Reactivity of Co-ordinated Ligands. Part XX.[1] Preparation and Reactions of Cyclo-octadiene Complexes of Iron, Ruthenium, and Osmium

By **Anthony J. Deeming** and **Shafi S. Ullah**, Department of Chemistry, University College, 20 Gordon Street, London WC1H 0AJ
António J. P. Domingos, Brian F. G. Johnson, and **Jack Lewis,*** University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW

The complexes tricarbonyl(η-cyclo-octa-1,5-diene)ruthenium, (I), and tricarbonyl(η-cyclo-octa-1,3-diene)-osmium, (II), have been prepared and their reactivities examined and compared to those of the corresponding iron complexes. On reaction with Ph_3CBF_4 hydride-ion abstraction occurs to give cyclo-octadienylium complexes $[(C_8H_{11})M(CO)_3]^+$. These react with anionic nucleophiles to give neutral complexes, some of which contain η-allyl groups and metal–carbon σ-bonds. Catalytic isomerisations of cyclo-octa-1,5-diene have been studied as well as those of the diene complexes, a novel ring contraction being observed in one case. Substitution of a carbonyl ligand by PPh_3 has been observed for the η-allyl complexes of iron and ruthenium, and a carbonylation reaction to give bicyclo[4.2.1]non-2-en-9-one is also described.

In contrast to the very large number of (cyclic diene) complexes of tricarbonyliron described in the literature, corresponding ruthenium and osmium complexes have received comparatively little attention.[2] This may reflect the now well documented tendency of both $[Ru_3(CO)_{12}]$ and $[Os_3(CO)_{12}]$ to form polymeric organometallic complexes with dienes rather than monomeric species.

Prior to this work the complexes tricarbonyl(η-cyclo-octa-1,5-diene)iron, (I), and tricarbonyl(η-cyclo-octa-1,3-diene)iron, (II), were known [3-5] but their reactivity unexplored. Previous workers [6] also reported that the reaction of cyclo-octa-1,3-diene with $[Ru_3(CO)_{12}]$ yields the complex $[(C_8H_{12})Ru_3(CO)_{10}]$. Here we describe the syntheses of the complexes tricarbonyl(η-cyclo-octa-1,5-diene)ruthenium, (I), tricarbonyl(4—6-η,1-σ-cyclo-octenediyl)ruthenium, (III), and tricarbonyl(η-cyclo-octa-1,3-diene)osmium, (II). We further describe the formation of cyclo-octadienylium complexes from (I) and (II) and Ph_3CBF_4, and their reactions with nucleophilic reagents. Brief reports of some aspects of this work have been given previously.[7,8]

RESULTS AND DISCUSSION

Preparation.— *Tricarbonyl*(η-*cyclo-octa*-1,5-*diene*)*iron*, (I), *and tricarbonyl*(η-*cyclo-octa*-1,3-*diene*)*iron*, (II). There are a number of reports [3-5] of complexes derived from cyclo-octa-1,5-diene and cyclo-octa-1,3-diene with tricarbonyliron, however these reports are inconsistent. Consider, for example, complex (I). This complex has been variously described as a liquid [4,5] and a crystalline solid (m.p. 90—90·5 °C).[3] Following the procedure of Koerner von Gustorf *et al.*,[3] we synthesised complex (I) and the corresponding cyclo-octa-1,3-diene complex (II) by photochemical treatment of $[Fe(CO)_5]$ and the appropriate diene. From cyclo-octa-1,3-diene only complex (II) was produced, but from the reaction with cyclo-octa-1,5-diene several complexes were isolated. Thus after a few hours the product was predominantly tetracarbonyl(η-cyclo-octa-1,5-diene)iron; this was successively converted to complex (I) over more extended irradiation times. Under the conditions of our experiment, the highest yields of complex (I) were obtained after irradiation for 44 h, while irradiation for 80 h gave complete conversion to complex (II). The intermediate tetracarbonyl(η-cyclo-octa-1,5-diene)iron complex and (I) and (II) were separated from the reaction mixture by a combination of chromatography and fractional crystallisation.

In contrast to some previous reports, we found that both complexes (I) and (II) are moderately stable thermally and also to oxidation by air. Previous reports that these complexes had considerable instability were probably due to the material being impure. For example, needle-shaped crystals of complex (II) grown on a glass surface remained unchanged in air at room temperature for weeks, whereas the same complex associated with small amounts of the tetracarbonyl complex or iron oxide decomposes under a dinitrogen atmosphere at 0 °C. Both complexes (I) and (II) when pure are indefinitely stable under dinitrogen at 0 °C.

Tricarbonyl(η-*cyclo-octa*-1,5-*diene*)*ruthenium*, (I), *and tricarbonyl*(4—6-η,1-σ-*cyclo-octenediyl*)*ruthenium*, (III). Dodecacarbonyl-*triangulo*-triruthenium reacted with cyclo-octa-1,5-diene heated under reflux in benzene (*ca.* 8 h) to give complex (I), and, although the excess of diene was considerably isomerised to its 1,4- and 1,3-isomers (see later), no other organoruthenium complexes were observed. Over more extended reaction times complex

---

[1] Part XIX, B. F. G. Johnson, J. Lewis, and D. J. Yarrow, *J.C.S. Dalton*, 1974, 1054.

[2] See, for example, B. L. Shaw, ' Organometallic Compounds, Comprehensive Inorganic Chemistry,' Pergamon Press, Oxford, 1973.

[3] E. Koerner von Gustorf and J. C. Hogan, *Tetrahedron Letters*, 1968, **28**, 3191.

[4] R. B. King, T. A. Manuel, and F. G. A. Stone, *J. Inorg. Nuclear Chem.*, 1961, **16**, 233.

[5] A. Nakamura and N. Hagihara, *Mem. Inst. Sci. Ind. Res.*, Osaka Univ., 1961, **17**, 187.

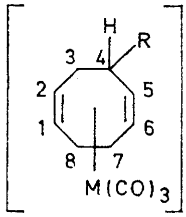
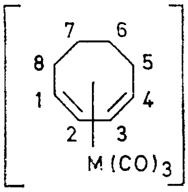
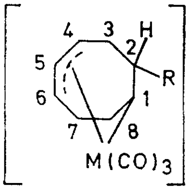
[6] J. P. Candlin, K. K. Joshi, and D. T. Thompson, *Chem. and Ind.*, 1966, 1960.

[7] 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.

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

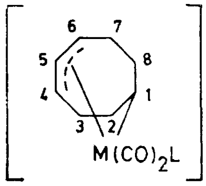
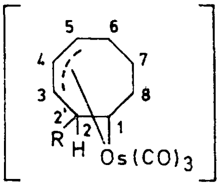
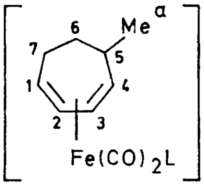
TABLE 1

N.m.r. data

Complex (solvent)	Assignment	Chemical shift, τ	Relative intensity	Multiplicity	*J*/Hz
					
(I) M = Fe, R = H	1, 2, 5, 6	6·20	4	m	
(C_6H_6)	3, 4, 7, 8	8·0—8·8	8	m	
(I) M = Ru, R = H	1, 2, 5, 6	6·28	4	m	
(C_6H_6)	3, 4, 7, 8	7·6—8·2	8	m	
(XVIII) M = Fe, R = $\mathrm{CH_2^{a}{\cdot}CH^{b}{:}CH_2^{c}}$	b	4·41	1	m	
(C_6H_6)	c	5·07	2	m	
	1, 2, 5, 6	6·69	4	m	
	3, 4, 7, 8, a	7·2—9·1	9	m	
(XVIII) M = Fe, R = $\mathrm{CH^{a}(COMe^{b})_2}$	a	5·72	1	m	
($CDCl_3$)	*	6·16	3	m	
	b	7·77	3	s	
	b	7·81	3	s	
	†	6·5—8·8		m	
					
(II) M = Fe	2, 3	5·23	2	m	
(C_6H_6)	1, 4	7·01	2	m	
	5—8	8·18	4	m	
		8·88	4	m	
(II) M = Os	2, 3	4·45	2	m	
($CDCl_3$)	1, 4	6·72	2	m	
	5—8	7·92	4	m	
		8·65	4	m	
					
