Allylation of Cobalt-co-ordinated Cyclo-octatetraene by the $[Fe\{P(OMe)_3\}(NO)_2(\eta^3\text{-allyl})]^+$ Cation: Ring Closure to 1,2,3,3a-Tetrahydropentalenyl Derivatives and the *X*-Ray Structure of $[Co(\eta^5\text{-}C_8H_8R)(\eta\text{-}C_5Me_5)][PF_6]$ $[R = CH_2C(Me){=}CH_2]$ *

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The reaction of $[Fe\{P(OMe)_3\}(NO)_2(\eta^3\text{-allyl})][PF_6]$ [**1**; allyl = CH_2CHCH_2, $CH_2CHCHMe$, or $CH_2C(Me)CH_2$] with $[Co(\eta^4\text{-cot})(\eta\text{-}C_5R'_5)]$ (**2**; R' = H or Me, cot = cyclo-octatetraene) results in C–C coupling and the formation of 1,2,3,3a-tetrahydropentalenyl derivatives $[Co(\eta^5\text{-}C_8H_8R)(\eta\text{-}C_5R'_5)][PF_6]$ [**3**; R = $CH_2CH{=}CH_2$, $CH_2CH{=}CHMe$, or $CH_2C(Me){=}CH_2$; R' = H or Me]. An *X*-ray diffraction study on $[Co(\eta^5\text{-}C_8H_8R)(\eta\text{-}C_5Me_5)][PF_6]$ [R = $CH_2C(Me){=}CH_2$] confirms the structure assignment with the cobalt atom co-ordinated to an η^5-1,2,3,3a-tetrahydropentalenyl ligand having the 2-methylallyl substituent *exo* to the metal. The co-ordination of the η^5-1,2,3,3a-tetrahydropentalenyl ligand is slightly asymmetric with the substituted carbons furthest from the cobalt. The observed structure shows that complexes (**3**) may also be regarded as substituted cobaltocenium salts, and as such undergo reversible one-electron reduction to the corresponding cobaltocenes at a platinum bead electrode in CH_2Cl_2.

The addition of an electrophile to a co-ordinated hydrocarbon as a route to C–C bonds is largely restricted by the lack of suitable, easily handled carbocations. However, there are now sufficient examples to suggest that stereo- and regio-specific C–C bond coupling can result from the reaction between a cationic hydrocarbon–metal complex, acting as a stable source of a carbonium ion, and a second organotransition-metal compound, acting as a nucleophile. Thus, the terminal carbon of the allyl group of $[Fe(\sigma\text{-allyl})(CO)_2(cp)]$ (cp = η-C_5H_5) couples[1] respectively with the ethylene and C_7 ring of $[Fe(CO)_2(\eta\text{-}C_2H_4)(cp)]^+$ and $[Fe(CO)_3(\eta^5\text{-}C_7H_9)]^+$ (C_7H_9 = cycloheptadienyl); $[Fe(CO)_2L(cp)]^+$ (L = CO or C_2H_4) reacts[2] with $[Fe(cp)(\eta^5\text{-}C_6Me_5CH_2)]^+$ at the exocyclic methylene group to yield $[Fe(cp)(\eta^5\text{-}C_6Me_5CH_2R)]^+$ [R = $(\eta^4\text{-}C_5H_4)Fe(CO)_3$ or $(CH_2CH_2)Fe(CO)_2(cp)$]; and $[M(CH_2)(CO)_n(cp)]^+$ (M = Fe, n = 2; M = Mo, n = 3) act[3] as sources of the methylene cation to alkylate, for example, $[Fe(\sigma\text{-}CH{=}CH_2)(CO)_2(cp)]$ and $[Fe(\sigma\text{-}CH_2CH{=}CH_2)(CO)_2(cp)]$ at the unco-ordinated vinylic and allylic double bonds.

We have recently noted that $[Fe\{P(OMe)_3\}(NO)_2(\eta^3\text{-allyl})][PF_6]$ (**1**; allyl = CH_2CHCH_2, $CH_2CHCHMe$, or $CH_2C(Me)CH_2$)[4] acts as an allyl transfer reagent towards $[M(CO)_2L(\eta^4\text{-cot})]$ (M = Fe, L = $CNBu^t$;[5] M = Ru, L = CO or PPh_3;[6] cot = cyclo-octatetraene), leading to the synthesis of allyl-substituted cot derivatives.[6] We now describe the allylation, by (**1**), of $[Co(\eta^4\text{-cot})(\eta\text{-}C_5R'_5)]$ (**2**; R' = H or Me) which not only results in C–C bond formation, between the C_8 and C_3 fragments, but also in rearrangement of the C_8 ring to give the co-ordinated 1,2,3,3a-tetrahydropentalenyl ligand, as shown by *X*-ray structural studies on $[Co(\eta^5\text{-}C_8H_8R)(\eta\text{-}C_5R'_5)][PF_6]$ [**3**; R = $CH_2C(Me){=}CH_2$, R' = Me]. The complexes (**3**) may be regarded alternatively as substituted cobaltocenium salts, in accord with their reversible one-electron reduction to the corresponding cobaltocenes at a platinum electrode.

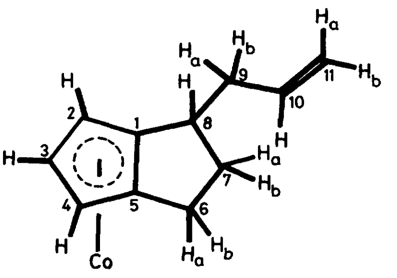

Figure 1. The 1,2,3,3a-tetrahydropentalenylcobalt group of (**3**), with the numbering scheme for the ^1H and ^{13}C n.m.r. spectra

Results and Discussion

The addition of $[Fe\{P(OMe)_3\}(NO)_2(\eta^3\text{-allyl})][PF_6]$ [**1**; allyl = CH_2CHCH_2, $CH_2CHCHMe$, or $CH_2C(Me)CH_2$] to $[Co(\eta^4\text{-cot})(\eta\text{-}C_5R'_5)]$ (**2**; R' = H or Me) in CH_2Cl_2 gives dark brown solutions from which moderate yields of the yellow crystalline salts $[Co(\eta^5\text{-}C_8H_8R)(\eta\text{-}C_5R'_5)][PF_6]$ (**3**; R = allyl, R' = H or Me) may be isolated after chromatography (twice) on alumina.

