Annelation of Ring-opened Arylcyclopropenium Ions to Co-ordinated Cyclo-octatetraene, and the *X*-Ray Crystal Structure of $[Fe(CO)_3(\sigma,\eta^3\text{-}C_{11}H_9Ph_3)]$ *

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The cyclo-octatetraene (cot) complexes $[M(CO)_3(\eta^4\text{-cot})]$ (M = Fe or Ru) undergo electrophilic addition reactions with arylcyclopropenium ions as their $[BF_4]^-$ salts, $[C_3Ph_2R][BF_4]$ (R = H or Ph), to give $[M(CO)_3(\eta^2:\eta^3\text{-}C_{11}H_8Ph_2R)][BF_4]$ (**1**; M = Fe or Ru, R = H or Ph); hydride addition to (**1**; M = Fe, R = Ph) yields $[Fe(CO)_3(\sigma,\eta^3\text{-}C_{11}H_9Ph_3)]$ (**2**). The *X*-ray structure of compound (**2**) shows the ring-opened cyclopropenium ion to be bonded to the original cot ring *via* three new carbon–carbon bonds. The resulting polycyclic hydrocarbon ligand is attached to the iron atom by a σ,η^3-bonded eight-membered ring, and also contains substituted cyclopentene, cyclohexane, and cyclohexenyl moieties. Complex (**2**) crystallises in the monoclinic space group $P2_1/n$, and the structure has been refined to $R(R') = 0.073$ (0.077) for 2 484 reflections [$I \geqslant 3.0\sigma(I)$].

The reactions of substituted cyclopropenium ions with transition-metal substrates generally result in metal–carbon bond formation; the products include σ-[1] and η^3-cyclopropenyls,[2–4] and four-membered metallacycles.[5] Carbon–carbon bond formation appears to be confined to those reactions in which η^3-oxocyclobutenyl ligands result from initial attack at co-ordinated CO,[2,4,6] and to those between $[C_3Bu^t_3]^+$ and $[M(CO)_3(cp)]^-$ (cp = η-C_5H_5) which give the cyclopropenyl-substituted cyclopentadienyl complexes $[MH(CO)_3\{\eta^5\text{-}C_5H_4(C_3Bu^t_3)\}]$ (M = Mo or W).[7]

We now give details[8] of the reactions between $[C_3Ph_2R][BF_4]$ (R = H or Ph) and $[M(CO)_3(\eta^4\text{-cot})]$ (M = Fe or Ru, cot = cyclo-octatetraene) which yield $[M(CO)_3(\eta^2:\eta^3\text{-}C_{11}H_8Ph_2R)][BF_4]$ (**1**; R = H or Ph) in which the ring-opened cyclopropenium ion is annelated to the co-ordinated eight-membered ring. The *X*-ray structure of $[Fe(CO)_3(\sigma,\eta^3\text{-}C_{11}H_9Ph_3)]$ (**2**), the hydride adduct of (**1**; M = Fe, R = Ph), confirmed the formation of three new carbon–carbon bonds.

Results and Discussion

The prolonged reaction of $[M(CO)_3(\eta^4\text{-cot})]$ (M = Fe or Ru, cot = cyclo-octatetraene) with $[C_3Ph_3][BF_4]$ in acetone gives an orange solution from which moderate yields of yellow crystalline $[M(CO)_3(\eta^2:\eta^3\text{-}C_{11}H_8Ph_2R)][BF_4]$ (**1**; M = Fe or Ru, R = Ph) are readily isolable. The empirical formula of the salts was established by elemental analysis, and the carbonyl i.r. spectrum (Table 1) confirmed the cationic nature of the metal-containing product and the retention of all three carbonyl ligands. The ^1H and ^{13}C n.m.r. spectra (Table 2) were, however, complex and the structure of compound (**1**) could not be assigned; suitable crystals for an *X*-ray diffraction study were also unavailable.

The reaction of (**1**; M = Fe, R = Ph) with $NaBH_4$ in tetrahydrofuran (thf) rapidly gave a solution of the complex $[Fe(CO)_3(\sigma,\eta^3\text{-}C_{11}H_9Ph_3)]$ (**2**), readily isolated after column chromatography as yellow crystals (Table 1). Although the ^1H and ^{13}C n.m.r. spectra (Table 2) were again impossible to assign, suitable crystals of (**2**) were obtained and an *X*-ray diffraction study was successfully completed.

