Ferrocenyl Carbene Complexes of Chromium, Tungsten, and Manganese. Models of the α-Ferrocenyl Carbonium Ion

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The preparation of a series of complexes, $[(CO)_5MC(Fc)X]$ (M = Cr, W; X = $O^-NMe_4^+$, OMe, OEt, NH_2, NMe_2, NC_4H_8) and $[(\pi\text{-}C_5H_4Me)(CO)_2MnC(Fc)OMe]$ (Fc = ferrocenyl) is reported. The results of spectroscopic (i.r., u.v.–visible, n.m.r., and mass) measurements are used to demonstrate the profound consequences of the introduction of a ferrocenyl substituent into the carbene ligand in the complexes. The ferrocenyl group acts as a potent electron donor by means of a resonance interaction with the carbene carbon atom. The nature of the stabilisation provided by the α-ferrocenyl group is discussed. Some of these new compounds function as specific hydrogenation catalysts. Attempts to prepare β-ferrocenyl carbene complexes are described. Ferrocenyl-lithium does not react with $(\pi\text{-}C_5H_5)Co(CO)_2$ or with $(\pi\text{-}C_5H_5)V(CO)_4$.

THE carbene species [RR'C:], is related to the carbonium ion $[RR'CH^+]$ as a base to its conjugate acid. A number of recent studies have described [1] the generation and reactions of α-ferrocenyl carbenes which are then related to their α-ferrocenyl carbonium ion counterparts. These latter systems show unusual stability which has been the subject of much interest.[2] We have studied a series of metal carbene complexes in which the carbene ligand contains a ferrocenyl, Fc, group adjacent to the co-ordinatively unsaturated carbon atom. This situation is analogous to that encountered in α-ferrocenyl carbonium ions.

Heteronuclear complexes of transition-metals in which the metal atoms are not directly bonded are of interest for the evidence they provide of the ability of one metal to transmit its influence to another. Recent studies of systems of this type, in which two metals are separated by one atom, have shown that some metal–metal interaction occurs in such compounds.[3]

RESULTS AND DISCUSSION

Preparation of Complexes.—Each of the complexes (I)—(IX) was prepared by adaptations of the general methods currently available.[4] Details are recorded in the Experimental section. Ferrocenyl-lithium was usually prepared either from bromoferrocene [5] or from ferrocenylmercury chloride.[6] Notwithstanding slightly lower yields, the latter precursor was preferred because of its greater ease of use and accessibility. The α-ferrocenyl carbene complexes of chromium and tungsten are all air-stable crystalline solids which are sparingly soluble in non-polar solvents (hexane, benzene) and readily soluble in polar solvents (ether, acetone). The manganese complex is both air and photo-sensitive but is thermally stable above its melting point; it is soluble in all organic solvents.

Infrared Spectra.—The assignment of the carbonyl stretching frequencies (Experimental section) is straightforward, and from these the force constants k_1 and k_2 have been calculated. Table 1 shows the effect of changing the group Y in the complexes $[(CO)_5Cr{\cdot}C(OEt)Y]$ and $[(CO)_5Cr{\cdot}C(NC_4H_8)Y]$ (Y = 2-furyl, Me, Ph, Fc) upon the force constants k_1 and k_2. The substitution of a ferrocenyl group produces a significant decrease in k_1 from its value in the other systems, suggesting that $(d \longrightarrow p)\pi$ donation in the $Cr\text{–}C(sp^2)$ bond decreases in the same manner as $(d \longrightarrow \pi^*)\pi$ donation in the Cr-*trans*(CO) bond increases. A comparable change is also observed when alkoxy-carbene complexes of tungsten and of manganese are compared (Y = Ph, Fc). Examination of this variation using Graham's method [7] to determine the σ- and π-parameters of the $M\text{–}C(sp^2)$ bond, does not distinguish between the inductive effects of the various groups Y, but confirms the alkoxy-groups as stronger π-acceptors than amino-groups.[8] The presence of two absorptions of medium

TABLE 1

Carbonyl stretching frequencies, cm^{-1}, force constants,[a] $N\ m^{-1}$, and σ-, π-parameters [b] for a series of carbene complexes, $[(CO)_5CrCXY]$

	$\nu(CO)\ cm^{-1}$				$N\ m^{-1}$			
	A''_1	B_1	A'_1	E	k_1	k_2	σ	π
X = OEt								
Y = Fu	2065	1995	1965	1950	1580	1591	−44	+58
Me	2064	1983	1961	1947	1576	1587	−48	+58
Ph	2062	1987	1963	1954	1576	1595	−32	+50
Fc	2056	1977	1949	1938	1555	1574	−53	+50
X = NC_4H_8								
Y = Fu	2067	1978	1933	1942	1527	1579	−15	+17
Me	2056	1968	1930	1936	1523	1572	−25	+20
Ph	2056	1975	1931	1937	1523	1573	−23	+19
Fc	2053	1969	1918	1930	1509	1569	−17	+9

Reference compound, $C_6H_{11}NH_2Mo(CO)_5$, $k_1 = 1508$, $k_2 = 1577\ N\ m^{-1}$ (ref. 7).

