Paramagnetic Carbenemetal Complexes. Part 1. Cationic Chromium(I) Complexes and the Chemistry of their Chromium(0) Precursors and of Related Molybdenum(0) and Tungsten(0) Complexes, especially with Bulky Carbene Ligands $C(OR')R$ [$R = CH(SiMe_3)_2$ or CH_2SiMe_3]

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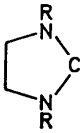
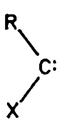
Carbenemetal complexes having bulky alkyl substituents at $C_{carb.}$, $[M(CO)_5\{C(OR')R\}]$ [M = Cr, Mo, or W; R = CH_2CMe_3, CH_2SiMe_3, or $CH(SiMe_3)_2$; R' = Me, Et, or $SiMe_3$], are reported; a noteworthy feature is the good thermal stability of the molybdenum(0) complexes. Photolysis of $[Cr(CO)_5L]$ [L = $C(OEt)CH(SiMe_3)_2$ or $\overline{\mathrm{CN(Et)CH_2CH_2N}}\mathrm{Et}$ (abbreviated as L^{Et})] in the presence of $P(OPh)_3$, dmpe, or dppe yields *fac*-$[Cr(CO)_3(L)L'_2]$ [L' = $P(OPh)_3$ or $L'_2 = Me_2P(CH_2)_2PMe_2$ (dmpe) or $Ph_2P(CH_2)_2PPh_2$ (dppe)]. Addition of $Ag[BF_4]$ to the latter in CH_2Cl_2 affords $[Cr(CO)_3(L)L'_2]^+$, characterised by e.s.r. spectroscopy. The dmpe complex with L = L^{Et} is stable at ambient temperature [unlike the other two chromium(I) analogues] and is well characterised, m.p. 95 °C, as is $[Cr(CO)_3\{C(OEt)CH(SiMe_3)_2\}(dmpe)][BF_4]$. The g_{av} factors for the 10 new chromium(I) salts are *ca.* 2.02 which suggests that significant unpaired spin is delocalised away from the metal, consistent with the low ^{53}Cr isotropic hyperfine coupling constant (*ca.* 1.3 mT). Detailed i.r., ^1H and ^{13}C n.m.r., and He(I) photoelectron spectroscopic, as well as mass spectrometric, data are described for the carbenemetal(0) complexes.

DESPITE the substantial literature now available on carbenemetal complexes,[1] a field first recognised in 1964 with the synthesis of $[W(CO)_5\{C(OPh)Me\}]$,[2] stable (at >20 °C) paramagnetic derivatives were unknown until 1977 when we briefly reported on some low-spin d^7 iron(I) complexes.[3] Compounds of this class are of interest because they allow specific physicochemical techniques to be applied, especially e.s.r. spectroscopy and paramagnetic susceptibility, which may contribute to an understanding of the nature of the $M-C_{carb.}$ bond. The synthesis of the stable carbeneiron(I) complexes, using ligands of type (A) (abbreviated as L^R), suggests that a wider range of unusual paramagnetic metal complexes may become accessible as their L^R-stabilised derivatives. It is a principal objective of the present series to explore this proposition. In the present paper much emphasis is, however, on diamagnetic precursors, especially those having bulky carbene ligands.

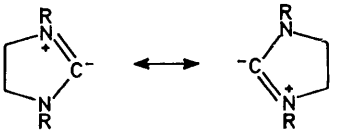


(A) (L^R)

We have previously published extensively on diamagnetic L^R complexes of Cr^0, Mo^0, Mo^{II}, W^0, W^{II}, Mn^I, Fe^0, Fe^{II}, Ru^0, Ru^{II}, Os^{II}, Co^I, Rh^I, Rh^{III}, Ir^I, Ni^0, Ni^{II}, Pd^{II}, Pt^{II}, and Au^I.[4] It is clear that such complexes derived from the carbene ligand (A) are generally much more stable than from type (B) (especially with X = OR', NR'_2, or NHR') (which we term Fischer-type carbenes), no doubt because of the more extensive π delocalisation in the former, (C).



(B)



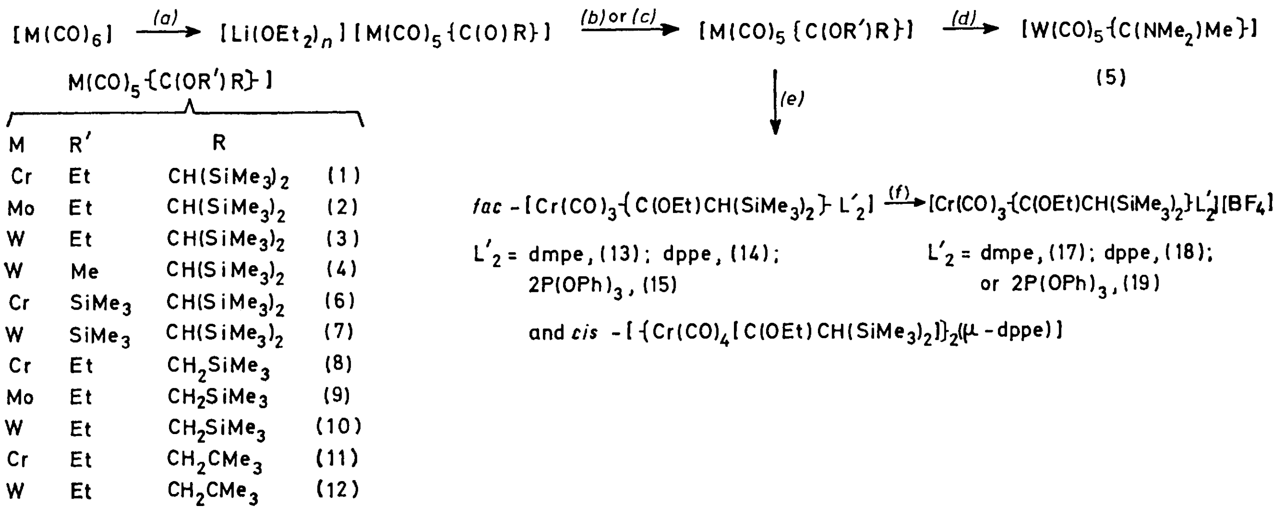
(C)

Fischer-type carbenemetal(0) complexes of chromium or tungsten of formula $[M(CO)_5L]$ (M = Cr or W, L = a carbene ligand) have received much attention. In contrast, the molybdenum analogues are sparsely documented, because of their much greater lability.

RESULTS AND DISCUSSION

Chromium(0), *Molybdenum*(0), *and Tungsten*(0) *Complexes*.—We now report the synthesis and chemical and spectroscopic characterisation of (*i*) new Fischer-type carbenemetal complexes $[M(CO)_5\{C(OR')R\}]$ (M = Cr, Mo, or W) in which R is the bulky group CH_2CMe_3, CH_2SiMe_3, or $CH(SiMe_3)_2$ (Scheme 1), and (*ii*) complexes $[Cr(CO)_3(L)L'_2]$ [L' = $P(OPh)_3$ or $L'_2 = Me_2P(CH_2)_2PMe_2$ (dmpe) or $Ph_2P(CH_2)_2PPh_2$ (dppe); L = a carbene ligand including C(OR')R or L^R] (Scheme 2). Additionally, (*iii*), the oxidation of the chromium(0) complexes is described whereby novel stable paramagnetic carbenechromium(I) complexes $[Cr(CO)_3(L)L'_2]^+$ are obtained (Scheme 2).

