Reactivity of Co-ordinated Ligands. Part XXI.† Ligand Substitution and Nucleophilic Reactivity of Cyclohexa-, Cyclohepta-, and Cyclo-octadienylium Complexes of Iron

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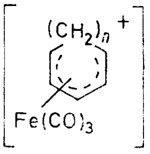
Cations $[L(C_7H_9)Fe(CO)_2]^+$ [IV; L = PPh$_3$, AsPh$_3$, SbPh$_3$, pyridine (py), MeCN, NH$_3$, or CH$_2$CHCN] have been prepared from dicarbonyl(1—5-η-cycloheptadienylium)iodoiron. In the cases where L = PPh$_3$ or AsPh$_3$, nucleophilic attack generates solely 3—5-η,1-σ-cycloheptenyl products, (VI), resulting from attack at the 2-position of the dienylium system. Studies on the nucleophilic reactivity of tricarbonyl(1—5-η-cycloheptadienylium)iron, (II), show that mixtures of η-cyclohepta-1,3-diene and 3—5-η,1-σ-cycloheptenyl products [(IX) and (X)] result, with the proportions being dependent on both the conditions and the nucleophile. Tricarbonyl(1—5-η-cyclohexadienylium)iron, (I), and its dicarbonyl(triphenylphosphine) analogue, (VIII), both react with nucleophiles to generate only the η-cyclohexa-1,3-diene product, (VII). Tricarbonyl(1-5-η-cyclo-octadienylium)iron, (III), gives only the η-cyclo-octa-1,3-diene product on treatment with tetrahydroborate, but evidence is presented suggesting that attack at the 2-position also occurs. These differences in reactivity are discussed in terms of steric, kinetic, and electronic factors.

TRICARBONYLIRON complexes of delocalized dienylium cations show great thermodynamic stability. In addition to electron donation from the 4π-electron system, stabilization of the cation is effected by back bonding from the filled metal orbitals to the empty non-bonding orbitals of the dienylium system. A wide variety of acyclic η-pentadienylium complexes have been synthesized by treatment of tricarbonyl(*trans*-penta-1,3-dienol)iron and its alkyl-substituted derivatives with strong acid.[1] Cyclic dienylium complexes of six-, seven-, and eight-membered rings (I)—(III) may be prepared by hydride abstraction or protonation of the appropriate diene or triene complex.



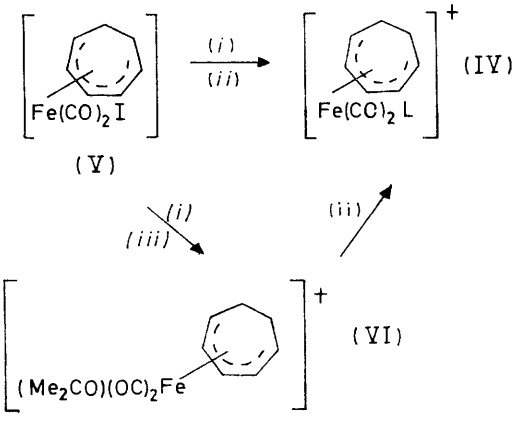
(I) $n = 1$
(II) $n = 2$
(III) $n = 3$

Reaction of tricarbonyl(η-cyclohexadienylium)iron, (I), with a wide variety of nucleophiles yields 5-substituted η-cyclohexa-1,5-diene complexes,[2] except in the case of iodide which results in displacement of a carbonyl group to give neutral dicarbonyl(η-cyclohexadienylium)iodoiron.[3] By analogy with known specific *exo*-nucleophilic attack on other ring systems, attack on (I) has been assumed to be *exo* and some substantiating evidence has been obtained.[2] A recent kinetic study of the reaction of complex (I) with pentane-2,4-dionate has been rationalized in terms of direct nucleophilic attack on the organic moiety, although a mechanism involving metal participation cannot be excluded.[4] Although reduction of tricarbonyl(η-cycloheptadienylium)iron, (II), with tetrahydroborate ion was originally reported to give only tricarbonyl(η-cyclohepta-1,3-diene)iron,[3] it has been shown recently that a mixture of 1,3-diene and σ,η-allyl products results.[5] Reaction of (II) with iodide generates the neutral dicarbonyl(η-cycloheptadienylium)iodoiron complex.[3] Tricarbonyl(η-cyclo-octadienylium)iron, (III), has been reported to yield only tricarbonyl(η-cyclo-octa-1,3-diene)iron on reduction.[6]

This work presents a study of the synthesis and reactivity of cations of the type $[L(C_7H_9)Fe(CO)_2]^+$, (IV), where L is a donor ligand other than carbonyl. Variation in this ligand has been found to lead to great changes in the reactivity of the organic moiety. A reinvestigation of the nucleophilic reactivity of the six-, seven-, and eight-membered dienylium systems (I)—(III) has also been undertaken.

RESULTS

Synthesis.—The only previously known derivative of the type (IV) is the complex where L = PPh$_3$, obtained



(*i*) AgPF$_6$; (*ii*) L = PPh$_3$, AsPh$_3$, SbPh$_3$, pyridine (py), MeCN, NH$_3$, or CH$_2$CHCN; (*iii*) Me$_2$CO. The counter ion is PF$_6^-$ in each case

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† Part XX, preceding paper.

