The Reaction of Co-ordinated Cyclo-octatetraene with Arenediazonium Ions: Azo-coupling *vs.* Arylation

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Arenediazonium ions, $[N_2C_6H_4R'\text{-}p][BF_4]$, react with $[Fe(CO)_{3-n}\{P(OMe)_3\}_n(\eta^4\text{-cot})]$ (1; n = 1 or 2, cot = cyclo-octatetraene) to give the azo-coupled cyclo-octatrienyl $[Fe(CO)_{3-n}\{P(OMe)_3\}_n(\eta^5\text{-}C_8H_8N_2C_6H_4R'\text{-}p)]X$ (2; n = 1, R′ = NO_2, X = BF_4; n = 1 or 2, R′ = F, X = BPh_4) which is deprotonated to give the fluxional, arylazo-substituted cot complex $[Fe(CO)_{3-n}\{P(OMe)_3\}_n(\eta^4\text{-}C_8H_7N_2C_6H_4R'\text{-}p)]$ (3). The reaction of (3; n = 2, R′ = F) with $NMe_3(O)\cdot 2H_2O$ yields the un-co-ordinated azo-compound $C_8H_7N_2C_6H_4F\text{-}p$ (4). The tricarbonyl $[Fe(CO)_3(\eta^4\text{-cot})]$ and $[N_2C_6H_4NO_2\text{-}p][BF_4]$ afford the arylated bicyclo[5.1.0]octadienyl complex $[Fe(CO)_3(\eta^5\text{-}C_8H_8C_6H_4NO_2\text{-}p)][BF_4]$ (5) which is deprotonated to the fluxional aryl-cot complex $[Fe(CO)_3(\eta^4\text{-}C_8H_7C_6H_4NO_2\text{-}p)]$ (6). Hydride-ion addition to (5) gives the bicyclo[5.1.0]octadiene compound $[Fe(CO)_3(\eta^4\text{-}C_8H_9C_6H_4NO_2\text{-}p)]$ (7), ^1H n.m.r. studies on which reveal an *endo*-aryl substituent. The mechanism of the reaction between (1) and $[N_2C_6H_4R'\text{-}p]^+$ involves competitive electrophilic attack at the metal and cot ring.

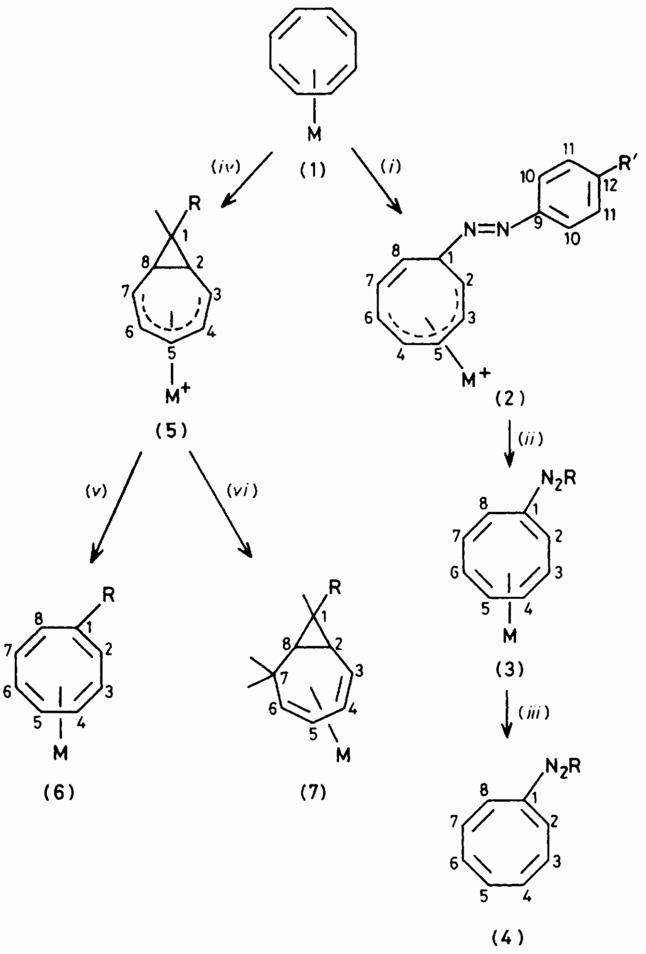
Transition-metal substrates and arenediazonium ions commonly afford arenediazenato-complexes[1] by addition or ligand substitution, the N_2R (R = aryl) ligand behaving as a one- or three-electron donor. In this respect there is a marked analogy with metal nitrosyl chemistry.[2] The diazonium ion may, however, undergo a variety of other reactions, acting as a weak one-electron oxidant,[3] inserting into metal–hydrogen bonds,[4] or undergoing dimerisation in the formation of tetrazene complexes.[5] Carbon–carbon bond formation has also been observed, in the arylation of ferrocene[6] and in the *ortho*-metallation reaction[7] with $[\{Ir(CO)_3(PPh_3)\}_2]$ to give $[\{Ir(CO)_2(PPh_3)(NH{=}NC_6H_3R'\text{-}p)\}_2]^{2+}$. We now present details[8] of C–C and C–N bond-forming reactions between $[N_2C_6H_4R'\text{-}p][BF_4]$ and $[Fe(CO)_{3-n}\{P(OMe)_3\}_n(\eta^4\text{-cot})]$ (1; cot = cyclo-octatetraene) which lead to the synthesis of complexes of both aryl- and arylazo-substituted cyclic polyolefins.

