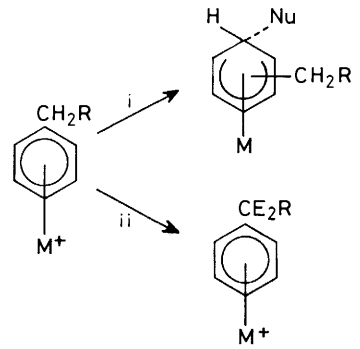
Metal-mediated Functionalization of Tetrahydronaphthalene, Octahydroanthracene, and Tetrahydroquinoline: Stereochemical Control of Nucleophilic Addition to Cationic Cyclopentadienyl(η^6-arene)iron(II) Complexes *via* Benzylic Substitution

Stephen L. Grundy, Anthony R. H. Sam, and Stephen R. Stobart
Department of Chemistry, University of Victoria, P.O. Box 1700, Victoria, B.C., Canada, V8W 2Y2

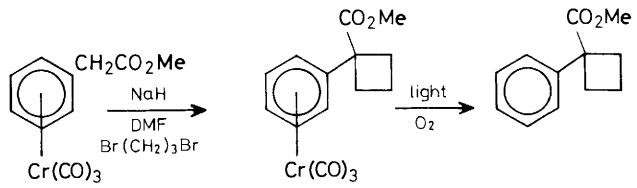
Treatment of the cationic tetrahydronaphthalene complex $[Fe(cp)(\eta^6\text{-}C_{10}H_{12})][PF_6]$ (**1**; cp = η^5-C_5H_5) with hydride or with carbon nucleophiles affords mixtures of isomeric neutral η^5-cyclohexadienyl complexes with low to moderate regioselectivity. Substitution at all four benzylic positions of the tetrahydronaphthalene ligand in compound (**1**) is achieved by treatment with an excess of Bu^{t}OK as base and in the presence of organic halide; by contrast with complex (**1**), the product tetra substituted tetrahydronaphthalene complexes, $[Fe(cp)(C_{10}H_8R_4)][PF_6]$ (**7**; R = Me), (**8**; R = CH_2:$CHCH_2$), and (**10**; R = CH_2Ph) exhibit a high degree of selectivity in the subsequent formation of substituted cyclohexadienyl complexes *via* addition of nucleophiles. With Bu^{t}OK–$PhCH_2Br$, trisubstitution can be effected, giving the complex $[Fe(cp)(C_{10}H_9BzI_3)][PF_6]$ (**9**; BzI = CH_2Ph) and leaving a single benzylic hydrogen which is substituted on further treatment with base and organic halide, to give diastereoisomeric mixtures of $[Fe(cp)(C_{10}H_8BzI_3R)][PF_6]$, (**11**; R = CH_2:$CHCH_2$), (12; R = Me), and (**13**; R = COPh). Under slightly different reaction conditions mono benzylic substitution is also possible, affording the compounds $[Fe(cp)(C_{10}H_{11}R)][PF_6]$, (**17**; R = Me) and (**18**; R = COPh). Octahydroanthracene and tetrahydroquinoline iron analogues $[Fe(cp)(Ar)][PF_6]$, (**14**; Ar = $C_{14}H_{18}$) and (**37**; Ar = $C_9H_{11}N$) of compound (**1**) have been synthesized and some deprotonations and substitutions have been cursorily examined. Hydrocarbon decomplexation from derivatives of (**1**) may be achieved by pyrolytic sublimation, completing Fe(cp) mediated synthesis of polysubstituted tetrahydronaphthalene derivatives including *inter alia* 1,1,4,4-tetramethyl-6-phenyltetrahydronaphthalene and 1,1,4,4-tetramethyl-6,7-diphenyltetrahydronaphthalene.

The depletion of electron density from aromatic systems which accompanies η^6-co-ordination at a transition-metal centre (*i.e.* metal-arene complex formation) introduces a susceptibility to attack by nucleophilic reagents that can function as a viable alternative to conventional electrophilic behaviour as a means for ring substitution. Simultaneous enhanced acidity of benzylic hydrogens establishes a complementary strategy for structural modification of substituted benzenes.[1] While each of these operations is well established for simple benzene derivatives (see Scheme 1, i and ii) application to synthetic adaptation of polycyclic frameworks has so far received very little attention. 1,2,3,4-Tetrahydronaphthalene (**A**) is the lowest member of a class of unsubstituted polyhydropolyaromatic compounds which are abundant components in crude oil. Derivatization of such readily available hydrocarbons may provide economical synthetic routes to polycyclic natural products or other desirable target molecules. Substitution reactions of the same family of hydroaromatics are also of interest as a means for modelling dissolution and liquefaction of coals.[2]

Selectivity in skeletal modification of polycarbocycles may be projected by analogy with Scheme 1, parallelling chemistry which has been developed principally through using the $Cr(CO)_3$ group as an electron sink and for blocking access to one face of the aromatic compound, the latter introducing stereospecificity into certain substitution steps. Of the several hundred examples which illustrate such transformations involving arenes, substituted arenes,[3] heteroarenes,[4] polyaromatics (*e.g.* pyrene[5] or naphthalene[6]), and cyclophanes,[7] most effect direct C–C bond formation at the aromatic nucleus but a significant number depend on benzylic activation (*i.e.*



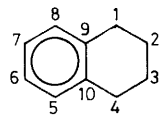
Scheme 1. *Reagents:* i, Nu = Nucleophile, *e.g.* H^-; ii, base + electrophile (E), *e.g.* MeI



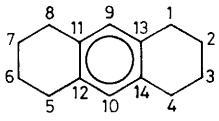
Scheme 2.

reaction centred at exocyclic carbon atoms); an interesting example is provided by the double alkylation of methyl phenylacetate[8] (Scheme 2).

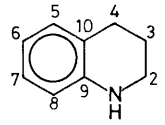
We have begun to test the scope of metal-assisted



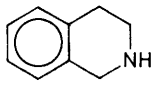
(A)



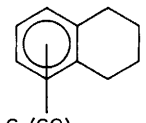
(B)



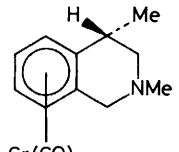
(C)



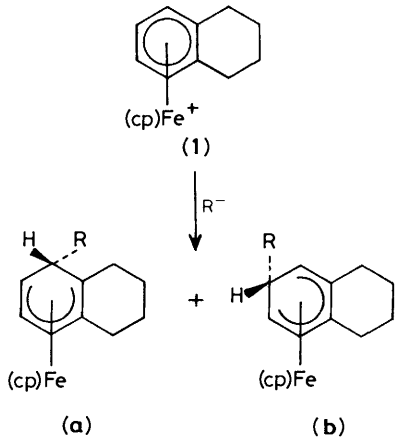
(D)



(E)



(F)



(a) (b)

(2a, b) R = H
(3a, b) R = D
(4a, b) R = Bu
(5a, b) R = Bu^t
(6a, b) R = Ph

Scheme 3.

modifications of polycyclic hydrocarbon structures by exploring changes in reactivity of tetrahydronaphthalene (**A**) and octahydroanthracene (1,2,3,4,5,6,7,8-isomer; **B**) that accompany complexation to the $Fe(cp)^+$ fragment (cp = C_5H_5). The latter was chosen because, although its utility in metal-assisted substitutions has received relatively little attention, the activating effect is predicted to be greater than that of $Cr(CO)_3$ through introduction of an overall positive charge on the complex. Further perceived advantages of the iron system included (*a*) the facility of product decomplexation by simple pyrolysis; (*b*) the prospects for recovery of the iron precursor [ferrocene, $Fe(cp)_2$] semi-stoicheiometrically, or completely by arene-exchange; and (*c*) circumventing the production of potentially toxic chromium-containing inorganic residues.

The potential for using operations (1, i) *vs.* (1, ii) (see Scheme 1) sequentially to direct stereochemistry each of the other, an idea hitherto ignored, has also been examined. Thus while only 1 and 4 positions (α,α') in the saturated ring of (**1**) can be modified *via* (1, ii) [with α,α' discrimination through *exo vs. endo* selectivity in the $Fe(cp)^+$ complex], we have found that such substitution may direct aromatic substitution (1, i) away from the (tetrahydronaphthalene) 8 carbon in favour of the more distant 6,7 atoms, regiospecificity which may be desirable in synthesis. Finally, and as a preliminary to developing corresponding heterocyclic chemistry, we have isolated the $Fe(cp)^+$ complex of tetrahydroquinoline (**C**), and have shown that it also reacts according to Scheme 1, i; by contrast (and in common with quinoline or isoquinoline) a related arene-iron cation is not accessible from tetrahydroisoquinoline (**D**) under conditions that are effective for synthesis of complexes (**A**)—(**C**).

Results and Discussion

Hydride or carbanion addition to the tetralin complex[9] (**1**) was observed to occur exclusively at the unsubstituted positions of the aromatic ring of the tetrahydronaphthalene framework; thus reaction with nucleophiles (H^-, D^-, Bu^-, Bu^{t-} or Ph^-), resulted in the formation of the neutral cyclohexadienyl complexes (**2a,b**)—(**6a,b**) (Scheme 3)). In every case a mixture of two isomers is formed, through attack at two distinguishable unsaturated positions in the aromatic nucleus (7,8 *vs.* 5,6), giving the products as red, air-sensitive oils; these were miscible with polar and non-polar solvents, and were characterized by mass spectrometry, i.r. spectroscopy, and n.m.r. measurements (^1H data, Table 1; ^{13}C data, Table 2). Attempts to separate the isomer mixtures using silica gel or alumina chromatography were unsuccessful. Relative isomer proportions (Table 3) are dependent on the nature of the reagent used: for example, (**2a**) and (**2b**) are formed in the ratio 48:52 on treatment of (**1**) with $NaBH_4$, but when $LiBEt_3H$ is used the isomer ratio changes to 71:29.

