Addition of Cyclopropenylium and Tropylium Ions to Cyclooctatetraene-cobalt and -rhodium Cyclopentadienyl Complexes*

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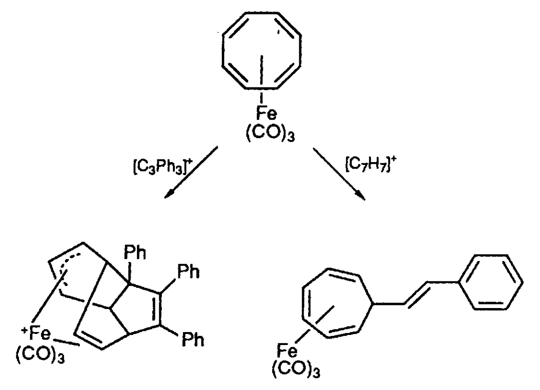
Cyclopropenylium ions $[C_3R'_3]^+$ (R' = Ph or Bu^t) react with $[Co(\eta^4\text{-cot})(\eta\text{-}C_5R_5)]$ (R = H or Me, cot = cyclooctatetraene) to give $[M\{\eta^5\text{-}C_8H_8(C_3R'_3)\}(\eta\text{-}C_5R_5)]^+$ **3** (M = Co; R = H, R' = Ph; R = Me, R' = Ph or Bu^t); X-ray structural studies on **3** (M = Co, R = H, R' = Ph) show an *exo*-cyclopropene substituent on the cyclooctatrienyl ring. The reaction of $[C_3Ph_3]^+$ with $[Rh(\eta^4\text{-cot})(\eta\text{-}C_5Me_5)]$ gives a similar product **3** (M = Rh, R = Me, R' = Ph) which rearranges to an unknown isomer **5** whereas $[Rh(\eta^4\text{-cot})(\eta\text{-}C_5H_5)]$ undergoes electrophilic substitution at the cyclopentadienyl ring to give $[Rh(\eta^2,\eta^3\text{-}C_8H_9)\{\eta\text{-}C_5H_4(C_3Ph_3)\}]^+$ **4**. The addition of $[C_7H_7]^+$ to $[Co(\eta^4\text{-cot})(\eta\text{-}C_5R_5)]$ (R = H or Me) gives $[Co\{\eta^5\text{-}C_8H_8(C_7H_7)\}(\eta\text{-}C_5R_5)]^+$ **6** (R = H or Me) which, in the case of **6** (R = Me), rearranges to the 1,2,3,3*a*-tetrahydropentalenyl complex $[Co\{\eta^5\text{-}C_8H_8(C_7H_7)\}(\eta\text{-}C_5Me_5)]^+$ **7**. Finally, the reactions between $[Rh(\eta^4\text{-cot})(\eta\text{-}C_5R_5)]$ (R = H or Me) and $[C_7H_7]^+$ give $[Rh(\eta^2,\eta^3\text{-}C_8H_9)\{\eta\text{-}C_5H_4(C_7H_7)\}]^+$ **8** and $[Rh\{\eta^2,\eta^3\text{-}C_8H_8(C_7H_7)\}(\eta\text{-}C_5Me_5)]^+$ **9** respectively.

The addition of carbon-based nucleophiles to co-ordinated hydrocarbons provides a useful route to the stereo- and regiospecific formation of new carbon–carbon bonds.[1] A quantitative understanding of the underlying principles governing the site of nucleophilic attack has been provided by molecular-orbital calculations[2] but in many cases that site may be predicted qualitatively by the Davies–Green–Mingos rules.[3] In principle, therefore, directed organic syntheses may readily be devised. Electrophilic addition to co-ordinated hydrocarbons[4] potentially provides a second general route to C–C bond formation but systematic studies are somewhat hampered both by the relative lack of suitable carbon-based electrophiles and by the absence of any predictive rules for site preference. Simply on the basis of charge effects, it might be predicted that the preferred site of electrophilic attack would be the opposite to that for nucleophilic attack. However, while charge control is likely in electrophilic addition for hard electrophiles (*e.g.* H^+) frontier orbital control [involving the highest occupied molecular orbital (HOMO) on the substrate and the lowest unoccupied molecular orbital (LUMO) on the electrophile] is more likely for soft electrophiles such as aromatic carbocations. The situation is therefore likely to be analogous (with roles reversed of course) to that in frontier orbital controlled nucleophilic reactions (where the initial interaction is likely to involve the LUMO on the substrate and the HOMO on the nucleophile).

The reactions of $[M(CO)_3(\eta^4\text{-cot})]$ (cot = cyclooctatetraene) with electrophiles provide good examples of the complexity of the problem. For example, in the case of iron,[5] protonation gives the cyclooctatrienyl cation $[Fe(CO)_3(\eta^5\text{-}C_8H_9)]^+$ which is converted into the bicyclo[5.1.0]octadienyl isomer whereas the ruthenium analogue gives[6] a third species, namely $[Ru(CO)_3(\eta^2,\eta^3\text{-}C_8H_9)]^+$. With carbocations the situation is even more complex. Thus, $[CPh_3]^+$ and $[Fe(CO)_3(\eta^4\text{-cot})]$ give[7] the simple adduct $[Fe(CO)_3\{\eta^5\text{-}C_8H_8(CPh_3)\}]^+$ but Friedel–Crafts acetylation yields[8] the bicyclo[3.2.1]octadienyl complex $[Fe(CO)_3\{\eta^2,\eta^3\text{-}C_8H_8(COMe)\}]^+$, and $[C_3Ph_3]^+$ and $[C_7H_7]^+$ gave **1**[9] and **2**[10] (Scheme 1) respectively, the products of complex rearrangement reactions following initial electrophilic addition.



Scheme 1

In order to clarify the chemistry of electrophilic addition to co-ordinated hydrocarbons in general, and to $[M(CO)_3(\eta^4\text{-cot})]$ in particular, we have studied the reactions of $[M(\eta^4\text{-cot})(\eta\text{-}C_5R_5)]$ (M = Co or Rh, R = H or Me) with $[C_3Ph_3]^+$ and $[C_7H_7]^+$. These studies shed further light on the dependence of the product on both the metal and the substituent R, and on the rearrangement of co-ordinated carbocations including that of the cyclooctatrienyl group to the 1,2,3,3*a*-tetrahydropentalenyl ligand.

Results and Discussion

The Reactions of $[C_3R'_3]^+$ (R' = Ph *or* Bu^t) *with* $[M(\eta^4\text{-cot})(\eta\text{-}C_5R_5)]$ (M = Co *or* Rh, R = H *or* Me).—The addition of 1 equivalent of $[C_3Ph_3][BF_4]$ to $[Co(\eta^4\text{-cot})(\eta\text{-}C_5H_5)]$ or $[Co(\eta^4\text{-cot})(\eta\text{-}C_5Me_5)]$ in CH_2Cl_2 rapidly gave orange solutions from which air-stable orange powders were isolated and characterised by elemental analysis (Table 1) and ^1H and ^{13}C NMR spectroscopy (Table 2). The 270 MHz ^1H NMR spectra of the two products are very similar and show that electrophilic attack has occurred at co-ordinated cot to give the monocyclic cations $[M\{\eta^5\text{-}C_8H_8(C_3R'_3)\}(\eta\text{-}C_5R_5)]^+$ **3** (M = Co, R = H

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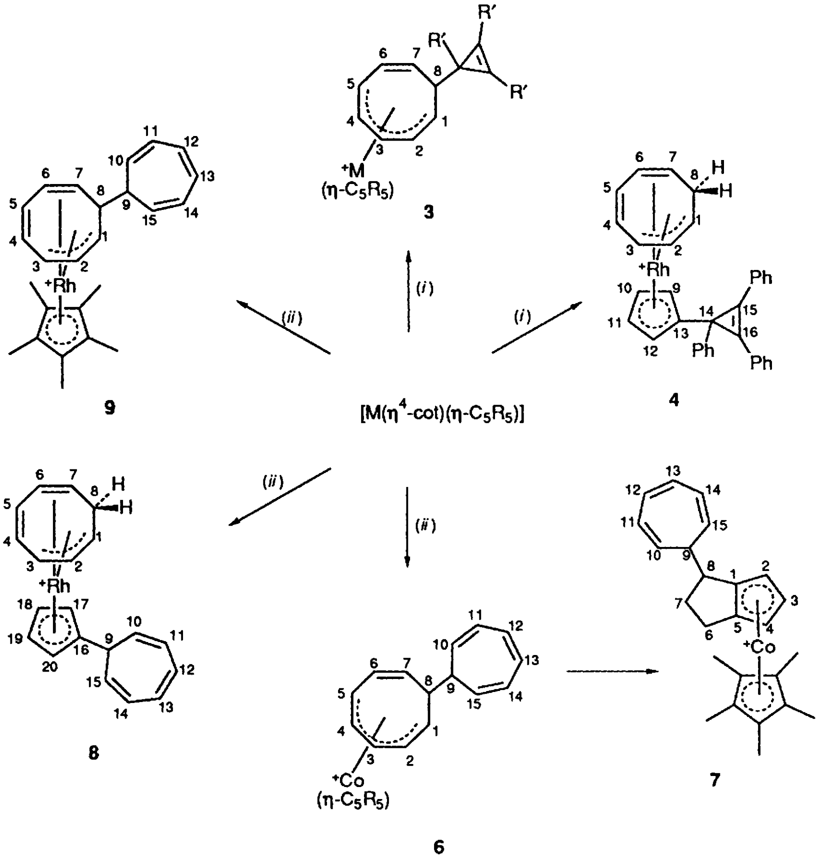
* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.