Results and Discussion

The Azo-coupling Reactions of $[Fe(CO)_{3-n}\{P(OMe)_3\}_n(\eta^4\text{-cot})]$.—The addition of solid $[N_2C_6H_4NO_2\text{-}p][BF_4]$ to a cold (0 °C) solution of $[Fe(CO)_{3-n}\{P(OMe)_3\}_n(\eta^4\text{-cot})]$ (1; n = 1) in CH_2Cl_2 leads to the isolation of yellow crystals of the azo-coupled salt $[Fe(CO)_{3-n}\{P(OMe)_3\}_n(\eta^5\text{-}C_8H_8N_2C_6H_4R'\text{-}p)]X$ (2; n = 1, R′ = NO_2, X = BF_4) (Scheme) which was characterised by elemental analysis and by i.r. (Table 1) and n.m.r. (Table 2) spectroscopy. The ^{13}C n.m.r. spectrum of $[Fe(CO)_2\{P(OMe)_3\}(\eta^5\text{-}C_8H_8N_2C_6H_4NO_2\text{-}p)]^+$, which is similar to that of $[Fe(CO)_3(\eta^5\text{-}C_8H_8CPh_3)]^+$,[9] suggests the presence of a cyclo-octatrienyl ring, verified by ^1H-$\{^1H\}$ decoupling of the ^{31}P-decoupled ^1H n.m.r. spectrum. The *trans* configuration at the N=N double bond of (2), as shown in the Scheme, is based only on analogy with azobenzene.

The addition of an electrophile, E^+, to $[Fe(CO)_3(\eta^4\text{-cot})]$ affords the cyclo-octatrienyl complex $[Fe(CO)_3(\eta^5\text{-}C_8H_8E)]^+$ as the first product. For proton addition, electrocyclic ring closure occurs above −60 °C to give the bicyclo[5.1.0]-octadienyl isomer.[10] The monocyclic form is stabilised by electron-withdrawing groups, E,[11] such as CPh_3 and, in the present case, $N_2C_6H_4R'\text{-}p$.[12]

Azo-coupling reactions also occur between $[N_2C_6H_4F\text{-}p][BF_4]$ and (1; n = 1 or 2) but the salts could only be characterised (Table 1) as (2; n = 1 or 2, R′ = F, X = BPh_4) after metathesis with $Na[BPh_4]$ in acetone. Although similar to that of $[Fe(CO)_2\{P(OMe)_3\}(\eta^5\text{-}C_8H_8N_2C_6H_4NO_2\text{-}p)][BF_4]$ the ^1H n.m.r. spectra were partially obscured by the tetraphenylborate resonances and, in the case of the monocarbonyl, broadened by trace paramagnetic impurities.



Scheme. M = $Fe(CO)_{3-n}\{P(OMe)_3\}_n$, R = aryl, R′ = NO_2 or F. (*i*) n = 1 or 2, $[N_2C_6H_4R'\text{-}p]^+$; (*ii*) Al_2O_3 or $Na[HCO_3]$; (*iii*) $NMe_3(O)\cdot 2H_2O$; (*iv*) n = 0, $[N_2C_6H_4NO_2\text{-}p]^+$; (*v*) pyridine; (*vi*) $Na[BH_4]$. The numbering of the aryl group is as shown for (2). The atom numbering shown differs from that used in the systematic names for the compounds (see Experimental section)

Table 1. Infrared and analytical data

Compound	$\tilde{\nu}$(CO) [a]/cm^{-1}	Analysis [b]/% C	H	N
$[Fe(CO)_2\{P(OMe)_3\}(\eta^5\text{-}C_8H_8N_2C_6H_4NO_2\text{-}p)][BF_4]$	2 061, 2 025	39.2 (39.5)	4.0 (3.6)	6.7 (7.3)
$[Fe(CO)_2\{P(OMe)_3\}(\eta^5\text{-}C_8H_8N_2C_6H_4F\text{-}p)][BPh_4]$	2 059, 2 023	65.3 (66.0)	5.6 (5.2)	3.4 (3.6)
$[Fe(CO)\{P(OMe)_3\}_2(\eta^5\text{-}C_8H_8N_2C_6H_4F\text{-}p)][BPh_4]$	1 997	61.8 (61.5)	6.0 (5.7)	2.9 (3.2)
$[Fe(CO)_2\{P(OMe)_3\}(\eta^4\text{-}C_8H_7N_2C_6H_4NO_2\text{-}p)]$	2 001, 1 949	45.7 (46.3)	3.9 (4.1)	7.9 (8.6)
$[Fe(CO)\{P(OMe)_3\}_2(\eta^4\text{-}C_8H_7N_2C_6H_4F\text{-}p)]$	1 927, 1 937 [c]	44.7 (45.2)	5.4 (5.2)	4.9 (5.0)
$[Fe(CO)_3(\eta^5\text{-}C_8H_8C_6H_4NO_2\text{-}p)][BF_4]$	2 109, 2 061 (sh), 2 055	45.3 (45.0)	3.0 (2.7)	2.9 (3.1)
$[Fe(CO)_3(\eta^4\text{-}C_8H_7C_6H_4NO_2\text{-}p)]$	2 047, 1 989 2 055, 1 997, 1 983 [c]	56.2 (55.9)	2.6 (3.0)	4.3 (3.8)
$[Fe(CO)_3(\eta^4\text{-}C_8H_9C_6H_4NO_2\text{-}p)]$	2 049, 1 975 2 055, 1 991, 1 985 [c]	55.6 (55.6)	3.4 (3.5)	3.7 (3.8)

