# Friedel–Crafts Acylation of Tricarbonyl(cyclo-octatetraene)iron. Preparation and Reactions of (8-Acylbicyclo[3.2.1]octadienylium)tricarbonyliron Hexafluorophosphates

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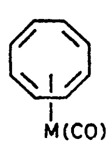
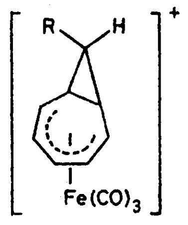
The acylation of the title complex $[Fe(C_8H_8)(CO)_3]$ (1a) has been found to give cations of molecular formula $[Fe\{C_8H_8(COR)\}(CO)_3]^+$ (3a; R = Me, 3b; R = Ph) which contain a co-ordinated bicyclo[3.2.1]octadienyl ligand in which the C(8) acyl group is stereospecifically *endo* to the C(6),C(7) double bond [in contrast, $[Ru(C_8H_8)(CO)_3]$ (1b) is unreactive towards acylating reagents]. Reaction of (3a) with $BH_4^-$ or $CN^-$ gives, as major products, complexes of the type $[Fe\{2—4\text{-}\eta,6\text{-}\sigma\text{-}C_8H_8X(COMe)\}(CO)_3]$ (6a; X = H, 7; X = CN), while $I^-$ displaces co-ordinated CO to give $[Fe\{2—4{:}6—7\text{-}\eta\text{-}C_8H_8(COMe)\}(CO)_2I]$ (9). The addition of $R'S^-$ (R' = $Pr^i$, $Bu^t$, or Ph) to (3a) or (3b) affords the diene complexes $[Fe\{3—4{:}6—7\text{-}\eta\text{-}C_8H_8(SR')(COR)\}(CO)_3]$ (11). The stereochemistry of addition of $R'S^-$ is exclusively $exo_M$. The thioethers (11) react with $HPF_6$ to regenerate their parent cations and this facility has been utilised to permit nucleophilic addition to the acyl carbonyl while retaining the co-ordinated dienyl in ' protected ' form. Subsequent removal of the thio-substituent leads to some novel co-ordinated cyclic ethers. Oxidative demetallation of (11) liberates a substituted bicyclo[3.2.1]octadiene in high yield. A possible mechanism for the rearrangement of the cyclo-octatetraene during the acylation reaction is discussed.

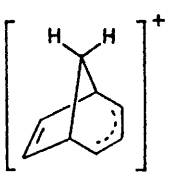
THE Friedel–Crafts acylation of tricarbonyl(cyclo-octatetraene)iron (1a) has been reported [1] to give a cationic adduct of molecular formula $[Fe\{C_8H_8(COMe)\}(CO)_3]^+$ along with small amounts of the substituted complex $[Fe\{1—4\text{-}\eta\text{-}C_8H_7(COMe)\}(CO)_3]$. By analogy with the protonation of (1a) which gives the bicyclo[5.1.0]octadienylium complex (2a),[2] the acetyl cation was assigned the similar structure (2b). However, reactions of this cation with a variety of nucleophiles gave products in which the mode of co-ordination of the organic fragment was different from that expected for the addition of $X^-$ to (2b). The basic $C_8$ unit of these complexes was found to have a bicyclo[3.2.1] arrangement and this observation prompted a re-examination of the acetyl salt. A single-crystal *X*-ray diffraction study confirmed the bicyclo[3.2.1] structure (3a) for this cation.[3,4]



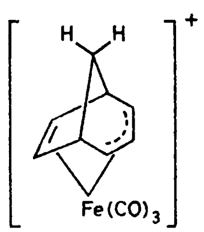
(1a) M = Fe
(1b) M = Ru



(2a) R = H
(2b) R = COMe



(4)



(5)

In this paper we report the reactions of the acetyl (3a) and benzoyl (3b) cations with a range of nucleophiles. The products of the addition of $RS^-$ to (3a) and (3b) have been examined in greater detail as possible routes to substituted bicyclo[3.2.1] compounds.

## RESULTS AND DISCUSSION

*Acylation of Cyclo-octatetraene Complexes.*—Acylation of $[Fe(C_8H_8)(CO)_3]$ (1a) by acetyl chloride and $AlCl_3$ in $CH_2Cl_2$ afforded the acetyl cation (3a) in 45% yield. If the acylation is performed using $MeCOBF_4$ the yield of cationic complex is almost quantitative.[5] The reaction of (1a) with benzoyl chloride and $AlCl_3$ gave the corresponding benzoyl cation (3b) in 75% yield.

The $^1H$ n.m.r. spectrum (Table 1, Figure) of these cations shows a closer similarity to the spectra of the uncomplexed (4) [6] and complexed (5) [7] bicyclo[3.2.1] cations that to that of the bicyclo[5.1.0]octadienylium complex (2a).[2] However, $^1H$ n.m.r. data alone were insufficient to prove that formulation of the acyl cation as (3a) or (3b) was correct and a single-crystal *X*-ray diffraction study of the acetyl cation was therefore undertaken, the results of which have been reported elsewhere.[3,4] This study confirmed the bicyclo[3.2.1] structure of the octadienylium ligand and, in particular, established the configuration of the C(8) acyl group as *endo* to the C(6), C(7) double bond.

The cyclo-octatetraeneiron complex (1a) is only attacked by strong electrophiles, *e.g.* $H^+$,[2] electron-withdrawing olefins,[8] and $Tl[NO_3]_3$.[9] No reaction was observed between (1a) and $EtBr–AlCl_3$ or $[OMe_3][PF_6]$. Tricarbonyl(cyclo-octatetraene)ruthenium is even less reactive than its iron counterpart. Reaction with $MeCOCl–AlCl_3$ gave a mixture of starting material and the HCl addition complex $[Ru(3—5\text{-}\eta\text{-}C_8H_9)(CO)_3Cl]$,[10]

## TABLE 1

Hydrogen-1 n.m.r. spectral data for the complexes [a]

| Complex | $H^{3}$ | $H^{2,4}$ | $H^{6,7}$ | $H^{1,5}$ | $H^{8}$ | Other |
|---|---|---|---|---|---|---|
| (3a) [a] | 4.74 (t) [6] | 5.06 (t) [6] | 5.58 (m) | 6.24 (m) | 7.42 (s) | 7.88 (s) Me |
| (3b) [b] | 4.62 (t) [6] | 4.96 (t) [6] | 5.50 (m) | 6.19 (m) | 6.49 (m) | 2.01 (dd) [8,2] *o*-Ph; 2.46 (m) *m, p*-Ph |

| | $H^{2}$ | $H^{3}$ | $H^{4}$ | $H^{5}$ | $H^{1}$ | $H^{7}$(*endo*$_M$) | $H^{8}$ | $H^{6}$ | Other |
|---|---|---|---|---|---|---|---|---|---|
| (6a) [c] | 4.6 (td) [6, 2.5] | 5.28 (t) [6] | 5.92 (m) | 6.73 (t) [7] | 7.18 (m) | 7.80—8.05 (m) | 8.12 (s) | 9.12 (m) | 8.02 (s) Me<br>8.44 (m) $H^{7}$(*exo*$_M$) |
| (6b) [c] | 4.6 (m) | 5.26 (t) [6] | 5.92 (m) | 6.73 (t) [7] | 7.18 | 7.8—8.1 (m) | 7.8—8.1 (m) | 9.12 (br d) [7] | 8.02 (s) Me |
| (7) [c] | 4.62 (td) [6, 2.5] | 5.19 (t) [6] | 5.86 (m) | 6.44 (t) [7] | 6.68 (br dd) [6, 2] | 7.20 (br s) | 8.0 (s) | 8.86 (dd) [7, 2] | 7.84 (s) Me |

| | $H^{3}$ | $H^{2,4}$ | $H^{1,5}$ | $H^{6,7}$ | $H^{8}$ | Other |
|---|---|---|---|---|---|---|
| (9) [c] | 5.10 (t) [6] | 5.59 (t) [6] | 7.17 (m) | 6.65 (m) | 8.10 (s) | 7.98 (s) Me |

| | $H^{2}$ | $H^{5,6}$ | $H^{3,4,7}$ | $H^{8}$ | $H^{1}$ | Other |
|---|---|---|---|---|---|---|
| (11a) [d] | 6.26 (dd) [5, 2] | 6.69 (m) | 7.08 (m) | 7.24 (s) | 7.46 (t) [5] | 7.08 (m) –C*H*Me$_2$<br>8.04 (s) MeC(O)–<br>8.75 (dd) [6, 3.5[e]] –CH*Me*$_2$ |
| (11b) [d] | 6.26 (dd) [5, 2] | 6.68 (m) | 7.0 (m) | 7.37 (s) | 7.46 (t) [5] | 8.01 (s) MeC(O)–<br>8.66 (s) Bu$^t$ |
| (11c) [d] | 5.78 (dd) [5, 2] | 6.60 (m) | ← 7.0 (m) → | | 7.38 (t) [5] | 2.72 (m) Ph<br>8.02 (s) MeC(O)– |
| (11d) [d] | 6.14 (dd) [5, 2] | 6.43 ($H^{6}$) (t) [5] and 6.57 ($H^{5}$) (t) [5] | 6.82—7.10 (m) | 6.34 | 7.40 (t) [5] | 2.01 (dd) [7, 2] *o*-Ph<br>2.64 (m) *m, p*-Ph<br>6.82—7.10 (m) –C*H*(Me)$_2$<br>8.64 (dd) [6, 3.5 [e]] –CH(*Me*) |

