$MoC_{35}H_{37}NO_2P_2Cl_3$: C, 54.74; H, 4.86; N, 1.82. Found: C, 55.04; H, 5.22; N, 1.51. Mol wt: calcd, 768; found (toluene solution), 764. Magnetic moment: 1.85 μ_B. IR: 1590 (w), 1439 (m), 1143 (vs), 1126 (s), 1099 (s), 1073 (w), 1032 (w), 1021 (w), 1000 (m), 840 (w), 823 (m), 752 (s), 731 (s), 699 (s), 542 (s), 520 (s), 487 (m), 440 (m) cm^{-1}.

Preparation of $[MoO_2Cl_2(OPEtPh_2)\cdot{}^1/_2C_6H_5CH_3]$. Hexane was added to a solution of $Mo(Ntol)Cl_3(EtPh_2P)_2$ (0.97 g; 1.32 mmol) in toluene (30 mL) until the point of incipient precipitation. The red-orange solution was then allowed to stand undisturbed, exposed to the atmosphere, for 2 days. During this time, the color of the solution became yellow and large pale yellow acicular crystals were deposited. These crystals were collected by filtration, washed with hexane, and dried in vacuo. Analysis of the mother liquor by GC/MS revealed the presence of *p*-toluidine and ethyldiphenylphosphine oxide. Anal. Calcd for $MoC_{31.5}H_{34}O_4Cl_2P_2$: C, 44.23; H, 4.03. Found: C, 44.20; H, 3.97; N, 0.00. Mol wt: calcd, 475; found (CH_2Cl_2 solution), 462. IR: 1591 (w), 1441 (s), 1174 (vs), 1150 (vs), 1126 (s), 1103 (s), 1076 (m), 1033 (w), 1002 (w), 947 (vs), 904 (vs), 764 (m), 750 (s), 723 (s), 703 (s), 545 (s), 513 (m) cm^{-1}.

Preparation of *cis,mer*-$Mo(Ntol)Cl_2(Me_3P)_3$. A stirred solution of $Mo(Ntol)Cl_3(Me_3P)_2$ (0.99 g; 2.16 mmol) and Me_3P (0.60 g; 7.84 mmol) in toluene (75 mL) was treated with sodium amalgam (0.08 g of Na (3.5 mmol) in 10 g of Hg). Over a 3-h period, the color of the solution changed from dark orange to green to blue and finally to green-brown. After being stirred an additional 12 h, the solution was filtered and the filtrate was taken to dryness. The green powdery product was washed with pentane (3 × 30 mL) and dried in vacuo. Large, dark green crystals of this material were readily obtained by slow cooling of a warm (40 °C) saturated toluene solution. The identity of the complex has been established by a single-crystal X-ray diffraction study.[22] ^1H NMR (C_6D_6): δ 6.87 (AB quartet, J_{AB} = 8.2 Hz, 4 H, $C_6H_4CH_3$), 1.88 (s, 3 H, $C_6H_4CH_3$), 1.42 (t, J_{HP} = 3.6 Hz, 18 H, PMe_3), 1.29 (d, J_{HP} = 7.8 Hz, 9 H, PMe_3). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 5.38 (t, J_{PP} = 18.1 Hz, area 1), −7.32 (d, J_{PP} = 18.1 Hz, area 2). IR: 1593 (w), 1416 (m), 1330 (s), 1301 (m), 1275 (s), 1106 (m), 1017 (m), 951 (vs), 853 (s), 826 (s), 783 (s), 674 (s), 554 (m), 444 (m) cm^{-1}.

Crystallographic Study. General operating procedures have been previously described.[38] Repeated attempts to cool suitable crystals to low temperatures (between −165 and −30 °C) resulted in crystal fracture; thus, data were collected at 20 °C. there was no evidence of decomposition during the course of the data collection as monitored by four reflections chosen as standards.

A systematic search of a limited hemisphere of reciprocal space located no systematic absences or symmetry, leading to a triclinic space group. The structure was readily solved by a combination of direct methods and Fourier techniques and refined by full-matrix least squares. Hydrogen atoms were not visible in difference Fourier maps phased on the non-hydrogen atoms but were included in the final cycles of refinement as idealized fixed-atom contributors (d(C–H) = 0.95 Å; B_{iso} = 1.0 + B_{iso}(riding atom)). A final difference Fourier was featureless, the largest peak being 0.21 e/Å^3. ψ scans of three reflections near χ = 90° were flat, indicating no absorption correction was necessary.

The thermal parameters are rather large for some parts of the molecule, indicative of the relatively "unstable" room-temperature form. The fact that a phase transition occurs slightly below room temperature is in agreement with these observations.

Acknowledgment. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Bureau of General Research at Kansas State University for support of this research. The WM-400 NMR spectrometer used in this work was purchased with the assistance of an NSF instrumentation award.

Supplementary Material Available: Complete listings of bond lengths, bond angles, anisotropic thermal parameters, and structure factor amplitudes (30 pages). Ordering information is given on any current masthead page.

---

(38) Huffman, J. C.; Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* **1980**, *19*, 2755.

Contribution from the Institut de Recherches sur la Catalyse CNRS, 69626 Villeurbanne Cedex, France,
and Laboratoire de Chimie Analytique et Laboratoire de Spectrochimie Infrarouge et Raman CNRS,
Université des Sciences et Techniques de Lille, 59655 Villeneuve d'Ascq Cedex, France

Electrochemical Generation and Study of Labile 19-Electron Dinitrosylmolybdenum Radicals

D. Ballivet-Tkatchenko,[†] A. Boughriet,[‡] and C. Brémard*[§]

Received January 4, 1985

Electrochemical reduction of dicationic, monocationic, and neutral dinitrosylmolybdenum complexes in acetonitrile are reported: $[Mo(NO)_2L_2L_2]^{2+}$, $[Mo(NO)_2L_2LCl]^+$, $[Mo(NO)_2L_2Cl_2]$; L = MeCN, L_2 = 2,2′-bipyridine. All of the compounds are reducible by one electron to yield stable 19-electron complexes. The radical complexes can be reduced by another electron to unstable 20-electron complexes. Cyclic voltammetry and controlled-potential coulometry have been used at several temperatures to characterize these processes. The dicationic complexes undergo a reversible one-electron reduction. IR, UV–vis, and ESR studies have shown that the unpaired electron is delocalized over both nitrosyl groups. One-electron transfer to the monochloro and dichloro complexes induces facile exchange of the chloro ligand in the 19-electron complexes with L = MeCN. The free Cl^- anions coordinate to the remaining 18-electron chloro complexes to give $[Mo(NO)_2Cl_3L]^-$ and $[Mo(NO)_2Cl_4]^{2-}$, which are more easily reduced than dichloro or monochloro complexes. The multiple-electrochemical-step system is therefore not catalytic, but is rather of the electroactivation type.

