d, $^2J = 2.6$ Hz, 2H, H1*E*, H5*E*); 2.49 (dd, 2H, H1′*E*, H4′*E*); 1.90 (s, 6H, 2Me); 1.68 (s, 9H, $^t$Bu); 1.26 (d, 2H, H1*Z*, H5*Z*); 1.07 (dd, 2H, H1′*Z*, H4′*Z*). $^{13}C$ NMR: 144.7 (s, Ru*C*N); 110.8 (s); 99.1 (d, $J = 167$ Hz); 91.4 (d, $J = 171$ Hz); 59.7 (s, RuCN*C*); 56.6, 46.9 (2t, $J = 161$ Hz); 30.5 (q, $J = 129$ Hz, $^t$Bu); 23.5 (q, $J = 128$ Hz). Anal. Found: C, 45.71; H, 6.39; N, 3.40. $C_{16}H_{26}BF_4NRu$ calc.: C, 45.73; H, 6.24; N, 3.33%.

*(t-Butylisocyanide)(η⁴-2,3-dimethylbutadiene)(η⁵-2,4-dimethylpentadienyl)ruthenium tetrafluoroborate (6).* 2,3-Dimethylbutadiene (5.0 ml, 44 mmol) was added to a solution of **2** (0.23 g, 0.50 mmol) in acetone (30 ml) and the mixture was refluxed for 4 h. Work-up as for **5** gave colourless crystals of **6** (0.16 g, 71%). M.p. 205°C (dec.). IR: 2186 $cm^{-1}$ (CN). $^1H$ NMR: 5.77 (s, 1H, H3); 3.52 (d, $^2J = 2.5$ Hz, 2H, H1*E*, H5*E*); 2.60 (d, $^2J = 1.8$ Hz, 2H, H1′*E*, H4′*E*); 2.09, 1.92 (each s, 12H, 2Me and 2Me′); 1.67 (s, 9H, $^t$Bu); 1.29 (d, 2H, H1*Z*, H5*Z*); 0.93 (d, 2H, H1′*Z*, H4′*Z*). $^{13}C$ NMR: 145.7 (s, Ru*C*N); 111.7, 103.0 (2s); 101.2 (d, $J = 164$ Hz); 59.7 (s, RuCN*C*); 55.2, 48.7 (2t, $J = 161$ Hz); 30.4 (q, $J = 129$ Hz, $^t$Bu); 22.8, 20.0 (2q, $J = 127$ Hz). Anal. Found: C, 48.04; H, 7.02; N, 3.28. $C_{18}H_{30}BF_4NRu$ calc.: C, 48.22; H, 6.74; N, 3.12%.

*(t-Butylisocyanide)(η⁴-cyclohexa-1,3-diene)(η⁵-2,4-dimethylpentadienyl)ruthenium tetrafluoroborate (7).* This was made by the method described as for **6**, from cyclohexa-1,3-diene (0.62 ml, 6.5 mmol) and **2** (0.15 g, 0.32 mmol). Reaction in refluxing acetone (30 ml) for 6 h gave pale yellow crystals of **7** (0.090 g, 62%). M.p. 159°C (dec.). IR: 2176 $cm^{-1}$ (CN). $^1H$ NMR: 6.13 (s, 1H, H3); 5.33 (dd, $^3J = 5.2$, $^4J = 2.6$ Hz, 2H, H2′, H3′); 3.55 (m, 2H, H1′, H4′); 3.52 (d, $^2J = 2.4$ Hz, 2H, H1*E*, H5*E*); 1.96 (s, 6H, 2Me); 1.76 (d, $^2J = 9.8$ Hz, 2H, H5′a, H6′a); 1.69 (s, 9H, $^t$Bu); 1.54 (d, 2H, H5′s, H6′s); 1.13 (d, 2H, H1*Z*, H5*Z*). $^{13}C$ NMR: 147.4 (s, Ru*C*N); 111.0 (s); 98.6 (d, $J = 161$ Hz); 89.5 (d, $J = 174$ Hz); 66.9 (d, $J = 161$ Hz); 59.7 (s, RuCN*C*); 57.7 (t, $J = 159$ Hz); 30.5 (q, $J = 135$ Hz, $^t$Bu); 24.4 (q, $J = 128$ Hz); 22.9 (t, $J = 130$ Hz). Anal. Found: C, 48.32; H, 6.39; N, 3.14. $C_{18}H_{28}BF_4NRu$ calc.: C, 48.44; H, 6.32; N, 3.14%.

*(t-Butylisocyanide)(η² : η²-cycloocta-1,5-diene)(η⁵-2,4-dimethylpentadienyl)ruthenium tetrafluoroborate (8).* This was made as described for **6**, but from cycloocta-1,5-diene (0.67 ml, 5.5 mmol) and **2** (0.13 g, 0.27 mmol). Reaction in refluxing acetone (30 ml) for 8 h gave pale yellow crystals of **8** (0.12 g, 88%). M.p. 174°C (dec.). IR: 2169 $cm^{-1}$ (CN). $^1H$ NMR: 6.47 (s, 1H, H3); 3.71, 3.69 (2m, 4H, 4CH′); 2.56, 2.35 (2m, 4H, $CH_2'$); 2.45 (d, $^2J = 2.4$ Hz, 2H, H1*E*, H5*E*); 2.17 (d, $^2J = 9.3$ Hz, 2H, $CH_2'$); 2.04 (s, 8H, 2Me and $CH_2'$); 1.72 (s, 9H, $^t$Bu); 1.03 (d, 2H, H1*Z*, H5*Z*). $^{13}C$ NMR: 150.2 (s, Ru*C*N); 119.8 (s); 94.3 (d, $J = 167$ Hz); 92.9 (d, $J = 159$ Hz); 84.3 (d, $J = 160$ Hz); 59.8 (s, RuCN*C*); 54.1 (t, $J = 160$ Hz); 31.7 (t, $J = 127$ Hz); 30.7 (q, $J = 135$ Hz, $^t$Bu); 29.7 (t, $J = 130$ Hz); 24.6 (q, $J = 133$ Hz). Anal. Found: C, 50.89; H, 6.77; N, 3.12. $C_{20}H_{32}BF_4NRu$ calc.: C, 50.64; H, 6.80; N, 2.95%.