(III) M = Fe, R = H	4, 6	4·80	2	m	
($CDCl_3$)	5	5·65	1	t	$J(H_{4,6}–H_5)$ 8·0
	1—3, 7, 8	7·3—8·8	9	m	
(III) M = Ru, R = H	4, 6	4·78	2	m	
(C_6H_6)	5	5·53	1	t	$J(H_{4,6}–H_5)$ 8
	1—3, 7, 8	7·6—8·2	9	m	
(XIV) M = Fe, R = CN	4	4·63	1	m	
($CDCl_3$)	6	5·01	1	m	
	5	5·55	1	t	$J(H_{4,6}–H_5)$ 8·2
	2	6·60	1	m	
	1, 3, 7, 8	7·3—8·4	8	m	
(XIV) M = Fe, R = Me^a	4, 6	5·30	2	m	
(C_6H_6)	5	6·08	1	t	$J(H_{4,6}–H_5)$ 8·1
	2	7·21	1	m	
	1, 3, 7, 8	7·7—9·1	8	m	
	a	9·35	3	d	$J(H_2–H_a)$ 6·5
(XIV) M = Fe, R = $\mathrm{CH_2^{a}{\cdot}CH^{b}{:}CH_2^{c}}$	b	4·45	1	m	
(C_6H_6)	c	5·10	4	m	
	4, 6	5·35		m	
	5	6·06	1	t	$J(H_{4,6}–H_5)$ 8·1
	1, 2, 3, 7, 8, a	7·22—8·95	10	m	

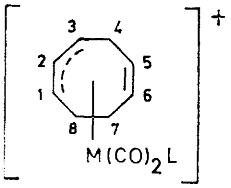
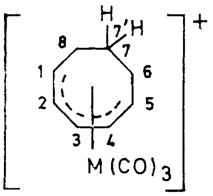
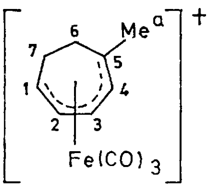
* Three olefin protons. † Remaining protons; the Me^b were non-equivalent.

TABLE 1 (*Continued*)

Complex (solvent)	Assignment	Chemical shift, τ	Relative intensity	Multiplicity	*J*/Hz
					
(XII) M = Fe, L = PPh_3	C_6H_5	2·66	15	m	
($CDCl_3$)	4, 6	5·63	2	m	$J(H_{4,6}–H_5)$ 8·0
	5	6·24	1	2t	$J(H_5–P)$ 19·0
	1—3, 7, 8	7·1—8·6	9	m	
(XII) M = Ru, L = PPh_3	C_6H_5	2·82	15	m	
($CDCl_3$)	4, 6	5·69	2	m	
	5	6·33	1	2t	$J(H_{4,6}–H_5)$ 8·0
	1	7·38	1	m	$J(H_5–P)$ 17·0
	2, 3, 7, 8	7·6—8·5	8	m	
(XIII) M = Fe, L = $Ph_2PCH_2CH_2PPh_2$	C_6H_5	2·65	20	m	
	4, 6	6·04 6·28	1 1	m m	
	5	6·56	1	m	
	Other protons	7·2—8·8	13	m	
					
(VI) R = H[1]	3—5	5·25 5·54 5·81	1 1 1	m m m	
($CDCl_3$)	2′	6·67	1	d	$J(H_2–H_{2'})$ 14·9
	2	7·32	1	8 line m	$J(H_2–H_3)$ 7·8
	1, 6—8	7·7—9·3	7	m	$J(H_1–H_2)$ 11·5
(VII) R = CN	3—5	5·48	3	m	
($CDCl_3$)	2	6·28	1	2d	$J(H_2–H_3)$ 7·0 $J(H_1–H_2)$ 10·7
	1, 6—8	7·7—9·3	7	m	
					
(IXa) L = CO	2, 3	5·35	2	m	
($CDCl_3$)	1, 4	7·36	2	m	
	5—7	8·2—9·2	8	m	
	a	9·52		d	$J(H_5–H_a)$ 6·2
(IXa) L = PPh_3	2, 3	5·45	2	m	$J(P–H_{2,3})$ 3·5
($CDCl_3$)	1, 4	7·61	2	m	
	5—7	8·0—9·1	8	m	
	a	9·43		d	$J(H_5–H_a)$ 6·1

For both complexes (IXa) the Me doublets integrated for 2·6 protons relative to the olefin signals and the signals between τ 8·0 and 9·2 (due to ring protons) for somewhat more than 5·0 protons. We suggest that this is due to a small amount of another isomer present.

TABLE I (*Continued*)

Complex (solvent)	Assignment	Chemical shift, τ	Relative intensity	Multiplicity	*J*/Hz
					
(V) M = Fe, L = CO (SO_2)	1, 3, 5, 6	4·90	4	m	
	2, 4, 7, 8	6·40	2	m	
		6·8—8·3	5	m	
(V) M = Ru, L = CO (SO_2)	6	4·26	1	m	$J(H_6-H_8)$ 4
	1	4·84	1	m	
	2	4·97	1	m	$J(H_{1,3}-H_2)$ 8
	3	5·32	1	m	
	5	5·96	1	m	$J(H_{4,6}-H_5)$ 4
	4	6·6	2	m	
	7, 8	7·2—7·9	4	m	
(V) M = Os, L = CO (SO_2)		4·44	1	m	
		5·04	2	m	
		5·49	1	m	
		5·6—9·0		m	
Signals between τ 4 and 6 were very similar in pattern to those of complex (V; M = Ru) and the structure has been assigned accordingly. No assignments of n.m.r. signals were attempted.					
(XV) M = Fe, L = PPh_3 ($CDCl_3$)	C_6H_5	2·5	15	m	
	Ring protons	4·0—5·0	3	m	
		6·0—6·7	2	m	
		7·1—8·7	6	m	
Spectrum poorly resolved; no assignments were made.					
					
(IV) M = Fe (SO_2)	3	2·75	1	m	
	2, 4	4·30	2	m	
	1, 5	5·57	2	m	
	6—8	7·4—9·5	6	m	
The spectrum was rather broad but agreed with that reported previously.[11]					
(IV) M = Os (SO_2)	3	2·65	1	t	$J(H_2-H_3) = J(H_3-H_4)$ 7·0
	2, 4	4·12	2	m	$J(H_1-H_2) = J(H_4-H_5)$ 10·2
	6, 7, 8	7·27	2	m	
		7·8—8·6	3	m	
	7′	9·21	1	m	
					
(X) (SO_2)	3	3·02	1	t	$J(H_{2,4}-H_3)$ 6·2
	2, 4	4·16	2	m	
	1	5·54	1	m	
	a	7·98	7	s	
	5—7	6·3—8·2		m	

(I) underwent slow isomerisation to (III). The ^1H n.m.r. spectrum of this complex (Table 1, which also contains data for the other complexes described) showed it to contain a ruthenium–carbon σ-bond as well as an η-allyl–ruthenium bond. The two outer protons of the η-allyl group gave a single resonance showing the symmetrical nature of this group.

We further established the nature of the bonding by an *X*-ray structural study of a cyano-derivative of complex (III).[8] This may be regarded as an octahedral complex of ruthenium(II) (d^6) with two CO groups *trans* to a bidentate η-allyl group with the third CO unique and *trans* to the ruthenium–carbon σ-bond. A bonding pattern of this type was first observed for the complex tricarbonyl(4—6-η,6-σ-cyclo-octatrienediyl)osmium which is a product of the reaction of $[Os_3(CO)_{12}]$ and cyclo-octatetraene.[9] More recently several examples of a cyclic ligand bonding to iron or ruthenium through an η-allyl group and a metal–carbon σ-bond have been noted,[10,11] and such bonding can now be regarded as a characteristically alternative way in which a cyclic ligand can donate four electrons to a metal atom other than as a diene.

We made a large number of attempts to prepare the complex (II; M = Ru) without success. From the reaction of cyclo-octa-1,3-diene with $[Ru_3(CO)_{12}]$ under a variety of conditions we were only able to isolate Ru_4 and Ru_3 derivatives which have been reported previously.[12] No monomeric complexes were observed. Attempts to cause cyclo-octa-1,3-diene to react with monomeric starting materials such as tricarbonyl(η-cyclohexadiene)ruthenium were unsuccessful.