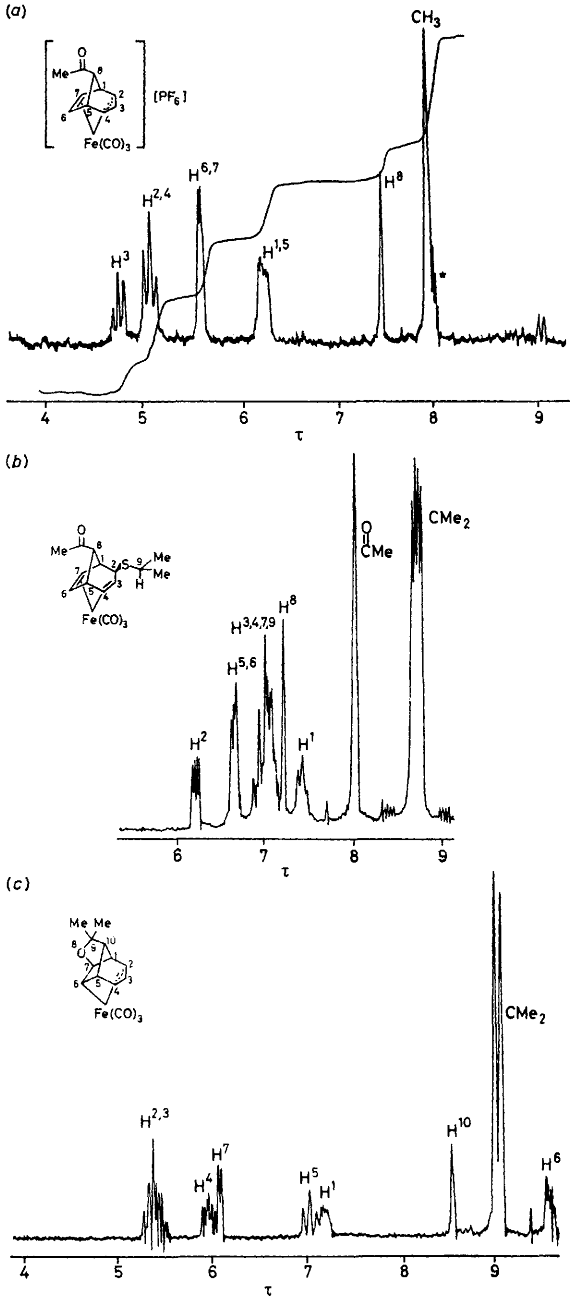
| | $H^{2}$ | $H^{5}$ or $^{6}$ | $H^{3,4,5}$ or $^{6,7}$ | $H^{1}$ | $H^{8}$ | OH | Other |
|---|---|---|---|---|---|---|---|
| (12a) [d] | 6.36 (br m) | ← 6.6—7.5 (m) → | | | 8.14 (d) | 8.0 (br m) | 6.36 (m) $H^{9}$<br>6.6—7.5 (m) –C*H*(Me)$_2$<br>8.90 (dd) [9, 4 [e]] –CH(*Me*)$_2$<br>8.97 (d) [9], –CH(OH)*Me* |
| (13a) [d] | 8.08 (m) (*endo*$_M$) [f] | ← 6.6—7.5 (m) → | | | 8.70 (m) | 8.26 (br m) | 6.36 (m) $H^{9}$<br>9.01 (d) [9] –CH(OH)*Me*<br>7.96 (m) $H^{2}$ (*exo*$_M$) [f] |
| (14) [d] | 6.26 (dd) [4, 2] | 6.66 (t) [4] | 6.80—7.15 | 7.70 (t) [4] | 8.18 (s) | 8.94 (s) | 8.72 (dd) [9, 4] [e] –SCH(*Me*)$_2$<br>8.86 (s) –C(OH)(*Me*)$_2$ |

| | $H^{3}$ | $H^{2,4}$ | $H^{6,7}$ | $H^{1,5}$ | OH | $H^{8}$ | Other |
|---|---|---|---|---|---|---|---|
| (15a) [b] | 4.82 (t) [6] | 5.1 (m) | 5.59 (m) | 6.4—6.7 (m) | | 8.63 (d) [8] | 6.4—6.7 (m) $H^{9}$<br>8.90 (d) [6] Me |
| (15b) [b] | 4.79 (t) [6] | 5.04 and 5.19 (m) | 5.50 (m) | 6.24 and 6.92 (m) | 5.50 (m) | 8.23 (d) [8] | 2.66 (s) Ph<br>5.50 (m) $H^{9}$ |
| (16) [b] | 4.84 [g] (t) [6] | 5.12 (t) [6] | 5.59 (m) | 6.46 (m) | 7.00 (br m) | 8.52 (s) | 8.86 (s) Me |

| | $H^{2,3}$ | $H^{4}$ | $H^{7}$ | $H^{5}$ | $H^{1}$ | $H^{10}$ | $H^{6}$ | Other |
|---|---|---|---|---|---|---|---|---|
| (17a) [a] | 5.40 (m) | ← 6.00 (m) → | | 7.06 (A) [h] (t) [7]<br>7.41 (B) (m) | 7.41 | 8.45 (d) [2]<br>8.53 (B) (s) | 9.61 (dd) [7.3] | 6.24 (qd) [6, 2] $H^{9}$ (A)<br>6.66 (q) [6] $H^{9}$ (B)<br>9.05 (d) [6] Me (A)<br>9.17 (d) [6] Me (B) |
| (17b) [i] | 6.08 (m) | 6.48 and 6.70 (A + B) (m) | 5.66 (dd) [4, 1] | 7.54—7.82 (A + B) (m) | | 8.60 (A + B) (m) | 9.43 (d) [7] | 2.80 (m) Ph<br>5.23 (d) [3] $H^{9}$ (A)<br>5.70 (s) $H^{9}$ (B) |
| (18) [b] | 5.40 (m) | 5.96 (m) | 6.08 (d) [3] | 7.02 (t) [7] | 7.18 (m) | 8.52 (m) | 9.58 (m) | 8.99 and 9.06 (s) Me |

| | $H^{6}$ | $H^{4}$ | $H^{7}$ | $H^{3}$ | $H^{8}$ | $H^{9}$ | $H^{1,5}$ | Other |
|---|---|---|---|---|---|---|---|---|
| (19) [c] | 3.54 [f] (dd) [5, 3] | 3.72 (td) [10, 6, 2] | 4.50 [f] (dd) [5, 3] | 6.64 (d, br) | 5.95 (s) | 6.60 (m) | 6.78 (m) | 1.88 (dd) [7, 2] *o*-Ph<br>2.53 (m) *m,p*-Ph<br>6.93 (spt) [6] –C*H*(Me)$_2$<br>8.66 (d) [6] Me |

[a] Chemical shift (τ), 100-MHz spectra unless otherwise specified. Coupling constants (*J*/Hz) in square brackets. [b] $(CD_3)_2CO$. [c] $CDCl_3$. [d] $CS_2$. [e] Methyl resonances split by chiral centre at C(2), 3.5 Hz. [f] See ref. 6. [g] 80 MHz. [h] Assignments of structures A and B are purely arbitrary and intended for clarity. [i] $C_6D_6$.



Proton n.m.r. spectra of (*a*) [Fe{2—4:6,7-η-$C_8H_8$(COMe)}$(CO)_3$]$^+$ (3a) (asterisk indicates solvent peak), (*b*) [Fe{3—4:6—7-η-$C_8H_8$-(COMe)(SPr$^i$)}$(CO)_3$] (11a), and (*c*) [Fe{2—4-η,6-σ-$C_8H_8$OC-$Me_2$}$(CO)_3$] (18)

the latter presumably formed during hydrolytic work-up. No cationic products were obtained. Reaction with $MeCOBF_4$ gave almost quantitative recovery of starting material; small amounts of [Ru(1—3:6—7-η-$C_8H_9$)-$(CO)_3$]$^{+11}$ were formed by protonation of (1b) with some $HBF_4$ formed by hydrolysis of the acylating reagent.

Such a reduction in reactivity towards electrophiles may be a continuing trend down the series Fe, Ru, Os. Tricarbonyl(cycloheptatriene)osmium[12] is not readily acylated by $MeCOBF_4$ and [Ru($C_6H_8$)$(CO)_3$] is reportedly less reactive towards attack by hexafluoropropene than the corresponding iron complex.[13]

*Nucleophilic Addition Reactions.*—The reactions of the acetyl and benzoyl cations with nucleophiles are summarised in Scheme 1. The parent cations were quite stable in acidic aqueous solution, but the acetyl cation (3a) reacted rapidly with $OH^-$ to give a complex mixture of products. In contrast to the behaviour of (2a), the acyl cations were not deprotonated by triethylamine.