Isomer distributions of Table 3 were calculated from the ^1H n.m.r. spectra: in particular, in isomer (**2a**) a low field doublet, δ 5.77, is attributable to 5-H, the proton most removed from the newly substituted carbon, while no corresponding resonance is observed for (**2b**). A similar distinction is evident (Table 1) for the products (**3a**), (**3b**) of deuteride attack on (**1**): the upfield doublets in the ^1H n.m.r. spectrum of (**2a**), (**2b**) assigned to H_{exo} are absent from that of (**3a**) and (**3b**). This is consistent with stereospecific addition of D^- to the *exo* face of complex (**1**), an observation supported by i.r. spectroscopy, where $\nu(CH_{exo})$ at 2 760 cm^{-1} in (**2a,b**) shifts to 2 040 cm^{-1} in (**3a,b**), corresponding to $\nu(CH)/\nu(CD)$ = 1.35, *vs.* 1.36 calculated on the basis of reduced masses. Indeed, no i.r. absorptions in the range 2 700—2 800 cm^{-1}, characteristic[10] of CH_{exo} bond stretching, could be found for any of the cyclohexadienyls (**3a,b**)—(**6a,b**), indicating that in each instance the incoming nucleophile is added to the *exo* face of the arene ligand, in accordance with results reported by Pauson and co-workers.[11] A purely steric view of substitution involving $NaBH_4$, $LiBEt_3H$, $LiBEt_3D$, or LiPh as nucleophilic reagents would suggest that in each case the predominant isomer should result from attack at the least hindered position. The observed regioselectivity (Table 3) shows that other factors must be involved with isomers (**2a**), (**3a**), and (**6a**) formed preferentially. This is in contrast to hydride addition to the related *o*-xylene complex,[12] where a 1:1 isomer ratio was encountered. The reaction of complex (**1**) with butyl-lithium or t-butyl-lithium proceeds in good yield, substituting to give roughly equal proportions of the two expected isomers, unlike the prototypal $[Fe(cp)(benzene)]^+$ cation[13] with which t-butyl-lithium induces disproportionation as a minor reaction that leaves much of the cation unchanged.

Enhanced acidity of hydrogens attached to carbon atoms α to the co-ordinated arene ring system is a characteristic of complexes related to (**1**) and offers a means whereby substitution in the saturated ring of (**1**) may be effected. Similar

Table 1. ^{1}H N.m.r. spectra for cyclohexadienyl complexes[a]

Complex	cp	H^1—H^4	H^5—H^4	R	CH_3
(2a)[b]	3.96 (s)	1.0—2.6[c]	5.77 (d, H^5), 4.08 (t, H^6), 2.38 (dd, $H^8{}_{endo}$), 2.13 (t, H^7)	1.96 (d, $H^8{}_{exo}$)[d]	
(2b)	3.98 (s)	1.0—2.6[c]	4.10 (d, H^5),[e] 2.50 (m, $H^7{}_{endo}$), 2.05 (d, H^8), H^6[f]	1.77 (d, $H^7{}_{exo}$)	
(3a)[b]	3.96 (s)	1.0—2.5[c]	5.76 (d, H^5), 4.09 (t, H^6), 2.20 (m, $H^8{}_{endo}$), 2.11 (t, H^7)		
(3b)	3.98 (s)	1.0—2.5[c]	4.1 (d, H^5),[e] 2.50 (m, $H^7{}_{endo}$), 2.03 (dd, H^8), H^6[f]		
(4a,b)	3.99 (s) 3.96 (s)	0.78—2.9[c]	5.58 (d, H^5)	0.78—2.9[c]	
(5a,b)	3.97 (s) 3.94(s)	1.0—2.8[c]	5.37 (d, H^5),[g] 4.06 (d, H^5), 1.0—2.8[c]	0.49 (s), 0.54 (s)	
(6a)[b]	3.97 (s)	1.0—1.9[c]	5.55 (d, H^5), 3.60 (d, $H^8{}_{endo}$), 2.2—2.7,[c] 2.63 (t, H^7), H^5[f]	6.90 (m), 7.1 (m)	
(6b)	4.00 (s)	1.0—1.9[c]	4.10 (d, H^5), 2.2—2.7,[c] 2.2—2.7[c]	6.90 (m), 7.10 (m)	
(22)	4.14 (s)	1.3—1.9[c]	2.02 (d, H^8), 2.11 (t, H^6), 2.56 (dt, $H^7{}_{endo}$),[d] 4.06 (d, H^8)	1.61 (d, $H^6{}_{exo}$)	1.52 (s), 1.49 (s), 1.15 (s), 0.75 (s)
(23)	4.13 (s)	1.3—1.9[c]	2.00 (dd, H^8),[h] 2.10 (td, H^6), 2.53 (tt, $H^7{}_{endo}$),[i] 4.06 (d, H^5)		1.51 (s), 1.48 (s), 1.14 (s), 0.75 (s)
(24)	4.16 (s)	1.2—1.7[c]	2.59 (td, H^6),[h] 2.65 (dd, H^8), 3.61 (t, $H^7{}_{endo}$), H^5[f]	6.8—7.5 (m)	1.44 (s), 1.36 (s), 0.88 (s), 0.77 (s)
(25)	4.14 (s)	1.2—1.8[c]	2.22 (m, $H^7{}_{endo}$), 2.37 (dd, H^8),[h] 2.47 (td, H^6), 3.95 (d, H^5)	0.83 (t, CH_3), 1.2—1.8	1.48 (s), 1.41 (s), 1.12 (s), 0.81 (s)
(27)	4.16 (s)	1.74 (m) 2.00 (m)	3.20 (d, H^5), 5.28 (d, H^8),[j] 6.70 (dd, $H^6{}_{endo}$), 6.88—7.67 (C_6H_5),[c]	6.88—7.67 (C_6H_5)[c]	1.79 (s), 1.56 (s), 0.90 (s), 0.77 (s)

[a] C_6D_5 Solution, all chemical shifts in p.p.m. All three bond aromatic couplings in the range 5—7 Hz. [b] Major isomer. [c] Series of overlapping signals. [d] $J(H_{endo}$–$H_{exo}) = 12$ Hz; H_{exo} only couples with H_{endo}. [e] Obscured by H^6 of other isomer. [f] Not located. [g] Corresponding to **(5a)**. [h] $J(H^5$–$H^7) = 1.7$ Hz. [i] $J(H^7{}_{endo}$–D) = 2.0 Hz. [j] $J(H^8$–$H^6{}_{endo}) = 1.2$ Hz.

Table 2. ^{13}C N.m.r. spectra for cyclohexadienyl complexes **(2a,b)**—**(6a,b)**[a]

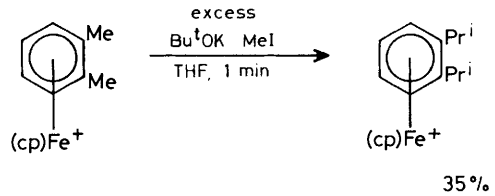
Complex	cp	CH_2	CH	Quaternary carbons	Others	CH_3
(2a)[b]	74.1	22.9, 23.4, 29.2, 33.2, 34.2 (C^8, C^1–C^4)	24.4 (C^7), 76.1 (C^6), 77.3 (C^5)	93.1, 93.7, 94.5 (C^9, C^{10})[c]		
(2b)	74.4	23.6, 27.4, 29.5, 30.5 (C^1–C^4)	20.7, 21.7 (C^8,C^6), 72.7 (C^5)	*d*		
(6a)[b]	74.3	23.1, 23.3, 29.5, 32.7 (C^1–C^4)	32.6 (C^7), 75.7 (C^6), 76.0 (C^5)	92.7, 93.0, 93.4 (C^9,C^{10})[e]	48.2 (C^8), 125—129,[f] 146.7[g]	
(6b)	74.5	23.5, 24.1, 29.0, 30.7 (C^1–C^4)	29.7, 30.8 (C^8,C^6), 75.9 (C^5)	*d*	41.8 (C^7), 125—129,[f] 149.3[g]	
(22)	73.9	36.1, 35.6, 27.5 (C^6,C^2,C^3)	13.2, 22.4 (C^8,C^6), 73.7 (C^5)	32.9, 33.9 (C^1,C^4), 104.2, 104.4 (C^9,C^{10})		28.9, 32.5, 33.4, 34.9
(24)	73.9	35.5, 35.8	24.3, 30.4 (C^8,C^6), 72.5 (C^5), 41.8 (C^7)	32.0, 33.4 (C^1,C^4), 101.6, 104.0 (C^9,C^{10}), 148.4 (C_6H_5)	125—128.9 (C_6H_5)[f]	29.1, 32.3, 32.8, 34.3
(25)	73.6	23.0, 26.8, 35.6, 36.0, 41.0 (C^2–C^4, C_4H_9)	22.0, 31.2, 37.0 (C^8,C^6,C^7), 71.2 (C^5)	32.8, 33.5 (C^1,C^4), 101.2, 103.9 (C^9,C^{10})	14.3 (C_4H_9)	29.0, 32.4, 33.4, 34.7
(27)	75.9	35.4, 35.9 (C^2,C^3)	74.1 (C^8), 25.3 (C^5), 43.6 (C^6)	101.5, 103.1 (C^9,C^{10}), (C^1,C^4,C^7),[h] 146.5, 146.8 (C_6H_5)	124.3—128.9 (C_6H)[f]	28.9, 32.5, 32.8, 34.1

[a] C_6D_6 Solution, all chemical shifts in p.p.m. [b] Major isomer. [c] Also contains quaternary carbons of **(2b)**. [d] Same as for isomer (a). [e] Also contains quaternary carbons of **(6b)**. [f] Obscured by solvent. [g] Quaternary phenyl resonance. [h] Not located.

Table 3. Isomer distribution for cyclohexadienyl complexes

Compound	Nucleophilic reagent	Isomer ratio[a] **(a)**:**(b)**
(2)	$NaBH_4$	48:52
(2)	$LiBEt_3H$	71:29
(3)	$LiBEt_3D$	68:32
(4)	BuLi	53:48
(5)	Bu^tLi	50:50
(6)	PhLi	64:36

[a] Calculated from ^{1}H n.m.r. spectra (see text).