The osmium complexes. In attempts to prepare monomeric cyclo-octadiene osmium complexes we reacted $[Os_3(CO)_{12}]$ with cyclo-octa-1,3-diene heated under reflux in benzene. No monomeric complexes, however, were formed and from this reaction we could only isolate in very low yield a complex of formula $[(C_8H_{12})Os_3(CO)_9]$ as determined by its mass spectrum. Like the ruthenium complexes this might also be correctly formulated as $[H_2(C_8H_{10})Os_3(CO)_9]$. Monomeric complexes of formula $[(C_8H_{12})Os(CO)_3]$ were, however, obtained by irradiating a mixture of $[Os_3(CO)_{12}]$ and either cyclo-octa-1,3- or 1,5-diene in benzene. In the case of the former the product was tricarbonyl(η-cyclo-octa-1,3-diene)osmium, (II), but an inseparable mixture of isomers was obtained from cyclo-octa-1,5-diene. This mixture probably contains η-allyl complexes analogous to complex (III) together with normal diene complexes. N.m.r. and i.r. data for the diene complexes so far described are given in Tables 1 and 2 respectively. All the data are consistent with the complexes as formulated.

Preparation and Study of Cationic Complexes $[(C_8H_{11})M(CO)_3]^+$.—The reactions now described are depicted in Scheme 1. All the complexes $[(C_8H_{12})M(CO)_3]$, (I) and (II), underwent hydride-ion abstraction reactions with Ph_3CBF_4 to yield cationic complexes $[(C_8H_{11})M(CO)_3]BF_4$. Thus the cyclo-octa-1,3-diene complexes (II; M = Fe or Os) reacted to give the tricarbonyl(1—5-η-cyclo-octadienylium) complexes, (IV), and the cyclo-octa-1,5-diene complexes (I; M = Fe or Ru) reacted to give the isomeric tricarbonyl(1—3:5,6-η-cyclo-octadienylium) complexes, (V). In each case hydride-ion abstraction has taken place at the carbon atom adjacent to a co-ordinated double bond without further rearrangement of the co-ordinated ligands. Complex (IV; M = Fe) has been reported previously[13] as the product of the reaction of tricarbonyl(η-cyclo-octatriene)iron complexes and H^-. ^1H N.m.r. and i.r. spectroscopic data (Tables 1 and 2) are fully consistent with these formulations.

TABLE 2

I.r. wavenumbers (cm^{-1})

Complex	Solvent	ν(CO)
(I; M = Fe)	C_6H_{12}	2 027s, 1 961s, br, 1 951s, br
(II; M = Fe)	C_6H_{12}	2 043s, 1 974s, 1971s
(I; M = Ru)	C_6H_{12}	2 043s, 1 982 (sh), 1 966s, br
(V; M = Fe)	$MeNO_2$	2 102s, 2 047s, br
(V; M = Ru)	CH_2Cl_2	2 122s, 2 077 (sh), 2 060s, br
(III; M = Fe)	C_6H_{12}	2 046s, 1 981s
(III; M = Ru)	C_6H_{12}	2 067s, 1 999s
(XIV; R = CN)	C_6H_{12}	2 055s, 1 991s
[XIV; R = $CH(COMe)_2$]	C_6H_{12}	2 048s, 1 981s
[XVIII; R = $CH(OMe)_2$]	C_6H_{12}	2 030s, 1 972s, 1 952s
[XIV; R = $CH(CO_2Et)_2$]	C_6H_{12}	2 051s, 1 982s
[XVIII; R = $CH(CO_2Et)_2$]	C_6H_{12}	2 029s, 1 968s, 1 952s
[XIV; R = $CPh(CO_2Et)_2$]	C_6H_{12}	2 051s, 1 980s
[XVIII; R = $CPh(CO_2Et)_2$]	C_6H_{12}	2 027s, 1 970s, 1 951s
(XIV; R = Me)	C_6H_{12}	2 046s, 1 980s, 1 972 (sh)
(XIV; R = allyl)	C_6H_{12}	2 043s, 1 977s
(XVIII; R = allyl)	C_6H_{12}	2 036s, 1 962s, 1 948s
(XII; M = Fe)	C_6H_{12}	1 979s, 1 926s
(II; M = Os)	C_6H_{12}	2 043s, 1 980s
(IV; M = Fe)	CH_2Cl_2	2 105s, 2 057s, 2 047s
(IV; M = Os)	CH_2Cl_2	2 121s, 2 062s, 2 053s
(VIII)	C_6H_{12}	2 046s, 1 982s, 1 975s
(VI)	C_6H_{12}	2 063s, 1 984s
(V)	CH_2Cl_2	2 119s, 2 059s, 2 047s
(IXa; L = CO)	C_6H_{12}	2 044s, 1 977s
(XII; M = Ru)	C_6H_{12}	2 002s, 1 947s
(IXa; L = PPh_3)	C_6H_{12}	1 963s, 1 924s
(XIII)	C_6H_{12}	1 975s, 1 922s
(VII)	C_6H_{12}	2 070s, 1 991s
(XV)	CH_2Cl_2	2 029s, 1 983s
(XVI)	C_6H_{12}	1 948s, 1 889s
(X)	CH_2Cl_2	2 105s, 2 054s

All the cationic complexes underwent reactions with nucleophiles. On reduction with sodium tetrahydroborate complex (V; M = Fe) yielded two isomeric products: the parent complex (I) (10%) and (III) (90%). In contrast the corresponding reaction of complex (V; M = Ru) gave (III) as the sole organometallic product. The formation of derivatives (III) in these reactions contrasts with the exclusive formation of η-cyclo-octa-1,5-diene derivatives in reactions of (1—3:5,6-η-cyclo-octadienylium)-(η-cyclopentadienyl)cobalt and

---

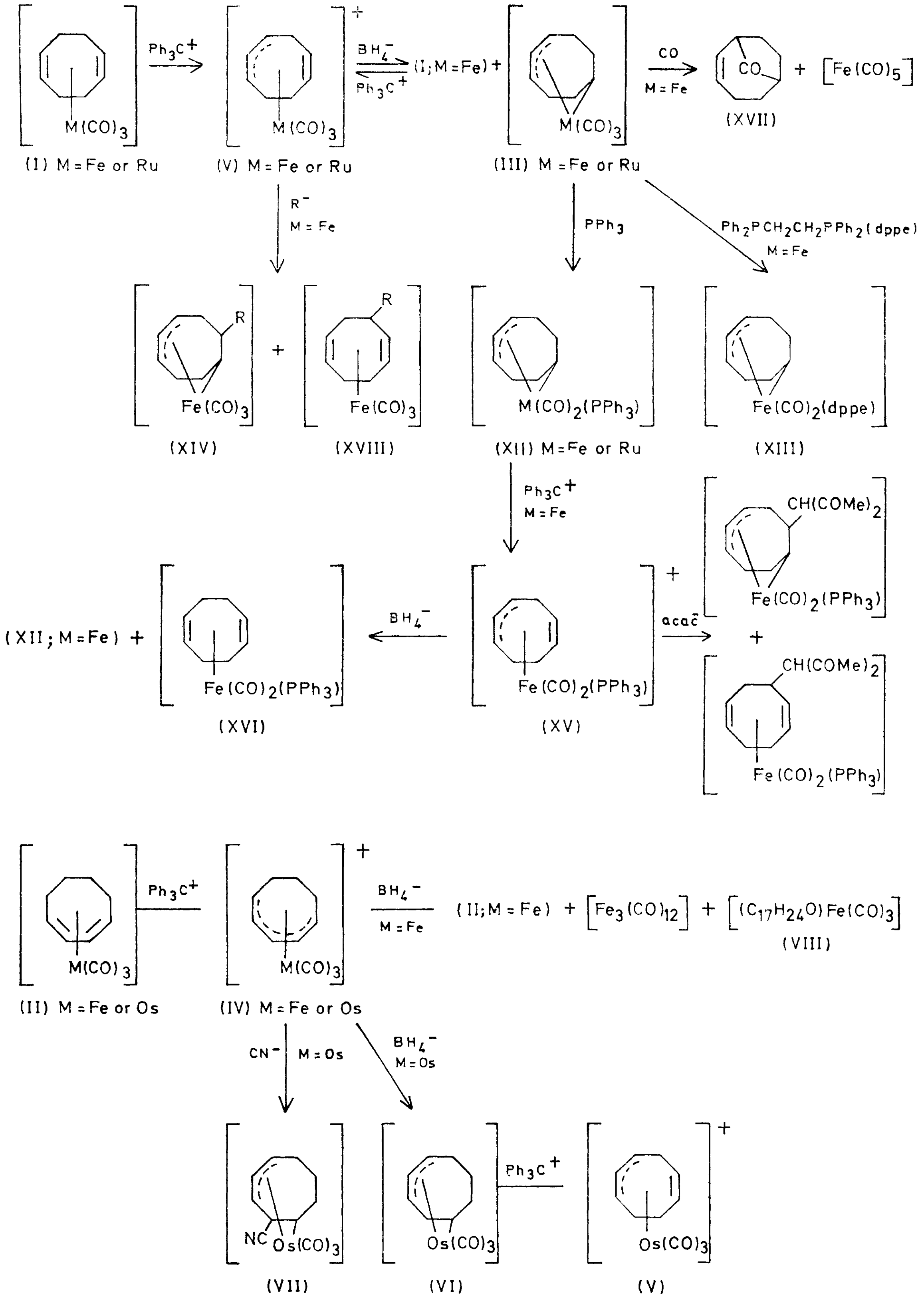
[9] M. I. Bruce, M. Cooke, M. Green, and D. J. Westlake, *J. Chem. Soc.* (*A*), 1969, 987.