*(η⁴-Butadiene)(carbonyl)(η⁵-2,4-dimethylpentadienyl)ruthenium tetrafluoroborate (9).* Butadiene was bubbled through a solution of **3** (0.17 g, 0.42 mmol) in acetone (30 ml) at room temperature for 1 h. Work-up as for **5** gave colourless crystals of **9**

(0.13 g, 85%). M.p. 164°C (dec.). IR ($CH_2Cl_2$ solution): 2064 $cm^{-1}$ (CO). $^1H$ NMR (acetone-$d_6$): 6.77 (t, $^4J$ = 1.0 Hz, 1H, H3); 5.81 (m, $^3J$ = 13.0, 6.0, $^4J$ = 5.0, 2.0 Hz, 2H, H2', H3'); 3.87 (dd, $^2J$ = 2.7 Hz, 2H, H1*E*, H5*E*); 2.99 (m, $^2J$ = 2.0 Hz, 2H, H1'*E*, H4'*E*); 2.05 (s, 6H, 2Me); 2.01 (m, 2H, H1'*Z*, H4'*Z*); 1.92 (d, 2H, H1*Z*, H5*Z*). $^{13}C$ NMR (acetone-$d_6$): 205.7 (s, CO); 114.6 (s); 101.8 (d, $J$ = 170 Hz); 93.5 (d, $J$ = 176 Hz); 57.2, 49.5 (2t, $J$ = 164 Hz); 23.4 (q, $J$ = 130 Hz). Anal. Found: C, 39.50; H, 4.74. $C_{12}H_{17}BF_4ORu$ calc.: C, 39.47; H, 4.69%.

*Carbonyl($\eta^4$-2,3-dimethylbutadiene)($\eta^5$-2,4-dimethylpentadienyl)ruthenium tetrafluoroborate (**10**).* 2,3-Dimethylbutadiene (3.0 ml, 26 mmol) was added to a solution of **3** (0.11 g, 0.27 mmol) in acetone (20 ml) and the mixture was stirred at room temperature for 3 h. Work-up as for **5** gave colourless crystals of **10** (0.080 g, 75%). M.p. 187°C. IR ($CH_2Cl_2$ solution): 2064 $cm^{-1}$ (CO). $^1H$ NMR ($CD_2Cl_2$): 6.18 (t, $^4J$ = 1.0 Hz, 1H, H3); 3.73 (dd, $^2J$ = 3.1 Hz, 2H, H1*E*, H5*E*); 2.81 (d, $^2J$ = 2.3 Hz, 2H, H1'*E*, H4'*E*); 2.21, 2.01 (2s, 12H, 2Me and 2Me'); 1.54 (d, 2H, H1*Z*, H5*Z*); 1.43 (d, 2H, H1'*Z*, H4'*Z*). $^{13}C$ NMR ($CD_2Cl_2$): 204.0 (s, CO); 115.3, 106.2 (2s); 103.5 (d, $J$ = 171 Hz); 55.6, 49.2 (2t, $J$ = 160 Hz); 22.3, 19.6 (2q, $J$ = 128 Hz). Anal. Found: C, 42.85; H, 5.85. $C_{14}H_{21}BF_4ORu$ calc.: C, 42.77; H, 5.38%.

*Carbonyl($\eta^2$:$\eta^2$-cycloocta-1,5-diene)($\eta^5$-2,4-dimethylpentadienyl)ruthenium tetrafluoroborate (**12**).* This was made as described for **10**, but from cycloocta-1,5-diene (1.1 ml, 8.9 mmol) and **3** (0.18 g, 0.44 mmol). Reaction in acetone (20 ml) for 8 h at room temperature gave pale yellow crystals of **12** (0.13 g, 70%). M.p. 164°C (dec.). IR: 2031 $cm^{-1}$ (CO). $^1H$ NMR (acetone-$d_6$): 7.13 (t, $^4J$ = 1.5 Hz, 1H, H3); 4.43, 4.17 (2m, 4H, 4CH'); 2.90 (dd, $^2J$ = 3.9 Hz, 2H, H1*E*, H5*E*); 2.80, 2.55 (2m, 4H, $CH_2'$); 2.42, 2.29 (2d, $^2J$ = 8.3 Hz, 4H, $CH_2'$); 2.25 (s, 6H, 2Me); 1.67 (d, 2H, H1*Z*, H5*Z*). $^{13}C$ NMR (acetone-$d_6$): 209.7 (s, CO); 123.8 (s); 98.1 (d, $J$ = 161 Hz, 3C); 89.8 (d, $J$ = 160 Hz, 2C); 53.5 (t, $J$ = 162 Hz); 31.5, 30.0 (2t, $J$ = 127 Hz); 24.4 (q, $J$ = 129 Hz). Anal. Found: C, 45.99; H, 5.53. $C_{16}H_{23}BF_4ORu$ calc.: C, 45.84; H, 5.53%.