Reduction of (3a) with Na[$BH_4$] gave a complex mixture of products. Chromatography of this mixture on silica and fractional crystallisation afforded a 25% yield of the σ,η-allyl complex (6a). The corresponding 7-deuterio-complex (6b) was obtained on reduction of (3a) with Li[$BD_4$]. The $^1H$ n.m.r. spectrum (Table 1) shows a characteristic σ,η-allyl pattern. The equivalence of the two outer allyl protons in the parent cation is removed: $H^2$ being shifted downfield and $H^4$ moving slightly upfield relative to $H^3$. In addition, a high-field resonance appears at τ 9.10 due to the $H^6$ proton geminal to the M–C σ bond. The $H^7$ resonance at τ 8.44 is absent in the deuteriated complex (6b). Nucleophilic addition to co-ordinated dienyl ligands commonly occurs with *exo*$_M$ stereospecifically (see below). Making this assumption, it follows that the resonance at τ 8.44 is due to $H^7$(*exo*$_M$). The assignment cannot be checked rigorously as $H^7$(*endo*$_M$) is obscured by the methyl proton signal.

An i.r. spectrum of the partially purified reaction mixture shows that in addition to the ν(MCO) bands due to (6), another tricarbonyliron complex is also present: ν(MCO) ($C_6H_{12}$) at 2 037, 1 974, 1 960; ν(CO) at 1 717 cm$^{-1}$. The $^1H$ n.m.r. spectrum of this crude mixture suggested that the second complex may be the product of C(2) addition of $BH_4^-$ to give the 3,4:6,7-η-diene. However, this product proved unstable and could not be further purified.

Reaction of (3a) with cyanide ion afforded a mixture of the 7-cyano-σ,η-allyl complex (7) (13%) and an isomeric compound which is probably the diene complex (8) (9%). The $^1H$ n.m.r. spectrum of the σ,η-allyl complex (Table 1, Figure) displayed features very similar to those of (6), but in addition, the $H^7$ resonance was shifted downfield from the methyl proton singlet and could thus be identified. Cyanide ion would also be expected to add in *exo*$_M$ fashion,[14] so this signal would correspond to $H^7$-(*endo*$_M$). The 60-MHz $^1H$ n.m.r. spectrum of (8) was not very informative due to overlapping signals: τ 6.45 (3 H, m), 6.85 (2 H, m), 7.2 (3 H, s, br), 7.85 (3 H, s, br). The i.r. spectrum [ν(MCO) at 2 046, 1 985, 1 976; ν(CO) at 1 720 cm$^{-1}$ ($C_6H_{12}$)] shows a slight lowering of ν(MCO) relative to the σ,η-allyl complex (Table 2), similar to that observed for the tetrahydroborate reduction mixture. It therefore seems likely that (8) is the 2-cyanodiene complex.

Iodide ion displaced CO from the acetyl cation (3a) to give the dicarbonyl iodide (9). The $^1H$ n.m.r. spectrum of the product shows that the plane of symmetry of the organic ligand is maintained, so ruling out attack at the

**Table 2**

Infrared and mass spectral data for the complexes

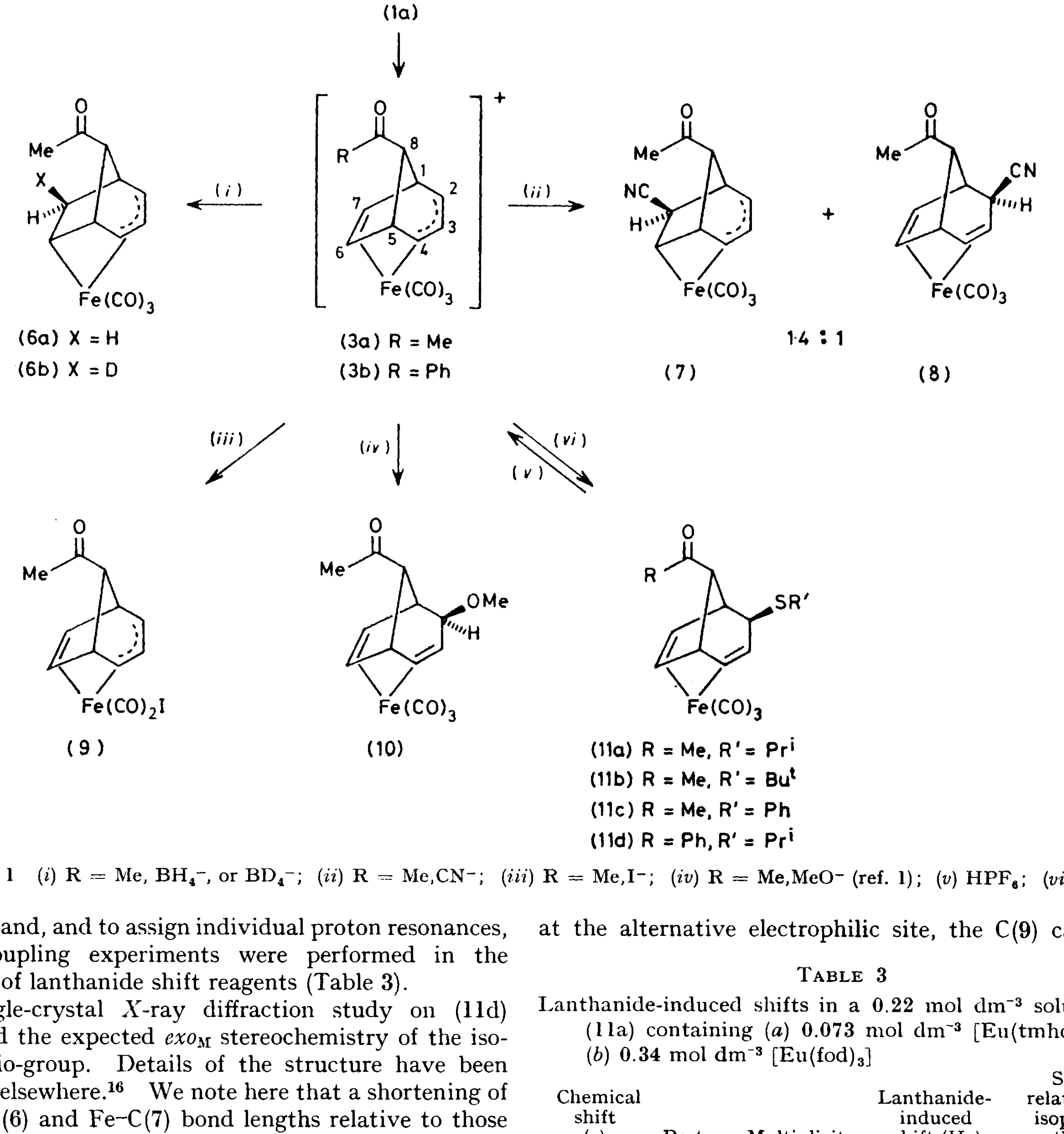
| | I.r. (cm$^{-1}$) | | |
|---|---|---|---|
| Complex | $\nu$(MCO) | $\nu$(other) | Mass spectrum (*m*/*e*) |
| (3a)<br>(see ref. 1) | 2 105[a]<br>2 070<br>2 042 | 1 710 C=O<br>840 P–F | |
| (3b) | 2 110[a]<br>2 060 (br) | 1 675 C=O<br>1 600 } Ph<br>1 560 }<br>850 P–F | |
| (6a) | 2 051[b]<br>1 984<br>1 979 | 1 716 C=O | 260 ($P^+$ − CO); 232 ($P^+$ − 2CO); 204 ($P^+$ − 3CO) |
| (7) | 2 061[b]<br>1 996<br>1 931 | 1 715 C=O | 313 ($P^+$); 285 ($P^+$ − CO); 257 ($P^+$ − 2CO); 229 ($P^+$ − 3CO) |
| (9) | 2 029[c]<br>1 984 | | 386 ($P^+$); 358 ($P^+$ − CO); 330 ($P^+$ − 2CO); 287 ($P^+$ − 2CO − MeCO) |
| (11a) | 2 035[b]<br>1 973<br>1 962 | 1 715 C=O | 362 ($P^+$); 306 ($P^+$ − 2CO); 278 ($P^+$ − 3CO) |
| (11b) | 2 035[b]<br>1 971<br>1 961 | 1 718 C=O | 396 ($P^+$); 340 ($P^+$ − 2CO); 312 ($P^+$ − 3CO) |
| (11c) | 2 037[b]<br>1 977<br>1 965 | 1 715 C=O | 376 ($P^+$); 348 ($P^+$ − CO); 320 ($P^+$ − 2CO); 292 ($P^+$ − 3CO) |
| (11d) | 2 035[b]<br>1 972<br>1 962 | 1 685 C=O | 424 ($P^+$); 396 ($P^+$ − CO); 368 ($P^+$ − 2CO); 340 ($P^+$ − 3CO) |
| (12a) +<br>(13a) | 2 033[b]<br>1 970<br>1 958 | 3 400[d] O–H | |
| (14) | 2 033[b]<br>1 970<br>1 959 | 3 400[d] O–H | 378 ($P^+$); 350 ($P^+$ − CO); 322 ($P^+$ − 2CO); 294 ($P^+$ − 3CO) |
| (15a) | 2 110[a]<br>2 075<br>2 030 | 3 620 O–H<br>850 P–F | |
| (15b) | 2 110[a]<br>2 060 (br) | 3 600 O–H<br>1 600 Ph<br>850 P–F | |
| (16) | 2 110[a]<br>2 060 (br) | 3 600 O–H<br>850 P–F | |
| (17a) | 2 048[b]<br>1 982<br>1 980 | | 288 ($P^+$); 260 ($P^+$ − CO); 232 ($P^+$ − 2CO); 204 ($P^+$ − 3CO) |
| (17b) | 2 051[b]<br>1 983 | | 350 ($P^+$); 322 ($P^+$ − CO); 294 ($P^+$ − 2CO); 266 ($P^+$ − 3CO) |
| (18) | 2 050[b]<br>1 981<br>1 979 | | 302 ($P^+$); 274 ($P^+$ − CO); 246 ($P^+$ − 2CO); 218 ($P^+$ − 3CO) |
| (19) | | 3 070[d] C–H(Ph) 1 600 Ph<br>3 040 1 580<br>2 970 C–H 1 480<br>1 685 C=O | 284 ($P^+$); 241 ($P^+$ − Pr$^i$); 209 ($P^+$ − SPr$^i$); 179 ($P^+$ − PhC=O) |