Scheme 2 (*i*) $[C_3R'_3]^+$, (*ii*) $[C_7H_7]^+$

Table 1 Analytical data for cobalt and rhodium complexes

Complex	Yield (%)	Colour	Analysis (%)[a] C	Analysis (%)[a] H
$[Co\{\eta^5\text{-}C_8H_8(C_3Ph_3)\}(\eta\text{-}C_5H_5)][BF_4]$ **3** (M = Co, R = H, R′ = Ph)	74	Orange	70.3 (70.1)	5.1 (4.9)
$[Co\{\eta^5\text{-}C_8H_8(C_3Ph_3)\}(\eta\text{-}C_5Me_5)][BF_4]$ **3** (M = Co, R = Me, R′ = Ph)	81	Orange	71.6 (71.8)	6.0 (5.9)
$[Rh(\eta^2,\eta^3\text{-}C_8H_9)\{\eta\text{-}C_5H_4(C_3Ph_3)\}][BF_4]$ **4**	69	Yellow	64.9 (65.2)	4.5 (4.5)
$[Co\{\eta^5\text{-}C_8H_8(C_7H_7)\}(\eta\text{-}C_5H_5)][PF_6]$ **6** (R = H)	53	Orange	51.1 (51.7)	4.4 (4.3)
$[Co\{\eta^5\text{-}C_8H_8(C_7H_7)\}(\eta\text{-}C_5Me_5)][PF_6]$ **7**	68	Dark orange	55.7 (56.2)	5.8 (5.7)
$[Rh(\eta^2,\eta^3\text{-}C_8H_9)\{\eta\text{-}C_5H_4(C_7H_7)\}][BPh_4]$ **8**[b]	62	Yellow	76.9 (76.8)	6.2 (6.3)
$[Rh\{\eta^2,\eta^3\text{-}C_8H_8(C_7H_7)\}(\eta\text{-}C_5Me_5)][PF_6]$ **9**[c]	77	Yellow	49.3 (49.3)	5.4 (5.0)

[a] Calculated values in parentheses. [b] Calculated for a 0.5 OEt_2 solvate (confirmed by ^1H NMR spectroscopy). [c] Calculated for a 0.5 CH_2Cl_2 solvate.

or Me, R′ = Ph) (Scheme 2). All of the eight signals observed for the protons of the C_8 ring are shifted to higher field when C_5H_5 is replaced by C_5Me_5. However, the shifts for protons H^1–H^5 (0.6–1.2 ppm) are much greater than those for protons H^6–H^8 (*ca.* 0.0–0.2 ppm) suggesting that the C_8 ring is η^5-bound to cobalt *via* C^1–C^5 rather than in the alternative η^2,η^3 mode (*i.e.* by C^1–C^3, C^6 and C^7). In order to confirm this suggestion, and to determine the conformation of the cobalt-bound C_8 ring and the stereochemistry at C^8 (*i.e. exo* or *endo* addition of the C_3 ring) an X-ray diffraction analysis of **3** (M = Co, R = H, R′ = Ph) was carried out.

The molecular structure of the cation **3** (M = Co; R = H, R′ = Ph) was determined by a room-temperature single-crystal structure analysis of its $[BF_4]^-$ salt, and is illustrated in Fig. 1. [Note that the X-ray atom numbering scheme differs from that used in the discussion of the NMR spectra (Scheme 2).] Selected bond lengths and angles are given in Table 3. The cation **3** (M = Co, R = H, R′ = Ph) consists of a cobalt atom carrying an η-C_5H_5 ligand and an η^5-C_8H_8X ligand where X is the *cyclo*-C_3Ph_3 substituent linked to C(34) and *exo* to the cobalt atom. The C_8 ring, a substituted cyclooctatrienyl, adopts a folded and slightly twisted conformation and is co-ordinated to Co(1) through carbon atoms C(29–33). The C_8 ligand geometry is therefore broadly similar to that observed[11] for $[Ru(\eta^5\text{-}C_8H_9)(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)]^+$. The C–C bond lengths of the η^5-dienyl unit [C(29–33)] of **3** [1.377(5)–1.439(5) Å] are as expected.[12] The C(27)–C(34) and C(33)–C(34) bond lengths [1.483(4) and 1.512(4) Å respectively] are comparable with the C–C single bond length of 1.478 Å in unco-ordinated cot,[13] but C(27)–C(28) [1.303(5) Å] is shorter than expected for a free double bond.[12] The fold angle, measured as the angle between the mean planes C(29–33) and C(27–29, 33, 34) is 126.5°. The C_8-ring angles in general show large deviations from ideal values. The angle C(27)–C(34)–C(33), at the sp^3 carbon, is 118.2(3)° and the other C_8-ring angles have a mean value of 127°, which is larger than expected for sp^2 carbon atoms. The C_8 ring bond angles are similar to those of $[Ru(\eta^5\text{-}C_8H_9)(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)]^+$ but are markedly greater than those of the isomer $[Ru(\eta^2,\eta^3-C_8H_9)(\eta-C_6H_3Me_3-1,3,5)]^+$.[11] The structural differences between the C_8 rings of the two arene-ruthenium isomers were taken to show that the isomerisation of the η^5-cyclooctatrienyl ligand to the η^2,η^3-octatrienyl cation might be driven by the relief of ring strain. It is interesting to note, however, that the angles within the C_8 ring of $[Ru(CO)_2(PPh_3)\{\eta^2,\eta^3-C_8H_8[CH_2C(Me)=CH_2]\}]^+$[14] are similar to those of the two structurally characterised η^5-cyclooctatrienyl rings.

The observation of the η^5-cyclooctatrienyl ring in **3** (M = Co, R = H, R′ = Ph) provides supporting evidence for the first step in the mechanism proposed[9] for the formation of **1**

Table 2 Proton and ^{13}C NMR spectroscopic data for cobalt and rhodium complexes[a]