[a] In CH_2Cl_2 unless stated otherwise. [b] Calculated values are given in parentheses. [c] In hexane.

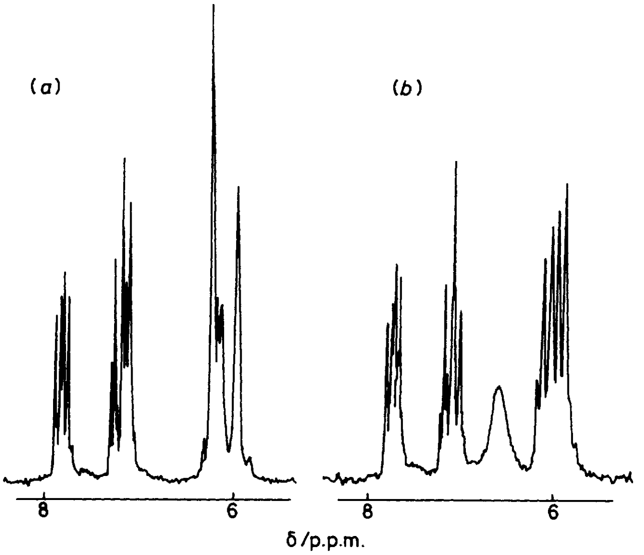


Figure. The ^1H n.m.r. spectrum of $C_8H_7N_2C_6H_4F\text{-}p$ (4): (a) at −20 °C; and (b) at +55 °C

Complex (2; $n = 2$, R′ = F) is deprotonated on column chromatography on Brockman Activity II alumina to give purple-black crystals of $[Fe(CO)_{3-n}\{P(OMe)_3\}_n(\eta^4\text{-}C_8H_7N_2C_6H_4R'\text{-}p)]$ (3; $n = 2$, R′ = F) (Tables 1 and 2). The electron-withdrawing nature of the arylazo-substituent is reflected in an increase in $\tilde{\nu}$(CO) of 12 cm^{-1} from the value of (1; $n = 2$). The presence of the monosubstituted cot ring was verified by n.m.r. spectroscopy. The observation of only five signals in the room-temperature ^{13}C n.m.r. spectrum of the C_8 ring is due to the fluxionality of the complex. The ^{31}P-decoupled ^1H n.m.r. spectrum is similarly simplified with oscillation of the $Fe(CO)\{P(OMe)_3\}_2$ group between C^3—C^6 and C^4—C^7 (Scheme) rendering pairs of protons (H^2H^8, H^3H^7, and H^4H^6) equivalent. No attempt was made to quantify the fluxional process further.

The deprotonation of (2; $n = 1$, R′ = NO_2) could not be carried out on alumina but was successfully achieved by adding $Na[HCO_3]$ to a solution of the cation in aqueous acetone. The relative concentrations of water and acetone appear to be crucial. While acting as a weak base in 60% aqueous acetone, $Na[HCO_3]$ serves as a source of hydroxide ion in a 90% mixture. Under the latter conditions $[Fe(CO)_2\{P(OMe)_3\}(\eta^5\text{-}C_8H_8N_2C_6H_4NO_2\text{-}p)]^+$ slowly gave a low yield of a yellow, crystalline, neutral complex with $\tilde{\nu}$(CO)(hexane) at 1 993 and 1 937 cm^{-1}. The full characterisation of this species was deterred by unsuccessful attempts to reproduce the exact experimental conditions. However, a strong peak at m/e 269 in the mass spectrum corresponds to $[C_8H_8(OH)(N_2C_6H_4NO_2\text{-}p)]^+$ and we tentatively formulate the yellow crystals as $[Fe(CO)_2\{P(OMe)_3\}\{\eta^4\text{-}C_8H_8(OH)(N_2C_6H_4NO_2\text{-}p)\}]$. It is noteworthy that column chromatography of $[Fe(CO)_2\{P(OMe)_3\}(\eta^5\text{-}C_8H_8N_2C_6H_4NO_2\text{-}p)]^+$ on alumina also gave low yields of an orange-yellow solid with $\tilde{\nu}$(CO) at 1 993 and 1 937 cm^{-1} and, in this case, a satisfactory elemental analysis was obtained for $[Fe(CO)_2\{P(OMe)_3\}\{\eta^4\text{-}C_8H_8(OH)(N_2C_6H_4NO_2\text{-}p)\}]$.

