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Preliminary communication

Electrochemical oxidation of isocyanide complexes of manganese and chromium

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The variations of infrared stretching frequencies (ν(CO), ν(CN)) in isocyanide substituted metal carbonyls as a function of the isocyanide ligand have been the subject o extensive comment[1]. In general, one observes for structurally analogous complexes $M(CO)_x(CNR)_y$ a lower value for ν(CO) and a smaller shift to lower wave numbers, $\Delta\nu$(C (= ν(CN) for the free ligand – ν(CN) for the complexed ligand) for alkyl isocyanides than for aryl isocyanides. On the basis of these data, aryl isocyanides are acknowledged to have greater capacity for electron withdrawal in a metal complex[1]. This conclusion is rationalized in terms of delocalization of metal electron density through π bonding into th aryl ring, whereas such delocalization is not possible with alkyl isocyanide. Of course this rationale was introduced when emphasis on ligand metal π bonding was popular, and may now be modified to include σ and π bonding contributions.

We observe, however, that though there is no apparent controversy over this conclusion, neither is there reported any substantial difference in chemical behavior of alkyl and aryl isocyanide complexes which can be directly attributed to these differences. The purpose of this communication is to point out that, indeed, such differences in chemical behavior do exist, and that they may have rather significant consequences.

We have looked at the electrochemical oxidations of manganese(I)[2,3] and chromium(0)[4,6] aryl isocyanide complexes, $Mn(CNR)_6^+$ and $Cr(CNR)_6$ ($R = C_6H_5$, p-$CH_3C_6H_4$, p-$CH_3OC_6H_4$, p-ClC_6H_4) and the manganese methyl isocyanide complex[5,6] $Mn(CNCH_3)_6^+$, by cyclic voltammetry using a stationary platinum bead working electrod These data are presented in Table 1.

The information from this study provides several important comparisons, foremost being the ease of oxidation of aryl and alkyl isocyanide complexes of a metal. The complex $Mn(CNCH_3)_6^+$ is seen to be substantially easier to oxidize than any of the analogous aryl isocyanide complexes $Mn(CNAr)_6^+$. Among the aryl isocyanide complexes there are smaller, though still substantial, differences in oxidation potentials depending on the nature of the *para*-substituent group. Electron-donating groups predictably increase th ease of oxidation, electron-withdrawing groups lower the ease of oxidation.

TABLE I

VOLTAMMETRIC DATA [a]

Compound	$\frac{1}{2}[E_{p,c} + E_{p,a}]$	*Process*
$[Mn(CNCH_3)_6]PF_6$	0.47	$+1 \rightarrow +2$
	1.59	$+2 \rightarrow +3$
$[Mn(CNC_6H_4OCH_3)_6]PF_6$	0.81	$+1 \rightarrow +2$
	1.68	$+2 \rightarrow +3$
$[Mn(CNC_6H_4CH_3)_6]PF_6$	0.93	$+1 \rightarrow +2$
	1.83	$+2 \rightarrow +3$
$[Mn(CNC_6H_5)_6]PF_6$	1.01	$+1 \rightarrow +2$
	1.91	$+2 \rightarrow +3$
$[Mn(CNC_6H_4Cl)_6]PF_6$	1.05	$+1 \rightarrow +2$
	1.90	$+2 \rightarrow +3$
$Cr(CNC_6H_4OCH_3)_6$	0.15	$0 \rightarrow +1$
	−0.43	$0 \rightarrow -1$
$Cr(CNC_6H_4CH_3)_6$	0.23	$0 \rightarrow +1$
	−0.39	$0 \rightarrow -1$
$Cr(CNC_6H_5)_6$	0.33	$0 \rightarrow +1$
	−0.29	$0 \rightarrow -1$
$Cr(CNC_6H_4Cl)_6$	0.33	$0 \rightarrow +1$
	−0.17	$0 \rightarrow -1$

[a] Cathodic and anodic peak potentials in volts, *vs.* saturated calomel electrode (aq. KCl). Solutions in CH_2Cl_2 (5×10^{-3} *M*) with $[n\text{-}Bu_4N][ClO_4]$ (0.1*M*) as base electrolyte. The electrode reactions appear reversible for the manganese salts. (Difference in peak potentials is 0.06 V for a one-electron reversible system.) Differences in peak potentials for the chromium complexes are 0.06–0.07 V.

The same trend toward oxidation is observed on the hexakis(aryl isocyanide)-chromium(0) species. For each complex, a one electron oxidation is observed. The lower potential when compared to the isoelectronic manganese species is anticipated due to the lower valency of chromium in these complexes. It would be interesting to compare these data with the oxidation potential for hexakis(methyl isocyanide)chromium(0). However it is appropriate to note that this compound is not yet known. We have observed that obvious methods for its synthesis are not successful; *e.g.*, the reaction of chromium(II) acetate and isocyanide failed to yield this species, although the aryl isocyanide complexes are easily prepared in this way.

There are several other points that deserve mention. All of the hexakis-isocyanide manganese(I) complexes are observed to undergo a second one electron oxidation at considerably higher potential. Presumably this represents an oxidation to the manganese(III) species. No second oxidation was observed for the analogous chromium complexes. However these species may be reduced by one electron, with potentials which indicate such a reduction should be reasonably accessible by chemical means.

Finally we note that the isoelectronic iron(II) species $[Fe(CNCH_3)_6]^{2+}$ gives neither a clean electrochemical oxidation nor a reduction. The lack of an oxidation seems somewhat surprising.

It is attractive to relate the ease of oxidation to the electron-withdrawing power ol the ligand, and most probably this is indeed the major point of importance. However, this conclusion is not fully justifiable; one must be aware that the $E_{1/2}$ measures an energy difference related to both the initial and final complexes in the reaction.

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REFERENCES

1 L. Malatesta and F. Bonati, *Isocyanide Complexes of Metals*, Wiley-Interscience, New York, N.Y., 1969.

2 A. Sacco, *Gazz. Chim. Ital.*, 86 (1956) 201.

3 A. Sacco and L. Naldini, *Gazz. Chim. Ital.*, 86 (1956) 207.

4 L. Malatesta, A. Sacco and S. Ghielmi, *Gazz. Chim. Ital.*, 82 (1952) 506.

5 A. Sacco, *Ann. Chim. (Rome)*, 48 (1958) 225.

6 F.A. Cotton and F. Zingales, *J. Amer. Chem. Soc.*, 83 (1961) 351.