[a] Force constants calculated by the method of F. A. Cotton and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, 1962, **84**, 4432.
[b] Ref. 7.

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[7] W. A. G. Graham, *Inorg. Chem.*, 1968, **7**, 315.

[8] M. Y. Darensbourg and D. J. Darensbourg, *Inorg. Chem.*, 1970, **9**, 32.

intensity on the region 1100—1000 cm^{-1} indicates that the ferrocene ring is monosubstituted throughout this series of complexes.[9]

N.m.r. Spectra.—Both of the apparent triplet signals of the $H_{2,5}$ and $H_{3,4}$ protons of the monosubstituted cyclopentadienyl ring are to lower field of the singlet of the unsubstituted ring, H_1. Analogy with other electron-attracting substituents (CN, NO_2) leads to the assignment of the lower-field triplet to the $H_{2,5}$ protons.[10] This contrasts with the n.m.r. spectra of α-ferrocenyl carbonium ions in which $H_{2,5}$ is to high field of H_1 and $H_{3,4}$.[11] In the n.m.r. spectra of substituted ferrocenes there are linear relations between (*a*) the Hammett substituent constant, σ_P, and $\Delta_{2,5}$ (for definition, see Table 2), and also between (*b*) the resonance substituent constant, σ_R, and the value of $(\Delta_{3,4} - \Delta_1)$.[12] The values of σ_P and σ_R for the carbene substituents in each of the complexes (I)—(IX) may be calculated in this way. Positive values of both parameters in all cases indicate the overall electron-withdrawing nature of the carbene carbon atom regardless of metal or of heteroatom. The substituent $[(CO)_5MC(OR)-]$ (M = Cr, W) is a stronger electron-attracting group than $[(CO)_5MC(NR_2)-]$. This may be attributed to the greater electron release from nitrogen which satisfies the electron deficiency of the carbene carbon atom to a greater extent than the more electronegative oxygen. The relative electron-donor ability of the heteroatom decreases in the order O^- (IV) > NR_2 (IX) > OR (III). Replacement of $[(CO)_5M]$ with $[(\pi-C_5H_4Me)Mn(CO)_2]$ brings about a reduction of both σ_P and σ_R [compare (I) and (V)], implying that the latter is a better electron-donating group. The σ_R values for the carbene substituents in the complexes (I)—(IX) are larger than any previously measured. The values indicate that a strong electron release from the ferrocenyl group to the empty carbene carbon p_z orbital takes place *via* a delocalised π-system rather than through inductive effects. This is consistent with the finding that the normal donor strength of the ferrocenyl group is considerably increased by interaction with strong electrophilic centres.[13]

TABLE 2

Ferrocene ring proton n.m.r. signals in the complexes (I)—(IX)

	Chemical shifts (p.p.m.)			Δ Values (Hz) *				
Complex †	H_1	$H_{2,3}$	$H_{3,4}$	Δ_1	$\Delta_{2,5}$	$\Delta_{3,4}$	σ_P	σ_R
(I) [a]	4·23	4·98	4·77	−9	−84	−63	+0·66	+0·67
(II) [a]	4·20	4·97	4·74	−6	−83	−60	+0·65	+0·68
(III) [a]	4·23	4·97	4·80	−9	−83	−66	+0·65	+0·69
(IV) [b]	4·09	4·57	4·17	+8	−40	0	+0·36	+0·26
(V) [a]	4·14	4·77	4·44	0	−63	−30	+0·52	+0·38
(VI) [a]	4·20	4·69	4·62	−6	−55	−48	+0·46	+0·53
(VII) [a]	4·19	4·50	4·36	−5	−36	−22	+0·32	+0·30
(VIII) [a]	4·16	4·46	4·46	−2	−32	−32	+0·31	+0·38
(IX) [a]	4·16	4·50	4·50	−2	−36	−36	+0·33	+0·43

* $\Delta_{i,j} = \delta(FcH) - \delta(H_{i,j}$ complex). † Solvent (*a*) $CDCl_3$, (*b*) $(CD_3)_2CO$.

Substituent parameters calculated[12] according to: $\Delta_{2,5} = -147\sigma_P + 13$; $(\Delta_{3,4} - \Delta_1) = -81\sigma_R + 0{\cdot}8$.

The n.m.r. spectra of many complexes $[(CO)_5CrC(OMe)Y]$ (Y = substituted phenyl ring), are temperature dependent,[14] the OCH_3 signal appearing as a doublet at temperatures below *ca.* 230 K. The spectrum of (I) remained unchanged at 210 K, suggesting that either the C–OMe bond has less double-bond character or that the bulk of the ferrocenyl group completely restricts rotation about this bond.[15]

Restricted rotation about the C–NMe_2 bond in the complexes $[(CO)_5Cr{\cdot}C(NMe_2)Y]$ results in the appearance of two N–Me resonances.[16] In (VII; Y = Fc) these two resonances are separated by 14 Hz, whereas for Y = Ph[17] and Y = Me the separations are 95 and 57 Hz respectively. ASIS Measurements have shown that the lower-field resonance in the latter complexes can be assigned to the N–Me group *trans* to Y.[18] In (VII; Y = Fc) it is the *cis* N–Me resonance which is so strongly deshielded, relative to its phenyl and methyl analogues, by the ferrocenyl group (Table 3).