[a] Nujol mull. [b] $C_6H_{12}$. [c] $CH_2Cl_2$. [d] Thin film.

dienyl carbons. Accompanying the loss of positive charge, the H$^{6,7}$ resonance shifts upfield of H$^{1,5}$ to $\tau$ 7.17. The i.r. (Table 2) shows only two metal carbonyl absorptions, indicating metal attack and CO substitution. In contrast the bicyclo[5.1.0] cation (2a) undergoes *addition* of I$^-$ to the metal and ring opening to give the monocyclic complex $[\mathrm{Fe}(\eta^3\text{-}C_8H_9)(CO)_3I]$.[15a] In the case of the bicyclo[3.2.1] cation (5), I$^-$ addition to the metal is accompanied by CO substitution.[15b]

Methoxide ion has been shown [1] to attack (3a) to give a low yield of an adduct which can now be reformulated as the 2-methoxy-3—4:6—7-$\eta$-diene complex (10). In a similar fashion thiolate anions (RS$^-$) were found to add to C(2) of (3a) or (3b) to give the thioether complexes (11a—d). These compounds were the only addition products isolated from the reaction (50—80% yield); no $\sigma,\eta$-allyl complexes similar to (6) or (7) were isolated. The 2-phenylthio-complex (11c) was found to decompose fairly readily. Small amounts of unidentified tricarbonyliron complexes were isolated from the reaction of (3a) with RS$^-$ but these did not contain an acyl group. Similar compounds were obtained from the reaction of (3a) with MeO$^-$ or OH$^-$, but not from the reaction of RS$^-$ with the benzoyl cation (3b). These compounds proved unstable and were not characterised further.

The $^1$H n.m.r. spectra of the thioethers (Table 1; see also Figure) were complicated by overlapping resonances. To clarify the identification of the site of addition to the



SCHEME 1 (*i*) R = Me, $BH_4^-$, or $BD_4^-$; (*ii*) R = Me,$CN^-$; (*iii*) R = Me,$I^-$; (*iv*) R = Me,$MeO^-$ (ref. 1); (*v*) $HPF_6$; (*vi*) $R'S^-$

dienyl ligand, and to assign individual proton resonances, spin-decoupling experiments were performed in the presence of lanthanide shift reagents (Table 3).

A single-crystal *X*-ray diffraction study on (11d) confirmed the expected *exo*$_M$ stereochemistry of the isopropylthio-group. Details of the structure have been reported elsewhere.[16] We note here that a shortening of the Fe–C(6) and Fe–C(7) bond lengths relative to those of the acetyl cation [4] was observed, with a corresponding lengthening of the C(6)–C(7) bond. This is consistent with the notion of more effective back donation of Fe *d* electrons into the alkene $\pi^*$ orbital when the effective charge on the metal is reduced. It was also found that the C–S bond distances (*ca.* 1.84 Å) are relatively long which may reflect the ease with which the isopropylthio-group can be removed (see below).

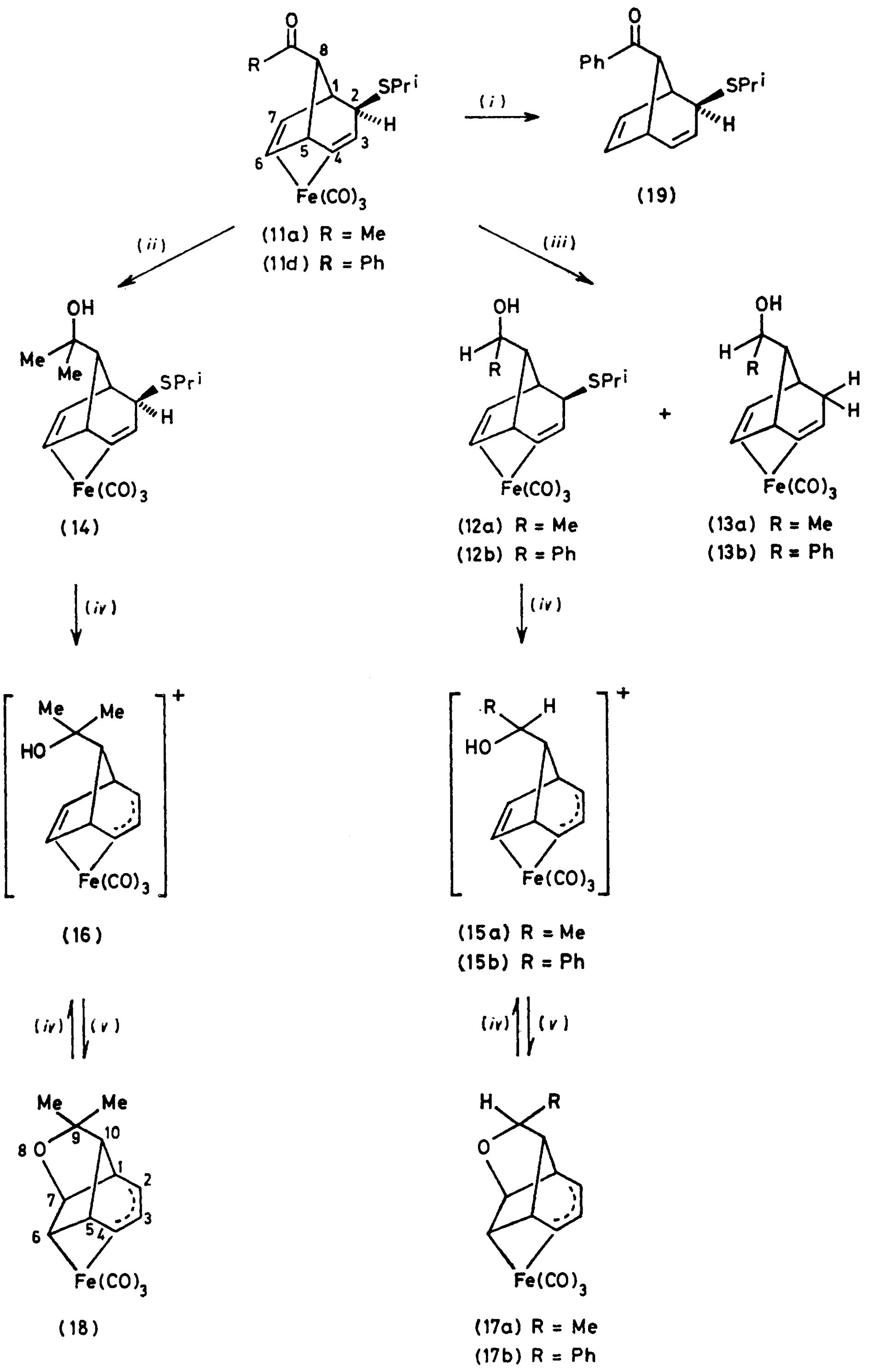
*Reactions of Co-ordinated Thioethers.*—The examples of nucleophilic addition to (3a) and (3b) discussed above reveal that the regiochemistry of nucleophilic attack on these cations is only partially governed by the extent to which the positive charge is delocalised over the co-ordinated dienyl carbons and the metal. The preference of a nucleophile for a particular site is controlled by a complex balance of coulombic and frontier-orbital factors that are not understood at present.[17,18] However, the wide range of products obtained on tetrahydroborate reduction of (3a) showed that, as expected, attack at the alternative electrophilic site, the C(9) carbonyl

TABLE 3

Lanthanide-induced shifts in a 0.22 mol $dm^{-3}$ solution of (11a) containing (*a*) 0.073 mol $dm^{-3}$ [Eu(tmhd)$_3$] and (*b*) 0.34 mol $dm^{-3}$ [Eu(fod)$_3$]

| Chemical shift ($\tau$) | Proton | Multiplicity | Lanthanide-induced shift (Hz) | Shift relative to isopropyl methyls ($\tau$) |
|---|---|---|---|---|
| (*a*) | | | | |
| 3.84 | $H^5$ | t | 285 | 6.7 |
| 4.13 | $H^8$ | s | 311 | 7.2 |
| 4.60 | Me | s | 344 | 8.0 |
| 4.76 | $H^1$ | br t | 270 | 6.3 |
| 5.17 | $H^6$ | t | 152 | 3.5 |
| 5.30 | $H^2$ | dd | 96 | 2.2 |
| 5.73 | $H^7$ | t | 135 | 3.1 |
| 6.17 | $H^4$ | t | 91 | 2.1 |
| 6.39 | $H^{3,9}$ | m | 69 | 1.6 |
| 8.32 | $CMe_2$ | d | 43 | 1.0 |
| (*b*) | | | | |
| −0.4 | *o*-Ph | m | 241 | 6.9 |
| 2.26 | *m*,*p*-Ph | m | 28 | 0.8 |
| 3.24 | $H^5$ | br t | 328 | 9.4 |
| 3.36 | $H^8$ | s | 294 | 8.4 |
| 4.69 | $H^6$ | overlapping t | 270 | 7.7 |
| 4.77 | $H^1$ | | 258 | 7.4 |
| 5.19 | $H^2$ | d | 89 | 2.5 |
| 5.74 | $H^7$ | t | 123 | 3.5 |
| 6.30 | $H^{3,4,9}$ | m | 67 | 1.9 |
| 8.25 | $CMe_2$ | d | 35 | 1.0 |

tmhd = 2,2,6,6-Tetramethylheptane-3,5-dionate; fod = 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctane-3,5-dionate.