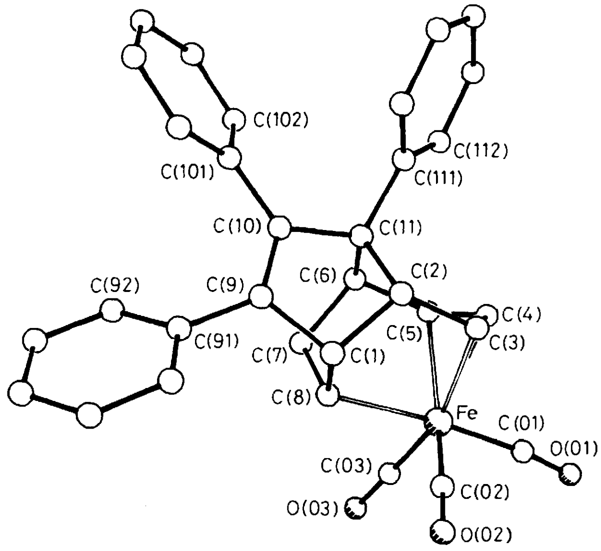

Figure 1. The molecular structure of $[Fe(CO)_3(\sigma,\eta^3\text{-}C_{11}H_9Ph_3)]$ (**2**) showing the atom numbering scheme. The hydrogen atoms are omitted for clarity

The results of the diffraction study are illustrated in Figure 1 which shows the molecular structure and crystallographic numbering scheme; selected bond lengths and angles are given in Table 3. The molecule consists of an eight-membered ring σ,η^3-bonded to the metal atom of an $Fe(CO)_3$ group and joined to a ring-opened triphenylcyclopropenium ion by three carbon–carbon bonds.

The bonding of the eight-membered ring to the metal atom is similar to that recently found in the octafluorocyclo-octatetraene complex $[Fe(CO)_3(\sigma,\eta^3\text{-}C_8F_8)]$,[9] and previously proposed for $[Os(CO)_3(\sigma,\eta^3\text{-}C_8H_8)]$ [10] (**A**). The σ bond Fe–C(8) is typical of other such bonds, for which values of 2.08—2.16 Å have been observed.[11] The allyl group C(3)–C(4)–C(5) is η^3-bound to iron with the Fe–C bond lengths [Fe–C(3) 2.184(6), Fe–C(4) 2.099(6), and Fe–C(5) 2.194(7) Å] very similar to those in, for example, $[\{Fe(CO)_3(\eta^3\text{-}C_3H_5)\}_2]$ (2.195, 2.104, and 2.208 Å)[12] and the cyclo-octenyl complex $[Fe\{P(OMe)_3\}_3(\eta^3\text{-}C_8H_{13})]$ (2.135, 2.028, and 2.170 Å).[13]

The eight-membered ring itself shows approximate mirror

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* Tricarbonyl(9—11-η-5,6,7-triphenyltricyclo[5.4.0.0^{4,8}]undeca-5,10-dien-9-yl)iron.

Supplementary data available (No. SUP 56144, 7 pp.): thermal parameters, H-atom co-ordinates, complete bond lengths and angles. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Table 1. Infrared spectroscopic and analytical data

		Analysis (%)	
Compound	$\tilde{\nu}$(CO)^a/cm^{-1}	C	H
$[Fe(CO)_3(\eta^2:\eta^3-C_{11}H_8Ph_3)][BF_4]$ (**1**; M = Fe, R = Ph)	2 104, 2 056, 2 042 (sh)	63.9 (64.2)	4.2 (3.8)
$[Ru(CO)_3(\eta^2:\eta^3-C_{11}H_8Ph_3)][BF_4]$ (**1**; M = Ru, R = Ph)	2 127, 2 078, 2 064	59.4 (59.7)	3.3 (3.6)
$[Fe(CO)_3(\eta^2:\eta^3-C_{11}H_9Ph_2)][BF_4]$ (**1**; M = Fe, R = H)	2 106, 2 056, 2 046	58.8 (59.8)	3.6 (3.7)
$[Ru(CO)_3(\eta^2:\eta^3-C_{11}H_9Ph_2)][BF_4]$ (**1**; M = Ru, R = H)	2 126, 2 075, 2 064	54.5 (55.0)	3.5 (3.4)
$[Fe(CO)_3(\sigma,\eta^3-C_{11}H_9Ph_3)]$ (**2**)	2 052, 1 989, 1 985 (sh)^c	75.5 (75.0)	4.8 (4.7)

^{a} In CH_2Cl_2 unless stated otherwise. ^{b} Calculated values in parentheses. ^{c} In n-hexane.

