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The Infrared Spectroelectrochemistry of Hexakis(xylyl isocyanide)molybdenum(0)

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Based upon previous electrochemical and chemical studies on hexakis(aryl isocyanide) complexes of molybdenum(0) and tungsten(0), we have proposed [1–3] that the following scheme (reactions (1)–(5)) provides a plausible mechanism for the observed conversion of $M(CNAr)_6$ to $[M(CNAr)_7]^{2+}$ following oxidation to $[M(CNAr)_6]^{2+}$. In this scheme, the

$$M(CNAr)_6 \rightleftharpoons [M(CNAr)_6]^+ + e^- \tag{1}$$

$$[M(CNAr)_6]^+ \longrightarrow [M(CNAr)_6]^{2+} + e^- \tag{2}$$

$$[M(CNAr)_6]^{2+} + [M(CNAr)_6]^+ \longrightarrow [M(CNAr)_7]^{2+} + \{[M(CNAr)_5]^+\} \tag{3}$$

$$\{[M(CNAr)_5]^+\} \longrightarrow \{[M(CNAr)_{5-x}]^+\} + ArNC \tag{4}$$

$$[M(CNAr)_6]^{2+} + ArNC \longrightarrow [M(CNAr)_7]^{2+} \tag{5}$$

species denoted { } are believed to be unstable and highly reactive species that were not detected electrochemically [1]. By utilizing spectroelectrochemical techniques, specifically FT-IR spectroscopy, we can now provide strong supporting evidence for the essential ingredients of this mechanism. In this report, we describe the results of such a study on a representative member of this class, *viz.* $Mo(CNxylyl)_6$ (xylyl = 2,6-dimethylphenyl).

The complexes $Mo(CNxylyl)_6$ and $[Mo(CNxylyl)_7](PF_6)_2$ were prepared using the methods previously reported [1, 3]. The dichloromethane and acetonitrile solvents (Burdick and Jackson) were vacuum distilled over CaH_2, while DMF and DMSO (Burdick and Jackson) were dried over size 4 Å molecular sieves which had been activated at 300 °C for 14 h under vacuum. Electrochemical measurements were carried out under a rigorously inert atmosphere which was achieved by utilizing a nitrogen filled dry box (Vacuum Atmospheres). Details of the cell configuration, instrumentation, and infrared OTTLE (optically transparent thin layer electrode) cell, in which a gold mesh working electrode was used, are provided elsewhere [4, 5].

TABLE I. Cyclic Voltammetric Parameters for $Mo(CNxylyl)_6$[a]

Solvent	$E_{1/2}$ (V) (+1/0)	$i_{p,c}/i_{p,a}$[b]	$E_{p,a} - E_{p,c}$ (mV)[b]	$E_{p,a}$ (V) (+2 ← +1)
CH_3CN	−0.28	<1	68	+0.35
DMF	−0.04	≈1	73	+0.62
DMSO	−0.25[c]	≪1	–	+0.80
CH_2Cl_2	−0.35	≈1	69	+0.48

[a] Recorded in 0.1 M TBAH using a Pt-bead electrode at ν = 200 mV/s and 25 °C *vs.* SCE. [b] These parameters relate to the properties of the (1+/0) couple. [c] $E_{p,a}$ value.

The IR spectra were recorded on an IBM/Bruker FTIR model 98-4A spectrometer, with a globar light source and a liquid N_2-cooled MCT narrow-band detector (Infrared Associates Model HCT-18A). Satisfactory spectra could be obtained within a few interferometer scans (*ca.* 10 s). Tetra-n-butylammonium hexafluorophosphate (TBAH) was used as the supporting electrolyte and measurements were carried out in approximately 1 mM solutions of the isocyanide complex and 0.1 M TBAH. It was necessary to deoxygenate solvents that were used in the OTTLE prior to addition of $Mo(CNxylyl)_6$ in order to prevent air oxidation of the complex.