SCHEME 2 (*i*) R = Ph, Ce$^{IV}$; (*ii*) R = Me, LiMe; (*iii*) R = Me or Ph; $BH_4^-$; (*iv*) $HPF_6$; (*v*) $NEt_3$

group, could only be achieved at the expense of competing addition to the more electrophilic dienyl system.

Since the usual syntheses of bicyclo[3.2.1]octadienes are based either on ring expansion of bicyclo[2.2.1]-heptenes or -heptadienes, or on dipolar cycloadditions to cyclopentadienes,[19] there are few routes available to such compounds stereospecifically functionalised at C(8). The rearrangement of (1a) to (3) provides a route to such compounds and we therefore sought a method whereby the C(9) carbonyl on the acyl cations could be selectively modified while retaining the facility for metal-directed nucleophilic attack at the dienyl carbons.

One possible method would involve ' protecting ' the cationic dienyl system by addition of a nucleophile which could then be easily removed after manipulations at C(9). Of the nucleophiles discussed above, the thiolate anions offered the most promise as they could be added to the acyl cation (3a) and (3b) both regio- and stereo-specifically, and, with the exception of the thiophenolate anion, in good yield. The products were moderately air-stable and easily purified by chromatography. Moreover, although stable to weak acids, the thioethers reacted rapidly with $HPF_6$ to regenerate the parent cations in quantitative yield.

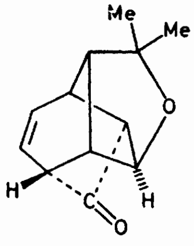
The chemistry of the 2-isopropylthio-complexes (11a,d) is summarised in Scheme 2. Reduction of the acyl group with $Na[BH_4]$ in ethanol gave moderate yields of the corresponding alcohols (12a,b), along with recovered starting material and some of the fully reduced complexes (13a,b). A variety of conditions was examined for the reduction but formation of (13) could not be altogether suppressed. Best results were obtained with $Li[AlH(OBu^t)_3]$–$Et_2O$ at low temperature where the ratio of (12) to (13) was about 2 : 1.

The mixture of reduced complexes could not be separated by chromatography, and the $^1H$ n.m.r. spectra are also complicated by the fact that each compound is present as a mixture of diastereomers formed by attack of tetrahydroborate at either face of the C(9) carbonyl. The situation is greatly simplified if the acyl reduction does not generate an asymmetric centre at C(9), and therefore we prepared the 9,9-dimethyl complex (14). Nucleophilic attack on the acetyl thioether (11a) with MgMeI proved unsatisfactory, resulting in either recovery of starting material or decomposition. However, treatment of (11a) with LiMe afforded the alcohol (14) in good yield. None of the 2-methyl complex analogous to (13) was obtained in this reaction. The two C(9) methyl groups resonate as a singlet (Table 1) at $\tau$ 8.86 and the remainder of the spectrum is similar to that of the parent thioether (11a). The $^1H$ n.m.r. spectrum of (15b) (Table 1) shows that the pairs of resonances $H^2$,$H^4$ and $H^1$,$H^5$ are split due to the epimeric centre at C(9). Surprisingly, $H^6$ and $H^7$ are not split significantly in this complex. The hydroxymethyl complex (15a) shows no such splitting, although it would be expected since both C(9) epimers are present in the sample. The 8-(1-hydroxy-1-methylethyl) cation (16) contains no chiral centre at C(9) and the two methyl groups resonate as a singlet at $\tau$ 8.86.

Although the mixtures of (12a,13a) and (12b,13b) could not be readily separated by chromatography, only the 2-isopropylthio-derivatives were protonated by $HPF_6$ to give the hydroxy-cations (15a,b), thus affording a convenient method of purification. Similarly, the alcohol (14) was protonated to form the cation (16). All three cations were characterised by $^1H$ n.m.r. spectra and microanalyses.

Generation of the hydroxy-cations (15a,b) and (16) permits further nucleophilic addition under the regio- and stereo-chemical control of the co-ordinated metal. Reaction of these cations with triethylamine deprotonated the alcohol, leading to the formation of the novel cyclic ethers (17a,b) and (18). The reaction is reversed by the addition of $HPF_6$. The 9-methyl and 9-phenyl derivatives (17a) and (17b) are present as a diastereomeric mixture A and B, as revealed by $^1H$ n.m.r. (Table 1). The 9,9-dimethyl complex (18) is free from this complication and the $^1H$ n.m.r. spectrum is much simplified (Figure).

It was hoped that the insertion of CO into the M–C $\sigma$ bond followed by demetallation and ring closure might lead to conversion of the ether (18) into the polycyclic ketone (20). However, two reagents which commonly serve this purpose, CO and $PPh_3$, failed to remove the metal or give any detectable insertion product. Compound (18) was recovered unchanged after treatment with CO at 100 atm,* 100 °C, for 18 h, and reaction with $PPh_3$ in refluxing toluene for 18 h led to CO substitution. Surprisingly, treatment with $Ce^{4+}$ at 0 °C for 15 min failed to give any reaction.[20,21]



(20)

Whereas the attempted demetallation of (18) was unsuccessful, treatment of (11d) with $Ce^{4+}$ in MeOH gave the 3,6-diene (19) in almost quantitative yield. The acylation rearrangement, therefore, represents a convenient route to C(8)-substituted bicyclo[3.2.1]octadienes. The complex (19) was obtained in 60% overall yield from $[Fe(C_8H_8)(CO)_3]$. As the acyl cations can be obtained from starting material in almost 100% yield using $RCOBF_4$,[5] the main limitation to this route is the yield of the thioether complexes.

*Mechanism of the Acyl Cation Rearrangement.*—The mechanism of formation of the 8-acyl cations (3a,b) from the monocyclic cyclo-octatetraene complex is uncertain. One attractive route is through the intermediacy of the bicyclo[5.1.0] cation (2b), which by analogy with the protonation of (1) [2] would be the expected product of acylation. Migration of the acyl-substituted C(8) of (2b) would then lead to the bicyclo[3.2.1] cation (Scheme 3).

Attempts to induce a similar rearrangement in the unsubstituted bicyclo[5.1.0] cation (2a) were unsuccessful. Heating or photolysis of (2a) in polar solvents such as acetone or acetonitrile lead to extensive decomposition of the sample. Cation (2a) was found to be stable on heating in trifluoroacetic acid but showed no detectable isomerisation.[22] Heating (2a) in acetic anhydride to 70 °C for several hours gave a mixture of recovered (2a)

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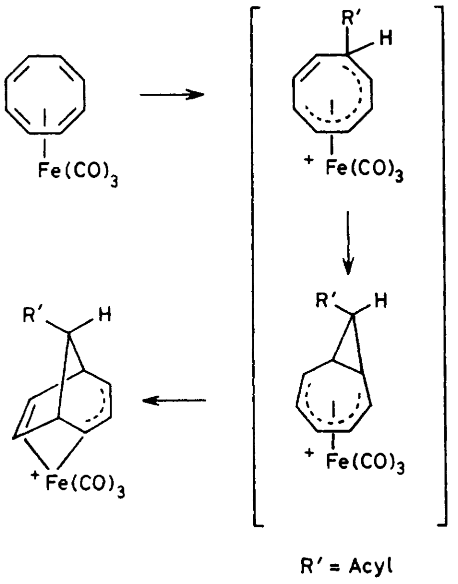
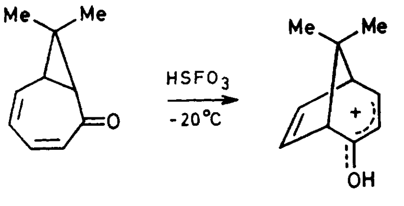
* Throughout this paper: 1 atm = 101 325 Pa; 1 mmHg ≈ 13.6 × 9.8 Pa.

and some (3a), again suggesting that the migration of C(8) may be related to its substitution pattern, as found for the cycloheptatriene–norcaradiene equilibrium.[23] Childs and Rogerson [24] have shown that the uncomplexed