Compound	^1H	^{13}C
$[Co\{\eta^5-C_8H_8(C_3Ph_3)\}(\eta-C_5H_5)][BF_4]$ **3** (M = Co, R = H, R′ = Ph)	4.64 (1 H, m, H^8), 5.16 [1 H, dd, $J(H^1H^8)$ 17, $J(H^1H^2)$ 10, H^1], 5.30 [1 H, dd, $J(H^5H^4)$ 9, $J(H^5H^6)$ 17, H^5], 5.39 [1 H, dd, $J(H^2H^3)$ 8, $J(H^2H^1)$ 10, H^2], 5.51 (1 H, m, H^6), 5.57 [1 H, dd, $J(H^4H^3)$ 8, $J(H^4H^5)$ 17, H^4], 5.84 (5 H, s, C_5H_5), 6.01 [1 H, dd, $J(H^7H^6)$ 11, $J(H^7H^8)$ 3, H^7], 6.89 [1 H, t, $J(H^3H^2 = J(H^3H^4)$ 8, H^3], 7.2–7.6 (15 H, m, C_3Ph_3)	37.0 (C^8), 45.5 (C^7), 67.3 (C^1), 68.9 (C^5), 88.0 (C^4), 89.6 (C_5H_5), 93.2 (C^2), 108.2 (C^3), 115.5 ($\mathit{C}_3\mathrm{Ph}_3$), 121.3 ($C^6$), 127.1–145.3 ($\mathrm{C}_3\mathit{Ph}_3$)
$[Co\{\eta^5-C_8H_8(C_3Ph_3)\}(\eta-C_5Me_5)][BF_4]$ **3** (M = Co, R = Me, R′ = Ph)	1.85 (15 H, s, C_5Me_5), 3.97 [1 H, dd, $J(H^1H^8)$ 6, $J(H^1H^2)$ 10, H^1], 4.38 [1 H, dd, $J(H^5H^6)$ 6, $J(H^5H^4)$ 10, H^5], 4.48 (1 H, m, H^8), 4.61 [1 H, dd, $J(H^2H^1)$ 10, $J(H^2H^3)$ 7, H^2], 5.00 [1 H, dd, $J(H^4H^5)$ 10, $J(H^4H^3)$ 7, H^4], 5.53 [1 H, ddd, $J(H^6H^7)$ 11, $J(H^6H^8)$ 2, $J(H^6H^5)$ 6, H^6], 5.89 [1 H, dd, $J(H^7H^6)$ 11, $J(H^7H^8)$ 2, H^7], 6.27 [1 H, t, $J(H^3H^2) = J(H^3H^4)$ 7, H^3], 7.2–7.8 (15 H, m, C_3Ph)	8.5 ($\mathrm{C}_5\mathit{Me}_5$), 36.7 ($C^8$), 43.2 ($C^7$), 70.0 ($C^1$), 71.1 ($C^5$), 92.2 ($C^4$), 95.9 ($C^2$), 100.1 ($\mathit{C}_5\mathrm{Me}_5$), 107.8 ($C^3$), 115.5 ($\mathit{C}_3\mathrm{Ph}_3$), 120.3 ($\mathit{C}_3\mathrm{Ph}_3$), 121.2 ($C^6$), 126.3–144.8 ($\mathrm{C}_3\mathit{Ph}_3$)
$[Co\{\eta^5-C_8H_8(C_3Bu^t_3)\}(\eta-C_5Me_5)][BF_4]$ **3** (M = Co, R = Me, R′ = Bu^t)	0.90 (9 H, s, $C_3Bu^t_3$), 1.02 (9 H, s, $C_3Bu^t_3$), 1.37 (9 H, s, $C_3Bu^t_3$), 1.82 (15 H, s, C_5Me_5), 3.52 (1 H, m, H^8), 3.73 [1 H, dd, $J(H^1H^8)$ 6, $J(H^1H^2)$ 11, H^1], 3.99 [1 H, dd, $J(H^5H^4)$ 10, $J(H^5H^6)$ 6, H^5], 4.74 [1 H, ddd, $J(H^2H^3)$ 8, $J(H^2H^1)$ 10, H^2], 4.81 [1 H, dd, $J(H^4H^3)$ 8, $J(H^4H^5)$ 6, H^4], 5.31 (1 H, m, H^6), 5.85 [1 H, dd, $J(H^7H^6)$ 14, $J(H^7H^8)$ 2, H^7], 6.41 [1 H, t, $J(H^3H^2) = J(H^3H^4)$ 7, H^3][b]	
$[Rh(\eta^2,\eta^3-C_8H_9)\{\eta-C_5H_4(C_3Ph_3)\}][BF_4]$ **4**	2.71 [1 H, m, $J(H^8H^{8'})$ 13, $J(H^8H^1) = J(H^8H^7)$ 7, H^8], 2.96 [1 H, ddd, $J(H^{8'}H^8)$ 13, $J(H^{8'}H^1)$ 9, $J(H^{8'}H^7)$ 7, $H^{8'}$], 3.68 [1 H, dq, $J(H^7H^6) = J(H^7H^8) = J(H^7H^{8'})$ 7, $J(H^7Rh)$ 2, H^7], 4.27 [1 H, dt, $J(H^2H^1) = J(H^2H^3)$ 8, $J(H^2Rh)$ 2, H^2], 4.63 [1 H, m, $J(H^1H^{8'})$ 9, $J(H^1H^2) = J(H^1H^8)$ 7, H^1], 5.19 [1 H, dd, $J(H^4H^5)$ 7, $J(H^4H^3)$ 4, H^4], 5.26 (2 H, m, H^3, H^5), 5.41 [1 H, d (br), $J(H^6H^7)$ 7, H^6], 5.70 (2 H, m, C_5H_4), 5.82 (2 H, m, C_5H_4), 7.2–7.9 (15 H, m, C_3Ph_3)[b]	19.7 (C^8), 40.9 [d, $J(C^7Rh)$ 6, C^7], 49.1 [d, $J(C^1Rh)$ 4, C^1], 79.9 [d, $J(C^3Rh)$ 10, C^3], 84.8 [d, $J(C^2Rh)$ 6, C^2], 89.7 [t, $J(CRh)$ 6, C^9 and C^{10}, or C^{11} and C^{12}], 90.7 [d, $J(C^6Rh)$ 10, C^6], 91.2 [t, $J(CRh)$ 6, C^9 and C^{10}, or C^{11} and C^{12}], 124.0 [d, $J(C^{13}Rh)$ 5, C^{13}], 127.5 (C^4, C^5), 128–133 (C_3Ph_3)
$[Rh\{\eta^5-C_8H_8(C_3Ph_3)\}(\eta-C_5Me_5)][BF_4]$ **3** (M = Rh, R = Me, R′ = Ph)	3.98 [1 H, ddt, $J(H^1H^2)$ 8, $J(H^1H^8)$ 6, $J(H^1Rh)$ 2, H^1], 4.39 (2 H, m, H^8, H^5), 5.03 [1 H, dt, $J(H^2H^1) = J(H^2H^3)$ 8, $J(H^2Rh)$ 2, H^2], 5.25 [1 H, dt, $J(H^4H^3) = J(H^4H^5)$ 8, $J(H^4Rh)$ 2, H^4], 5.67 [1 H, m, $J(H^6H^5)$ 9, $J(H^6H^7)$ 11, H^6], 5.90 [1 H, ddd, $J(H^7H^6)$ 11, $J(H^7H^8)$ 3, H^7], 6.33 [1 H, t, $J(H^3H^2) = J(H^3H^4)$ 7, H^3], 7.20–8.00 (15 H, m, C_3Ph_3)[c]	
$[Rh\{C_8H_8(C_3Ph_3)\}(\eta-C_5Me_5)][BF_4]$ **5**	1.46 (15 H, C_5Me_5), H^1–H^8: 3.20 (1 H, m), 3.86 (2 H, m), 4.65 [1 H, dd, $J(HH)$ 2, $J(HH)$ 9], 5.16 [1 H, dd, $J(HH)$ 3, $J(HH)$ 6], 5.29 (1 H, m), 5.86 [1 H, dd, $J(HH)$ 3, $J(HH)$ 4], 6.31 [1 H, dd, $J(HH)$ 6, $J(HH)$ 3], 6.8–8.0 (15 H, m, C_3Ph_3)	8.0 ($\mathrm{C}_5\mathit{Me}_5$), C^1–C^9: 57.9, 59.9, 73.3, 80.7 [d, $J(C^6Rh)$ 10], 91.0, 92.6 [d, $J(CRh)$ 5, $J(CRh)$ 13], 104.7 [d, $J(CRh)$ 5, $\mathit{C}_5\mathrm{Me}_5$], 122.8–145.6 ($\mathrm{C}_3\mathit{Ph}_3$)
$[Co\{\eta^5-C_8H_8(C_7H_7)\}(\eta-C_5H_5)][BF_4]$ **6** (R = H)	1.74 [1 H, q, $J(H^9H^8) = J(H^9H^{10}) = J(H^9H^{15})$ 6, H^9], 3.42 (1 H, m, H^8), 4.77 [1 H, dd, $J(H^1H^8)$ 6, $J(H^1H^2)$ 10, H^1], 5.33 (2 H, m, H^2, H^4), 5.59 (2 H, m, H^5, H^6), 5.90 (2 H, m, H^{10}, H^{15}), 5.95 (5 H, s, C_5H_5), 6.18 (3 H, m, H^7, H^{11}, H^{14}), 6.66 [2 H, t, $J(H^{12}H^{11}) = J(H^{13}H^{14})$ 3, H^{12}, H^{13}], 7.36 [1 H, t, $J(H^3H^2) = J(H^3H^4)$ 7, H^3]	35.2 (C^9), 41.8 (C^8), 44.1 (C^7), 77.9 (C^1), 78.1 (C^5), 86.6 (C_5H_5), 86.9 (C^2), 110.3 (C^3), 115.8 (C^6), 124.3–132.4 (C_7H_7)
$[Co\{\eta^5-C_8H_8(C_7H_7)\}(\eta-C_5Me_5)][BF_4]$ **6** (R = Me)	1.76 (1 H, m, H^9), 3.35 [1 H, dd, $J(H^8H^7)$ 5, $J(H^8H^1)$ 10, H^8], 4.43 (2 H, m, H^1, H^7), 4.64 [1 H, dd, $J(H^5H^6)$ 6, $J(H^5H^4)$ 9, H^5], 4.99 [1 H, dd, $J(H^2H^3)$ 8, $J(H^2H^1)$ 10, H^2], 5.25 [1 H, dd, $J(H^4H^3)$ 7, $J(H^4H^5)$ 9, H^4], 5.39 [1 H, dd, $J(H^6H^5)$ 6, $J(H^6H^7)$ 9, H^6], 5.70 (2 H, m, H^{10}, H^{15}), 6.18 [2 H, m, $J(H^{11}H^{10}) = J(H^{14}H^{13})$ 10, H^{11}, H^{14}], 6.65 [2 H, t, $J(H^{12}H^{11}) = J(H^{13}H^{14})$ 3, H^{12}, H^{13}], 6.77 [1 H, t, $J(H^3H^4) = J(H^3H^2)$ 7, H^3][c]	
$[Co\{\eta^5-C_8H_8(C_7H_7)\}(\eta-C_5Me_5)][BF_4]$ **7**	1.66 (1 H, m, H^9), 2.03 (15 H, s, C_5Me_5), 2.40–2.60 (4 H, m, H^6, $H^{6'}$, H^7, $H^{7'}$), 3.08 [1 H, dt, $J(H^8H^7) = J(H^8H^{7'})$ 2, $J(H^8H^9)$ 9, H^8], 4.94 [1 H, d, $J(H^2H^3)$ 2, H^2], 5.09 [1 H, d, $J(H^4H^3)$ 2, H^4], 5.15 [1 H, t, $J(H^3H^2) = J(H^3H^4)$ 2, H^3], 5.28 [1 H, dd, $J(HH)$ 6, $J(HH)$ 9, H^{10} or H^{15}], 5.35 [1 H, dd, $J(HH)$ 6, $J(HH)$ 9, H^{10} or H^{15}], 6.26 (2 H, m, H^{11}, H^{14}), 6.69 [2 H, t, $J(H^{12}H^{11}) = J(H^{13}H^{14})$ 2, H^{12}, H^{13}][d,e]	9.0 ($\mathrm{C}_5\mathit{Me}_5$), 21.5 ($C^7$), 33.4 ($C^6$), 37.8 ($C^8$), 43.6 ($C^9$), 79.6 ($C^2$, C^4), 90.1 (C^3), 96.8 ($\mathit{C}_5\mathrm{Me}_5$), 111.2, 112.4 ($C^1$, C^5), 124.1, 124.3 (C^{10}, C^{15}), 125.8, 131.1, 131.2 (C^{11}, C^{12}, C^{13}, C^{14})
$[Rh(\eta^2,\eta^3-C_8H_9)\{\eta-C_5H_4(C_7H_7)\}][BPh_4]$ **8**	2.61 [1 H, t, $J(H^9H^{15}) = J(H^9H^{10})$ 6, H^9], 3.00 [1 H, m, $J(H^8H^{8'})$ 13, $J(H^8H^1) = J(H^8H^7)$ 7, H^8], 3.47 [1 H, ddd, $J(H^{8'}H^8)$ 13, $J(H^{8'}H^1)$ 11, $J(H^{8'}H^7)$ 7, $H^{8'}$], 4.21 [1 H, dq, $J(H^7H^6) = J(H^7H^8) = J(H^7H^{8'})$ 7, $J(H^7Rh)$ 2, H^7], 4.80 [1 H, dt, $J(H^2H^1) = J(H^2H^3)$ 7, $J(H^2Rh)$ 2, H^2], 5.15 [1 H, m, $J(H^1H^{8'})$ 11, $J(H^1H^2) = J(H^1H^8)$ 6, H^1], 5.43 (2 H, m, H^{10}, H^{15}), 5.49 [1 H, dd, $J(H^4H^5)$ 7, $J(H^4H^3)$ 4, H^4], 5.55 [1 H, dt, $J(H^5H^4) = J(H^5H^6)$ 7, H^5], 5.70 [1 H, dd, $J(H^3H^4)$ 4, $J(H^3H^2)$ 8, H^3], 5.87 [1 H, dt, $J(H^6H^5) = J(H^6H^7)$ 8, H^6], 6.04 [2 H, dd, $J(H^{18}H^{17}) = J(H^{19}H^{20})$ 2, $J(H^{18}Rh) = J(H^{19}Rh) < 1$, H^{18}, H^{19}], 6.10 [1 H, dd, $J(HH)$ 2, $J(HRh) < 1$, H^{17} or H^{20}], 6.20 [1 H, dd, $J(HH)$ 2, $J(HRh) < 1$, H^{17} or H^{20}], 6.32 (2 H, m, H^{11}, H^{14}), 6.76 (2 H, m, H^{12}, H^{13}), 6.79 (4 H, m, *p*-Ph], 6.93 [8 H, t, $J(HH)$ 7, *o*- or *m*-Ph], 7.33 (8 H, m, *o*- or *m*-Ph)[d,f]	19.8 (C^8), 38.0 (C^9), 41.4 [d, $J(C^7Rh)$ 5, C^7], 48.2 [d, $J(C^1Rh)$ 5, C^1], 80.4 [d, $J(C^3Rh)$ 11, C^3], 85.3 [d, $J(C^2Rh)$ 5, C^2], 89.7 [d, $J(CRh)$ 5, C^{17}, C^{18} or C^{19}, C^{20}], 90.0 [d, $J(C^6Rh)$ 10, C^6], 90.7 [d, $J(C^{16}Rh)$ 5, C^{16}], 91.4 [d, $J(CRh)$ 5, C^{17}, C^{18} or C^{19}, C^{20}], 122.8 (*p*-Ph), 123.5, 123.6 (C^{10}, C^{15}), 126.6 (*m*-Ph), 131.4 (C^4, C^5), 132.2 (C^{11}, C^{14}), 132.9, 133.0 (C^{12}, C^{13}), 136.7 (*o*-Ph), 165.0 [$J(BPh)$ (?) 50, Ph][b]