[1] M. Haas, *Organometallic Chem. Rev.* (*A*), 1969, 307.

[2] E. O. Fischer and R. D. Fischer, *Angew. Chem.*, 1960, **72**, 919.

[3] M. A. Hashmi, J. D. Munro, P. L. Pauson, and J. M. Williamson, *J. Chem. Soc.* (*A*), 1967, 240.

[4] L. A. P. Kane-Maguire, *J. Chem. Soc.* (*A*), 1971, 1602.

[5] R. Aumann, *J. Organometallic Chem.*, 1973, **47**, C28.

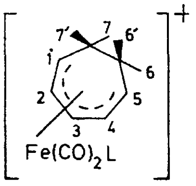
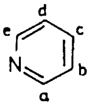
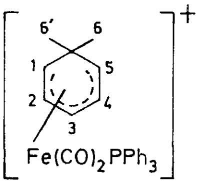
[6] W. McFarlane, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 1963, 2162.

by hydride abstraction from dicarbonyl(η-cyclohepta-1,3-diene)triphenylphosphineiron.[7] The method of preparation used here involved reaction of dicarbonyl(1—5-η-cycloheptadienylium)iodoiron, (V), with silver(I) hexafluorophosphate in the presence of the ligand L. The ligand was used as the solvent medium, as in the preparation of (IV; L = MeCN or NH_3) or, alternatively, the new complexes were prepared by addition of an acetone solution of silver(I) hexafluorophosphate to a solution of (V) in dichloromethane, to generate in solution (acetone)-dicarbonyl(1—5-η-cycloheptadienyl)iron from which the acetone may be displaced by addition of ligand L. All complexes (IV) are yellow solids stable under a dinitrogen atmosphere or in solution, except for (IV; L = NH_3) which loses ammonia in solution.

In the i.r. spectra of complexes (IV), two carbonyl bands of equal intensity were observed at 2 050—2 080 and 2 010—2 030 cm^{-1} (see Table 1). The wavenumbers are *ca.* 35 cm^{-1} higher than those of (V) and *ca.* 50 cm^{-1} higher than those found for neutral dicarbonyl(diene)triphenylphosphineiron complexes (see Table 2), consistent with the introduction of a positive charge. Cyanide-stretching

TABLE 1

Spectral data for dienylium complexes

	Proton [a]	Chemcal shift, τ	Intensity	Multiplicity	J/Hz	$\bar{\nu}$(CO) [b]/cm^{-1}
						
(IV) L = PPh_3	PPh_3	2·24	15	m		
	$H_{1,5}$	5·51	2	m		
	$H_{2,4}$	4·18	2	m		
	H_3	2·68	1	t	6·0	2 050, 2 007
	$H_{6,7}$	7·32	2	m		
	$H_{6',7}$	8·25	2	m		
(IV) L = $AsPh_3$	$H_{1,4}$	5·62	2	m		2 046, 2 005
	$H_{2,4}$	4·26	2	m		
	H_3,$AsPh_3$	2·4—2·6	16	m		
	$H_{6,7}$	7·45	2	m		
	$H_{6',7'}$	8·40	2	m		
(IV) L = $SbPh_3$	$H_{1,5}$	5·27	2	m		
	$H_{2,4}$	4·02	2	m		
	H_3,$SbPh_3$	2·4—2·6	16	m		2 045, 2 006
	$H_{6,7}$	7·23	2	m		
	$H_{6',7'}$	8·33	2	m		
Et_2O	CH_2	6·58	1	q	6·7	
	CH_3	8·89	1·5	t		
(IV) L =	$H_{a,e}$	1·09	2	d		2 057, 2 010
	$H_{3,c}$	1·95	2	m		
	$H_{b,d}$	2·48	2	m		
	$H_{1,5}$	5·73	2	m		
	$H_{2,4}$	4·34	2	m		
	$H_{6,7}$	7·34	2	m		
	$H_{6',7'}$	8·41	2	m		
(IV) L = MeCN	$H_{1,5}$	5·75	2	m		
	$H_{2,4}$	4·14	2	m		
	H_3	2·12	1	t	6·9	2 076, 2 035; 2 326 [ν(CN)] [c]
	$H_{6,7}$	7·49	2	m		
	$H_{6',7'}$	8·49	2	m		
	CH_3CN	7·64	3	s		
(IV) L = NH_3 [d]						2 052, 2 008; 3 377, 3 306 (NH_3) [c]
	$H_{1,5}$	5·60	2	m		
	$H_{2,4}$	4·21	2	m		
	H_3,PPh_3	2·4—2·6	16	m		2 045, 1 983
(VIII)	H_6 (*endo*)	7·25	1	m		
	$H_{6'}$ (*exo*)	8·11	1	m		

[a] $(CD_3)_2CO$ Solution. [b] CH_2Cl_2 Solution. [c] Nujol mull. [d] Decomposes in $(CD_3)_2CO$.

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[7] F. M. Chaudhari and P. L. Pauson, *J. Organometallic Chem.*, 1966, **5**, 73.