The organoazo-ligand of $[Fe(CO)\{P(OMe)_3\}_2(\eta^4\text{-}C_8H_7N_2C_6H_4F\text{-}p)]$ is decoupled from the metal on reaction of the complex with $NMe_3(O)\cdot 2H_2O$ in benzene under reflux. The yellow, crystalline solid $C_8H_7N_2C_6H_4F\text{-}p$ (4) was characterised by elemental analysis and mass spectrometry. Like other monosubstituted cot compounds, (4) is fluxional, undergoing both inversion of the tub conformation and bond-shift processes.[13] The variable-temperature ^1H n.m.r. spectra of (4) are insufficiently well resolved to afford activation energies for the fluxional processes but the limiting spectra are shown in the Figure. The ^{13}C n.m.r. spectrum at −50 °C (Table 2) confirms that the molecule is static at this temperature. At room temperature the signals associated with carbon atoms C^2—C^4 and C^6—C^8 are broad although that due to C^5 remains sharp.

The overall yield of (4) from (1) is poor but the reaction sequence described represents the only route to arylazo-derivatives of cot. Although the direct reaction between diazonium salts and dienes such as 2,3-dimethylbuta-1,3-diene[14] results in azo-coupling, that with cot is not successful. In acetone, cot and $[N_2C_6H_4NO_2\text{-}p][BF_4]$ gave an uncharacterised purple-brown polymer, and in aqueous solution only low yields of the biaryl, $p\text{-}NO_2C_6H_4C_6H_4NO_2\text{-}p$, were isolable.

The Arylation of $[Fe(CO)_3(\eta^4\text{-cot})]$.—In contrast to the reactions described above, $[Fe(CO)_3(\eta^4\text{-cot})]$ and $[N_2C_6H_4NO_2\text{-}p][BF_4]$ in cold (−20 °C) acetone give good yields of the ring-arylated salt $[Fe(CO)_3(\eta^5\text{-}C_8H_8C_6H_4NO_2\text{-}p)][BF_4]$ (5). The complex was fully characterised by elemental analysis and i.r. spectroscopy (Table 1) and by the n.m.r. spectrum (Table 2) which revealed the presence of the monosubstituted bicyclo[5.1.0]octadienyl group (Scheme). The ^{13}C n.m.r. spectra of (5) and the dimer $[Fe_2(CO)_6(\eta^5{:}\eta^{5'}\text{-}C_{16}H_{16})]^{2+}$, known[15] to contain two bicyclo[5.1.0]octadienyl groups C–C bonded at C^1, are very similar. In addition, the ^1H-$\{^1H\}$ decoupled spectra of (5), although complicated by overlap of the resonances due to H^1, H^2, and H^8, verified the bicyclic structure. A detailed study of the reaction of (5) with hydride ion (see below) showed the aryl group bonded to C^1 to be *endo* to the metal.

Deprotonation of (5), with pyridine in cold (−20 °C)

Table 2. Proton and ^{13}C n.m.r. data [a]