The elemental analyses of (**3**) (Table 1) suggested that allyl transfer from (**1**) to (**2**) had occurred, as found for $[M(CO)_2L(\eta^4\text{-cot})]$ (M = Fe, L = $CNBu^t$;[5] M = Ru, L = CO or PPh_3[6]), but the ^1H and ^{13}C n.m.r. spectra of (**3**) were unlike those of either $[Ru(CO)_2L(\eta^2,\eta^3\text{-}C_8H_8R)]^+$ (L = CO or PPh_3, R = allyl)[6] or the two observed isomers of $[Fe(CO)_2(CNBu^t)(\eta^5\text{-}C_8H_8R)]^+$ (R = allyl).[5] An *X*-ray study of the ruthenium complex [L = PPh_3, R = $CH_2C(Me)CH_2$] showed an η^2,η^3-bonded cyclo-octatrienyl ring,[6] and the iron complexes contain either η^5-cyclo-octatrienyl or η^5-bicyclo[5.1.0]octadienyl ligands. The n.m.r. spectra of (**3**), however, can only be assigned (Table 1) on the basis of the 1,2,3,3a-tetrahydropentalenyl structure shown in Figure 1.

Only one isomer of (**3**) is formed when (**2**; R' = H or Me) reacts with [**1**; allyl = CH_2CHCH_2 or $CH_2C(Me)CH_2$] but the 1-methylallyl complex [**1**; allyl = $CH_2CHCHMe$] gives a mixture of three isomers, in an approximate 1:1:1 ratio, with

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* (η-Pentamethylcyclopentadienyl)[3a,4—6,6a-η-1,2,3,3a-tetrahydro-1-(2-methylallyl)pentalenyl]cobalt(III) hexafluorophosphate.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Table 1. Analytical, cyclic voltammetric, and n.m.r. spectroscopic data for $[Co(\eta^5\text{-}C_8H_8R)(\eta\text{-}C_5R'_5)][PF_6]$