Table 2. Proton and ^{13}C n.m.r. spectral data (δ/p.p.m.)^a

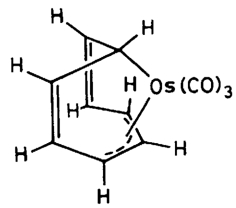
Complex	^{1}H^b	^{13}C^c
(**1**; M = Fe, R = Ph)	3.66 [1 H, m, $J(H^2H^1)$ 6, $J(H^2H^3)$ 6, H^2], 4.11 [1 H, t, $J(H^7H^6)$ 7, $J(H^7H^8)$ 7, H^7], 4.36 [1 H, dd, $J(H^1H^2)$ 6, $J(H^1H^8)$ 5, H^1], 4.77 [1 H, td, $J(H^3H^4)$ 6, $J(H^3H^2)$ 6, $J(H^3H^5)$ 2, H^3], 4.87 [1 H, ddd, $J(H^6H^5)$ 7, $J(H^6H^7)$ 7, $J(H^6H^2)$ 2, H^6], 5.88 [1 H, ddd, $J(H^5H^6)$ 7, $J(H^5H^4)$ 6, $J(H^5H^3)$ 2, H^5], 6.05 [1 H, dd, $J(H^4H^5)$ 6, $J(H^4H^3)$ 6, H^4], 6.50 [1 H, ddd, $J(H^8H^7)$ 7, $J(H^8H^1)$ 5, $J(H^8H^2)$ 1, H^8], 7.21 (15 H, m, C_6H_5)	31.20 (C^1), 53.24, 54.30, 54.70, 58.04 (C^2, C^3, C^5, C^6), 58.89 (C^{11}), 70.86 (C^4), 95.83, 96.11 (C^7, C^8), 128.19, 128.25, 128.76, 128.87, 128.97, 129.14, 129.44, 130.06, 134.79, 136.32, 138.97, 139.45, 149.65 (C_6H_5), 205.27, 206.47, 206.81 (CO)^d
(**1**; M = Ru, R = Ph)	3.86 (1 H, m, H^6), 4.18 (2 H, m, H^1, H^7), 4.68 [1 H, td, $J(H^5H^4)$ 7, $J(H^5H^6)$ 7, $J(H^5H^3)$ 2, H^5], 4.79 [1 H, ddd, $J(H^2H^3)$ 8, $J(H^2H^1)$ 6, $J(H^2H^6)$ 2, H^2], 5.24 [1 H, ddd, $J(H^3H^4)$ 6, $J(H^3H^2)$ 8, $J(H^3H^5)$ 2, H^3], 5.81 [1 H, dd, $J(H^4H^3)$ 6, $J(H^4H^5)$ 7, H^4], 6.59 [1 H, m, $J(H^8H^1)$ 5, $J(H^8H^7)$ 7, H^8], 7.22 (15 H, m, C_6H_5)	33.31 (C^1), 49.50, 56.00, 58.65, 61.00, 66.07 (C^2, C^3, C^4, C^5, C^6), 59.67 (C^{11}), 100.70, 102.87 (C^7, C^8), 128.66, 128.76, 129.17, 129.34, 129.58, 129.92, 130.63, 131.93, 137.13, 139.96 (C_6H_5)
(**1**; M = Fe, R = H)	3.31 [1 H, ddd, $J(H^2H^3)$ 7, $J(H^2H^1)$ 6, $J(H^2H^6)$ 2, H^2], 3.75 [1 H, t, $J(H^7H^8)$ 6, $J(H^7H^6)$ 6, H^7], 3.97 [1 H, ddd, $J(H^1H^9)$ 3, $J(H^1H^8)$ 6, $J(H^1H^2)$ 6, H^1], 4.46 [1 H, ddd, $J(H^3H^4)$ 7, $J(H^3H^2)$ 7, $J(H^3H^5)$ 2, H^3], 4.89 [1 H, ddd, $J(H^6H^7)$ 6, $J(H^6H^5)$ 6, $J(H^6H^2)$ 2, H^6], 5.92 (3 H, m, H^5, H^4, H^8), 6.64 [1 H, d, $J(H^9H^1)$ 3, H^9], 7.25 (10 H, m, C_6H_5)	31.52 (C^1), 52.62, 52.87, 54.43, 58.93 (C^2, C^3, C^5, C^6), 56.68 (C^{11}), 70.65 (C^4), 94.89, 95.72 (C^7, C^8), 127.87, 128.26, 128.56, 128.75, 128.90, 129.09, 129.39, 129.68, 135.69, 139.79, 145.71 (C_6H_5), 138.38 (C^9)^{e,f}
(**1**; M = Ru, R = H)	3.53 [1 H, m, $J(H^2H^1)$ 6, H^2], 3.79 [1 H, m, $J(H^1H^2)$ 6, $J(H^1H^8)$ 5, H^1], 3.96 [1 H, t, $J(H^7H^6)$ 7, $J(H^7H^8)$ 7, H^7], 4.51 [1 H, td, $J(H^3H^4)$ 7, $J(H^3H^2)$ 7, $J(H^3H^5)$ 2, H^3], 4.92 [1 H, ddd, $J(H^6H^5)$ 7, $J(H^6H^7)$ 7, $J(H^6H^2)$ 2, H^6], 5.39 [1 H, ddd, $J(H^5H^4)$ 6, $J(H^5H^6)$ 7, $J(H^5H^3)$ 2, H^5], 5.83 [1 H, dd, $J(H^4H^3)$ 7, $J(H^4H^5)$ 6, H^4], 6.33 [1 H, ddd, $J(H^8H^1)$ 5, $J(H^8H^7)$ 7, $J(H^8H^2)$ 1, H^8], 6.70 [1 H, d, $J(H^9H^1)$ 3, H^9], 7.25 (10 H, m, C_6H_5)	33.34 (C^1), 48.00, 54.65, 59.83, 60.71, 65.41 (C^2, C^3, C^4, C^5, C^6), 57.00 (C^{11}), 99.72, 101.97 (C^7, C^8), 127.78, 128.08, 128.86, 129.44, 139.32 (C_6H_5), 144.99 (C^9), 217.83 (CO)^{d,f}
(**2**; M = Fe)	2.16 (1 H, m, H^8), 2.54 [1 H, m, $J(H^7H^{7'})$ 13, H^7], 2.68 [1 H, m, $J(H^7H^{7'})$ 13, H$^{7'}$], 3.26 (1 H, m, H^6), 3.43 (1 H, m, H^2), 4.19 [1 H, t, $J(H^1H^2)$ 6, $J(H^1H^8)$ 6, H^1], 4.44 [1 H, ddd, $J(H^3H^2)$ 6, $J(H^3H^4)$ 7, $J(H^3H^5)$ 2, H^3], 5.27 [1 H, m, $J(H^4H^3)$ 7, $J(H^4H^5)$ 7, H^4], 6.02 [1 H, td, $J(H^5H^4)$ 7, $J(H^5H^6)$ 7, $J(H^5H^3)$ 2, H^5], 6.95 (15 H, m, C_6H_5)^g	