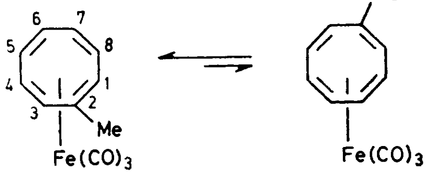


SCHEME 3

8,8-dimethylhomotropone (8,8-dimethylbicyclo[5.1.0]-octa-3,5-dien-2-one] (21) rearranged in $FSO_3H$ at −20 °C to the bicyclo[3.2.1] cation (22), whereas no similar rearrangement has been detected for the unsubstituted homotropone.[25] Related rearrangements have also been reported for co-ordinated olefins. Tricarbonyl-chromium [26] and -molybdenum [27] complexes of bicyclo[6.1.0]-nonatriene rearrange on heating to the bicyclo[4.2.1] complexes with retention of configuration at the migrating centre.[28] In an attempt to learn more about this rearrangement we studied the reaction of tricarbonyl-(methylcyclo-octatetraene)iron (23) with PhCOCl–$AlCl_3$. Whereas the unsubstituted cyclo-octatetraene complex (1) is fluxional on the $^1$H n.m.r. time scale at the lowest attainable temperatures,[29] at − 145 °C (23) exists as 90% of the isomer (23a).[30,31] At room temperature (23) is present predominantly as the isomer (23a) (80%) in equilibrium with (23b) (20%), but the methyl group still provides a useful label on the cyclo-octatetraene ring.[8b]



(21) (22)



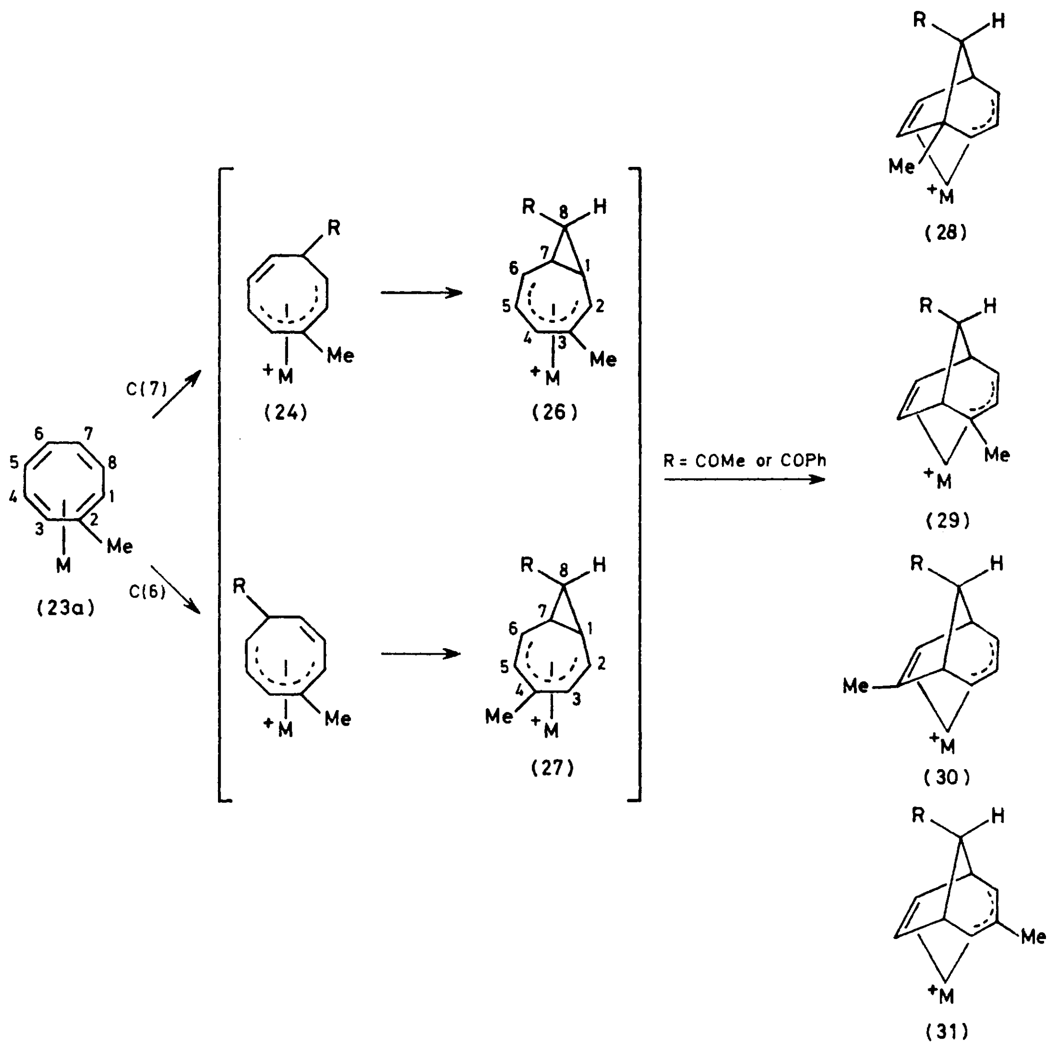
(23a) (23b)

Benzoylation of (23) afforded a mixture of cationic complexes (Scheme 4). The two major products, formed in roughly equal amounts, are assigned the structures (28) and (29). The $^1$H n.m.r. spectrum (Table 4) showed three methyl singlets at τ 7.57, 7.70, and 8.57 in the approximate ratio 4 : 1 : 5, integrating in total for three protons. The high-field methyl resonance at τ 8.57 has to be Me–C($sp^3$), while the other major singlet at τ 7.56 is Me–C($sp^2$). Comparison with the spectrum of the unmethylated benzoyl cation (Table 1) shows that two $H^8$ and two $H^3$ resonances are distinguishable. Therefore, the Me–C($sp^3$) resonance has to represent the 5-methyl cation (28) (Scheme 4). The two $H^3$ resonances visible are a triplet at τ 4.60 ($J$ = 6 Hz) and a doublet at τ 4.71 ($J$ = 6 Hz). Since the triplet must correspond to (28), the $H^3$ doublet and the Me–C($sp^2$) singlet are due to complex (29). Due to its low relative concentration, no positive assignment can be made for the remaining minor isomer. The position of the methyl resonance at τ 7.70 suggests Me–C($sp^2$). This would be consistent with either of the two complexes (30) and (31).

TABLE 4

Hydrogen-1 n.m.r. spectrum of methylated benzoyl cations

| Chemical shift (τ) | Proton (cation) | Multiplicity | $J$/Hz |
|---|---|---|---|
| (*a*) Solvent $(CD_3)_2CO$ | | | |
| 2.0 | *o*-Ph | dd | 8,2 |
| 2.44 | *m,p*-Ph | m | |
| 4.60 | $H^3$ (28) | t | 6 |
| 4.71 | $H^3$ (29) | d | 6 |
| 5.0 | $H^2$ (28 or 29) | t | 6 |
| 5.40 | $H^{4,7}$ (28)<br>$H^{2,6,7}$ (29) | m | |
| 5.76 | $H^6$ (28) | d | 3 |
| 6.22 | $H^1$ (28)<br>$H^{1,5}$ (29) | m | |
| 6.44 | $H^8$ (28 or 29) | s | |
| 6.53 | $H^8$ (28 or 29) | s | |
| 7.57 | Me (29) | s | |
| 7.70 | Me (30 or 31) | s | |
| 8.57 | Me (28) | s | |
| (*b*) Solvent $CD_2Cl_2$ | | | |
| 2.13 | *o*-Ph | dd | 8,2 |
| 2.48 | *m,p*-Ph | m | |
| 4.86 | $H^3$ (28) | t | 6 |
| 5.04 | $H^3$ (29) | d | 6 |
| 5.20 | $H^2$ (28 or 29) | t | 6 |
| 5.42 | $H^2$ (28 or 29) | dd | 6,5 |
| 5.56 | $H^4$ (28) | dd | 6,2 |
| 5.78 | $H^7$ (28)<br>$H^{6,7}$ (29) | | |
| 6.20 | $H^6$ (28) | d | 3 |
| 6.40 | $H^1$ (28)<br>$H^{1,5}$ (29) | | |
| 6.68 | $H^8$ (28 or 29) | s | |
| 6.82 | $H^8$ (28 or 29) | s | |
| 7.68 | Me (29) | s | |
| 7.77 | Me (30 or 31) | s | |
| 8.63 | Me (28) | s | |



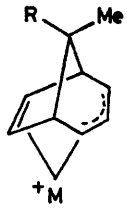
Scheme 4

Assuming that the formation of the bicyclo[3.2.1] cations proceeds through a bicyclo[5.1.0] intermediate, it is possible to predict which products might be formed on benzoylation of (23). This is shown in Scheme 4 for the isomer (23a). It is known that protonation of (23a) at low temperature takes place at either C(6) or C(7) to give the intermediates (24) and (25) (R = H) which rearrange on warming to the bicyclo[5.1.0] cations (26) and (27) (R = H).[31] We propose that acylation of (23a) follows a similar pathway to give the intermediates (26) and (27) (R = COPh or COMe) which then undergo either a 1,3 or 1,4 shift of the C(1)–C(8) or C(7)–C(8) bonds to produce the bicyclo[3.2.1] cations (28)—(31).

A similar analysis of the expected products from the benzoylation of the minor isomer (23b) would predict formation of the bicyclo[3.2.1] cations (29)—(32), to the exclusion of (28). As the 5-methyl isomer (28) is a major product from the benzoylation of (23) and we see no (32), we suggest that most of the reaction is proceeding from attack on (23a).