The Fischer-type carbenemetal complexes $[M(CO)_5\{C(OR')R\}]$ (M = Cr, Mo, or W) (1)—(4) and (6)—(12) were prepared by standard procedures (Scheme 1). They are readily soluble in pentane, crystallisation at low temperature affording materials which are (at ambient temperature) yellow crystals [R' = Me, Et, or $SiMe_3$; R = $CH(SiMe_3)_2$] or oils (R' = Et, R = CH_2SiMe_3 or CH_2CMe_3). Corresponding electron-rich olefin-derived complexes $[M(CO)_5L^{Et}]$ [M = Cr, Mo, or W, L^{Et} = $\overline{\mathrm{CN(Et)CH_2CH_2N}}\mathrm{Et}$] have been previously reported.[5] The thermal stabilities of the various metal(0) complexes $[M(CO)_5L]$ decrease in the following sequences (and these parallel the yields obtained): (*i*) M = W > Cr > Mo, and (*ii*) L = L^{Et} > $C(OEt)CH(SiMe_3)_2$ ≫ $C(OEt)CH_2SiMe_3$ > $C(OEt)CH_2CMe_3$ > $C(OSiMe_3)CH(SiMe_3)_2$.



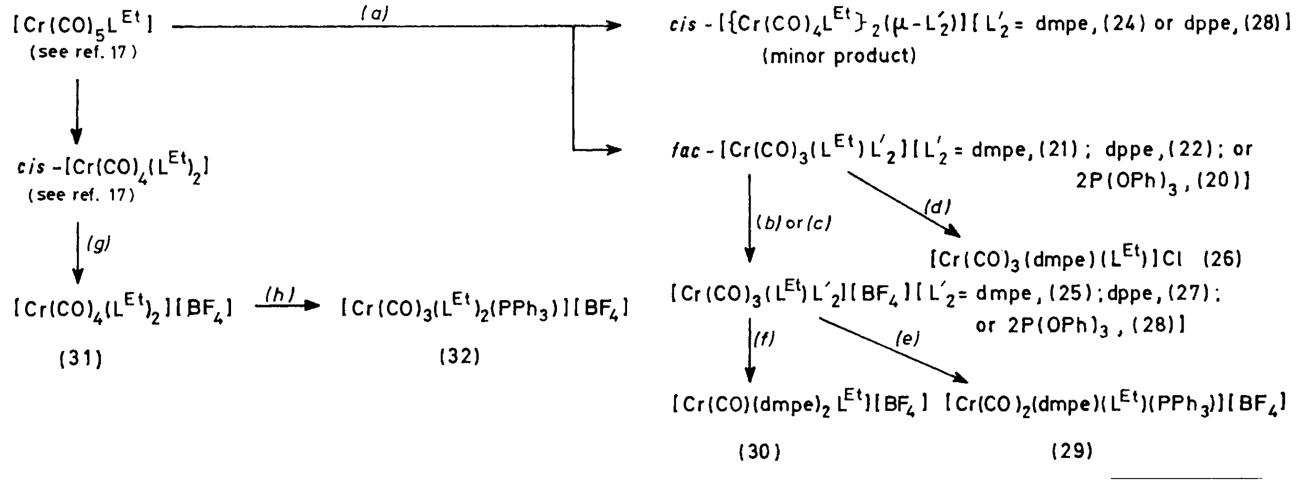
SCHEME 1 Synthetic routes to complexes of Cr^0 and Cr^I containing bulky carbene ligands of the Fischer type. (*a*) OEt_2, LiR [R = $CH(SiMe_3)_2$, CH_2SiMe_3, or CH_2CMe_3], 25 °C; (*b*) OEt_2–CH_2Cl_2, $[OEt_3][BF_4]$ or $SFO_2(OMe)$ (R′ = Et or Me), 0 °C; (*c*) OEt_2, $SiMe_3Cl$ (R′ = $SiMe_3$), −30 °C; (*d*) C_6H_6, 5 °C, $NHMe_2$; (*e*) C_6H_{14}, *hν*, 11 h, L'_2 = dppe, dmpe, or $2P(OPh)_3$, 20 °C; (*f*) CH_2Cl_2, 0 °C (L'_2 = dmpe), −30 °C (L'_2 = dppe), $Ag[BF_4]$

Analytical (Table 1) and/or spectroscopic data (Tables 2—7) for the new complexes are consistent with their formulations.

When R = $CH(SiMe_3)_2$ the carbenemetal complexes $[M(CO)_5\{C(OR')R\}]$ are the most stable. This has allowed the preparation and full characterisation of $[Mo(CO)_5\{C(OEt)CH(SiMe_3)_2\}]$. Previously only the very labile Fischer-type pentacarbonyl(carbene)molybdenum(0) complexes $[Mo(CO)_5\{C(OPh)R\}]$ (R = Me or Ph) [6] and two molybdenum(0) complexes having the secondary carbene ligand [7] $C(NMe_2)H$ had been described; [5] electron-rich olefin-derived analogues $[Mo(CO)_5L^R]$ (R = Me, Et, Bu^n, or CH_2Ph) are much more inert.[5] However, the relatively stable substituted derivatives *cis*-$[Mo(CO)_4\{C(OMe)Me\}(PPh_3)]$ [8] and *cis*-$[Mo(CO)_4\{C(OMe)Me\}L^{Me}]$ [5] are known. Recently the preparation of the compounds $[Mo(CO)_5\{C(OR')(SiPh_3)\}]$ (R′ = Me or Et), which are somewhat less labile than $[Mo(CO)_5\{C(OMe)Me\}]$, was reported.[9]

The enhanced stability of $[M(CO)_5\{C(OR')R\}]$ when R = $CH(SiMe_3)_2$ may reflect the difficulty of associative decomposition pathways. Consistent with this is the reduced sensitivity to aerobic or aqueous attack. The stability of the electron-rich olefin-derived complexes $[M(CO)_5L^R]$ has been considered to be thermodynamic in origin.[5] The complexes $[M(CO)_5\{C(OEt)CH_2SiMe_3\}]$ (M = Mo or W), (9) and (10), are sensitive to water, hydrolysing at room temperature giving (by ^1H n.m.r. spectroscopy) the known $[M(CO)_5\{C(OEt)Me\}]$.[10] This is in accord with the ready ethanolysis and aminolysis of $[Cr(CO)_5\{C(OEt)CH_2SiMe_3\}]$ (8), yielding $[Cr(CO)_5\{C(OEt)Me\}]$ and $[Cr(CO)_5\{C(NH_2)Me\}]$, respectively.[11]

The ^1H n.m.r. spectroscopic data (simple first-order spectra) for the new complexes are given in Table



SCHEME 2 Synthetic routes to chromium(0) and chromium(I) complexes containing the carbene ligand L^{Et} = $\overline{CN(Et)CH_2CH_2N}Et$. (*a*) Hexane, *hν*, 8 h, L'_2 = dmpe, dppe, or $2P(OPh)_3$, 20 °C; (*b*) thf or CH_2Cl_2, L'_2 = dmpe, 5 °C, $Ag[BF_4]$; (*c*) CH_2Cl_2, L'_2 = dppe or $2P(OPh)_3$, −40 °C, $Ag[BF_4]$; (*d*) CH_2Cl_2, −20 °C, CCl_4; (*e*) CH_2Cl_2, PPh_3, *hν*, 0 °C; (*f*) CH_2Cl_2, 24 h, 25 °C; (*g*) CH_2Cl_2, $Ag[BF_4]$, −50 °C; (*h*) CH_2Cl_2, PPh_3, −40 °C

TABLE 1

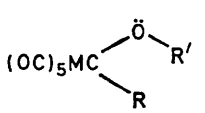
Analytical data for some carbene complexes [a] of Cr^0, Cr^I, Mo^0, and W^0

