Inorganica Chimica Acta, *97* (1985) L51–L53

Electrochemical Redox Behaviour of the Hexakis(aryl isocyanide) Complexes of Molybdenum(0) and Tungsten(0)

DAVID A. BOHLING, KENT R. MANN

Department of Chemistry, University of Minnesota, Minneapolis, Minn. 55455, U.S.A.

STARLA ENGER, THOMAS GENNETT, MICHAEL J. WEAVER and RICHARD A. WALTON[*]

Department of Chemistry, Purdue University, West Lafayette, Ind. 47907, U.S.A.

Received October 10, 1984

The hexakis(alkyl isocyanide) and hexakis(aryl isocyanide) complexes of chromium, $[Cr(CNR)_6]^{n+}$ and $[Cr(CNAr)_6]^{n+}$, are noteworthy for their well-defined redox chemistry and the range of accessible stable oxidation states (n can be 3, 2, 1 or 0) [1–7]. In contrast to this situation, solutions of the hexakis(phenyl isocyanide) complexes $Mo(CNPh)_6$ and $W(CNPh)_6$ in 0.2 M tetra-n-butylammonium hexafluorophosphate(TBAH)-dichloromethane possess a reversible one-electron oxidation at $E_{1/2} \simeq -0.2$ V *vs.* SCE, and a second oxidation at $E_{p,a} = +0.48$ V (Mo), or +0.44 V (W) *vs.* SCE, that is chemically irreversible [8]. Single scan cyclic voltammetric measurements showed conclusively [8] that following the second oxidation, the $[M(CNPh)_6]^{2+}$ cations decomposed chemically, by a process that was rapid on the time scale of the electrochemical experiment. The product(s) could not be identified because it was not stable chemically. However, when the bulk electrolyses of solutions of $Mo(CNPh)_6$ and $W(CNPh)_6$ in 0.2 M TBAH–CH_2Cl_2 were carried out at a potential (+0.6 V) that was positive of the second (irreversible) oxidation then the corresponding seven coordinate dication $[M(CNPh)_7]^{2+}$ was the major product[**], implying that the very reactive 16-electron six-coordinate species $[M(CNPh)_6]^{2+}$ can scavenge phenyl isocyanide. In an effort to explore the significance of these redox properties insofar as they pertain to other aryl isocyanide complexes of the types $Mo(CNAr)_6$ and $W(CNAr)_6$, and to ascertain the mechanism whereby $[M(CNAr)_7]^{2+}$ is formed by the electrochemical oxidation of $M(CNAr)_6$, we have examined further the electrochemical redox properties of $M(CNAr)_6$, with emphasis upon the more readily synthesized molybdenum complexes. Several key points emerging from these investigations are addressed herein.

TABLE I. Cyclic Voltammetric Half-Wave Potentials for $Mo(CNAr)_6$ Complexes in 0.1 M TBAH-Dichloromethane.[a]

Complex	$E_{1/2}$	$E_{p,a}$
$Mo(CNPh\text{-}4\text{-}Cl)_6$	−0.03	+0.56
$Mo(CNPh)_6$	−0.18 (−0.19)[b]	+0.45 (+0.48)[b]
$Mo(CNPh\text{-}4\text{-}Me)_6$	−0.19	+0.47
$Mo(CNPh\text{-}2\text{-}Me)_6$	−0.20	+0.53
$Mo(CNPh\text{-}4\text{-}OMe)_6$	−0.28	+0.37
$Mo(CNPh\text{-}2,6\text{-}DIP)_6$[c]	−0.25	+0.71
$Mo(CNxylyl)_6$	−0.35[d]	+0.48[d]

[a] Data recorded at 100 mV/s *vs.* Ag/AgCl unless otherwise stated. [b] Data from ref. 8 *vs.* SCE. [c] DIP = di-iso-propyl. [d] *Vs.* SCE as reference electrode.