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

[11] R. Aumann, *Angew. Chem. Internat. Edn.*, 1971, **10**, 188—190; 1973, **12**, 574.

[12] A. J. Canty, A. J. P. Domingos, B. F. G. Johnson, and J. Lewis, *J.C.S. Dalton*, 1973, 2056.

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



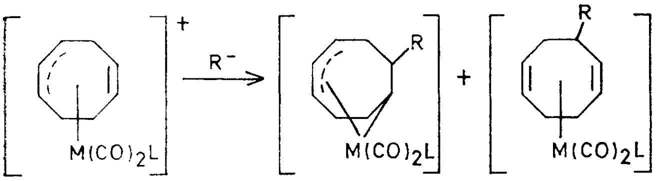
SCHEME 1

BF_4^- Is the counter ion for all the cations shown

-[η-(triphenylmethyl)cyclopentadienyl]rhodium.[14] Formation of a mixture of products is a feature of reactions of complex (V; M = Fe) with the nucleophilic reagents $NaCH(CO_2Et)_2$, $NaCPh(CO_2Et)_2$, NaCN, MeMgI, and $(CH_2{=}CHCH_2)MgBr$. The approximate ratios of the two isomers formed in each case were estimated from i.r. spectra of the mixtures and are given in Table 3.

TABLE 3

Approximate percentages of products for the reaction:



(A) (B)

M	L	Nucleophilic reagent	Percentage (A)	(B)
Ru	CO	$NaBH_4$	100	0
Fe	CO	$NaBH_4$	90	10
Fe	CO	KCN	70	30
Fe	CO	Na(acac)	50	50
Fe	CO	$Na[CH(CO_2Et)_2]$	60	40
Fe	CO	$Na[CPh(CO_2Et)_2]$	60	40
Fe	PPh_3	$NaBH_4$	92	8
Fe	PPh_3	Na(acac)	55	45

Attack of sodium tetrahydroborate on complexes (IV; M = Fe or Os) was also studied. The osmium complex gave a single product (VI), in which the C_8 ring system is bonded in a 3—5-η,1-σ-manner, that is with an η-allyl fragment and a metal–carbon σ-bond. Support for this bonding mode comes from ^1H n.m.r. evidence which indicated that the three allylic protons were inequivalent as expected for a non-symmetrical η-allyl group (Table 1). The related 2-cyano-derivative $[(\eta\text{-}C_8H_{11}CN)Os(CO)_3]$, (VII), was also prepared. It had an n.m.r. spectrum similar to that of complex (VI), except that the unique hydrogen on the carbon atom α to the cyano-substituent appeared as a doublet of doublets at τ 6·28 (J_{H-H} 10·7 and 11·0 Hz); these values are consistent only with an *exo*-cyano-substituent. Additional evidence for the nature of the bonding in complex (VI) comes from its reaction with Ph_3CBF_4 to produce (V). We were able to prepare complex (V; M = Os) in only very small yields and as a consequence were unable to establish the site of tetrahydroborate attack.

Complex (VI) is formed by hydride-ion attack at the 2-position of the 1—5-η-cyclo-octadienylium system in (IV; M = Os). Until very recently such behaviour was rare but now seems to be an emerging pattern for dienylium complexes. However, the analogous reaction of complex (IV; M = Fe) followed a different path to give a mixture of products. The major component of this mixture was complex (II) but even this was obtained in small yield (see Experimental section). Low yields of $[Fe_3(CO)_{12}]$ and of a yellow complex (VIII) were also observed. From its mass spectrum, complex (VIII) has the composition $C_{20}H_{24}FeO_4$. The i.r. spectrum in the carbonyl region (Table 2) was characteristic of a complex containing an $Fe(CO)_3$ group, and this was confirmed by the mass spectrum which showed sequential loss of only three carbonyl groups from the parent ion. The spectrum also showed peaks due to the ions $C_{17}H_{24}OFe^+$ and $C_{17}H_{24}O^+$. On these grounds we formulate the complex as $[(C_{17}H_{24}O)Fe(CO)_3]$. To date we have been unable to characterise this species further.

Complexes (III; M = Fe or Ru) underwent reaction with Ph_3CBF_4 to regenerate (V).

Isomerisation Reactions.—The results described above show that isomerisations can be carried out by a process of hydride-ion abstraction from the diene complexes followed by hydride-ion addition to the dienylium products. We wished to examine the relation of isomerisations achieved in this way to catalytic isomerisation of cyclo-octadienes by iron,[15] ruthenium, and osmium carbonyl catalysts. We have already mentioned that in the preparation of complex (I; M = Ru) from $[Ru_3(CO)_{12}]$ there is considerable isomerisation of the excess of cyclo-octa-1,5-diene and by monitoring the composition of the diene mixture during the course of the reaction by vapour-phase chromatography we have shown that the cyclo-octa-1,4-diene is produced as an intermediate in the formation of cyclo-octa-1,3-diene. These results are shown graphically in the Figure. By additional experiments complex (I) was shown to catalyse a similar isomerisation of cyclo-octa-1,5-diene and during these experiments the catalyst itself was converted to complex (III; M = Ru) which was itself shown to function as a catalyst in these reactions. A plausible mechanism for such isomerisations [16] is shown in Scheme 2 and the experimental results strongly suggest that

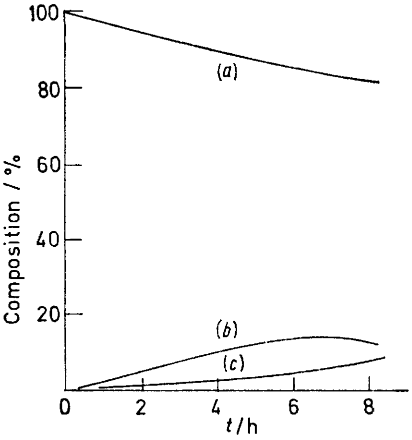


FIGURE 1 Isomeration of cyclo-octa-1,5-diene as a function of time: (*a*) 1,5-; (*b*) 1,4-; and (*c*) 1,3-diene