Complex	M.p. (θ_c/°C)	Yield (%)	Colour	Analysis (%) [b] C	H	N
(1) $[Cr(CO)_5\{C(OEt)CH(SiMe_3)_2\}]$	42—44	60	Yellow	44.1 (44.1)	5.8 (5.9)	
(2) $[Mo(CO)_5\{C(OEt)CH(SiMe_3)_2\}]$	44—46	42	Yellow	39.6 (39.9)	5.3 (5.3)	
(3) $[W(CO)_5\{C(OEt)CH(SiMe_3)_2\}]$	43—45	90	Yellow	33.9 (33.4)	4.8 (4.5)	
(4) $[W(CO)_5\{C(OMe)CH(SiMe_3)_2\}]$	71—72	86	Yellow	32.2 (32.0)	4.1 (4.2)	
(5) $[W(CO)_5\{C(NMe_2)Me\}]$	61—62	90	Yellow	27.3 (27.3)	2.4 (2.3)	3.5 (3.5)
(6) $[Cr(CO)_5\{C(OSiMe_3)CH(SiMe_3)_2\}]$	135—140 (decomp.)	84	Yellow	42.1 (42.5)	6.2 (6.2)	
(7) $[W(CO)_5\{C(OSiMe_3)CH(SiMe_3)_2\}]$	152—155 (decomp.)	87	Yellow	31.9 (32.9)	5.0 (4.8)	
(20) *fac*-$[Cr(CO)_3(L^{Et})\{P(OPh)_3\}_2]$ [c]	126—129	65	White	62.7 (62.6)	5.4 (5.0)	2.9 (3.1)
(21) *fac*-$[Cr(CO)_3(dmpe)(L^{Et})]$ [c]	135—140	70	Yellow	46.4 (46.6)	6.9 (7.3)	6.8 (6.8)
(22) *fac*-$[Cr(CO)_3(dppe)(L^{Et})]$ [c]	>155 (slow decomp.)	70	Cream	65.5 (65.5)	5.8 (5.8)	4.0 (4.2)
(25) $[Cr(CO)_3(dmpe)(L^{Et})][BF_4]$ [c]	95	90	Dark golden yellow	37.7 (38.5)	5.7 (6.0)	5.5 (5.6)

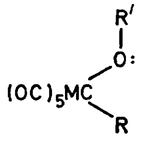
[a] Other complexes were characterised solely by ^1H n.m.r., i.r., e.s.r., or ^{13}C n.m.r. spectroscopic data. [b] Calculated values are given in parentheses. [c] L^{Et} = $\overline{\text{CN(Et)CH}_2\text{CH}_2\text{N}}\text{Et}$, dmpe = $(Me_2PCH_2)_2$, dppe = $(Ph_2PCH_2)_2$.

2(*a*) and 2(*b*). The chemical shifts of the protons of the co-ordinated carbene appear to be independent of the metal. However, the CH proton when R = C*H*$(SiMe_3)_2$ in $[M(CO)_5\{C(OR')R\}]$ is deshielded by τ *ca.* 1.0 compared with the CH_2 protons when R = CH_2SiMe_3 or CH_2CMe_3. For complexes $[M(CO)_5\{C(OSiMe_3)R\}]$ [R = $CH(SiMe_3)_2$, M = Cr or W], (6) or (7), two sharp $SiMe_3$ singlets are observed, the $OSiMe_3$ resonance being τ *ca.* 0.3 to lower field than those of $CH(SiMe_3)_2$, and the unique CH proton is deshielded by τ *ca.* 0.7 compared with the OEt analogues. These values may be compared with the somewhat higher shifts (M = Cr, τ 10.0; M = W, τ 10.12) for the $OSiMe_3$ methyls in $[M(CO)_5\{C(OSiMe_3)Me\}]$.[12]

The high double-bond character of the $C_{carb.}$–O bond in carbene–metal complexes of the type $[M(CO)_5\{C(OR')R\}]$ has been the subject of much spectroscopic investigation.[13] The Me signals observed for $[Cr(CO)_5\{C(OMe)Me\}]$ at 40 °C in $(CD_3)_2CO$ broaden upon cooling and, at −40 °C, resolve into two pairs of sharp singlets, each pair corresponding to one of the *cis* and *trans* isomers, (D) and (E).[14] A detailed variable-temperature ^1H n.m.r. spectroscopic study has shown[15] that steric



(D) (*cis*)



(E) (*trans*)

rather than electronic effects of R are more important in determining the coalescence temperature (T_c) for such *cis* $\rightleftharpoons$ *trans* isomerisations; for example in $[Cr(CO)_5\{C(OMe)(C_6H_2Me_3\text{-}2,4,6)\}]$ T_c is 36 °C. Variable-temperature ^1H n.m.r. experiments on the new complexes

TABLE 2

Hydrogen-1 n.m.r. data for new carbenemetal complexes

(*a*) Complexes containing a [C(OR')R] ligand [a]

Complex	OCH_2	OCH_2CH_3	–CH–	$Si(CH_3)_3$	$-CH_2-$	Others
(1)	5.15 (q)	8.74 (t)	5.67	9.77		
(2)	5.25 (q)	8.73 (t)	5.67	9.77		
(3)	5.37 (q)	8.88 (t)	5.70	9.78		
(4)			5.64	9.77		5.84 (OCH_3)
(5)						6.62 (*cis*-NCH_3), 6.10 (*trans*-NCH_3), 7.17 (CCH_3)
(6)			5.00	9.68		9.32 $[OSi(CH_3)_3]$
(7)			5.10	9.67		9.37 $[OSi(CH_3)_3]$
(8)	5.37 (q)	8.88 (t)		9.85	6.65	
(9)	5.37 (q)	8.77 (t)		9.85	6.65	
(10)	5.37 (q)	8.67 (t)		9.85	6.63	
(11)	5.15 (q)	8.78 (t)			6.67	8.98 $[C(CH_3)_3]$
(12)	5.38 (q)	8.80 (t)			6.80	8.97 $[C(CH_3)_3]$

(*b*) Carbenechromium(0) complexes containing the L^{Et} ligand [b]

Complex	Solvent	NCH_2CH_3	Ring CH_2	NCH_2CH_3	Resonances due to L'_2 ligand(s)
(20)	C_6H_6	6.1 (q)	7.6	8.9 (t)	*c*
(21)	C_6H_6	6.0 (q)	7.1	8.8 (t)	8.4—9.1 (m)
(22)	CH_2Cl_2	6.5 (m)	6.65 (br)	9.05 (t) [d]	2.7, 7.7 (m)
(24)	C_6H_6	6.2 (q)	7.2	8.8 (t)	8.4—9.1 (m)

[a] Spectra obtained at 30 °C, C_6D_6 solvent (reference C_6H_6, τ 2.73); values quoted in τ. All resonances singlets unless stated: q = quartet, t = triplet. [b] All resonances, quoted in τ using the solvent resonance as standard, were singlets unless stated: q = quartet, t = triplet, m = multiplet or complex, br = broad. L^{Et} = $\overline{\text{CN(Et)CH}_2\text{CH}_2\text{N}}\text{Et}$. [c] Solvent obscures resonances. [d] Doublet of triplets, $J_{AX} \simeq J_{BX}$.

TABLE 3

Carbon-13 n.m.r. spectroscopic data for new carbenemetal complexes [a]

Complex	$C_{carb.}$	4 × *cis*-CO	*trans*-CO	OCH_3	–CH–	$-OCH_2CH_3$	$Si(CH_3)_3$	Others
(1)	357.0	217.5	223.0	76.5	72.0	15.0	1.4	
(2)	350.6	207.2	213.8	78.9	72.1	15.4	2.0	
(3)	332.5	198.5	202.5	79.5	72.5	15.0	1.5	
	(^1J = 102.5)	(^1J = 127.1)	(^1J = 119.0)					
(4)	335.8 [b]	199.1 [b]	203.1 [b]		73.2		1.9	68.9 [c]
(5)	248.0 [b]	200.4 [b]	204.2 [b]					40.3,[d] 42.0,[e] 55.3 [f]
(6)	349.5	218.5	223.1		80.6		2.1	2.7 [g]
(7)	331.7 [b]	199.5 [b]	202.9 [b]		72.4		1.6	1.8 [g]
(9)	346.5	206.5	213.5	79.0		15.0	0.0	61.0 [h]
(10)	329.0	198.5	203.5 [b]	79.5		15.0	0.0	63.0 [h]
	(^1J = 101.1)	(^1J = 127.5)						
(11)	365.0	217.0	223.5	78.5		14.5		75.0 [h] 34.5,[i] 30.5 [j]
(12)	339.0 [b]	198.0 [b]	202.0 [b]	81.0		14.5		76.5,[h] 34.5,[i] 30.5 [j]

[a] C_6D_6 solvent, values in p.p.m. relative to $SiMe_4$ (δ 0 p.p.m.); spectra obtained at 25 °C with a sweep width of 10 000 Hz. ^1J refers to $^1J(^{183}W-^{13}C)$. [b] Solution too dilute to measure $^1J(^{183}W-^{13}C)$. [c] OCH_3. [d] *cis*-NCH_3. [e] *trans*-NCH_3. [f] CCH_3. [g] $OSi(CH_3)_3$. [h] $-CH_2-$. [i] $C(CH_3)_3$. [j] $C(CH_3)_3$.