The highly reactive nature of the monocation and the even more unstable dication $[Mo(CNxylyl)_6]^{2+}$ is exemplified by the dependence of the chemical reversibility of the anodic–cathodic cyclic voltammograms as a function of solvent. In all the solvents studied (acetonitrile, dichloromethane, DMF, and DMSO) the cyclic voltammograms for the +2/+1 redox couple were irreversible, but the reversibility of the +1/0 couple was greatly affected (Table I). Based upon these measurements, dichloromethane was judged to be the most suitable solvent for carrying out the spectroelectrochemistry studies.

The infrared spectral data obtained during electrolysis supports the scheme outlined in reactions (1)–(5). The neutral complex exhibits a strong ν(CN) mode at 1951 cm^{-1} with two weak shoulders at 2017 and 2048 cm^{-1} (Fig. 1a). Upon generation of the monocation by electrolysis at 0.0 V, the frequency of the major ν(CN) band shifts to 2048 cm^{-1} (Fig. 1b). These spectral changes can be reversed by re-reducing $[Mo(CNxylyl)_6]^+$ to $Mo(CNxylyl)_6$ at a potential negative to that for the +1/0 couple. After electrolysis of $Mo(CNxylyl)_6$ at +0.90 V (*i.e.* beyond the second oxidation – reaction (2)) three bands appear in the ν(CN) region; an intense feature centered at ~2120 cm^{-1} with a shoulder at 2106 cm^{-1}, and a very weak band at 2225 cm^{-1} (Fig. 1c). These spectral changes can be seen to proceed via the intermediacy of $[Mo(CNxylyl)_6]^+$ (ν(CN) at

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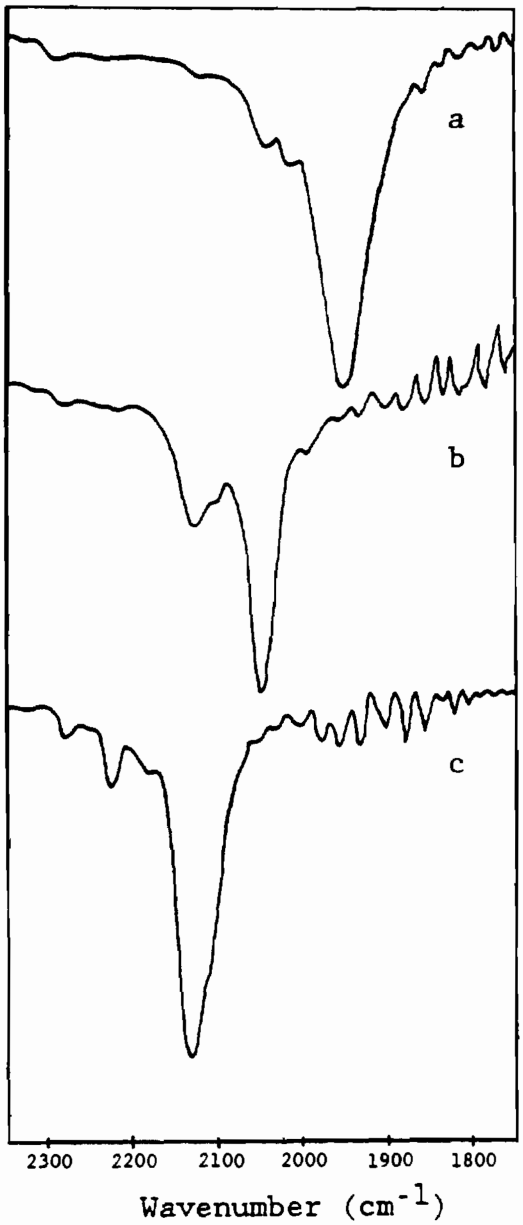

Fig. 1. FT-IR spectroelectrochemical study of Mo(CNxylyl)$_6$. Timed study of the ν(CN) region upon electrolysis at +0.9 V: (a) t = 0 min; (b) t = 3 min; (c) t = 5 min.

2048 cm^{-1}) by monitoring the spectra with time. A comparison of the spectrum in Fig. 1c with the spectrum of an authentic sample of [Mo(CNxylyl)$_7$]-(PF$_6$)$_2$, ν(CN) at 2125 cm^{-1} in CH$_2$Cl$_2$, confirmed this to be the predominant species that is formed following bulk electrolysis at +0.90 V. It should be noted here that free xylylNC exhibits a ν(CN) mode whose frequency, 2121 cm^{-1}, is coincident with the ν(CN) band of [Mo(CNxylyl)$_7$]$^{2+}$, although the latter band is markedly broader.