Substitution reactions involving the removal of halide ions from halo complexes such as dinitrosyl complexes and replacement by neutral two-electron-donor ligands such as phosphine, nitrile, olefin, or alkyne lead to useful cationic complexes.[1-4] In particular, cationic olefin complexes have been thoroughly investigated because of their applications in catalytic organic synthesis.[5-7] The conventional associative and dissociative mechanisms for ligand exchanges are usually considered to involve even-numbered 16- and 18-electron intermediates.[8] Recently, efficient chain mechanisms of ligand substitution in metal carbonyls involving odd-electron radical intermediates have been proposed.[9] Fur-

---

[†] Institut de Recherches sur la Catalyse CNRS. Present address: Laboratoire de chimie de coordination CNRS, 205 Route de Narbonne, 31400 Toulouse, France.

[‡] Laboratoire de Chimie Analytique CNRS.

[§] Laboratoire de Spectrochimie Infrarouge et Raman CNRS.

(1) Regina, F. J.; Wojciki, A. *Inorg. Chem.* **1980**, *19*, 3803.
(2) Legzdins, P.; Nurse, C. R. *Inorg. Chem.* **1982**, *21*, 3110.
(3) Fisher, E. O.; Fichtel, K. *Chem. Ber.* **1962**, *94*, 1200.
(4) (a) Foxman, B. M.; Klemarczyk, P. T.; Liptrot, R. E.; Rosemblum, M. *J. Organomet. Chem.* **1980**, *187*, 253. (b) Reger, D. L.; Coleman, C. J. *Inorg. Chem.* **1979**, *18*, 3155. (c) Davison, A.; Green, M. L. H.; Wilkinson, G. *J. Chem. Soc.* **1961**, 3172. (d) Mattson, B. M.; Graham, W. A. G. *Inorg. Chem.* **1981**, *20*, 3186. (e) Ballivet-Tkatchenko, D.; Brémard, C. *J. Chem. Soc., Dalton Trans.* **1983**, 1143 and references therein. See also: Johnson, B. F. G.; Khair, A.; Savory, C. G.; Walter, R. H.; Alobaidi, K. H.; Al Hassam, T. J. *Transition Met. Chem.* (*Weinheim, Ger.*) **1978**, *3*, 81.
(5) Lennon, P.; Rosen, A. M.; Rosenblum, M. *J. Am. Chem. Soc.* **1977**, *99*, 8476 and references therein.

thermore, it has been suggested that reductive elimination of chloride ions produces vacant sites on the coordination sphere of $[Fe(NO)_2Cl_2]_2$.[10]

A few 19-electron dinitrosylmolybdenum and -tungsten complexes have been generated and stabilized with dithiocarbamate,[11] η^5-C_5H_5,[12] and 2,2′-bipyridine[13] ligands. We have previously reported stereochemical studies[14] of a series of octahedral 18-electron dichlorodinitrosylmolybdenum complexes $Mo(NO)_2L_2Cl_2$ with L = MeCN or py and L_2 = 2,2′-bipyridine. However, the chemistry of these compounds was found to be limited by their kinetic inertness toward ligand substitution reactions.[15] Nevertheless, it was possible to carry out the chloride-elimination reaction by the treatment of the organometallic chloride with various silver(I) salts. The cationic complexes thus produced are 18-electron species in which a donor solvent molecule has replaced the halide in the coordination sphere of the metal. The monocationic and dicationic dinitrosyl complexes containing coordinated acetonitrile have been isolated as the perchlorate salts $[Mo(NO)_2L_2Cl(MeCN)][ClO_4]$ and $[Mo(NO)_2L_2(MeCN)_2][ClO_4]_2$ (L = MeCN, L_2 = 2,2′-bipyridine).[4c] Electrochemical methods have been employed to generate the 19-electron complexes required for the reductive elimination of the chloride ion of the coordination sphere of the metal.

This paper presents the results of an electrochemical study of cationic complexes. Our objective was to establish the electrochemical mechanisms for the elimination of chloride ion.

Experimental Section

Materials. Reagent grade acetonitrile (Merck) was further purified by distillation from calcium hydride. It was then redistilled from P_4O_{10} under argon and stored under argon. Prior to use the acetonitrile was filtered through a dry alumina column under argon. Tetraethylammonium perchlorate (TEAP) (Carlo Erba) and tetraethylammonium chloride (Merck) were dried in vacuo at 50 °C over P_4O_{10}. All preparative reactions were carried out under argon atmosphere.

(1) Dicationic compounds were obtained by chloride abstraction from $Mo(NO)_2L_2Cl_2$ with $AgClO_4$, as previously described:[4c] $[Mo(NO)_2(MeCN)_4][ClO_4]_2$ (**[1]**$[ClO_4]_2$), $[Mo(NO)_2(bpy)(MeCN)_2][ClO_4]_2$ (**[2]**$[ClO_4]_2$), $[Mo(NO)_2(bpy)_2][ClO_4]_2$ (**[3]**$[ClO_4]_2$).

(2) Monocationic compounds were obtained by chloride abstraction from $Mo(NO)_2L_2Cl_2$ with $AgClO_4$, as previously described:[4c] $[Mo(NO)_2(MeCN)_3Cl][ClO_4]$ (**[4]**$[ClO_4]$), $[Mo(NO)_2(bpy)(MeCN)Cl][ClO_4]$ (**[5]**$[ClO_4]$).

(3) Neutral dichlorodinitrosyl compounds were prepared as described in previous works:[14,16] $[Mo(NO)_2(MeCN)_2Cl_2]$ (**6**), $[Mo(NO)_2(bpy)Cl_2]$ (**7**).

Instrumentation. Electrochemical measurements were performed with a Tacussel PRT 20-10 potentiostat in combination with a Tacussel UAP 4 Universal programmer. This instrument is equipped with a current-to-voltage converter that provides feedback compensation for the ohmic drop between working and reference electrodes. Rotating-disk-electrode voltammograms and slow-scan cyclic voltammograms were recorded on a Sefram TGM 164 X-Y recorder. Fast-scan cyclic voltammograms were obtained from photographs of the trace on tektronix R 5111 storage oscilloscope. Controlled-potential electrolyses were carried out with a Tacussel PRT 100-1 potentiostat in combination with a Tacussel ING 5 coulometer; the potential was controlled with a Tacussel ISIS 4000 instrument. Conductivities of 10^{-2}–10^{-3} mol·dm^{-3} complex solutions were measured with a CD 75 Tacussel conductivity bridge from 0 to 40 °C.

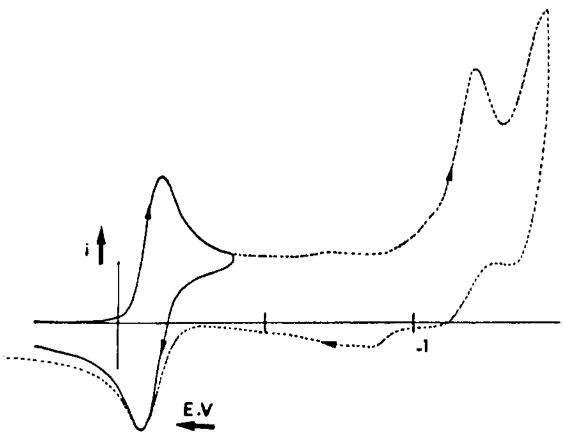

Figure 1. Cyclic voltammograms of 10^{-3} mol·dm^{-3} $[Mo(NO)_2(bpy)_2]^{2+}$ in acetonitrile containing 0.1 mol·dm^{-3} TEAP at 20 °C and at a scan rate of 0.1 V·s^{-1} vs. SCE.