$[W(CO)_5\{C(OR')R\}]$ [R = $CH(SiMe_3)_2$, R′ = Me or Et], (3) and (4), in the range −70 to 70 °C in $[^2H_8]$toluene showed only one isomer, almost certainly due to the steric demands of the bulky $CH(SiMe_3)_2$ group ' locking ' the molecules in the least sterically demanding isomeric *trans* form, (E).

The ^{13}C n.m.r. spectroscopic data for the new carbenemetal complexes are given in Table 3. The $C_{carb.}$ resonance is at low field, typically *ca.* 330—350 p.p.m. relative to $SiMe_4$. The values of $\delta(C_{carb.})$ for $[M(CO)_5\{C(OSiMe_3)R\}]$ [R = $CH(SiMe_3)_2$, M = Cr or W], (6) or (7), are slightly to higher field than those reported[12] for $[M(CO)_5\{C(OSiMe_3)Me\}]$ [M = Cr, $\delta(C_{carb.})$ 374.9; M = W, $\delta(C_{carb.})$ 346.1 p.p.m.]. It is interesting that $C_{carb.}$ in $[M(CO)_5\{C(OR')(SiPh_3)\}]$ (M = Cr, Mo, or W; R′ = Et or Me) is more deshielded, and occurs invariably below 400 p.p.m.[9]

TABLE 4

Infrared spectroscopic data (cm^{-1})

(*a*) For $[M(CO)_5\{C(OR')R\}]$ (M = Cr, Mo, or W) and $[W(CO)_5\{C(NMe_2)Me\}]$ [a]

Complex	ν(CO)			
	A_1^1	B_1	A_1^2	E
(1)	2 062m	1 966w	1 952s	1 940s, br
(2)	2 070m	1 977w	1 949s	1 946s, br
(3)	2 068m	*b*	1 952s	1 938s, br
(4)	2 068m	*b*	1 952s	1 938s, br
(5)	2 066m	1 970w	1 932s	1 930s
(6)	2 058m	1 974w	1 958s	1 946s, 1 930s
(7)	2 064m	1 974w	1 956s	1 944s, 1 926s
(8) [c]	2 062m	1 958w	1 936s	1 948s, 1 944s
(9)	2 068m	*b*	1 939s	1 954s, 1 951s
(10)	2 067m	*b*	1 932s	1 948s, 1 944s
(11)	2 062m	*b*	1 959s	1 944s, br
(12)	2 071m	*b*	1 955s	1 941s, br

(*b*) For phosphine- and phosphite-substituted carbene complexes [d] of Cr^0 and Cr^I

Complex	ν(CO)	$\nu(CN_2)$ [e]
(13) [f]		
(14) [f]	1 925s, 1 859s, br	
(15) [f]	1 966s, 1 913s, br	
(16) [g]	2 010m, (1 930—1 840)s, br	
(20) [g]	1 978s, 1 874s, br	1 490mw
(21) [g]	1 901s, 1 806s, br	1 491mw
(22) [g]	1 913s, 1 827s, br	1 490mw
(23) [g]	1 995m, (1 900—1 850)s, br	1 490mw
(24) [g]	1 990m, (1 880—1 820)s, br	1 491mw
(25) [g]	2 010mw, 1 930mw, 1 890s	1 501m
(27) [g]	2 002mw, 1 936mw, 1 902s	

[a] Spectra recorded in C_6H_{14} solution, assigned to C_{4v} symmetry; calibrated against polystyrene film (1 602 cm^{-1}); w = weak, m = medium, s = strong, br = broad. [b] Not observed. [c] See also ref. 11. [d] Spectra calibrated against polystyrene film. [e] Nujol mull spectrum. [f] Hexane solution. [g] CH_2Cl_2 solution.

As found previously,[16] substitution of W for Cr in isoleptic carbenemetal complexes results in the $C_{carb.}$ atom being more shielded; *e.g.* for $[M(CO)_5\{C(OEt)R\}]$ [R = $CH(SiMe_3)_2$, M = Cr or W], (1) or (3), $\Delta\delta(C_{carb.})$ = −26 p.p.m., and, as expected, the value for the molybdenum analogue (2) is intermediate between those for Cr and W. There is little variation (*ca.* 2—4 p.p.m.) in the chemical shifts of $C_{carb.}$ as a function of R′. Complexes (6) and (7), as expected, have two distinct silylmethyl singlets ($\Delta\delta \approx 0.5$ p.p.m.), and the $OSiMe_3$ shifts [M = Cr, (6), δ = 2.69 p.p.m.; M = W, (7), δ = 1.80 p.p.m.] may be compared with those found for $[M(CO)_5\{C(OSiMe_3)Me\}]$ (M = Cr, δ = 0.00 p.p.m.; M = W, δ = −0.12 p.p.m.).[12]

Coupling constants $^1J(^{183}W-^{13}C)$ for the new tungsten complexes (3) and (10) [for $C_{carb.}$, *cis*-CO, and *trans*-CO] are comparable with those for other Fischer-type carbenetungsten complexes,[16] $[W(CO)_5L^{Et}]$, and *cis*-$[W(CO)_4\{C(OR')R\}L^{Me}]$.[7,17]

Selected i.r. spectroscopic data for the new complexes are in Table 4(*a*) and 4(*b*). Absorptions at *ca.* 1 260, 850, and 725 cm^{-1} for complexes $[M(CO)_5\{C(OR')R\}]$ [R = $CH(SiMe_3)_2$ or CH_2SiMe_3] are assigned to vibrations involving the $SiMe_3$ moiety. Solution spectra for the pentacarbonylcarbenemetal(0) complexes in the 1 900—2 100 cm^{-1} region are generally characterised by three predominant bands ($2A_1$ and E) consistent with an idealised C_{4v} geometry. However, occasionally the

TABLE 5

Relative abundance of ions in mass spectra of some carbenemetal complexes [a]

Complex	M^+	$[M - CO]^+$	$[M - 2CO]^+$	$[M - 3CO]^+$	$[M - 4CO]^+$	$[M - 5CO]^+$
(1)	7	5	10	3	33	100
(2)	6	14	25	39	69	100
(3)	30	8	9	18	100	19
(4)	100	0	0	10	40	30
(5)	40	0	35	60	100	0
(6)	10	50	40	20	85	100
(7)	5	4	1	4	60	100
(20) [b]	0	0	0	0		
(21)	100	50	10	100		
(22)	15	0	0	100		
$[Cr(CO)_5L^{Et}]$	42	21	21	14	71	100
$[Mo(CO)_5L^{Et}]$	60	45	35	65	100	100
trans-$[Mo(CO)_4(L^{Me})_2]$ [c]	25	26	33	11	100	
$[Mo(CO)_5L^{Me}]$ [d]	100	84	53	58	63	81
$[Mo(CO)_5L'^{Me}]$ [e,f]	1	1	<1	100	13	18

[a] Source at 80—115 °C, sample at ambient temperature, 70 eV except where otherwise stated. [b] No peaks at *m*/*e* >320. [c] Source at 80 °C, sample at 115 °C. [d] Source at 115 °C, sample at ambient temperature. [e] Source at 115 °C, sample at ambient temperature, 70 eV. [f] $L'^{Me} = CN(Me)CH_2CH_2CH_2NMe$.