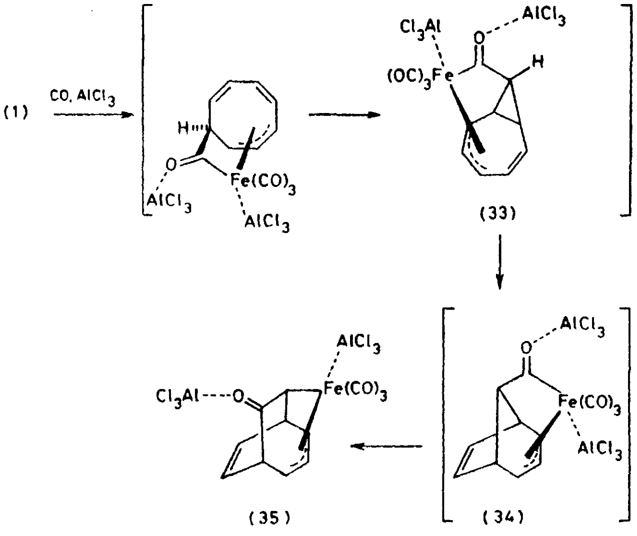
According to our scheme, a 1,3 shift of the cyclopropyl bonds in the intermediates (26) and (27) (R = COMe or COPh) could afford the [3.2.1] complexes (28), (29), and (30), while a 1,4 shift would lead to (28), (29), and (31). We cannot distinguish between these two mechanisms in this experiment but the data suggest only one of the two is the major pathway.

Since the exact mechanism leading to formation of the bicyclo[3.2.1] cation from [Fe($C_8H_8$)(CO)$_3$] is not known, we are unable to establish the initial stereochemistry of electrophile attack on the cyclo-octatetraene ring, although we might expect it to be *exo*$_M$.[31-34] The final


(32) R = COMe or COPh

product, however, contains the C(8) acyl group *syn* to the C(6), C(7) double bond. The reason for this striking stereospecificity is unknown, but its observation poses the question of whether the rearrangement proceeds under control of orbital symmetry.

The rearrangement observed in the acylation reaction may be related to the reaction of (1) with $AlCl_3$ and CO to give complex (35) derived from barbaralone.[5,35] Insertion of CO into the $C_8$ ring could be achieved by initial electrophilic attack to give the bicyclo[5.1.0] intermediate (33), followed by rearrangement to the [3.2.1] skeleton (34) and finally ring expansion to the σ,η-allyl complex (35) (Scheme 5). In this connection, we note that [Ru($C_8H_8$)(CO)$_3$] is neither readily acylated nor does it undergo a ' barbaralone-type ' reaction with $AlCl_3$–CO.



SCHEME 5

## EXPERIMENTAL

All reactions were carried out under an atmosphere of pure dry nitrogen. Melting points were measured in open capillary tubes on a Gallenkamp apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 257 spectrometer using a CO calibrant. Mass spectra were obtained on an A.E.I. MS 12 spectrometer. Elemental analyses were determined by the microanalytical department of this laboratory. Hydrogen-1 n.m.r. spectra were recorded on a Varian Associates HA 100 and XL 100 spectrometer, operating at 100 MHz, and on a Varian Associates CFT 20 spectrometer operating in the Fourier-transform mode at 80 MHz, employing a solvent deuterium lock.

Tricarbonyl(cyclo-octatetraene)iron,[36] tricarbonyl(cyclo-octatetraene)ruthenium,[10] tricarbonyl(methylcyclo-octatetraene)iron,[31] and acetyl tetrafluoroborate [37] were prepared by the literature methods. Anhydrous $AlCl_3$ was sublimed immediately before use.

(2—4:6—7:-η-8-*Acetylbicyclo*[3.2.1]*octadienylium*)*tricarbonyliron Hexafluorophosphate* (3a).—This was prepared following the method of Johnson *et al.*[1] Anhydrous $AlCl_3$ (3.3 g, 25 mmol) was added to dry dichloromethane (60 cm$^3$). Freshly distilled acetyl chloride (4.5 cm$^3$, 63.5 mmol) was added from a syringe. The resulting deep red solution was added dropwise to a stirred solution of [Fe($C_8H_8$)(CO)$_3$] (6 g, 25 mmol) in dichloromethane (60 cm$^3$) at 0 °C over a 20 min period. Stirring was continued for another 10 min at 0 °C, and the reaction mixture then hydrolysed with ice-cold 5% hydrochloric acid solution (75 cm$^3$). Diethyl ether (60 cm$^3$) was added and the organic phase separated, then washed with water (3 × 50 cm$^3$). The combined aqueous fractions were extracted with diethyl ether (3 × 50 cm$^3$) and the golden yellow aqueous solution cooled to 0 °C. Addition of 15% ammonium hexafluorophosphate solution (50 cm$^3$) gave a pale yellow precipitate which was collected and washed with diethyl ether, then dried *in vacuo* at 35 °C to give the *product*, which could be further purified by dissolving in the minimum volume of acetone and reprecipitating with diethyl ether (yield 5.2 g, 47%).

(2—4:6—7-η-8-*Benzoylbicyclo*[3.2.1]*octadienylium*)*tricarbonyliron Hexafluorophosphate* (3b).—This was prepared by the method described above, using benzoyl chloride and anhydrous $AlCl_3$. The *product* was obtained as a pale yellow precipitate (yield 9.0 g, 74%) (Found: C, 43.2; H, 2.8. $C_{18}H_{13}F_6FeO_4P$ requires C, 43.7; H, 2.65%).

*Reaction of* [Fe($C_8H_7$Me)(CO)$_3$] *with Benzoyl Chloride and Anhydrous* $AlCl_3$.—The above procedure was followed and the product analysed by $^1$H n.m.r. spectroscopy.

*Attempted Acylation of* [Ru($C_8H_8$)(CO)$_3$].—Tricarbonyl(cyclo-octatetraene)ruthenium was treated with acetyl chloride and anhydrous $AlCl_3$ under similar conditions to those described above. No cationic ruthenium complex was found in the aqueous layer. The organic residue was found to contain a mixture of [Ru($C_8H_8$)(CO)$_3$] and tricarbonyl(3—5-η-cyclo-octatrienyl)ruthenium chloride by i.r. spectroscopy.

In another attempt, [Ru($C_8H_8$)(CO)$_3$] was treated with acetyl tetrafluoroborate at −78 °C in dichloromethane. Addition of dry diethyl ether gave a small amount of precipitate which was found to be *tricarbonyl*(1—3:6—7-η-*cyclo-octatrienylium*)*ruthenium tetrafluoroborate* by $^1$H n.m.r. The ether-soluble fraction contained only starting material.

(2—4-η,6-σ-8-*Acetylbicyclo*[3.2.1]*octenediyl*]*tricarbonyliron* (6a).—Compound (3a) (1 g, 2.3 mmol) was added in small amounts to a 10% solution of sodium tetrahydroborate (10 cm$^3$) in diethyl ether (15 cm$^3$) at 0 °C. After stirring for 1 h, water (25 cm$^3$) was added and the two layers separated. The aqueous layer was extracted with diethyl ether, and the combined ether extracts were washed with water. After drying over Mg[SO$_4$], the ether was removed and the residue chromatographed twice on silica plates using 10% diethyl ether–benzene as eluant. Two major bands were obtained (in addition to several minor ones) and the faster running band was purified by crystallisation to give the *product* (145 mg, 25%) (Found: C, 54.4; H, 4.3. $C_{13}H_{12}FeO_4$ requires C, 54.2; H, 4.15%).

The slower running band gave the unstable isomeric compound which was probably the 3,6-η-diene.

(2—4-η,6-σ-8-*Acetyl-7-deuteriobicyclo*[3.2.1]*octenediyl*)*tricarbonyliron* (6b).—A deuterium oxide solution (20 cm$^3$) of lithium tetradeuterioborate (250 mg, 9.6 mmol) and (3a) (430 mg, 0.99 mmol) were mixed at 0 °C and stirred for 30 min. The mixture was extracted with diethyl ether and the extracts dried over Mg[SO$_4$]. The residue left after removal of ether was chromatographed twice on silica plates in 10% diethyl ether–benzene. The faster running band was extracted and purified by crystallisation to give the *product*.

(2—4-η,6-σ-8-*Acetyl-7-cyanobicyclo*[3.2.1]*octenediyl*)*tricarbonyliron* (7).—Compound (3a) (0.5 g, 1.5 mmol) was added in small amounts to a saturated aqueous solution (5 $cm^3$) of sodium cyanide with vigorous stirring. After 30 min the mixture was extracted with diethyl ether, the extracts dried over $Mg[SO_4]$, and the solvent removed. The residue was chromatographed on silica plates using 20% ethyl acetate–benzene as eluant. Two major bands were obtained and the slower running band was extracted and crystallised from hexane–dichloromethane to give almost colourless crystals of the *product* (yield 50 mg, 13%) (Found: C, 53.3; H, 3.7. $C_{14}H_{11}FeNO_4$ requires C, 53.7; H, 3.55%).

The faster running band gave yellow crystals of an isomeric compound, probably the diene complex (8) (yield 35 mg, 9%).