Solutions of a series of hexakis(aryl isocyanide) complexes of Mo(0) in 0.1 M tetra-n-butylammonium hexafluorophosphate(TBAH)-dichloromethane (Table I) were found[†] to exhibit cyclic voltammetric behavior essentially the same as that reported previously for $M(CNPh)_6$ (M = Mo or W) in 0.2 M TBAH–CH_2Cl_2, thereby establishing the generality of this redox behavior and emphasizing the differences that exist with the chromium analogues $[Cr(CNAr)_6]^{n+}$. Compared to the analogous $Cr(CNAr)_6$ compounds [5], only a limited correlation of the cyclic voltammetric half-wave potentials $E_{1/2}$ with Hammett σ_p and σ_o functions exists for the electrode reaction depicted in eqn. 1[††]. These couples (eqn. 1) are characterized

$$[Mo(CNAr)_6]^+ + e^- \longrightarrow Mo(CNAr)_6 \qquad (1)$$

by $E_{1/2}$ values in the potential range 0 to −0.3 V, peak separations of less than 100 mV and peak ratios $i_{p,c}/i_{p,a}$ equal to one in the 0.1 M TBAH-CH_2Cl_2 solvent system.

---

[*] Author to whom correspondence should be addressed.

[**] The species $[Mo(CNPh)_7]^{2+}$ and $[W(CNPh)_7]^{2+}$ themselves possess very characteristic and well-defined electrochemical properties, *viz.* in 0.2 M TBAH–CH_2Cl_2 a reversible one-electron oxidation at $E_{1/2}$ = +1.41 V (for Mo) or +1.32 V (for W), and an irreversible two-electron reduction at $E_{p,c}$ = −1.12 V (for Mo) or −1.02 V (for W) *vs.* SCE; for full details see ref. 8(b).

[†] These measurements were carried out at the University of Minnesota using the experimental set-up described previously [5]. All potentials are quoted relative to a Ag/AgCl reference electrode, which therefore makes them very similar, although not exactly identical to, the data presented in ref. 8, for which an SCE reference was used.

[††] Further details are available in D. A. Bohling, *Ph.D. Thesis*, University of Minnesota, 1984.

0020-1693/85/$3.30

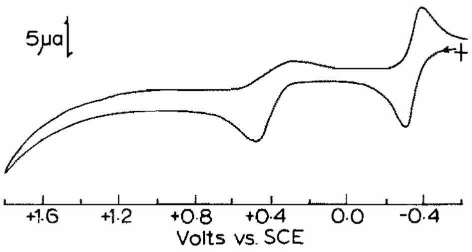

Fig. 1. Anodic–cathodic cyclic voltammogram of a solution of $Mo(CNxylyl)_6$ in 0.1 M $TBAH–CH_2Cl_2$ recorded at ν = 100 mV/s using a Pt-bead electrode (other experimental conditions are as described in footnote [§]).

In contrast to the reversible character of the +1/0 couple, the conversion of $[Mo(CNAr)_6]^+$ to $[Mo(CNAr)_6]^{2+}$ is followed in all instances by a chemical transformation that is rapid on the electrochemical time scale, thereby yielding very little response corresponding to the reverse process, at least for sweep rates up to 10 V/s. This irreversibility contrasts with the reversible nature of the $[Cr(CNAr)_6]^{2+/1+}$ couple [5]. In an attempt to identify the chemical reactions that follow the formation of $[Mo(CNAr)_6]^{2+}$, we have focused our attention upon the behavior of one such system, *viz.*, $Mo(CNxylyl)_6$ (xylyl = 2,6-dimethylphenyl), a complex that appears to be representative of the series[†††].

