Electrochemical Oxidation of Organometallic Complexes. Carbene and Lewis Base Complexes of Chromium, Molybdenum, and Tungsten Carbonyls

By **Malcolm K. Lloyd, Jon A. McCleverty,*** and **David G. Orchard,** Department of Chemistry, University of Sheffield, Sheffield S3 7HF
Joseph A. Connor,* Michael B. Hall, Ian H. Hillier, E. Malcolm Jones, and **Gerald K. McEwen,** Department of Chemistry, University of Manchester, Manchester M13 9PL

Tha oxidative one-electron transfer reactions of a wide variety of Group VI metal carbonyl derivatives have been detected by voltammetry. The compounds studied are of the type $M(CO)_{6-n}L_n$ or $M(CO)_{6-2n}(LL)_n$ (M = Cr, Mo, W; L = monodentate Lewis base, n = 1 or 2; LL = bidentate Lewis base, n = 1 or 2) and carbene complexes of the type $M(CO)_5C(X)Y$. The value of the potential, $E_{\frac{1}{2}}$, is influenced by each of the variables M, L(or LL), n, X, and Y. The order of $E_{\frac{1}{2}}$-values follows closely the apparent π-acceptor/σ-donor ratio of the ligand, but comparison with the results of molecular orbital calculations suggests that the influence of L (or of $\{C(X)Y\}$) upon the redox orbital is indirect. Steric effects are shown to influence the value of $E_{\frac{1}{2}}$, especially where bidentate ligands are present. The oxidation potentials are related to synthetic chemistry in these systems.

IT has been known for many years that dibenzenechromium may be readily oxidised to the stable, paramagnetic monocation, $[(\pi\text{-}C_6H_6)_2Cr]^+$.[1] Treatment of $[Cr(CO)_5I]^-$ with iodine [2] and of $(\pi\text{-}C_6H_6)W(CO)_3$ with $SbCl_5$ [3] has also afforded oxidised species of varying stability, namely $Cr(CO)_5I$ and $[\pi\text{-}C_6H_6W(CO)_3Cl]SbCl_6$. Furthermore $[\{HB(pyz)_3\}Mo(CO)_3]^-$ † undergoes two discrete one-electron oxidation reactions which have been detected polarographically.[4]

Considering these facts, it seemed apparent that Group VI metal carbonyl derivatives in general should undergo simple, oxidative, one-electron transfer reactions, and that these could be detected by voltammetry. Accordingly, we have investigated a series of derivatives of the hexacarbonyls of chromium, molybdenum, and tungsten of the type $ML_n(CO)_{6-n}$ (L = alternative ligand, usually a Lewis base and $n \leqslant 4$). Some of our preliminary results have been reported.[5,6] In this paper we discuss the results obtained from $CrL(CO)_5$, where L = Lewis base or carbene, C(X)Y, from $ML_2(CO)_4$ or $M(LL)(CO)_4$, where L or LL is a Lewis base and M = Cr, Mo, or W, and from $Mo(LL)_2(CO)_2$. In the following paper we shall discuss the results obtained from certain arene and cycloheptatriene complexes.

RESULTS

The anodic oxidation behaviour of the organometallic species has been investigated in dichloromethane solution at room temperature using a rotating platinum electrode and $[Et_4N]ClO_4$ as base electrolyte. Dichloromethane is effectively inert towards the compounds studied (as is the base electrolyte) under the conditions of the experiment. On the other hand, the use of dimethylformamide or acetonitrile for example, causes decomposition of some of the complexes under similar conditions. Our results (Tables 1, 2, and 3) indicate that the use of a dropping mercury working electrode would not be practical since mercury oxidises at *ca.* +0·7 V. Platinum wire happened to form the most convenient electrode, but carbon rod would be equally useful.