Compound	^1H (δ) [b]	^{13}C (p.p.m.) [b]
$[Fe(CO)_2\{P(OMe)_3\}(\eta^5\text{-}C_8H_8N_2C_6H_4NO_2\text{-}p)][BF_4]$ [c]	8.10 [2 H, d, $J(H^{10}H^{11})$ 9, H^{10}], 7.20 [2 H, d, $J(H^{11}H^{10})$ 9, H^{11}], 7.10 [1 H, dd, $J(H^4H^3)$ 5, H^4], 6.48 (1 H, s, H^1), 5.96 [1 H, m, $J(H^3H^2)$ 8, $J(H^3H^4)$ 5, H^3], 5.68 [1 H, m, $J(H^5H^6)$ 8, H^5], 5.58 [1 H, dd, $J(H^7H^6)$ 7, $J(H^7H^8)$ 6, H^7], 4.88 [1 H, m, $J(H^6H^5)$ 8, $J(H^6H^7)$ 7, H^6], 4.70 [2 H, m, $J(H^2H^3)$ 8, $J(H^8H^7)$ 6, H^2, H^8], 3.90 [9 H, d, J(PH) 12, $P(OMe)_3$]	55.70, 56.24, 56.61 [C^1, $P(OMe)_3$], 69.65, 83.73 (C^2,C^6), 102.41, 103.14, 103.69 (C^3—C^5), 113.3, 127.05, (C^{10},C^{11}), 141.06, 145.80, 148.83 (C^7,C^9,C^{12}) [d]
$[Fe(CO)\{P(OMe)_3\}_2(\eta^4\text{-}C_8H_7N_2C_6H_4F\text{-}p)]$ [e]	7.81 [2 H, dd, $J(H^{10}H^{11})$ 8, $J(H^{10}F)$ 6, H^{10}], 7.11 [2 H, dd, $J(H^{11}H^{10})$ 8, $J(H^{11}F)$ 8, H^{11}], 6.56 [2 H, d, $J(H^2H^3)$ = $J(H^8H^7)$ 9, H^2 and H^8], 5.16 [4 H, m, $J(H^3H^2)$ = $J(H^7H^8)$ 9, $J(H^4H^5)$ = $J(H^6H^5)$ 8, H^3, H^4, H^6, and H^7], 4.29 [1 H, t, $J(H^5H^4)$ = $J(H^5H^6)$ 8, H^5], 3.52 [18 H, t, J(PH) 4, $P(OMe)_3$]	51.63 [$P(OMe)_3$], 66.86 (C^5), 97.62, 99.86, 100.35 (C^2—C^4,C^6—C^8), 109.45 (C^1), 115.67 [d, J(CF) 23, C^{11}], 123.44 [d, J(CF) 8, C^{10}]
$[Fe(CO)_3(\eta^5\text{-}C_8H_8C_6H_4NO_2\text{-}p)][BF_4]$ [c]	8.34 [2 H, d, $J(H^{10}H^{11})$ 10, H^{10}], 7.28 [3 H, m, $J(H^{11}H^{10})$ 10, H^5 and H^{11}], 5.52 (4 H, m, H^3, H^4, H^6, H^7), 3.46 (3 H, m, H^1, H^2, H^8)	41.98 (C^2,C^8), 65.83 (C^1), 98.11 (C^5), 101.87, 102.05 (C^3,C^4,C^6,C^7), 125.65, 133.84 (C^{10},C^{11}), 142.16, 148.83 (C^9,C^{12})
$[Fe(CO)_3(\eta^4\text{-}C_8H_7C_6H_4NO_2\text{-}p)]$ [e]	8.16 [2 H, d, $J(H^{10}H^{11})$ 8, H^{10}], 7.46 [2 H, d, $J(H^{11}H^{10})$ 8, H^{11}], 5.80 [2 H, d, $J(H^2H^3)$ = $J(H^8H^7)$ 10, H^2, H^8], 5.40 [2 H, dd, $J(H^3H^2)$ = $J(H^7H^8)$ 10, $J(H^3H^4)$ = $J(H^7H^6)$ 10, H^3, H^7], 5.02 [2 H, dd, $J(H^4H^3)$ = $J(H^6H^7)$ 10, $J(H^4H^5)$ = $J(H^6H^5)$ 8, H^4, H^6], 4.78 [1 H, t, $J(H^5H^4)$ = $J(H^5H^6)$ 8, H^5]	87.25 (C^5), 91.98, 97.92, 109.15 (C^2—C^4,C^6—C^8), 123.59, 128.02 (C^{10},C^{11}), 128.56, 146.58, 153.01 (C^1,C^9,C^{12}), 211.38 (CO)
$[Fe(CO)_3(\eta^4\text{-}C_8H_9C_6H_4NO_2\text{-}p)]$ [e,f]	1.28 [1 H, t, $J(H^1H^8)$ 5, $J(H^1H^2)$ 5, H^1], 1.40 [1 H, m, $J(H^8H^7)$ = $J(H^8H^{7'})$ 4, $J(H^8H^1)$ 5, $J(H^8H^2)$ 8, H^8], 1.83 [1 H, m, $J(H^2H^3)$ 6, $J(H^2H^1)$ 5, $J(H^2H^8)$ 8, H^2], 2.40 [2 H, t, $J(H^7H^6)$ = $J(H^{7'}H^6)$, 4, $J(H^7H^8)$ = $J(H^{7'}H^8)$ 4, $H^7H^{7'}$], 3.17 [1 H, m, $J(H^6H^5)$ 6, $J(H^6H^7)$ = $J(H^6H^{7'})$ 4, H^6], 3.65 [1 H, t, $J(H^3H^4)$ 6, $J(H^3H^2)$ 6, H^3], 5.09 [1 H, t, $J(H^4H^5)$ 6, $J(H^4H^3)$ 6, H^4], 5.28 [1 H, t, $J(H^5H^4)$ 6, $J(H^5H^6)$ 6, H^5], 6.99 [2 H, d, $J(H^{11}H^{10})$ 9, H^{11}], 8.06 [2 H, d, $J(H^{10}H^{11})$ 9, H^{10}]	23.68 (C^7), 28.10, 29.22, 36.13 (C^1,C^2,C^8), 60.59, 61.10 (C^3,C^6), 85.97, 88.59 (C^4,C^5), 123.63, 125.01 (C^{10},C^{11}), 145.50, 151.83 (C^9,C^{12}), 211.02 (CO)
$C_8H_7N_2C_6H_4F\text{-}p$ [e,f]	7.79 [2 H, dd, $J(H^{10}H^{11})$ 9, $J(H^{10}F)$ 5, H^{10}], 7.13 [2 H, dd, $J(H^{11}H^{10})$ 9, $J(H^{11}F)$ 9, H^{11}], [7.03 (1 H, m), 6.13 (3 H, m), 5.88 (3 H, m) H^2—H^8]	115.91 [d, J(CF) 23, C^{11}], 124.42 [d, J(CF) 9, C^{10}], 128.10, 129.73, 132.17, 133.53, 133.80, 143.99 (C^2—C^4,C^6—C^8), 130.96 (C^5), 155.53 (C^1 or C^9), 164.05 [d, J(CF) 251, C^{12}]

[a] Numbering as in Scheme. Room-temperature spectrum unless stated otherwise. [b] Downfield from $SiMe_4$, J values in Hz. When not quoted, quaternary carbon resonances were not detected. [c] In CD_3NO_2. [d] The resonance due to C^8 is obscured by that of the aromatic carbon atom at 127.05 p.p.m. [e] In $CDCl_3$. [f] ^{13}C spectrum at −50 °C.