---

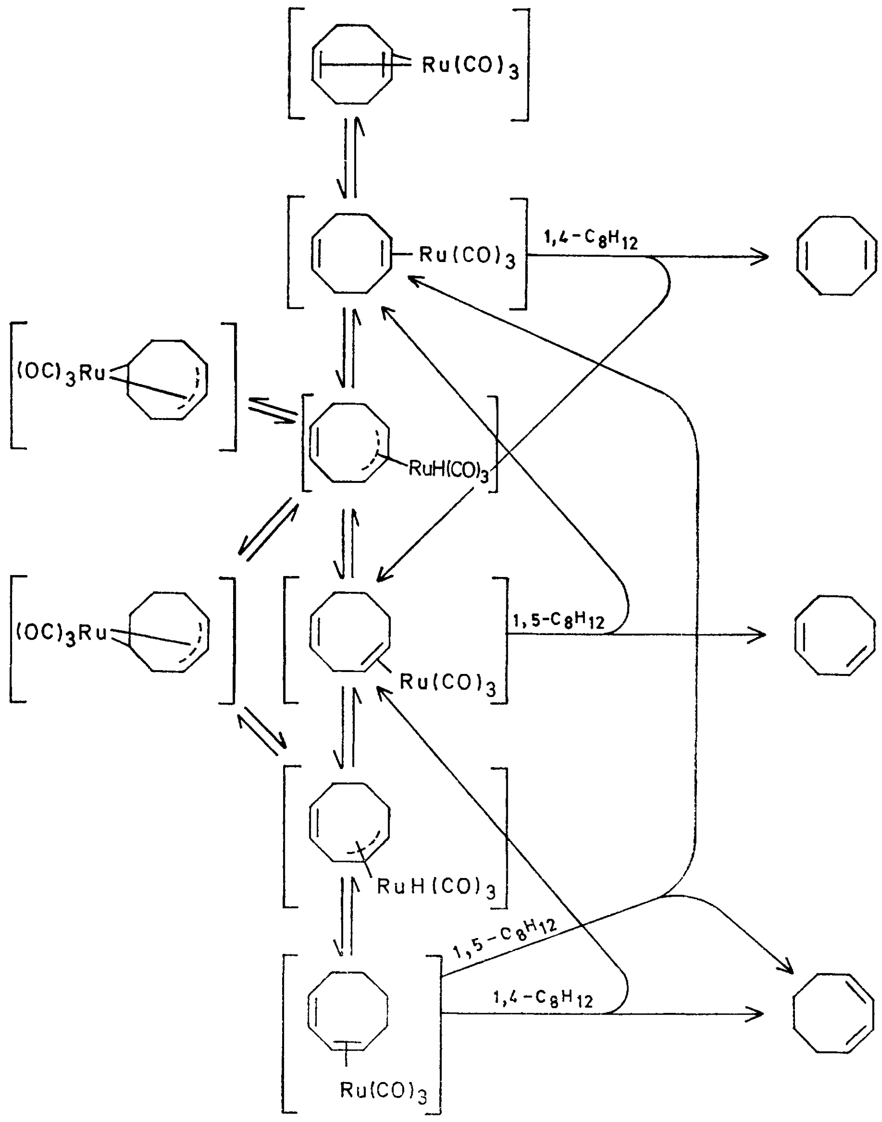
[14] J. Lewis and A. Parkins, *J. Chem. Soc. (A)*, 1967, 1150; 1969, 953.

[15] J. E. Arnett and R. Pettit, *J. Amer. Chem. Soc.*, 1968, **83**, 2954.

[16] H. Alper, P. C. LePort, and S. Wolfe, *J. Amer. Chem. Soc.*, 1969, **91**, 7553.

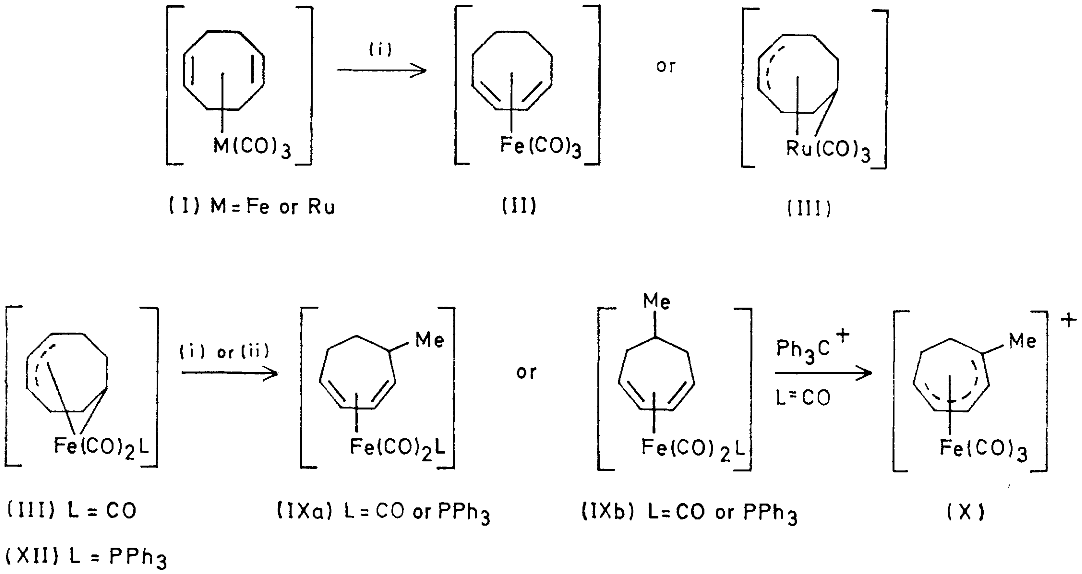
complex (I) also catalyses the diene isomerisation in the reaction with $[Ru_3(CO)_{12}]$.

The iron complexes behave differently. For example, complex (I) isomerises when heated under reflux in benzene or on irradiation at room temperature to complex (II); this is in contrast to the behaviour of the analogous ruthenium complex which isomerises to the η-allyl complex (III). We wished to examine whether (I; M = Fe) is initially isomerised to the η-allyl complex (III) and then further isomerised to complex (II), or whether the reaction path for the iron and ruthenium complexes are quite distinct. The following results showed that the two paths are in fact distinct. By spectroscopic means we were able to show that complex (III; M = Fe) did not occur at any detectable concentration during the isomerisation of (I) to (II) and cannot be an intermediate in the isomerisation of the diene. On heating complex (III) under reflux in benzene isomerisation to a 1,3-diene complex (IX) of formula $[(C_8H_{12})\text{-}Fe(CO)_3]$ occurred. The n.m.r. signals of the olefinic protons of this complex and of (II) were almost identical in pattern but somewhat different in chemical shift (see Table 1). The main difference was a doublet corresponding to three protons at τ 9·35 which occurred in the spectrum of complex (IX) and which we assign to methyl protons of a CH_3CH group. On this evidence we tentatively propose that the organic ring has contracted to give the methylcyclohepta-1,3-diene complex (IXa) or (IXb). We favour the former on the evidence of the n.m.r. spectrum of its derivative tricarbonyl[1—5-η-(5-



Scheme 2

Suggested mechanism for the catalytic isomerisation of cyclo-octa-1,5-diene methylcycloheptadienylium)iron]tetrafluoroborate, (X), formed by abstraction of hydride ion from (IX). In this spectrum the methyl signal was a singlet, suggesting the structure shown in Scheme 3 since a hydride ion must have been abstracted from a carbon atom adjacent to the Me substituent. The considerable change in chemical shift of this Me signal from τ 9·51 in complex (IX) to τ 7·98 in (X) also agrees with the suggested change in hybridisation of the carbon atom to which it is attached on abstraction of hydride ion. These results indicate that complex (III) isomerises by a totally different path and is thus not an intermediate in the isomerisation of (I) to (II). This is consistent with the mechanism shown in Scheme 2.



Scheme 3

Isomerisation reactions: (i) 80 °C, benzene; (ii) 125 °C, n-octane [for (XII)]

Reaction of Complexes (III) *with Neutral Ligands*.—(a) *Tertiary phosphines*. We found that the behaviour of complexes (III) towards tertiary phosphines or CO is in marked contrast to that of (I) and (II) which readily gave [$Fe(CO)_3(PPh_3)_2$], (XI), and the appropriate diene on reaction with Ph_3P. On the other hand complexes (III) underwent substitution of one of the CO groups to give dicarbonyl(4—6-η,1-σ-cyclo-octenediyl)triphenylphosphine derivatives (XII; M = Fe or Ru). The reactions were complete within a few minutes at 80 and 40 °C respectively. Complexes (XII) both showed n.m.r. spectra characteristic of symmetrical η-allyl groups (Table 1) and thus it is the carbonyl group *trans* to the metal–carbon σ-bond that has been substituted. No further carbonyl substitution of complex (XII; M = Fe) occurred even under very much more vigorous reaction conditions such as heating under reflux in cyclohexane in the presence of an excess of PPh_3 for 8 h. This illustrates the stability of the 4—6-η,1-σ-system and the relative inertness of the remaining two carbonyl groups. On heating at even higher temperatures (125 °C, refluxing n-octane, 6 h) the main product was the result of isomerisation of the ring system rather than further substitution of carbonyl groups. We believe that a ring contraction like that previously described for the unsubstituted complex (III; M = Fe) occurs to give dicarbonyl[η-(5-methylcyclohepta-1,3-diene)triphenylphosphineiron, (IX). The assignment of this structure is based on the very close similarity of the n.m.r. spectra of complexes (IX; L = CO or PPh_3) (see Table 1).