R′	R	Yield (%)	Analysis[a] (%)		$^1H(\delta)$[b]	^{13}C (p.p.m.)[b]	E°[c]/V
			C	H			
H	$CH_2CH{=}CH_2$	35	46.4 (46.4)	4.6 (4.4)	2.14 (1 H, m, H^{9a} or H^{9b}), 2.23 (1 H, m, H^{9a} or H^{9b}), 2.2—2.7 (4 H, m, H^{6a}, H^{6b}, H^{7a}, H^{7b}), 3.00 (1 H, m, H^8), 5.00 [1 H, dddd, $J(H^{11a}H^{10})$ 16.9, $J(H^{11a}H^{11b})$ 1.6, $J(H^{11a}H^{9a})$ = $J(H^{11a}H^{9b})$ 1.5, H^{11a}], 5.07 [1 H, dddd, $J(H^{11b}H^{10})$ 10.3, $J(H^{11b}H^{11a})$ 1.8, $J(H^{11b}H^9)$ = $J(H^{11b}H^{9b})$ 0.9, H^{11b}], 5.46 [1 H, d, $J(H^2H^3)$ 2.4, H^2], 5.50 [1 H, d, $J(H^4H^3)$ 2.4, H^4], 5.56 (5 H, s, C_5H_5), 5.58 [1 H, dddd, $J(H^3H^2)$ = $J(H^3H^4)$ 2.6, H^3], 5.73 [1 H, dddd, $J(H^{10a}H^{11a})$ 17.2, $J(H^{10a}H^{11b})$ 9.9, $J(H^{10a}H^{9a})$ = $J(H^{10a}H^{9b})$ 7.01, H^{10a}]	24.53 (C^7), 35.78 (C^6), 38.35 (C^8), 38.95 (C^9), 76.61 (C^2, C^4), 85.40 (C_5H_5), 86.04 (C^3), 114.18, 116.24 (C^1, C^5), 118.23 (C^{11}), 135.12 (C^{10})	−0.95
H	$CH_2C(Me){=}CH_2$	46	47.7 (47.7)	4.8 (4.7)	1.76 (3 H, s, Me), 2.09 (2 H, m, $H^{9a}H^{9b}$), 2.1—2.7 (4 H, m, H^{6a}, H^{6b}, H^{7a}, H^{7b}), 3.09 [1 H, m, $J(H^8H^{7a})$ 6.7, $J(H^8H^{9a})$ = $J(H^8H^{9b})$ 7.6, H^8], 4.60 (1 H, m, H^{11a}), 4.84 (1 H, m, H^{11b}), 5.42 [1 H, d, $J(H^2H^3)$ 2.4, H^2], 5.50 [1 H, d, $J(H^4H^3)$ 2.4, H^4], 5.57 (6 H, br s, C_5H_5, H^3)	22.19 (Me), 24.19 (C^7), 35.68 (C^6), 36.62 (C^8), 42.69 (C^9), 76.58 (C^2, C^4), 85.35 (C_5H_5), 85.91 (C^3), 113.51 (C^{11}), 113.96, 116.53 (C^1, C^5), 142.88 (C^{10})	−0.95
H	$CH(Me)CH{=}CH_2$[d]	30	48.1 (47.7)	4.7 (4.7)	1.04 [3 H, d, $J(MeH^9)$ 6.8, Me], 2.0—2.7 (5 H, m, H^{6a}, H^{6b}, H^{7a}, H^{7b}, H^9), 2.86 [1 H, dd, $J(H^8H^9)$ = $J(H^8H^{7a})$ 7.4, H^8], 4.94 [1 H, m, $J(H^{11a}H^{10})$ 17.2, H^{11a}], 4.99 [1 H, m, $J(H^{11b}H^{10})$ 9.9, H^{11b}], 5.3—5.6 (1 H, m, H^{10}), 5.43 [1 H, d, $J(H^2H^3)$ 2.4, H^2], 5.45 [1 H, d, $J(H^4H^3)$ 2.8, H^4], 5.55 (5 H, s, C_5H_5), 5.59 [1 H, t, $J(H^3H^2)$ = $J(H^3H^4)$ 2.3, H^3]	18.27 (Me), 25.29 (C^7), 34.34 (C^6), 42.72, 44.35 (C^8, C^9), 76.64 77.24 (C^2, C^4), 85.45 (C_5H_5), 85.94 (C^3), 114.58, 115.40 (C^1, C^5), 116.28 (C^{11}), 140.48 (C^{10})	
H	*trans*-$CH_2CH{=}CHMe$[d]				1.64 [3 H, d, $J(MeH^{11a})$ 5.0, Me], 2.0—2.7 (6 H, m, H^{6a}, H^{6b}, H^{7a}, H^{7b}, H^{9a}, H^{9b}), 2.93 (1 H, m, H^8), 5.3—5.6 (2 H, m, H^{10}, H^{11a}), 5.47 (1 H, m, H^2), 5.50 (1 H, m, H^4), 5.55 (5 H, s, C_5H_5), 5.58 [1 H, t, $J(H^3H^2)$ = $J(H^3H^4)$ 2.5, H^3]	18.07 (Me), 24.57 (C^7), 35.75 (C^6), 37.83 (C^9), 38.94 (C^8), 76.46, 76.50, 76.56 (C^2, C^4),[e] 85.34 (C_5H_5), 86.02 (C^3), 114.20, 116.48 (C^1C^5), 127.37 (C^{11}), 129.32 (C^{10})	
H	*cis*-$CH_2CH{=}CHMe$[d]				1.46 [3 H, d, $J(MeH^{11b})$ 6.8, Me], 2.0—2.7 (6 H, m, H^{6a}, H^{6b}, H^{7a}, H^{7b}, H^{9a}, H^{9b}), 2.93 (1 H, m, H^8), 5.3—5.6 (2 H, m, $H^{10}H^{11a}$), 5.47 (1 H, m, H^2), 5.50 (1 H, m, H^4), 5.55 (5 H, s, C_5H_5), 5.58 [1 H, t, $J(H^3H^2)$ = $J(H^3H^4)$ 2.5, H^3]	13.05 (Me), 24.62 (C^7), 31.94 (C^9), 36.00 (C^6), 38.81 (C^8), 76.46, 76.50, 76.56 (C^2, C^4),[e] 85.34 (C_5H_5), 86.07 (C^3), 114.16, 116.48 (C^1, C^5), 126.59 (C^{11}), 127.59 (C^{10})	
Me	$CH_2CH{=}CH_2$	35	51.9 (52.1)	6.0 (5.8)	1.94 (15 H, s, C_5Me_5), 2.1—2.5 (6 H, m, H^{6a}, H^{6b}, H^{7a}, H^{7b}, H^{9a}, H^{9b}), 2.68 (1 H, m, H^8), 4.77 [1 H, d, J (H^2H^3) 2.4, H^2], 4.79 [1 H, d, $J(H^4H^3)$ 2.6, H^4], 5.01 [1 H, dd, $J(H^3H^2)$ = $J(H^3H^4)$ 2.5, H^3], 5.01 [1 H, dddd, $J(H^{11a}H^{10})$ 16.9, H^{11a}], 5.07 [1 H, dddd, $J(H^{11b}H^{10})$ 10.3, H^{11b}], 5.70 [1 H, dddd, $J(H^{10}H^{11a})$ 17.1, $J(H^{10}H^{11b})$ 10.0, $J(H^{10}H^{9a})$ = $J(H^{10}H^{9b})$ 7.0, H^{10}]	9.97 ($C_5\mathit{Me}_5$), 21.94 (C^7), 34.81 (C^6), 35.84 (C^8), 39.45 (C^9), 78.92, 79.21 (C^2, C^4), 89.72 (C^3), 96.78 (C_5Me_5), 110.64, 113.21 (C^1, C^5), 118.21 (C^{11}), 135.28 (C^{10})	−1.26
Me	$CH_2C(Me){=}CH_2$	23	52.6 (53.0)	6.3 (6.1)	1.74 (3 H, s, Me), 1.95 (15 H, s, C_5Me_5), 2.0—2.5 (6 H, m, H^{6a}, H^{6b}, H^{7a}, H^{7b}, H^{9a}, H^{9b}), 2.79 (1 H, m, H^8), 4.62 (1 H, br s, H^{11a}), 4.74 [1 H, d, $J(H^2H^3)$ 2.6, H^2], 4.80 [1 H, d, $J(H^4H^3)$ 2.4, H^4], 4.85 (1 H, br s, H^{11b}), 5.01 [1 H, dd, $J(H^3H^2)$ = $J(H^3H^4)$ 2.6, H^3]	9.92 ($C_5\mathit{Me}_5$), 21.65 (C^7) 22.35 (Me), 34.05 (C^8), 34.76 (C^6), 43.22 (C^9), 79.02, 79.21 (C^2, C^4), 89.67 (C^3), 96.74 (C_5Me_5), 110.55, 113.28 (C^1, C^5), 113.37 (C^{11}), 143.01 (C^{10})	−1.25
Me	$CH(Me)CH{=}CH_2$[d]	43	53.0 (53.0)	6.3 (6.1)	0.98 [3 H, d, $J(MeH^9)$ 6.8, Me], 1.94 (15 H, s, C_5Me_5), 2.0—2.5 (5 H, m, H^{6a}, H^{6b}, H^{7a}, H^{7b}, H^9), 2.55 (1 H, m, H^8), 4.78 (2 H, m, H^2, H^4), 4.96 [1 H, m, $J(H^{11b}H^{10})$ 9.5, H^{11b}], 4.99 (1 H, m, H^{11a}), 5.02 [1 H, t, $J(H^3H^2)$ = $J(H^3H^4)$ 2.4, H^3], 5.24—5.64 (1 H, m, H^{10})	9.91 ($C_5\mathit{Me}_5$), 18.03 (Me), 22.54 (C^7), 33.29 (C^6), 41.67, 42.76 (C^8, C^9), 79.18, 79.42 (C^2, C^4), 89.64 (C^3), 96.69 (C_5Me_5), 111.15, 112.13 (C^1, C^5), 116.05 (C^{11}), 140.78 (C^{10})	
Me	*trans*-$CH_2CH{=}CHMe$[d]				1.64 [3 H, m, $J(MeH^{11a})$ 6.0, Me], 1.94 (15 H, s, C_5Me_5), 2.0—2.5 (6 H, m, H^{6a}, H^{6b}, H^{7a}, H^{7b}, H^{9a}, H^{9b}), 2.63 (1 H, m, H^8), 4.73 [1 H, d, $J(H^2H^3)$ 2.6, H^2], 4.78 (1 H, m, H^4), 5.01 [1 H, t, $J(H^3H^2)$ = $J(H^3H^4)$ 2.5, H^3], 5.24—5.64 (2 H, m, H^{10}, H^{11a})	9.91 ($C_5\mathit{Me}_5$), 17.79 (Me), 21.89 (C^7), 34.65 (C^6), 36.22 (C^8), 38.26 (C^9), 78.88, 79.10 (C^2, C^4), 89.64 (C^3), 96.69 (C_5Me_5), 110.56, 113.39, (C^1, C^5), 127.61 (C^{11}), 129.10 (C^{10})	