We had noted previously [8] that following the second oxidation, *i.e.* $(Mo)^{1+} \rightarrow (Mo)^{2+}$, 'product waves' appeared in the single scan cyclic voltammograms of $M(CNPh)_6$ (M = Mo or W) at potentials more positive than +1.1 V. Similar cyclic voltammetric scans in the case of the other complexes listed in Table I confirmed that all these systems behaved in a comparable fashion. Subsequently, we have found that the appearance of these waves at potentials > +1.1 V results from the reaction of $[Mo(CNAr)_6]^{2+}$ with impurities in the solvent and/or supporting electrolyte because, as shown in Fig. 1, the single-scan cyclic voltammogram of $Mo(CNxylyl)_6$ in 0.1 M $TBAH–CH_2Cl_2$ is free of such waves when recourse was made to a highly purified solvent and supporting electrolyte[§]. For this system, the +1/0 couple was characterized by $E_{1/2} = -0.35$ V *vs.* SCE and $i_{p,c}/i_{p,a} = 1$, while the +2/+1 couple had $E_{p,a} = +0.48$ V *vs.* SCE and $i_{p,c}/i_{p,a} \ll 1$ at a scan rate (ν) of 100 mV/s. Even with fast scans (up to 10 V/s) the ratio $i_{p,c}/i_{p,a}$ was much less than unity. Within the potential range +1.9 to −2.4 V, there were no other significant features discernible in the cyclic voltammogram under these experimental conditions.

Exhaustive electrolysis of solutions of $Mo(CNPh)_6$ and $W(CNPh)_6$ at potentials positive of the second (irreversible) oxidation gives seven coordinate $[Mo(CNPh)_7]^{2+}$ and $[W(CNPh)_7]^{2+}$ as the predominant chemical products [8], although the product yields were not previously determined. This behavior is typical of that found for the other $Mo(CNAr)_6$ species, as exemplified by the present results for $Mo(CNxylyl)_6$. Controlled potential electrolysis on 0.1 M $TBAH–CH_2Cl_2$ solutions of $Mo(CNxylyl)_6$ was conducted at 0.0 V in order to achieve complete conversion to the paramagnetic monovalent cation[§§]. The electrolysis was assumed concluded when only cathodic current was exhibited using a rotating platinum electrode, at which time 0.98 electron had been removed. The cation's half life is significantly

---

[†††] The complex $Mo(CNxylyl)_6$, like others of this type described in Table I, was prepared from the reaction of $Mo_2(O_2CCH_3)_4$ with excess of ArNC using a slight modification of the synthetic route described by Mann *et al.* [9]. An alternative procedure employs a sodium/mercury reduction method as proposed by Chiu *et al.* [10]. Methanol (50 ml), which had been dried over molecular sieves for two days prior to use, was added to 40 g of a 4% Na/Hg amalgam. The subsequent addition of 0.5 g of $Mo_2(O_2CCH_3)_4$ immediately produced a dark brown colored solution. Shortly thereafter, 1.0 g (7.6 mmol) of xylyl isocyanide was added. The flask was shaken for 15 min and the contents changed to a deep red color. The resulting mixture was separated from the remaining Na/Hg amalgam and cooled to 0 °C in an ice bath. The solid was filtered off, and the $Mo(CNxylyl)_6$ was extracted into diethyl ether. Evaporation of the diethyl ether extract was achieved under a stream of nitrogen gas; yield 40%. This product had identical spectroscopic ($\nu(N{\equiv}C)$ at 1939 cm^{-1}) and electrochemical properties to that found for samples isolated using the other procedure. Purification was effected by recrystallization from toluene using oxygen-free and anhydrous conditions. *Anal.* Calcd. for $C_{54}H_{54}MoN_6$: C, 73.45; H, 6.16. Found: C, 72.82; H, 6.61.

[§] The supporting electrolyte $n-Bu_4NPF_6$ was purified by recrystallizing it several times from absolute ethanol, followed by thorough vacuum drying. The dichloromethane solvent (Burdick and Jackson) was purified utilizing CaH_2 as the drying agent, followed by three freeze-pump-thaw cycles, and vacuum distillation (10^{-6} mm). Rigorous inert atmosphere conditions (N_2, Vacuum Atmospheres dry box) were used in all subsequent measurements. The electrochemical cell configuration used was the typical one [11], but with a double-fritted SCE reference cell to hinder the diffusion of water into the working compartment of the cell. Measurements were carried out at 25 °C using a Pt-bead electrode that had been cleaned in boiling nitric acid followed by a saturated ferrous ammonium sulfate solution. Instrumentation consisted of a PAR 173 potentiostat, a PAR 175 Universal Programmer, and a PAR 179 coulometer.