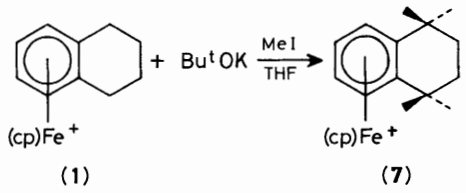
Scheme 4.

chemistry has been developed for the *o*-xylene complex,[14] (Scheme 4), which represents one-step multiple carbon–carbon bond formation. At room temperature, complex **(1)** reacts with a large excess (*ca.* 50-fold) of Bu^tOK and MeI to give an orange amorphous solid; formulation of this product as the tetramethyl derivative **(7)** (Scheme 5) was supported by spectroscopic measurements and microanalytical data, implying that under such conditions alkylation predominates over Williamson synthesis. The ^{1}H n.m.r. spectrum (Table 4) contains two prominent singlets at δ 1.28 and 1.69 assigned respectively to the

Table 4. ^{1}H N.m.r. spectra for substituted tetrahydronaphthalene complexes[a]

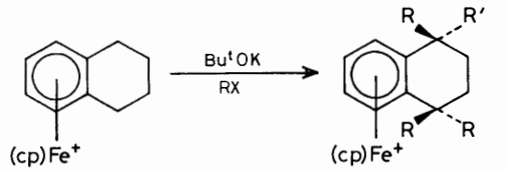
Complex	cp	H^5—H^6	R1′R4′	R1″R4″	H^2H^3	Others
(7)	5.21 (s)	6.52 (m)	1.69 (s)	1.28 (s)	1.95 (m, $H^{2'}$,$H^{3'}$), 1.76 (m, $H^{2''}$,$H^{3''}$)	
(8)	5.25 (s)	6.51 (m)	6.09 (m, –CH=), 4.9 (=CH_2),[e] 3.08 (dd, –CH*H*–),[g] 2.73 (dd, –C*H*H–)[i]	5.55 (m, –CH=), 5.3 (=CH_2),[e] 2.45 (dd, –CH*H*–),[h] 2.26 (dd, –C*H*H–)[j]	1.98 (m, $H^{2'}$,$H^{3'}$), 1.89 (m, $H^{2''}$,$H^{3''}$)	
(9)	5.29 (s)	6.08 (dd, H^6),[k] 6.36 (t, H^7),[n] 6.63 (m, H^5,H^6)[e]	3.72 (d, –C*H*H–),[l] 3.55 (d, –CH*H*–), (3.20 m, H^1), 6.86—7.55 (m, Ph)	3.32 (d, –C*H*H–),[m] 2.53 (d, –CH*H*–), 2.18 (dd, –C*H*H),[o] 1.80 (dd, –CH*H*–),[p] 6.86—7.55 (m, C_6H_5)[e]	1.66—1.94 (m)[e]	
(10)[q]	5.02 (s)	5.94 (m)[e]	3.50 (d, –C*H*H–),[r] 3.15 (d, –CH*H*–), 6.3—7.6 (m, Ph)	2.92 (d, –C*H*H–),[s] 2.15 (d, –CH*H*–), 6.3—7.6 (m, Ph)	1.5—2.0 (m)[e]	
(11)	5.44 (s)	6.68 (m)	3.86 (d, –C*H*H),[l] 3.71 (d, –CH*H*–), 3.39 (dd, –C*H*H–),[t] 4.25 (d, =CH_2)[u] 4.66 (d, =CH),[w] 5.15 (m, =CH–),[e] 7.0—7.7 (C_6H_5)	3.55 (d, –C*H*H–),[l] 3.25 (d, –C*H*H),[o] 2.28 (d, –CH*H*),[v] 7.0—7.7 (C_6H_5)	2.0 (m)[e]	
(12)[b]	5.31 (s)[c]	6.59 (m),[e] 6.39 (m)[e]	1.53 (s, –CH_3), 3.2—3.9 (m, –CH_2–), 6.75—7.70 (C_6H_5)	2.1—2.6 (m, –CH_2),[x] 3.2—3.9 (m, –CH_2–),[x] 6.75—7.70 (C_6H_5), 0.46 (s, CH_3)	1.83 (m)[e]	
(13)[b]	5.45 (s),	6.35 (m), 6.56 (m)	6.95—7.53 (C_6H_5), 3.27—3.56 (–CH_2–), 2.35—2.70 (–CH_2–)	6.95—7.72 (C_6H_5), 3.27—3.56 (–CH_2–), 2.35—2.70 (–CH_2–)	1.75—1.87 (m)[e]	
(17)[b]	5.21 (s)[c]	6.30 (m)	3.30 (q, H^1), 3.10 (m, $H^{4'}$)[e]	1.31 (d, CH_3),[d] 2.84 (m, $H^{4''}$)[e]	1.6—2.3 (m)[b]	
(18)	5.25 (s)	6.34 (m), 6.44 (m)	7.59, 7.71, 8.16 (C_6H_5), 3.15 (m, $H^{4'}$)	5.48 (t, $H^{1''}$),[f] 2.88 (m, $H^{4''}$)	1.84 (m), 2.88 (m), 2.62 (m), 3.15 (m)	
(26)	5.11 (s)	6.70 (d, H^6),[k] 6.91 (dd, H^7),[y] 6.91 (d, H^5)	1.83 (s), 1.77 (s)	1.47 (s), 1.35 (s)	2.0 (s)	7.59, 8.06
(28)	5.26 (s)	6.75 (s, H^5,H^6)	1.43 (s)	1.83 (s)	1.89 (m) 2.04 (m)	7.43 (m)

[a] $(CD_3)_2CO$ Solutions. [b] Mixture of two isomers. [c] Major isomer. [d] $J(H_{1\alpha}$–$CH_3)$ = 6.9 H_3. [e] Poorly resolved. [f] $J(H_{1\beta}$–$CH_2)$ = 6.1 H_3. [g] J(*H*–H) = 13.3 Hz. [h] J(*H*–H) – 13.8 Hz, J(*H*–CH=) = 6.2 Hz. [i] J(*H*–CH=) = 7.4 Hz. [j] J(*H*–CH=) = 8.2 Hz. [k] $J(H^8$–$H^7)$ = 6.7 Hz, $J(H^8$–$H^6)$ = 1.0 Hz. [l] J(*H*–H) = 13.0 Hz. [m] J(*H*–H) = 13.3 Hz. [n] $J(H^7$–$H^6)$ = 6.3 Hz. [o] J(*H*–H) = 13.8 Hz, $J(H_\alpha$–CH) = 7.1 Hz. [p] $J(H_\alpha$–CH) = 9.6 Hz. [q] CD_3CN Solution. [r] J(*H*–H) = 13.1 Hz. [s] J(*H*–H) = 13.7 Hz. [t] J(*H*–H) = 13.9 Hz, J(H–CH*H*) = 7.0 Hz. [u] J(*H*–H)$_{trans}$ = 16.5 Hz. [v] J(H–H) = 14.2 Hz. [w] J(*H*–H)$_{cis}$ = 10.9 Hz. [x] Complex series of doublets. [y] $J(H^7$–$H^5)$ = 1.7 H_3.



(1) (7)

Scheme 5.

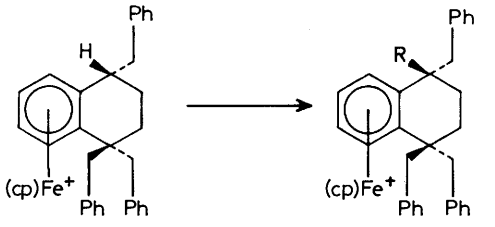


(1) (8) R = R′ = C_3H_5
(9) R = $PhCH_2$, R′ = H

Scheme 6.

exo- and *endo*-methyl groups; an isolated singlet at δ 5.21 corresponds to the cp group. Although no specific distinction between *exo vs. endo* methyl resonances has been suggested in Table 4, n.m.r. assignments for *exo*- and *endo*-methylated fluorene complexes[15] have shown that the *exo*-methyl group resonates at higher field. The purity of complex (**7**) appears to be dependent on the synthetic regimen applied. Thus, complex (**7**) is obtained free of impurity upon addition of a solution in THF of iodomethane to a dry mixture of complex (**1**) and Bu^{t}OK; if iodomethane is added to a THF solution containing complex (**1**) and Bu^{t}OK, however, several compounds containing the (cp)Fe^+ fragment appear to be formed in varying proportions. In a similar reaction the tetra-allyltetrahydronaphthalene compound (**8**) was produced by treatment of complex (**1**) with allyl iodide and Bu^{t}OK (Scheme 6), in a manner insensitive to the method of reagent addition.

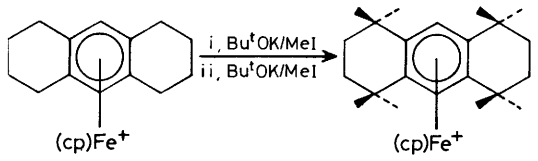
Attempted per-α-substitution of complex (**1**) by using Bu^{t}OK and benzyl bromide resulted in formation of the trisubstituted complex (**9**), a pale beige solid characterized by microanalysis and spectroscopic data. Two isomers can arise from trisubstitution of the tetrahydronaphthalene benzylic sites, but resolution in the ^{1}H n.m.r. spectrum of only a single cp signal at δ 5.29 implied that a single isomer is produced. A multiplet at δ 3.20 was assigned to the unsubstituted benzylic proton, the deshielded position[15] suggesting occupation of an *endo* site. It was found also that a fourth benzyl group could be introduced by treatment of complex (**9**) with more benzyl bromide and base (Scheme 7), resembling the forcing conditions required[16] for perbenzylation of $[Fe(cp)(C_6Me_6)]^+$. The tribenzyl derivative (**9**) proved to be a useful precursor for the synthesis of tetrahydronaphthalene complexes containing other α-substituents. Thus, treatment in the presence of Bu^{t}OK with allyl iodide, methyl iodide, or benzoyl chloride gave complexes (**11**), (**12**),



(9)

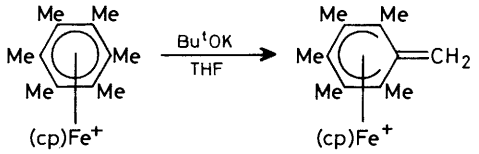
(10) R = $PhCH_2$
(11) R = C_3H_5
(12) R = Me
(13) R = PhCO

Scheme 7.



(14) (15)

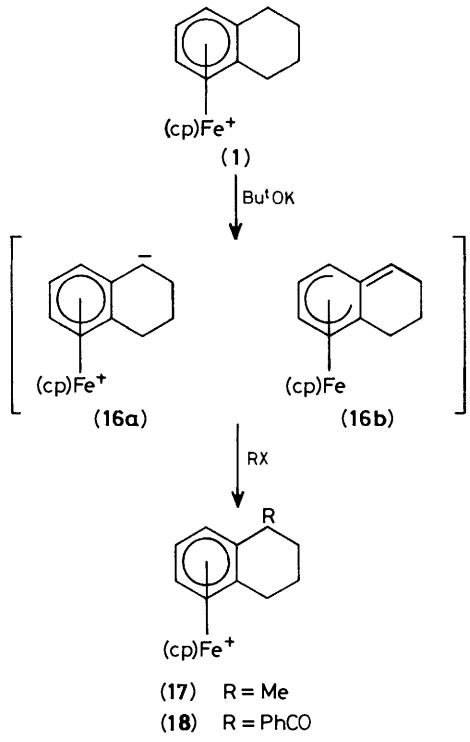
Scheme 8.



Scheme 9.

and (**13**) respectively. The methylated and benzoylated species (**12**) and (**13**) were formed as a mixture of *exo*- and *endo*-isomers. By contrast, spectroscopic data for the allyl derivative (**11**) suggested (Tables 4 and 5) that only a single stereoisomer was present: in particular, there was a sharp cp resonance (δ 77.7 p.p.m.) in the ^{13}C n.m.r. spectrum. Permethylation of the novel octahydroanthracene analogue (**14**) of (**1**) also proved to be possible, but only when a mixture of partially alkylated products produced initially was re-exposed to the MeI–Bu^{t}OK reagent mixture (Scheme 8). Isolation of the air-sensitive carbanions (*i.e.* intermediates generated by deprotonation) has been shown to be unnecessary [14] for the success of single-step polysubstitution reactions.