TABLE 2

Spectral data for neutral diene and dienyl complexes

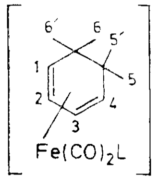
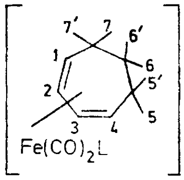
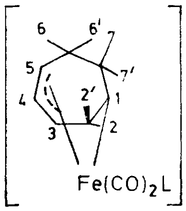
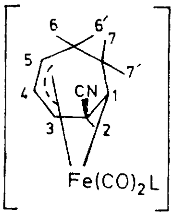
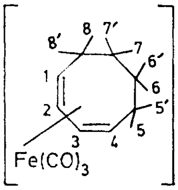
	Proton [a]	Chemical shift τ,	Intensity	Multiplicity	$\bar{\nu}$(CO) [b]/cm^{-1}	Parent ion (P^+), *m/e*
 (VII) L = CO	$H_{1,4}$	6·86	2	m	2 055, 1 986, 1 981	220
	$H_{2,3}$	4·76	2	m		
	$H_{5,6}$	8·37	4	m		
(VII) L = PPh$_3$	$H_{1,4}$	7·38	2	m	1 981, 1 927	(P − PPh$_3$)$^+$ 192
	$H_{2,3}$	5·20	2	m		
	$H_{5,6}$	8·35	4	m		
	PPh$_3$	2·4—2·8	15	m		
 (IX) L = CO	$H_{1,4}$	6·99	2	m	2 044, 1 981, 1 977	234
	$H_{2\ 3}$	4·76	2	m		
	$H_{5',5',7,7'}$	8·05	4	m		
	$H_{6,6'}$	8·55	2	m		
(IX) L = PPh$_3$	$H_{1,4}$	7·44	2	m	1 979, 1 925	206 (P − PPh$_3$)$^+$
	$H_{2,3}$	5·37	2	m		
	$H_{5,5',7,7'}$	8·08	4	m		
	$H_{6,6'}$	8·76	2	m		
	PPh$_3$	2·4—3·1	15	m		
 (VI) L = PPh$_3$	H_2 (pseudo-equatorial)	7·08	1	m	1 979, 1 921	206 (P − PPh$_3$)$^+$
	$H_{2'}, H_{1,6,6'}$	7·48—8·22	4	m		
	H_3	6·22	1	m		
	H_4	6·43	1	m		
	H_5	5·98	1	m		
	$H_{7\ \text{or}\ 7'}$					
	$H_{7\ \text{or}\ 7'}$, H_1	8·54	2	m		
	PPh$_3$	2·4—3·1	15	m		
(VI) L = AsPh$_3$	H_2	7·10	1	m	1 975, 1 919	206 (P − AsPh$_3$)$^+$
	$H_{2'}, H_{6,6'}$	7·4—8·2	4	m		
	H_3	5·97	1	m		
	H_4	6·20	1	m		
	H_5	5·57	1	m		
	H_7 or $_{7'}$					
	H_7 or $_{7'}$, H_1	8·51	2	m		
	AsPh$_3$	2·95	15	m		
 (VI) L = PPh$_3$	H_1	8·80	1	m	1 985,1 929	231 (P − PPh$_3$)$^+$
	H_{2-4}	6·60	3	m		
	H_5	5·98	1	m		
	$H_{6,6',7,7'}$	7·92	4	m		
	PPh$_3$	2·80	15	m		

TABLE 1 (*Continued*)

	Proton[a]	Chemical shift τ	Intensity	Multiplicity	$\bar{\nu}$(CO)[b]/cm^{-1}	Parent ion (P^+), m/e
(VI) L = $AsPh_3$	H_2	6·57	1	m		
	$H_{3,4}$	6·39	2	m		
	H_5	5·69	1	m	1 988, 1 935	231 (P − $AsPh_3$)$^+$
	H_1	8·85	1	m		
	$H_{6,6',7,7'}$	7·80—8·0	4	m		
	$AsPh_3$	2·79	15	m		
	$H_{1,4}$	6·2	2	m		
	$H_{2,3}$	5·3	2	m	2 043, 1 974	248
	$H_{5,5',8,8'}$	8·0	4	m		
	$H_{6,6',7,7'}$	8·8	4	m		

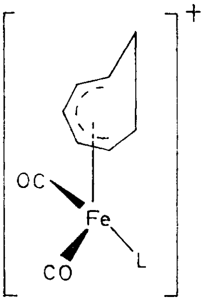
[a] C_6D_6 Solution. [b] Cyclohexane solution.

frequencies in (IV; L = MeCN or CH_2CHCN) at 2 326 and 2 270 cm^{-1} are comparable to those found for the corresponding salts [(cp)Fe(CO)$_2$L]PF$_6$ (cp = η-cyclopentadienyl) at 2 320 and 2 288 cm^{-1}.[8,9] The two expected ammine vibrations of complex (IV; L = NH_3) were observed at 3 377 and 3 306 cm^{-1}.