The voltammograms of all of the complexes examined, with the exception of $Cr(CO)_6$ and $Cr(CO)_5PF_3$, exhibited at least one oxidation wave, and some exhibited two waves. The primary oxidation process appears to correspond to a one-electron-transfer reaction, although this was not checked by coulometry. Such an assumption is, however, reasonable and entirely consistent both with the known chemistry [2] of $[Cr(CO)_5I]^-$ and with the electrode behaviour [7] (i_d/c; Table 1) of the well characterised $[Ni\{S_2C_2(CN)_2\}_2]^{2-}$. Some of the electrode reactions were studied by cyclic voltammetry and were shown to be either reversible or quasi-reversible with coupled chemical reactions; the nature of the coupled chemical reactions and the products thereof will be reported on later.

Lewis Base Complexes. Monosubstituted Compounds, $[Cr(CO)_5L_5]^Z$.—Inspection of the results obtained from $[Cr(CO)_5L]^Z$ (Table 1; Z is the charge) shows that, when $Z = -1$ (L = halide or cyanide), the $E_{\frac{1}{2}}$-values for the oxidation are relatively low, in the range +0·31 to +0·50 V. The potential values appear to be influenced by the electronegativity and by the π-bonding properties of L.

In the neutral compounds ($Z = 0$), $E_{\frac{1}{2}}$ is high (>1·10 V) when L is a good π-acceptor (poor σ-donor), for example phosphite, phosphine, or aryl isocyanide. The results suggest that $P(OMe)_3$ is a better π-acceptor (poorer σ-donor) than $P(OPh)_3$, that PH_3 is a good π-acceptor (poor σ-donor), comparable with the phosphites and certainly more effective than PPh_3, and that, in these complexes, PMe_3 and PPh_3 have comparable donor–acceptor properties.

A steady decrease in the π-acceptor properties of L, accompanied by an increase in σ-donor ability, leads to a progressive cathodic shift of the $E_{\frac{1}{2}}$-values. Thus, in the amine series, $E_{\frac{1}{2}}$-values are in the range +0·71 to +0·77 V, but, surprisingly, they do not correlate with the basicity of the free amine as indicated by the pK_a-value: the value of $E_{\frac{1}{2}}$ for the oxidation of $Cr(CO)_5NH_3$ is lower than those of the cyclic amine complexes containing ethyleneimine

---

† pyz = 1-Pyrazolyl.

[1] I. A. Kershunov, L. N. Vertyulina, and G. A. Domrachev, *Zhur. Obshchei Khim.*, 1962, **32**, 9 (*Chem. Abs.*, 1962, **57**, 14884g).

[2] H. Behrens and H. Zizlsperger, *Z. Naturforsch.* (*B*), 1961, **16**, 349.

[3] M. R. Snow and M. H. B. Stiddard, *Chem. Comm.*, 1968, 580.

[4] S. Trofimenko, *J. Amer. Chem. Soc.*, 1969, **91**, 588.

[5] J. A. McCleverty, D. G. Orchard, J. A. Connor, E. M. Jones, J. P. Lloyd, and P. D. Rose, *J. Organometallic Chem.*, 1971, **30**, C75.

[6] J. A. Connor, E. M. Jones, G. K. McEwen, M. K. Lloyd, and McCleverty, *J.C.S. Dalton*, 1972, 1246.

[7] D. G. Orchard, Ph.D. Thesis, University of Sheffield, 1971.

TABLE 1

Voltammetric data obtained from Lewis base complexes, $Cr(CO)_5L$

L	$E_{\frac{1}{2}}$ [a]	$E_{\frac{3}{4}} - E_{\frac{1}{4}}$ [b]	i_d/c [c]	Cyclic voltammetry [d] E_a [e]	E_c [f]	PS [g]	Remarks [h]
$P(OMe)_3$	1·54	72	5·1(1)	1·65	1·44	210	R
PH_3	1·43	71	5·8(1)	1·20			EC
$P(OPh)_3$	1·32	52	7·5(2)				
PMe_3	1·18	80	4·9(1)	1·30	1·07	237	R
p-ClC_6H_4NC	1·16	58				195	QR/CCR
PPh_3	1·15	59	8·2(2)				
p-MeC_6H_4NC	1·14	60				200	
MeNC	1·10	58	9·0(2)				
Bu^tNC	1·10	85				200	
Pyridine	0·91	64	8·0(2)				
MeCN	0·90	54	6·9(2)				
C_4H_8NH [i]	0·77	57	9·1(2)				
C_2H_4NH	0·76	55	7·6(2)				
NH_3	0·71	56	8·1(2)				
CN^-	0·50	60	5·3(1)			165	R
I^-	0·35	57	9·0(2)				
Cl^-	0·31	56	7·4(2)				