symmetry is lowered, as shown by the appearance of a formally i.r.-forbidden B_1 mode together with a lifting of the degeneracy of the E mode, giving in these cases five i.r.-active ν(CO) bands. It is interesting that in complexes (1)—(3), (9), and (10) the E-mode degeneracy is lifted when R is the apparently less sterically demanding CH_2SiMe_3 group, but not when R = $CH(SiMe_3)_2$. Five i.r. ν(CO) modes have been reported for $[Cr(CO)_5\{C(OSiMe_3)Ph\}]$ [12] and $[W(CO)_5\{C(OMe)(SiPh_3)\}]$.[9] The position of the A_1^2 ν(CO) band may provide an insight into the electronic properties of the carbene ligand, since this band is mainly due (assuming limited coupling) to the unique CO *trans* to $C_{carb.}$, and on this basis the carbene ligands may be ranked (see ref. 9) according to their decreasing σ donor : π acceptor ratio as follows: $C(OEt)CH_2SiMe_3 > C(OEt)CH(SiMe_3)_2 > C(OEt)CH_2CMe_3 \sim C(OSiMe_3)CH(SiMe_3)_2$. Extending this to literature data, the series can be widened to include other carbene ligands: $CN(Et)CH_2CH_2NEt$ (L^{Et}) > $C(NMe_2)(SiPh_3) \sim C(NMe_2)Me > C(OEt)CH_2SiMe_3 > C(OEt)CH(SiMe_3)_2 > C(OEt)CH_2CMe_3 > C(OEt)Me > C(OSiMe_3)Me \sim C(OEt)(SiPh_3)$.

TABLE 6

Average vertical first ionisation potentials (eV) from photoelectron spectroscopy

Complex	First vertical i.p. (eV)	Ref.
$[M(CO)_5L^{Et}]$		
M = Cr	7.12	*
Mo	6.90	*
W	7.02	*
fac-$[Cr(CO)_3(dmpe)L^{Et}]$	6.70	*
$[M(CO)_5\{C(OEt)CH(SiMe_3)_2\}]$		
M = Cr	7.57	*
Mo	7.27	*
W	7.55	*
$[M(CO)_6]$		
M = Cr	8.40	20
Mo	8.50	20
W	8.56	20
cis-$[Mo(CO)_2(dmpe)_2]$	6.00	23
$[Cr(CO)_5L]$		
L = NH_3	7.56	21
NMe_3	7.45	21
PH_3	7.90	21
PMe_3	7.56	21

* This work; results obtained by Mr. A. W. Coleman, using a Perkin-Elmer PS15 He(I) spectrometer.

Parent ions of weak to medium intensities are observed in the mass spectra of complexes (1)—(7), (9), or (10), or $[M(CO)_5L^{Et}]$ (M = Cr or Mo) (Table 5). Attempts to obtain spectra from other carbene–Group 6 metal complexes gave $[M(CO)_6]^+$ as the highest *m*/*e* peaks. Fragmentation of the parent ion was normally by successive loss of CO ligands, but the $[M - CO]^+$ and $[M - 2CO]^+$ ions were obtained in low abundance.

The He(I) photoelectron spectra of $[M(CO)_5\{C(OEt)R\}]$ [R = $CH(SiMe_3)_2$] (M = Cr, Mo, or W), (1)—(3), and four electron-rich olefin-derived carbenemetal complexes were recorded (by Mr. A. W. Coleman). The first vertical ionisation potentials (i.p.s) are listed in Table 6. Comparative data on other Fischer-type carbenemetal complexes show first i.p.s at 7.25—7.75 eV,[18,*] the electron being removed from a predominantly metal-centred molecular orbital. Values for $[M(CO)_5L^{Et}]$ are slightly lower (Table 6), consistent with the higher σ donor : π acceptor ratio of these complexes and all are substantially lower than first i.p.s for $[M(CO)_6]$ (M = Cr, Mo, or W),[19] because of the replacement of CO by the poorer π-acceptor carbene ligand; similarly, phosphine- or amine-substituted carbonylmetal complexes have lower first i.p.s than the parent carbonyls.[20,21] The particularly low first i.p. found for *fac*-$[Cr(CO)_3(dmpe)L^{Et}]$ (21) may account for its ready oxidation (see below) to $[Cr(CO)_3(dmpe)L^{Et}]^+$.

Attempts to synthesise $[W(CO)_5\{C(OEt)N(SiMe_3)_2\}]$ by treatment of $[W(CO)_6]$ with $Li[N(SiMe_3)_2]$ failed, possibly due to the relatively low nucleophilicity of the amide. Likewise, there was no reaction between $[W(CO)_5\{C(OEt)R\}]$ [R = $CH(SiMe_3)_2$], (3), and $NH(SiMe_3)_2$, whereas the more nucleophilic $NHMe_2$ caused C–Si scission to occur, affording $[W(CO)_5\{C(NMe_2)Me\}]$ (5); a reaction formally similar to the ammonolysis of $[Cr(CO)_5\{C(OEt)CH_2SiMe_3\}]$ to yield $[Cr(CO)_5\{C(NH_2)$-

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* Throughout this paper: 1 eV ≈ 1.60×10^{-19} J.

Table 7

E.s.r. spectroscopic data

(*a*) For carbenechromium(I) complexes [a]

	Complex assignment	Structure	*g* Value	A_P [b]	A_{Cr} [b]	Temperature (°C) at which there is negligible decomposition
(17)	$[Cr(CO)_3\{C(OEt)CH(SiMe_3)_2\}(dmpe)][BF_4]$	1 : 2 : 1 (t)	2.022 1	2.00	1.34	>20
(18)	$[Cr(CO)_3\{C(OEt)CH(SiMe_3)_2\}(dppe)][BF_4]$	1 : 2 : 1 (t)	2.015 4	1.93	1.24	<-40
(25)	$[Cr(CO)_3(dmpe)L^{Et}][BF_4]$ [c]	1 : 2 : 1 (t)	2.019 9	2.23	1.34	>20
(26)	$[Cr(CO)_3(dmpe)L^{Et}]Cl$	1 : 2 : 1 (t)	2.020 2	2.20	1.37	>20
(27)	$[Cr(CO)_3(dppe)L^{Et}][BF_4]$	1 : 2 : 1 (t)	2.020 5	2.16	1.35	<10
(28)	$[Cr(CO)_3(L^{Et})\{P(OPh)_3\}_2][BF_4]$	1 : 2 : 1 (t)	2.022 7	2.05	*d*	<-30
(29)	$[Cr(CO)_2(dmpe)(L^{Et})(PPh_3)][BF_4]$	1 : 3 : 3 : 1 (q)	2.010 5	2.78	*d*	>20
(30)	$[Cr(CO)(dmpe)_2L^{Et}][BF_4]$	1 : 4 : 6 : 4 : 1 (p)	2.016	2.98	*d*	>20
(31)	$[Cr(CO)_4(L^{Et})_2][BF_4]$	(br s)	2.018		*d*	<-50
(32)	$[Cr(CO)_3(L^{Et})_2(PPh_3)][BF_4]$	1 : 1 (d)	2.012	1.56	*d*	<-40

(*b*) Some comparative data for chromium(I) complexes

Complex	*g* Value	A_P [b]	A_{Cr} [b]	Ref.
$[Cr(CO)_6]^+$	1.842		*e*	27
trans-$[Cr(CO)_2(dppm)_2]^+$	2.00	2.74	*e*	26
$[Cr(C_{10}H_8)_2]^+$	1.986		1.82	*f*
$[Cr(CN)_5(NO)]^{3-}$	1.994 9		1.85	*f*
trans-$[Cr(CO)_2(dmpe)_2]^+$	2.003	3.00	*e*	26
$[Cr(NH_3)_5(NO)]^{2+}$	1.979		2.35	*f*
$[Cr(OH_2)_5(NO)]^{2+}$	1.967 1		2.69	*f*
$[Cr(bipy)_3]^+$ [g]	1.997 2		2.18	*f*

[a] All spectra obtained in CH_2Cl_2 solution under argon or dinitrogen. [b] Coupling constants in mT. [c] This spectrum showed 'satellites' due to impurity of $[Cr(CO)_2(dmpe)_2]^+$. [d] Value not determined. [e] Values not reported. [f] B. A. Goodman and J. B. Raynor, *Adv. Inorg. Chem. Radiochem.*, 1970, **13**, 135 and refs. therein. [g] bipy = 2,2′-Bipyridyl.