^{a} In CD_3NO_2 unless stated otherwise. Numbering as in Scheme. *J* values in Hz. ^{b} 200-MHz Spectra. Chemical shifts downfield from SiMe$_4$. ^{c} 50-MHz Spectra unless stated otherwise. Chemical shifts downfield from SiMe$_4$. ^{d} In $(CD_3)_2CO$. ^{e} In CD_3CN. ^{f} 22.5-MHz Spectrum. ^{g} In $CDCl_3$.

symmetry (maximum deviation 0.06 Å) with the pseudo-mirror plane passing through C(4) and C(8) and lying perpendicular to the vectors C(1) ··· C(7), C(2) ··· C(6), and C(3) ··· C(5). The four atoms C(2), C(3), C(5), and C(6) are exactly coplanar (plane A) and show a dihedral angle of 111° with the mean plane of C(1), C(2), C(6), and C(7) (plane B). The atom C(8) is displaced towards the iron atom such that the mean plane of C(1), C(7), and C(8) (plane C) describes an angle of 121° with plane B. The

Table 3. Selected interatomic distances (Å) and angles (°) for $[Fe(CO)_3(\sigma,\eta^3\text{-}C_{11}H_9Ph_3)]$ (**2**) with estimated standard deviations in parentheses

Fe–C(01)	1.822(7)	Fe–C(02)	1.762(7)	C(5)–C(6)	1.534(9)	C(6)–C(7)	1.516(8)
Fe–C(03)	1.732(9)	Fe–C(3)	2.184(6)	C(8)–C(1)	1.540(8)	C(8)–C(7)	1.499(10)
Fe–C(4)	2.099(6)	Fe–C(5)	2.194(7)	C(92)–C(93)	1.395(0)	C(93)–C(94)	1.395(0)
Fe–C(8)	2.122(6)	C(01)–O(01)	1.142(8)	C(94)–C(95)	1.395(0)	C(95)–C(96)	1.395(0)
C(02)–O(02)	1.148(9)	C(03)–O(03)	1.177(11)	C(91)–C(92)	1.395(0)	C(91)–C(96)	1.395(0)
C(9)–C(10)	1.359(8)	C(9)–C(1)	1.529(9)	C(102)–C(103)	1.395(0)	C(103)–C(104)	1.395(0)
C(9)–C(91)	1.492(7)	C(10)–C(11)	1.545(8)	C(104)–C(105)	1.395(0)	C(105)–C(106)	1.395(0)
C(10)–C(101)	1.481(7)	C(11)–C(2)	1.555(10)	C(101)–C(102)	1.395(0)	C(101)–C(106)	1.395(0)
C(11)–C(6)	1.576(8)	C(11)–C(111)	1.531(7)	C(112)–C(113)	1.395(0)	C(113)–C(114)	1.395(0)
C(1)–C(2)	1.520(8)	C(3)–C(2)	1.525(9)	C(114)–C(115)	1.395(0)	C(115)–C(116)	1.395(0)
C(3)–C(4)	1.400(9)	C(4)–C(5)	1.368(11)	C(111)–C(112)	1.395(0)	C(111)–C(116)	1.395(0)
C(01)–Fe–C(02)	97.0(3)	C(01)–Fe–C(03)	89.9(3)	Fe–C(3)–C(2)	105.9(4)	Fe–C(3)–C(4)	67.6(3)
C(02)–Fe–C(03)	99.1(4)	C(01)–Fe–C(3)	103.9(3)	C(2)–C(3)–C(4)	118.2(7)	Fe–C(4)–C(3)	74.3(4)
C(02)–Fe–C(3)	89.4(3)	C(03)–Fe–C(3)	163.0(4)	Fe–C(4)–C(5)	75.3(4)	C(3)–C(4)–C(5)	118.3(6)
C(01)–Fe–C(4)	84.7(3)	C(02)–Fe–C(4)	124.6(3)	Fe–C(5)–C(4)	67.7(4)	Fe–C(5)–C(6)	106.1(4)