Table I. Cyclic Voltammetry Parameters and Infrared Characteristics of Dinitrosylmolybdenum Complexes[a]

no.	complex	E_p^{red}, V[b]	$E_p^{red} + E_p^{ox}/2$, V[b]	i_p^c/i_p^a	ν_s-(NO), cm^{-1}	ν_{as}-(NO), cm^{-1}
1	$[Mo(NO)_2(MeCN)_4]^{2+}$	−0.03	0.00	1.0	1860	1750
2	$[Mo(NO)_2(bpy)(MeCN)_2]^{2+}$	−0.12	−0.09	1.0	1830	1730
3	$[Mo(NO)_2(bpy)_2]^{2+}$	−0.17	−0.14	1.0	1830	1730
4	$[Mo(NO)_2(MeCN)_3Cl]^+$	−0.31	−0.27	1.6	1830	1720
5	$[Mo(NO)_2(bpy)Cl(MeCN)]^+$	−0.38	−0.35	1.0	1810	1690
6	$[Me(NO)_2(MeCN)_2Cl_2]$	−0.65	−0.62	2.0	1805	1685
7	$[Mo(NO)_2(bpy)Cl_2]$	−0.62	−0.57	1.0	1780	1650
8	$[Mo(NO)_2(MeCN)Cl_3]^-$	−0.95	−0.91			
9	$[Mo(NO)_2Cl_4]^{2-}$	−1.15	−1.10			

[a] Cyclic voltammetry performed at a Pt microelectrode with solutions 10^{-3} mol·dm^{-3} in substrate and 0.1 mol·dm^{-3} in TEAP (tetraethylammonium perchlorate) for MeCN; the scan rate was 0.1 V·s^{-1}, and T = 25 °C. [b] Potentials are reported in volts (±0.01 V) vs. SCE.

The ESR spectra of solutions and frozen solutions were obtained on a Varian E-109 spectrometer operating at 9.315 GHz between 20 and −160 °C. The radical complexes were generated in cylindrical quartz ESR tubes by electrolysis at −30 °C at potentials above the reduction potential of the complexes. UV–vis absorption spectra were recorded with a Jobin-Yvon DUOSPAC 203 spectrophotometer. IR spectra were recorded with a Perkin-Elmer 457 spectrometer.

Electrochemical Methods. All experiments were carried out in the dark in a thermostated cell between −30 and 40 °C and under argon. A conventional three-electron three-compartment cell was used. In addition, the large-area working electrode chamber was employed in order to allow coulometric experiments to be carried out as desired. Cyclic voltammograms were obtained with a platinum- or vitreous-carbon-disk electrode and a platinum-sheet auxiliary electrode of about 78 mm^2. The reference electrode system Ag/Ag^+ consisted of a silver wire immersed in a solution of 0.1 mol dm^{-3} electrolyte and 0.01 mol·dm^{-3} $AgClO_4$ in the desired solvent. All potentials were referred to the saturated calomel electrode (SCE). All test solutions were 1.0×10^{-2} mol·dm^{-3} in the metal complex. A "blank" was run before each manipulation to ensure that the solvent and supporting electrolyte were pure and that concentrations of water and oxygen in solution were low. The residual water was found by Karl Fischer measurements to be less than 10^{-3} mol·dm^{-3} in the cell.

Results

Dicationic Complexes. (1) Cyclic Voltammetry. The cyclic voltammograms of acetonitrile solutions of the dicationic complexes $[Mo(NO)_2(MeCN)_4]^{2+}$ (**1**), $[Mo(NO)_2(bpy)(MeCN)_2]^{2+}$

---

(6) Ballivet, D.; Tkatchenko, I. *J. Mol. Catal.* **1975**, *1*, 319.

(7) Ballivet, D.; Billard, C.; Tkatchenko, I. *J. Organomet. Chem.* **1977**, *124*, C9.

(8) (a) Basalo, F.; Pearson, R. G. "Mechanisms of Inorganic Reactions", 2nd ed.; Wiley-Interscience: New York, 1967; p 533. (b) Dobson, G. R. *Acc. Chem. Res.* **1976**, *9*, 300. (c) Deeming, A. *Inorg. React. Mech.* **1981**, *7*, 275.

(9) (a) Kidd, D. R.; Brown, T. L. *J. Am. Chem. Soc.* **1978**, *100*, 4095. (b) Absi-Halabi, M.; Atwood, J. D.; Forbus, N. P.; Brown, T. L. *Ibid.* **1980**, *102*, 6248. (c) Summers, D. P.; Luong, J. C.; Wrighton, M. S. *Ibid.* **1981**, *103*, 5238. (d) Hershberger, J. W.; Klingler, R. J.; Kochi, J. K. *Ibid.* **1982**, *104*, 3034. (e) Hershberger, J. W.; Klingler, R. J.; Kochi, J. K. *Ibid.* **1983**, *105*, 61.

(10) Ballivet-Tkatchenko, D.; Riveccie, M.; El Murr, N. *J. Am. Chem. Soc.* **1979**, *101*, 2763.

(11) Budge, J. R.; Broomhead, J. A.; Boyd, P. D. W. *Inorg. Chem.* **1982**, *21*, 1031.

(12) Yu, Y. S.; Jacobson, R. A.; Angelici, R. J. *Inorg. Chem.* **1982**, *21*, 3106.

(13) Masek, J.; Fiedler, J.; Klima, J.; Seyferth, K.; Taube, R. *Collect. Czech. Chem. Commun.* **1982**, *47*, 1721.

(14) Ballivet-Tkatchenko, D.; Brĕmard, C.; Abraham, F.; Nowogrocki, G. *J. Chem. Soc., Dalton Trans.* **1983**, 1137.

(15) Silverthorn, W. E. *Inorg. Chem.* **1979**, *18*, 1835.

(16) (a) Anker, M. W.; Colton, R.; Tomkins, I. B. *Aust. J. Chem.* **1968**, *21*, 1149. (b) Johnson, B. F. G.; Cotton, F. A. *Inorg. Chem.* **1964**, *3*, 1609. (c) Hugher, W. B.; Zuech, E. A. *Inorg. Chem.* **1973**, *12*, 471. (d) Bencze, L. *J. Organomet. Chem.* **1973**, *56*, 303.