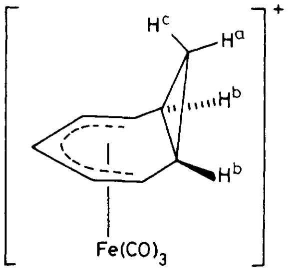
acetone, gives good yields of the red-orange cot derivative $[Fe(CO)_3(\eta^4\text{-}C_8H_7C_6H_4NO_2\text{-}p)]$ (6) (Tables 1 and 2). The reaction not only involves the removal of a proton but also cyclopropane ring opening as previously described for $[Fe(CO)_3(\eta^5\text{-}C_8H_9)]^+$.[16] Complex (6) is fluxional in the same sense as (3), with positions 2 and 8, 3 and 7, and 4 and 6 rendered equivalent by metal migration. The overall yield of (6) from $[Fe(CO)_3(\eta^4\text{-cot})]$ suggests a viable new route to arylated cot complexes.[17]

The Mechanism of the Reaction between (1) *and Arenediazonium Ions.*—We have shown [15] previously that $[Fe(CO)_{3-n}\{P(OMe)_3\}_n(\eta^4\text{-cot})]$ (1) undergoes one-electron oxidation at a potential markedly lowered by an increase in *n*; chemical oxidation with $[N(C_6H_4Br\text{-}p)_3]^+$ leads to dimerisation. Thus, we had hoped to induce coupling between (1; $n = 1$ or 2) and arenediazonium ions *via* one-electron oxidation followed by reaction between the cation radical $[Fe(CO)_{3-n}\{P(OMe)_3\}_n(C_8H_8)]^+$ and $N_2C_6H_4R'\text{-}p$ (or $C_6H_4R'\text{-}p$) radicals. We are now convinced, however, that the azo-coupling and arylation reactions described above occur *via* competitive electrophilic attack at the co-ordinated ring and metal centre. The reaction of (1; $n = 0$) and $[N_2C_6H_5][BF_4]$ in acetone gives small yields of $[Fe(CO)_3(\eta^4\text{-}C_8H_7N_2C_6H_5)]$ (m/e = 348) and clearly a redox-based mechanism cannot operate; the oxidation potential for $[Fe(CO)_3(\eta^4\text{-cot})]$ is too positive for $[N_2C_6H_4R'\text{-}p]^+$ to cause radical-cation formation.† It might be noted here that spontaneous deprotonation of the intermediate $[Fe(CO)_3(\eta^5\text{-}C_8H_8N_2C_6H_5)]^+$ is facilitated by the absence of phosphite ligands (which drastically increase the basicity of the metal centre).

Although direct attack of the electrophile $[N_2C_6H_4R'\text{-}p]^+$ occurs at the ring to give the azo-coupled products it is most unlikely that the arylated compounds are subsequently formed by N_2 loss from (2). We therefore propose that arylation occurs by electrophilic attack at the metal followed by aryl migration to the C_8 ring. Similar metal-induced loss of N_2 is involved in, for example, the Sandmeyer reaction of diazonium salts.[19] Such a mechanism suggests that the aryl substituent in (5) should be *endo* to the metal. Although the ^1H n.m.r. spectrum of (5) is inconclusive, the *endo* geometry is confirmed by treating the cation with hydride ion.

The addition of $Na[BH_4]$ to $[Fe(CO)_3(\eta^5\text{-}C_8H_8C_6H_4NO_2\text{-}p)][BF_4]$ in cold (−78 °C) tetrahydrofuran (thf) gives bright yellow $[Fe(CO)_3(\eta^4\text{-}C_8H_9C_6H_4NO_2\text{-}p)]$ (7). The ^1H n.m.r. spectrum shows not only that the bicyclic ring system is retained but that the aryl substituent is *endo* to the metal.

The ^1H n.m.r. spectra of a range of cyclopropane derivatives [20] gave J_{cis} = 8—11 Hz and J_{trans} = 5—8 Hz. Further, in the complex $[Fe(CO)_3(\eta^5\text{-}C_8H_9)]^+$ (see below) the couplings for H^aH^b and H^cH^b are 8.0 and 4.5 Hz respectively.[21] For complex (7), $J(H^1H^2) = J(H^1H^8)$ = 5 Hz, thereby defining the *endo* geometry of the aryl group.



A similar aryl-ligand migration, from niobium to a co-ordinated cot ligand, occurs in the reaction between $[Nb(C_6H_5)(cot)_2]$ and $Ph_2PCH_2PPh_2$ (dppm). The complex $[Nb(dppm)(\eta^4\text{-cot})(\eta^5\text{-}C_8H_8Ph)]$ contains an η^5-bicyclo[5.1.0]-octadienyl ring with an *endo*-phenyl substituent, as verified by *X*-ray crystallography.[22]

Conclusion

Arenediazonium ions react with $[Fe(CO)_{3-n}\{P(OMe)_3\}_n(\eta^4\text{-cot})]$ to give arylazo- or aryl-substituted cot derivatives. The former result by direct ring attack whereas the latter are formed by addition to the metal followed by *endo* migration to the ring and loss of nitrogen.