TABLE 3

(N–Me) Proton resonances in the n.m.r. spectra of the complexes $[(CO)_5CrC(NMe_2)R]$ in $CDCl_3$ solution

	Chemical shifts, δ/p.p.m.	
R	N–CH_3 (*trans*)	N–CH_3 (*cis*)
Me	3·87	3·30
Ph	3·99	3·04
Fc	4·04	3·90

U.v.–visible Spectra.—The spectra of the complexes (I)—(IX) are dominated by two intense charge-transfer absorptions in the region 200—700 nm. The assignment of these bands follows from previous work on related

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[11] M. Hisatome and K. Yamakawa, *Tetrahedron*, 1971, **27**, 2101.

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[16] E. Moser and E. O. Fischer, *J. Organometallic Chem.*, 1968, **13**, 387.

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systems.[19] The lower energy M → L charge-transfer band is sensitive to the nature of M. While slight differences are observed between chromium and tungsten analogues [(II) and (III); (VIII) and (IX)], the manganese complex, (V), shows this absorption at considerably higher energy than (I), consistent with the greater π-electron donor strength of the manganese-containing group. Comparison with other compounds of the type $[(CO)_5CrC(OEt)Y]$ shows that the ferrocenyl group causes a large increase in the energy of the M → L charge-transfer band compared to other groups, Y, which is again indicative of the superior electron-donor strength of the ferrocenyl substituent. (Table 4).

TABLE 4

U.v.–visible spectra of the complexes

Compound †	$\lambda_{max.}$ (nm)	log ε	$\lambda_{max.}$ (nm)	log ε	$\lambda_{max.}$ (nm)	log ε	$\lambda_{max.}$ (nm)	log ε
(I) [a]	255	4·34	(340)	3·5	420	3·88	515	3·44
(II) [a]	238	4·36	(335)	3·2	414	3·56	510	3·20
(III) [a]	240	4·66	355	3·83	405	4·15	520	3·68
(IV) [b]	237	4·39	*		345	3·61	(450)	3·3
(V) [a]	225	4·30	*		396	3·46	475	3·46
(VI) [a]	255	4·41	350	3·54	405	3·72	*	
(VII) [a]	232	4·42	*		392	3·68	(460)	3·1
(VIII) [a]	235	4·43	*		388	3·66	(450)	2·9
(IX) [a]	240	4·40	350	4·3	387	3·65	445	3·61

* Absorptions obscured by intensity of neighbouring charge-transfer maxima. † Solvent (*a*) hexane, (*b*) CH_2Cl_2. Shoulder peaks are listed in parentheses, energy values and extinction coefficients being only approximate.

In addition to the two intense charge-transfer absorptions, one and sometimes two weaker bands are observed at *ca.* 340 and *ca.* 480 nm in the complexes (I)—(IX), which are assigned to the ferrocenyl chromophore.[20] The intensities of these bands are consistent with the carbene substituent (*e.g.* $[(CO)_5CrC(OR)-]$) being electron attracting.[9] The position of the better resolved, lower-energy band shows a large bathochromic shift relative to ferrocene. From the variation in the position of this band it is clear that $[(CO)_5CrC(OR)-]$ is a stronger electron-withdrawing group than $[(CO)_5CrC(NR_2)-]$. The distinction drawn between the $[(\pi\text{-}C_5H_4Me)Mn(CO)_2]$ group and the $[(CO)_5M]$ (M = Cr, W) group is reinforced by the shift of this lower-energy band to shorter wavelength from (I) to (V).

Mass Spectra.—Unlike the carbene complexes which have been studied in the past, the present series of compounds do not show all the ions $[LM(CO)_n]^+$ which arise by successive loss of carbonyl groups from the molecular ion. The ion $[LM(CO)_4]^+$ is present only in (I), while the molecular ion is also missing from the spectra of (VII) and (VIII). For the purposes of comparison, the ion $[MC(Fc)X]^+$ (X = OR, NR_2) has been assigned a relative abundance of 100 (Table 5).

The most abundant ion in the alkoxy-carbene complexes (I)—(III) is $[M - Fc]^+$. Metastable transitions show that this ion arises in the usual manner [21] from $[MC(Fc)OR]^+$, but the greatly enhanced stability of the daughter compared to other systems may be a consequence of metal–metal interaction. The spectrum of the manganese complex, (V), shows a novel metal-extrusion process, in that the ion $[(\pi\text{-}C_5H_4Me)MnFc]^+$ (*m/e* 319) loses manganese to give $[MeC_5H_4{\cdot}Fc]^+$ (*m/e* 264; M^* 218·5). Additional peaks in the mass spectrum of (II) at *m/e* values greater than that of the molecular ion can be assigned to the olefin, $[FcC(OEt)]_2$, formed by dimerisation of the carbene ligand in the ion source.[22]

While the principal features of the fragmentation of the amino-carbene complex (VI) are very similar to those of the analogous compounds $[(CO)_5CrC(R)NH_2]$ (R = Me, Ph), those of the tertiary amino-complexes (VII)—(IX) are very different. Metastable transitions indicate that the fragmentation of $[M - C(Fc)NR_2]^+$ follows the path shown in the Scheme, to give $[Fc{\cdot}CH_2]^+$, the most abundant ion in the spectra of these complexes.