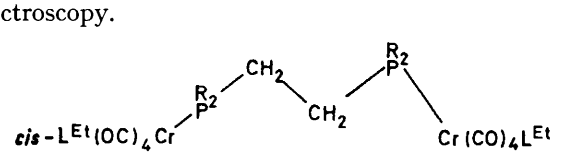
Me}].[11] These observations offer a contrast with the behaviour towards $NHMe_2$ of complexes $[M(CO)_5\{C(OR')(SiPh_3)\}]$ (M = Cr, Mo, or W; R′ = Me or Et) [9] or $[M(CO)_5\{C(OR')Me\}]$ [1] which give $[M(CO)_5\{C(NMe_2)(SiPh_3)\}]$ or $[M(CO)_5\{C(NMe_2)Me\}]$, respectively.

The restricted rotation about the $C_{carb.}\overset{...}{-}N$ bond in complex (5) gives rise to the three methyl signals in both the ^1H and ^{13}C n.m.r. spectra (assigned to the $C_{carb.}$-Me, *cis*-NMe, and *trans*-NMe groups), a similar phenomenon to that found for the chromium analogue,[22] and related to the *cis–trans* isomerism in $[W(CO)_5\{C(NHMe)Me\}]$.[19] Carbon-13 n.m.r. spectroscopic data show [23] that both isomers exist independently in solution, $C_{carb.}$ being at 255.7 (*cis* isomer) and 258.7 p.p.m. (*trans* isomer). These are at lower field than $\delta(C_{carb.})$ for (5), being at 248 p.p.m., reflecting the substitution of H by the more electron-donating Me group.

Unsuccessful attempts were made to prepare stable dialkylcarbenemetal complexes, $[M(CO)_5(CR_2)]$ [M = Cr or W; R = $CH(SiMe_3)_2$], by an established method [24] from $[M(CO)_5\{C(OEt)R\}]$, (1) or (3), and LiR. Complexes (1) and (3) were also unreactive towards BBr_3 in the range −40 to 40 °C, conditions generally yielding carbynemetal complexes *trans*-$[MBr(CO)_4(CR)]$ (M = Cr or W) from less hindered analogues.[12] These results provide further illustration of the kinetic stability conferred by the bulky $C(OEt)CH(SiMe_3)_2$ ligand on derived complexes $[M(CO)_5L]$.

The isolation of the complex $[NMe_4][W(CO)_5\{C(O)CH(SiMe_3)_2\}]$ was attempted by treatment of a solution believed to contain $[Li(OEt_2)_x][W(CO)_5\{C(O)CH(SiMe_3)_2\}]$ [an intermediate in the synthesis of the carbenetungsten complex (3)] with $[NMe_4]Br$. The exceedingly oxygen-sensitive yellow needles obtained appeared to be of the unchanged lithium salt, on the basis of the ^1H n.m.r. spectrum {CH (τ 6.3), $SiCH_3$ (τ 9.2), CH_3CH_2O [τ 6.6(q), 8.9(t)]}.

Photolysis of $[Cr(CO)_5\{C(OEt)R\}]$ [R = $CH(SiMe_3)_2$], (1), in the presence of a phosphite or a phosphine gave only a small quantity of the tricarbonyl complex (13), (14), or (15) (Scheme 1). By contrast, similar photolysis of $[Cr(CO)_5L^{Et}]$ gave a good yield of the *fac*-tricarbonyl derivative (20), (21), or (22) (Scheme 2). Infrared results confirm the *fac* geometry, a sharp *A* and broad *E* modes being observed [Table 4(*b*)]. Two of these complexes, (21) and (22), gave molecular ions in the mass spectrum, fragmenting by successive loss of CO (Table 5). For the bis(phosphite) derivative (20), ions above *m*/*e* = 320 were not observed. The ^1H n.m.r. spectroscopic data for complexes (20) and (21) are shown in Table 2(*b*). In the products derived from the chelating phosphines, small specimens of the binuclear complexes (23) and (24) were isolated, characterised by i.r. [ν(CO)] and ^1H n.m.r. spectroscopy.



(23) R = Ph; (24) R = Me

Carbenechromium(I) *Cationic Complexes*.—Addition of $Ag[BF_4]$ to a degassed CH_2Cl_2 solution of *fac*-$[Cr(CO)_3(L^{Et})L'_2]$ [L′ = $P(OPh)_3$ or L'_2 = dmpe or dppe], (20), (21), or (22), in the cavity of an e.s.r. spectrometer at low temperature gave, in each case, a 1 : 2 : 1 triplet assigned to the corresponding Cr^I-containing salt (25), (27), or (28), containing two apparently magnetically equivalent ^{31}P nuclei (100%, $I = \frac{1}{2}$), *cf.* Figure 1 and Table 7(*a*). A

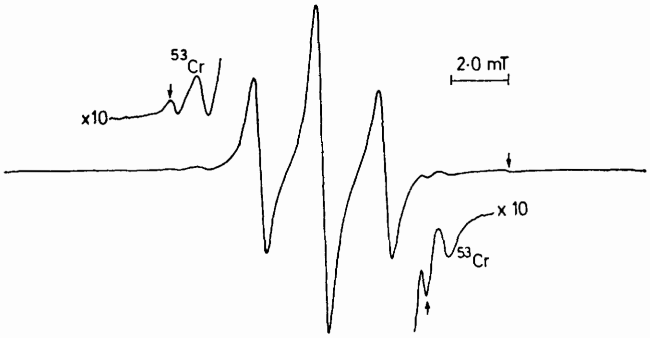


FIGURE 1 E.s.r. spectrum of $[Cr(CO)_3(dmpe)L^{Et}][BF_4]$ in CH_2Cl_2 under argon at 20 °C. The arrowed peaks are assigned to traces of $[Cr(CO)(dmpe)_2L^{Et}][BF_4]$ (see Figure 2 and text); ^{53}Cr indicates chromium satellites

silver mirror was deposited. The stability of the salts is markedly dependent upon the nature of the phosphorus ligand, the dmpe complex (25) being isolable at 20 °C, the $P(OPh)_3$ complex (28) stable below -30 °C, and the dppe analogue (27) of intermediate stability. The relative thermal and aerial stability of these salts reflect the changing electron density at the metal centre, being greatest for L'_2 = dmpe, (25), and this is also noted in the position of the ν(CO) bands which decrease in wavenumber in the order $L'_2 = 2P(OPh)_3 >$ dppe $>$ dmpe. This stability sequence is the same as that observed for ease of oxidation of the corresponding chromium(0) precursor.