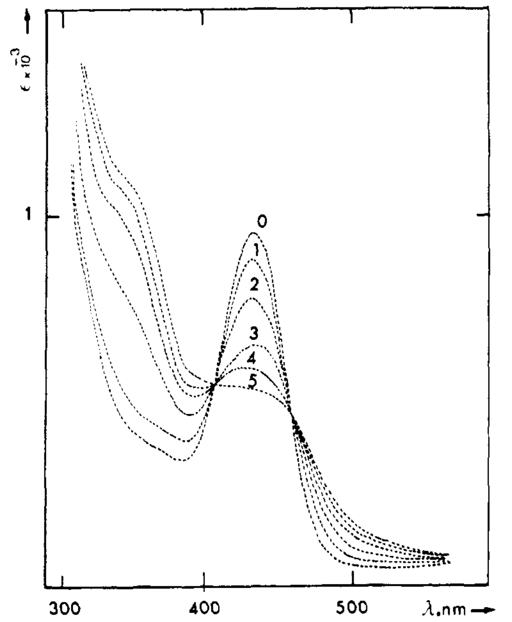

Figure 2. Changes occurring in the UV-visible spectrum during the exhaustive electrolysis at E = 0.3 V vs. SCE of 10^{-2} mol·dm^{-3} [Mo(NO)$_2$(MeCN)$_4$]$^{2+}$ in acetonitrile containing 0.1 mol·dm^{-3} TEAP at −30 °C.

(**2**), and [Mo(NO)$_2$(bpy)$_2$]$^{2+}$ (**3**) each exhibit a well-defined cathodic wave, together with the coupled anodic wave on the reverse scan. A typical example is given in Figure 1.

The peak current ratio $i_p^c/i_p^a = 1$ and the potential separation $\Delta E = E_p^c - E_p^a = 0.060$ V of the cathodic and anodic waves at all the scan rates and temperatures used correspond to the expected values for a one-electron reversible electrochemical couple. However, above 30 °C the ratio i_p^c/i_p^a is greater than unity for **1** and indicates some decomposition of the 19-electron complex above this temperature, on the cyclic voltammetry time scale of 5 s. Nevertheless, the 19-electron complexes **1**–**3** are stable at room temperature, at least on the cyclic voltammetry time scale. The electrochemical standard redox potentials $E° \simeq (E_p^c + E_p^a)/2$ are listed in Table I.

At more reducing potentials, the cyclic voltammograms of the dicationic complexes **2** and **3** exhibit supplementary irreversible cathodic peaks at −0.95 and −1.23 V, respectively. The absence of anodic peaks, even at rates up to 2 V·s^{-1} and at low temperatures, indicates the rapid decomposition of the 20-electron complexes (Figure 1) (eq 1–3). In the case of complex **1**, the supplementary cathodic peak is weak and ill-defined, due perhaps to adsorption of nonelectroactive species on the platinum electrode.[17]

$$[\mathrm{Mo(NO)_2L_2L_2}]^{2+} + e^- \rightleftarrows [\mathrm{Mo(NO)_2L_2L_2}]^+ \qquad (1)$$

$$[\mathrm{Mo(NO)_2L_2L_2}]^{+} + e^- \rightleftarrows [\mathrm{Mo(NO)_2L_2L_2}] \qquad (2)$$

$$[\mathrm{Mo(NO)_2L_2L_2}] \xrightarrow{\text{fast}} \text{products} \qquad (3)$$

(2) Coulometry. Exhaustive controlled-potential electrolysis of the dicationic complexes **1**–**3** past the first reduction wave consumed 1 mol of electrons/mol of complex (n = 1.0 ± 0.1 faradays) at 20 °C. However, at this temperature, the height of the wave observed on the rotating-disk voltammograms of the reduced solutions does not remain constant and indicates some decomposition of the radical complex [Mo(NO)$_2$L$_2$L$_2$]$^+$. Provided that the temperature was not allowed to rise above −30 °C, the reoxidation of [Mo(NO)$_2$L$_2$L$_2$]$^+$ could be effected quantitatively back to the dicationic precursor. Bulk electrolysis of dicationic complexes must be carried out at relatively low temperatures to minimize the decomposition of the labile 19-electron complexes. Such a lability is consistent with the reversible reduction observed by cyclic voltammetry, since a half-life of the order of seconds is sufficient to yield a i_p^c/i_p^a ratio of unity.

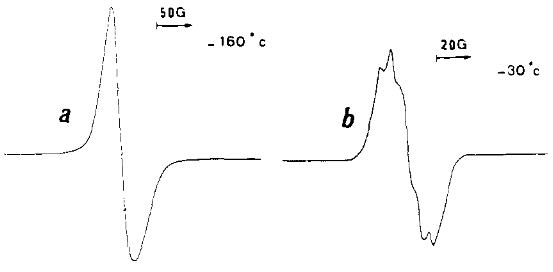

Figure 3. ESR spectra (a) of a frozen acetonitrile solution (0.1 mol·dm^{-3} TEAP) of [Mo(NO)$_2$(MeCN)$_4$]$^+$ and (b) of an isotropic acetonitrile solution (0.1 mol·dm^{-3} TEAP) of [Mo(NO)$_2$(MeCN)$_4$]$^+$.

(3) Spectroscopy of 19-Electron Complex 1. For some understanding of the nature of the radical cations, several spectroscopic measurements were investigated. The UV–visible spectra of the 18-electron dinitrosyl complexes show several absorption bands. The most characteristic absorption occurs near 420 nm for the dicationic complexes. During the electrolysis of **1**, the strong absorption at 420 nm decreases, and concomitantly a shoulder appears at 350 nm (Figure 2). It is difficult to make a definite assignment of the electronic transition due to the limited information available on the electronic spectra of dinitrosyl complexes. We have assigned the absorption at 420 nm to a dπ → π^*(NO) transition, 1b$_2$ → 2a$_1$ with C_{2v} symmetry.[4c] The ν(NO) frequencies, in the infrared region, of **1** (1860, 1750 cm^{-1}) are 170 and 160 cm^{-1} higher than those (1690, 1590 cm^{-1}) in the 19-electron reduced complex. These IR studies show that the additional electron is substantially on the two NO ligands.[11,12] The ESR spectrum of the frozen acetonitrile solution of [Mo(NO)$_2$(MeCN)$_4$]$^+$ exhibits a broad signal centered at g = 2.007 (Figure 3a). However, at −30 °C the spectrum consists of five poorly resolved lines (Figure 3b). This pattern results from coupling of the unpaired electron with the two equivalent ^{14}N's (I = 1): g = 2.005, a_N = 7 G. In the ESR spectra of the 19-electron complexes, there is no evidence of metal nuclear hyperfine interaction from either 15.72% ^{95}Mo (I = $^5/_2$) or 9.46% ^{97}Mo (I = $^5/_2$). The ESR spectra of the present and other 19-electron dinitrosyl species generated by irradiation[18] or electrochemistry[11-13] were interpreted as indications that the unpaired electron is largely confined to the NO ligands.