Astruc *et al.*[17] have isolated a stable crystalline product from deprotonation of the hexamethylbenzene complex {[Fe(η^5-C_5H_5)(η^6-C_6Me_6)]PF_6} (Scheme 9), an *X*-ray crystal structure determination for which is best interpreted in terms of a cyclohexadienyl formalism [*cf.* (**16a**), (**16b**), Scheme 10]. Attempts at isolation of corresponding stable species following deprotonation of either the tetrahydronaphthalene complex (**1**) or its octahydroanthracene analogue (**14**) were unsuccessful, in accord with earlier conclusions [18] that deprotonated arene complexes are kinetically unstable with less than fully substituted aromatic nuclei; however the red solution formed by deprotonation of (**1**) [formulated as either a zwitterionic complex (**16a**) or a cyclohexadienyl complex (**16b**)], was found to react with methyl iodide or benzoyl chloride to give the mono substituted derivatives (**17**) and (**18**) respectively. Complex (**14**) was deprotonated with Bu^{t}OK to give a red solution (Scheme 11) that was somewhat more stable than that containing (**16a,b**); the ^1H n.m.r. spectrum showed a cp resonance at δ 3.86, *i.e.* shifted to higher field by *ca.* 1 p.p.m. *vs.* compound (**14**), indicative of neutral Fe^{II} character. Inequivalence introduced between 9-H and 10-H resulted in chemical shifts of δ 3.51 and 4.12, positions that are in good agreement with those for known



(17) R = Me
(18) R = PhCO

Scheme 10.

cyclohexadienyls, although no comparable data are available relating to an alternative zwitterionic structure. Solutions of (**19a, b**) reacted with methyl iodide and benzoyl chloride to give compounds (**20**) and (**21**). The monomethyl derivatives (**17**) and (**20**) were formed as mixtures of *exo*- and *endo*-isomers, with the *exo*-methylated isomer predominating [19] as would be expected from steric arguments. The monobenzyl compound (**18**) was recovered contaminated with its precursor (**1**) but was separated successfully using alumina chromatography. For products (**18**) and (**21**) only a single isomer was detected, evidence for stereospecific addition under steric control. These results are in contrast to those reported [15] for the analogue [Fe(cp)(fluorene)]$^+$, where addition of methyl iodide was stereospecific and addition of benzoyl chloride resulted in disubstitution, indicating a lower acidity for benzylic hydrogens in co-ordinated tetrahydronaphthalenes *vs.* those in fluorene analogues.

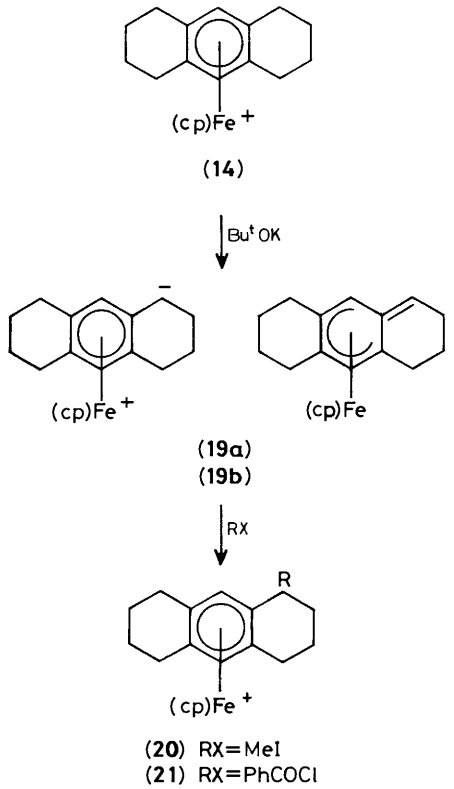
Addition of nucleophiles to compound (**1**) results in substitution at the 7 and 8 positions. In order to determine if substitution in the saturated ring of the tetrahydronaphthalene complex (**1**) had any influence on the pattern of nucleophilic addition to the co-ordinated ring system, the reactivity of the tetramethyltetrahydronaphthalene complex (**7**) with various nucleophiles was investigated (Scheme 12). In sharp contrast to similar additions of nucleophiles to complex (**1**), those represented by Scheme 13 each afforded a single product. The compounds (**22**)—(**25**) were characterized by ^1H n.m.r., i.r., ^{13}C n.m.r., and mass spectroscopy. In all cases a single cp resonance was observed; regiospecific addition to the 6 position was demonstrated by the absence from ^1H n.m.r. spectra of features attributable (as proposed above) to the 5-H resonances characteristic of 8-substituted derivatives. A C–H_{exo} stretch at 2 760 cm^{-1} was observed only in the hydride addition product (**22**), indicating also that each addition was regiospecific to the 7 position and stereospecifically *exo*.

In order to add a second phenyl substituent *via* nucleophilic attack, reoxidation of the neutral cyclohexadienyl complex (**24**) to a cationic species is required. Previous workers have reported

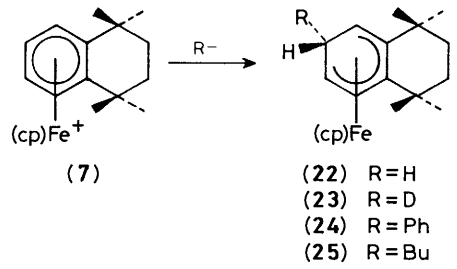
Table 5. ^{13}C N.m.r. spectra for substituted tetrahydronaphthalene complexes[a]

Complex	cp	C^1—C^4	C^5—C^8	C^9—C^{10}	Others
(7)	76.3	34.0 (C^1,C^4), 34.1 (C^2,C^3)	83.8 (C^5,C^8), 86.1 (C^6,C^7)	113.9	31.3, 32.5 (CH_3)
(8)[e]	77.4	40.1 (C^1,C^4), 27.4 (C^2,C^3)	85.4 (C^5,C^8), 86.6 (C^6,C^7)	113.9	45.0, 46.1 (–CH_2–), 134.4 (=CH–), 119.9, 120.1 (=CH_2)
(9)[e]	77.9	41.1 (C^1), 22.5, 22.6 (C^2,C^3), 44.4 (C^4)	87.0, 87.5, 87.3, 86.6	108.1 (C^9), 115.9 (C^{10})	42.1, 47.6, 48.2 (–CH_2), 127.3—139.8 (C_6H_5)
(10)[f]	77.7	42.3 (C^1,C^4), 26.8 (C^2,C^3)	85.6 (C^5,C^6)	115.1	44.6, 47.8 (–CH_2–), 127.7—132.9 (C_6H_5)
(11)[f]	77.7	40.9, 42.2 (C^1,C^4), 24.9, 28.3 (C^2,C^3)	85.4, 86.3, 86.4, 86.9	114.1, 115.6	43.5, 46.6, 46.8, 49.8 (–CH_2), 119.9 (=CH_2), 134.0 (=CH–), 127.3—132.8 (C_6H_5)
(12)	77.6,[b] 77.7	23.2, 24.0 (C^2,C^3), 37.8, 38.8 (C^1,C^4)[g]	87.3, 86.4[g]	113.5, 116.1[g]	27.5 (CH_3), 46.9, 47.3,[c] 49.2 (–CH_2–), C_6H_5,[c] 39.9 (–CH_3)[f]
(13)[h]	78.0, 77.8	22.3, 22.4, 25.1, 26.7 (C^2,C^3), 57.3 (C^1)	*i*	107.9, 109.1, 115.6, 117.1	204.6, 210.1 (CO), 127—133 (C_6H_5)
(17)	78.1[b]	33.3 (C^1), 20.1, 29.7, 30.8 (C^2—C^4)	*c*	*c*	23.2 (CH_3)
(18)[d]	78.7	48.2 (C^1), 28.1, 29.3 (C^2,C^3), 20.4 (C^3)	87.8, 88.4, 88.5, 89.1	103.6, 106.0	130.1, 130.4, 130.6 (C_6H_5), 136.8 (C_6H_5, quat.), 202.3 (*C*=O)
(26)	78.5	35.1 (C^1,C^4), 34.7, 35.0 (C^2,C^3)	82.5, 84.4, 84.8 (C^5,C^7,C^8), 102.6 (C^6)	114.7, 115.2	31.5, 32.76, 32.81 (CH_3), 128.9 130.4, 131.1, 135.9 (C_6H_5)
(28)	79.5	35.0 (C^1,C^4), 34.9 (C^1,C^3)	85.7 (C^5,C^8), 103.5 (C^6,C^7)	114.8	129.5, 130.2, 131.8, 136.2 (C_6H_5), 31.4, 32.9 (CH_3)

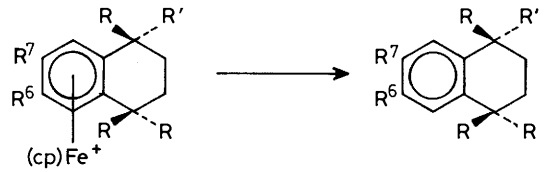
[a] $CDCL_3$ solution, all chemical shifts in p.p.m. [b] Major isomer. [c] Obscured by overlapping resonances. [d] CD_3NO_2 Solution. [e] $(CD_3)_2CO$ Solution. [f] CD_3CN Solution. [g] Signals for the minor isomer obscured by those of the major isomer and starting material. [h] Mixture of *exo*- and *endo*-benzoylated complexes *ca.* 55:45 ratio. [i] Obscured by overlapping resonances.



Scheme 11.



Scheme 12.



(7)	R = R'= Me, R^6=R^7=H	(29)
(8)	R = R'= C_3H_5, R^6=R^7=H	(30)
(9)	R = $PhCH_2$, R'= H, R^6=R^7=H	(31)
(10)	R = R'= $PhCH_2$, R^6=R^7=H	(32)
(12)	R = $PhCH_2$, R'= Me, R^6=R^7=H	(33)
(13)	R = $PhCH_2$, R'= COPh, R^6=R^7=H	(34)
(26)	R = R'= Me, R^6=H, R^7=Ph	(35)
(28)	R = R'= Me, R^6=R^7=Ph	(36)

Scheme 13.