Table 1 (*continued*)

R′	R	Yield (%)	Analysis[a] (%) C	Analysis[a] (%) H	^{1}H(δ)[b]	^{13}C (p.p.m.)[b]
Me	*cis*-$CH_2CH{=}CHMe$[d]				1.49 [3 H, m, J(MeH^{11b}) 6.8, Me], 1.94 (15 H, s, C_5Me_5), 2.0—2.5 (6 H, m, H^{6a}, H^{6b}, H^{7a}, H^{7b}, H^{9a}, H^{9b}), 2.63 (1 H, m, H^8), 4.78 (2 H, m, H^2, H^4), 5.01 [1 H, t, J(H^{3}H^2) = J(H^{3}H^4) 2.5, H^3], 5.24—5.64 (2 H, m, H^{10}H^{11a})	9.91 (C_5Me_5), 13.10 (Me), 21.97 (C^7), 32.37 (C^9), 34.99 (C^6), 36.19 (C^8), 78.88, 79.10, (C^2, C^4), 89.64 (C^3), 96.69 (C_5Me$_5$), 110.56, 113.39 (C^1, C^5), 126.77 (C^{11}), 127.39 (C^{10})

[a] Calculated values in parentheses. [b] In CD_2Cl_2. [c] Potentials are *versus* the aqueous saturated calomel electrode, at a platinum bead in CH_2Cl_2 with 0.1 mol dm^{-3} $[NBu^n_4][PF_6]$ as supporting electrolyte. Under these conditions, the E° value for the couple $[Fe(\eta\text{-}C_5H_5)_2]$–$[Fe(\eta\text{-}C_5H_5)_2]^+$ is 0.47 V. [d] The yield and elemental analysis refer to the mixture of three isomers (see text). The n.m.r. spectrum of each isomer has been taken from that of the mixture. [e] Peaks due to the *cis* and *trans* isomers overlap.

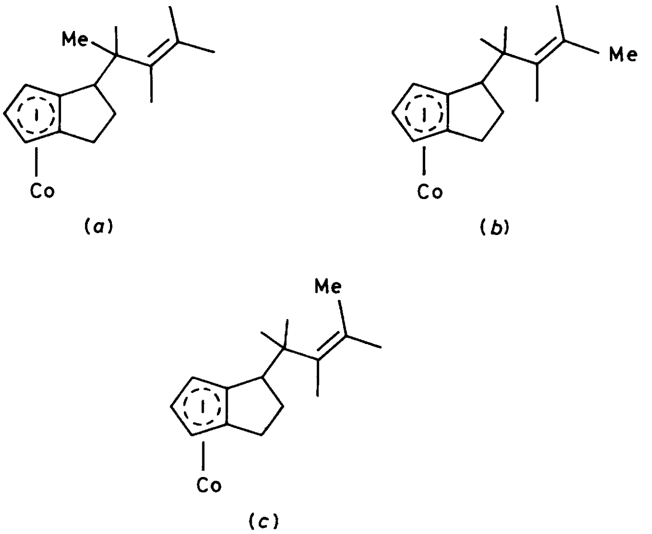

Figure 2. The 1,2,3,3a-tetrahydropentalenylcobalt groups of the three isomers of (3; R = $CH_2CHCHMe$)