TABLE 5

Mass spectra of the complexes, $[(CO)_5MC(Fc)X]$

Complex		(I)	(II)	(III) [a]	(VI)	(VII)	(VIII)	(IX) [a]
	M	Cr	Cr	W	Cr	Cr	Cr	W
Ion	X	OMe	OEt	OEt	NH_2	NMe_2	NC_4H_8	NC_4H_8
$(CO)_5ML^+$		12 [b]	21	29	7			24
$(CO)_4ML^+$		19						
$(CO)_3ML^+$		15	33	21	14	20	11	54
$(CO)_2ML^+$		15	28	19	8	20	13	54
$(CO)ML^+$		25	45	46	19	20	16	28
ML^+		100	100	100	100	100	100	100
$MC(Fc)O^+$		13	21	119				
MFc^+		200	251	456				
$FeCH_2NR_2^+$						248	33	58
$FcCH_3N^+$						204	23	50
$FcCH_2N^+$					45			
$FcCN^+$					57			
$FcCH_2^+$					2	400	156	104
FcH^+		11	9	34	25	420	56	112
$FeC_5H_4CH_2^+$						80	19	25
$FeC_5H_5^+$		20	11	190	65	648	136	90

[a] Abundance based on ^{184}W. [b] Relative abundance in percent.

When the sample pressure of (VIII) in the ion source is allowed to increase, a number of peaks appear in a regular manner at *m/e* values greater than the molecular ion. The results, together with those for the complex $[(CO)_5CrC(Ph)NMe_2]$ are reported in Table 6.

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[21] J. Müller and J. A. Connor, *Chem. Ber.*, 1969, **102**, 1148.

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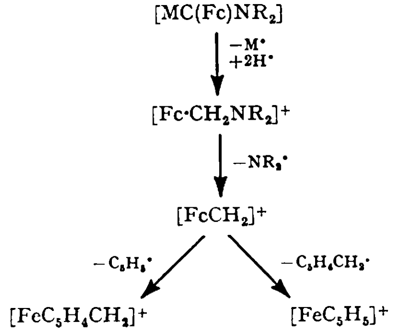
The ions are assigned to ion–molecule and ion–ion collisional complexes of the kind described recently in other organometallic compounds.[23] The same features are observed in the spectra of other compounds described here.



SCHEME

Following our preliminary report of certain aspects of this work,[24] the preparation and certain physical properties of (II) have been reported by others.[25] Their results are in complete agreement with ours where comparison is possible.

TABLE 6

Ion–molecule and ion–ion collisional complexes in the mass spectra of [(CO)$_5$CrC(NR$_2$)Y] compounds

Ion	R = Me Y = Ph	R = C$_4$H$_8$ Y = Fc
(CO)$_5$Cr$_2$L$_2$$^+$	12	
(CO)$_4$Cr$_2$L$_2$$^+$	14	11
(CO)$_3$Cr$_2$L$_2$$^+$	48	
(CO)$_2$Cr$_2$L$_2$$^+$	16	39
(CO)Cr$_2$L$_2$$^+$	83	
Cr$_2$L$_2$$^+$	100	100
L$_2$$^+$	270	1750
(L$_2$–NR$_2$)$^+$		8750
(CO)$_5$CrL$^+$	930	
(CO)$_3$CrL$^+$	1790	8500
CrL$^+$	6640	58000

Attempted Preparation of β-Ferrocenyl Carbene Complexes.—A number of unsuccessful attempts were made to prepare the compound [(CO)$_5$CrC(CH$_2$Fc)OMe]. The addition of ferrocenylmethyl lithium,[26] FcCH$_2$Li, to hexacarbonylchromium and alkylation of the resulting salt with Me$_3$O$^+$BF$_4$$^-$ gave 1,2-diferrocenylethane and FcCH$_2$OMe as the only iron-containing products.

Analogy with the successful preparation of benzyllithium from the reaction of butyl-lithiumtetramethylethylenediamine, BuLi–tmen, with toluene,[27] suggested that a similar reaction between BuLi–tmen and methylferrocene would afford FcCH$_2$Li. Accordingly, a solution containing BuLi, tmen, and FcMe (1 : 1 : 1) was added to hexacarbonylchromium in ether. In addition to unchanged methylferrocene, the products included *cis*-[(tmen)Cr(CO)$_4$] and, after alkylation, [(CO)$_5$CrC(OEt)Bu] together with a mixture of two isomeric methylferrocenyl carbene complexes [(CO)$_5$CrC(OEt){C$_{10}$H$_8$(Me)Fe}]. Attempts to separate the mixture have not been successful.