Table 2 (*continued*)

Compound	^{1}H	^{13}C
$[Rh\{\eta^2,\eta^3-C_8H_8(C_7H_7)\}(\eta-C_5Me_5)][PF_6]$ **9**	3.82 [1 H, dt, $J(H^7Rh)$ 2, $J(H^7H^8) = J(H^7H^6)$ 9, H^7], 4.24 [1 H, dt, $J(H^8H^7) = J(H^8H^1)$ 9, $J(H^8H^9)$ 12, H^8], 4.44 [1 H, dt, $J(H^2Rh)$ 2, $J(H^2H^1) = J(H^2H^3)$ 9, H^2], 4.86 [1 H, t, $J(H^1H^8) = J(H^1H^2)$ 9, H^1], 4.96 (2 H, m, H^3, H^6), 5.06 [1 H, dd, J(HH) 6, J(HH) 10, H^{10} or H^{15}], 5.12 [1 H, dd, $J(H^4H^3)$ 4, $J(H^4H^5)$ 7, H^4], 5.34 [1 H, dd, J(HH) 6, J(HH) 10, H^{10} or H^{15}], 5.47 [1 H, m, $J(H^5H^4) = J(H^5H^6)$ 7, H^5], 6.19 (2 H, m, H^{14}, H^{11}), 6.56 [2 H, t, $J(H^{12}H^{11}) = J(H^{13}H^{14})$ 5, H^{12}, H^{13}]^{g}	9.4 (C_5Me_5), 9.6 ($C_5Me'_5$), 39.2 (C^9, $C^{9'}$), 45.2 (C^8), 57.2 [d, $J(C^7Rh)$ 4, C^7], 59.3 [d, $J(C^1Rh)$ 5, C^1], 70.3 [d, $J(C^{1'}Rh)$ 15, $C^{1'}$], 73.8 [d, $J(C^{5'}Rh)$ 13, $C^{5'}$], 85.6 [d, $J(C^3Rh)$ 12, C^3], 93.0 [d, $J(C^{4'}Rh)$ 5, $C^{4'}$], 95.2 [d, $J(C^{2'}Rh)$ 4, $C^{2'}$], 95.6 [d, $J(C^2Rh)$ 4, C^2), 101.5 [d, $J(C^6Rh)$ 10, C^6], 104.4 [d, J(CRh) 6, C_5Me_5], 105.1 [d, J(CRh) 6, $C_5Me'_5$), 109.7 ($C^{3'}$), 121.8 (C^4, C^5), 124.2 ($C^{6'}$), 126.3 ($C^{10'}$, $C^{15'}$), 126.8, 126.9 (C^{10}, C^{15}), 130.3 ($C^{11'}$, $C^{14'}$), 131.4 (C^{11} or C^{14}), 131.5 ($C^{12'}$ or $C^{13'}$), 131.6 (C^{11} or C^{14}), 131.8 ($C^{12'}$ or $C^{13'}$), 132.4, 133.1 (C^{12}, C^{13})

[a] Atom numbering as in Scheme 2. *J* Values are in Hz. 270 MHz spectra, in $[^2H_6]$acetone unless stated otherwise. [b] In CD_3CN. [c] C_5Me_5 resonance obscured by solvent. [d] 400 MHz spectrum. [e] In CD_3NO_2. [f] In CD_2Cl_2. [g] The signal for H^9 is obscured by the solvent, but H^8, H^{10} and H^{15} are coupled to H^9 by 10, 6 and 6 Hz respectively.

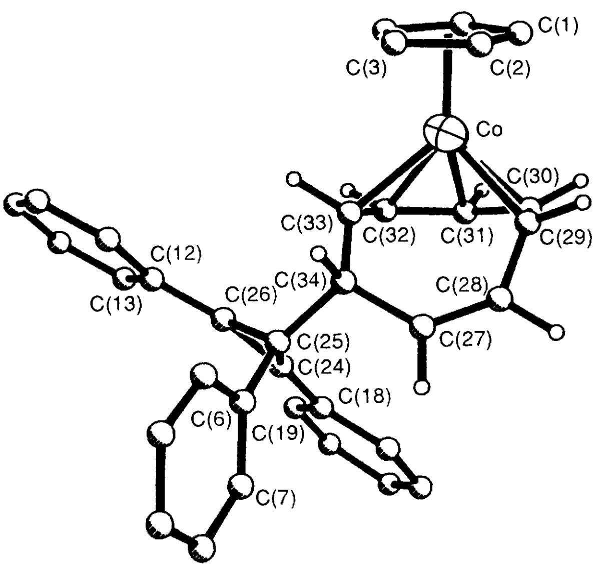


Fig. 1 The molecular structure of the cation **3** (M = Co, R = H, R′ = Ph) showing the labelling scheme; phenyl and cyclopentadienyl group hydrogen atoms have been omitted for clarity

Table 3 Selected bond distances (Å) and bond angles (°) for $[Co\{\eta^5-C_8H_8(C_3Ph_3)\}(\eta-C_5H_5)][BF_4]$

Co–C(1)	2.056(3)	Co–C(2)	2.034(3)	Co–C(3)	2.030(3)
Co–C(4)	2.041(5)	Co–C(5)	2.089(4)	Co–C(29)	2.118(4)
Co–C(30)	2.005(4)	Co–C(31)	2.055(4)	Co–C(32)	2.016(3)
Co–C(33)	2.078(3)	C(1)–C(2)	1.392(5)	C(1)–C(5)	1.367(5)
C(2)–C(3)	1.365(6)	C(3)–C(4)	1.419(6)	C(4)–C(5)	1.409(6)
C(6)–C(7)	1.386(4)	C(6)–C(11)	1.391(4)	C(6)–C(25)	1.503(4)
C(7)–C(8)	1.376(5)	C(8)–C(9)	1.364(6)	C(9)–C(10)	1.377(5)
C(10)–C(11)	1.378(5)	C(12)–C(13)	1.393(5)	C(12)–C(17)	1.396(5)
C(12)–C(26)	1.437(5)	C(13)–C(14)	1.374(7)	C(14)–C(15)	1.373(7)
C(15)–C(16)	1.369(7)	C(16)–C(17)	1.386(6)	C(18)–C(19)	1.386(4)
C(18)–C(23)	1.390(5)	C(18)–C(24)	1.448(4)	C(19)–C(20)	1.364(5)
C(20)–C(21)	1.362(7)	C(21)–C(22)	1.367(6)	C(22)–C(23)	1.388(5)
C(24)–C(25)	1.509(4)	C(24)–C(26)	1.300(5)	C(25)–C(26)	1.500(4)
C(25)–C(34)	1.563(4)	C(27)–C(28)	1.303(5)	C(27)–C(34)	1.483(4)
C(28)–C(29)	1.458(5)	C(29)–C(30)	1.377(5)	C(30)–C(31)	1.384(6)
C(31)–C(32)	1.417(7)	C(32)–C(33)	1.439(5)	C(33)–C(34)	1.512(4)