A similar enhanced oxidative lability of dmpe complexes has previously been observed in the oxidation of various Group 6 metal(0) carbonylphosphine complexes.[23] Upon oxidation the ν(CO) frequencies of complexes (20)—(22) show the expected increase of *ca.* 100 cm^{-1} [Table 4(*b*)]. Likewise, addition of CCl_4 to the chromium(0) complex (21) in the cavity of the e.s.r. spectrometer resulted in the formation of a 1 : 2 : 1 triplet, assigned to $[Cr(CO)_3(dmpe)L^{Et}]Cl$ (26) [equation (1)].

$$\underset{(21)}{fac\text{-}[Cr(CO)_3(dmpe)L^{Et}]} \xrightarrow{CCl_4} [Cr(CO)_3(dmpe)L^{Et}]^+CCl_4{}^{\bullet -} \longrightarrow \underset{(26)}{[Cr(CO)_3(dmpe)L^{Et}]Cl} + {}^{\bullet}CCl_3 \quad (1)$$

The e.s.r. parameters of the salt (26) are very similar to those of the analogous tetrafluoroborate, (25) (Table 7). It was not possible to spin-trap the $^{\bullet}CCl_3$ radical with nitrosodurene, nor in the oxidation[25] of *cis*-$[Mo(CO)_2(dmpe)_2]$ with CCl_4. Photolysis of $[Cr(CO)_3(dmpe)L^{Et}][BF_4]$ (25) in the presence of PPh_3 in the e.s.r. spectrometer cavity gave rise to a new signal, a 1 : 3 : 3 : 1 quartet which suggests two overlapping triplets in which the ^{31}P coupling constants of dmpe and PPh_3 are approximately equal. After ⩾24 h at 20 °C the signal due to (25) decays and a minor residual e.s.r. signal is revealed (Figure 2), a 1 : 4 : 6 : 4 : 1 quintet, assigned tentatively to $[Cr(CO)(dmpe)_2L^{Et}]^+$ (30) on the basis of a computer-simulated spectrum. This may be formed by phosphine exchange from the salt (25), or by oxidation of $[Cr(CO)(dmpe)_2L^{Et}]$ {a minor impurity in $[Cr(CO)_3(dmpe)L^{Et}]$}. The chromium(I) salt with two dmpe ligands is clearly more stable than that with only one dmpe, and thus the signal of the former is observed when that from the latter, (25), has decayed. It is known that oxidation of $[Fe(CO)_3(L^{Me})(PPh_3)]$ with Ag$^+$ at -20 °C affords $[Fe(CO)_3(L^{Me})(PPh_3)]^+$ which upon warming (*ca.* 25 °C) produces the exceedingly stable iron(I) cation $[Fe(CO)_2(L^{Me})(PPh_3)_2]^+$.

Oxidation of the Fischer-type complex *fac*-$[Cr(CO)_3\{C(OEt)R\}\{P(OPh)_3\}_2]$ [R = $CH(SiMe_3)_2$], (15), by Ag[BF_4] occurs (a silver mirror is formed), but even at -60 °C the resulting salt (19) decomposes too rapidly for a satisfactory e.s.r. spectrum to be recorded; in contrast, oxidation of the dppe–chromium(0) analogue (14) gives a 1 : 2 : 1 triplet, assigned to the corresponding cation (18), decaying at >-40 °C. Similarly, oxidation of the dmpe complex (13) gives the chromium(I) salt (17). Addition of Ag[BF_4] to $[Cr(CO)_5\{C(OEt)R\}]$ [R = $CH(SiMe_3)_2$], (1), effected no reaction. Oxidation of *cis*-$[Cr(CO)_4(L^{Et})_2]$ by Ag$^+$ gave e.s.r. signals attributable to $[Cr(CO)_4(L^{Et})_2]^+$ (31) which produced a doublet in the presence of PPh_3 at <-40 °C, consistent with the formation of the complex $[Cr(CO)_3(L^{Et})_2(PPh_3)]^+$ (32) which was unexpectedly labile. Alternatively for $[Cr(CO)_4(L^{Et})_2]$, tetracyanoethylene (tcne) or trityl chloride were tried as oxidants, but the only observed e.s.r. signals were those of tcne$^{\bullet -}$ or $^{\bullet}CPh_3$, respectively.

The *g* factors reported here, typically *ca.* 2.02, are all substantially higher than the free-electron value of 2.002 3. From the data shown in Table 7(*a*) and 7(*b*) it is noted that for many of the known transient chromium(I) complexes the *g* value is often less than that of the free electron. The family of complexes $[CrL_5(NO)]^{2+}$ (L = H_2O or NH_3) has been studied; an increase in the delocalisation of the unpaired electron causes a *g*-value shift towards 2.002 3 and a decrease in the isotropic coupling to ^{53}Cr. Measurement of the *g* tensor in such complexes indicates that the odd electron is predominantly in the d_{xy} orbital, but for complex (25) the frozen-solution spectrum in CH_2Cl_2 consists of a broad (no phosphorus or chromium coupling resolved) singlet, $g = 2.020\,6$; these e.s.r. parameters resemble those

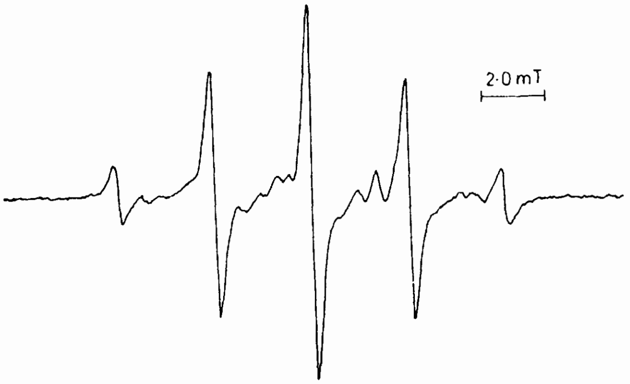


FIGURE 2 E.s.r. spectrum of $[Cr(CO)(dmpe)_2L^{Et}][BF_4]$ in CH_2Cl_2 under argon at 20 °C, obtained when the sample used for Figure 1 was set aside for ⩾24 h in CH_2Cl_2 at 20 °C

found for *trans*-[$Cr(CO)_2(L'_2)_2$]$^+$ (L'_2 = dmpe or dppe),[26] for which the *g* values are *ca.* 2.00. The higher values reported here may reflect substantial delocalisation of the unpaired electron, consistent with the small isotropic coupling to ^{53}Cr, typically 1.3 mT (Table 7). An alternative explanation (proposed by a referee) is that in these carbene complexes, with different ligands and lower symmetry than [$CrL_5(NO)$]$^{2+}$, the unpaired electron is in an orbital (possibly d_{z^2} rather than d_{xy}), which is mixed by spin–orbit coupling with filled, rather than unfilled, metal *d* orbitals giving $g > 2.002\,3$; additionally, the orbital may have a little Cr 4*s* character and hence have a reduced isotropic hyperfine ^{53}Cr coupling.

The chromium(I) complexes reported here are the first characterised (i.r. and e.s.r.) examples of Group 6 carbenemetal paramagnetic complexes, and some are isolable at ambient temperature. There is a report of the electrochemical oxidation of carbenemetal(0) complexes at a platinum electrode,[27] and an unstable carbenechromium(−I) complex was obtained by reduction of [$Cr(CO)_5\{C(OMe)Ph\}$] by K–Na alloy in tetrahydrofuran (thf) at low temperature in the cavity of an e.s.r. spectrometer.[28]

Molecular-orbital calculations on [$Cr(CO)_5\{C(OMe)Me\}$] reveal that the lowest unoccupied molecular orbital (l.u.m.o.) is energetically isolated and spatially localised on $C_{carb.}$,[29] a result which seems to be supported by e.s.r. data on [$Cr(CO)_5\{C(OMe)Ph\}$].[28] Reduction of a series of (arylmethoxycarbene)pentacarbonylmetal(0) (M = Cr, Mo, or W) compounds has been studied by cyclic voltammetry;[30] it was suggested that the aryl ring of the metal(0) complex lies in the plane perpendicular to the M–$C_{carb.}$–O plane, but in the plane in the metal(−I) complex. The highest occupied molecular orbital (h.o.m.o.) of the metal(0) complex is insensitive to this conformational change but the l.u.m.o. is significantly less stable for the perpendicular case. For our $Cr^0 \xrightarrow{-e^{-1}} Cr^I$ oxidations, the ^{31}P and ^{53}Cr hyperfine couplings observed for the chromium(I) complex suggest that electron loss from the chromium(0) precursor is predominantly from the h.o.m.o. extending over Cr–P.