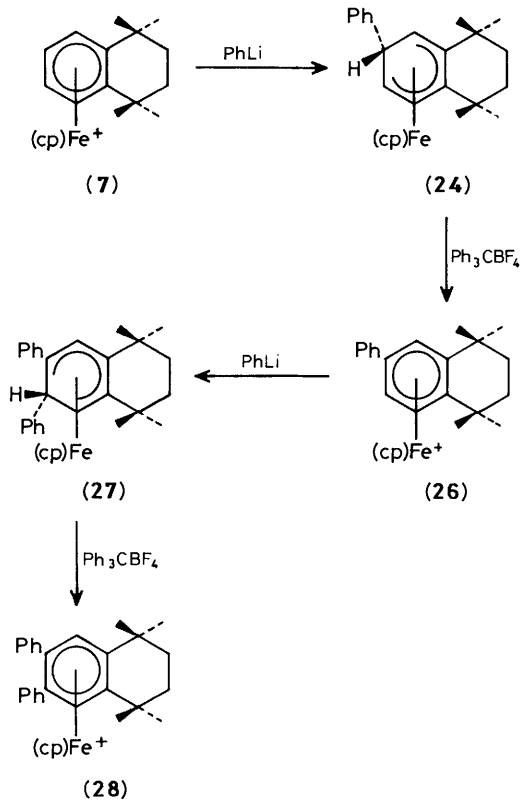
that in related cyclohexadienyl complexes, hydride abstraction to yield the cationic derivative may be accomplished successfully using *N*-bromosuccinimide[20] or triphenylmethyl tetrafluoroborate[14] $(Ph_3C)BF_4$. Thus it was found that treatment of complex (**24**) with Ph_3CBF_4 gave the phenyl-(tetramethyl)tetrahydronaphthalene cation (**26**), *via* endo-hydride abstraction (Scheme 14); whereupon subsequent treatment with PhLi gave the expected neutral cyclohexadienyl complex (**27**). Both ^1H and ^{13}C n.m.r. data were consistent with a high symmetry structure, which is possibly only if the second Ph group has attached at the 6 position. The product (**27**) could also be oxidized (Ph_3CBF_4) to a further cation (**28**), for which the ^1H and ^{13}C n.m.r. spectra confirmed a symmetrical disposition of the six ring-substituents.

Pyrolytic sublimation[21] of compound (**7**) afforded the free

Table 6. ^{1}H N.m.r. spectra for uncomplexed tetrahydronaphthalenes[a]

Compound	H^6—H^8	$R^{1'}R^{4'}$	$R^{1''}R^{4''}$	H^2—H^3	Others
(**29**)	7.31 (m), 7.12 (m)	1.28 (s, CH_3)		1.69 (s)	
(**30**)	7.14 (m), 7.25 (m)	5.59 (m, –CH=), 5.02 (m), 4.99 (m),[c] 4.95 (m)[c]	2.50 (dd, –C*H*H–),[b] 2.21 (dd, –CH*H*–)[d]	1.69 (s)	
(**31**)	7.75 (d),[e] 7.37 (t),[f] 7.02 (m)	2.8 (m, H_a), 3.49 (d, –C*H*H–), 3.27 (d, –CH*H*–),[g] 6.91 (m, C_6H_5), 7.22 (m, C_6H_5)	2.94 (d, –C*H*H–), 2.81 (d, –CH*H*–),[g] 2.37 [dd, CH_a(C*H*H–)–],[i] 1.88 [dd, CH_a(CH*H*–)][j]	1.97 (m), 1.57 (dt),[h] 1.33 (m)	
(**32**)[k]	7.20 (m),[l] 7.45 (m)	2.90 (d, –C*H*H–), 2.59 (d, –CH*H*–),[m] 6.83 (m, C_6H_6), 7.12 (m, C_6H_5)		1.53 (s)	
(**33**)	6.75 (m), 6.85 (m), 6.92 (m), 7.26 (m)	0.95 (s, CH_3), 3.28 (d, –CH*H*–),[n] 3.23 (d,–CH*H*),[n] 7.12 (m, C_6H_5)	2.85 (d, –C*H*H–), 2.71 (d, –CH*H*–), 2.32 (d, –CH*H*–), 2.19 (d,–CH*H*–), 7.12 (m, C_6H_5)	1.2 (m)	
(**34**)	6.6—8.1[c]	3.46 (d, –CHH–), 3.25 (d, –C*H*H–), 3.22 (d, –C*H*H–), 3.19 (d, –C*H*H–), 2.91 (d, –C*H*H–), 2.78 (d, –C*H*H)[o]		1.5—2.0[c]	
(**35**)	7.24—7.58 (m)[c]	1.31 (s), 1.33 (s)		1.71 (s)	7.24, –7.58 (m), (C_6H_5)
(**36**)	7.33 (s)	1.33 (s)		1.73 (s)	7.15 (m), (C_6H_5)

[a] $CDCl_3$ Solution, all chemical shifts in p.p.m. [b] J(*H*–H) = 14.0 Hz, J(H–CH=) = 6.4 Hz. [c] Poorly resolved. [d] J(H–CH=) = 8.0 Hz. [e] $J(H–H)_{ortho}$ = 7.6 Hz. [f] J(H–H) = 1.1 Hz. [g] J(H–H) = 13.3 Hz. [h] $J(H^2_\alpha–H^2_\beta)$ = 14.3 Hz, $J(H^2–H^3)$ = 3.8 Hz. [i] J(*H*–H) = 13.7 Hz, $J(H_\alpha–CH)$ = 6.2 Hz. [j] $J(H_\alpha–CH)$ = 9.9 Hz. [k] $(CD_3)_2CO$ Solution. [l] $J(H–H)_{ortho}$ = 6.0 Hz. [m] J(*H*–H) = 13.5 Hz. [n] J(*H*–H) = 13.7 Hz. [o] J(*H*–H) = 13.1 Hz.



Scheme 14.

hydrocarbon, 1,1,4,4-tetramethyltetrahydronaphthalene (**29**), as a clear colourless oil (Scheme 13). The preparation of this compound was reported[22] by condensation of 2,5-dichloro-2,5-dimethylhexane with benzene in the presence of an excess of $AlCl_3$, although no spectroscopic characterization has since appeared. For the iron complexes (**7**) and (**8**), signals arising from *exo*- and *endo*-R groups are distinguishable by n.m.r., but generation of the corresponding uncomplexed materials (**29**) and (**30**) re-establishes in each case a molecular plane of symmetry with concomitant simplification of the spectra. Spectroscopic comparison between the complexed and uncomplexed species was thus very informative as an aid to structural identification. The ^{1}H n.m.r. and ^{13}C n.m.r. data are collected in Tables 6 and 7 respectively. Similar reactions were possible for iron complexes in which the hydrocarbon ligand contains a chiral centre due to the presence of more than one type of R group in the saturated ring. Thus complexes (**12**) and (**13**) gave on pyrolysis hydrocarbons (**33**) and (**34**). For each of these the n.m.r. spectra (Tables 6 and 7) show only one set of signals: for example, the ^{1}H n.m.r. spectrum of complex (**33**) displays a singlet at δ 0.95 assigned to the methyl group. Since compounds (**33**) and (**34**) would be predicted to exist as diasteroisomeric mixtures, the observation of only one signal due to ring substituents implies that the saturated ring is sufficiently flexible to allow rapid conformational inversion.[23] Compound (**35**), obtained by pyrolytic sublimation of complex (**26**) (see Scheme 14), showed spectroscopic properties similar to those reported in the literature;[24] this class of compound was previously only accessible by the reaction of biphenyl and 2,5-dimethylhexane-2,5-diol in the presence of $AlCl_3$. The diphenyltetramethyltetrahydronaphthalene (**36**) has not been synthesized previously, although a related compound 1,2,3,4-tetrahydro-6,7-diphenylnaphthalene has been prepared by Vollhardt and co-workers.[25]

Many simple substituted heterocyclic compounds exhibit significant pharmacological activity, accounting in part for recent interest in heteroarene iron[26] and chromium[27] chemistry. In order to explore heterocycle substitution chemistry related to that described above for (**1**) and (**14**), the tetrahydroquinoline complex (**37**) was made using a procedure similar to that reported by Helling and Hendrickson[28] (Scheme 15). Spectroscopic data are collected in Table 8. Attempts at synthesizing the isomeric complex derived from tetrahydroisoquinoline were unsuccessful, although the chromium complex (**E**) has been reported.[27] Problems associated with the formation of the iron complex may be due to decomposition of the heterocyclic ligand in the presence of $AlCl_3$. VonBorn cleavage[29] of amines in the presence of electrophiles is well documented, so that in this case $AlCl_3$ may be acting as the electrophile.

Electrophilic substitution chemistry of the tetrahydro-

Table 7. ^{13}C N.m.r. spectra for uncomplexed substituted tetrahydronaphthalenes[a]

Compound	C^1—C^4	C^5—C^8	C^9—C^{10}	Others
(29)	34.2 (C^1,C^4), 35.2 (C^2,C^3)	125.5 (C^5,C^6), 126.4 (C^6,C^7)	144.8	31.9 ($-CH_3$)
(30)	40.0 (C^1,C^4), 26.8 (C^2,C^3)	125.5 (C^5,C^8), 127.2 (C^6,C^7)	142.7	46.3 ($-CH_2$), 135.5 (–CH=), 117.2 ($=CH_2$)
(31)	40.5 (C^1), 22.3, 25.0 (C^2,C^3), 42.9 (C^4)	*b*	138.7, 138.8	42.3, 47.4, 50.5 ($-CH_2-$), 125.5—142.3 (C_6H_5)
(32)	42.7 (C^1,C^4), 26.2 (C^2,C^3)	125.0 (C^5,C^8), 128.8 (C^6,C^7)	142.4	47.4 ($-CH_2-$), 125.9—130.9 (C_6H_5)
(33)	43.1 (C^1,C^4), 28.6, 30.9 (C^2,C^3)	*b*	141.0, 146.0	25.6 ($-CH_3$), 47.9, 48.0, 49.7 ($-CH_2-$), 125.2—131.0 (C_6H_5)
(34)	57.3 (C^1), 24.9 (C^2), (C^3,C^4)[c]	125.7—131.0[d]	137.9—142.3	40.4, 42.3, 47.7, 50.4 ($-CH_2-$), 205.2 (C=O), 137.9—142.3[e]
(35)	34.1, 34.4 (C^1,C^4), 35.1, 35.2 (C^2,C^3)	124.4, 125.3, 126.8, 126.9 (C^5,C^7,C^8, C_6H_4)	138.4, 141.6, 144.0, 145.2, (C^9,C^{10},C^6,C_6H_5)	127.1, 128.6 (C_6H_5), 31.85, 31.9 (CH_3)
(36)	34.2 (C^1,C^4), 35.3 (C^2,C^3)	126.2, 128.8 (C^5, C^8, C_6H_5)	137.6, 141.9, 144.2 (C^9,C^{10}, C_6H_5)	127.8, 130.0 (C_6H_5), 31.9 (CH_3)

[a] $CDCl_3$ solution, all chemical shifts in p.p.m. [b] Poorly resolved. [c] Not located. [d] Complex series of lines. [e] Quaternary carbons on aromatic rings.

Table 8. N.m.r. spectra for heterocyclic compounds[a]

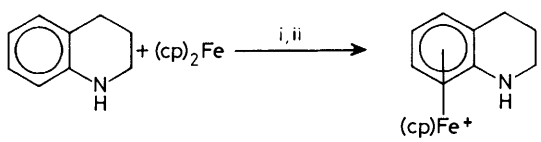
^1H N.m.r.