C(18)–C(24)–C(25)	145.7(3)	C(18)–C(24)–C(26)	150.3(3)
C(25)–C(24)–C(26)	64.0(2)	C(6)–C(25)–C(24)	119.5(2)
C(6)–C(25)–C(26)	117.1(3)	C(24)–C(25)–C(26)	51.2(2)
C(6)–C(25)–C(34)	113.5(2)	C(24)–C(25)–C(34)	120.2(3)
C(26)–C(25)–C(34)	121.7(2)	C(12)–C(26)–C(24)	152.9(3)
C(12)–C(26)–C(25)	141.9(3)	C(24)–C(26)–C(25)	64.8(2)
C(28)–C(27)–C(34)	126.5(3)	C(27)–C(28)–C(29)	130.0(3)
C(28)–C(29)–C(30)	125.0(3)	C(29)–C(30)–C(31)	124.8(4)
C(30)–C(31)–C(32)	124.9(3)	C(31)–C(32)–C(33)	127.5(3)
C(32)–C(33)–C(34)	130.8(3)	C(25)–C(34)–C(27)	109.6(2)
C(25)–C(34)–C(33)	109.6(2)	C(27)–C(34)–C(33)	118.2(3)

from $[C_3Ph_3]^+$ and $[Fe(CO)_3(\eta^4\text{-cot})]$, namely *exo* addition of the electrophile to the co-ordinated cot ligand. In order to investigate subsequent steps in the mechanism of formation of **1**, complexes **3** (M = Co, R = H or Me, R′ = Ph) were heated under reflux both in nitromethane and in acetone; in neither case was isomerisation observed before decomposition. The reactions of $[C_3Bu^t{}_3]^+$ with $[Co(\eta^4\text{-cot})(\eta-C_5R_5)]$ (R = H or Me) were also investigated. The electron-donating properties of the tertiary butyl groups render $[C_3Bu^t{}_3]^+$ a weaker electrophile than $[C_3Ph_3]^+$ and consequently $[C_3Bu^t{}_3][BF_4]$ did not react with $[Co(\eta^4\text{-cot})(\eta-C_5H_5)]$ either at room or elevated temperatures. However, with the more electron-rich complex $[Co(\eta^4\text{-cot})(\eta-C_5Me_5)]$, $[Co\{\eta^5-C_8H_8(C_3Bu^t{}_3)\}(\eta-C_5Me_5)][BF_4]$ **3** (M = Co, R = Me, R′ = Bu^t) was rapidly formed at room temperature. The orange product could not be isolated entirely free from unreacted $[C_3Bu^t{}_3][BF_4]$ and satisfactory elemental analyses were therefore not obtained. Nevertheless, the ^1H NMR spectrum of **3** (M = Co, R = Me, R′ = Bu^t), contaminated only by a singlet for the free $[C_3Bu^t{}_3]^+$ ion, showed signals for the C_8-ring protons very similar to those of **3** (M = Co, R = Me, R′ = Ph) (Table 2) and the η^5-bonding mode is clearly adopted once again. For **3** (M = Co, R = H, R′ = Bu^t), the three singlet signals observed for the Bu^t groups of the substituent C_3 ring reflect the asymmetry of the C_8 ring. In addition the replacement of C_3Ph_3 by $C_3Bu^t{}_3$ at C^8 results in a significant shift to high field of the signal due to H^8.

The reactions of $[Rh(\eta^4\text{-cot})(\eta-C_5H_5)]$ and $[Rh(\eta^4\text{-cot})(\eta-C_5Me_5)]$ with equimolar quantities of $[C_3Ph_3][BF_4]$ in CH_2Cl_2 are very different from those of the cobalt complexes and also from each other. The reaction of $[Rh(\eta^4\text{-cot})(\eta-C_5H_5)]$ resulted in an orange solution from which $[Rh(\eta^2,\eta^3-C_8H_9)\{\eta-C_5H_4(C_3Ph_3)\}][BF_4]$ **4** (Tables 1 and 2, Scheme 2) was isolated in good yield as a yellow, air-stable powder. In contrast to the ^1H NMR spectra of the cobalt complexes **3**, that of **4** shows that substitution of the $\eta-C_5H_5$ ring, rather than electrophilic addition to the cot ligand, has occurred. Thus the signals for the four C_5-ring protons appear as two multiplets at δ 5.70 and 5.82 rather than as the doublet expected for an η-C_5H_5 group bonded to rhodium (^{103}Rh, $I = \frac{1}{2}$). The chemical shifts of the protons attached to the C_8 ring are very similar to those of $[Rh(\eta^2,\eta^3\text{-}C_8H_9)(\eta\text{-}C_5H_5)]^+$[15] and $[Rh(\eta^2,\eta^3\text{-}C_8H_9)\{\eta\text{-}C_5H_4(CHCH{=}CH_2)\}]^+$[16] and the assignment of the η^2,η^3-bonding mode is also supported by the observation of ^{103}Rh coupling of *ca.* 2 Hz for the signals for protons H^2, H^3 and H^7, somewhat smaller and less well resolved couplings to H^1 and H^6, but no coupling for H^4, H^5 and H^8.

The C_8-ring signals in the ^{13}C NMR spectrum are very similar to those reported for $[Rh(\eta^2,\eta^3\text{-}C_8H_9)(\eta\text{-}C_5H_5)]^+$[15] and $[Rh(\eta^2,\eta^3\text{-}C_8H_9)\{\eta\text{-}C_5H_4(CHCH{=}CH_2)\}]^+$,[16] and the five co-ordinated carbon atoms all show coupling to the rhodium atom of 4–10 MHz. Because of the asymmetry of the C_8 ring there are three signals (in the ratio of 2:2:1) for the C_5 ring carbons of **4**. That for C^{13} is a doublet [δ 124, $J(^{13}C^{103}Rh)$ 5 Hz] and those for C^9, C^{10}, C^{11} and C^{12} appear as two superimposed pairs of doublets (*i.e.* they appear to be pseudo triplets) at δ 89.7 and 91.2.

There is ample precedent for the preferential attack of an electrophile at the η-C_5H_5 group rather than at the co-ordinated diene of complexes such as $[Rh(\eta^4\text{-diene})(\eta\text{-}C_5H_5)]$ *e.g.* during the Friedel–Crafts acylation[17] of $[Rh(\eta^4\text{-chd})(\eta\text{-}C_5H_5)]$ (chd = cyclohexa-1,3-diene) to give $[Rh(\eta^4\text{-chd})\{\eta\text{-}C_5H_4(COMe)\}]$, in the reaction[18] of $[Rh(\eta^4\text{-cod})(\eta\text{-}C_5H_5)]$ with $[CPh_3][BF_4]$ to give $[Rh(\eta^4\text{-cod})\{\eta\text{-}C_5H_4(CPh_3)\}]$, and in the allylation of $[Rh(\eta^4\text{-cot})(\eta\text{-}C_5H_5)]$ by $[Fe\{P(OMe)_3\}(NO)_2(\eta^3\text{-allyl})]^+$ to give $[Rh(\eta^2,\eta^3\text{-}C_8H_9)\{\eta\text{-}C_5H_4(CHCH{=}CH_2)\}]^+$.[16] However, it remains unclear why electrophiles add respectively to the C_5 and C_8 rings of rhodium and cobalt analogues. At this point we tentatively raise the possibility that the divergent behaviour is a consequence of the differing degree of covalency in first- and second-row transition-metal to ligand bonding. Enhanced metal–ligand covalency, as observed for second-row metals, is likely to have two consequences of relevance to this problem. First, the M–L bonding orbitals (*e.g.* those involved in M–C_5H_5 and/or M–cot bonding) are at lowered energy relative to those ligand π orbitals not interacting with the metal (*i.e.* generally those of cot rather than C_5H_5). Secondly, the transfer of charge from ligand to metal through the interacting orbitals and atoms will be enhanced. Both of these effects will make those ligand atoms and π orbitals *not* directly interacting with the metal relatively more attractive as sites for electrophilic attack since to a first approximation these atoms and orbitals will have charge and energy characteristics independent of the metal. This argument therefore gives predictions in accord with the site preferences observed in this system. It is of course probable that other factors, such as the larger atomic radius of the second-row metal, might play a part in controlling these reactions.

The mechanism for the formation of **4** is likely to be the same as that proposed for the allylic alkylation[16] of $[Rh(\eta^4\text{-cot})(\eta\text{-}C_5H_5)]$. First, *exo* addition of $[C_3Ph_3]^+$ to the η-C_5H_5 ring gives the 16-electron intermediate $[Rh(\eta^4\text{-cot})\{\eta^4\text{-}C_5H_5(C_3Ph_3)\}]^+$. The *endo* proton of the $C_5H_5(C_3Ph_3)$ ligand then migrates to the C_8 ring *via* the metal (*i.e.* with the 18-electron metal hydride $[RhH(\eta^4\text{-cot})\{\eta^5\text{-}C_5H_5(C_3Ph_3)\}]^+$ as intermediate). Metal hydride intermediates are also presumably formed in the reactions of $[Rh(\eta^4\text{-diene})(\eta\text{-}C_5H_5)]$ (diene = chd or cod) with the carbon-based electrophiles noted above. However, in these cases the metal cannot regain a stable 18-electron configuration by proton migration (η^3-allyl rather than η^5-dienyl groups would result as the hydrocarbon has no unco-ordinated double bonds). Proton loss from the metal therefore occurs, giving the neutral species $[Rh(\eta^4\text{-diene})(\eta\text{-}C_5H_4R)]$.