The reaction between the salt, Me$_4$N[(CO)$_5$CrC(O)Fc], and an excess of tmen in methylene chloride at reflux gives *cis*-[(tmen)Cr(CO)$_4$] in good yield. This reaction is similar to that between R$_4$N[(CO)$_5$CrCl] and tmen which is usually used for the preparation of *cis*-[(diamine)Cr(CO)$_4$] compounds.[17] It suggests that the use of aminelithium reagents for the preparation of carbene complexes of metal carbonyls will usually be accompanied by the formation of amine-substituted products.

Reaction of (π-C$_5$H$_5$)M(CO)$_n$ *with Organolithium Reagents.*—Attempts to prepare the complexes (π-C$_5$H$_5$)Co(CO)[C(Fc)OR] and (π-C$_5$H$_5$)V(CO)$_3$[C(Fc)OR] from the reaction of FcLi with (π-C$_5$H$_5$)Co(CO)$_2$ and (π-C$_5$H$_5$)V(CO)$_4$ respectively, followed by alkylation were unsuccessful. In each case ferrocene together with the starting material were recovered. This is in marked contrast to the reactivity of (π-C$_5$H$_4$Me)Mn(CO)$_3$ described earlier. It has been suggested that the susceptibility of coordinated carbon monoxide to nucleophilic attack may be determined by the force constant, k, of the group, attack occurring when $k > 1530$ N m^{-1}.[28] This arbitrary distinction has been contradicted by the recent report of a carbene complex derived from [mesitylene Cr(CO)$_3$] ($k = 1497$ N m^{-1}).[29] We find that BuLi reacts with (π-C$_5$H$_5$)V(CO)$_4$ ($k = 1490$ N m^{-1}) and with (π-C$_5$H$_5$)Co(CO)$_2$ to give deeply coloured solids which have so far eluded characterisation because they decompose very rapidly in aqueous solution during attempts either to isolate the salt product or to alkylate the same.

General Conclusions.—The presence of a ferrocenyl group adjacent to the carbene carbon atom leads to significant changes in the physical properties of metal–carbene complexes when these are compared with those of carbene complexes containing simple organic substituents. The i.r. spectra show the ferrocenyl group to be a strong electron donor and this is substantiated by the electronic spectra. The n.m.r. spectra indicate that this donation is principally a resonance interaction with the empty p_z orbital on the carbene carbon atom. These results imply that the carbene ligand, [C(Fc)X] (X = OR, NR$_2$), is a poor π-acceptor, a conclusion which is also supported by electrochemical measurements.[30] The mass spectra show remarkable changes

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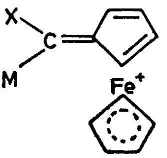
in both fragmentation and abundance from those encountered for carbene complexes previously, many of which changes are attributable to stabilisation gained by the presence of the ferrocenyl group.

These observations show that when a ferrocenyl group is present, the resonance canonical form (Figure) must contribute to the representation of the carbene complex. This structure is very similar to others which have been discussed in connection with the properties of α-ferrocenylcarbonium ions. The dominance of a resonance interaction between the ferrocenyl group and the carbene carbon atom might indicate support for vertical stabilisation[31] of the carbocationic centre by the ferrocenyl group.



FIGURE

Catalytic Activity of the Complexes.—Some of the compounds described here have been tested for their catalytic activity, especially in hydrogenation reactions. Under standard conditions (100 °C/180 atm. H_2/dioxan), the most active system studied, (I), was found to catalyse the hydrogenation of a variety of simple amides and nitriles to give amines. Internal olefins were not reduced. The activity of the catalyst was reduced when an amino-substituent, as in (VII), replaced the alkoxy-substituent. Changing the metal from chromium to tungsten, (III), removed all activity as a catalyst in these reactions. Under similar conditions, both ferrocene and [(arene)Cr(CO)$_3$] compounds are inactive. The observed behaviour is to be contrasted with that of Raney nickel which requires both higher temperature and higher pressure.

EXPERIMENTAL

Materials and Methods.—These were similar to those described earlier.[17] In addition, bromoferrocene was prepared from ferrocenylmercury chloride.[32] Chromatographic purification of the crude product was found to be unnecessary; a solution of the orange oil in light petroleum, when allowed to evaporate slowly to dryness gave a pure brown crystalline product, m.p. 30—32° (lit.[32] 31—32°), yield 66% (lit.,[32] 57%).