[a] In V, error ±10 mv. [b] In mV, for a reversible couple, *e.g.* $[Ni\{S_2C_2(CN)_2\}_2]^- + e \rightleftharpoons [Ni\{S_2C_2(CN)_2\}_2]^{2-}$, $E_{\frac{3}{4}} - E_{\frac{1}{4}} = 59$ mV. [c] In μA mmol⁻¹ for the reversible couple $[Ni\{S_2C_2(CN)_2\}_2]^- + e^- \rightleftharpoons [Ni\{S_2C_2(CN)_2\}_2]^{2-}$ this depends on the electrode used: for electrode (1) $i_d/c = 5·3$ and for electrode (2) 8·4. [d] Using Pt wire and sweeps of 0·05 V s^{-1}. [e] Anodic peak. [f] Cathodic peak. [g] Peak separation, for a reversible wave, based on the couple in (*b*), PS varies between 170 and 230 mV. [h] R = Reversible wave, QR = quasi-reversible, IR = irreversible, CCR = coupled chemical reaction, EC = electrode coating. [i] $W(CO)_5(NEt_3)$ has $E_{\frac{1}{2}} = +0·88$ V, $E_{\frac{3}{4}} - E_{\frac{1}{4}} = 53$ mV, $i_d/c = 5·2$ μA mmol⁻¹, $E_a = 0·99$, E_c not detected, QR.

and pyrrolidine. When L is pyridine or MeCN, the value of $E_{\frac{1}{2}}$ falls in the intermediate range at *ca.* +0·90 V. Alkylation of $[Cr(CO)_5CN]^-$ to give $Cr(CO)_5CNR$ causes an increase of at least 500 mV in the oxidation potential, as has been observed in electrochemical studies of iron cyanide and isocyanide complexes.[8]

Lewis Base Complexes. $M(CO)_4L_2$, $M(CO)_4(LL)$, *and* $M(CO)_2(LL)_2$.—The results (Table 2) indicate clearly that there is a correlation between the apparent π-acceptor/σ-donor ratio of the ligand L (or L–L) and the $E_{\frac{1}{2}}$-values of the complexes. In general, the half-wave potential value of a particular compound, $Cr(CO)_5L$, (L = PMe_3, pyridine, or amine) is more anodic (+1·18 to +0·71 V) than that of its analogue in the $Cr(CO)_4(L–L)$ series [L–L = $(Me_2PCH_2)_2$ (dmpe), bipyridyl, or diamine, respectively] (+0·89 to +0·14 V). This is consistent with our earlier finding[6] that when *n* decreases in the series $Cr(CO)_n(L)_{6-n}$ and CO is replaced by an increasing number of less effective π-acceptor ligands, the value of $E_{\frac{1}{2}}$ decreases.

The oxidation potentials for the $Cr(CO)_4(LL)$ complexes in which LL is *o*-phenanthroline or *NNN'N'*-tetramethyl-*o*-phenylenediamine are more positive than those for the corresponding bipyridyl and *NNN'N'*-tetramethylethylenediamine compounds, showing that, as found elsewhere,[9] increased π-conjugation within a comparable ligand system leads to a decrease in the ease of oxidation of the complex as a whole.

As mentioned above for the class of $Cr(CO)_5L$ compounds, there appears to be an inverse relationship between the basicity of an amine, LL, and the $E_{\frac{1}{2}}$-value of the complex $Cr(CO)_4(LL)$; methylation at nitrogen causing a large increase in the potential. In contrast to this, methyl substitution of the ethylenic backbone of the diamine ligands caused no change in $E_{\frac{1}{2}}$. However the potential of the stilbenediamine complex was significantly higher than that of its ethylenediamine analogue.