^{1}H N.m.r. spectra of the complexes were characteristic of the η-cycloheptadienylium system, showing, in the case of (IV; L = MeCN) for example, the central (3-) dienylium proton as a triplet (J 6·7 Hz) at τ 2·12, the two inner (2-,4-) protons as a doublet of doublets at τ 4·14, and the two outer (1-,5-) protons as a multiplet at τ 5·75. The two *endo*-methylenic protons were observed as a multiplet at τ 7·49, while the two *exo*-protons were found at τ 8·49. The ^{13}C n.m.r. spectrum of the complex (IV; L = $AsPh_3$) establishes the stereochemistry of the cations. At room temperature, the proton-decoupled spectrum showed the dienylium carbon atoms as three singlets at 106·4 (C_1), 104·7 ($C_{2,3}$), and 92·7 ($C_{4,5}$) p.p.m. downfield from tetramethylsilane. A singlet was observed for the methylene carbon atoms at 36·7 p.p.m., while the triphenylarsine carbons were observed at 135·6—138·0 p.p.m. A singlet was found for the carbonyl resonance at 215·0 p.p.m. No temperature dependence of either the dienylium or the carbonyl resonances was observed down to −60 °C. On the basis of pseudo-octahedral co-ordination, the symmetry of the dienylium and the singlet carbonyl resonances are consistent with a structure (A) in which the ligand L is *trans* to the central dienylium carbon atom. A structure involving *trans*-carbonyl would be expected to give two carbonyl resonances and an unsymmetrical dienylium spectrum.

Reactivity.—As a consequence of the positive charge on complexes (IV), even the weakest σ-donors remain inert to displacement by other σ- and π-donor ligands. Whereas cyanides may be easily displaced by olefins from several neutral complexes, methyl cyanide was not displaced by olefins from (IV) under either thermal or photochemical conditions. It was displaced by triphenylphosphine to give (IV; L = PPh_3) only after heating under reflux in dichloromethane for 2 h.

Reaction of complexes (IV) with potassium iodide resulted in nucleophilic attack at the metal atom, with regeneration of (V) and displacement of the ligand L. Only the triphenylphosphine complex was unaffected by iodide; this is consistent with displacement of iodide in the reaction of dicarbonyl(η-cyclopentadienyl)iodoiron with triphenylphosphine.[10] Reaction of the complexes (IV; L = py, MeCN, NH_3, or CH_2CHCN) with strong nucleophiles such as hydride, methoxide, or cyanide gave only decomposition. These reactions proceed *via* attack on the organic moiety rather than the metal atom to generate corresponding η-cycloheptadiene complexes which appear to be too unstable to characterize. The instability of related chromium complexes has previously been noted.[11] Reaction of the complexes (IV; L = PPh_3 or $AsPh_3$) with hydride and cyanide did give stable products of nucleophilic attack on the organic ligand. The products were, however, exclusively σ,η-allyl complexes resulting from attack at the 2-position of the dienylium system.



(A)

Products involving co-ordination in a 4—6-η,1-σ-manner have been isolated on reduction of the 1—3:5,6-η-cyclooctadienylium derivatives of tricarbonyl-iron and -ruthenium.[12,13] It has previously been shown that reaction of $Fe_2(CO)_9$ with polycyclic olefins containing a cyclo-

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[8] E. O. Fischer and E. Moser, *Z. anorg. Chem.*, 1966, **342**, 156.

[9] E. O. Fischer and E. Moser, *Z. Naturforsch.*, 1965, **B20**, 184.

[10] P. M. Treichel, R. L. Subkin, K. W. Barnett, and D. Reichard, *Inorg. Chem.*, 1966, **5**, 1177.

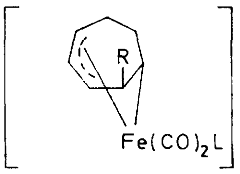
[11] W. P. Anderson, W. G. Blenderman, and K. A. Drews, *J. Organometallic Chem.*, 1972, **42**, 139.

[12] F. A. Cotton, A. J. Deeming P. L. Josty, S. S. Ullah, A. J. P. Domingos, B. F. G. Johnson, and J. Lewis, *J. Amer. Chem. Soc.*, 1971, **93**, 4624.

[13] F. A. Cotton, M. D. LaPrade, B. F. G. Johnson, and J. Lewis, *J. Amer. Chem. Soc.*, 1971, **93**, 4626.

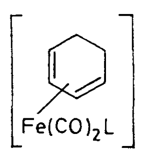
propane ring gives products involving co-ordination in a 3—5-η,1-σ-manner to a tricarbonyliron group. Complexes of bullvalene,[14a] tetracyclo[4.4.0.0^{5,7}.0^{2,10}]deca-3,8-diene,[14b] isobullvalene,[14c] semibullvalene,[15] and barbaralone [16] have been isolated. On the other hand, the reaction of Fe$_2$(CO)$_9$ with cyclopropylstyrene produced only 1,3-diene tricarbonyliron complexes,[17] although a σ,η-allyl intermediate was postulated. The stability of the 3—5-η,1-σ-complexes mentioned above has been attributed [14a] to the fact that the methylenic C$_2$ carbon atom forms the bridgehead of a polycyclic system. Our results, and those of Aumann,[5] show that such a structural arrangement is not necessary.