C(03)–Fe–C(4)	136.3(4)	C(3)–Fe–C(4)	38.1(2)	C(4)–C(5)–C(6)	119.3(5)	C(11)–C(6)–C(5)	111.7(5)
C(01)–Fe–C(5)	99.7(3)	C(02)–Fe–C(5)	152.7(2)	C(11)–C(6)–C(7)	111.1(5)	C(5)–C(6)–C(7)	106.1(5)
C(03)–Fe–C(5)	102.4(4)	C(3)–Fe–C(5)	65.7(3)	C(6)–C(7)–C(8)	106.0(6)	Fe–C(8)–C(1)	108.5(4)
C(4)–Fe–C(5)	37.1(3)	C(01)–Fe–C(8)	172.4(3)	Fe–C(8)–C(7)	103.3(4)	C(1)–C(8)–C(7)	111.4(5)
C(02)–Fe–C(8)	84.4(3)	C(03)–Fe–C(8)	82.5(3)	C(93)–C(92)–C(91)	120.0(0)	C(92)–C(93)–C(94)	120.0(0)
C(3)–Fe–C(8)	83.6(2)	C(4)–Fe–C(8)	100.7(2)	C(93)–C(94)–C(95)	120.0(0)	C(94)–C(95)–C(96)	120.0(0)
C(5)–Fe–C(8)	81.9(2)	Fe–C(01)–O(01)	174.0(7)	C(95)–C(96)–C(91)	120.0(0)	C(9)–C(91)–C(92)	120.7(3)
Fe–C(02)–O(02)	176.3(6)	Fe–C(03)–O(03)	178.4(7)	C(9)–C(91)–C(96)	119.3(3)	C(92)–C(91)–C(96)	120.0(0)
C(10)–C(9)–C(1)	109.0(5)	C(10)–C(9)–C(91)	130.0(6)	C(103)–C(102)–C(101)	120.0(0)	C(102)–C(103)–C(104)	120.0(0)
C(1)–C(9)–C(91)	119.7(5)	C(9)–C(10)–C(11)	109.0(5)	C(103)–C(104)–C(105)	120.0(0)	C(104)–C(105)–C(106)	120.0(0)
C(9)–C(10)–C(101)	128.1(5)	C(11)–C(10)–C(101)	122.9(5)	C(105)–C(106)–C(101)	120.0(0)	C(10)–C(101)–C(102)	120.3(2)
C(10)–C(11)–C(2)	99.5(4)	C(10)–C(11)–C(6)	109.2(5)	C(10)–C(101)–C(106)	119.6(2)	C(102)–C(101)–C(106)	120.0(0)
C(2)–C(11)–C(6)	105.7(5)	C(10)–C(11)–C(111)	113.9(4)	C(113)–C(112)–C(111)	120.0(0)	C(112)–C(113)–C(114)	120.0(0)
C(2)–C(11)–C(111)	113.4(5)	C(6)–C(11)–C(111)	114.0(4)	C(113)–C(114)–C(115)	120.0(0)	C(114)–C(115)–C(116)	120.0(0)
C(9)–C(1)–C(2)	101.4(5)	C(9)–C(1)–C(8)	109.5(5)	C(115)–C(116)–C(111)	120.0(0)	C(11)–C(111)–C(112)	122.1(2)
C(2)–C(1)–C(8)	106.5(4)	C(11)–C(2)–C(1)	100.2(5)	C(11)–C(111)–C(116)	117.9(2)	C(112)–C(111)–C(116)	120.0(0)
C(11)–C(2)–C(3)	112.7(5)	C(1)–C(2)–C(3)	115.4(5)				



(A)

π-allyl fragment is inclined away from the iron atom making an angle of 152° with plane A.

The annelation of the ring-opened cyclopropenium ion, C(9)—C(11), to the original cot ligand of $[Fe(CO)_3(\eta^4\text{-cot})]$ results in three new rings. Thus, the formation of bonds between C(9) and C(1), C(2) and C(11), and C(6) and C(11) generates a cyclopentene ring [C(1)C(2)C(11)C(10)C(9), ring D], a cyclohexane ring [C(1)C(2)C(3)C(11)C(6)C(7)C(8), ring E], and a cyclohexenyl ring [C(2)C(3)C(4)C(5)C(6)C(11), ring F]; rings D and E are fused along C(1)–C(2) and C(2)–C(11), and ring F is fused to both D and E along C(2)–C(11).