[*Ferrocenyl(methoxy)carbene*]*pentacarbonylchromium*, (I).—A suspension of ferrocenyl-lithium, prepared from the reaction between ferrocenylmercury chloride (4·20 g, 10 mmol) and n-butyl-lithium (20 mmol) in hexane,[6] was added dropwise to a stirred solution of hexacarbonylchromium (2·10 g, 10 mmol) in diethyl ether (250 ml) at room temperature during 0·5 h. The resulting dark brown mixture was refluxed for a further 2 h. The solvent was removed under reduced pressure to give a brown oil. Repeated washing of this oil with hexane (3 × 50 ml) to remove dibutylmercury gave a brown powder on removal of the solvent. The brown powder was dissolved in water (75 ml) and solid trimethyloxonium tetrafluoroborate (1·63 g, 1 mmol) was added to the solution. The aqueous solution was extracted with ether (4 × 50 ml) and the ethereal extracts were combined and dried (Na_2SO_4); finally the organic solvent was removed under reduced pressure. Recrystallisation of the residue from ether–hexane (3 : 1 v/v) gave deep purple *crystals* of (I), m.p. 134—135° (dec) (1·95 g, 4·7 mmol, 47% based in FcHgCl) [Found ($C_{17}H_{12}CrFeO_6$ requires): C, 48·8 (48·6); H, 3·1 (2·9); Cr, 12·5% (12·4)], $\nu_{max.}$ (hexane) 2059m, 1980w, 1940s, and 1953vs; $\nu_{max.}$ (CS_2–$CHCl_3$) 2955m, 1430m, 1378m, 1322m, 1260s, and 1220s cm^{-1}; δ ($CDCl_3$) 4·67 (3H, s, CH_3) p.p.m.

[*Ethoxy(ferrocenyl)carbene*]*pentacarbonylchromium*, (II).—A similar procedure to that described for the preparation of (I), with the exception that triethyloxonium tetrafluoroborate (2·1 g, 11 mmol) was used, produced purple needles of (II) (2·0 g, 4·6 mmol, 47% based on FcHgCl), m.p. 129—130° (lit.,[25] m.p. 129°), $\nu_{max.}$ (hexane) 2056m, 1977w, 1938s, 1949vs; $\nu_{max.}$ (CS_2) 1260s, 1220s, 1200s, 1064s, 1044s, 831s cm^{-1}; δ ($CDCl_3$) 2·58 (3H, t, CH_3) and 5·03 (2H, q, CH_2) p.p.m.

[*Amino(ferrocenyl)carbene*]*pentacarbonylchromium*, (VI).—Ammonia was bubbled through a stirred solution of (I) (0·67 g, 1·6 mmol) in ether (50 ml) at room temperature until the solution became orange (*ca.* 5 min). Orange-red *crystals* of (VI) were obtained from ether–hexane (3 : 1 v/v) (0·51 g. 1·25 mmol, 78%), m.p. 153—154° (dec) [Found ($C_{16}H_{11}CrFeNO_5$ requires) C, 47·7 (47·4); H, 2·8 (2·7); N, 3·4 (3·5); Cr, 12·7% (12·8)]; $\nu_{max.}$ (hexane); 2058m, 1974w, 1942s, and 1934vs; $\nu_{max.}$ (CS_2/$CHCl_3$) 3450m, 1630s, 1520m, 1250m, 1110m, and 1042m cm^{-1}; δ ($CDCl_3$) 8·14 (2H, s, NH_2) p.p.m.

[*Dimethylamino(ferrocenyl)carbene*]*pentacarbonylchromium*, (VII).—Freshly distilled dimethylamine (1 ml) was added to a solution of (I) (0·17 g, 0·4 mmol) in ether (50 ml) at 0°. Reaction was complete after 1 week. Orange-red *crystals* of (VII) were obtained from ether–hexane (3 : 1 v/v) (0·11 g, 0·26 mmol, 65%), m.p. 107—108° [Found ($C_{18}H_{15}CrFeNO_5$ requires): C, 49·9 (49·9), H 3·6 (3·5), N 3·4 (3·2), Fe 13·3% (12·9)]; $\nu_{max.}$ (hexane) 2055m, 1971w, 1932s, and 1923vs; $\nu_{max.}$ (CS_2/$CHCl_3$) 3095m, 1660m, 1515m, 1450m, 1390m, and 1235s cm^{-1}.

[*Ferrocenyl(1-pyrrolidinyl)carbene*]*pentacarbonylchromium*, (VIII).—Freshly distilled pyrrolidine (1 ml) was stirred at room temperature with a solution of (I) (0·3 g, 0·7 mmol) in ether (25 ml) for 5 h. Orange *crystals* of (VIII) were obtained from ether–hexane (3 : 1 v/v) (0·16 g, 0·33 mmol, 50%), m.p. 132—133° (dec) [Found ($C_{20}H_{17}CrFeNO_5$ requires): C 52·3 (52·3), H 3·8 (3·7), N 2·9 (3·0), Cr 11·1 (11·3), Fe 12·3% (12·2)]; $\nu_{max.}$ (hexane) 2053m, 1969w, 1930s, 1918 vs; $\nu_{max.}$ (CS_2/$CHCl_3$) 2975m, 2875m, 1485m, 1445m, 1225s, 1115s cm^{-1}; δ ($CDCl_3$) 2·10 (4H, m, CH_2-β), 4·23 [2H, s, α-CH_2 (*cis* to Fc)], 4·31 [2H, s, α-CH_2 (*trans* to Fc)] p.p.m.

