Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

Preliminary communication

The electrochemical oxidation of low-valent chromium, tungsten and manganese complexes

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(Received June 1st, 1971)

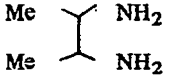
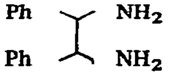
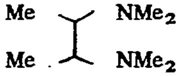
A variety of chromium carbonyl derivatives undergo polarographic reduction giving mono- or di-anions[1]. There are no examples, however, of the electrochemical oxidation of chromium carbonyls, presumably because of the use of the dropping mercury electrode in the previous polarographic experiments. By employing a rotating platinum electrode in dichloromethane solution, we have shown that many chromium carbonyl complexes may be oxidised in one-electron transfer reactions, most of which are voltammetrically and chemically reversible.

The half-wave potentials for the oxidation of the Lewis base compounds $[Cr(CO)_5L]$ are dependent on the π-acceptor/σ-donor abilities of L. Thus, when L is a good π-acceptor, $E_{1/2}$ is greater than +1.00 V (Table 1), and when L is a poor π-acceptor but is a good σ-donor, $E_{1/2}$ is less than ca. +0.80 V. In the tetracarbonyl series, $[Cr(CO)_4(\text{diamine})]$[2], the $E_{1/2}$-values occur ca. 400 mV lower than those of the pentacarbonyl amine species, suggesting that the effect of the donor atom is additive, and dependent both on the substituent at the N-donor atom and on the ligand backbone.

In the carbene complexes, $[Cr(CO)_5(CXY)]$, the oxidation potentials were significantly dependent upon both X and Y. Thus, when Y = 2-furyl[3], the $E_{1/2}$-values decreased in the order $X = OR > SR > NR_2 \gg O^-$ (Table 2). However, when Y = 1-ferrocenyl[4], $E_{1/2}$ occurred ca. 200 mV lower than any other comparable carbene complex system containing the same substituent X. Ferrocene undergoes a one-electron oxidation process ($E_{1/2}$ 0.39V), so that it is surprising that the voltammograms of these ferrocenyl carbene complexes exhibit only one one-electron oxidation wave. A possible explanation is that $E_{1/2}$ for the oxidation of the $[Cr(CO)_5X\text{—}]$ moiety occurs outside the limits of the voltage scan (*cf.* $Cr(CO)_6$, where no wave was detected from 0 to +1.80 V) in these compounds, and it is the ferrocenyl oxidation wave, which is known to be substituent dependent[5], which is detected. The fact that $E_{1/2}$ is greater than in ferrocene itself, reflects the donor character of the metallocenyl group and may be related to the known ability of the ferrocenyl group to stabilise α-carbonium ions[6].

TABLE 1

VOLTAMMETRIC DATA OBTAINED FROM SOME LEWIS BASE COMPLEXES $[Cr(CO)_5L]$ AND $[Cr(CO)_4(diamine)]$

L	Diamine	$E_{1/2}$ [a]
$P(OPh)_3$		1.32
PPh_3		1.15
CNMe		1.10
NCMe		0.90
NH_3		0.71
I^- [b]		0.35
Cl^- [b]		0.31
		0.14
		0.22
		0.36

[a] In V, *vs.* SCE; in CH_2Cl_2 (10^{-3} *M*) with $[Et_4N][ClO_4]$ (0.05 *M*) as base electrolyte; at 20°.
[b] As NEt_4^+ salts.

TABLE 2

VOLTAMMETRIC DATA OBTAINED FROM SOME CHROMIUM, TUNGSTEN AND MANGANESE CARBENE COMPLEXES

Metal fragment	(CXY)		$E_{1/2}$
	X	Y	(V)
$Cr(CO)_5$	OEt	2-furyl	0.92
	SEt	2-furyl	0.82
	NC_4H_8 [a]	2-furyl	0.71
	O^-	2-furyl	0.06
	OEt	1-ferrocenyl	0.70
	OEt	2-thienyl	0.93
$W(CO)_5$	OEt	1-ferrocenyl	0.68
$(\pi\text{-}C_5H_4Me)Mn(CO)_2$	OMe	1-ferrocenyl	0.26 0.99
	OMe	Ph	0.45 1.3 [b]

[a] *N*-Pyrrolidyl. [b] Wave-height reduced by electrode coating.

Voltammetric oxidation is not restricted to the Group VIB metal carbonyl complexes. Thus, the manganese carbenes, $\{(\pi\text{-}C_5H_4Me)Mn(CO)_2[C(OMe)Y]\}$ (Y = 1-ferrocenyl or Ph) undergo two one-electron oxidation processes, and the nitrosyl cations $[(\pi\text{-}C_5H_5)Mn(NO)LL']^+$ (L = L′ = phosphines, pyridines, isonitriles, bipyridyl, etc.)[7] may be oxidised in a one-electron step which is also dependent on the π-acceptor/σ-donor characteristics of L and L′ (Table 3).

TABLE 3

VOLTAMMETRIC DATA OBTAINED FROM SOME MANGANESE NITROSYL COMPLEXES, $[(\pi\text{-}C_5H_5Mn(NO)LL'][PF_6]$

L	L'	$E_{½}$ (V)
CO	PPh_3	1.62
$4\text{-}MeC_5H_4N$ [a]	$P(OPh)_3$	1.16
PMe_2Ph	PMe_2Ph	0.90
bipyridyl		0.90
$4\text{-}MeC_5H_4N$	PPh_3	0.84

[a] 4-Methylpyridine.

The half-wave potential data indicate that formation of the oxidised species by "wet chemical" methods is largely impracticable. However, the unstable $[Cr(CO)_5I]$ has been obtained[8] by iodine oxidation of $[Cr(CO)_5I]^-$; our attempts to prepare the analogous $[Cr(CO)_5Cl]$ have so far been unsuccessful as have our attempts to obtain $[Cr(CO)_4(\text{diamine})]^+$ by oxidation of the natural species with Ag^+. However, treatment of $\{(\pi\text{-}C_5H_4Me)Mn(CO)_2[C(OMe)(1\text{-ferrocenyl})]\}$ with I_2 in CH_2Cl_2/Me_2CO afforded a species which exhibited, in solution at room temperature, a characteristic six-line ESR signal (^{55}Mn, I 5/2; 100% abundant; $\langle g \rangle$ 2.037 and $\langle a \rangle_{Mn}$ 91.6 gauss) which we attribute to the monocationic species.

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