*($\eta^4$-Butadiene)($\eta^5$-2,4-dimethylpentadienyl)(trimethylphosphite)ruthenium tetrafluoroborate (**13**).* Butadiene was bubbled through a solution of **4** (0.18 g, 0.36 mmol) in acetone (30 ml) at reflux for 1 h. Work-up as for **5** gave colourless crystals of **13** (0.13 g, 79%). M.p. 182°C (dec.). $^1H$ NMR: 6.39 (d, $J$(PH) = 2.4 Hz, 1H, H3); 5.39 (m, $^3J$ = 9.0, 6.0, $^4J$ = 2.0 Hz, 2H, H2', H3'); 3.95 (d, $J$(PH) = 11.5 Hz, 9H, OMe); 3.47 (d, $^2J$ = 3.1 Hz, 2H, H1*E*, H5*E*); 2.40 (m, $^2J$ = 2.0 Hz, H1'*E*, H4'*E*); 1.93 (s, 6H, 2Me); 0.90 (dd, $J$(PH) = 6.8 Hz, 2H, H1*Z*, H5*Z*); 0.85 (ddd, 2H, H1'*Z*, H4'*Z*). $^{13}C$ NMR: 110.1 (s); 100.7, 91.1 (2d, $J$ = 168 Hz); 57.4, 45.7 (2t, $J$ = 161 Hz); 54.5 (q, $J$ = 148 Hz, OMe); 23.5 (q, $J$ = 130 Hz). Anal. Found: C, 36.12; H, 5.97; P, 6.62. $C_{14}H_{26}BF_4O_3PRu$ calc.: C, 36.46; H, 5.68; P, 6.72%.

*($\eta^4$-2,3-Dimethylbutadiene)($\eta^5$-2,4-dimethylpentadienyl)(trimethylphosphite)ruthenium tetrafluoroborate (**14**).* 2,3-Dimethylbutadiene (5.0 ml. 44 mmol) was added to a solution of **4** (0.33 g, 0.66 mmol) in acetone (30 ml) and the mixture was refluxed for 3 h. Work-up as for **5** gave colourless crystals of **14** (0.25 g, 78%). M.p. 193°C (dec.). $^1H$ NMR: 5.83 (d, $J$(PH) = 2.0 Hz, 1H, H3); 3.94 (d, $J$(PH) = 11.3 Hz, 9H, OMe); 3.53 (d, $^2J$ = 3.3 Hz, 2H, H1*E*, H5*E*); 2.46 (d, $^2J$ = 2.2 Hz, H1'*E*, H4'*E*); 2.05 (d, $J$(PH) = 0.8 Hz, 6H, 2Me); 1.91 (s, 6H, 2Me'); 0.84 (dd, $J$(PH) = 8.5 Hz, 2H, H1*Z*, H5*Z*); 0.66 (dd, $J$(PH) = 18.1 Hz, 2H, H1'*Z*, H4'*Z*). $^{13}C$ NMR: 110.8, 102.8 (2s); 102.4 (d, $J$ = 162 Hz); 56.1, 47.6 (2t, $J$ = 160 Hz); 54.9 (q, $J$ = 150 Hz, OMe); 22.6, 20.0 (2q, $J$ = 128 Hz). Anal. Found: C, 39.89; H, 6.44; P, 6.24. $C_{16}H_{30}BF_4O_3PRu$ calc.: C, 39.28; H, 6.18; P, 6.33%.

*($\eta^4$-Cyclohexa-1,3-diene)($\eta^5$-2,4-dimethylpentadienyl)(trimethylphosphite)ruthenium tetrafluoroborate (15).* This was made as described for **14**, but from cyclohexa-1,3-diene (0.80 ml, 8.4 mmol) and **4** (0.21 g, 0.42 mmol). Reaction in refluxing acetone (30 ml) for 3 h gave pale yellow crystals of **15** (0.14 g, 67%). Alternatively, cyclohexa-1,4-diene (0.06 ml, 0.64 mmol) and **4** (0.16 g, 0.32 mmol) in refluxing acetone (30 ml) for 6 h gave **15** (0.080 g, 53%). M.p. 151°C (dec.). $^1$H NMR: 6.33 (d, $J$(PH) = 2.9 Hz, 1H, H3); 5.30 (dd, $^3J$ = 5.0, $^4J$ = 2.0 Hz, 2H, H2′, H3′); 3.96 (d, $J$(PH) = 11.4 Hz, 9H, OMe); 3.65 (d, $^2J$ = 2.7 Hz, 2H, H1$E$, H5$E$); 3.48 (m, 2H, H1′, H4′); 2.02 (s, 6H, 2Me); 1.67 (dd, $^2J$ = 11.3, $^3J$ = 2.0 Hz, 2H, H5′s, H6′s); 1.35 (dd, $J$(PH) = 7.3 Hz, 2H, H5′a, H6′a); 0.60 (dd, $J$(PH) = 6.5 Hz, 2H, H1$Z$, H5$Z$). $^{13}$C NMR: 109.5 (s); 100.6 (dd, $J$ = 163, $J$(PC) = 7 Hz); 89.1 (d, $J$ = 173 Hz); 66.2 (d, $J$ = 160 Hz); 58.6 (td, $J$ = 152, $J$(PC) = 7 Hz); 54.0 (q, $J$ = 155 Hz, OMe); 24.3 (q, $J$ = 131 Hz); 22.5 (td, $J$ = 134, $J$(PC) = 11 Hz). Anal. Found: C, 39.66; H, 5.63; P, 6.29. $C_{16}H_{28}BF_4O_3PRu$ calc.: C, 39.44; H, 5.79; P, 6.36%.