[§§] Electrochemically generated solutions of $[Mo(CNxylyl)_6]^+$ are, as expected, ESR-active and display a well-defined spectrum. At −150 °C, the X-band ESR spectrum is characterized by g values of 2.085 and 2.006; a weak broad feature at g ≃ 1.91 is attributable to an impurity, the intensity of which increases with time as the complex cation slowly decomposes.

$$\mathrm{Mo(CNAr)_6} \rightleftharpoons \mathrm{[Mo(CNAr)_6]^+} + e^- \qquad (1)$$

$$\mathrm{[Mo(CNAr)_6]^+} \longrightarrow \mathrm{[Mo(CNAr)_6]^{2+}} + e^- \qquad (2)$$

$$\mathrm{[Mo(CNAr)_6]^{2+}} + \mathrm{[Mo(CNAr)_6]^+} \longrightarrow \mathrm{[Mo(CNAr)_7]^{2+}} + \{\mathrm{[Mo(CNAr)_5]^+}\} \qquad (3)$$

$$\{\mathrm{[Mo(CNAr)_5]^+}\} \longrightarrow \{\mathrm{[Mo(CNAr)_{5-x}]^+}\} + x\mathrm{ArNC} \qquad (4)$$

$$\mathrm{[Mo(CNAr)_6]^{2+}} + \mathrm{ArNC} \longrightarrow \mathrm{[Mo(CNAr)_7]^{2+}} \qquad (5)$$

Scheme 1. Note: reaction (4) may well be solvent assisted; { } denotes an unstable and highly reactive species that has not been detected electrochemically.

greater at lower temperatures, *i.e.* $t_{1/2}^{25\,°C} \approx 30-60$ s and $t_{1/2}^{-40\,°C} \approx 24$ h. Our attempts to isolate analytically pure $\mathrm{[Mo(CNxylyl)_6]PF_6}$ using $\mathrm{[(\eta\text{-}C_5Me_5)_2Fe]PF_6}$ as the oxidant have not yet been successful.

In contrast to the reversibility of the +1/0 couple, attempts to generate the divalent $\mathrm{[Mo(CNxylyl)_6]^{2+}}$ cation are thwarted by its rapid decomposition. Upon bulk electrolysis of solutions of $\mathrm{Mo(CNxylyl)_6}$ at +0.80 V, ~1.50 equivalents of electrons are consumed; subsequent voltammetry of the solution showed that the only electrochemically-active product is $\mathrm{[Mo(CNxylyl)_7]^{2+}}$ and that it is formed in ~75% yield. Its electrochemical properties are representative of this class of complex as a whole and resemble very closely the behavior of $\mathrm{[Mo(CNPh)_7]^{2+}}$ as reported previously in ref. 8*. This coulometric measurement clearly implies that the putative, coordinatively unsaturated $\mathrm{[Mo(CNxylyl)_6]^{2+}}$ ion scavenges for xylylNC to give the stable seven-coordinate dication and, as a consequence, a portion of the molybdenum containing-species is sacrificed. This conversion of $\mathrm{[Mo(CNAr)_6]^{2+}}$ to $\mathrm{[Mo(CNAr)_7]^{2+}}$ resembles that in which $\mathrm{[Cr(CNR)_7]^{2+}}$ can be formed by the reaction of RNC with $\mathrm{[Cr(CNR)_6]^{2+}}$ [3, 4]. A feasible mechanism is that shown in Scheme 1, where steps (3) and (5) can both lead to the formation of $\mathrm{[Mo(CNxylyl)_7]^{2+}}$, and step (4) accounts for the 'loss' of electrochemically-active molybdenum**. Support for this mechanism comes from observing the influence of added xylylNC (varied from 0 to 20 mM) upon the electrochemical results for solutions that were ~1 mM in complex. At 0 mM xylylNC, the occurrence of the 1.50 electron count (measured relative to Mo(0)) after the second oxidation to the divalent cation (step 2) suggests that a reaction occurs with the monovalent cation (step 3). This accounts for the failure to achieve a two electron count, since $\mathrm{[Mo(CNAr)_6]^+}$ is consumed prior to its complete conversion to $\mathrm{[Mo(CNAr)_6]^{2+}}$. This postulate is supported by the effect of increasing the bulk concentration of free xylyl isocyanide ligand. Bulk electrolysis at +0.8 V in the presence of 2-fold and 20-fold excesses of the ligand produced an 80% and 96% yield of the seven-coordinate species with 1.7 and 2.0 electrons removed, respectively. Voltammetric procedures were utilized in determining that the first oxidation (step **1**) was unaffected by this increase in ligand concentration. Clearly then, step (5) dominates, essentially to the exclusion of steps (3) and (4), when excess isocyanide ligand is added. This simple mechanism accords with previous synthetic results which showed [8] that the chemical oxidation (using $\mathrm{NOPF_6}$) of $\mathrm{M(CNPh)_6}$ (M = Mo or W) in the presence of excess PhNC can give high preparative yields of $\mathrm{[M(CNPh)_7](PF_6)_2}$.