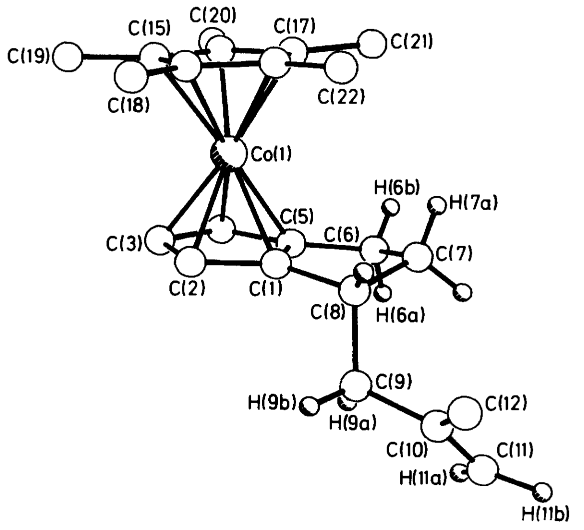

Figure 3. Molecular structure of the $[Co(\eta^5\text{-}C_8H_8R)(\eta\text{-}C_5Me_5)]^+$ [R = $CH_2C(Me){=}CH_2$] cation showing the atomic labelling scheme used. Hydrogen atoms of methyl groups and on carbons C(2), C(3), and C(4) have been omitted for clarity

the 1,2,3,3a-tetrahydropentalenylcobalt groups shown in Figure 2. A partial assignment of the ^{1}H and ^{13}C n.m.r. spectra of the mixtures of isomers is given in Table 1. For the isomer in which the CHMe group is directly attached to the C_5 ring [Figure 2(*a*)], diastereoisomerism is also possible. In the case of the pentamethylcyclopentadienyl compound, only one diastereomer was found, but for the cp complex a trace (< 1%) of the second was detected by the methyl signal at δ 0.983 [d, J(MeH^9) 7 Hz] in the ^{1}H n.m.r. spectrum.

The complexes (3) may also be regarded as substituted cobaltocenium salts and as such undergo one-electron reduction at a platinum bead electrode, to uncharacterised cobaltocene derivatives. Thus, the cyclic voltammograms of [3; R = $CH_2CH{=}CH_2$ or $CH_2C(Me){=}CH_2$, R′ = H or Me] in CH_2Cl_2 show reversible reduction waves at the potentials (Table 1) expected on the basis of those for the reductions of $[Co(cp)_2]^+$ (E^0 = −0.86 V) and $[Co(\eta\text{-}C_5Me_5)_2]^+$ (E^0 −1.48 V) in CH_2Cl_2.[7]

The n.m.r. spectra and electrochemistry of (3) provide good evidence for the rearrangement of co-ordinated cot to the 1,2,3,3a-tetrahydropentalenyl ligand on allylation of (2). However, the structure of [3; R = $CH_2C(Me){=}CH_2$, R′ = Me] was only fully resolved by a single-crystal *X*-ray diffraction study.

The molecular structure of the cation of $[Co(\eta^5\text{-}C_8H_8R)(\eta\text{-}C_5Me_5)][PF_6]$ [R = $CH_2C(Me){=}CH_2$] is illustrated in Figure 3; the atomic co-ordinates are given in Table 2 and selected bond lengths and angles are given in Tables 3 and 4. The cation may be viewed as a substituted cobaltocenium ion formed with η^5-pentamethylcyclopentadienyl and substituted η^5-1,2,3,3a-tetrahydropentalenyl (thp) ligands. The 1,2,3,3a-tetrahydropentalenyl ligand has a 2-methylallyl substituent *exo* to the cobalt on C(8) of the cyclopentene ring. While the C_5Me_5 ring is symmetrically bonded to Co(1) (mean Co–C, 2.040 Å) the η^5-thp ligand is somewhat slipped, with the substituted carbons C(1), C(5) having the longer Co–C distances [2.070(4) and 2.071(4) Å] and C(3) the shortest [2.004(4) Å]. The amount of slip is indicated by the distance, Δ, between the centroid of C(1—5) and the projection of Co(1) on to the plane of that ring, Δ = 0.061 Å. There is no significant variation of C–C bond lengths within the η^5 rings. The two rings are eclipsed [C(19)–C(15)–Co(1)–C(3) 0.1°] and are inclined to one another by 5.3°, presumably to minimise repulsions between methyl groups C(21), C(22) and the second ring of the thp ligand.

The cyclopentene ring of the thp ligand shows a slightly twisted envelope conformation with intraring torsion angles C(8)–C(1)–C(5)–C(6) −2.4, C(7)–C(8)–C(1)–C(5) 17.4, C(6)–C(7)–C(8)–C(1) −25.3, C(5)–C(6)–C(7)–C(8) 24.1, and C(1)–C(5)–C(6)–C(7) −13.6°. The *exo*-2-methylallyl substituent at C(8) [Co(1)–C(1)–C(8)–C(9) 177.2°] adopts a *gauche* conformation with respect to C(8)–C(7) [C(10)–C(9)–C(8)–C(7) 64.1°]. Finally, the terminal methylene group adopts a conformation in which the CH_2 eclipses the C(9)–H(9a) bond.

Table 2. Atomic co-ordinates (× 10^4)

Atom	*x*	*y*	*z*
Co(1)	2 132(1)	717(1)	1 778(1)
C(1)	3 364(3)	1 525(3)	1 893(3)
C(2)	2 824(3)	2 001(4)	2 552(4)
C(3)	2 685(3)	1 221(4)	3 319(4)
C(4)	3 124(3)	273(4)	3 134(4)
C(5)	3 550(3)	467(3)	2 254(4)
C(6)	4 180(4)	−49(4)	1 640(5)
C(7)	4 156(4)	723(4)	669(4)
C(8)	3 885(3)	1 815(3)	1 047(4)
C(9)	4 747(3)	2 475(4)	1 615(4)
C(10)	5 375(3)	2 767(3)	882(4)
C(11)	6 238(4)	2 461(5)	1 072(6)
C(12)	4 958(4)	3 455(6)	−75(6)
C(13)	1 333(3)	751(4)	209(3)
C(14)	859(3)	1 246(3)	942(4)
C(15)	769(3)	471(3)	1 751(4)
C(16)	1 190(3)	−483(3)	1 509(4)
C(17)	1 532(3)	−312(3)	545(4)
C(18)	504(4)	2 366(4)	867(5)
C(19)	306(4)	640(5)	2 693(5)
C(20)	1 251(4)	−1 492(4)	2 166(5)
C(21)	2 000(4)	−1 119(4)	−14(5)
C(22)	1 554(4)	1 269(5)	−783(4)
P(1)	2 356(1)	5 230(1)	1 244(1)
F(1)	1 891(4)	6 066(3)	1 772(5)
F(2)	1 728(3)	5 449(4)	144(4)
F(3)	1 675(3)	4 428(4)	1 484(4)
F(4)	3 045(3)	6 012(4)	1 044(4)
F(5)	2 995(3)	4 976(4)	2 368(3)
F(6)	2 828(4)	4 364(5)	753(4)
F(1′)	2 500(4)	4 809(5)	2 399(3)
F(2′)	2 210(3)	5 622(4)	70(3)
F(3′)	2 381(4)	6 339(3)	1 653(4)
F(4′)	2 332(4)	4 104(3)	819(5)
F(5′)	3 385(3)	5 252(6)	1 362(5)
F(6′)	1 325(3)	5 192(5)	1 115(10)