TABLE 2

Voltammetric data obtained from Lewis base complexes, $M(CO)_4L_2$, $M(CO)_4(LL)$, and $Mo(CO)_2(LL)_2$

M	L (or LL)	$E_{\frac{1}{2}}$ [a]	$E_{\frac{3}{4}} - E_{\frac{1}{4}}$ [b]	i_d/c [c]	Cyclic voltammetry [d]			
					E_a [e]	E_c [f]	PS [g]	Remarks [h]
Cr	*o*-phen	0·89	57	5·4(1)	1·00	0·81	190	R
	p-ClC_6H_4NC	0·76	65		0·825	0·67	155	R
	p-MeC_6H_4NC	0·67	67		0·765	0·60	165	R
	PMe_2H	0·61	100	5·1(1)	0·705			QR/CCR
	bipy	0·61	62	4·7(1)	0·71	0·53	175	R
	Pr^iNC	0·58	74		0·61	0·41	250	QR
	Bu^tNC	0·57	62		0·65	0·49	160	R
	$(Me_2PCH_2)_2$ [i]	0·46	70	5·3(1)	0·59	0·325	265	QR
	o-$Me_2NC_6H_4NMe_2$	0·44	57	7·2(2)				
	$(Me_2NCH_2)_2$	0·36	52	7·0(2)				
	$(Me_2NCHMe)_2$	0·36	50	7·1(2)				
	$(H_2NCHPh)_2$	0·22	60	7·2(2)				
	$(H_2NCHMe)_2$	0·14	53	7·1(2)				
	$(H_2NCH_2)_2$	0·14	60	6·9(2)				
Mo	*p*-ClC_6H_4NC	0·98	60		1·05			EC
	p-MeC_6H_4NC	0·89	93					
	Pr^iNC	0·81	101					
	Bu^tNC	0·80	87					
	bipy	0·62	98	5·9(1)				
	$(Me_2PCH_2)_2$ [j]	0·61	85	4·4(1)				EC
W	Pr^iNC	0·76	100		0·90			QR/CCR
	Bu^tNC	0·75	70		0·90			QR/CCR
	$(Me_2PCH_2)_2$	0·61	55	6·7(1)	0·71			QR/CCR
Mo	$[(Me_2PCH_2)_2]_2$ [k]	−0·23	83		−0·18			QR/CCR
	$[(Ph_2PCH_2)_2]_2$	−0·02	61	7·9(2)				

[a-h] As in Table 1. [i] Second oxidation wave, $E_{\frac{1}{2}} = +1·08$ V, $E_{\frac{3}{4}} - E_{\frac{1}{4}} = 80$ mV; $i_d/c = 11·03$; no cyclic voltammograms because of EC. [j] Second oxidation wave $E_{\frac{1}{2}} = 1·44$ V, $E_{\frac{3}{4}} - E_{\frac{1}{4}}$ *ca.* 130 mV. [k] Second oxidation wave $E_{\frac{1}{2}} = +0·82$ V, $E_{\frac{3}{4}} - E_{\frac{1}{4}} = 90$ mV, $E_a = 0·95$, E_c not observed.

Considering the results obtained from the class of

---

[8] M. K. Lloyd and J. A. McCleverty, unpublished work.

[9] J. A. McCleverty and D. G. Orchard, *J. Chem. Soc.* (*A*), 1971, 3784.

$M(CO))_4L_2$ and $M(CO)_4(LL)$ compounds in general, it is clear that changing M from chromium to molybdenum leads to an increase in the value of $E_{\frac{1}{2}}$, but this increase does not extend to tungsten.

The dicarbonyl complexes, $Mo(CO)_2\{(R_2P)_2CH_2\}_2$ (R = Me or Ph), exhibit two oxidation processes, and, of the Lewis bases studied had the lowest potentials for the primary oxidation step. This is consistent with the observation[10] that the diphos complex (R = Ph) is readily oxidised by iodine to give $[Mo(CO)_2(diphos)I]I_3$.