*($\eta^2$ : $\eta^2$-Cycloocta-1,5-diene)($\eta^5$-2,4-dimethylpentadienyl)(trimethylphosphite) ruthenium tetrafluoroborate (16).* This was made as described for **14**, but from cycloocta-1,5-diene (1.3 ml, 11 mmol) and **4** (0.26 g, 0.52 mmol). Reaction in refluxing acetone (40 ml) for 6 h gave pale yellow crystals of **16** (0.20 g, 76%). M.p. 174°C (dec.). $^1$H NMR: 6.51 (d, $J$(PH) = 3.0 Hz, 1H, H3); 4.01 (d, $J$(PH) = 10.7 Hz, 9H, OMe); 3.63, 3.58 (2m, 4H, 4CH′); 2.47 (d, $^2J$ = 3.3 Hz, 2H, H1$E$, H5$E$); 2.40, 2.29 (2m, 4H, $CH_2'$); 2.04 (s, 6H, 2Me); 2.09–1.97 (m, 4H, $CH_2'$); 0.54 (dd, $J$(PH) = 4.4 Hz, 2H, H1$Z$, H5$Z$). $^{13}$C NMR: 119.6 (s); 95.2 (dd, $J$ = 168, $J$(PC) = 12 Hz); 92.9 (d, $J$ = 159 Hz); 83.7 (d, $J$ = 161 Hz); 55.6 (qd, $J$ = 158, $J$(PC) = 10 Hz, OMe); 53.8 (t, $J$ = 159 Hz); 31.6, 30.3 (2t, $J$ = 127 Hz); 24.8 (q, $J$ = 128 Hz). Anal. Found: C, 42.40; H, 6.40; P, 5.88. $C_{18}H_{32}BF_4O_3PRu$ calc.: C, 42.12; H, 6.26; P, 6.01%.

*(t-Butylisocyanide)($\eta^5$-cyclopentadienyl)($\eta^4$-2,4-dimethylpenta-1,3-diene)ruthenium tetrafluoroborate (17).* This was made as described for **6**, from freshly distilled cyclopentadiene (0.080 ml, 0.87 mmol) and **2** (0.27 g, 0.58 mmol). Reaction in refluxing acetone (30 ml) for 5 h, gave pale yellow crystals of **17** (0.19 g, 75%). M.p. 218°C (dec.). IR: 2162 cm$^{-1}$ (CN). $^1$H NMR: 5.68 (s, 1H, H3′); 5.26 (s, 5H, Cp); 3.36 (d, $^2J$ = 2.8 Hz, 1H, H1′$E$); 2.27, 1.81 (2s, 6H, 2Me′); 1.60 (s, 10H, $^t$Bu and H1′$Z$); 1.02 (s, 3H, Me′). $^{13}$C NMR: 147.8 (s, Ru$C$N); 103.1 (s); 87.7 (d, $J$ = 182 Hz, Cp); 86.4 (d, $J$ = 165 Hz); 83.3 (s); 60.1 (s, RuCN$C$); 45.9 (t, $J$ = 162 Hz); 34.2 (q, $J$ = 127 Hz); 31.2 (q, $J$ = 129 Hz, $^t$Bu); 26.9 (q, $J$ = 125 Hz); 22.8 (q, $J$ = 128 Hz). Anal. Found: C, 47.23; H, 6.09; N, 3.24. $C_{17}H_{26}BF_4NRu$ calc.: C, 47.24; H, 6.06; N, 3.24%.

*(t-Butylisocyanide)($\eta^4$-2,4-dimethylpenta-1,3-diene)($\eta^5$-pentamethylcyclopentadienyl)ruthenium tetrafluoroborate (18).* This was made as described for **6**, from 1,2,3,4,5-pentamethylcyclopentadiene (0.13 ml, 0.78 mmol) and **2** (0.24 g, 0.52 mmol). Reaction in refluxing acetone (30 ml) for 4 h, gave pale yellow crystals of **18** (0.21 g, 80%). M.p. 154°C (dec.). IR: 2151 cm$^{-1}$ (CN). $^1$H NMR: 4.69 (s, 1H, H3′); 2.54 (d, $^2J$ = 3.4 Hz, 1H, H1′$E$); 2.05 (s, 3H, Me′); 1.77 (s, 15H, $C_5Me_5$); 1.59 (s, 9H, $^t$Bu); 1.55 (s, 4H, Me′ and H1′$Z$); 0.96 (s, 3H, Me′). $^{13}$C NMR: 155.0 (s, Ru$C$N); 102.5 (s); 98.5 (s, $C_5Me_5$); 89.4 (d, $J$ = 159 Hz); 80.9 (s); 59.5 (s, RuCN$C$); 45.1 (t, $J$ = 161 Hz); 31.3 (q, $J$ = 129 Hz, $^t$Bu); 30.9, 23.3, 23.0 (3q, $J$ = 128 Hz); 10.2 (q, $J$ = 128 Hz, $C_5Me_5$). Anal. Found: C, 52.86; H, 7.24; N, 2.69. $C_{22}H_{36}BF_4NRu$ calc.: C, 52.60; H, 7.22; N, 2.79%.