---

*For $\mathrm{[Mo(CNxylyl)_7]^{2+}}$ in 0.1 M TBAH–$\mathrm{CH_2Cl_2}$, $E_{1/2}$ = +1.55 V, and $E_{p,c}$ = −0.97 *vs.* SCE. The first process corresponds to a reversible one-electron oxidation, the second to an irreversible two-electron reduction.

**Note that single scan cyclic voltammetry on solutions of $\mathrm{Mo(CNxylyl)_6}$ does not show the presence of significant quantitites of $\mathrm{[Mo(CNxylyl)_7]^{2+}}$ (Fig. 1). This can be attributed to the very low concentration of free xylylNC that is formed at the electrode surface and the relative slowness of step (3) on this electrochemical time scale.

Acknowledgements

Support of the National Science Foundation (Grant No. CHE82-06117 to R.A.W.) is gratefully acknowledged. We thank Dr. Charles J. Cameron and Kay A. Conner for experimental advice and assistance.

References

1 (a) P. M. Treichel and G. J. Essenmacher, *Inorg. Chem.*, *15*, 146 (1976);
(b) P. M. Treichel, D. W. Firsich and G. J. Essenmacher, *Inorg. Chem.*, *18*, 2405 (1979).
2 G. J. Essenmacher and P. M. Treichel, *Inorg. Chem.*, *16*, 800 (1977).
3 W. S. Mialki, T. E. Wood and R. A. Walton, *J. Am. Chem. Soc.*, *102*, 7105 (1980).
4 W. S. Mialki, D. E. Wigley, T. E. Wood and R. A. Walton, *Inorg. Chem.*, *21*, 480 (1982).
5 D. A. Bohling, J. F. Evans and K. R. Mann, *Inorg. Chem.*, *21*, 3546 (1982).
6 D. A. Bohling and K. R. Mann, *Inorg. Chem.*, *22*, 1561 (1983).
7 D. A. Bohling and K. R. Mann, *Inorg. Chem.*, *23*, 1426 (1984).
8 (a) D. D. Klendworth, W. W. Welters, III and R. A. Walton, *J. Organomet. Chem.*, *213*, C13 (1981);
(b) D. D. Klendworth, W. W. Welters, III and R. A. Walton, *Organometallics*, *1*, 336 (1982).
9 K. R. Mann, M. Cimolino, G. L. Geoffroy, G. S. Hammond, A. A. Orio, G. Albertin and H. B. Gray, *Inorg. Chim. Acta*, *16*, 97 (1976).
10 K. W. Chiu, C. G. Howard, G. Wilkinson, A. M. Galas and M. R. Hursthouse, *Polyhedron*, *1*, 803 (1982).
11 T. C. Zietlow, D. D. Klendworth, T. Nimry, D. J. Salmon and R. A. Walton, *Inorg. Chem.*, *20*, 947 (1981).