Carbene Complexes, $Cr(CO)_5C(X)Y$.—The potential measurements obtained from these complexes are summarised in Table 3. The values of $E_{\frac{1}{2}}$ span the range $-0{\cdot}10$ to $+0{\cdot}93$ V. For any particular heteroatom substituent, X (X = OR, SR, NRR′, $O^-NR_4^+$), the value of $E_{\frac{1}{2}}$ is not greatly influenced by the organic group, Y, when this is any of 2-thienyl, 2-furyl, (substituted) phenyl, or alkyl; however, when Y is ferrocenyl the potential falls by *ca.* 200 mV from its value in the other compounds. As the substituents on the phenyl become more electron-releasing, $E_{\frac{1}{2}}$ decreases in the order $Y = p\text{-}ClC_6H_4 > C_6H_5 > p\text{-}MeOC_6H_4$. This order is the same as that found for the ionisation potentials of the complexes measured by mass spectroscopy.[11]

TABLE 3

Voltammetric data obtained from carbene complexes $M(CO)_5C(X)Y$

M	X	Y	$E_{\frac{1}{2}}$ [a]	$E_{\frac{3}{4}} -$ $E_{\frac{1}{4}}$ [b]	i_d/c [c]
Cr	OEt	2-Thienyl	0·93	59	8·0
	OEt	2-Furyl	0·92	66	8·7
	OPh	2-Furyl	0·92	55	7·9
	OMe	p-ClC_6H_4	0·92 [d]	70	8·6
	OEt	C_6H_5	0·90	63	8·0
	OMe	p-$MeOC_6H_4$	0·86 [d]	75	7·7
	SPh	2-Furyl	0·84	54	7·4
	SEt	2-Furyl	0·82	52	7·5
	Aziridin-1-yl	C_6H_5	0·81	77	10·8
	Azetidin-1-yl	C_6H_5	0·78	76	8·4
	Pyrrolidin-1-yl	C_6H_5	0·76	57	10·0
	Piperidin-1-yl	C_6H_5	0·75	58	8·0
	NMe_2	C_6H_5	0·75	71	6·7
	NEt_2	Me	0·74	68	8·0
	NH_2	2-Furyl	0·74	61	7·5
	NH_2	2-Thienyl	0·74	54	8·0
	NHC_6H_{11}	Et	0·74	67	8·0
	NMe_2	Me	0·72	66	6·5
	Pyrrolidin-1-yl	2-Furyl	0·71	64	8·2
	Pyrrolidin-1-yl	2-Thienyl	0·70 [d]	75	5·0
	NHMe	Me	0·70	64	9·0
	OEt	Ferrocenyl	0·70	58	8·0
	OMe	Ferrocenyl	0·69	62	9·0
	Pyrrolidin-1-yl	Ferrocenyl	0·51	65	6·4
W	OEt	Ferrocenyl	0·68	59	8·0
	Pyrrolidin-1-yl	Ferrocenyl	0·50	56	7·0
Cr	$O^-NMe_4^+$	2-Furyl	0·06	63	
	$O^-NMe_4^+$	2-NMe-pyrryl	−0·09	80	
	$O^-NMe_4^+$	CH_2SiMe_3	−0·04	100	8·0
W	$O^-NMe_4^+$	Ferrocenyl	−0·04	73	

[a,b] As in Table 1. [c] As in Table 2, using electrode (2). [d] Waves were quasi-reversible with a coupled chemical reaction as established by cyclic voltammetry.

Variation of the group X causes the value of $E_{\frac{1}{2}}$ to increase in the order $X = O^-NMe_4^+ < NRR' < SR < OR$, which parallels the established order of decreasing donor strength of these groups with respect to the carbene carbon empty p_z-orbital.[12] The value of $E_{\frac{1}{2}}$ appears to correlate with the ring size in the cycloalkylamino-substituted complexes, but this does not reflect the changing basicity of the nitrogen, as indicated by pK_a measurements[13] of the free bases, $(CH_2)_nNH$, or the ASI shift of the α-CH_2 groups in the n.m.r. spectra of the complexes.[14] This lack of correlation with basicity, which has already been mentioned above, is apparent in the comparison of $Cr(CO)_5C(X)(C_4H_3S)$ ($X = NH_2, NC_4H_8$), for which $E_{\frac{1}{2}}$ is the same in each case, and the comparison of $Cr(CO)_5C(X)Me$ ($X = NHMe, NMe_2, NEt_2$), for which $E_{\frac{1}{2}}$ increases as the bulk of the substituents at nitrogen increases.