Experimental

The preparation, purification, and reactions of the complexes described were carried out under an atmosphere of dry nitrogen. Unless stated otherwise, the solid complexes are air-stable and dissolve in polar organic solvents such as CH_2Cl_2 and acetone to give moderately air-sensitive solutions. The compounds $[Fe(CO)_{3-n}\{P(OMe)_3\}_n(\eta^4\text{-cot})]$ ($n = 0$,[23] 1 or 2 [15]) and $[N_2C_6H_4R'\text{-}p][BF_4]$ (R′ = F or NO_2) [24] were prepared by published methods. Infrared spectra were recorded on a Perkin-Elmer PE 457 spectrophotometer and calibrated against the absorption band of polystyrene at 1 601 cm^{-1}. Proton n.m.r. spectra were obtained on Varian Associates HA100 or JEOL PS100 or FX200 spectrometers, and ^{13}C n.m.r. spectra on JEOL PFT100 or FX200 instruments; both were calibrated against tetramethylsilane as internal reference. Mass spectra were recorded on an A.E.I. MS 902 instrument.

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

Dicarbonyl(1—5-η-8-p-*nitrophenylazocyclo-octatrienyl*)(*trimethyl phosphite*)*iron Tetrafluoroborate*, $[Fe(CO)_2\{P(OMe)_3\}(\eta^5\text{-}C_8H_8N_2C_6H_4NO_2\text{-}p)][BF_4]$.—To a stirred, cooled (0 °C) solution of $[Fe(CO)_2\{P(OMe)_3\}(\eta^4\text{-cot})]$ (0.65 g, 1.90 mmol) in CH_2Cl_2 (85 cm^3) was added solid $[N_2C_6H_4NO_2\text{-}p][BF_4]$ (0.45 g, 1.90 mmol). After 90 min, dissolution of the arenediazonium salt was complete and the resulting pale red solution was filtered and evaporated to dryness. The residue was dried *in vacuo* for 2 h and then washed with acetone (5 cm^3) to give the *product* as a bright yellow solid. The yield could be improved by careful addition of diethyl ether to the acetone washings. Yellow *crystals* of the product were obtained by recrystallisation from acetone–diethyl ether, yield 0.49 g (45%).

The compound $[Fe(CO)_2\{P(OMe)_3\}(\eta^5\text{-}C_8H_8N_2C_6H_4F\text{-}p)][BPh_4]$ was prepared by the addition of $Na[BPh_4]$ to an acetone solution of $[Fe(CO)_2\{P(OMe)_3\}(\eta^5\text{-}C_8H_8N_2C_6H_4F\text{-}p)][BF_4]$. Evaporation to dryness, extraction with CH_2Cl_2, filtration, and addition of hexane gave the tetraphenylborate salt as a yellow *solid*, yield 66%. Low yields of $[Fe(CO)\{P(OMe)_3\}_2(\eta^5\text{-}C_8H_8N_2C_6H_4F\text{-}p)][BPh_4]$ were similarly obtained as a yellow *solid* after recrystallisation of the crude product from thf–water.

Carbonyl(3—6-η-1-p-*fluorophenylazocyclo-octatetraene*)*bis*(*trimethyl phosphite*)*iron*, $[Fe(CO)\{P(OMe)_3\}_2(\eta^4\text{-}C_8H_7N_2C_6H_4F\text{-}p)]$.—Crude $[Fe(CO)\{P(OMe)_3\}_2(\eta^5\text{-}C_8H_8N_2C_6H_4F\text{-}p)][BF_4]$, prepared as above from $[Fe(CO)\{P(OMe)_3\}_2(\eta^4\text{-cot})]$ (0.50 g, 1.15 mmol), was dissolved in acetone (10 cm^3) and

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† For the oxidation of $[Fe(CO)_3(\eta^4\text{-cot})]$, $(E_p)_{ox}$ = 0.88 V *vs.* a calomel electrode (1 mol dm^{-3} in LiCl), at a cyclic voltammetric scan rate of 100 mV s^{-1}, in CH_2Cl_2.[15] For the reduction of $[N_2C_6H_5][BF_4]$, E_0 = 0.295 V *vs.* a saturated calomel electrode in sulpholane (tetrahydrothiophen 1,1-dioxide).[18]

added to an alumina–CH_2Cl_2 column. Elution with acetone gave a broad purple-brown band which yielded the product as a purple oil on removal of the solvent. Dissolution of the oil in diethyl ether, addition to an alumina–hexane column, elution with diethyl ether, and recrystallisation from pentane (−78 °C) gave purple-black *crystals*, yield 77 mg {13% based on $[Fe(CO)\{P(OMe)_3\}_2(\eta^4\text{-cot})]$}, m.p. 86—88 °C, *m/e* 558. The compound is sparingly soluble in n-hexane but more soluble in polar solvents to give deep purple, air-stable solutions.