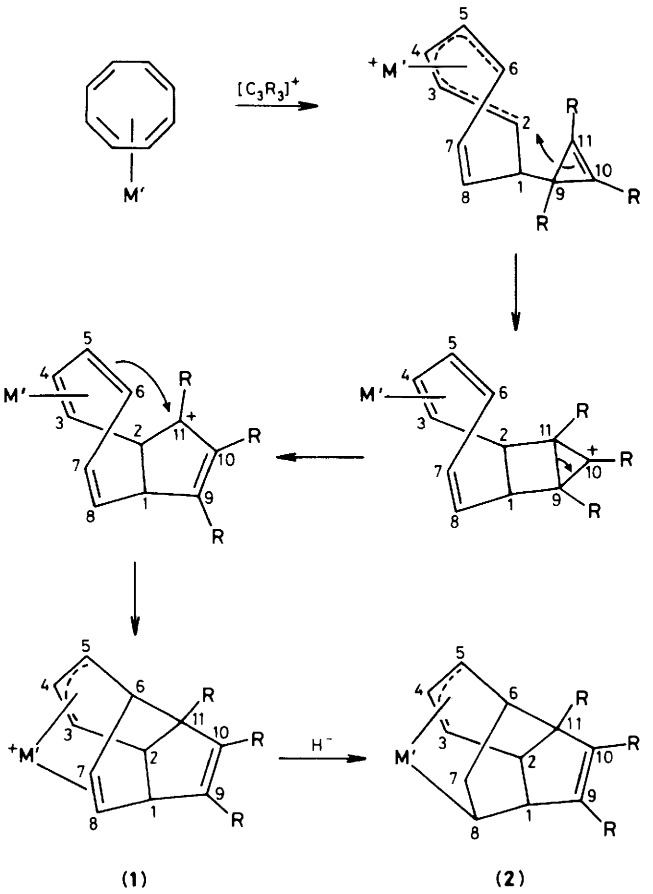
The cyclopentene ring D, containing the C–C double bond C(9)–C(10), has an envelope conformation with the fold about C(1) · · · C(11) (dihedral angle 134°). The cyclohexane ring E has a chair conformation, with the C–C distances close to those found[14] in C_6H_{12} itself and the planes C and C(2)C(11)C(6) (plane G) folded with respect to plane B by 121° (see above) and 116°, respectively. The cyclohexenyl ring F has a boat conformation in which the folding of the π-allyl group with respect to plane A is described above, and the latter plane is more acutely inclined at 133° to plane G.

In the light of the *X*-ray structure of compound (**2**), the ^1H and ^{13}C n.m.r. spectra have been rationalised (Table 2); the assignments of the ^1H n.m.r. spectra are fully consistent with ^1H-$\{^1H\}$ decoupling experiments.

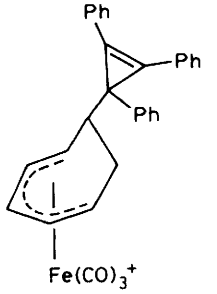
The presence of two hydrogen atoms bonded to atom C(7) of (**2**) suggests this to be the site of hydride attack on (**1**), and on this assumption complex (**1**) is assigned the formula $[M(CO)_3(\eta^2{:}\eta^3\text{-}C_{11}H_8Ph_2R)]^+$ (M = Fe or Ru, R = H or Ph) and the structure shown in the Scheme. The ^1H and ^{13}C n.m.r. spectra (Table 2) are fully in accord with this structure, and nucleophilic addition reactions are to be expected at a co-ordinated alkene, rather than an allyl group, according to the Davies–Green–Mingos rules.[15]

The proposed mechanism for the formation of compound (**1**; R = Ph) from $[M(CO)_3(\eta^4\text{-cot})]$ and $[C_3Ph_3]^+$ is shown in the Scheme. The first step in the sequence, namely the electrophilic addition of the intact cyclopropenium ion to the C_8 ligand, has precedence in the reaction between $[M(CO)_3(cp)]^-$ and $[C_3Bu^t_3]^+$,[7] and in the observation that $[Fe(CO)_3(\eta^4\text{-}C_7H_8)]$ (C_7H_8 = cycloheptatriene) and $[C_3Ph_3]^+$ afford[16] the η^5-cycloheptadienyl derivative $[Fe(CO)_3\{\eta^5\text{-}C_7H_8(C_3Ph_3)\}]^+$ (**B**). In an attempt to verify the subsequent steps in the mechanism, the reactions between $[M(CO)_3(\eta^4\text{-cot})]$ (M = Fe or Ru) and $[C_3Ph_2H]^+$ have been investigated.