The observation that the first carbonyl group of complex (III; M = Fe) is much more readily substituted than the second is confirmed by the reaction of (III) with $Ph_2PCH_2CH_2PPh_2$ which gives [1,2-bis(diphenylphosphino)ethane]dicarbonyl(4—6-η,1-σ-cyclo-octenediyl)-iron, (XIII), in which the potentially bidentate phosphorus ligand is bonded to iron through one phosphorus atom only. The assignment of the structure of this complex is not unambiguous, but the non-equivalence of the outer protons of the η-allyl group suggests that the phosphine has substituted one of the CO groups *trans* to the η-allyl group rather than that *trans* to the σ-bonded carbon atom. It appears from *X*-ray studies on the tricarbonyl[4—6-η,1-σ-(2-cyanocyclo-octenediyl)]ruthenium, (XIV),[8] complex and a related iron complex [17] that M–C bonds are significantly longer for the CO group *trans* to the M–C σ-bond than for those *trans* to the η-allyl group. This would suggest that the *trans*-influence of the alkyl is greater than that of the allyl group and it is possible that the *trans*-effect of the alkyl group is also greater. This may account for the ready substitution of only one carbonyl group. A detailed examination of the kinetics of these reactions has been carried out.[18]

---

[17] J. Weaver and P. Woodward, *J. Chem. Soc.* (*A*), 1971, 3521.

[18] B. F. G. Johnson, J. Lewis, and M. V. Twigg, *J.C.S. Dalton*, 1974, 241.

We also carried out some reactions with the complex (XII; M = Fe) in order to compare its reactivity with that of the parent (III). Substitution of a carbonyl group from complex (III) by PPh_3 to give (XII) should result in an increase in electron density on the metal atom which might be expected to change the reactivity of the organic ligand. Our studies showed, however, that the reactivities of the complexes are qualitatively similar. Thus abstraction of a hydride ion from (XII) yielded the dicarbonyl(1—3:5,6-η-cyclo-octadienylium)-triphenylphosphineiron complex (XV) which is directly related to (V), and attack by hydride ion on this complex occurs at both the olefin group to give the original complex (XII) and at the η-allyl group to give dicarbonyl(η-cyclo-octa-1,5-diene)triphenylphosphineiron, (XVI). The ratio of (XII) and (XVI) formed in this reaction was *ca.* 11 : 1, which may be compared to the 9 : 1 ratio obtained in the case of the unsubstituted tricarbonyl complexes. Thus there is no significant difference in product ratios in the two cases and it is suggested that substitution of CO by PPh_3 increases the reactivity of the η-allyl and of the olefin groups towards nucleophiles almost equally. This was confirmed by attack of pentane-2,4-dionate (acac) on (XII) which gave a mixture of 4—6-η,1-σ-cyclo-octenyl [ν(CO) at 1 982 and 1 930 cm^{-1}] and η-cyclo-octa-1,5-diene derivatives [ν(CO) at 1 957 and 1 899 cm^{-1}] in the ratio 55 : 45 compared with 50 : 50 for the tricarbonyl complexes described earlier. This mixture was not separated.

(b) *Carbon monoxide.* As with tertiary phosphines the reactivity of complex (III; M = Fe) with carbon monoxide is quite different from that of (I) and (II). Cyclo-octa-1,5- or -1,3-diene were displaced from complexes (I) or (II) respectively on treatment with carbon monoxide (85 atm, room temperature) in cyclohexane for 2 d. The only iron-containing product in either case was iron pentacarbonyl. Complex (III), however, gave $[Fe(CO)_5]$ and a ketonic compound $C_9H_{12}O$. We formulate this as the five-membered ring ketone, bicyclo-[4.2.1]non-2-en-9-one, (XVII) [ν(CO) at 1 743 cm^{-1} in CCl_4 and 1 749 cm^{-1} in cyclohexane]. Brewis and Hughes [19] have shown that cyclo-octa-1,5-diene can be catalytically carbonylated by a palladium(II) complex to give an isomeric ketone, bicyclo[3.3.1]non-2-en-9-one [ν(CO) at 1 733 cm^{-1}]. In the six-membered ring ketone synthesised by Brewis and Hughes [19] the ketonic stretching frequency is lower than that of the ketone we synthesised, as expected for the different size rings. We did not determine whether there is preliminary carbonyl insertion into the iron–carbon σ-bond or whether there is insertion at the 4-position of the η-allyl group. In either case, as might be expected, the ketone carbon has linked the σ-bonded carbon atom to one of the outer carbons of the η-allyl group of complex (III).

EXPERIMENTAL

All reactions were carried out under a dinitrogen atmosphere as were work-up procedures except for rapid transferences. Compounds were stored under dinitrogen below 0 °C. Although complexes (I) and (II) are known we include preparative details as these have not been fully reported previously.

*Preparation of the Diene Complexes.—Tricarbonyl(η-cyclo-octa-*1,5-*diene)iron,* (I). A solution of cyclo-octa-1,5-diene (40·0 g) and iron pentacarbonyl (40·0 g) in benzene (160 cm^3) was irradiated with a medium-pressure Hg lamp for 44 h. The reaction mixture was then reduced to dryness under vacuum and the residue extracted with pentane. On cooling the pentane solution to −78 °C, brown-yellow crystals of complexes (I) and (II) precipitated while tetracarbonyl-(η-cyclo-octa-1,5-diene)iron remained in solution. Separation of this precipitated material on silica, eluting with pentane, gave complex (I) as orange-yellow crystals (22·0 g), m.p. 76 °C, and complex (II) as yellow needles (20·0 g), m.p. 36 °C. Both complexes gave satisfactory elemental analyses and parent ions were observed in their mass spectra.

*Tricarbonyl(η-cyclo-octa-*1,3-*diene)iron,* (II). A solution of cyclo-octa-1,3-diene (25·0 g) and iron pentacarbonyl (20·0 g) in benzene (160 cm^3) was irradiated for 48 h and the solvent and unreacted starting material then removed under vacuum to give green crystals. Purification by chromatography on silica gave complex (II) as yellow needles (20·0 g, 80%), m.p. 36 °C. The complex was characterised by elemental analysis and by its n.m.r., i.r., and mass spectra.

*Tricarbonyl(η-cyclo-octa-*1,5-*diene)ruthenium,* (I). The complex $[Ru_3(CO)_{12}]$ (960 mg, 1·5 mmol) was heated under reflux for 8 h with cyclo-octa-1,5-diene (15 cm^3, 0·12 mol) in benzene (75 cm^3). The solvent was removed and the excess of diene distilled off (30 °C, 7 mmHg). Unreacted $[Ru_3(CO)_{12}]$ (307 mg, 32%) was separated by treating the residue with pentane. The pentane solution was then concentrated and chromatographed with pentane on a silica column to separate traces of complex (III), a major band which on concentration gave a yellowish oil, and small amounts of $[Ru_3(CO)_{12}]$. The yellowish oil was sublimed at 0 °C and 0·005 mmHg on to a cold finger at −30 °C. A second chromatography and sublimation yielded complex (I) (684 mg, 58%) as white *crystals* melting at room temperature (Found: C, 44·54; H, 4·35. Calc. for $C_{11}H_{12}O_3Ru$: C, 45·05; H, 4·10%). The complex is unstable even at −20 °C under a dinitrogen atmosphere, but may be kept unchanged for 1 month in frozen benzene solution.

Tricarbonyl(1—3:5,6-*η-cyclo-octadienylium)ruthenium tetrafluoroborate,* (V). Dichloromethane solutions of complex (I) (673 mg, 2·3 mmol in 1 cm^3) and Ph_3CBF_4 (825 mg, 2·5 mmol in 5 cm^3) were mixed and shaken for 30 min. On addition of diethyl ether a pale yellow precipitate formed which was left in the air to hydrolyse the unreacted Ph_3CBF_4. Recrystallisation from dichloromethane with addition of diethyl ether gave complex (V) (540 mg, 1·4 mmol, 62%) as air-stable white *crystals* which decompose at 209 °C without melting (Found: C, 34·4; H, 3·10. Calc. for $C_{11}H_{11}BF_4O_3Ru$: C, 34·85; H, 2·95%).