The addition of 1 equivalent of $[C_3Ph_3][BF_4]$ to $[Rh(\eta^4\text{-cot})(\eta\text{-}C_5Me_5)]$ gave a yellow solution from which a microcrystalline powder was isolated in good yield on addition of diethyl ether. The ^{1}H NMR spectrum of a freshly prepared sample of the powder was similar to that of **3** (M = Co, R = Me, R′ = Ph) indicating the formation of $[Rh\{\eta^5\text{-}C_8H_8(C_3Ph_3)\}(\eta\text{-}C_5Me_5)][BF_4]$ **3** (M = Rh, R = Me, R′ = Ph). However, over a period of 10 d in CH_2Cl_2 this complex was completely converted into a new species in a process which could be accelerated by heating a solution of **3** (M = Rh, R = Me, R′ = Ph) in CH_2Cl_2 under reflux for 4 h. Addition of diethyl ether then precipitated an orange powder **5** the ^{1}H NMR spectrum of which shows a doublet at δ 1.46 for the intact C_5Me_5 ring, and seven resonances for the eight different C_8-ring protons, including two at high field (δ 3.20 and 3.86). A full assignment of the ^{1}H NMR spectrum could not be made despite ^{1}H–^{1}H decoupling and ^{1}H–^{1}H two-dimensional correlation (COSY) experiments but it is inconsistent with either η^2,η^3-octatrienyl or η^5-bicyclo[5.1.0]octadienyl structures for the C_8 ring. It is possible that the C_3Ph_3 ring has opened, as observed in the reaction of $[C_3Ph_3]^+$ with $[Fe(CO)_3(\eta^4\text{-cot})]$ (Scheme 1), but the ^{1}H NMR spectrum of **5** is not similar to that of **1**. If C_3 ring opening has occurred, a different isomerisation pathway appears to be followed when **3** (M = Rh, R = Me, R′ = Ph) is converted into **5**. Unfortunately, suitable crystals could not be grown for an X-ray diffraction study on **5** and its structure remains unknown.

The Reactions of $[C_7H_7]^+$ *with* $[M(\eta^4\text{-cot})(\eta\text{-}C_5R_5)]$.—The reaction of $[Co(\eta^4\text{-cot})(\eta\text{-}C_5H_5)]$ with $[C_7H_7][PF_6]$ is very similar to that with $[C_3Ph_3][BF_4]$, giving a moderate yield of the orange adduct $[Co\{\eta^5\text{-}C_8H_8(C_7H_7)\}(\eta\text{-}C_5R_5)][PF_6]$ **6** (R = H) (Tables 1 and 2, Scheme 2). The unco-ordinated cycloheptatriene unit shows four signals in the ^{1}H NMR spectrum in the ratio of 2:2:2:1, again reflecting the asymmetry in the co-ordinated C_8 ring. The complex is air-stable in the solid state but over a period of several hours decomposes in solution.

The reaction of $[C_7H_7][PF_6]$ with $[Co(\eta^4\text{-cot})(\eta\text{-}C_5Me_5)]$ in acetone is initially similar to that with $[Co(\eta^4\text{-cot})(\eta\text{-}C_5H_5)]$ giving, after 20 min, a red-orange solution **6** (R = Me) which showed a ^{1}H NMR spectrum consistent with an η^5-bound C_8 ring of the type found for **3** (M = Co, R = Me, R′ = Ph). Over a period of 4 h, the red-orange solution became paler in colour, and a dark orange air-stable solid **7** was then isolated and fully characterised by elemental analysis and ^{1}H and ^{13}C NMR spectroscopy (Tables 1 and 2).

The ^{1}H NMR spectrum of **7** shows the C_8 ring protons as three signals at low field and three signals in the range δ 2–3. The first set of signals, a triplet and two doublets, is typical of the protons of disubstituted η^5-$C_5H_3R_2$ groups,[19] and the second set occurs as two overlapping multiplets (δ 2.4–2.6) for H^6, $H^{6'}$ and H^7,$H^{7'}$, and a doublet of triplets at δ 3.08 for H^8. The C_7H_7 ring is in a more asymmetric environment than that of **6** (R = Me) showing five signals in the ratio 2:2:1:1:1; the signal for the bridgehead proton (H^9) occurs as a high-field multiplet. The ^{1}H NMR spectrum of **7** is very different from that of **6** (R = Me) and from that expected for either a η^2,η^3-cyclooctatrienyl or a η^5-bicyclo[5.1.0]octadienyl C_8H_8R ligand. However, it is compatible with the presence of a monosubstituted η^5-1,2,3,3*a*-tetrahydropentalenyl ligand (Scheme 2), as found in $[Co\{\eta^5\text{-}C_8H_8[CH_2C(Me){=}CH_2]\}(\eta\text{-}C_5Me_5)]^+$ the product of the reaction between $[Co(\eta^4\text{-cot})(\eta\text{-}C_5Me_5)]$ and $[Fe\{P(OMe)_3\}(NO)_2\{\eta^3\text{-}CH_2C(Me){=}CH_2\}]^+$.[20] The inequivalence of protons H^2 and H^4 shows the C_7H_7 substituent to be at C^8, as observed in **6** (R = Me). The complexity of the ^{1}H NMR spectrum in the region δ 2–3 prevented a distinction to be made between *exo* and *endo* geometries for the C_7H_7 substituent. However, X-ray structural studies on **3** (M = Co, R = H, R′ = Ph) and $[Co\{\eta^5\text{-}C_8H_8[CH_2C(Me){=}CH_2]\}(\eta\text{-}C_5Me_5)]^+$ have shown the substituent *exo* to the metal atom.

The presence of an η^5-1,2,3,3*a*-tetrahydropentalenyl ligand is also supported by electrochemistry in that the cyclic voltammogram of **7** shows a reversible one-electron reduction wave at −1.28 V. This behaviour is very similar to that of $[Co(\eta\text{-}C_5Me_5)_2]^+$, which is reduced to $[Co(\eta\text{-}C_5Me_5)_2]$ at −1.48 V,[21] and $[Co\{\eta^5\text{-}C_8H_8[CH_2C(Me){=}CH_2]\}(\eta\text{-}C_5Me_5)]^+$ (reversibly reduced[20] at −1.25 V); given the structure proposed **7** can, of course, be formulated alternatively as a cobaltocenium salt. As in the allylation of $[\text{Co}(\eta^4\text{-cot})(\eta\text{-C}_5\text{H}_5)]$ with $[\text{Fe}\{\text{P(OMe)}_3\}(\text{NO})_2(\eta^3\text{-allyl})]^+$,[20] the η^5-1,2,3,3*a*-tetrahydropentalenyl ligand is formed from $[\text{C}_7\text{H}_7][\text{PF}_6]$ with $[\text{Co}(\eta^4\text{-cot})(\eta\text{-C}_5\text{Me}_5)]$ much more rapidly, and under milder conditions, than in reactions involving the isomerisation of neutral complexes of monocyclic C_8 ligands.[22]

The addition of 1 equivalent of $[\text{C}_7\text{H}_7][\text{BF}_4]$ to $[\text{Rh}(\eta^4\text{-cot})(\eta\text{-C}_5\text{H}_5)]$ in CH_2Cl_2 gave a yellow solution from which only an impure green oil could be isolated. However, dissolution of the green oil in acetone and addition of $\text{Na}[\text{BPh}_4]$ resulted in metathesis to give a yellow powder the ^{1}H NMR spectrum of which initially showed a mixture of three species. Two of these were readily identified as the η^5-bicyclo[5.1.0]octadienyl and η^2,η^3-cyclooctatrienyl complexes $[\text{Rh}(\eta^5\text{-C}_8\text{H}_9)(\eta\text{-C}_5\text{H}_5)]^+$ and $[\text{Rh}(\eta^2,\eta^3\text{-C}_8\text{H}_9)(\eta\text{-C}_5\text{H}_5)]^+$, previously prepared[15] by the direct protonation of $[\text{Rh}(\eta^4\text{-cot})(\eta\text{-C}_5\text{H}_5)]$; the third product is $[\text{Rh}(\eta^2,\eta^3\text{-C}_8\text{H}_9)\{\eta\text{-C}_5\text{H}_4(\text{C}_7\text{H}_7)\}]^+$ **8** (Scheme 2). After 24 h in solution the mixture contained only $[\text{Rh}(\eta^2,\eta^3\text{-C}_8\text{H}_9)(\eta\text{-C}_5\text{H}_5)]^+$ and **8** (in an approximate 1:1 ratio) the bicyclo[5.1.0]octadienyl isomer having converted into the η^2,η^3-cyclooctatrienyl analogue as observed previously.[15] Complex $[\text{Rh}(\eta^2,\eta^3\text{-C}_8\text{H}_9)(\eta\text{-C}_5\text{H}_5)]^+$ and **8** proved impossible to separate completely but slow diffusion of diethyl ether into a CH_2Cl_2 solution of the mixture afforded yellow crystals which were partially separated by hand; the 400 MHz ^{1}H NMR spectrum of **8** was then obtained using one of the appropriate crystals. This spectrum showed that, as in the reaction of $[\text{C}_3\text{Ph}_3]^+$ with $[\text{Rh}(\eta^4\text{-cot})(\eta\text{-C}_5\text{H}_5)]$, electrophilic addition occurs at the C_5 ring rather than at the cot ligand. The signals for the C_5 ring are in the ratio 1:1:2 [rather than the doublet expected for a $\text{Rh}(\eta\text{-C}_5\text{H}_5)$ moiety], and the chemical shifts of the C_8 ring protons are virtually identical to those observed[15] for the protonated species $[\text{Rh}(\eta^2,\eta^3\text{-C}_8\text{H}_9)(\eta\text{-C}_5\text{H}_5)]^+$ indicating that the C_8 ligand of **8** is also bound in an η^2,η^3 fashion. Protons H^1, H^2, H^3, H^6 and H^7 all exhibit coupling to the rhodium atom (of *ca.* 2 Hz for H^2 and H^7, but smaller for the rest). The signal for the bridgehead proton, H^{14}, occurs as a triplet at δ 2.61, shifted to high field (relative to the corresponding protons in other C_7H_7 units) by the proximity of the $\eta^5\text{-C}_5$ ligand; the remaining cycloheptatriene protons give signals at low field in the ratio 2:2:2. Since a sufficient quantity of pure **8** could not be isolated, a ^{13}C NMR spectrum of the mixture was obtained; the close similarity of the shift values for corresponding C_8-ring carbons emphasised the similarity of the two C_8H_9 ligands. All the co-ordinated carbon atoms show rhodium coupling of 4–10 Hz (Tables 1 and 2).