*(t-Butylisocyanide)($\eta^5$-cyclohexadienyl)($\eta^4$-2,4-dimethylpenta-1,3-diene)ruthenium tetrafluoroborate (19).* This was made as described for **6**, from cyclohexa-1,4-diene (0.05 ml, 0.53 mmol) and **2** (0.17 g, 0.37 mmol). Reaction in refluxing acetone (40 ml) for 8 h gave yellow crystals of **19** (0.14 g, 85%). M.p. 142°C (dec.). IR: 2163 $cm^{-1}$ (CN). $^1H$ NMR: 6.04 (m, $^3J$ = 5.4, 5.2 Hz, 1H, H3); 5.36 (s, 1H, H3′); 5.36 (m, $^3J$ = 6.6, 5.2 Hz, 1H, H2 or H4); 4.66 (m, $^3J$ = 7.2, 5.4 Hz, 1H, H4 or H2); 4.06 (m, $^3J$ = 6.6, 5.7 Hz, 1H, H1 or H5); 3.75 (m, $^3J$ = 7.2, 5.7 Hz, 1H, H5 or H1); 2.73 (m, $^2J$ = 14.2, $^3J$ = 5.7, 5.7 Hz, 1H, H6s); 2.54 (d, $^2J$ = 2.4 Hz, 1H, H1′*E*); 2.38 (d, $^2J$ = 14.2 Hz, 1H, H6a); 2.11 (s, 3H, Me′); 1.76 (s, 9H, $^t$Bu); 1.68 (d. 1H, H1′*Z*); 1.34, 1.13 (2s, 6H, 2Me′). $^{13}C$ NMR: 152.9 (s, Ru*C*N); 103.3 (s); 99.3, 96.4 (2d, $J$ = 171 Hz); 92.6 (d, $J$ = 175 Hz); 89.3 (d, $J$ = 164 Hz); 81.1 (s); 59.7 (s, RuCN*C*); 55.8 (d, $J$ = 167 Hz); 54.9 (d, $J$ = 170 Hz); 45.8 (t, $J$ = 161 Hz); 30.9 (q, $J$ = 127 Hz, $^t$Bu); 30.3 (q, $J$ = 129 Hz); 28.4 (t, $J$ = 136 Hz); 24.0, 22.2 (2q, $J$ = 128 Hz). Anal. Found: C, 48.51; H, 6.66; N, 3.30. $C_{18}H_{28}BF_4NRu$ calc.: C, 48.44; H, 6.32; N, 3.14%.

*Carbonyl($\eta^5$-cyclohexadienyl)($\eta^4$-2,4-dimethylpenta-1,3-diene)ruthenium tetrafluoroborate (20).* This was made as described for **10**, from cyclohexa-1,4-diene (0.060 ml, 0.64 mmol) and **3** (0.14 g, 0.34 mmol). Reaction in acetone (20 ml) at room temperature for 60 h gave colourless crystals of **20** (0.10 g, 78%). M.p. 133°C (dec.). IR: 2037 $cm^{-1}$ (CO). $^1H$ NMR (acetone-$d_6$): 6.57 (m, $^3J$ = 5.4, 5.2 Hz, 1H, H3); 5.81 (s, 1H, H3′); 5.70 (m, $^3J$ = 6.8, 5.4 Hz, 1H, H2 or H4); 5.26 (m, $^3J$ = 6.8, 5.2 Hz, 1H, H4 or H2); 4.61 (m, $^3J$ = 6.8, 5.9 Hz, 1H, H5 or H1); 4.47 (m, $^3J$ = 6.8, 5.9 Hz, 1H, H1 or H5); 3.05 (m, $^2J$ = 14.6, $^3J$ = 5.9, 5.9 Hz, 1H, H6s); 3.00 (d, $^2J$ = 2.8 Hz, 1H, H1′*E*); 2.51 (d, $^2J$ = 14.6 Hz, 1H, H6a); 2.32 (s, 4H, Me′ and H1′*Z*); 1.57, 1.44 (2s, 6H, 2Me′). $^{13}C$ NMR (acetone-$d_6$): 209.9 (s, CO); 107.5 (s); 102.0, 99.4 (2d, $J$ = 173 Hz); 96.9 (d, $J$ = 178 Hz); 92.0 (s); 91.0 (d, $J$ = 168 Hz); 59.7 (d, $J$ = 155 Hz); 58.0 (d, $J$ = 170 Hz); 47.9 (t, $J$ = 159 Hz); 30.6 (q, $J$ = 128 Hz); 28.8 (t, $J$ = 140 Hz); 24.3, 23.0 (2q, $J$ = 128 Hz). Anal. Found: C, 42.61; H, 4.91. $C_{14}H_{19}BF_4ORu$ calc.: C, 42.99; H, 4.90%.