Thus, complex (IV; L = PPh$_3$) reacted with a 10% aqueous solution of sodium tetrahydroborate at 0 °C to give dicarbonyl(3—5-η,1-σ-cycloheptenyl)triphenylphosphineiron, (VI), in 70% yield. The i.r. spectrum showed two carbonyl vibrations at 1 979 and 1 921 cm^{-1}. The mass spectrum did not show a parent ion, but peaks due to [(C$_7$H$_{10}$)Fe(CO)$_{2-n}$] (n = 0—2) and PPh$_3$ were observed. The assignment of complex (VI) as 3—5-η,1-σ follows from its n.m.r. spectrum, which was assigned with the aid of spin decoupling, and preparation of the monodeuterio-complex by reduction of (IV; L = PPh$_3$) with lithium tetradeuterioborate (see Table 2). For comparison purposes, a sample of dicarbonyl(η-cyclohepta-1,3-diene)triphenylphosphineiron was prepared.[7] The n.m.r. spectrum was completely different (see Table 2) and consistent with the symmetric nature of the molecule. Reduction of the complex (IV; L = AsPh$_3$) with sodium tetrahydroborate gave as product the corresponding complex (VI), whose spectroscopic properties were essentially identical to those of the PPh$_3$ derivative (see Table 2). Cyanide attack on the complexes (IV; L = PPh$_3$ or AsPh$_3$) also generated derivatives of (VI), whose structures readily followed from their n.m.r. spectra (see Table 2).

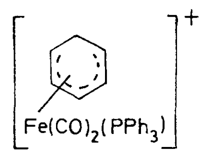


(VI) R=H or CN, L=PPh$_3$ or AsPh$_3$

The observation of nucleophilic attack at only the 2-position of the dienylium system is in marked contrast to the reported reactivity of the tricarbonyl analogue (II).[5] Thus, a reinvestigation of the nucleophilic reactivity of (II), as well as both the six- and eight-membered ring dienylium systems, was undertaken. Reduction of tricarbonyl(1—5-η-cyclohexadienylium)iron, (I), under the conditions previously described gave only tricarbonyl-(η-cyclohexa-1,3-diene)iron, (VII), in agreement with previous results.[18] Dicarbonyl(1—5-η-cyclohexadienylium)-triphenylphosphineiron, (VIII), was also reduced only to (VII; L = PPh$_3$). In contrast, reduction of tricarbonyl(1—5-η-cycloheptadienylium)iron, (II), under the same conditions resulted in attack at both the 1- and 2-positions to generate a mixture of the tricarbonyl(η-cyclohepta-1,3-diene)iron (IV), and tricarbonyl(3—5-η,1-σ-cycloheptenyl)iron, (X), in a ratio of 1 : 2·3 (total yield 84%), in agreement with the results of Aumann.[5] A change in the reaction conditions greatly alters the product ratio. When reduction was carried out in dichloromethane–ethanol (1 : 1) at room temperature, a ratio of 1·2 : 1 was obtained.

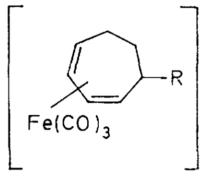


(VII) L=CO or PPh$_3$



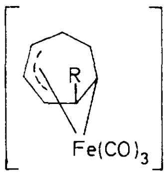
(VIII)

The mixture of complexes (IX) and (X) (R = H) reacted with triphenylmethylium tetrafluoroborate to regenerate only (II). The two complexes may be differentiated chemically, however, by their reaction with triphenylphosphine. When the mixture was heated under reflux with triphenylphosphine in benzene [conditions under which isomerization of (X) to (IX) does not occur], only (X) underwent substitution to give (VI). Labilization of carbonyl has been noted previously in the thermal reaction of tricarbonyl(4—6-η,1-σ-cyclo-octadienyl)iron with triphenylphosphine, where substitution of the carbonyl group *trans* to the iron–carbon σ-bond takes place *via* a CO-dissociative mechanism.[15,19] Reaction of complex (II) with other nucleophiles such as cyanide or cp also produced mixtures of (IX) and (X). The proportions (see Experimental section) were assigned using i.r. and n.m.r. spectra of the mixtures.



R=H, cp, or CN

(IX)



(X)

The nucleophilic reactivity of tricarbonyl-(1—5-η-cyclo-octadienylium)iron, (III), was also re-investigated. Reduction with aqueous tetrahydroborate gave a 10% yield of only tricarbonyl(η-cyclo-octa-1,3-diene)-iron. Reaction with cyanide, however, provided evidence that attack also occurs at the 2-position of the dienyl system.[20] When (III) was treated with potassium cyanide under an atmosphere of carbon monoxide, 4-cyanobicyclo-[3.3.1]non-2-en-9-one, (XI), was isolated (yield 8%). Its formation may be rationalized by carbonylation of unstable tricarbony[3—5-η,1-σ-(2-cyanocyclo-octenyl)]iron, (XII), which was not isolated. When the reaction was carried

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[14] (*a*) R. Aumann, *Angew. Chem. Internat. Edn.*, 1971, **10**, 188; (*b*) *ibid.*, p. 189; (*c*) *ibid.*, p. 190.

[15] R. H. Moriarty, C. L. Yeh, and R. C. Ramey, *J. Amer. Chem. Soc.*, 1971, **93**, 6709.

[16] A. Eisenstadt, *Tetrahedron Letters*, 1972, 2005.

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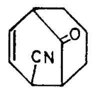
[18] A. J. Birch, P. E. Cross, J. Lewis, D. A. White, and S. B. Wild, *J. Chem. Soc.* (*A*), 1968, 332.