Complex **8** is presumably formed by the same mechanism proposed for the addition of $[\text{C}_3\text{Ph}_3]^+$ to $[\text{Rh}(\eta^4\text{-cot})(\eta\text{-C}_5\text{H}_5)]$ (see above). However, in the present case the competing formation of the protonated product $[\text{Rh}(\eta^2,\eta^3\text{-C}_8\text{H}_9)(\eta\text{-C}_5\text{H}_5)]^+$ is also observed. The mechanism for this second reaction is not clear, and the origin of the extra proton is unknown. We have shown previously[23] that the oxidative dimerisation of $[\text{Rh}(\eta^4\text{-cot})(\eta\text{-C}_5\text{H}_5)]$ by Ag^+ ions is accompanied by the formation of the bicyclo[5.1.0]octadienyl complex $[\text{Rh}(\eta^5\text{-C}_8\text{H}_9)(\eta\text{-C}_5\text{H}_5)]^+$, most probably by the reaction between the radical cation $[\text{Rh}(\eta^4\text{-cot})(\eta\text{-C}_5\text{H}_5)]^+$ and water. A similar mechanism may operate with the tropylium ion although the potentials for the oxidation of $[\text{Rh}(\eta^4\text{-cot})(\eta\text{-C}_5\text{H}_5)]$ (irreversible peak potential, 0.55 V[23]) and the reduction of $[\text{C}_7\text{H}_7]^+$ (−0.18 V) are highly thermodynamically unfavourable.

Treatment of a CH_2Cl_2 solution of $[\text{Rh}(\eta^4\text{-cot})(\eta\text{-C}_5\text{Me}_5)]$ with $[\text{C}_7\text{H}_7]^+$ gave a dark yellow solution from which an air-stable yellow microcrystalline powder was isolated and characterised by elemental analysis and ^{1}H and ^{13}C NMR spectroscopy (Tables 1 and 2). The presence of the methyl groups precluded electrophilic attack on the pentamethylcyclopentadienyl ring. As expected therefore, the ^{1}H NMR spectrum shows tropylium addition to the C_8 ring. However, it also indicated that the product is present in two isomeric forms. The major isomer **9** shows a singlet for the C_5Me_5 ring at δ 2.0, and the chemical shifts of the signals for the C_8 ring, assigned by ^{1}H–^{1}H COSY NMR experiments, indicate η^2,η^3 bonding to the rhodium. Thus the values obtained are very similar to those reported[15] for $[\text{Rh}(\eta^2,\eta^3\text{-C}_8\text{H}_9)(\eta\text{-C}_5\text{H}_5)]^+$; protons H^2 and H^7 show coupling of *ca.* 2 Hz to the rhodium, while the multiplet corresponding to H^3 and H^6 and the signal for H^1 also show evidence of rhodium coupling. The ^{13}C NMR spectrum also supports the proposed structure with the signal for the C_5Me_5 ring carbons appearing as a doublet at δ 104.4 (coupling of 6 Hz to rhodium) and the signals for C^6, C^2, C^3, C^1 and C^7 as doublets with rhodium coupling of 4–12 Hz.

The ^{1}H NMR spectrum of the minor isomer **10**, present in *ca.* 10% yield, is generally obscured by that of **9** but a low field triplet at δ 6.9 is indicative of an η^5-co-ordinated octatrienyl ligand as found in $[\text{Co}\{\eta^5\text{-C}_8\text{H}_8(\text{C}_7\text{H}_7)\}(\eta\text{-C}_5\text{R}_5)]^+$ **6** (R = H or Me); the ^{13}C NMR spectrum of **10** was more obviously similar to that of **6** (R = Me) adding strong support for the proposed formula.

Conclusion

The complexes $[\text{M}(\eta^4\text{-cot})(\eta\text{-C}_5\text{R}_5)]$ (R = H or Me) react with $[\text{C}_3\text{Ph}_3]^+$ and $[\text{C}_7\text{H}_7]^+$ to give a range of new complexes *via* electrophilic addition. The results show: (*i*) that the preferred site of electrophilic addition is metal dependent; the cobalt complexes are attacked at the C_8 ring whereas the cyclopentadienyl ligand of the rhodium complex is attacked unless that ring is permethylated, (*ii*) that η^5 and η^2,η^3 co-ordination of the cyclooctatrienyl ligand is preferred by Co and Rh respectively, and (*iii*) the rearrangement of the η^5-cyclooctatrienyl ligand to the 1,2,3,3*a*-tetrahydropentalenyl skeleton is favoured by permethylation at the cobalt cyclopentadienyl ligand; the rearrangement process is much faster for the cationic complexes than for previously described neutral analogues.

Experimental

The preparation, purification and reactions of the complexes described were carried out under an atmosphere of dry nitrogen, using dried, distilled and deoxygenated solvents. Purification was achieved by dissolving the complex in an appropriate solvent, filtration through Celite, and reducing the solvent volume *in vacuo*. Addition of a solvent in which the product is insoluble led to precipitation. Unless otherwise stated, the complexes are air-stable solids dissolving in polar solvents such as CH_2Cl_2 to give moderately air-sensitive solutions. The complexes $[\text{Co}(\eta^4\text{-cot})(\eta\text{-C}_5\text{R}_5)]$ (R = H[24] or Me[25]), $[\text{Rh}(\eta^4\text{-cot})(\eta\text{-C}_5\text{R}_5)]$ (R = H[23] or Me[26]) and $[\text{C}_3\text{Ph}_3][\text{BF}_4]$[27] were prepared by literature methods and $[\text{C}_7\text{H}_7][\text{PF}_6]$ was purchased from Aldrich. Proton and ^{13}C NMR spectra were recorded on JEOL GX270 or GX400 spectrometers and calibrated against SiMe_4 as an internal reference. Two-dimensional NMR spectroscopy employed the COSY-45 pulse sequence.[28] Electrochemical studies were carried out as previously described.[29] Under the conditions used, E° for the couple $[\text{Fe}(\eta\text{-C}_5\text{H}_5)_2]^+$–$[\text{Fe}(\eta\text{-C}_5\text{H}_5)_2]$, used as an internal standard, is 0.47 V.

$[\text{Co}\{\eta^5\text{-C}_8\text{H}_8(\text{C}_3\text{Ph}_3)\}(\eta\text{-C}_5\text{H}_5)][\text{BF}_4]$ **3** (M = Co, R = H, R′ = Ph).—To a stirred solution of $[\text{Co}(\eta^4\text{-cot})(\eta\text{-C}_5\text{H}_5)]$ (0.1 g, 0.44 mmol) in CH_2Cl_2 (20 cm^3) was added $[\text{C}_3\text{Ph}_3][\text{BF}_4]$ (155 mg, 0.44 mmol). After 20 min the orange solution was filtered through Celite and reduced to low volume *in vacuo*. Addition of diethyl ether precipitated the product as an orange solid. Purification from CH_2Cl_2–diethyl ether gave an orange powder, yield 190 mg (74%).

The compounds $[\text{Co}\{\eta^5\text{-C}_8\text{H}_8(\text{C}_3\text{Ph}_3)\}(\eta\text{-C}_5\text{Me}_5)][\text{BF}_4]$ **3**

Table 4 Atomic coordinates ($\times 10^4$) for $[\mathrm{Co}\{\eta\text{-}C_8H_8(C_3Ph_3)\}(\eta\text{-}C_5H_5)][BF_4]$

Atom	x	y	z	Atom	x	y	z
Co	−1120(1)	6930(1)	4086(1)	C(22)	−3963(2)	3383(5)	1617(3)
C(1)	−179(2)	8132(4)	4149(2)	C(23)	−3560(2)	3368(4)	2416(2)
C(2)	−68(2)	7054(4)	4744(2)	C(24)	−3410(2)	4133(3)	3859(2)
C(3)	−547(2)	7272(5)	5245(2)	C(25)	−2756(2)	3536(3)	4461(2)
C(4)	−972(2)	8519(5)	4955(3)	C(26)	−3339(2)	4562(3)	4610(2)
C(5)	−720(2)	9050(4)	4276(2)	C(27)	−1678(2)	3250(3)	3818(2)
C(6)	−2780(2)	2009(3)	4772(2)	C(28)	−1224(2)	3730(4)	3386(2)
C(7)	−3253(2)	975(4)	4347(2)	C(29)	−919(2)	5179(4)	3345(2)
C(8)	−3308(2)	−390(4)	4662(3)	C(30)	−1285(2)	6327(5)	2913(2)
C(9)	−2899(2)	−767(4)	5410(3)	C(31)	−1933(2)	6921(4)	3041(2)
C(10)	−2419(2)	233(4)	5843(2)	C(32)	−2220(2)	6695(3)	3748(3)
C(11)	−2356(2)	1597(3)	5526(2)	C(33)	−1951(2)	5711(3)	4412(2)
C(12)	−3595(2)	5285(3)	5255(2)	C(34)	−1962(1)	4070(3)	4446(2)
C(13)	−4233(2)	6124(4)	5116(3)	B	1094(3)	5214(5)	2947(3)
C(14)	−4465(2)	6786(4)	5750(3)	F(1)	1624(1)	5454(3)	2536(1)
C(15)	−4068(3)	6611(5)	6534(3)	F(2)	491(2)	4674(9)	2520(3)
C(16)	−3442(3)	5785(5)	6696(3)	F(4)	1424(3)	4003(5)	3477(3)
C(17)	−3201(2)	5127(4)	6058(2)	F(3)	1012(3)	6233(7)	3477(3)
C(18)	−3807(2)	4143(3)	3016(2)	F(2A)	440(4)	5889(13)	2385(6)
C(19)	−4453(2)	4931(4)	2783(2)	F(3A)	873(7)	3934(9)	3068(7)
C(20)	−4837(2)	4942(5)	1993(3)	F(4A)	1160(11)	6129(18)	3604(8)
C(21)	−4603(2)	4157(5)	1410(3)				

(M = Co, R = Me, R′ = Ph) and $[\mathrm{Rh}(\eta^2, \eta^3\text{-}C_8H_9)\{\eta\text{-}C_5H_4(C_3Ph_3)\}][BF_4]$ **4** were prepared by similar methods; both were precipitated from the reaction mixture by the addition of hexane, and the second was purified by adding its solution in CH_2Cl_2 to a large volume of diethyl ether.