We are unable to obtain sufficient comparative data from molybdenum and tungsten carbene complexes, due largely to the instability of these species (molybdenum) and to electrode coating (tungsten).

DISCUSSION

All the complexes examined here, except $Cr(CO)_6$ and $Cr(CO)_5PF_3$, undergo at least one one-electron oxidation whose potential value is dependent upon the metal atom, the electronic properties of the ligand L or [C(X)Y], and the number of CO groups present in the molecule. The failure to observe anodic electrode behaviour in $Cr(CO)_6$ and $Cr(CO)_5PF_3$ may be attributed to the occurrence of the appropriate oxidation wave within or above the decomposition wave of the medium (*i.e.* $E_{\frac{1}{2}} > 1{\cdot}6$ V); CO and PF_3 are better π-acceptor ligands than, say, $P(OR)_3$, and so the oxidation potential should be greater than $+1{\cdot}54$ V.

It seems intuitively reasonable to assume that the redox orbital in metal complexes is the highest occupied molecular orbital. However molecular orbital calculations[15] on the compounds $Cr(CO)_5L$ ($L = NH_3, PH_3, PMe_3$) and $Cr(CO)_5C(X)Me$ (X = OMe, NHMe), using a semi-empirical method similar to that used[16] in calculations of the anion $[Cr(CO)_5Cl]^-$, when scaled to *ab initio* calculations[15] of $Cr(CO)_5NH_3$, have shown that both the highest occupied molecular orbital (b_2) and the next most tightly bound orbitals (e) are composed exclusively (>99·4%) of Cr $3d$, C $2p$, and O $2s$ atomic orbital contributions. The validity of these calculations is corroborated by photoelectron spectroscopic measurements[17] on these and other similar compounds.

In the case of the carbene complexes, the calculations indicate a small (<16%) contribution of the carbene ligand [C(X)Y] to the third least tightly bound orbital. This contribution is absent in the compounds $Cr(CO)_5L$ ($L = NH_3, PH_3, PMe_3, Cl^-$) in which the '$e$' orbitals are degenerate. In every case the principal metal–ligand σ-bonding orbital (denoted σ) is more tightly

---

[10] P. F. Crossing and M. R. Snow, *J. Chem. Soc. (A)*, 1971, 610.

[11] E. O. Fischer, C. G. Kreiter, H. J. Kollmeier, J. Müller, and R. D. Fischer, *J. Organometallic Chem.*, 1971, **28**, 237.

[12] J. A. Connor and E. M. Jones, *J. Chem. Soc. (A)*, 1971, 3368.

[13] D. D. Perrin, *Austral. J. Chem.*, 1964, **17**, 484.

[14] J. A. Connor and P. D. Rose, *Tetrahedron Letters*, 1970.

[15] M. B. Hall and I. H. Hillier, unpublished work.

[16] M. B. Hall and R. F. Fenske, *Inorg. Chem.*, 1972, 11.

[17] M. Barber, J. A. Connor, M. F. Guest, M. B. Hall, I. H. Hillier, and W. N. E. Meredith, *Faraday Discuss. Chem. Soc.*, 1972, **54**, 219.

bound than both the b_2 and the e orbitals. The calculated energy separation in volts, $|b_2 - \sigma|$, increases in the order [C(OMe)Me] (1·0) < PMe_3 < [C(NHMe)Me] < PH_3 < NH_3 (5·6). The order of increasing binding energy of both b_2 and σ follows that of the ionisation potentials of the free ligands (PMe_3 8·6, PH_3 9·9, NH_3 10·8 eV), whereas the order of increasing $E_{\frac{1}{2}}$ is given by L = NH_3 < PMe_2 < PH_3 (see Table 1).