(2—4:6—7-η-8-*Acetylbicyclo*[3.2.1]*octadienyl*)*dicarbonyliodoiron* (9).—Compound (3a) (1 g, 2.3 mmol) was resuspended in dry acetone (30 $cm^3$) and potassium iodide (400 mg, 2.4 mmol) was added. The solution was stirred for 3 h and the solvent removed. The residue was dissolved in benzene, filtered through Celite, and then eluted through a short alumina column. The solvent was removed *in vacuo* and the residue recrystallised from hexane–dichloromethane to give the *product* as dark maroon crystals (yield 455 mg, 52%) (Found: C, 29.7; H, 2.4. $C_{12}H_{11}FeIO_3$ requires C, 29.6; H, 2.25%).

{3—4:6—7-η-8-*Acetyl-2-*(*isopropylthio*)*bicyclo*[3.2.1]*octa-*3,6-*diene*}*tricarbonyliron* (11a).—n-Butyl-lithium (7 mmol) in hexane was added by syringe to a solution of $Pr^iSH$ (0.66 mmol) in dry acetonitrile (50 $cm^3$) at 0 °C. The resultant precipitate was slowly transferred *via* a cannula to a stirred solution of (3a) (2 g, 4.64 mmol) in acetonitrile (100 $cm^3$) at 0 °C. The reaction mixture was stirred on ice for 5 min, then slowly hydrolysed with ice-cold 1% hydrochloric acid solution (60 $cm^3$). Diethyl ether (100 $cm^3$) was added and the light orange organic layer separated, washed with water (2 × 40 $cm^3$), and dried over $K_2[CO_3]$. The solvent was removed and the residue chromatographed on alumina (Grade 1), eluting first with benzene to remove the leading pale red band, then with benzene–1% ethyl acetate to collect the second, bright yellow band. The latter afforded the *product* as a yellow oil which could be further purified by distillation onto a cold-finger at 45—50 °C (0.05—0.001 mmHg) (yield 820 mg, 50%) (Found: C, 53.7; H, 4.95. $C_{16}H_{18}FeO_4S$ requires C, 53.1; H, 5.00%).

The 8-*acetyl*-2-(*t-butylthio*) (11b) and 8-*acetyl*-2-*phenylthio* (11c) complexes were prepared in similar fashion [Found: C; 54.8; H, 5.4. $C_{17}H_{20}FeO_4S$ (11b) requires C, 54.4; H, 5.35%. No satisfactory analysis for (11c)].

{3—4:6—7-η-8-*Benzoyl-2-*(*isopropylthio*)*bicyclo*[3.2.1]-*octa-*3,6-*diene*}*tricarbonyliron* (11d).—This was prepared by adding a suspension of $Li[SPr^i]$ in acetonitrile to a stirred solution of (3b) in acetonitrile at 0 °C in similar fashion to the procedure described above. Work-up and chromatography [benzene–alumina (Grade 1)] gave the *product* as yellow crystals which were recrystallised from pentane (m.p. 65—65.5 °C) (yield 80%) (Found: C, 59.6; H, 4.9. $C_{21}H_{20}FeO_4S$ requires C, 59.4; H, 4.25%).

*Reduction of Thioether Complexes.*—A solution of $Na[BH_4]$ (34.2 mg, 0.91 mmol) in ethanol (25 $cm^3$) was added dropwise over a 15-min period to a solution of (11a) (493 mg, 1.21 mmol) in ethanol (50 $cm^3$) at −15 °C. The reaction mixture was stirred at this temperature for 40 min, then acetone (5 $cm^3$) and water (50 $cm^3$) were added, followed by diethyl ether (25 $cm^3$) and sufficient extra water to achieve a good phase separation. The aqueous layer was extracted with diethyl ether (4 × 25 $cm^3$) and the combined organic extracts dried ($K_2[CO_3]$) and then concentrated *in vacuo* and chromatographed on alumina (Grade 1). The first red band eluted in benzene contained a mixture of unidentified tricarbonyliron complexes while a second yellow band contained starting material (152 mg, 46%). Another yellow band was eluted in 25% ethyl acetate–benzene, which contained a mixture of the alcohols (12a) and (13a) which could not be separated further by chromatography.

In an alternative procedure, $Bu^tOH$ (488 mg, 6.6 mmol) in dry diethyl ether (10 $cm^3$) was added at −78 °C to lithium aluminium hydride (84 mg, 2.2 mmol) in dry diethyl ether (10 $cm^3$). The mixture was stirred at −78 °C for 30 min, then (11a) (400 mg, 1.1 mmol) in diethyl ether (10 $cm^3$) was added dropwise and the reaction stirred for 3 h at −78 °C. Addition of 1% hydrochloric acid (20 $cm^3$) and work-up as described above gave a yellow oil which was chromatographed in the usual way to give the *product* as a 2 : 1 mixture of (12a) and (13a).

The 8-benzoylthioether (11d) was reduced in similar fashion to give a mixture of the alcohols (12b) and (13b).

*Tricarbonyl*{3—4:6—7-η-8-(1-*hydroxy*-1-*methylethyl*)-2-(*isopropylthio*)*bicyclo*[3.2.1]*octa*-3,6-*diene*}*iron* (14).—Methyl-lithium (1.5 mmol) in diethyl ether was added by syringe to a stirred solution of (11a) (400 mg, 1.1 mmol) in dry diethyl ether (30 $cm^3$) at 0 °C, and the reaction mixture stirred at this temperature for 4 h. Hydrolysis with 1% hydrochloric acid (60 $cm^3$) gave a yellow organic layer. The aqueous phase was washed with diethyl ether (2 × 20 $cm^3$) and the combined organic phases washed once with cold water (20 $cm^3$), then dried ($K_2[CO_3]$). Removal of solvent and chromatography (Fluka 507C alumina, Grade 1) with 1% ethyl acetate–benzene eluted starting material. Elution with 35% ethyl acetate–benzene gave the *product* as a yellow oil (yield 160 mg, 37%). This could be further purified by distillation onto a cold-finger at reduced pressure (Found: C, 53.7; H, 5.85. $C_{17}H_{22}FeO_4S$ requires C, 53.95; H, 5.80%).

*Protonation of Thioether Complexes.*—Ether solutions of the thioethers were protonated by adding a 60% aqueous solution of hexafluorophosphoric acid dropwise at 0 °C. The *precipitates* were collected, washed in diethyl ether, dried *in vacuo*, and then dissolved in the minimum volume of acetone and reprecipitated with diethyl ether. The cations (15a, b) were obtained by protonation of the mixture of alcohols (12a, b) and (13a, b) [Found: C, 35.6; H, 3.0. $C_{13}H_{13}F_6FeO_4P$ (15a) requires C, 35.95; H, 3.0%. Found: C, 43.2; H, 2.8. $C_{18}H_{13}F_6FeO_4P$ (15b) requires C, 43.7; H, 2.65%]. The alcohol cation (16) was obtained by protonation of the 8-(1-hydroxy-1-methylethyl) complex (14) (Found: C, 37.5; H, 3.4. $C_{14}H_{15}F_6FeO_4P$ requires C, 37.5; H, 3.3%).

*Reaction of Alcohol Cations with Triethylamine.*—A slight excess of triethylamine was added to a stirred suspension of the alcohol cations (15a, b) or (16) in dichloromethane at 0 °C. The resulting clear solutions were stirred for 2 min at 0 °C and then hydrolysed with 1% hydrochloric acid (5 $cm^3$) and water (10 $cm^3$). The organic layers were separated, washed, and dried over $K_2[CO_3]$. Removal of solvent gave the *cyclic ethers* (17a, b) and (18) in quantitative yield [Found: C, 54.8; H, 4.35. $C_{13}H_{12}FeO_4$ (17a) requires C, 54.15; H, 4.15%. Found: C, 61.9; H, 4.5. $C_{18}H_{14}FeO_4$ (17b) requires C, 61.7; H, 4.1%. Found: C, 55.75; H, 5.0. $C_{14}H_{14}FeO_4$ (18) requires C, 55.6; H, 4.7%].

*8-Benzoyl-2-(isopropylthio)bicyclo*[3.2.1]*octa-3,6-diene* (19).—Ammonium cerium(IV) nitrate (1.03 g, 1.88 mmol) was dissolved in ethanol (50 $cm^3$) and added dropwise to a solution of the thioether (11d) (200 mg, 0.47 mmol) in ethanol (50 $cm^3$) at 0 °C. The solution was stirred for 5 min, then hydrolysed with water (200 $cm^3$). The aqueous layer was washed with diethyl ether ($2 \times 50$ $cm^3$), the organic fractions combined, and dried ($K_2[CO_3]$). The solvent was removed to give the *product* as a colourless oil which was further purified by distillation onto a cold-finger at 55—60 °C (0.01 mmHg) (yield 132 mg, 98%) (Found: C, 76.1; H, 7.4; S, 11.15. $C_{18}H_{20}OS$ requires C, 76.05; H, 7.05; S, 11.25%).

We are grateful to Dr. A. V. Rivera and Dr. G. M. Sheldrick for crystallographic structure determinations, and to Johnson Matthey Ltd. for a loan of $RuCl_3$. We also thank the S.R.C. (A. D. C.) and N.A.T.O. (P. D.) for financial support.

[0/832 *Received, 2nd June,* 1980]

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