On adding $[C_3Ph_2H][BF_4]$ to $[M(CO)_3(\eta^4\text{-cot})]$ in CH_2Cl_2, near-quantitative yields of the crystalline yellow (M = Fe) or white (M = Ru) salts $[M(CO)_3(\eta^2{:}\eta^3\text{-}C_{11}H_8Ph_2R)][BF_4]$ (**1**; M = Fe or Ru, R = H) (Table 1) are rapidly precipitated. The ^1H and ^{13}C n.m.r. spectra (Table 2) are very similar to those of the triphenylcyclopropenium ion derivatives, differing mainly in the appearance of a doublet at *ca.* δ 6.7 (*J* = 3 Hz). Proton–proton decoupling experiments show that this signal is due to the proton, attached to C(9), which originated from the



Scheme. M' = Fe(CO)$_3$ or Ru(CO)$_3$



(B)

[C_3Ph_2H]$^+$ ion. While this observation serves to confirm that electrophilic attack at C(1) is the first step in the mechanism, subsequent steps remain undefined. Attempts to identify products from the reactions of [M(CO)$_2$(PPh$_3$)(η^4-cot)] (M = Fe or Ru) with [C$_3$Bu$^t_3$]$^+$ were unsuccessful.

Experimental

The preparation, purification, and reactions of the complexes described were carried out under an atmosphere of dry nitrogen. Unless stated otherwise, the purification of a complex involved dissolution in CH_2Cl_2, filtration, addition of n-hexane, and partial evaporation of the solvent mixture *in vacuo* to induce precipitation; the solid products are air-stable, dissolving in polar solvents such as acetone and CH_2Cl_2 to give moderately air-sensitive solutions. The compounds [M(CO)$_3$(η^4-cot)] (M = Fe[17] or Ru[18]) and [C$_3$Ph$_2$R][BF$_4$] (R = H[19] or Ph[20]) were prepared by published methods.

I.r. spectra were recorded on Perkin-Elmer 257 or Nicolet FT 7199 instruments and calibrated against the absorption band of polystyrene at 1 601 cm^{-1}. Proton n.m.r. spectra were recorded on a JEOL FX 200 spectrometer, and ^{13}C n.m.r. spectra on JEOL FX 90Q or FX 200 instruments; both were calibrated against SiMe$_4$ as an internal standard.

Microanalyses were by the staff of the Microanalytical Service of the School of Chemistry, University of Bristol. Melting points are uncorrected.

Syntheses.—[Fe(CO)$_3$(η^2:η^3-C$_{11}$H$_8$Ph$_3$)][BF$_4$](**1**; M = Fe, R = Ph). After stirring a solution of [C$_3$Ph$_3$][BF$_4$] (1.45 g, 4.10 mmol) and [Fe(CO)$_3$(η^4-cot)] (1.0 g, 4.10 mmol) for 10 d in acetone (200 cm^3) the solvent was removed *in vacuo*. Unreacted [Fe(CO)$_3$(η^4-cot)] was extracted into n-hexane, and the remaining yellow solid was recrystallised from acetone–diethyl ether to give the product as pale yellow microcrystals, yield 1.12 g (46%). The complex [Ru(CO)$_3$(η^2:η^3-C$_{11}$H$_8$Ph$_3$)][BF$_4$] was prepared similarly as a pale yellow solid, in 76% yield.

[Fe(CO)$_3$(η^2:η^3-C$_{11}$H$_9$Ph$_2$)][BF$_4$] (**1**; M = Fe, R = H). To a stirred solution of [C$_3$Ph$_2$H][BF$_4$] (1.17 g, 4.22 mmol) in CH$_2$Cl$_2$ (80 cm^3) was added a solution of [Fe(CO)$_3$(η^4-cot)] (1.03 g, 4.22 mmol) in CH$_2$Cl$_2$ (80 cm^3). A yellow precipitate was formed rapidly, which was filtered off, washed with diethyl ether (10 cm^3), and dried in air. Recrystallisation from nitromethane–diethyl ether gave the *product* as yellow crystals, yield 1.43 g (65%). The complex (**1**; M = Ru, R = H) was prepared similarly as a white solid in 52% yield.

[Fe(CO)$_3$(σ,η^3-C$_{11}$H$_9$Ph$_3$)] (**2**). A large excess of NaBH$_4$ was added to a stirred solution of [Fe(CO)$_3$(η^2:η^3-C$_{11}$H$_8$Ph$_3$)][BF$_4$] (0.3 g, 0.50 mmol) in thf (25 cm^3). After 10 min the red solution was filtered and evaporated to dryness. Chromatography on an alumina–n-hexane column, eluting with n-hexane, gave a yellow solution. Yellow crystals of the product were obtained by partial evaporation *in vacuo* and cooling to −78 °C, yield 0.06 g (23%). The compound is soluble in all common organic solvents.

Crystal Structure Determination of [Fe(CO)$_3$(σ,η^3-C$_{11}$H$_9$Ph$_3$)] (**2**).—Yellow crystals of compound (**2**) were grown from n-hexane at −78 °C, and diffracted intensities were measured at 293 K for a crystal of approximate dimensions 0.26 × 0.25 × 0.24 mm. Of the 4 673 independent reflections measured for $2.9 \leqslant 2\theta \leqslant 55°$ on a Nicolet $P3/m$ diffractometer, 2 484 satisfied the criterion $I \geqslant 3.0\sigma(I)$ and were used in the final refinement of the structure. Two check reflections were remeasured every 50 reflections and indicated no significant crystal decay during the 156 h of exposure to *X*-rays. Corrections were applied for Lorentz, polarisation, and *X*-ray absorption effects, the last by using an empirical method based on azimuthal scan data ($\mu R = 0.12$).