$[\mathrm{Co}\{\eta^5\text{-}C_8H_8(C_3Bu^t_3)\}(\eta\text{-}C_5Me_5)][BF_4]$ **3** (M = Co, R = Me, R′ = Bu^t).—A mixture of $[\mathrm{Co}(\eta^4\text{-cot})(\eta\text{-}C_5Me_5)]$ (102 mg, 0.35 mmol) and $[C_3Bu^t_3][BF_4]$ (81 mg, 0.28 mmol) in CH_2Cl_2 (20 cm^3) was stirred for 5 min. The dark brown solution was filtered through Celite and evaporated to low volume *in vacuo*. Addition of diethyl ether precipitated an orange solid, and purification from acetone–diethyl ether gave the product as an orange powder, yield 118 mg (59% based on $[\mathrm{Co}(\eta^4\text{-cot})(\eta\text{-}C_5Me_5)]$). Unreacted $[C_3Bu^t_3][BF_4]$ could not be fully removed from the final product and satisfactory elemental analyses were not obtained.

Synthesis of Complex **5**.—A solution of $[\mathrm{Rh}(\eta^4\text{-cot})(\eta\text{-}C_5Me_5)]$ (74 mg, 0.22 mmol) and $[C_3Ph_3][BF_4]$ (75 mg, 0.22 mmol) in CH_2Cl_2 (25 cm^3) was heated under reflux for 2 h. The resulting orange solution was filtered through Celite and evaporated to low volume *in vacuo*. Addition of diethyl ether gave an orange solid, and purification from CH_2Cl_2–diethyl ether afforded an orange microcrystalline powder, yield 90 mg (59%).

$[\mathrm{Co}\{\eta^5\text{-}C_8H_8(C_7H_7)\}(\eta\text{-}C_5H_5)][PF_6]$ **6** (R = H).—To a stirred solution of $[\mathrm{Co}(\eta^4\text{-cot})(\eta\text{-}C_5H_5)]$ (78 mg, 0.34 mmol) in acetone (30 cm^3) was added $[C_7H_7][PF_6]$ (84 mg, 0.36 mmol). After 5 min the orange solution was filtered through Celite and the solvent volume reduced *in vacuo*. Addition of diethyl ether and purification from CH_2Cl_2–hexane afforded the product as an orange solid, yield 102 mg (53%).

$[\mathrm{Co}\{\eta^5\text{-}C_8H_8(C_7H_7)\}(\eta\text{-}C_5Me_5)][PF_6]$ **7**.—To a stirred solution of $[\mathrm{Co}(\eta^4\text{-cot})(\eta\text{-}C_5Me_5)]$ (103 mg, 0.35 mmol) in acetone (25 cm^3) was added $[C_7H_7][PF_6]$ (97 mg, 0.41 mmol). After 4 h the orange solution was filtered through Celite and the solvent volume reduced *in vacuo*. Addition of diethyl ether gave a red-brown precipitate which was purified from acetone–diethyl ether to give a dark orange powder, yield 0.13 g (68%).

$[\mathrm{Rh}(\eta^2,\eta^3\text{-}C_8H_9)\{\eta\text{-}C_5H_4(C_7H_7)\}][BPh_4]$ **8**.—To a stirred solution of $[\mathrm{Rh}(\eta^4\text{-cot})(\eta\text{-}C_5H_5)]$ (100 mg, 0.37 mmol) in CH_2Cl_2 (20 cm^3) was added $[C_7H_7][BF_4]$ (65 mg, 0.37 mmol). After 30 min the orange solution was evaporated to dryness. The residue was then dissolved in acetone (5 cm^3), treated with $NaBPh_4$ (130 mg, 0.38 mmol) and evaporated to dryness once more. Extraction into CH_2Cl_2, filtration, and addition of diethyl ether to the extract gave a yellow solid which was purified from CH_2Cl_2–diethyl ether to give the product as a yellow solid, yield 164 mg (62%).

$[\mathrm{Rh}\{\eta^2,\eta^3\text{-}C_8H_8(C_7H_7)\}(\eta\text{-}C_5Me_5)][PF_6]$ **9**.—To a stirred solution of $[\mathrm{Rh}(\eta^4\text{-cot})(\eta\text{-}C_5Me_5)]$ (50 mg, 0.15 mmol) in CH_2Cl_2 (25 cm^3) was added $[C_7H_7][PF_6]$ (35 mg, 0.15 mmol). After 1 h the dark yellow solution was filtered through Celite and the solvent volume reduced *in vacuo*. Addition of diethyl ether and purification from CH_2Cl_2–diethyl ether afforded the product as a yellow microcrystalline solid, yield 65 mg (77%).

Crystal Structure Analysis of $[\mathrm{Co}\{\eta^5\text{-}C_8H_8(C_3Ph_3)\}(\eta\text{-}C_5H_5)][BF_4]$.—*Crystal data*. $C_{34}H_{28}BCoF_4$, $M = 582.3$, monoclinic, space group $P2_1/c$ (no. 14), $a = 18.618(5)$, $b = 9.208(2)$, $c = 16.776(5)$ Å, $\beta = 102.43(2)°$, $U = 2808.6(13)$ Å^3, $Z = 4$, $D_c = 1.38$ g cm^{-3}, $\lambda = 0.710\,69$ Å, $\mu = 6.6$ cm^{-1}, $F(000) = 1200$, $T = 295$ K.

Diffraction measurements were made with a Siemens four-circle P3m diffractometer using graphite-monochromated X-radiation on a single crystal (approximate dimensions $0.78 \times 0.46 \times 0.50$ mm) mounted in a thin-walled glass capillary under N_2. Cell dimensions were determined from the setting angle values of 24 centred reflections. A total of 5861 diffracted intensities (including checks) were measured in a unique quadrant of reciprocal space for $4.0 < 2\theta < 50.0°$ by ω Wyckoff scans of width 0.55°. Three check reflections (4 0 −8, 5 4 −6, 6 −2 4) remeasured after every 50 ordinary data showed *ca*. 3% decay and *ca*. 2% variation over the period of data collection; an appropriate correction was therefore applied. Of the 5459 non-check intensity data collected, 4932 unique observations remained after averaging of duplicate and equivalent measurements ($R_{\mathrm{int}} = 0.018$) and deletion of systematic absences. Of these 3695 with $I > 2\sigma(I)$ were retained for use in structure solution and refinement. An absorption correction was applied on the basis of 432 azimuthal scan data; maximum and minimum transmission coefficients were 0.395 and 0.369 respectively. Lorentz and polarisation corrections were applied. The structure was solved by heavy atom (Patterson and Fourier difference) methods, and refined by full-matrix least squares against F. All non-hydrogen atoms were assigned anisotropic displacement parameters except the low-occupancy fluorine atoms (see below). All hydrogen atoms were assigned fixed isotropic displacement parameters and were constrained to ideal geometries with C–H 0.96 Å. The $[BF_4]^-$ anion showed a two-fold site disorder corresponding to two orientations differing by rotation about the F(1)–B(1) bond. Fluorine atoms F(2–4) were assigned (refined) site occupancies of 0.76(1), and F(2A–4A) site occupancies of 0.24(1). Restraints were applied to B–F and F $\cdots$ F distances so as to ensure approximately tetrahedral geometry for each of the two orientations of the $[BF_4]^-$ anion. Refinement of the 374 least-squares variables converged smoothly to residual indices $R = 0.042$, $R' = 0.049$, $S = 1.95$.* Weights, w, were set equal to $[\sigma_c^2(F_o) + gF_o^2]^{-1}$. Here $\sigma_c^2(F_o)$ is the variance in F_o due to counting statistics and $g = 0.0002$ was chosen to minimise the variation in S as a function of F_o. Final difference electron density maps showed no features outside the range +0.4 to −0.3 e Å^{-3}. Table 4 reports the positional parameters for the non-hydrogen atoms.

All calculations were made with programs of the SHELXTL-PLUS[30] system as implemented on a Siemens R3m/V structure determination system. Complex neutral-atom scattering factors were taken from ref. 31.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Acknowledgements

We thank the SERC for a Studentship (to P. M. H.) and Johnson Matthey plc for a generous loan of rhodium trichloride.

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Received 2nd June 1992; *Paper* 2/02896D

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* $R = \Sigma|\Delta|/\Sigma|F_o|$, $R' = [\Sigma w\Delta^2/\Sigma wF_o^2]^{\frac{1}{2}}$, $S = [\Sigma w\Delta^2/(N_o - N_v)]^{\frac{1}{2}}$, $\Delta = F_o - F_c$, N_o = number of observations and N_v = number of variables.