Table 3. Bond lengths (Å)

Co(1)–C(1)	2.070(4)	Co(1)–C(2)	2.037(4)
Co(1)–C(3)	2.004(4)	Co(1)–C(4)	2.038(4)
Co(1)–C(5)	2.071(4)	Co(1)–C(13)	2.033(4)
Co(1)–C(14)	2.042(4)	Co(1)–C(15)	2.040(4)
Co(1)–C(16)	2.037(4)	Co(1)–C(17)	2.049(4)
C(1)–C(2)	1.411(7)	C(1)–C(5)	1.418(6)
C(1)–C(8)	1.495(6)	C(2)–C(3)	1.423(7)
C(3)–C(4)	1.410(7)	C(4)–C(5)	1.412(7)
C(5)–C(6)	1.493(8)	C(6)–C(7)	1.549(8)
C(7)–C(8)	1.543(7)	C(8)–C(9)	1.551(6)
C(9)–C(10)	1.499(7)	C(10)–C(11)	1.306(7)
C(10)–C(12)	1.486(8)	C(13)–C(14)	1.424(7)
C(13)–C(17)	1.419(6)	C(13)–C(22)	1.502(8)
C(14)–C(15)	1.435(6)	C(14)–C(18)	1.507(7)
C(15)–C(16)	1.423(6)	C(15)–C(19)	1.511(8)
C(16)–C(17)	1.428(7)	C(16)–C(20)	1.508(7)
C(17)–C(21)	1.496(8)		

The Mechanism of the Allylation of (**2**) *by* (**1**).—The mechanism of formation of the 1,2,3,3a-tetrahydropentalenyl group in (**3**) *via* allylation of the cot ligand of (**2**) is complex. The first step is clearly C–C bond coupling between (**1**) and (**2**) to give (**A**) (Scheme), presumably *via* a bimetallic intermediate in which the Fe{P(OMe)$_3$}(NO)$_2$ group is attached to the exocyclic double bond of (**A**). This bimetallic species has not been detected, and complexes of the type [FeL(η^2-alkene)(NO)$_2$] are, as yet, unknown.*

Table 4. Bond angles (°)