*(t-Butylisocyanide)($\eta^5$-cycloocta-2,4-dien-1-yl)($\eta^4$-2,4-dimethylpenta-1,3-diene) ruthenium tetrafluoroborate (21).* This was made as described for **6**, from cycloocta-1,3-diene (0.80 ml, 6.5 mmol) and **2** (0.14 g, 0.30 mmol). Reaction in refluxing acetone (30 ml) for 10 h gave pale yellow crystals of **21** (0.10 g, 68%). M.p. 168°C (dec.). IR: 2165 $cm^{-1}$ (CN). $^1H$ NMR: 6.33 (dd, $^3J$ = 7.1, 7.1 Hz, 1H, H3); 5.20 (s, 1H, H3′); 4.88 (dd, $^3J$ = 9.3, 7.1 Hz, 1H, H2); 4.35 (m, 1H, H5); 4.04 (dd, $^3J$ = 9.3, 7.1 Hz, 1H, H4); 3.72 (m, 1H, H1); 2.39 (d, $^2J$ = 2.5 Hz, 1H, H1′*E*) 2.31 (m, 2H, H6*E*, H8*E*); 2.06 (s, 4H, Me′ and H1′*Z*); 1.87 (m, 2H, H6*Z*, H8*Z*); 1.74 (s, 9H, $^t$Bu); 1.32 (s, 3H, Me′); 1.26 (m, 1H, H7a); 1.16 (s, 3H, Me′); 0.21 (qt, $^2J$ = 14.6, $^3J$ = 14.0, 14.0, 3.0, 3.0 Hz, 1H, H7s). $^{13}C$ NMR: 153.7 (s, Ru*C*N); 111.1 (d, $J$ = 166 Hz); 107.7 (s); 93.2, 91.8, 90.4 (3d, $J$ = 166 Hz); 84.4 (s); 68.1, 64.7 (2d, $J$ = 154 Hz); 59.2 (s, RuCN*C*); 50.7 (t, $J$ = 159 Hz); 31.2 (q, $J$ = 128 Hz, $^t$Bu); 31.0, 28.2 (2q, $J$ = 128 Hz); 28.8 (t, $J$ = 123 Hz); 28.3 (t, $J$ = 127 Hz); 22.4 (q, $J$ = 128 Hz); 18.6 (t, $J$ = 130 Hz). Anal. Found: C, 50.45; H, 6.68; N, 3.05. $C_{20}H_{32}BF_4NRu$ calc.: C, 50.64; H, 6.80; N, 2.95%.

*Carbonyl($\eta^5$-cycloocta-2,4-dien-1-yl)($\eta^4$-2,4-dimethylpenta-1,3-diene)ruthenium tetrafluoroborate (22).* A solution of cycloocta-1,3-diene (0.070 ml, 0.56 mmol) and **3** (0.18 g, 0.44 mmol) in acetone (30 ml) was stirred at room temperature for 4 d. Solvent evaporation and recrystallisation of the residue from $EtOH/Et_2O$ gave

yellow crystals of **22** (0.13 g, 70%). M.p. 143°C (dec.). IR: 2035 $cm^{-1}$ (CO). $^1H$ NMR (acetone-$d_6$): 6.77 (dd, $^3J$ = 7.3, 7.1 Hz, 1H, H3); 5.57 (s, 1H, H3'); 5.20 (dd, $^3J$ = 9.5, 7.1 Hz, 1H, H2); 4.81 (m, 1H, H5); 4.62 (dd, $^3J$ = 9.5, 7.3 Hz, 1H, H4); 4.26 (m, 1H, H1); 2.97 (d, $^2J$ = 2.5 Hz, 1H, H1'*E*); 2.70 (d, 1H, H1'*Z*); 2.42 (m, 2H, H6*E*, H8*E*); 2.23 (s, 3H, Me'); 2.12 (m, 2H, H6*Z*, H8*Z*); 1.56 (s, 3H, Me'); 1.47 (s, 3H, Me'); 1.39 (m, 1H, H7a); 0.33 (qt, $^2J$ = 14.0, $^3J$ = 14.0, 14.0, 2.9, 2.9 Hz, 1H, H7s). $^{13}C$ NMR ($CD_2Cl_2$): 207.7 (s, CO); 112.3 (d, $J$ = 166 Hz); 110.3, 96.3 (2s); 93.3 (d, $J$ = 168 Hz); 93.2 (d, $J$ = 160 Hz); 91.5 (d, $J$ = 172 Hz); 71.7, 67.7 (2d, $J$ = 154 Hz); 50.8 (t, $J$ = 164 Hz); 28.2 (q, $J$ = 128 Hz); 28.1 (t, $J$ = 135 Hz); 27.8 (t, $J$ = 128 Hz); 22.7 22.1 (2q, $J$ = 128 Hz); 17.8 (t, $J$ = 129 Hz). Anal. Found: C, 45.67; H, 5.61. $C_{16}H_{23}BF_4ORu$ calc.: C, 45.84; H, 5.53%.