Complex	cp	H^5—H^8	H^2—H^3	R^1	$R^{4'}R^{4''}$
(37)	4.91 (s)	5.68 (d), 5.88 (t), 5.96 (t), 6.05 (d)	3.45 (m), 3.24 (m), 2.20 (m), 2.05 (m)	6	2.91 (dt, $H^{4'}$),[c] 2.96 (m, $H^{4''}$)
(39)	4.97 (s)	5.74 (dd), 5.95 (td), 5.98 (dd), 6.04 (td)[d]	3.44[e] (m), 2.24, 2.05 (m)	3.10 (s)	2.95 (m, $H^{4''}$), 2.71 (m, $H^{4''}$)
(40)	4.96 (s)	6.17 (d), 6.10 (t), 5.96 (t), 5.82 (d)	3.48[e] (m), 2.33 (m), 1.89 (dt)[f]	3.08 (s)	1.21 (s), 1.60 (s)

^{13}C N.m.r.

Complex	cp	C^5—C^{10}	C^2—C^4	R^1	$R^{4'}R^{4''}$
(37)	76.6	68.2, 79.9, 85.3, 86.8, 125.1 (C^9)	41.0 (C^2), 26.8 (C^4), 21.2 (C^3)		
(39)	76.1	65.5, 80.2, 85.1, 86.9 (C^{9-10})	50.8 (C^2), 27.4 (C^4), 21.3 (C^3)	39.0	
(40)	75.7	66.4, 79.2, 83.0, 85.3, 93.5 (C^{10}), 125.4 (C^9)	47.3 (C^2), 35.8 (C^3), C[4][b]	39.0	28.3, 30.0

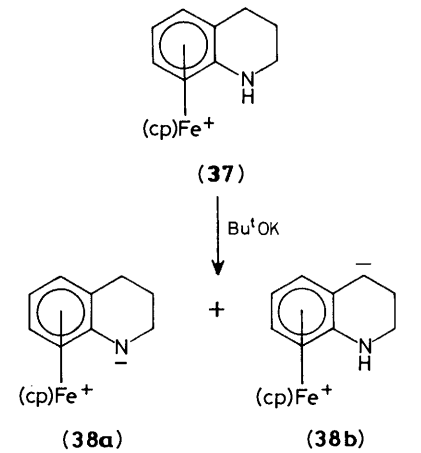
[a] $(CD_3)_2CO$ Solution, all chemical shifts in p.p.m.; 3 bond aromatic couplings in the range 5.7—6.4 Hz. [b] Not located. [c] $J(H^{4'}-H^{4''})$ = 16.7 Hz, $J(H^{4'}-H^{3'}, H^{3''})$ = 5.3 Hz. [d] $J(H-H)_{meta}$ = 1.4 Hz. [e] Corresponding to two hydrogens. [f] $J(H^{3'}-H^{3''})$ = 13.6 Hz.



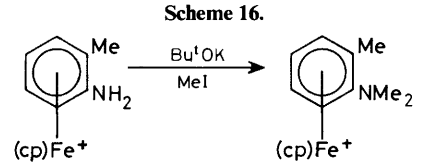
(37)

Scheme 15. *Reagents and conditions:* i, $AlCl_3$, Al, decahydronaphthalene, reflux; ii, water, NH_4PF_6

quinoline complex (**37**) has been investigated; as a preliminary, the deprotonation of complex (**37**) by Bu^{t}OK (Scheme 16) was followed using ^1H n.m.r. spectroscopy. Two singlet cp resonances were evident, in 81:19 ratio; the spectroscopic data are consistent with formation of products (**38a**):(**38b**) (Scheme 16) with the major constituent resulting from deprotonation at nitrogen. For the major isomer (**38a**), the aromatic protons resonate in the range δ 6.29—7.02; although a cyclohexadienyl structure could be postulated, the relatively deshielded position of these protons favours an aromatic (*i.e.* zwitterionic) structure as is indicated. In a related *o*-toluidine iron complex,[30] deprotonation followed by methylation produced solely the substitution product at nitrogen (Scheme 17). Similarly treatment of (**37**) with Bu^{t}OK and MeI gave the methylated complex (**39**). Further α-substitution was achieved by the subsequent reaction of complex (**39**) with Bu^{t}OK and MeI yielding the pure compound (**40**) (Scheme 18). The only other example of a heterocyclic arene complex in which substitution

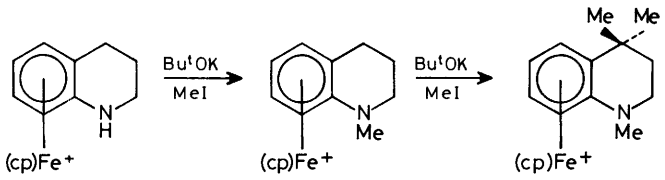


Scheme 16.



Scheme 17.

at both benzylic and amino sites has been achieved is that reported recently by Davies (**F**).[27] From our results, it seems that the Fe(cp) group may be less effective in 'face blocking' of



(37) (39) (40)

Scheme 18.

arene nuclei than is the $Cr(CO)_3$ fragment, and is unlikely to be able to exert sufficient influence to direct a first methyl group stereospecifically *exo*.

Experimental

(*A*) *General.*—Solvents were dried and distilled prior to use and experimental manipulations were carried out under an atmosphere of dinitrogen gas. Elemental analyses were performed by the Canadian Microanalytical Services Ltd., Vancouver. The n.m.r. spectra were recorded on a Bruker WM250 spectrometer operating at 250.0 MHz (^{1}H) and 62.9 MHz (^{13}C); i.r. spectra were obtained using a Perkin-Elmer 283 instrument and mass spectra were recorded using a Finnigan 3300 Mass Spectrometer. The tetrahydronaphthalene complex $[Fe(cp)(C_{10}H_{12})][PF_6]$ (**1**), was prepared by literature methods;[8] other reagents were used as received.

(*B*) *Nucleophilic Addition to Complex* (**1**).—(a) *With hydride: formation of* $[Fe(cp)(C_{10}H_{13})]$ (**2a,b**). Method A. A stirred suspension of compound (**1**) (0.50 g, 1.3 mmol) in THF (10 ml) was treated with $NaBH_4$ (0.15 g, 3.9 mmol). Addition of methanol (3 ml) to destroy excess of $NaBH_4$ left a clear bright red solution, which was subsequently evaporated to dryness. The orange residue was extracted with light petroleum (b.p. 30—60 °C) (15 ml) and then washed with water (10 ml). The orange organic layer was chromatographed on a neutral alumina column (8 × 3 cm^3). Elution with diethyl ether followed by evaporation of the solvent afforded a mixture of isomers (**2a**) and (**2b**) as a red viscous oil (0.23 g, 70%); *m/z* 254 (M^+) and 121 [$(cp)Fe^+$].

Method B. In a procedure similar to that described in method A above, $LiEt_3BH$ was used instead of $NaBH_4$. The addition of methanol was omitted, and the product was recovered as a red oil (0.32 g, 97%).

(b) *With deuteride: formation of* $[Fe(cp)(C_{10}H_{12}D)]$ (**3a,b**). Addition to a suspension of compound (**1**) (0.30 g, 0.75 mmol) in THF (10 ml) of $LiEt_3BD$ (0.11 g, 1 mmol) resulted in formation of a clear red solution. Volatiles were removed under reduced pressure after which the mixture treated as in (a) to give the product as a red oil (0.18 g, 95%); *m/z* (e.i.), 255 (M^+), 186 [$(cp)_2Fe^+$], and 121 [$(cp)Fe^+$].

(c) *With butyl-lithium: formation of* $[Fe(cp)(C_{10}H_{12}Bu)]$ (**4a,b**). A suspension of (**1**) (0.20 g, 0.50 mmol) in THF (15 ml) at −78 °C was treated with BuLi (8 mmol, 5 ml) in hexane. The resulting clear orange-brown solution was allowed to warm to room temperature and then evaporated to dryness. The residue was extracted with diethyl ether (15 ml) and washed with distilled water (10 ml). The orange organic layer was separated, dried ($MgSO_4$), and chromatographed on a neutral alumina column (8 × 3 cm^2); elution with diethyl ether followed by removal of the solvent afforded the product as a red viscous oil (*ca.* 60% yield).

(d) *With t-butyl-lithium, phenyl-lithium: formation of* $[Fe(cp)(C_{10}H_{12}Bu^t]$ (**5a,b**), $[Fe(cp)(C_{10}H_{12}Ph)]$ (**6a,b**). Using a procedure identical with that outlined in the synthesis of (**4a,b**), treatment of compound (**1**) with Bu^{t}Li or PhLi gave the products (**5a,b**) 80% and (**6a,b**) 96%: (**5a,b**) *m/z* (e.i.), 310 (M^+), 253, and 121; (**6a,b**) *m/z* (e.i.) 330 (M^+) and 253.

(*C*) *Benzylic Substitution of Complex* (**1**).—(a) *With methyl iodide or benzoyl chloride: formation of* $[Fe(cp)C_{10}H_{11}Me][PF_6]$ (**17**) *and* $[Fe(cp)C_{10}H_{11}COPh][PF_6]$ (**18**). To a solid mixture of complex (**1**) (1.0 g, 2.5 mmol) and Bu^{t}OK (0.84 g, 7.5 mmol) was added THF (20 ml), to give a dark red solution. This was stirred for 5 min, after which the solvent was removed under reduced pressure and hexane (60 ml) was added. The solution was then filtered through Celite, concentrated to 15 ml, and cooled to 0 °C; addition of iodomethane (5.3 g, 38 mmol) resulted in the deposition of a light orange precipitate. The mixture was stirred for 1 h, after which the supernatant was removed and the residual yellow solid washed with diethyl ether. Shaking of the latter with aqueous NH_4PF_6 precipitated a yellow salt which was filtered off and dissolved in CH_2Cl_2. The solution was dried ($MgSO_4$), concentrated to 5 ml, and diluted with diethyl ether to precipitate a pure yellow product (**17**) (0.10 g, 10%), m.p. 164—171 °C (Found: C, 46.7; H, 4.6. Calc. for $C_{16}H_{19}F_6FeP$: C, 46.63; H, 4.65%). Use of benzoyl chloride (3.6 g, 26 mmol) in place of iodomethane gave the product (**18**) (0.18 g, 47%) as a yellow powder (Found: C, 52.85; H, 4.4. Calc. for $C_{22}H_{21}F_6OP$: C, 52.61; H, 4.21%).