Anation Reactions by Cl$^-$ of the Dicationic Complexes. The course of the anation reactions by Cl$^-$ of the dicationic complexes **1** and **2** can be followed by spectrophotometry,[4e] conductometry,[4e] and cyclic voltammetry at room temperature (Figure 4). Thus, reactions 4 and 5 are instantaneous and follow the reverse path of halide abstraction. The reversible system [Mo(NO)$_2$(bpy)(MeCN)$_2$]$^{2+}$/[Mo(NO)$_2$(bpy)(MeCN)$_2$]$^+$, $E°$ = −0.09 V, is quantitatively converted to the reversible system [Mo(NO)$_2$(bpy)(MeCN)Cl]$^+$/[Mo(NO)$_2$(bpy)(MeCN)Cl], $E°$ = −0.35 V. The following anation reaction (5) is equilibrated at room temperature and gives the reversible system [Mo(NO)$_2$(bpy)Cl$_2$]/[Mo(NO)$_2$(bpy)Cl$_2$]$^-$, $E°$ = −0.57 V. The anation reaction pathways are analogous for [Mo(NO)$_2$(MeCN)$_4$]$^{2+}$ (**1**). The reversible system [Mo(NO)$_2$(MeCN)$_4$]$^{2+}$/[Mo(NO)$_2$(MeCN)$_4$]$^+$, $E°$ = 0.0 V, is quantitatively converted to the quasi-reversible system [Mo(NO)$_2$(MeCN)$_3$Cl]$^+$/[Mo(NO)$_2$(MeCN)$_3$Cl], $E°$ =

$$[\mathrm{Mo(NO)_2L_2(MeCN)_2}]^{2+} + \mathrm{Cl}^- \rightarrow [\mathrm{Mo(NO)_2L_2\ (MeCN)Cl}]^+ + \mathrm{MeCN} \qquad (4)$$

$$[\mathrm{Mo(NO)_2L_2(MeCN)Cl}]^{+} + \mathrm{Cl}^- \rightleftarrows [\mathrm{Mo(NO)_2L_2Cl_2}] + \mathrm{MeCN} \qquad (5)$$

---

[17] Bard, A. J.; Faulkner, L. R. "Electrochemical Methods. Fundamentals and Applications"; Masson: Paris, New York, 1983; p 603.

[18] (a) Couture, C.; Morton, J. R.; Preston, K. F.; Strach, S. J. *J. Magn. Reson.* **1980**, *41*, 88. (b) Morton, J. R.; Preston, K. F.; Strach, S. J. *J. Phys. Chem.* **1980**, *84*, 2478.

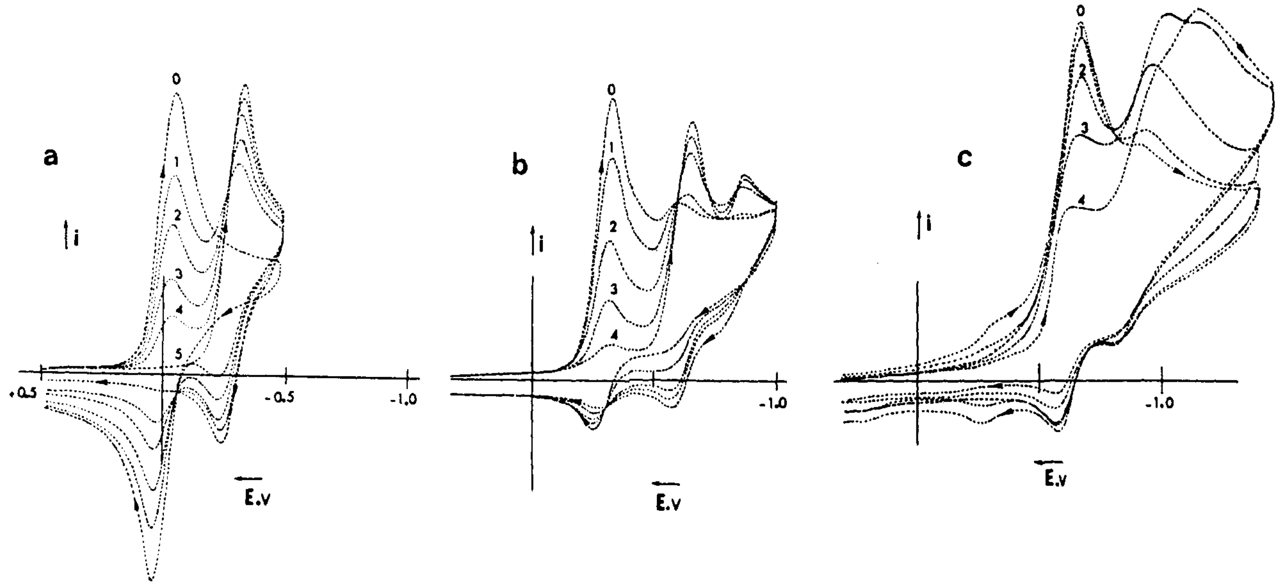

Figure 4. Changes occurring in the cyclic voltammogram during the addition of Et_4NCl to (a) $[Mo(NO)_2(MeCN)_4]^{2+}$, (b) $[Mo(NO)_2(MeCN)_3Cl]^+$, and (c) $[Mo(NO)_2(MeCN)_2Cl_2]$ in acetonitrile (0.1 mol·dm^{-3} TEAP) at 25 °C and at a scan rate of 0.1 V·s^{-1}.

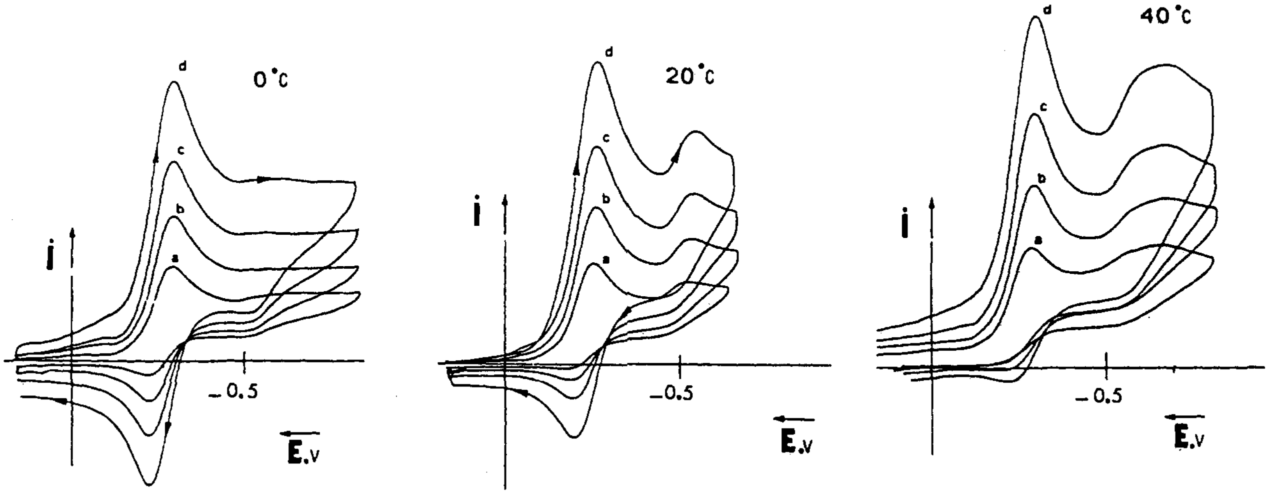

Figure 5. Cyclic voltammograms of a solution of 5×10^{-3} mol·dm^{-3} $[Mo(NO)_2(MeCN)_3Cl]^+$ in acetonitrile containing 0.1 mol·dm^{-3} TEAP at 0, 20, and 40 °C and at scan rates of (a) 0.02, (b) 0.05, (c) 0.1, and (d) 0.2 V·s^{-1}.