There is a direct linear relation between $E_{\frac{1}{2}}$ for the complexes $Cr(CO)_5L$ [L = PPh_3, PMe_3, PH_3, $P(OMe)_3$] and the ionisation potential of the free ligand, L. This might be interpreted to show that oxidation takes place by electron loss from the Cr–L bond, as was proposed[18] for the analogous molybdenum compounds. However such an interpretation is not consistent with the results of the molecular orbital calculations if it is accepted that the redox orbital is synonymous with the highest occupied molecular orbital. The possibility that the energies of the orbitals b_2, e, and σ change in solution in such a manner as to make σ the least tightly bound, must be discounted on the basis of energy considerations. A reorganisation of this kind would require a change of *ca.* 250 kJ mol^{-1} in the energy of the system accompanying dissolution in a relatively non-polar solvent, methylene chloride.

A series of both *ab initio* and approximate molecular orbital calculations[19] on the molecules $Mn(CO)_5X$ (X = Me, Cl, H) showed that in the approximate treatment the (Mn–X) σ orbital was more tightly bound than both b_2 and e. However, in the *ab initio* calculation this ordering was reversed so that σ is the least tightly bound molecular orbital. Unfortunately, attempts to determine the oxidation potentials of $Mn(CO)_5Me$ and of $Mn(CO)_5X$ (X = Cl, Br, I) were hindered by rapid decomposition and coating of the platinum electrode. It appears reasonable to suggest that the instability with respect to oxidation in these manganese compounds may be related to the ordering of the orbitals ($\sigma < b_2, e$) in these molecules.

The relationship between $E_{\frac{1}{2}}[Cr(CO)_5L]$ and the ionisation potential of L for other complexes in which L is a nitrogen or carbon (carbene) donor is of the inverse linear type. This type of relationship has been interpreted[18] as showing that ionisation results in loss of an electron from a ligand molecular orbital rather than from the M–L σ orbital. This interpretation is not supported by the molecular orbital calculations on $Cr(CO)_5NH_3$ and $Cr(CO)_5C(X)Me$ (X = OMe, NHMe) outlined above.

The effect of the ligand, L, upon the value of $E_{\frac{1}{2}}$ for the complex $Cr(CO)_5L$ is clearly much more subtle than might have been suspected. While the molecular orbital calculations indicate that L does not participate to any significant extent in the highest occupied molecular orbital (b_2), the values of $E_{\frac{1}{2}}$ indicate that, if this orbital is correctly assumed to be the redox orbital, then it is quite sensitive to the nature of L. This contradiction may be resolved by suggesting that L exerts a remote or indirect influence upon the energy of the b_2 orbital in the $Cr(CO)_5L$ compounds, without changing the atomic orbital composition of the molecular orbital.

The lack of correlation between $E_{\frac{1}{2}}$ and the basicity of the Lewis base in $Cr(CO)_5L$ (L = PR_3 or NH_3) and $Cr(CO)_4(LL)$ (LL = diamine) is surprising. The only explanation we can offer is that the steric interactions between the more bulky phosphines, phosphites, or amines [those carrying aryl (P) or alkyl (N) groups] and the CO groups attached to the metal are relieved by increasing the Cr–P and Cr–N bond lengths relative to their 'equilibrium distance' in species containing less bulky substituents [H or alkyl (P) or H (N)]. Such an increase in bond length would lead to a decrease in the effective basicity (donor strength) of L with respect to chromium, that is, to a decrease in the ligand field strength. The consequent increase in the binding energy of the redox orbital would, in turn, increase the value of $E_{\frac{1}{2}}$.

The ferrocenyl carbene complexes exhibit a single one-electron oxidation wave in their voltammograms. Initially, this is surprising since (i) ferrocene and its substituted derivatives exhibit anodic electrode behaviour corresponding to the generation of $[(\pi\text{-}C_5H_4R)_2Fe]^+$, and (ii) the $Cr(CO)_5Q$ group, where Q = L or C(X)Y, has oxidation behaviour in its own right. We would have anticipated, therefore, the detection of either two one-electron oxidation waves, or possibly an apparemt two-electron process. There can be two explanations for the experimental results; that the process observed is due to one of the redox centres, say A in A–B, and that the oxidation wave of B is increased so much by the electron-withdrawing properties of A that it occurs within or above the decomposition wave of the medium (this would be represented by A^{+}–B), or that the redox orbital of the $Cr(CO)_5C(X)Fc$ complex encompasses both potential redox centres which corresponds to the generation of $[A–B]^+$. The latter explanation, in our opinion, seems to be more reasonable, and is consistent with other properties of the compounds.[20]