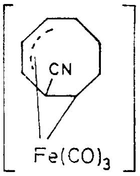
[19] B. F. G. Johnson, J. Lewis, and M. V. Twigg, *J. Organometallic Chem.*, 1973, **52**, C31.

[20] J. Evans, B. F. G. Johnson, and J. Lewis, *J.C.S. Dalton*, 1972, 2668.

out under a dinitrogen atmosphere, only the dimer $(C_8H_{11})_2$ was produced.



(XI)



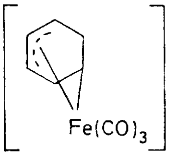
(XII)

DISCUSSION

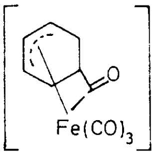
Any reasonable explanation of the trends and differences observed must involve an interrelated combination of kinetic, steric, and electronic factors. The free valencies of the carbon atoms of the dienylium ligands may be calculated from the molecular-orbital description of the free ions.[21] These values, which are directly proportional to the susceptibility of the carbon atom to nucleophilic attack, are in the order $F_1 > F_3 > F_2$. On bonding to the metal atom, however, the strict π-symmetry of the dienylium molecular orbitals is destroyed and σ–π-mixing occurs, corresponding to an effective change from sp^2 to sp^3 hybridization of the dienylium carbons, either in the ground state or in an activated transition state. In particular, a decrease in the free valency of C_1 and C_3 relative to C_2 would be expected, due to directional properties of the metal *d* orbitals in the pseudo-octahedral situation shown in (A).

The observance of no products of attack at the 2-position of the dienylium ligand in the cases of the six-membered ring complexes (I) and (VIII) may be due to instability of the resulting σ,η-allyl products. Tricarbonyl(3—5-η,1-σ-cyclohexenyl)iron, (XIII) has been only postulated as an intermediate in decarbonylation and isomerization of the carbonyl-bridged complex (XIV) to (VII; L = CO).[5] On the other hand, the seven-membered-ring complex (X; R = H) is kinetically stable, although thermodynamically unstable relative to the 1,3-diene (IX).[5] Thus, in nucleophilic attack on the seven-membered-ring complex (II), products of attack at both the 1- and 2-positions are observed. Very recently, it has been shown that tetrahydroborate reduction of the (1—5-η-bicyclo-[5.1.0]octadienylium)tricarbonyliron cation also leads to a mixture of 1,3-diene and σ,η-allyl products.[22] In the case of the eight-membered-ring complex (III), the evidence presented shows that attack at the 2-position probably occurs, although the product appears to be too unstable to be isolated. Although in none of the complexes (I)—(III) is there any evidence of attack at the 3-position, it is to be noted that, to date, there have been no reports of monocyclic 1,4-diene complexes of tricarbonyliron. Reaction of monocyclic 1,4-dienes with iron carbonyls invariably leads to isomerization to the 1,3-derivative.

Substitution of a carbonyl group by phosphine in complex (II) leads first to a decrease in the rate of nucleophilic attack due to greater σ-donor and poorer π-acceptor properties of phosphine relative to carbonyl.[4] Secondly, in consideration of the stereochemistry shown in (A), the *trans*-effect of this phosphine ligand is such that deactivation of the 3-position (and, through the symmetry of the molecular orbitals, the 1-position also) with respect to nucleophilic attack occurs, and only the product of attack at the 2-position is isolated. Very recently, another example of this type of behaviour was noted.[23] Reduction of carbonyl(1—5-η-cycloheptadienylium)(η-cyclohexa-1,3-diene)iron, (XV),

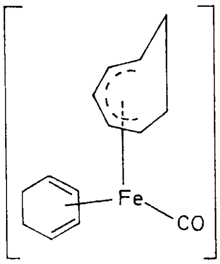


(XIII)

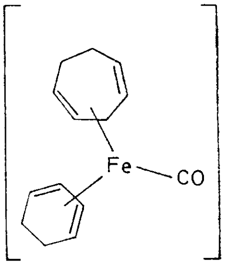


(XIV)

generates exclusively carbonyl(η-cyclohepta-1,4-diene)-(η-cyclohexa-1,3-diene)iron, (XVI), the first example of a monocyclic 1,4-diene complex of iron. The ^{13}C n.m.r. spectrum of complex (XV) shows the unique carbonyl group to be *trans* to the 3-position. Thus, in this complex, in contrast to (A), the ligand of least σ-donor strength is *trans* to the 3-position.



(XV)



(XVI)

Finally, the effect of a change in the metal atom may be noted. Tetrahydroborate reduction of complex (II; M = Ru) gives a mixture of 75% (X) and 25% (IX),[24] which is roughly similar to the results obtained for the iron system. In contrast, the complex (III; M = Os) is reduced to give only tricarbonyl(3—5-η,1-σ-cyclooctenyl)osmium.[12] It has been observed that both ruthenium and osmium carbonyls show a greater tendency than iron to form σ,η-allyl derivatives in their reactions with dienes.

EXPERIMENTAL

Reactions were carried out under a dry dinitrogen atmosphere. I.r. spectra were recorded on a Perkin-Elmer

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[23] B. F. G. Johnson, J. Lewis, T. W. Matheson, I. G. Ryder, and M. V. Twigg, *J.C.S. Chem. Comm.*, 1974, 269.