[*Ethoxy(ferrocenyl)carbene*]*pentacarbonyltungsten*, (III).—This complex was prepared by the procedure described for (II) and isolated as dark brown *needles* of (III) from ether–hexane (3:1 v/v), yield 40% based on FcHgCl, m.p. 155—156° [Found ($C_{18}H_{14}FeO_6W$ requires) C, 38·4 (38·2); H, 2·2 (2·5); Fe, 10·1 (9·9); W, 32·0% (32·5)] $\nu_{max.}$ (hexane) 2066m, 1976w, 1936s, and 1948vs; $\nu_{max.}$ (CS_2/$CHCl_2$) 1430m,

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[31] T. G. Traylor, W. Hanstein, H. J. Berwin, N. A. Clinton, and R. S. Brown, *J. Amer. Chem. Soc.*, 1971, **93**, 5715.

[32] R. W. Fish and M. Rosenblum, *J. Org. Chem.*, 1965, **30**, 1253.

1380m, 1325m, 1240s, 1220s, 1195s cm^{-1}; δ 2·58 (3H, t, CH_3), 4·85 p.p.m. (2H, q, CH_2).

Tetramethylammonium[*ferrocenyl*(*oxido*)*carbene*]*pentacarbonyltungsten*, (IV).—The brown solid (1·8 g, 2·8 mmol) obtained from the reaction of hexacarbonyltungsten (1·7 g, 4·7 mmol) and ferrocenyl-lithium was dissolved in water (15 ml). A saturated solution of Me_4NBr (1 g, 6·5 mmol) in water (2 ml) was added to it, causing precipitation of a brown oil. The oil was isolated, mixed with methylene chloride (20 ml), filtered, and reprecipitated as an oil by addition of hexane (50 ml). Removal of the solvent under reduced pressure followed by extensive trituration resulted in solidification. The reprecipitation process was repeated to give (IV) as a brown *powder* (0·65 g, 1·1 mmol, 24% based on FcHgCl), m.p. 105—106° (dec) [Found ($C_{20}H_{21}FeNO_6W$ requires) C, 39·1 (39·3); H, 3·5 (3·4); N, 2·1 (2·3); W, 29·7 (30·0)]; $\nu_{max.}$ (CH_2Cl_2); 2044m, 1898s, and 1874s; $\nu_{max.}$ (Nujol/HCB) 3400m, 3025m, 2920m, 1490m, 1202s, and 1183s cm^{-1}.

[*Ferrocenyl*(*pyrrolidin*-1-*yl*)*carbene*]*pentacarbonyltungsten*, (IX).—Acetyl chloride (0·055 g, 0·7 mmol) in methylene chloride (3 ml) was added dropwise to a stirred solution of (IV) (0·2 g, 0·3 mmol) in methylene chloride (70 ml). The solution immediately became green, affording a green solid on removal of the solvent. The green solid was dissolved in ether (50 ml) and filtered; pyrrolidine (0·05 g, 7 mmol) in ether (25 ml) was added dropwise to the stirred solution. Removal of the solvent under reduced pressure from the resulting solution gave a brown solid. This was clarified by chromatography on alumina (Grade III, 15 × 3 cm, C_6H_6) to give a red eluate. The eluate was separated by fractional crystallisation of the residue, after evaporation of the solvent, with hexane and gave deep red *crystals* of (IX) {(57 mg, 0·097 mmol, 29%) m.p. 146—147° (dec) Found ($C_{20}H_{17}FeNO_5W$ requires) C, 40·6 (40·6); H, 2·6 (2·9); N, 2·7% (2·4) $\nu_{max.}$ (hexane) 2062m, 1967w, 1932s, and 1923vs; $\nu_{max.}$ ($CS_2/CHCl_3$) 2970m, 1485m, 1445s, 1255m, 1228s, and 1109s cm^{-1}; δ ($CHCl_3$) 2·10 (4H, m, β-CH_2), 5·84 (4H, m, α-CH_2, partly obscured by $-C_5H_5$ resonance) p.p.m.} and yellow *crystals* of 1-*pyrrolidin*-1-*ylpentacarbonyltungsten* (29 mg, 0·073 mmol 24%) m.p. 78—79° (dec): [Found ($C_9H_8NO_5W$ requires): C, 27·6 (27·4); H, 2·6 (2·3); N, 3·5 (3·6)%]; $\nu_{max.}$ (hexane) 2073m, 1932s, and 1921m; $\nu_{max.}$ ($CS_2/CHCl_3$) 3250w, 1605w, 1212m, and 902m cm^{-1}.