C(1)–Co(1)–C(2)	40.2(2)	C(1)–Co(1)–C(3)	67.9(2)
C(2)–Co(1)–C(3)	41.2(2)	C(1)–Co(1)–C(4)	68.1(2)
C(2)–Co(1)–C(4)	69.1(2)	C(3)–Co(1)–C(4)	40.8(2)
C(1)–Co(1)–C(5)	40.0(2)	C(2)–Co(1)–C(5)	67.8(2)
C(3)–Co(1)–C(5)	67.5(2)	C(4)–Co(1)–C(5)	40.2(2)
C(1)–Co(1)–C(13)	111.1(2)	C(2)–Co(1)–C(13)	123.5(2)
C(3)–Co(1)–C(13)	158.0(2)	C(4)–Co(1)–C(13)	160.9(2)
C(5)–Co(1)–C(13)	126.8(2)	C(1)–Co(1)–C(14)	124.7(2)
C(2)–Co(1)–C(14)	106.4(2)	C(3)–Co(1)–C(14)	120.2(2)
C(4)–Co(1)–C(14)	155.8(2)	C(5)–Co(1)–C(14)	161.9(2)
C(13)–Co(1)–C(14)	40.9(2)	C(1)–Co(1)–C(15)	158.9(2)
C(2)–Co(1)–C(15)	121.1(2)	C(3)–Co(1)–C(15)	104.0(2)
C(4)–Co(1)–C(15)	119.3(2)	C(5)–Co(1)–C(15)	156.7(2)
C(13)–Co(1)–C(15)	68.8(2)	C(14)–Co(1)–C(15)	41.2(2)
C(1)–Co(1)–C(16)	160.1(2)	C(2)–Co(1)–C(16)	157.1(2)
C(3)–Co(1)–C(16)	120.2(2)	C(4)–Co(1)–C(16)	105.3(2)
C(5)–Co(1)–C(16)	123.0(2)	C(13)–Co(1)–C(16)	68.7(2)
C(14)–Co(1)–C(16)	69.1(2)	C(15)–Co(1)–C(16)	40.9(2)
C(1)–Co(1)–C(17)	125.8(2)	C(2)–Co(1)–C(17)	160.3(2)
C(3)–Co(1)–C(17)	157.9(2)	C(4)–Co(1)–C(17)	123.1(2)
C(5)–Co(1)–C(17)	110.4(2)	C(13)–Co(1)–C(17)	40.7(2)
C(14)–Co(1)–C(17)	68.9(2)	C(15)–Co(1)–C(17)	68.8(2)
C(16)–Co(1)–C(17)	40.9(2)	Co(1)–C(1)–C(2)	68.7(2)
Co(1)–C(1)–C(5)	70.0(2)	C(2)–C(1)–C(5)	108.2(4)
Co(1)–C(1)–C(8)	132.1(3)	C(2)–C(1)–C(8)	140.1(4)
C(5)–C(1)–C(8)	111.1(4)	Co(1)–C(2)–C(1)	71.2(2)
Co(1)–C(2)–C(3)	68.1(2)	C(1)–C(2)–C(3)	106.8(4)
Co(1)–C(3)–C(2)	70.7(2)	Co(1)–C(3)–C(4)	70.9(3)
C(2)–C(3)–C(4)	109.4(4)	Co(1)–C(4)–C(3)	68.3(2)
Co(1)–C(4)–C(5)	71.2(2)	C(3)–C(4)–C(5)	106.8(4)
Co(1)–C(5)–C(1)	69.9(2)	Co(1)–C(5)–C(4)	68.7(3)
C(1)–C(5)–C(4)	108.7(4)	Co(1)–C(5)–C(6)	129.7(3)
C(1)–C(5)–C(6)	110.4(4)	C(4)–C(5)–C(6)	140.7(4)
C(5)–C(6)–C(7)	102.9(4)	C(6)–C(7)–C(8)	106.5(4)
C(1)–C(8)–C(7)	102.3(4)	C(1)–C(8)–C(9)	108.6(3)
C(7)–C(8)–C(9)	112.0(4)	C(8)–C(9)–C(10)	114.8(4)
C(9)–C(10)–C(11)	122.9(5)	C(9)–C(10)–C(12)	115.7(4)
C(11)–C(10)–C(12)	121.5(6)	Co(1)–C(13)–C(14)	69.9(2)
Co(1)–C(13)–C(17)	70.3(2)	C(14)–C(13)–C(17)	109.0(4)
Co(1)–C(13)–C(22)	127.6(3)	C(14)–C(13)–C(22)	125.1(4)
C(17)–C(13)–C(22)	125.9(5)	Co(1)–C(14)–C(13)	69.2(2)
Co(1)–C(14)–C(15)	69.3(2)	C(13)–C(14)–C(15)	107.1(4)
Co(1)–C(14)–C(18)	127.4(3)	C(13)–C(14)–C(18)	126.3(5)
C(15)–C(14)–C(18)	126.6(5)	Co(1)–C(15)–C(14)	69.5(2)
Co(1)–C(15)–C(16)	69.4(2)	C(14)–C(15)–C(16)	108.1(4)
Co(1)–C(15)–C(19)	126.8(3)	C(14)–C(15)–C(19)	125.8(4)
C(16)–C(15)–C(19)	126.1(4)	Co(1)–C(16)–C(15)	69.7(2)
Co(1)–C(16)–C(17)	70.0(2)	C(15)–C(16)–C(17)	108.2(4)
Co(1)–C(16)–C(20)	126.2(3)	C(15)–C(16)–C(20)	125.1(5)
C(17)–C(16)–C(20)	126.7(4)	Co(1)–C(17)–C(13)	69.0(2)
Co(1)–C(17)–C(16)	69.1(2)	C(13)–C(17)–C(16)	107.5(4)
Co(1)–C(17)–C(21)	128.0(3)	C(13)–C(17)–C(21)	126.6(5)
C(16)–C(17)–C(21)	125.9(4)		

The subsequent conversion of (**A**) to (**3**) involves not only C–C bond formation (transannular ring closure) but also the breaking and making of two C–H bonds, a complex reaction sequence which nevertheless occurs at room temperature.† Several examples exist of the formation of pentalene or pentalenyl ligands from monocyclic C_8 rings (cyclo-octadienes,

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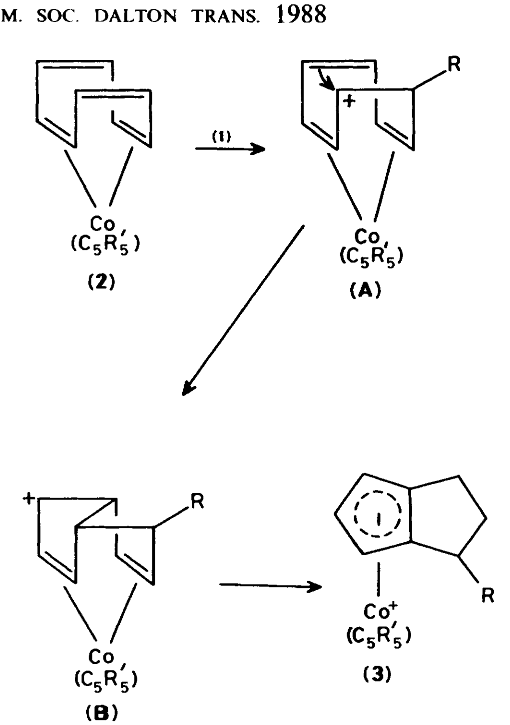
* *Note added in proof:* U.v. photolysis of [Fe(CO)$_2$(NO)$_2$] with 1-butene in liquid xenon at −104 °C gives [Fe(CO)$_{2-n}$(η^2-CH$_2$=CHCH$_2$CH$_3$)$_n$(NO)$_2$] [*n* = 1 or 2) [G. E. Gadd, M. Poliakoff, and J. J. Turner, *Inorg. Chem.*, 1986, **25**, 3604; *trans*-cyclo-octene analogues are also noted in ref. 21 of this paper].

† It should be noted that the isomerisation of (**A**) to (**3**) does not occur during chromatography on alumina; ^{1}H n.m.r. spectroscopy clearly shows the presence of (**3**) in the crude reaction product.