(b) *With methyl iodide: formation of* $[Fe(cp)(C_{10}H_8Me_4)][PF_6]$ (**7**).—A mixture of complex (**1**) (3.0 g, 113 mmol) and Bu^{t}OK (12.6 g, 113 mmol) was treated with a solution of MeI (16 g, 113 mmol) in THF (100 ml). The solution refluxed vigorously and changed from dark red to orange with the formation of a beige precipitate. After the mixture had been stirred for 16 h, the volatiles were removed under reduced pressure and the resulting creamy solid was washed in diethyl ether and then water (100 ml). The solid was filtered off and dissolved in CH_2Cl_2 and this solution was dried ($MgSO_4$), and concentrated under reduced pressure; the residue was chromatographed on a neutral alumina column (15 × 3 cm^2). Elution with acetone, followed by concentration of the eluant to 10 ml and subsequent dilution with ether afforded the product as an orange powder (2.2 g, 64%) (Found: C, 50.6; H, 5.8. Calc. for $C_{19}H_{25}F_6FeP$: C, 50.24; H, 5.55%).

(c) *With allyl iodide and benzyl bromide: formation of* $[Fe(cp)\{C_{10}H_8(C_3H_5)_4\}][PF_6]$ (**8**) *and* $[Fe(cp)\{C_{10}H_9(CH_2Ph)_3\}][PF_6]$ (**9**). Following a procedure similar to that described in (b) above, treatment of complex (**1**) (0.41 g, 1.0 mmol) with Bu^{t}OK (2.2 g, 20 mmol) and allyl bromide (6.1 g, 50 mmol) gave the product (**8**) as a light orange powder (0.28 g, 49%). Similarly, treatment of complex (**1**) (0.82 g, 2.1 mmol) with Bu^{t}OK (1.1 g, 10 mmol) and benzyl bromide (3.4 g, 20 mmol) afforded the product (**9**) as a light beige powder (0.92 g, 67%): (**8**) (Found: C, 58.4; H, 5.65. Calc. for $C_{23}H_{33}F_6FeP$: C, 58.08; H, 5.96%); (**9**) (Found: C, 64.85; H, 5.8. Calc. for $C_{36}H_{35}F_6FeP$: C, 64.68; H, 5.28%).

(*D*) *Nucleophilic Addition to Complex* (**7**).—(a) *With hydride and deuteride: formation of* $[Fe(cp)(C_{10}H_9Me_4)]$ (**22**) *and* $[Fe(cp)(C_{10}H_8DMe_4)]$ (**23**). Using procedures identical to those outlined in the synthesis of (**2a,b**) and (**3a,b**), treatment of compound (**7**) with $LiBEt_3H$ or $LiBEt_3D$ afforded the products (**22**) 95% and (**23**) 92% as red oils: (**22**) *m/z* (c.i.), 311 (M + 1), 310, 295, 281, 267, 253; (**23**) *m/z* (e.i.) 311 (M^+).

(b) *With phenyl-lithium and butyl-lithium: formation of* $[Fe(cp)(C_{10}H_8PhMe_4)]$ (**24**) *and* $[Fe(cp)(C_{10}H_8BuMe_4)]$ (**25**). Using the method indicated in the preparation of (**4a,b**), treatment of complex (**7**) with phenyl-lithium or butyl-lithium gave the products (**24**) 59% and (**25**) 58% as orange viscous oils: (**24**) *m/z* (c.i.), 387 (M + 1); (**25**) (c.i.) 367 (M + 1).

(*E*) *Hydride Abstraction of Complex* (**24**).—(a) *Formation of* $[Fe(cp)(C_{10}H_7PhMe_4)][PF_6]$ (**26**). A stirred solution of complex (**24**) (0.34 g, 0.88 mmol) in CH_2Cl_2 (15 ml) was treated with triphenylmethyl tetrafluoroborate (0.33 g, 1 mmol). After 10 min the solvent was removed under reduced pressure and the oily brown material washed with diethyl ether. Dichloromethane (15 ml) and water saturated with NH_4PF_6 (20 ml) was added and the red organic layer separated, dried ($MgSO_4$), and purified by passage through a neutral alumina column. Elution with acetone gave an orange solution. The product (**26**) was obtained as a light yellow solid after concentration and addition of diethyl ether (Found: C, 57.05; H, 5.65. Calc. for $C_{25}H_{29}F_6FeP$: C, 56.62; H, 5.51%), m.p. 208 °C.

(*F*) *Synthesis of* (η^5-*Cyclopentadienyl*)(η^6-*octahydroanthracene*)*iron*(II) *Hexafluorophosphate* $[Fe(cp)(C_{14}H_{18})][PF_6]$ (**14**).—A mixture of octahydroanthracene (4.0 g, 21.5 mmol), ferrocene (4.0 g, 21.5 mmol), $AlCl_3$ (5.74 g, 43.0 mmol), and Al (0.58 g, 21.5 mmol) was suspended in decahydronaphthalene (100 ml) at 150 °C for 20 h. The mixture was cooled in an ice-bath and then extracted with 15% aqueous methanol (2 × 30 ml); the aqueous portion was then washed with ether (5 × 20 ml), after which solid NH_4PF_6 was added to give a yellow precipitate. This was collected, redissolved in CH_2Cl_2, and the solution dried ($MgSO_4$); crystallization was induced by the slow addition of ether to give the product as orange microcrystals (5.0 g, 50%) (Found: C, 50.45; H, 5.2. Calc. for $C_{19}H_{23}F_6FeP$: C, 50.47; H, 5.13%); $\delta[(CD_3)_2CO]$ 6.14 (2 H, s, H^9—H^{10}), 4.99 (5 H, s, cp), 3.02 (4 H, dt, $H^{1''}$,$H^{4''}$,$H^{5''}$,$H^{8''}$), 1.96 (4 H, m, $H^{2'}$,$H^{3'}$,$H^{6'}$,$H^{7'}$), and 1.84 (4 H, n, $H^{2''}$,$H^{3''}$,$H^{6''}$,$H^{7''}$); $\delta_C[(CD_3)_2CO]$ 102.4 (C^{11}—C^{14}), 86.6 (C^9—C^{10}), 78.7 (cp), 28.4 (C^1,C^4,C^5,C^6), and 22.6 (C^2,C^3,C^6,C^7).

(*G*) *Benzylic Substitution of Complex* (**14**).—(a) *With methyl iodide or benzoyl chloride: formation of* $[Fe(cp)(C_{14}H_{17}Me)][PF_6]$ (**20**) *and* $[Fe(cp)(C_{14}H_{17}COPh)][PF_6]$ (**21**). A solution of (**14**) (500 mg, 1.11 mmol) in THF (20 ml) was treated with Bu^{t}OK (600 mg, 6.36 mmol) and then stirred for 10 min. Volatiles were removed under reduced pressure after which the solid residue was extracted into hexane (20 ml). Methyl iodide (0.5 ml, 8 mmol) was added to the hexane solution to give a creamy brown precipitate. The solvent was removed and then the residue was dissolved in hot water (80 °C, 100 ml). After filtration, the clear solution was treated with sufficient NH_4PF_6 to form an oily precipitate. The water was decanted off and the solid residue was dried *in vacuo*; it was then redissolved in CH_2Cl_2 (2 ml). The latter solution was poured into ether to precipitate a solid which settled slowly; decanting off the ether gave the product (**20**) as a yellow powder (310 mg, 60%) (Found: C, 51.4; H, 5.2. Calc. for $C_{20}H_{25}F_6FeP$: C, 51.52; H, 5.41%); $\delta[(CD_3)_2CO]$ 1.29 (d, Me_{exo}), 1.60 (d, Me_{endo}), 1.9 (n, CH_2), 2.8, 3.1 (m, CH_2), 4.994 (s, cp_{exo}), 4.998 (s, cp_{endo}), and 6.32 and 6.16 (m, ArH). A similar procedure using benzoyl chloride in place of iodomethane yielded compound (**21**) (90%) (Found: C, 56.5; H, 4.65. Calc. for $C_{26}H_{27}F_6FeOP$: C, 56.14; H, 4.89%); $\delta(CD_3NO_2)$ 4.33 (br), 4.99 (s, cp), 5.98, 6.18 (s), 7.6—8.3 (m, Ph); $\delta_C(CD_3NO_2)$ 28.2, 29.0, 28.7, 28.1, 22.9, 20.3 (C^2—C^8), 47.6, 79.3 (cp), 87.2, 87.7 (C^9—C^{10}), 101.4, 103.4, 103.5, 104.2 (C^{11}—C^{14}), 130.1, 130.4, 135.3 (Ph), and 202.3 (C=O).

(b) *With methyl iodide: formation of* $[Fe(cp)(C_{14}H_{10}Me_8)][PF_6]$ (**15**). A solution of (**14**) (1.00 g, 2.21 mmol) in THF (100 ml) was treated with a large excess of Bu^{t}OK (12.0 g, 107 mmol) and MeI (5.0 g, 35 mmol) and the mixture stirred for 48 h. The reaction was quenched by the addition of aqueous NH_4PF_6. The aqueous suspension was extracted into CH_2Cl_2 (2 × 20 ml) and the extract dried ($MgSO_4$) to give an orange solution. Reduction in volume of the latter, followed by dilution with ether precipitated an orange compound (600 mg) shown by ^{1}H n.m.r. to be a complex mixture of compounds. Using this mixture in place of compound (**14**), the same procedure was repeated to afford the product as an orange powder (200 mg, 17%) (Found: C, 56.95; H, 6.75. Calc. for $C_{27}H_{39}F_6FeP$: C, 57.46; 6.97%); $\delta[(CD_3)_2CO]$ 1.29 (s, Me), 1.73 (s, Me), 1.5—2.2 (m, CH_2), 5.20 (s, cp), and 6.46 (s, CH); $\delta_C[(CD_3)_2CO]$ 31.3, 33.2 (Me), 34.9 (C^2,C^3,C^5,C^8), 76.7 (cp), 79.4 (C^9—C^{10}), and 112.8 (C^{11}—C^{14}).

(*H*) *Benzylic Substitution of Complex* (**9**).—(a) *With benzyl bromide: formation of* $[Fe(cp)\{C_{10}H_8(CH_2Ph)_4\}][PF_6]$ (**10**).—A stirred suspension of complex (**9**) (1.0 g, 1.5 mmol) in THF (40 ml) was treated with Bu^{t}OK (1.8 g, 15.6 mmol) to afford a dark red solution. Benzyl bromide (6.7 g, 39 mmol) was added after which the mixture was stirred for 22 h; during this time a gradual colour change occurred to pale orange. Volatiles were removed under reduced pressure after which any excess of benzyl bromide was extracted into diethyl ether. The residual orange solid was filtered off, washed with water, and dissolved in acetone–acetonitrile (1:1); the solution was then dried ($MgSO_4$). Chromatography of the latter on a neutral alumina column (15 × 3 cm^2) with acetonitrile as eluant, followed by recrystallization of the product from methanol–diethyl ether yielded orange microcrystals (0.81 g, 71%) (Found: C, 68.4; H, 5.75. Calc. for $C_{43}H_{41}F_6FeP$: C, 68.08; H, 5.45%).