[*Ferrocenyl*(*methoxy*)*carbene*]*methylcyclopentadienyldicarbonylmanganese*, (V).—A suspension of ferrocenyl-lithium (20 mmol) was added dropwise during 1 h to [(π-C_5H_4Me)$Mn(CO)_3$] (4·5 g, 20 mmol) in diethyl ether (250 ml). After 3 h at reflux a dark brown solution was obtained which afforded a red oil on removal of the solvent. Repeated washing with hexane (3 × 50 ml) left a highly air-sensitive red-brown powder. This powder was alkylated in aqueous solution (50 ml) with solid $Me_3O^+BF_4^-$

crystals of (V) (0·5 g, 1·2 mmol, 6% based on Mn), m.p. 53—54° [Found ($C_{20}H_{19}FeMnO_3$ requires) C, 57·5 (57·5); H, 4·6 (4·5); Mn, 13·0 (13·0)%]; $\nu_{max.}$ (hexane) 1938 and 1879s; $\nu_{max.}$ ($CS_2/CHCl_3$) 3095m, 1460m, 1430m, 1250s, 1212s, and 1191vs cm^{-1}; δ ($CHCl_3$) 1·72 (3H, t, C–CH_3), 4·19 2H, t, $H_{2,5}$), 4·30 (2H, t, $H_{3,4}$), and 4·53 p.p.m. (3H, s, O–CH_3); mass spectrum (*m*/*e*, *I*): 418, 12; 362, 54; 319, 100; 264, 31; 186, 14; 121, 19.

Attempted Preparations of [*Ferrocenylmethyl*(*methoxy*)*carbene*]*pentacarbonylchromium*.—(*a*) A solution of ferrocenylmethyl-lithium, prepared [26] from $FcCH_2OMe$ (1·75 g, 7·6 mmol) and lithium shot (1·4 g, 200 mmol) in THF, was filtered (G3) and added dropwise to hexacarbonylchromium (1·75 g, 8 mmol) in ether (150 ml). The mixture was refluxed for 2 h, after which time the solvent was removed *in vacuo* to give a brown oil. Methylation ($Me_3O^+BF_4^-$) in aqueous solution followed by extraction of the products with hexane–ether (150 ml; 2 : 1 v/v) gave a brown oil on removal of the solvent. Chromatography of a benzene solution of the oil on alumina (Grade III, 150 × 2 cm, hexane) gave two fractions which were shown to be 1,2-*diferrocenylethane* [(0·54 g), m.p. 190—192 (lit.,[33] 192°); mass spectrum (*m*/*e*, %): 398, 14 (M^+); 334, 4; 245, 4; 230, 10; 200, 10; 200, 100; 199, 93, 186, 18; 134, 38; 121, 66] together with $FcCH_2OMe$ (0·91 g, 52% recovery).

(*b*) Butyl-lithium (5·6 mmol in hexane) was added to *NNN'N'*-tetramethylethylenediamine (0·65 g, 5·6 mmol) in hexane (20 ml). The solution was stirred for 5 min and methylferrocene [34] (1·14 g, 5·7 mmol) in hexane (10 ml) was added to it. The mixture was stirred for 3 h and the resulting deep red solution was added dropwise to hexacarbonylchromium (1·25 g, 5·6 mmol) in ether (150 ml). The mixture was refluxed for 1 h, and the solvent was then removed *in vacuo* giving a brown oil which was subsequently washed with hexane (3 × 30 ml). The hexane extracts were shown to contain unchanged methylferrocene (0·5 g, 2·5 mmol, 45% recovery) and [(tmen)$Cr(CO)_4$]. The brown oily material which was insoluble in hexane was mixed with methylene chloride (100 ml) and alkylated ($Et_3O^+BF_4^-$). Evaporation of the solvent and dissolution of the residue in ether gave a dark red solution which was filtered and once again evaporated. The resulting dark red oil was mixed with benzene and chromatographed (alumina Grade III; 150 × 2 cm). Elution with hexane produced one yellow fraction which was shown to be [$(CO)_5CrC(OEt)Bu$] (0·15 g, 0·51 mmol) (i.r. and mass spectrum). Elution with hexane–benzene (10 : 1 v/v) provided a dark red fraction. Attempted crystallisation of the resulting red oil from cold pentane was not successful (0·11 g). The material was identified as [(*ethoxy*)-*methylferrocenylcarbene*]*pentacarbonylchromium* on the following evidence; mass spectrum (*m*/*e*, %): 448, 10(M^+); 392, 21; 364, 22; 336, 15; 308, 40; 279, 10; 251, 100 requires): C, 49·8 (50·1); H, 4·6 (4·4); N, 2·9 (2·9); Fe, 12·0% (11·7)].

Reaction of (X) *with NNN'N'-Tetramethylethylenediamine.*—The brown salt, (X) (0·26 g, 0·53 mmol) was dissolved in methylene chloride (150 ml) and tmen (2 g, 17 mmol) was added to the solution. The mixture was refluxed for 3 h after which time the solvent was evaporated. The residual pale orange solid was extracted with ether and the resulting solution was filtered. Evaporation of the ether left an orange oil which was crystallised from methanol–water (3 : 1 v/v) to give yellow plates of [(tmen)Cr(CO)$_4$] (83 mg, 0·31 mmol, 58%), m.p. 227° (dec) [lit.,[17] 228° (dec)]. I.r. spectrum identical with standard material.

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