Scheme. R = allyl, R′ = H or Me

cot, *etc.*). Almost invariably, however, these reactions have involved the thermolysis of uncharged species at elevated temperatures,[8] and the mechanisms proposed for the ring closures have involved hydrogen atom migrations. In the Scheme a mechanism is proposed for the formation of (**3**) based on the assumption that a carbocation ligand is bound to cobalt, and that proton rather than hydrogen atom migration is the more likely. The ring-closure step involves nucleophilic attack of the unco-ordinated double bond on the positively charged carbon atom to give (**B**), a process assisted by the 'tub' conformation in (**A**) (a conformation deriving from that of the precursor in which the cot ligand is 1,5-co-ordinated). Here it should be noted that no such ring closure occurs on allylation of $[M(CO)_2L(\eta^4\text{-cot})]$ (M = Fe, L = $CNBu^t$;[5] M = Ru, L = CO or PPh_3[6]) where the cot ligand is 1,3-bonded to the metal and therefore more nearly planar. The formation of (**3**) from (**B**) can then involve a sequence of two deprotonation–protonation reactions, either metal-assisted or intermolecular, with the driving force the eventual creation of the stable cyclopentadienyl-like ligand. That protons must be removed from positions *exo* to the metal may favour the intermolecular pathway.

Experimental

The preparation, purification, and reactions of the complexes described were carried out under an atmosphere of dry nitrogen.

The complexes $[Co(\eta\text{-}C_5R_5)(\eta^4\text{-cot})]$ (R = H[9] or Me[10]) and $[Fe\{P(OMe)_3\}(NO)_2(\eta^3\text{-allyl})][PF_6]$ [allyl = $CH_2CH{=}CH_2$, $CH_2CH{=}CHMe$, $CH_2C(Me){=}CH_2$][4] were prepared by published methods.

Proton and ^{13}C n.m.r. spectra were recorded on a JEOL GX 270 instrument and were calibrated against $SiMe_4$ as an internal reference. Cyclic voltammetric measurements were carried out as previously described.[11] Microanalyses were by the staff of the Microanalytical Service of the School of Chemistry, University of Bristol.

Synthesis of $[Co(\eta^5\text{-}C_8H_8R)(\eta\text{-}C_5H_5)][PF_6]$ [R = $CH_2C(Me){=}CH_2$].—To a stirred solution of $[Co(\eta^4\text{-cot})(\eta\text{-}C_5H_5)]$ (0.15 g, 0.7 mmol) in CH_2Cl_2 (25 cm^3) was added $[Fe\{P(OMe)_3\}(NO)_2\{\eta^3\text{-}CH_2C(Me)CH_2\}][PF_6]$. After 1 h the dark brown solution was filtered, and addition of diethyl ether (*ca.* 100 cm^3) gave a brown solid. Extraction of the solid with CH_2Cl_2 and chromatography on a CH_2Cl_2–alumina column (2 × 15 cm) gave, on elution with acetone–CH_2Cl_2 (1:19), an orange solution, which was evaporated to dryness. The residue was then chromatographed again, in the same manner, and treatment of the yellow eluate with diethyl ether gave the product as a yellow solid, yield 0.08 g (46%).

$[Co(\eta^5\text{-}C_8H_8R)(\eta\text{-}C_5R'_5)][PF_6]$ [R′ = H, R = CH_2CHCH_2; R′ = Me, R = CH_2CHCH_2 or $CH_2C(Me)CH_2$] were prepared similarly. All of the complexes are air-stable yellow solids which dissolve in polar solvents such as CH_2Cl_2 and acetone to give air-stable yellow solutions.

Crystal Structure Analysis of $[Co(\eta^5\text{-}C_8H_8R)(\eta\text{-}C_5Me_5)][PF_6]$ [**3**; R = $CH_2C(Me){=}CH_2$].—*Crystal data.* $C_{22}H_{30}CoF_6P$, M = 498.4, monoclinic, a = 18.849(3), b = 12.645(3), c = 12.465(3) Å, β = 103.78(2)°, U = 2 273.2(9) Å^3, D_c = 1.466 g cm^{-3}, $F(000)$ = 1 032, space group $P2_1/c$ (no. 14), Mo-K_α X-radiation (graphite monochromator), $\bar{\lambda}$ = 0.710 69 Å, $\mu(\text{Mo-}K_\alpha)$ = 8.75 cm^{-1}.

Diffraction measurements were made on a single crystal of [**3**, R = $CH_2C(Me)CH_2$] (dimensions *ca.* 0.88 × 0.2 × 0.07 mm), mounted in air on a glass fibre, using a Nicolet *P*3*m* diffractometer at room temperature. Intensity data were collected for a unique quadrant of reciprocal space by $\theta/2\theta$ scans in the range $4 < 2\theta < 50°$. Of 4 710 intensities measured, 3 989 remained after averaging of duplicate and symmetry equivalent data; of these, 2 929 with $I > \sigma(I)$ were used in structure solution and refinement. An absorption correction was applied to these intensities, based on 315 azimuthal scan data; transmission coefficients varied between 0.748 and 0.623. The structure was solved by conventional heavy-atom methods, and refined by blocked-cascade least squares. All non-hydrogen atoms were assigned anisotropic vibrational parameters; hydrogen atoms having isotropic parameters were constrained to idealised geometries (C–H 0.96 Å), except for the terminal methylene group which was not so constrained. The $[PF_6]^-$ anion has two-fold disorder with F(1)–F(6) having occupancy 0.498(5) and F(1′)–F(6′) 0.502(5). Refinement converged to final residuals R = 0.053, R' = 0.065, and S = 1.54* where weights $w = [\sigma_c^2(F_o) + 0.000\,85\,F_o^2]^{-1}$ were assigned to intensity data [$\sigma_c^2(F_o)$ being variance in F_o due to counting statistics]. Final electron-density difference maps showed no features of magnitude >0.4 e Å^{-3}. Complex neutral-atom scattering factors were taken from ref. 12. All calculations were made using the SHELXTL program system.[13] Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters, H-atom co-ordinates, and remaining bond lengths and angles.

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* $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}}$, $S = [\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{var})]^{\frac{1}{2}}$.

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