*($\eta^5$-Cycloocta-2,4-dien-1-yl)($\eta^4$-2,4-dimethylpenta-1,3-diene)(trimethylphosphite) ruthenium tetrafluoroborate (23).* This was made as described for **14**, from cycloocta-1,3-diene (0.070 ml, 0.56 mmol) and **4** (0.15 g, 0.30 mmol). Reaction in refluxing acetone (30 ml) for 7 h gave colourless crystals of **23** (0.11 g, 74%). M.p. 116°C (dec.). $^1H$ NMR: 6.28 (m, $^3J$ = 6.9, 6.9, $J$(PH) = 2.8 Hz, 1H, H3); 5.06 (s, 1H, H3'); 4.81 (dd, $^3J$ = 9.3, 6.9 Hz, 1H, H2); 4.24 (m, 1H, H5); 4.03 (d, $J$(PH) = 10.9 Hz, 9H, OMe); 3.85 (dd, $^3J$ = 9.3, 6.9 Hz, 1H, H4); 3.75 (m, 1H, H1); 2.51 (d, $^2J$ = 2.5 Hz, H1'*E*); 2.06 (s, 3H, Me'); 2.02 (m, 2H, H6*E*, H8*E*); 1.87 (d, 1H, H1'*Z*); 1.85 (m, 2H, H6*Z*, H8*Z*); 1.21 (s, 3H, Me'); 1.18 (m, 1H, H7a); 0.92 (d, $J$(PH) = 2.5 Hz, 3H, Me'); 0.19 (qt, $^2J$ = 14.5, $^3J$ = 14.0, 14.0, 3.0, 3.0 Hz, 1H, H7s). $^{13}C$ NMR: 110.9 (dd, $J$ = 175, $J$(PC) = 12 Hz); 108.0 (s); 91.4 90.7, 89.5 (3d, $J$ = 165 Hz); 84.1 (s); 68.8 (dd, $J$ = 152, $J$(PC) = 5 Hz); 63.7 (d, $J$ = 146 Hz); 55.0 (q, $J$ = 137 Hz, OMe); 51.0 (td, $J$ = 154, $J$(PC) = 5 Hz); 27.5 (q, $J$ = 133 Hz); 26.7 (t, $J$ = 133 Hz); 25.8 (t, $J$ = 130 Hz); 22.4, 21.4 (2q, $J$ = 127 Hz); 18.4 (t, $J$ = 128 Hz). Anal. Found: C, 41.98; H, 6.15; P, 6.18. $C_{18}H_{32}BF_4O_3PRu$ calc.: C, 41.96, H, 6.26; P, 6.01%.

*(t-Butylisocyanide)($\eta^4$-cyclohexa-1,3-diene)($\eta^5$-cyclohexadienyl)ruthenium tetrafluoroborate (24).* This was made as described for **6**, from cyclohexa-1,4-diene (0.73 ml, 7.8 mmol) and **2** (0.18 g, 0.39 mmol). Reaction in refluxing acetone (40 ml) for 12 h gave pale yellow crystals of **24** (0.12 g, 72%). Alternatively, cyclohexa-1,3-diene (0.30 ml, 3.2 mmol) and **19** (0.070 g, 0.16 mmol) in refluxing acetone (30 ml) for 6 h, gave **24** (0.050 g, 74%). M.p. 176°C (dec.). IR: 2170 $cm^{-1}$ (CN). $^1H$ NMR: 6.34 (t, $^3J$ = 5.4 Hz, 1H, H3); 5.43 (dd, $^3J$ = 5.3, $^4J$ = 2.6 Hz, 2H, H2', H3'); 5.24 (dd, $^3J$ = 7.0, 5.4 Hz, 2H, H2, H4); 4.19 (dd, $^3J$ = 7.0, 5.9 Hz, 2H, H1, H5); 3.74 (m, 2H, H1', H4'); 2.81 (dt, $^2J$ = 14.2, $^3J$ = 5.9 Hz, 1H, H6s); 2.60 (d, 1H, H6a); 1.80 (s, 9H, $^t$Bu); 1.78 (m, $^2J$ = 11.8 Hz, 2H, H5'a, H6'a); 1.50 (m, 2H, H5's, H6's). $^{13}C$ NMR: 151.4 (s, Ru*C*N); 94.6, 88.5, 81.1 (3d, $J$ = 174 Hz); 66.5 (d, $J$ = 162 Hz); 59.8 (d, $J$ = 168 Hz); 59.7 (s, RuCN*C*); 30.6 (q, $J$ = 127 Hz, $^t$Bu); 28.7 (t, $J$ = 135 Hz); 22.9 (t, $J$ = 130 Hz). Anal. Found: C, 47.78; H, 5.60; N, 3.15. $C_{17}H_{24}BF_4NRu$ calc.: C, 47.46; H, 5.62; N, 3.25%.

*Carbonyl($\eta^4$-cyclohexa-1,3-diene)($\eta^5$-cyclohexadienyl)ruthenium tetrafluoroborate (25).* A solution of cyclohexa-1,3-diene (1.2 ml, 12.6 mmol) and **20** (0.060 g, 0.15 mmol) in acetone (10 ml) was stirred at room temperature for 6 h. Solvent evaporation and recrystallisation of the residue from EtOH/$Et_2O$ gave pale orange crystals of **25** (0.050 g, 87%). A similar procedure but with cyclohexa-1,4-diene and reaction for 12 h at room temperature also gave **25** (73%). Characterisation details for **25** are in accord with those we have reported previously [13b].