Tricarbonyl(4—6-*η*,1-*σ-cyclo-octenediyl)ruthenium,* (III). Aqueous solutions of complex (V) (270 mg, 0·71 mmol) and excess of $NaBH_4$ (472 mg, 12·5 mmol) were mixed at 0 °C and stirred for 15 min. The mixture was extracted with diethyl ether (3 × 10 cm^3) and the extracts dried over magnesium sulphate. The yellow-brown oil obtained after evaporation of diethyl ether was chromatographed on a silica column with pentane and sublimed (0 °C, 0·005 mmHg, −18 °C cold finger), to yield complex (III) (135 mg, 0·46 mmol, 65%) as white *crystals* melting at room temperature

---

[19] S. Brewis and P. R. Hughes, *Chem. Comm.*, 1966, 6.

(Found: C, 44·54; H, 4·15. Calc. for $C_{11}H_{12}O_3Ru$: C, 45·05; H, 4·10%). The complex is stable under dinitrogen.

Tricarbonyl(η-*cyclo-octa*-1,3-*diene*)*osmium*, (II). A suspension of dodecacarbonyl-*triangulo*-triosmium (0·50 g) in benzene (160 cm^3) with cyclo-octa-1,3-diene (3·0 g) was irradiated for 90 h. After removal of the solvent under vacuum pentane was added. Unreacted $[Os_3(CO)_{12}]$ was removed by filtration and the solution evaporated down to a viscous brown oil which was distilled twice at 0·1 mmHg (70 °C) and at 0·05 mmHg (50 °C) to give complex (II) as a yellow oil (0·11 g, 35% based on the carbonyl used) (Found: C, 39·25; H, 2·65. Calc. for: $C_{11}H_{12}O_3Os$: C, 39·4; H, 3·15%). The mass spectrum showed the parent ion corresponding to $[(C_8H_{12})^{192}Os(CO)_3]^+$ at *m/e* 384. A similar reaction with cyclo-octa-1,5-diene gave a yellow oil having a mass spectrum similar to that of complex (II), but with a very complicated n.m.r. spectrum suggesting that a mixture of isomers had been produced. The unreacted diene was shown by g.l.c. analysis to have been partly converted to the 1,3-form. No pure compounds were isolated from this reaction.

Hydride-ion Abstraction from the Diene Complexes.—*Tricarbonyl*(1—5-η-*cyclo-octadienylium*)*iron tetrafluoroborate*, (IV). Complex (II) (1·40 g) dissolved in a minimum volume of dry dichloromethane was treated with Ph_3CBF_4 (1·90 g). After 1 h, a dark precipitate was formed which was separated and washed with diethyl ether. Recrystallisation from dichloromethane–diethyl ether gave complex (IV) as a pale yellow solid (0·9 g) (Found: C, 39·3; H, 3·35. Calc. for $C_{11}H_{11}BF_4FeO_3$: C, 39·55; H, 3·35%). This complex has previously been prepared by protonation of the cyclo-octatriene complex.[13]

Tricarbonyl(1—3:5,6-η-*cyclo-octadienylium*)*iron tetrafluoroborate*, (V). Complex (I) gave complex (IV) as a yellow solid (90%) by a similar route to that above (Found: C, 39·4; H, 3·30. Calc. for $C_{11}H_{11}BF_4FeO_3$: C, 39·55; H, 3·35%).

Tricarbonyl(1—5-η-*cyclo-octadienylium*)*osmium tetrafluoroborate*, (IV). This was prepared in a similar manner from complex (II) to give a white *powder* (yield 50—75%) (Found: C, 28·35; H, 2·7. Calc. for $C_{11}H_{11}BF_4O_3Os$: C, 28·15; H, 2·35%).

Reactions of the Cationic Complexes with Nucleophiles.—*Complex* (V; M = Fe) *with sodium tetrahydroborate*. Complex (V) (3·70 g) dissolved in water (100 cm^3) was treated with $NaBH_4$ (1·1 mol per Fe) in small portions at 0 °C. After 5 min the mixture was extracted with diethyl ether, the extract giving a green-yellow solid (2·16 g, 80%). The i.r. spectrum of this solid in the carbonyl-stretching region showed that it was a mixture of two neutral complexes, containing $Fe(CO)_3$ groups, in the ratio 9 : 1. Separation of the mixture on alumina gave *tricarbonyl*(4—6-η,1-σ-*cyclo-octenediyl*)*iron*, (III), m.p. 105 °C, as the major product (Found: C, 52·75; H, 4·85. Calc. for $C_{11}H_{12}FeO_3$: C, 53·2; H, 4·85%). The other species in the mixture was shown to be complex (I) (10% abundance) by spectral analysis.

Similar treatments of complex (V) with sodium cyanide or sodium pentane-2,4-dionate in water, $Na[CH(CO_2Et)_2]$ or $Na[CPh(CO_2Et)_2]$ in tetrahydrofuran (thf), methylmagnesium iodide or allylmagnesium bromide in diethyl ether gave in each case mixtures of 2-substituted tricarbonyl(4—6-η,1-σ-cyclo-octenyl)iron, (XIV), and of 4-substituted tricarbonyl(η-cyclo-octa-1,5-diene)iron, (XVIII). The ratios of the two isomers as estimated from i.r. spectra in the carbonyl-stretching region are given in Table 1. In most cases it was not possible to separate these isomers; however, in certain cases it was possible and the following complexes were isolated and characterised: *tricarbonyl*-[4—6-η,1-σ-(2-*cyanocyclo-octenyl*)]*iron* as a white solid, m.p. 120 °C (7%) (Found: C, 52·05; H, 4·0; N, 5·1. Calc. for $C_{12}H_{11}FeNO_3$: C, 52·55; H, 4·05; N, 5·0%); *tricarbonyl*-{η-[4-(*diacetylmethyl*)*cyclo-octa*-1,5-*diene*]}*iron* as yellow needles, m.p. 68·5 °C (Found: C, 55·8; H, 5·2. Calc. for $C_{16}H_{14}FeO_5$: C, 55·4; H, 5·2%); *tricarbonyl*[4—6-η,1-σ-(2-*methylcyclo-octenediyl*)]*iron* as a yellow oil (30%) (Found: C, 54·65; H, 5·3. Calc. for $C_{12}H_{14}FeO_3$: C, 54·75; H, 5·3%); [4—6-η,1-σ-(2-*allylcyclo-octenyl*)]*tricarbonyliron* as a viscous orange oil (23%) (Found: C, 57·9; H, 5·35. Calc. for $C_{14}H_{16}FeO_3$: C, 58·6; H, 5·55%); and [η-(4-*allylcyclo-octa*-1,5-*diene*)]*tricarbonyliron* as a viscous orange oil (23%) (Found: C, 58·2; H, 5·4. Calc. for $C_{14}H_{16}FeO_3$: C, 58·6; H, 5·55%).

Complex (IV; M = Fe) *with sodium tetrahydroborate*. Complex (IV) (1·5 g) dissolved in water (50 cm^3) was treated with sodium tetrahydroborate (1·1 mol per Fe). The solution deposited a black gummy material which was extracted with diethyl ether. The ether solution gave a green viscous oil (0·26 g) which, on chromatography on alumina, yielded three bands corresponding to complex (II) (0·15 g), $[Fe_3(CO)_{12}]$ (0·04 g), and a yellow solid (VIII) (0·023 g). Complex (VIII) exhibited an i.r. spectrum characteristic of a complex containing an $Fe(CO)_3$ group (see Table 2) and a mass spectrum showing a parent ion corresponding to $[(C_{17}H_{24}O)Fe(CO)_3]^+$ with sequential loss of three CO groups. A peak due to the ion $C_{17}H_{24}O^+$ was also present in the spectrum.

Complex (IV; M = Os) *with sodium tetrahydroborate*. Sodium tetrahydroborate (1·1 mol per osmium atom) was added to a solution of complex (IV) (0·132 g) in water–acetone (30 cm^3, 4 : 1 v/v) and the mixture stirred for 20 min at room temperature. A diethyl ether extract of the mixture gave a residue which was distilled twice (80 °C, 0·05 mmHg) to give tricarbonyl(3—5-η,1-σ-cyclo-octenediyl)osmium, (VI), as a colourless oil (0·055 g, 51%) (Found: C, 39·6; H, 2·9. Calc. for $C_{11}H_{12}O_3Os$: C, 39·24; H, 2·65%). Its mass spectrum showed the parent ion and the expected fragmentation pattern.