−0.31 V (Figure 4a). The resulting anation (5) is equilibrated at room temperature and gives the system $[Mo(NO)_2(MeCN)_2Cl_2]/[Mo(NO)_2(MeCN)_2Cl_2]^-$, $E° = -0.65$ V (Figure 4b). For complex 1, addition of excess chloride anion generates the trichloro and tetrachloro species $[Mo(NO)_2(MeCN)Cl_3]^-$ and $[Mo(NO)_2Cl_4]^{2-}$ (eq 6 and 7); thereby, we have detected by means

$$[Mo(NO)_2(MeCN)_2Cl_2] + Cl^- \rightarrow [Mo(NO)_2(MeCN)Cl_3]^- + MeCN \quad (6)$$

$$[Mo(NO)_2(MeCN)Cl_3]^- + Cl^- \rightarrow [Mo(NO)_2Cl_4]^{2-} + MeCN \quad (7)$$

of cyclic voltammetry the redox system $[Mo(NO)_2(MeCN)_3Cl]^-/[Mo(NO)_2(MeCN)_3Cl]^{2-}$, $E° = -0.91$ V, and the well-known couple[13] $[Mo(NO)_2Cl_4]^{2-}/[Mo(NO)_2Cl_4]^{3-}$, $E° = -1.10$ V (Figure 4c).

Monocationic Complexes. In acetonitrile the cyclic voltammograms of the acetonitrile monochloro complexes $[Mo(NO)_2L_2(MeCN)Cl]^+$ (L = MeCN, L_2 = 2,2′-bipyridine) at 0 °C are characterized by ratios of the cathodic and anodic currents (i_p^c/i_p^a) of unity and by anodic and cathodic peak separation ($E_p^c - E_p^a$) near 0.060 V for reversible one-electron processes according to eq 8. At room temperature and at low scan rates, the peak

$$[Mo(NO)_2L_2(MeCN)Cl]^+ + e^- \rightleftarrows [Mo(NO)_2L_2(MeCN)Cl] \quad (8)$$

current ratio is more than unity for $[Mo(NO)_2(MeCN)_3Cl]^+$ (**4**) (Figure 5); $[Mo(NO)_2(bpy)(MeCN)Cl]^+$ (**5**) exhibits a reversible system according to (8) even at room temperature. At more reducing potentials, the cyclic voltammograms of **5** exhibits a supplementary irreversible cathodic peak at −1.17 V. As for **2** and **3** (Figure 1), the absence of the associated anodic peak on the reverse scan indicates the rapid decomposition of the 20-electron complex. Bulk electrolysis of **5** at −0.5 V and 0 °C required 1.0 faraday/mol of **5**.

When the peak current ratios are more than unity for $[Mo(NO)_2(MeCN)_3Cl]^+$ (**4**), a supplementary peak appears at a more reducing potential corresponding to the reduction of the 18-electron dichloro complex $[Mo(NO)_2(MeCN)_2Cl_2]$ (**6**) (Figure 5).

It is obvious that chloride exchange is necessary for the formation of $[Mo(NO)_2(MeCN)_2Cl_2]$ according to reaction 5. However, only a weak anodic current is detected on the reverse scan at a potential corresponding to the oxidation of the expected 19-electron complex $[Mo(NO)_2(MeCN)_4]^+$; see supplemental Figure 5. This cannot explain the source of Cl^- through a rapid solvation in the 19-electron complex (eq 9). It is more reasonable

$$[Mo(NO)_2(MeCN)_3Cl] \xrightarrow{CH_3CN} [Mo(NO)_2(MeCN)_4]^+ + Cl^- \quad (9)$$

to assume a chloride exchange between the 19-electron complex $[Mo(NO)_2(MeCN)_3Cl]$, which diffuses toward the solution, and

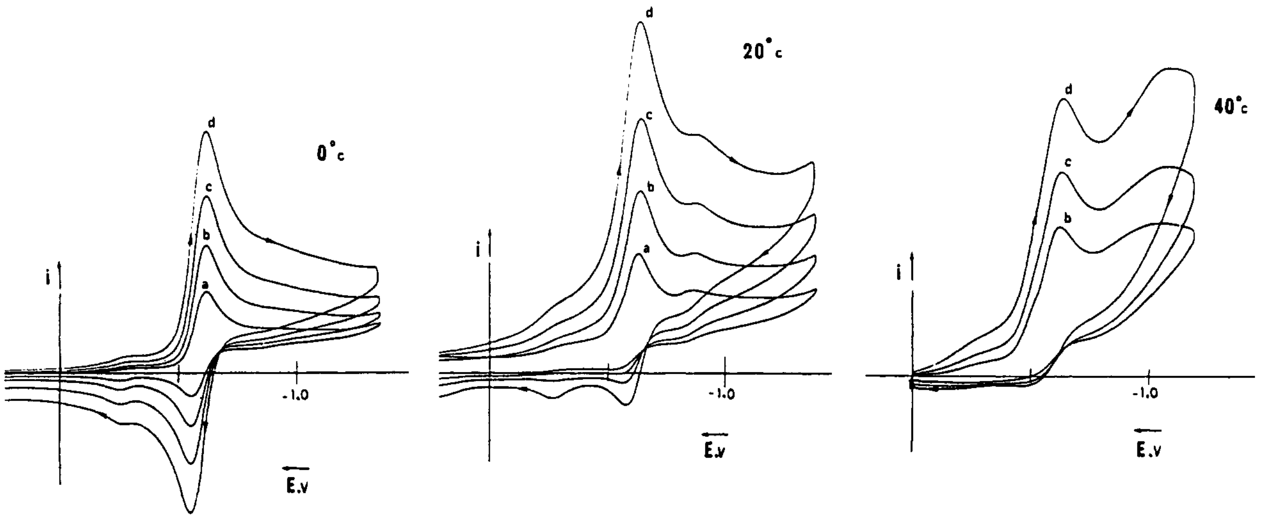

Figure 6. Initial scan CV of 2 × 10^{-3} mol·dm^{-3} [$Mo(NO)_2(MeCN)_2Cl_2$] in acetonitrile containing 0.1 mol·dm^{-3} TEAP at 0, 20, 40 °C and at scan rates of (a) 0.02, (b) 0.05, (c) 0.1, and (d) 0.02 V·s^{-1}.

the 18-electron complex [$Mo(NO)_2(MeCN)_3Cl$]$^+$, which diffuses toward the electrode, to give the neutral 18-electron complex [$Mo(NO)_2(MeCN)_2Cl_2$] (**6**) and a hypothetical 17-electron complex [$Mo(NO)_2(MeCN)_3$]$^+$. This latter species should be less stable than the 19-electron solvated complex, and denitrosylation can occur[19] before solvation.