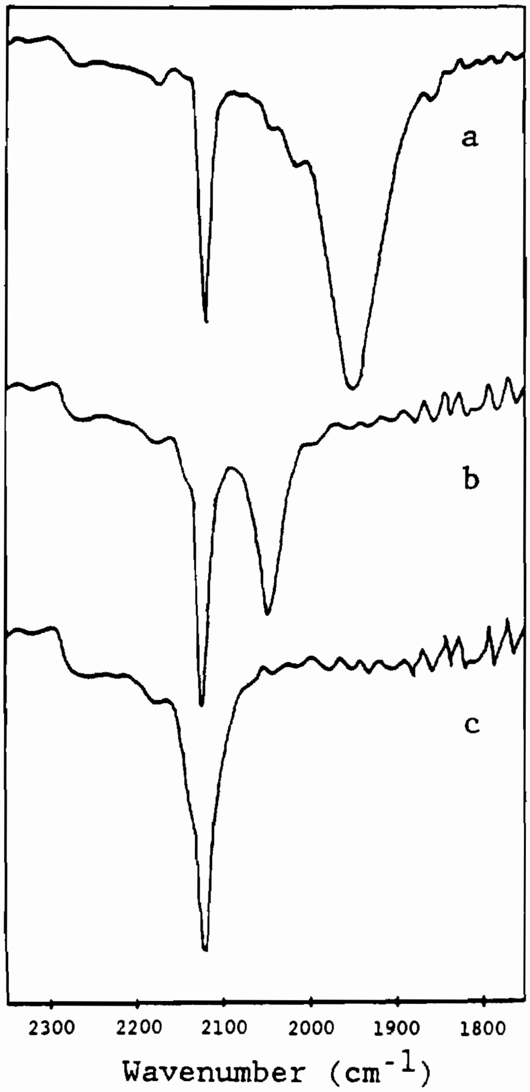

Fig. 2. FT IR spectroelectrochemical study of Mo(CNxylyl)$_6$. Timed study of the ν(CN) region upon electrolysis at +0.9 V in the presence of added excess xylylNC (ν(CN) = 2121 cm^{-1}): (a) t = 0 min; (b) t = 3 min; (c) t = 5 min.

An important point concerns whether isocyanide-deficient species such as {[Mo(CNxylyl)$_5$]$^+$} and {[Mo(CNxylyl)$_{5-x}$]$^+$} (see reactions (3) and (4)) can be detected. We find no evidence from the FT-IR spectra that they are present in other than very low concentrations. Although the weak feature at ~2225 cm^{-1} in Fig. 1c remains unassigned, it cannot be attributed to [Mo(CNxylyl)$_5$]$^+$ (or the like) since the ν(CN) mode(s) of such a species can be expected to occur at frequencies below that of [Mo(CN-xylyl)$_6$]$^+$ (ν(CN) at 2048 cm^{-1}). Since the presence of free xylylNC inhibits the formation and decomposition of {[Mo(CNxylyl)$_5$]$^+$} (reaction (4)), by favoring reaction (5), we would also expect to see the absence of these isocyanide-deficient species in spectra which are recorded when an excess of xylyl isocyanide is present. This can be seen to be the case in Fig. 2 where the oxidation of Mo(CNxylyl)_6 (at +0.9 V) in the presence of an excess of added xylylNC (ν(CN) at 2121 cm^{-1}) proceeds cleanly to give $[\text{Mo(CNxylyl)}_7]^{2+}$ (Fig. 2c) via the intermediacy of $[\text{Mo(CNxylyl)}_6]^+$ (Fig. 2b). Under these latter conditions reactions (1), (2) and (5) almost certainly predominate.

We believe that these results clearly demonstrate the value of FT-IR spectroelectrochemical techniques in probing the time-resolved redox characteristics of transition metal isocyanide complexes and will, we hope, presage increased use of such methodology.

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