(b) *With allyl iodide: formation of* $[Fe(cp)\{C_{10}H_8(CH_2Ph)_3C_3H_5\}][PF_6]$ (**11**). Using the method outlined in the preparation of complex (**10**), the reaction of complex (**9**) (0.40 g, 0.60 mmol) with Bu^{t}OK (0.34 g, 3.0 mmol) and allyl iodide (2.2 g, 13 mmol) afforded the product (0.10 g, 25%) as a beige solid (Found: C, 66.2; H, 5.6. Calc. for $C_{39}H_{39}F_6FeP$: C, 66.11; H, 5.55%).

(c) *With methyl iodide: formation of* $[Fe(cp)\{C_{10}H_8(CH_2Ph)_3Me\}][PF_6]$ (**12**). A stirred suspension of complex (**9**) (0.4 g, 2.7 mmol) in THF (40 ml) was treated with Bu^{t}OK (0.3 g, 2.7 mmol) to give a dark red solution. After 5 min iodomethane (6.8 g, 48 mmol) was added to give a creamy white precipitate and an orange solution. The mixture was stirred for 20 h after which volatiles were removed under reduced pressure. The residue was dissolved in CH_2Cl_2 (20 ml) and the solution shaken with distilled water (50 ml). The orange organic layer was separated, dried ($MgSO_4$), and concentrated, and the residue purified by elution down a neutral alumina column (20 × 3 cm^2) with acetone as eluant. The eluate was concentrated and then diluted with ether to precipitate the product as a light orange solid (0.16 g, 39%) (Found: C, 65.4; H, 5.7. Calc. for $C_{37}H_{37}F_6FeP$: C, 65.11; H, 4.56%).

(d) *With benzoyl bromide: formation of* $[Fe(cp)\{C_{10}H_8(CH_2Ph)_3COPh\}][PF_6]$ (**20**). A stirred suspension of complex (**9**) (0.30 g, 0.45 mmol) was treated with Bu^{t}OK (0.15 g, 1.4 mmol). Benzoyl chloride (2.4 g, 17 mmol, 2 ml) was added to give a clear light orange solution which was stirred for a further 1 h. Volatiles were removed under reduced pressure and the remaining oily material was washed in diethyl ether to precipitate a solid. The mixture was treated described in (c) above to give the product as a light beige solid (0.10 g, 29%).

(*I*) *Pyrolysis of Complexes*.—A sample of complex (**7**) (0.24 g, 0.53 mmol) was pyrolysed by heating *in vacuo* and the volatiles were collected on a cold finger at −78 °C. The yellowish sublimate was dissolved in diethyl ether and then purified by passage down a short alumina column (5 × 3 cm^2); the solvent was removed to afford the product (**29**) as a clear colourless oil (*ca.* 45% yield). In a similar fashion pyrolysis of compounds (**8**), (**9**), (**10**), (**12**), (**13**), (**26**), and (**28**) gave the products (**30**), (**31**), (**32**), (**33**), (**34**), (**35**), and (**36**) respectively: (**29**) *m*/*z* (e.i.) 188 (M^+); (**30**) *m*/*z* (c.i.), 293 (M + 1), 251, 211, and 169; (**31**) *m*/*z*

(c.i.) 403 (M + 1), 325, and 311; (**32**) m/z (e.i.) 493 (M^+), 401, and 324; (**35**) m/z (c.i.) 265 (M + 1); (**36**) m/z (c.i.) 341 (M + 1).

(J) Synthesis of (η^5-*Cyclopentadienyl*)(η^6-*tetrahydroquinoline*)*iron*(II) *Hexafluorophosphate* [Fe(cp)($C_9H_{11}N$)][PF_6] (**37**).—A mixture of ferrocene (5.5 g, 30 mmol), $AlCl_3$ (40 g, 300 mmol), Al powder (0.81 g, 30 mmol), and tetrahydroquinoline (10.6 g, 80 mmol) was refluxed in decahydronaphthalene (80 ml) for 4 h. The resulting dark mixture was cooled in an ice-bath and ice was added slowly to destroy the excess of $AlCl_3$. After filtration, the bright orange aqueous layer was separated and washed with light petroleum (b.p. 30—60 °C). The addition of NH_4PF_6 precipitated an orange solid which was filtered off and dissolved in CH_2Cl_2, and the solution dried ($MgSO_4$), concentrated under reduced pressure, and then chromatographed on a neutral alumina column (20 × 3 cm^2) with acetone as eluant. The eluate was evacuated to dryness and the residue dissolved in methanol. Addition of an excess of diethyl ether and light petroleum precipitated the product as a bright orange powder (3.6 g, 30%) (Found: C, 42.5; H, 4.35; N, 3.15. Calc. for $C_{14}H_{16}F_6FeNP$: C, 42.13; H, 4.04; N, 3.51%).

(K) Benzylic Substitution of Complex (**37**).—(a) *With methyl iodide: formation of* [Fe(cp)($C_{10}H_{10}NMe$)][PF_6] (**39**). A stirred suspension of complex (**37**) (0.15 g, 0.38 mmol) in THF (15 ml) was treated with Bu^{t}OK (0.13 g, 1.1 mmol) to afford a bright red solution which was stirred for 5 min. The volatiles were removed under reduced pressure and the residue was extracted with hexane (40 ml). The extract was filtered to yield a clear orange solution which was diluted with iodomethane (4.6 g, 32 mmol) to give a yellow precipitate. The supernatant was decanted off after which the solid was dissolved in water and reprecipitated as an orange solid using NH_4PF_6. The sample was purified by passage through a neutral alumina column (15 × 3 cm^2) using acetone as eluant. Concentration of the eluate followed by dilution with ether precipitated the complex as an orange powder (80 mg, 50%) (Found: C, 43.7; H, 4.35; N, 3.25. Calc. for $C_{15}H_{18}F_6FeNP$: C. 43.61; H, 4.39; N, 3.39%).

(b) *With methyl iodide: formation of* [Fe(cp)($C_{10}H_8Me_2$-NMe)][PF_6] (**40**). Using the method outlined in the synthesis of complex (**14**), the reaction of complex (**37**) (0.4 g, 1.0 mmol) with Bu^{t}OK (1.4 g, 12 mmol) and iodomethane (3.7 g, 26 mmol) afforded the product (**40**) as a bright orange powder (0.22 g, 50%) (Found: C, 46.7; H, 5.1; N, 2.9. Calc. for $C_{17}H_{22}F_6FeNP$: C, 46.28; H, 5.03; N, 3.17%).

References

1 M. F. Semmelhack, *Ann. N.Y. Acad. Sci.*, 1977, **295**, 36.
2 S. R. Stobart and M. J. Zaworotko, *Fuel*, 1985, **64**, 1623; *J. Chem. Soc., Chem. Commun.*, 1984, 1700.
3 D. Astruc, *Tetrahedron*, 1983, **39**, 4027; S. L. Grundy and P. M. Maitlis, *J. Organomet. Chem.*, 1984, **272**, 265.
4 R. G. Sutherland, C. C. Lee, and B. R. Steele, *J. Organomet. Chem.*, 1980, **186**, 265.
5 C. C. Lee, K. J. Demchuk, and R. G. Sutherland, *Can. J. Chem.*, 1979, **57**, 933.
6 R. G. Sutherland, S. C. Chen, J. Pannekoek, and C. C. Lee, *J. Organomet. Chem.*, 1975, **101**, 221.
7 A. R. Koray, *J. Organomet. Chem.*, 1981, **212**, 233.
8 G. Jaouen, A. Meyer, and G. J. Simonneaux, *J. Chem. Soc., Chem. Commun.*, 1975, 813.
9 N. A. Nesmeyanov, A. N. Vol'kenau, and I. N. Bolesova, *Tetrahedron Lett.*, 1963, 1725.
10 P. H. Bird and M. R. Churchill, *J. Chem. Soc., Chem. Commun.*, 1967, 777.
11 I. U. Khand, P. L. Pauson, and W. E. Watts, *J. Chem. Soc.*, 1969, 116.
12 I. U. Khand, P. L. Paulson, and W. E. Watts, *J. Chem. Soc.*, 1968, 2261.
13 A. N. Nesmeyanov, N. A. Vol'kenau, and L. A. Shilovtsva, *Akad. Nauk. SSSR, Ser. Khim.*, 1969, 726.
14 A. N. Nesmeyanov, N. A. Vol'kenau, L. A. Shilovtsva, and V. A. Petrakova, *J. Organomet. Chem.*, 1975, **85**, 365.
15 J. W. Johnson and P. M. Treichel, *J. Am. Chem. Soc.*, 1977, **99**, 1427.
16 A. R. Hamon, J. Y. Saillard, A. L. Beuze, M. J. McGlinchey, and D. Astruc, *J. Am. Chem. Soc.*, 1982, **104**, 7549.
17 D. Astruc, E. Roman, J. R. Hamon, and P. Batail, *J. Am. Chem. Soc.*, 1979, **101**, 2240.
18 D. Astruc, E. Roman, J. R. Hamon, and P. Michaud, *J. Am. Chem. Soc.*, 1981, **103**, 7502.
19 R. G. Sutherland, B. R. Steele, K. J. Demchuk, and C. C. Lee, *J. Organomet. Chem.*, 1981, **206**, 89.
20 M. L. H. Green, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 1960, 989.
21 R. G. Sutherland, W. J. Pannekoek, and C. C. Lee, *Can. J. Chem.*, 1978, **56**, 1782.
22 J. W. Kroeger and H. A. Bruson, *J. Am. Chem. Soc.*, 1940, **62**, 36.
23 F. A. L. Anet and M. Z. Haq, *J. Am. Chem. Soc.*, 1965, **87**, 3147.
24 R. Guilhemat, M. Pereyre, and M. Petraud, *Bull. Soc. Chim. Fr.*, 1980, 334.
25 R. L. Hillard and K. P. C. Vollhardt, *Angew. Chem., Int. Ed. Engl.*, 1975, **14**, 712.
26 C. C. Lee, A. Piorko, and R. G. Sutherland, *J. Organomet. Chem.*, 1983, **248**, 357.
27 J. Blagg, S. G. Davies, and B. E. Mobbs, *J. Chem. Soc., Chem. Commun.*, 1985, 619.
28 J. F. Helling and W. A. Hendrickson, *J. Organomet. Chem.*, 1979, **168**, 87.
29 J. March, Advanced Organic Chemistry, John Wiley and Sons Inc., New York, 1985, 3rd edn., pp. 387, 220, 221.
30 C. C. Lee, U. S. Gill, and R. G. Sutherland, *J. Organomet. Chem.*, 1981, **208**, 89.

Received 11*th August* 1988; *Paper* 9/00298G