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257 spectrometer; n.m.r. spectra were recorded on Perkin-Elmer R12B and Varian Associates HA100 spectrometers; mass spectra were recorded on an A.E.I. MS12 spectrometer. Elemental analyses were carried out by the microanalytical department of this laboratory.

Preparations.—(a) *Dicarbonyl*(1—5-η-*cycloheptadienylium*)*triphenylphosphineiron hexafluorophosphate*, (IV). Dicarbonyl(1—5-η-cycloheptadienylium)iodoiron, (V) [6] (3·0 g) was dissolved in dichloromethane (25 cm^3) and a solution of silver(I) hexafluorophosphate in acetone (15 cm^3) was added dropwise. The resulting solution was stirred for 15 min and silver(I) iodide removed by filtration. To the remaining red solution was added triphenylphosphine (2·6 g). After stirring for 30 min, the solvent was removed. The residue was dissolved in dichloromethane, filtered, and poured into stirred diethyl ether (150 cm^3). The resulting light yellow precipitate was filtered off and washed with diethyl ether to give *complex* (IV) (3·0 g, 69%). The complexes $[L(C_7H_9)Fe(CO)_2]PF_6$ (L = $AsPh_3$, $SbPh_3$, py, and CH_2CHCN) were prepared in the same manner. Complex (IV; L = $SbPh_3$) was obtained with 0·5 mol diethyl ether of crystallization [Found: C, 53·9; H, 4·20. (IV; L = PPh_3) requires C, 53·2; H, 3·95. Found: C, 49·3; H, 3·80. (IV; L = $AsPh_3$) requires C, 49·4; H, 3·65. Found: C, 47·9; H, 3·80. (IV; L = $SbPh_3$) requires C, 47·2; H, 3·90. Found: C, 39·1; H, 3·40; N, 3·25. (IV; L = py) requires C, 39·2; H, 3·25; N, 3·25. Found: C, 36·1; H, 3·05; N, 3·50. (IV; L = CH_2CHCN) requires C, 35·7; H, 3·00; N, 3·45%].

(b) *Dicarbonyl*(1—5-η-*cycloheptadienylium*)(*methyl cyano*)*iron hexafluorophosphate*, (IV). Complex (V) (3·0 g) was dissolved in methyl cyanide (50 cm^3), and a solution of silver(I) hexafluorophosphate (2·3 g) in methyl cyanide (15 cm^3) was added. The solution was stirred for 2 h and silver(I) iodide was then filtered off. The resulting yellow solution was reduced in volume to *ca.* 10 cm^3 and added to stirred diethyl ether (150 cm^3). The bright yellow precipitate was filtered off and washed with diethyl ether to give the *complex* (IV) (2·8 g, 80%). Liquid ammonia was used as solvent medium to prepare complex (IV; L = NH_3) [Found: C, 34·5; H, 3·25; N, 3·24. (IV; L = MeCN) requires C, 33·8; H, 3·05; N, 3·60. Found: C, 29·4; H, 3·70; N, 3·55. (IV; L = NH_3) requires C, 29·4; H, 3·25; N, 3·8%].

(c) *Dicarbonyl*(3—5-η,1-σ-*cycloheptenyl*)*triphenylphosphineiron*, (VI). Complex (VI; L = PPh_3) (2·0 g) was added in small amounts to a 10% aqueous solution of sodium tetrahydroborate (15 cm^3) covered with diethyl ether (30 cm^3) at 0 °C. After stirring for 30 min, water (50 cm^3) was added and the two layers separated. The water layer was extracted with diethyl ether (50 cm^3) and the combined extracts were washed with water (2 × 50 cm^3). After drying over $MgSO_4$, the diethyl ether was removed and the residue chromatographed on silica using benzene, which eluted a single yellow band. Evaporation of solvent, followed by crystallization from pentane, gave the complex as light yellow crystals (1·2 g, 78%). The triphenylarsine analogue was prepared similarly [Found: C, 69·1; H, 5·25. (VI; L = PPh_3) requires C, 69·3; H, 5·35. Found: C, 63·6; H, 4·65. (VI; L = $AsPh_3$) requires C, 63·4; H, 4·90%].

Dicarbonyl(η-cyclohepta-1,3-diene)triphenylphosphineiron was prepared by the method of Pauson.[7]

(d) *Dicarbonyl*[3—5-η,1-σ-(2-*cyanocycloheptenyl*)]*triphenylarsineiron*, (VI). Complex (IV; L = $AsPh_3$) (2·0 g) was added in small amounts to a solution of potassium cyanide (1·0 g) in 1 : 1 acetone–water (25 cm^3) at room temperature. After stirring for 15 min water (100 cm^3) was added and the whole extracted with diethyl ether (3 × 75 cm^3). The extracts were dried with $MgSO_4$ and the solvent removed. The residue was chromatographed on alumina using 5% ethyl acetate–benzene. Removal of solvent from the yellow band collected, followed by crystallization from pentane–benzene, gave the *complex* as light yellow crystals (1·4 g, 85%). The phosphine analogue was prepared similarly [Found: C, 68·3; H, 5·10; N, 2·50. (VI; L = PPh_3) requires C, 68·0; H, 4·85; N, 2·85. Found: C, 63·1; H, 4·70; N, 2·55. (VI; L = $AsPh_3$) requires C, 62·6; H, 4·45; N, 2·60%].