For [$Mo(NO)_2(bpy)(MeCN)Cl$]$^+$ (**5**), no supplementary peaks are detected in the cyclic voltammograms. The 19-electron complex is less labile than [$Mo(NO)_2(MeCN)_3Cl$], and chloride exchange does not occur at room temperature on the cyclic voltammetry time scale.

Neutral Complexes. Cyclic voltammograms of the neutral dinitrosyl complex [$Mo(NO)_2(MeCN)_2Cl_2$] (**6**) in acetonitrile are shown in Figure 6. Below 0 °C, the scans are all characterized by the cathodic and anodic peak separation ($E_p^c - E_p^a$) near 0.060 V and peak current ratios near unity (eq 10). At more reducing

$$[Mo(NO)_2L_2Cl_2] + e^- \rightleftarrows [Mo(NO)_2L_2Cl_2]^- \qquad (10)$$

potentials, the cyclic voltammograms of **7** exhibit a supplementary irreversible cathodic peak at −1.17 V. The absence of the associated anodic peak indicates the rapid decomposition of the 20-electron complex. The magnitudes of the i_p^c/i_p^a ratios at room temperature and a typical scan rate are strongly dependent upon the nature of the ligand L. The chelating ligand L_2 = bpy stabilizes the 19-electron complex even at 40 °C.

On the other hand, it should be noted that a weak cathodic current is observed in the cyclic voltammograms of Figure 6 as well as in the rotating-disk voltammograms (supplemental Figure 9) at a potential corresponding to the reduction of monochloro complexes, obtained by using a platinum or glassy-carbon electrode (Figure 6). The relative intensity of the prewave is more important at low concentrations of the complex and is suppressed by the addition of small amounts of [$N(C_2H_5)_4$][Cl]. The supplementary wave is attributed to the reverse solvation reaction (5). The intensity of the weak prewave increases with $v^{1/2}$, where v is the scan rate, and therefore the prewave possesses no kinetic character at room temperature and indicates a slow equilibration of the reaction (5).

Whereas for **7** with L = bpy, the peak current ratio of the main peak is near unity, for **6** with L = MeCN, the ratio i^c/i^a is greater than unity at room temperature and the system appears irreversible at 40 °C (Figure 6), indicating a significant decomposition of the 19-electron radical anion formed at the platinum electrode. Concomitantly, supplementary peaks appear at the more reducing potentials −0.95 and −1.15 V, corresponding to the anionic 18-electron complexes **8** and **9** (Figure 6). The chloride exchange occurs probably between the 19-electron complex [$Mo(NO)_2(MeCN)_2Cl_2$]$^-$, which diffuses toward the solution, and the 18-electron complex [$Mo(NO)_2(MeCN)_2Cl_2$] (**6**), which diffuses toward the electrode, to give the anionic 18-electron species [$Mo(NO)_2(MeCN)Cl_3$]$^-$ (**8**) and [$Mo(NO)_2Cl_4$]$^{2-}$ (**9**) through the two sequential reactions (6) and (7). Likewise, when the peak current ratio of the main peak is more than unity for complex **6**, the minor anodic peak at 0.24 V corresponding to the oxidation of the 19-electron complex [$Mo(NO)_2(MeCN_3)Cl$] increases slightly on the reverse scan. However, no anodic current corresponding to the oxidation of the solvated 19-electron species [$Mo(NO)_2(MeCN)_4$]$^+$ is clearly detected at +0.03 V. On the other hand, another minor peak is evidenced at +0.20 V (at room temperature) on the reverse scan. On a subsequent cathodic scan, reduction peaks corresponding to dicationic complexes are absent, and the weak height of the reduction peak of the 18-electron complex [$Mo(NO)_2(MeCN)_3Cl$] is identical with that found in the first scan. These results are not surprising, since the anation reactions (4) and (5)[4e] are fast in the 18-electron complexes.

Bulk electrolysis of [$Mo(NO)_2(bpy)Cl_2$] (**7**) at −0.75 V and 0 °C in acetonitrile required 1.0 faraday/mol. The reduced solution exhibits ESR spectra with five poorly resolved lines.[13] This pattern results from coupling of the unpaired electron of [$Mo(NO)_2(bpy)Cl_2$]$^-$ with the two equivalent ^{14}N's (I = 1).[13]

Discussion

Having previously observed[4e] inactivity in the thermal substitution of 18-electron [$Mo(NO)_2L_2Cl_2$], we believe the replacement of chloride by MeCN in these complexes proceeds only by chloride abstraction by Ag^+ upon refluxing an acetonitrile solution overnight to give the dicationic complexes in quantitative yield. On the other hand, in the 19-electron state these complexes exhibit rapid exchange of the chloro ligand and the lability of the ligand depends on the nature of the ligand L.

Spectroscopic data of the 19-electron dinitrosylmolybdenum complexes presented in this paper and other 19-electron dinitrosyl complexes of iron,[18] cobalt,[18] tungsten,[12] and molybdenum[11,13] demonstrate the existence of an energetically accessible dinitrosyl-based molecular orbital as the LUMO. This molecular orbital is delocalized over the two nitrosyl groups and possesses little or no metal orbital character. It should be noted that in 19-electron mononitrosylmolybdenum complexes, the unpaired electron is predominantly metal-centered.[21]

Although the structures of 19-electron dinitrosylmolybdenum complexes are not available yet, it is possible to obtain structural information about the [$Mo(NO)_2$]^7 moiety[19] by comparison with the recently reported single-crystal X-ray diffraction study of

---

(19) Seyferth, K.; Taube, R. *J. Organomet. Chem.* **1984**, *262*, 179.

(20) Enemark, J. H.; Feltham, R. D. *Coord. Chem. Rev.* **1974**, *13*, 339.

(21) Greehough, T. J.; Kolthammer, B. W. S.; Legzdins, P.; Trotter, J. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1980**, *B36*, 795.