*(t-Butylisocyanide)($\eta^2$:$\eta^2$-cycloocta-1,5-diene)($\eta^5$-cycloocta-2,4-dien-1-yl)ruthenium tetrafluoroborate (26).* A solution of cycloocta-1,5-diene (0.70 ml, 5.7 mmol) and **21** (0.26 g, 0.55 mmol) was refluxed in acetone (40 ml) for 7 h. Work-up as for **5** gave pale yellow crystals of **26** (0.20 g, 75%). M.p. 174°C (dec.). IR: 2161 $cm^{-1}$ (CN). $^1H$ NMR: 7.20 (t, $^3J = 7.1$ Hz, 1H, H3); 4.83 (dd, $^3J = 9.0$, 7.1 Hz, 2H, H2, H4); 4.21 (m, 2H, 2CH'); 3.61 (m, 2H, 2CH'), 3.23 (m, 2H, H1, H5); 2.53, 2.44 (2m, 4H, $CH_2'$); 2.17, 2.11 (2d, $^2J = 9.2$ Hz, 4H, $CH_2'$); 2.14 (m, 2H, H6*E*, H8*E*); 1.77 (s, 9H, $^t$Bu); 1.61 (m, 2H, H6*Z*, H8*Z*); 1.22 (m, 1H, H7a); 0.21 (qt, $^2J = 14.1$, $^3J = 14.1$, 3.0 Hz, 1H, H7s). $^{13}C$ NMR: 155.1 (s, Ru*C*N); 105.2 (d, $J = 168$ Hz); 98.7 (d, $J = 164$ Hz); 96.2, 87.8 (2d, $J = 159$ Hz); 64.5 (d, $J = 149$ Hz); 59.9 (s, RuCN*C*); 33.0 (t, $J = 127$ Hz); 31.4 (q, $J = 129$ Hz); 30.1, 27.7 (2t, $J = 130$ Hz); 19.1 (t, $J = 127$ Hz). Anal. Found: C, 52.03; H, 6.71; N, 3.08. $C_{21}H_{32}BF_4NRu$ calc.: C, 51.86; H, 6.63; N, 2.88%.

**Acknowledgements**

We thank the Swiss National Science Foundation for financial support and Johnson Matthey plc for a loan of $RuCl_3 \cdot nH_2O$.

**References**

1 For example: (a) J.R. Bleeke and A.J. Donaldson, Organometallics, 5 (1986) 2401; (b) G.H. Lee, S.M. Peng, S.F. Lush, M.Y. Liao and R.S. Liu, Organometallics, 6 (1987) 2094; (c) J.R. Bleeke and A.J. Donaldson, Organometallics, 7 (1988) 1588; (d) J.R. Bleeke, M.K. Hays and R.J. Wittenbrink, Organometallics, 7 (1988) 1417; (e) J.R. Hinchliffe and M.W. Whiteley, J. Organomet. Chem., 402 (1991) C50.
2 (a) R.D. Ernst, Acc. Chem. Res., 18 (1985) 56; (b) R.D. Ernst, Chem. Rev., 88 (1988) 1255.
3 D.N. Cox and R. Roulet, J. Chem. Soc., Chem. Commun., (1988) 951.
4 R. Gleiter, I. Hyla-Kryspin, M.L. Ziegler, G. Sergeson, J.C. Green, L. Stahl and R.D. Ernst, Organometallics, 8 (1989) 298.
5 D.N. Cox and R. Roulet, J. Chem. Soc., Chem. Commun., (1989) 175.
6 G. Michael, J. Kaub and C.G. Kreiter, Angew. Chem., Int. Ed. Engl., 24 (1985) 502.
7 J.R. Bleeke, J.J. Kotyk, D.A. Moore and D.J. Rauscher, J. Am. Chem. Soc., 109 (1987) 417.
8 T. Lumini, D.N. Cox, R. Roulet, G. Chapuis and F. Nicolo, Helv. Chim. Acta, 73 (1990) 1931.
9 T.D. Newbound, L. Stahl, M.L. Ziegler and R.D. Ernst, Organometallics, 9 (1990) 2962.
10 T. Lumini, D.N. Cox, R. Roulet and K. Schenk, J. Organomet. Chem., 434 (1992) 363.
11 D.N. Cox, R.W.H. Small and R. Roulet, J. Chem. Soc., Dalton Trans., (1991) 2013.
12 (a) B.F.G. Johnson, J. Lewis, T.W. Matheson, I.E. Ryder and M.V. Twigg, J. Chem. Soc., Chem. Commun., (1974) 269; (b) J. Ashley-Smith, D.V. Howe, B.F.G. Johnson, J. Lewis and I.E. Ryder, J. Organomet. Chem., 82 (1974) 257; (c) E.K.G. Schmidt and C.H. Theil, J. Organomet. Chem., 220 (1981) 87; (d) M.J. Hynes, M.F.T. Mahon and P. McArdle, J. Organomet. Chem., 320 (1987) C44.
13 (a) M. Crocker, M. Green, C.E. Morton, K.R. Nagle and A.G. Orpen, J. Chem. Soc., Dalton Trans., (1985) 2145; (b) D.N. Cox and R. Roulet, Organometallics, 5 (1986) 1886.
14 M.O. Albers, D.J. Robinson, A. Shaver and E. Singleton, Organometallics, 5 (1986) 2199.
15 P.J. Fagan, W.S. Mahoney, J.C. Calabrese and I.D. Williams, Organometallics, 9 (1990) 1843.
16 A.J. Domingos, B.F.G. Johnson and J. Lewis, J. Chem. Soc., Dalton Trans., (1975) 2288.
17 D. Bingham, B. Hudson, D.E. Webster and P.B. Wells, J. Chem. Soc., Dalton Trans., (1974) 1521.
18 T.V. Ashworth, A.A. Chalmers, D.C. Liles, E. Meintjies and E. Singleton, Organometallics, 6 (1987) 1543.