Reduction of Tricarbonyl(1—5-η-*cyclohexadienylium*)*iron*, (I), *and Dicarbonyl*(1—5-η-*cyclohexadienylium*)*triphenylphosphine iron*, (VIII), *with Sodium Tetrahydroborate*.—Reduction of the tetrafluoroborate salt (I) under the conditions described in (c) gave tricarbonyl(η-cyclohexa-1,3-diene)iron (VII) only, identified by its i.r., n.m.r., and mass spectra (see Table 2). Reduction of the tetrafluoroborate salt (VIII) under the conditions described in (c) gave only dicarbonyl(η-cyclohexa-1,3-diene)triphenylphosphineiron (VII), identified spectroscopically (see Table 2).

Nucleophilic Reactivity of Tricarbonyl(1—5-η-*cycloheptadienylium*)*iron* (II).—(i) *With sodium tetrahydroborate*. The reduction was carried out as in (c). Sublimation of the resulting oil at 50 °C (0·01 mmHg) gave a mixture consisting of 30% tricarbonyl(η-cyclohepta-1,3-diene)iron, (IX), and 70% tricarbonyl(3—5-η,1-σ-cycloheptenyl)iron, (X) (total yield 84%). The reduction was also carried out by addition of sodium tetrahydroborate (0·5 g) in small amounts to a stirred suspension of complex (II) (2·0 g) in 1 : 1 dichloromethane–ethanol (30 cm^3). After stirring for 15 min, water (75 cm^3) was added and the solution extracted with diethyl ether (3 × 75 cm^3). The extracts were dried over $MgSO_4$ and the solvent removed. The residue was chromatographed on alumina using light petroleum (b.p. 30—40 °C). Removal of solvent from the yellow band collected and sublimation at 50 °C (0·01 mmHg) gave a mixture consisting of 55% (IX) and 45% (X) (Found: C, 51·5; H, 4·30. Mixture requires C, 51·3; H, 4·30%).

(ii) *With cyanide*. The reaction was carried out as in (d). The resulting oil was distilled on to a cold finger [60 °C (0·01 mmHg)] to give a mixture of 22% tricarbonyl[η-(5-cyanocyclohepta-1,3-diene)]iron, (IX), and 78% tricarbonyl[3—5-η,1-σ-(2-cyanocycloheptenyl)]iron, (X), (total yield 53%) (Found: C, 51·2; H, 3·60; N, 5·60. Mixture requires C, 50·9; H, 3·50; N, 5·40%).

(iii) *With cyclopentadienide*. Complex (II) (2·0 g) and cyclopentadienylthallium (1·7 g) were stirred for 12 h in dichloromethane (20 cm^3) with exclusion of light. The resulting orange solution was filtered and the solvent removed. The residue was chromatographed on alumina using 5% ethyl acetate–light petroleum (b.p. 30—40 °C). Evaporation of the solvent from the orange band collected, followed by sublimation at 70 °C (0·01 mmHg) (some decomposition), gave a mixture of 85% tricarbonyl[η-(5-cyclopentadienylcyclohepta-1,3-diene)]iron, (IX), and 15% tricarbonyl[3—5-η,1-σ-(2-cyclopentadienylcycloheptenyl)]iron, (X) (total yield 55%) (Found: C, 61·4; H, 4·20. Mixture requires C, 60·8; H, 4·05%).

Nucleophilic Reactivity of Tricarbonyl(1—5-η-*cyclo-octadienylium*)*iron*, (III).—(i) *With sodium tetrahydroborate*. Reduction of complex (III) with sodium tetrahydroborate was carried out as in (*c*). The sole product isolated was tricarbonyl(η-cyclo-octa-1,3-diene)iron, identified spectroscopically (see Table 2).

(ii) *With cyanide.* The tetrafluoroborate salt of (III) (1·51 g) was added to a solution of sodium cyanide in aqueous acetone (20 cm^3) under a carbon monoxide atmosphere and the mixture was stirred for 40 min. The mixture was then poured into water (50 cm^3) and extracted with diethyl ether (5 × 20 cm^3). The combined extracts were washed with water and dried over $MgSO_4$. The solvent was removed to give a yellow oil which was chromatographed on a thick-layer plate with benzene. Two products were obtained: a fast-moving band yielded an oil [$(P - 214)^+$, $C_{16}H_{22}$; $\nu_{max.}$ (CS_2) at 1 640 cm^{-1} (C=C)]; a slow-moving band yielded 4-cyanobicyclo[3.3.1]non-2-en-9-one, (XI), (8%) [$(P - 163)^+$, $C_{10}H_{13}NO$; $\nu_{max.}$ (diethyl ether) at 2 215 (CN), 1 735 (CO), and 1 642 cm^{-1} (C=C); τ ($CDCl_3$) 3·12 (dd) and 4·09(t), two vinyl protons]. When the reaction was carried out under a dinitrogen atmosphere only the dimer $C_{16}H_{22}$ was obtained.

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