Finally, the electrochemical results may be related to the known synthetic oxidation chemistry of this class of compounds. Iodine oxidation of $[Cr(CO)_5I]^-$ afforded[2] $Cr(CO)_5I$ and this is consistent with an oxidation potential of +0·35 V. However, our attempts to oxidise the corresponding compounds $[Cr(CO)_5X]^-$ (X = Cl, CN) or even $Cr(CO)_4(H_2NCH_2)_2$, using $AgPF_6$ or I_2 were unsuccessful; reactions do occur but the products decomposed very rapidly, and we were unable to detect paramagnetic intermediates using e.s.r. spectral methods. The very easy oxidation of $[Mo(CO)_2\{Ph_2PCH_2)_2\}_2]$ to the corresponding cation using acid in air,[10] is clearly reflected in the very low $E_{\frac{1}{2}}$-value for this process (−0·02 V); oxidation of $[Mo(CO)_2$-

---

[18] G. Distefano, G. Innorta, S. Pignataro, and A. Foffani, *J. Organometallic Chem.*, 1968, **14**, 168.

[19] M. B. Hall, M. F. Guest, and I. H. Hillier, *Chem. Phys. Letters*, 1972, **15**, 592.

[20] J. A. Connor and J. P. Lloyd, *J.C.S. Dalton*, 1972, 1470.

$\{(Me_2PCH_2)_2\}_2]$ is even easier, as will be described in detail elsewhere.[21] * The trend towards increasingly negative values of $E_{\frac{1}{2}}$ as the number of phosphorus donor atoms at the metal increases is consistent with the known extreme sensitivity to oxidation of the tris-diphosphine complexes, $[M(R_2PCH_2CH_2PR_2)_3]$.[22] The insolubility of the compounds (M = Cr, Mo, W; R = Me) in solvents suitable for electrochemical measurements but with which they do not react has prevented a direct measurement of $E_{\frac{1}{2}}$.

EXPERIMENTAL

The voltammetric data were obtained using a Beckmann Electroscan 30 polarograph. The cell was of conventional H-type design, used in both two-electrode and three-electrode configuration, with a saturated calomel electrode (1M in aqueous LiCl) as reference. The test electrode was a platinum wire rotated at 620 rev. min^{-1}, and the auxiliary electrode, when used, was also of platinum wire. The solvent was dichloromethane carefully purified and dried prior to use. The complexes were 10^{-3}M in solution, and the base electrolyte, $[Et_4N]ClO_4$, was 0·075M; all measurements were carried out at room temperature (20 ± 2°) in draught-free conditions. The cyclic voltammograms were obtained using a stationary platinum wire and sweep scans of 0·05 V s^{-1}. The data were corrected for *iR* drop where necessary, and the estimated error in the results is ±10 mV.

The compounds listed in Tables 1—3 were prepared by standard methods and characterised by analysis and by the usual spectroscopic techniques. Solid compounds and their solutions were handled in an inert atmosphere.

We thank the S.R.C. for financial support (M. K. L., D. G. O., M. B. H., E. M. J., and G. K. McE.), and Mrs. J. Bray and Mr. G. A. Wright for technical assistance. We are grateful to the Royal Society for providing the funds which purchased the Beckman Electroscan 30 polarograph.

[2/2545 *Received, 10th November*, 1972]

---

* It might be expected that the isoelectronic $[Mo(N_2)_2(R_2P\text{-}CH_2CH_2PR_2)_2]$ would be more easily oxidised than the carbonyl species, since N_2 is a poorer π-acceptor than CO. This expectation has recently been realised (T. A. George and C. D. Seibold, *J. Amer. Chem. Soc.*, 1972, **94**, 6859).

[21] J. A. Connor and G. K. McEwen, unpublished work.

[22] J. Chatt and H. R. Watson, *J. Chem. Soc.*, 1962, 2545.