$[(\eta^5\text{-}C_5H_5)W(NO)_2(P(OPh)_3)]$.[12] There is little difference in the average W–N–O bond angles between the 19-electron complex and the 18-electron $[(\eta^5\text{-}C_5H_5)W(NO)_2Cl]$[20] complex. However, there is much discussion in the literature[20] about the influence of electron density on M–N–O bond angles in metal nitrosyl complexes. The major difference in structure is the substantially larger N–W–N bond angle in this 19-electron complex compared to that in the 18-electron analogue.[21]

The differences between the 18- and 19-electron structures are readily interpreted in terms of a MO calculation by Hall and co-workers.[22] These authors indicate that the 19th electron will occupy an orbital that has substantial 2π(NO) character. Nevertheless, in the case of $[Mo(NO)_2L_2Cl_2]$, the other ligands such as Cl contribute to this MO. Two kinds of stereochemistry are observed for $Mo(NO)_2L_2Cl_2$ complexes: *cis*-dinitrosyl-*cis*-dichloro (L = MeCN, py) and *cis*-dinitrosyl-*trans*-dichloro (L_2 = bpy). For the first type, the Mo–Cl bond is labilized in the 19-electron state; for the second type, the Mo–Cl bond is more stable in the 19-electron state. The key features of the chloride elimination are (i) the reduction of the $[Mo(NO)_2L_2Cl_2]$ complexes to their 19-electron anions and (ii) the rapid chloro ligand exchange of the paramagnetic intermediate. The multistep reduction produces trichloro and tetrachloro complexes, which are reducible at a more negative potential than the dichloro complexes. The multiple-step system is clearly not catalytic, but is rather of the electroactivation type.[23] The labile species "$Mo(NO)_2^{+}$", which is a potentially efficiency catalyst such as "$Fe(NO)_2$",[10] can be generated by electroreduction. The values of the standard potential $E°$ of the redox systems (Table I) give an estimation of the energy difference between the respective LUMO's. A decrease in the ν(NO) frequencies indicates stabilization of the LUMO. The energy of the LUMO is in the following order: dicationic > monocationic > neutral > monoanionic > dianionic. Among these classes of dinitrosyl complexes, the energy of the LUMO becomes more stabilized with increasing σ-donor and decreasing π-acceptor properties of ligand L.

Registry No. **1**$^{2+}$, 63087-71-8; **1**$^{+}$, 99948-14-8; **2**$^{+}$, 99948-22-8; **2**$^{2+}$, 100018-91-5; **3**$^{+}$, 99948-23-9; **3**$^{2+}$, 67158-74-1; **4**, 99948-17-1; **4**$^{+}$, 100018-92-6; **4**$^{-}$, 99948-19-3; **4**$^{2-}$, 99948-20-6; **5**, 99948-15-9; **5**$^{+}$, 100018-93-7; **6**, 99948-18-2; **6**$^{-}$, 69254-57-5; **7**, 14324-79-9; **7**$^{-}$, 99948-16-0; **8**$^{-}$, 99948-13-7; **8**$^{2-}$, 99948-24-0; **9**$^{2-}$, 65085-25-8; **9**$^{3-}$, 99948-21-7; MeCN, 75-05-8; Et_4NCl, 56-34-8; Cl_2, 7782-50-5.

Supplementary Material Available: Figures showing cyclic voltammograms of $[Mo(NO)_2(MeCN)_4]^{2+}$, $[Mo(NO)_2(bpy)(MeCN)_2]^{2+}$, $[Mo(NO)_2(MeCN)_3Cl]^{+}$, $[Mo(NO)_2(bpy)(MeCN)Cl]^{+}$, $[Mo(NO)_2(MeCN)_2Cl_2]$, and $[Mo(NO)_2bpyCl_2]$ and rotating-disk electrovoltammograms of the 19-electron complexes $[Mo(NO)_2(MeCN)_4]^{+}$ and $[Mo(NO)_2(MeCN)_2Cl_2]$ (9 pages). Ordering information is given on any current masthead page.

---

(22) Morris-Sherwood, B. J.; Kolthammer, B. W. S.; Hall, M. B. *Inorg. Chem.* **1981**, *20*, 2771.

(23) Savéant, J. M. *Acc. Chem. Res.* **1980**, *13*, 323.

Contribution from the Departments of Chemistry, The Ohio State University,
Columbus, Ohio 43210, and Wright State University, Dayton, Ohio 45435

Electrochemistry of Niobium(IV) and Tantalum(IV) Complexes: Ligand Additivity in d^1 Octahedral Complexes

B. E. Bursten,*[1a,c] M. R. Green,[1a] V. Katović,*[1b] J. R. Kirk,[1b] and D. Lightner, Jr.[1b]

Received July 8, 1985

The electrochemistry of the octahedral complexes $[MCl_{6-n}(NCMe)_n]^{-2+n}$ (M = Nb, Ta; n = 0, 1, 2 (cis)) has been investigated by using cyclic voltammetry. The ease with which these d^1 systems are oxidized to the corresponding d^0 systems decreases with increasing substitution of chloride by acetonitrile. The electrochemical data are in good accord with the model of ligand additivity and with Fenske–Hall molecular orbital calculations on the Nb series. It is concluded that NCMe is a more stabilizing ligand than Cl, largely because the latter acts as a π donor whereas the former is a weak π acceptor.

Introduction

The continuing growth in the high-valent chemistry of the early transition metals places new demands on the experimental techniques commonly used to elucidate the nature of the metal–ligand bonding. Such complexes often exhibit featureless electronic spectra and many are paramagnetic, hindering analysis by NMR. Further, the ligands generally used to stabilize early transition metals in high oxidation states (e.g. halides, nitriles, and phosphines) are not as amenable to spectroscopic probing as those commonly found in low-valent systems, such as CO.[2]

A technique of paramount importance in providing information about the energetics of high-valent systems is electrochemistry. The redox potentials of such systems provide, in principle, a measure of the ligand and metal atom influences on the electron energetics, data of great import given the attention focused on high-valent systems as potentially controllable oxidants.

We have previously advanced a model,[3] called ligand additivity, which we have used to correlate the trends in the redox potentials and ionization energies of low-spin d^6 octahedral complexes. This model has been used successfully on the ligand substitution series $ML_nL'_{6-n}$ where L and L′ are π-acid ligands such as CO, CNR, or PR_3, and M is a low-valent d^6 metal atom such as Cr(0), Mo(0), Mn(I), or Re(I).[3-5] The ligand additivity model not only correlates the experimental data but, in so doing, provides direct information about the relative bonding capabilities of L and L′.

As our previous research on the ligand additivity model has been limited to low-valent organometallic systems containing π-acid ligands, we were interested in determining whether the model could be extended to encompass high-valent coordination complexes containing classical donor ligands. In this paper we report a combined experimental and theoretical study of some

---

(1) (a) The Ohio State University. (b) Wright State University. (c) Camille and Henry Dreyfus Foundation Teacher-Scholar 1984–1989 and Fellow of the Alfred P. Sloan Foundation 1985–1987.

(2) See, for example: (a) Fowles, G. W. A.; Tidmarsh, D. J.; Walton, R. A. *Inorg. Chem.* **1969**, *8*, 631–638. (b) Luetkens, M. L., Jr.; Elcesser, W. L.; Huffman, J. C.; Sattelberger, A. P. *Inorg. Chem.* **1984**, *23*, 1718–1726. (c) Cotton, F. A.; Duraj, S. A.; Roth, W. J. *Inorg. Chem.* **1984**, *23*, 3592–3596.

(3) Bursten, B. E. *J. Am. Chem. Soc.* **1982**, *104*, 1299–1304.

(4) Bursten, B. E.; Darensbourg, D. J.; Kellogg, G. E.; Lichtenberger, D. L. *Inorg. Chem.* **1984**, *23*, 4361–4365.

(5) Bancroft, G. M.; Dignard-Bailey, L.; Puddephatt, R. J. *Inorg. Chem.* **1984**, *23*, 2369–2370.

0020-1669/86/1325-0831$01.50/0