Crystal data. C$_{32}$H$_{24}$FeO$_3$, $M = 512$, monoclinic, space group $P2_1/n$ (non-standard setting of no. 14), $a = 13.651(6)$, $b = 12.744(3)$, $c = 14.932(6)$ Å, $\beta = 107.35(3)°$, $U = 2\,479.5(5)$ Å^3, $D_m = 1.36$ g cm^{-3}, $Z = 4$, $D_c = 1.37$ g cm^{-3}, $F(000) = 1\,064$, Mo-K_α *X*-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 6.37 cm^{-1}.

The structure was solved by conventional heavy-atom methods and refined by blocked-cascade least squares. All non-hydrogen atoms were refined with anisotropic thermal parameters. The phenyl-group hydrogen atoms were constrained to idealised geometries (C–H 0.96 Å) and refined with isotropic thermal parameters; the remaining hydrogen atoms were refined freely. Weights were applied according to the scheme $w = [\sigma^2(F_o) + 0.000\,87|F_o|^2]^{-1}$, and refinement converged to $R(R')$ 0.073 (0.077) where $R' = \Sigma(F_o - F_c)w^{\frac{1}{2}}/\Sigma F_o w^{\frac{1}{2}}$.

Table 4. Atomic positional (fractional co-ordinates) parameters for [Fe(CO)$_3$(σ,η^3-C$_{11}$H$_9$Ph$_3$)] (**2**) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Fe	0.146 64(8)	0.222 65(7)	0.088 23(6)	C(92)	0.051 8(3)	0.065 3(4)	−0.322 2(4)
C(01)	0.185 1(6)	0.266 5(6)	0.209 9(5)	C(93)	0.023 8(3)	−0.026 7(4)	−0.374 3(4)
O(01)	0.213 8(5)	0.285 9(5)	0.288 1(4)	C(94)	−0.065 6(3)	−0.079 7(4)	−0.374 0(4)
C(02)	0.034 4(6)	0.156 0(5)	0.090 6(5)	C(95)	−0.126 9(3)	−0.040 7(4)	−0.321 7(4)
O(02)	−0.040 4(5)	0.112 6(4)	0.086 9(4)	C(96)	−0.098 8(3)	0.051 2(4)	−0.269 7(4)
C(03)	0.233 1(7)	0.119 7(7)	0.118 9(6)	C(91)	−0.009 5(3)	0.104 2(4)	−0.269 9(4)
O(03)	0.289 9(6)	0.048 1(6)	0.138 8(5)	C(102)	0.180 4(3)	0.370 7(4)	−0.316 3(3)
C(9)	0.019 8(5)	0.202 0(5)	−0.213 2(4)	C(103)	0.195 8(3)	0.405 9(4)	−0.399 5(3)
C(10)	0.069 4(5)	0.289 0(5)	−0.229 7(4)	C(104)	0.119 5(3)	0.391 4(4)	−0.484 7(3)
C(11)	0.106 3(5)	0.353 8(5)	−0.138 3(4)	C(105)	0.027 9(3)	0.341 6(4)	−0.486 6(3)
C(1)	0.017 0(5)	0.204 2(5)	−0.111 7(4)	C(106)	0.012 5(3)	0.306 4(4)	−0.403 4(3)
C(2)	0.023 2(6)	0.321 3(5)	−0.091 5(5)	C(101)	0.088 8(3)	0.320 9(4)	−0.318 2(3)
C(3)	0.052 0(6)	0.351 2(5)	0.012 0(5)	C(112)	0.194 0(3)	0.533 3(3)	−0.106 1(3)
C(4)	0.153 1(6)	0.382 4(5)	0.056 6(5)	C(113)	0.196 1(3)	0.640 0(3)	−0.126 2(3)
C(5)	0.230 2(6)	0.337 1(5)	0.028 9(5)	C(114)	0.114 4(3)	0.685 5(3)	−0.194 7(3)
C(6)	0.210 3(5)	0.306 3(5)	−0.074 3(5)	C(115)	0.030 6(3)	0.624 3(3)	−0.243 1(3)
C(7)	0.208 1(5)	0.187 4(5)	−0.076 8(5)	C(116)	0.028 4(3)	0.517 6(3)	−0.222 9(3)
C(8)	0.116 5(5)	0.155 6(5)	−0.047 4(5)	C(111)	0.110 2(3)	0.472 1(3)	−0.154 4(3)

A final electron-density difference synthesis showed no peaks > 0.7 or < -0.7 e Å^{-3}. Scattering factors were taken from ref. 21, and all computations were carried out within the laboratory on a Data General Eclipse S230 computer with the SHELXTL system of programs.[22] The final atom co-ordinates are listed in Table 4.

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