EXPERIMENTAL

General Procedures.—All reactions were carried out under an atmosphere of dry dinitrogen or argon. Hydrocarbon and ether solvents were dried over sodium wire and distilled before use and chlorinated solvents were distilled from phosphorus(V) oxide. Analyses were carried out in our microanalytical laboratory by Mr. and Mrs. A. G. Olney, and ^{13}C n.m.r. spectra were obtained by Mr. T. M. Siverns on a JEOL PFT-100 Fourier-transform spectrometer. Infrared spectra were examined as either Nujol mulls using a Perkin-Elmer 457 grating spectrophotometer or in hydrocarbon or CH_2Cl_2 solution using a Perkin-Elmer 257 grating spectrophotometer, and ^1H n.m.r. spectra were recorded on a Varian Associates T60 spectrometer. E.s.r. spectra were obtained on a Varian E3 spectrometer with *g* values measured relative to polycrystalline diphenylpicrylhydrazyl (dpph). Photoelectron spectra were recorded by Mr. A. W. Coleman on a Perkin-Elmer PS 15 instrument with a modified high-energy lamp. Mass spectra were obtained by Mr. A. M. Greenway using an A.E.I. MS30 instrument.

Melting points were determined in sealed evacuated tubes and are uncorrected. The complexes [$M(CO)_6$] (M = Cr or Mo) were obtained from B.D.H. Ltd., and [$W(CO)_6$] from Koch–Light Ltd.; [$M(CO)_5L^{Et}$] (M = Cr, Mo, or W) were prepared by standard literature methods.[5,17]

Preparation of Carbenemetal Complexes of the Type [$M(CO)_5\{C(OR')R\}$] [M = Cr, Mo, *or* W; R′ = Et, Me, *or* $SiMe_3$; R = $CH(SiMe_3)_2$, CH_2SiMe_3, *or* CH_2CMe_3].—Typically, to a stirred suspension of hexacarbonylmetal(0) (2 mmol) in OEt_2 (25 cm^3) was slowly added an OEt_2 solution of the appropriate lithium reagent LiR (2 mmol) at room temperature. The progress of the reaction was followed by the rate of disappearance of suspended [$M(CO)_6$] and development of a deep yellow solution. Once all the suspended [$M(CO)_6$] had disappeared, the solution was stirred (1 h). To this mixture was slowly added a solution of either triethyloxonium tetrafluoroborate [OEt_3][BF_4] (2.0 mmol) or ' magic methyl ' $SFO_2(OMe)$ (2.0 mmol) in CH_2Cl_2 (10 cm^3) at 0 °C, or, alternatively, a solution of $SiMe_3Cl$ (2.0 mmol) in OEt_2 (10 cm^3) at −30 °C. The resulting solution was stirred (1 h) and then solvent was removed *in vacuo*. The solid was extracted with pentane (2 × 15 cm^3), the extract filtered, and the combined extracts were reduced in volume to *ca.* 10 cm^3 and cooled (−30 °C) overnight. The supernatant was then decanted, leaving any unchanged [$M(CO)_6$]. Cooling the supernatant to −78 °C gave the desired yellow crystals of *carbenemetal*(0) *complex*.

Attempted Preparation of trans-[$W(CO)_4\{CCH(SiMe_3)_2\}Br$].—To a stirred solution of pentacarbonyl{ethoxy[bis(trimethylsilyl)methyl]methylene}tungsten(0) (0.054 g, 0.1 mmol) at −30 °C in hexane (5 cm^3) was added a slight excess of boron tribromide (0.031 g, 0.12 mmol). No reaction was discernable [by i.r., ν(CO), or ^1H n.m.r. spectroscopy]. The solution was allowed to warm to room temperature, but again no reaction was observed. On warming, (1 h, 40 °C), no carbyne complex was detected by i.r. [ν(CO)] spectroscopy.

Attempted Preparation of [$W(CO)_5(CR_2)$] [R = $CH(SiMe_3)_2$].—To a stirred solution of [$W(CO)_5\{C(OEt)CH(SiMe_3)_2\}$] (1.08 g, 2.0 mmol) in OEt_2 (30 cm^3) at −78 °C was slowly added a solution of Li[$CH(SiMe_3)_2$] (0.353 g, 2.25 mmol) in OEt_2 (5 cm^3) to produce a yellow-orange solution. After 2 h a solution of dry hydrogen chloride (0.09 g, 2.5 mmol) in OEt_2 (1.25 cm^3) was added, giving a pale yellow solution. After 10 min the reaction mixture was allowed to warm to room temperature. Solvent was removed *in vacuo*, and the residue extracted with pentane (2 × 15 cm^3) and cooled to −78 °C. The yellow crystals deposited were identified as starting material by ^1H n.m.r. spectroscopy (95% recovery).

Other Preparations.—[$W(CO)_5\{C(NMe_2)Me\}$]. To a solution of [$W(CO)_5\{C(OEt)CH(SiMe_3)_2\}$] (0.54 g, 1.0 mmol) in benzene (20 cm^3) at 5 °C was added dimethylamine (0.25 cm^3, an excess) and the solution stirred (5 h). Solvent was removed *in vacuo* and the residue extracted with pentane (2 × 10 cm^3). The combined extracts were reduced to *ca.* 10 cm^3 and cooled to −40 °C to give pale yellow needles of *pentacarbonyl*[*dimethylamino*(*methyl*)*methylene*]*tungsten*(0).

fac-[$Cr(CO)_3\{C(OEt)CH(SiMe_3)_2\}\{P(OPh)_3\}_2$]. A dilute solution of pentacarbonyl{ethoxy[bis(trimethylsilyl)methyl]methylene}chromium(0) (0.05 g, 0.125 mmol) and triphenyl phosphite (0.15 g, 0.375 mmol) in hexane was irradiated (11 h) with u.v. light from a Hanovia lamp to give the desired product, fac-*tricarbonyl{ethoxy[bis(trimethylsilyl)methyl]methylene}bis(triphenyl phosphite)chromium-*(0). The dmpe and dppe analogues were prepared in a similar manner.

fac-[Cr(CO)$_3$(dmpe)L$^{\mathrm{Et}}$]. A dilute solution of pentacarbonyl(1,3-diethylimidazolidin-2-ylidene)chromium(0) (0.55 g, 2.4 mmol) and dmpe (0.35 g, 2.4 mmol) was irradiated in hexane (8 h). The pale yellow precipitate formed was collected and recrystallised from thf–hexane at −30 °C to give pale yellow crystals of fac-[1,2-*bis(dimethylphosphino)ethane*]*tricarbonyl*(1,3-*diethylimidazolidin*-2-*ylidene*)-*chromium*(0). The dppe and P(OPh)$_3$ complexes were prepared in a similar manner.

fac-[Cr(CO)$_3$(dmpe)L$^{\mathrm{Et}}$][BF$_4$]. To a solution of *fac*-[Cr(CO)$_3$(dmpe)L$^{\mathrm{Et}}$] (0.5 g, 1.2 mmol) in thf (20 cm^3) at 0 °C was slowly added a solution of Ag[BF$_4$] (0.24 g, 1.2 mmol) in thf (10 cm^3). After stirring for a few minutes to coagulate the deposit of silver, the mixture was filtered through a ***clean*** [*] sinter and the orange solution reduced to *ca.* 5 cm^3. Addition of OEt$_2$ and cooling (−40 °C) gave dark orange crystals of fac-[1,2-*bis(dimethylphosphino)-ethane*]*tricarbonyl*(1,3-*diethylimidazolidin*-2-*ylidene*)-*chromium*(I) *tetrafluoroborate.*

We thank the S.R.C. for the award of a Fellowship (to P. I. R.) and other support, and Mr. A. W. Coleman for the photoelectron spectroscopic data.

[9/078 *Received*, 17*th January*, 1979]

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[*] Decomposition was found to occur readily on the surface of the sinter (a clean transfer wire is to be preferred).

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