Dicarbonyl(3—6-η-1-p-*nitrophenylazocyclo-octatetraene*)(*trimethyl phosphite*)*iron*, $[Fe(CO)_2\{P(OMe)_3\}(\eta^4\text{-}C_8H_7N_2C_6H_4NO_2\text{-}p)]$.—To a stirred solution of $[Fe(CO)_2\{P(OMe)_3\}(\eta^5\text{-}C_8H_8N_2C_6H_4NO_2\text{-}p)][BF_4]$(0.12 g, 0.21 mmol) in aqueous acetone (15 cm^3 water : 10 cm^3 acetone) was added $Na[HCO_3]$ (0.175 g, 2.08 mmol). An immediate colour change from yellow to purple was accompanied by the formation of a purple-black precipitate which was collected by filtration after 2 h, yield 84 mg (82%), m.p. 114—118 °C.

p-*Fluorophenylazocyclo-octatetraene*, $C_8H_7N_2C_6H_4F\text{-}p$.—A stirred mixture of $[Fe(CO)\{P(OMe)_3\}_2(\eta^4\text{-}C_8H_7N_2C_6H_4F\text{-}p)]$ (0.50 g, 0.90 mmol) and $NMe_3(O)\cdot 2H_2O$ (3.5 g, 31.5 mmol) in benzene (60 cm^3) was heated under reflux for 4 h. After removing the solvent, the purple-brown residue was extracted with diethyl ether (10 cm^3) and chromatographed on an alumina–hexane column. Elution of an orange-yellow band with hexane–diethyl ether (4 : 1) and removal of the solvent gave an orange-yellow solid. Dissolution in hexane (5 cm^3) and careful chromatography on a silica–hexane column, eluting with hexane–diethyl ether (50 : 1), gave a broad yellow band and a narrow orange band. Removal of the solvent from the yellow eluate gave yellow crystals of the *product*, yield 30 mg (15%), m.p. 86—88 °C, *m/e* 226 (Found: C, 74.2; H, 5.6; N, 12.5. $C_{14}H_{11}FN_2$ requires C, 74.3; H, 4.9; N, 12.4%). The compound is soluble in all common organic solvents to give air-stable, yellow solutions.

Tricarbonyl(2—6-η-8-p-*nitrophenylbicyclo*[5.1.0]*octadienyl*)*iron Tetrafluoroborate*, $[Fe(CO)_3(\eta^5\text{-}C_8H_8C_6H_4NO_2\text{-}p)][BF_4]$.—To a stirred, cooled (−20 °C) solution of $[Fe(CO)_3(\eta^4\text{-cot})]$ (0.50 g, 2.03 mmol) in acetone (15 cm^3) was added $[N_2C_6H_4NO_2\text{-}p][BF_4]$ (0.48 g, 2.03 mmol) in acetone (35 cm^3). Rapid gas evolution occurred, and after 40 min the red solution was filtered and reduced in volume. Addition of diethyl ether gave a yellow precipitate which was recrystallised from acetone–diethyl ether to give the product as a bright yellow *solid*, yield 0.45 g (50%).

Tricarbonyl(3—6-η-1-p-*nitrophenylcyclo-octatetraene*)*iron*, $[Fe(CO)_3(\eta^4\text{-}C_8H_7C_6H_4NO_2\text{-}p)]$.—To a stirred, cooled (−20 °C) solution of $[Fe(CO)_3(\eta^5\text{-}C_8H_8C_6H_4NO_2\text{-}p)][BF_4]$ (0.48 g, 1.06 mmol) in acetone (40 cm^3) was added an excess of pyridine (*ca.* 0.3 g, 3.8 mmol). After warming to 30 °C and stirring for 30 min the resulting red solution was evaporated to dryness. The residue, dissolved in diethyl ether (10 cm^3), was chromatographed on an alumina–hexane column giving an orange-red band on elution with hexane–diethyl ether (1 : 1). Partial removal of the solvent *in vacuo* gave the product as an orange-red *solid*, yield 0.2 g (50%), m.p. 128—131 °C, *m/e* 365. The compound is only sparingly soluble in hexane.

Tricarbonyl(2—5-η-8-p-*nitrophenylbicyclo*[5.1.0]*octa*-2,4-*diene*)*iron*, $[Fe(CO)_3(\eta^4\text{-}C_8H_9C_6H_4NO_2\text{-}p)]$.—To a stirred cold (−78 °C) suspension of $[Fe(CO)_3(\eta^5\text{-}C_8H_8C_6H_4NO_2\text{-}p)][PF_6]$ (1.67 g, 3.27 mmol) in thf (60 cm^3) was added an excess of $Na[BH_4]$ (0.66 g, 17.4 mmol). After 1 h the yellow solution was evaporated to dryness and the residue dissolved in CH_2Cl_2 (10 cm^3). Chromatography on a silica–hexane column gave a yellow band which was eluted with hexane–diethyl ether (2 : 1). The eluate was reduced to low volume (10 cm^3) and cooled (−78 °C) to give the product as a bright yellow *solid*, yield 0.73 g (61%), m.p. 168—170 °C (with decomposition), *m/e* 367. The complex is soluble in hexane and polar solvents to give air-stable yellow solutions.

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