Complex (IV; M = Os) *with sodium cyanide*. An analogous treatment of complex (IV) with sodium cyanide gave a product which was distilled at 80 °C (0·1 mmHg) and at 60 °C (0·05 mmHg) to give tricarbonyl[3—5-η,1-σ-(2-cyanocyclo-octenediyl)]osmium, (VII), as colourless crystals, m.p. 115 °C (Found: C, 35·4; H, 2·7; N, 3·35. Calc. for $C_{12}H_{11}NO_3Os$: C, 35·4; H, 2·7; N, 3·4%). The parent ion was observed in the mass spectrum.

Reactions of Complexes (III) *with Neutral Ligands*.—*Complex* (III; M = Fe) *with triphenylphosphine*. A solution of complex (V) (0·496 g) with PPh_3 (0·524 g) in cyclohexane (50 cm^3) was heated under reflux for 20 min by which time the i.r. spectrum showed that no starting material remained. After removal of solvent the solid residue was recrystallised from pentane–diethyl ether at −78 °C to give dicarbonyl(4—6-η,1-σ-cyclo-octenediyl)triphenylphosphine-iron, (XII), as yellow crystals (0·95 g), m.p. 126 °C (Found: C, 69·9; H, 5·75; P, 6·2. Calc. for $C_{28}H_{27}FeO_3P$: C, 69·7; H, 5·6; P, 6·45%). The parent ion was not observed in the mass spectrum, the highest mass peak corresponding to the loss of PPh_3 from this ion.

Complex (III; M = Fe) *with* 1,2-*bis*(*diphenylphosphino*)-*ethane*. Using an analogous procedure to that above the related complex [1,2-bis(diphenylphosphino)ethane]dicarbonyl(4—6-η,1-σ-cyclo-octenediyl)iron, (XIII), was obtained as a yellow solid, m.p. 130 °C (decomp.) (Found: C, 70·25; H, 5·9; P, 10·15. Calc. for $C_{36}H_{36}FeO_3P_2$: C, 69·9; H, 5·8; P, 10·45%). The highest mass peak in the mass spectrum corresponded to the ion $[(C_8H_{12})Fe(CO)_2]^+$.

Abstraction of hydride ion from complex (XII; M = Fe). Reaction of complex (XII) with Ph_3CBF_4 in dichloromethane gave dicarbonyl(1—3:5,6-η-cyclo-octadienylium)-triphenylphosphineiron tetrafluoroborate, (XV), as a yellow solid (Found: C, 60·1; H, 4·75; P, 5·4. Calc. for $C_{28}H_{26}BF_4FeO_3P$: C, 59·25; H, 4·6; P, 5·45%).

Complex (III; M = Fe) *with carbon monoxide.* A solution of complex (III) (0·70 g) in cyclohexane (75 cm³) was treated with carbon monoxide (85 atm) at 25 °C for 50 h. The i.r. spectrum in the carbonyl-absorption region showed the presence of starting material and $[Fe(CO)_5]$. The solvent and $[Fe(CO)_5]$ were removed from the filtered solution under vacuum and the residual yellow oil was chromatographed on silica. Elution with pentane gave a small quantity of starting material and further elution with methanol gave bicyclo[4.2.1]non-2-en-9-one (64%), (XVII), as a colourless oil which freezes below 5 °C (Found: C, 79·1; H, 8·8. Calc. for $C_9H_{12}O$: C, 79·4; H, 8·8%). Two derivatives of this ketone were prepared: the 2,4-dinitrophenylhydrazone as orange needles, m.p. 150—152 °C (Found: C, 56·7; H, 6·05; N, 17·2. Calc. for $C_{14}H_{16}N_4O_4$: C, 56·95; H, 6·05; N, 17·7%); and the semicarbazone as colourless needles, m.p. 185 °C (Found: C, 62·2; H, 7·7; N, 21·95. Calc. for $C_{10}H_{15}N_3O$: C, 62·15; H, 7·75; N, 21·75%). The ketone and its hydrazone derivative showed parent ions in their mass spectra while the semicarbazone showed only fragmentation ions such as $C_8H_{12}^+$.

Reactions of Complexes (I) *and* (II) *with Carbon Monoxide.*—There was no evidence for the formation of ketonic species on similar treatments of complexes (I) and (II) (M = Fe). In each case the only products were $[Fe(CO)_5]$ and the appropriate diene as characterised by mass, i.r., and n.m.r. spectra.

Isomerisation Reactions.—Complex (I; M = Fe). The isomerisation of complex (I) to complex (II) was carried out in refluxing cyclohexane or by irradiating a benzene solution with a medium-pressure mercury u.v. lamp at room temperature. By following changes in the i.r. spectrum a half-life of *ca.* 1 h was obtained for the thermal reaction.

Complex (III; M = Fe). A solution of complex (III) (0·50 g) in cyclohexane (60 cm³) was heated under reflux for 8 h by which time the i.r. spectrum showed almost complete absence of starting material. The yellow oil obtained by removal of the solvent was chromatographed on silica, eluting with pentane, to give a very small quantity of complex (III) and a yellow oil which was distilled twice (25 °C, 0·1 mmHg) to give tricarbonyl[η-(5-methylcyclohepta-1,3-diene)]iron, (IXa), as a yellow oil (0·49 g) (Found: C, 53·05; H, 4·8. Calc. for $C_{11}H_{12}FeO_3$: C, 53·1; H, 4·85%). The mass spectrum showed the parent-ion peak.

Complex (XII; M = Fe). A solution of complex (XII) (0·50 g) in n-octane (4; cm³) was heated under reflux for 6 h. After this time no starting material was detectable by i.r. spectroscopy and chromatography on silica gave dicarbonyl[η-(5-methylcyclohepta-1,3-diene)]triphenylphosphineiron, (IXa), as yellow crystals (0·49 g), m.p. 82 °C (Found: C, 69·9; H, 5·8. Calc. for $C_{29}H_{26}FeO_3P$: C, 69·7; H, 5·6%).

Hydride-ion Abstraction from Complex (IXa; L = CO).—A solution of complex (IXa) (0·050 g) in dichloromethane (20 cm³) was shaken with Ph_3CBF_4 (1 mol per Fe atom). After 30 min diethyl ether was added to give a yellow precipitate which was recrystallised from dichloromethane-diethyl ether to give tricarbonyl[1—5-η-(5-methylcycloheptadienylium)iron tetrafluoroborate, (X), as a pale yellow powder (0·036 g) (Found: C, 39·1; H, 3·6. Calc. for $C_{11}H_{11}BF_4FeO_3$: C, 39·55; H, 3·35%).

Kinetic Experiments.—Kinetic experiments were carried out at 90·0 ± 0·1 °C, in the absence of light and under a dinitrogen atmosphere. Reactors fitted with condensors were used. Two types of procedure were used to prepare the solutions: (*i*) in experiments with the complex $[Ru_3(CO)_{12}]$, the temperature of the $[Ru_3(CO)_{12}]$ solution was stabilised for 5 min and the appropriate amount of cyclo-octa-1,5-diene added; (*ii*) in experiments with complexes (I; M = Ru) or (III; M = Ru) an appropriate volume of a standard solution of one of these complexes was added to a stabilised solution of the solvent and the diene. Aliquot portions were taken every 2 h and analysed by i.r. spectrometry and gas–liquid chromatography. In the former case the solvent was evaporated (20 °C, 12 mmHg), n-heptane added and then evaporated, and the spectrum run in n-heptane. Aliquot portions for gas–liquid chromatography were analysed without any preliminary treatment. A 6·4 m × 3 mm column of 10% 1,2,3-tris(2-cyanoethoxy)propane on Cromsorb W and flame-ionisation detection were used. Experimental conditions for the chromatographies were: oven, 80 °C; carrier gas, N_2, 2·8 atm; detection, 1·8 atm H_2; 2·3 atm air; sample, 0·15 mm³. The peaks were integrated by a weighing procedure.

We thank the S.R.C. for support (to A. J. D. and A. J. P. D.) and Johnson, Matthey and Co. Ltd. for their generous loan of ruthenium and osmium salts.

[3/2312 *Received, 12th November,* 1973]