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Electrochemical Studies of Seven-Coordinate Isocyanide Complexes of Molybdenum(II) and Tungsten(II)[1,2]

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The redox properties of the seven-coordinate cations $[M(CNR)_6X]^+$, $[Mo(CNR')_6I]^+$, and $[M(CNR)_7]^{2+}$ (M = Mo, W; R = alkyl; R′ = aryl; X = Cl, Br, I, CN, or $SnCl_3$) have been investigated by cyclic voltammetry and controlled-potential coulometry in dichloromethane solutions. All of the alkyl isocyanide complexes, with the exception of $[Mo(CN\text{-}t\text{-}C_4H_9)_6(SnCl_3)](PF_6)$, exhibit a quasi-reversible one-electron oxidation to form seven-coordinate Mo(III) or W(III) cations and also show an irreversible reduction. The cations $[Mo(CN\text{-}t\text{-}C_4H_9)_4((CNH\text{-}t\text{-}C_4H_9)_2)X]^+$ (X = I, CN) behave similarly. The half-wave potentials increase in the order $[Mo(CNR)_4((CNHR)_2)I]^+ < [Mo(CNR)_6X]^+$ (X = halide) $< [Mo(CNR)_6CN]^+ < [Mo(CNR)_7]^{2+} < [Mo(CNR)_6(SnCl_3)]^+$, a trend that reflects the electron-donor/acceptor properties of the ligands. The tungsten analogues studied show similar trends but are easier to oxidize by ~0.1 V. The $[Mo(CNR')_6I]^+$ (R′ = aryl) cations display a reversible oxidation wave ~0.4 V more anodic than their alkyl analogues as well as two additional, irreversible oxidations at higher potentials. They also undergo an irreversible reduction. A correlation is drawn between the ease of oxidation of these complexes and the ability of their isocyanide ligands to undergo reductive coupling in reactions with chemical reducing agents such as zinc in a protic solvent. No evidence was found for electrochemical reductive coupling of any of the compounds studied.

Introduction

Seven-coordinate alkyl isocyanide complexes of Mo(II) and W(II), $[M(CNR)_6X]^+$, undergo an interesting reductive coupling reaction to form the $[Mo(CNR)_4((CNHR)_2)X]^+$ cations which contain a coordinated *N*,*N*′-dialkyldiaminoacetylene molecule.[3-6] This ligand can be removed oxidatively and isolated as the corresponding dialkyl oxamide with the newly formed C–C bond intact.[6] The reductive coupling reaction has been effected with zinc in a protic solvent and with photochemically excited benzophenone or the trityl radical in ethanol.

The present study was undertaken to learn whether the $[M(CNR)_6X]^+$ complexes could be reductively coupled electrochemically. We also wanted to use electrochemical methods to characterize the electronic properties of these cations and thereby gain further insight into the factors[6] affecting the reductive coupling reaction. Cyclic voltammetric and controlled-potential electrolysis experiments were therefore carried out in which the ligand X (for M = Mo, X = Cl, Br, I, CN, and $SnCl_3$ and R = *t*-Bu; for M = W, X = Cl, Br, and I and R = $t\text{-}C_4H_9$) and the R groups (for M = Mo, X = I, R = CH_3, $c\text{-}C_6H_{11}$, $t\text{-}C_4H_9$, $p\text{-}C_6H_4CH_3$, C_6H_5, $p\text{-}C_6H_4Cl$) were systematically varied. The complexes $[Mo(CNR)_7]^{2+}$ (R = CH_3, $c\text{-}C_6H_{11}$, $t\text{-}C_4H_9$), $[Mo(CN\text{-}c\text{-}C_6H_{11})_5(dppm)]^{2+}$ (dppm = $Ph_2PCH_2PPh_2$), $[W(CN\text{-}t\text{-}C_4H_9)_7]^{2+}$, and two examples of complexes containing the bis(*tert*-butylamino)acetylene ligand, $[Mo(CN\text{-}t\text{-}C_4H_9)_4((CNH\text{-}t\text{-}C_4H_9)_2)X]^+$ (X = I, CN), were also investigated. Electrochemical studies on $[Mo(CNR)_7]^{2+}$ (R = CH_3, $c\text{-}C_6H_{11}$, $t\text{-}C_4H_9$), $[Mo(CN\text{-}c\text{-}C_6H_{11})_5(dppm)]^{2+}$, $[W(CN\text{-}t\text{-}C_4H_9)_7]^{2+}$, $[Mo(CNPh)_6I]^+$, and related complexes have been carried out independently by Walton and coworkers.[7-9]

Experimental Section

The molybdenum and tungsten complexes used for electrochemical studies were available from previous work,[10] except for $[Mo(CNPh)_6I](BPh_4)$ and $[Mo(CN\text{-}c\text{-}C_6H_{11})_5(dppm)](PF_6)_2$, which were gifts from H. B. Gray and R. A. Walton, respectively. Compounds that contained an easily oxidized counterion (e.g., BPh_4^-, I^-) were converted to the BF_4^- or PF_6^- salt by one of the two following methods:

Method A. A methanol solution of 100–200 mg of the desired cation was passed through a 0.5-cm diameter column containing a 20-fold excess of Dowex 2X-8 (20–50 mesh) anion exchanger which had been previously converted to the BF_4^- or PF_6^- form.

Method B. A concentrated methanol solution containing approximately 5-fold excess of $NaBF_4$ or $NaPF_6$ was added to a methanol solution containing 50–100 mg of the desired cation. The precipitate was collected by suction filtration and rinsed with cold methanol. Samples were considered to be pure if an oxidation wave attributable to the interfering anion could not be detected.

Dichloromethane was freshly distilled under nitrogen from P_2O_5. Tetra-*n*-butylammonium perchlorate (TBAP) was purchased from Eastman Organic Chemicals, recrystallized three times from warm ethyl acetate/pentane (Aldrich Chemical Co. "Gold Label"), and dried in vacuo at 100 °C. Ferrocene, AgI, and tetra-*n*-butylammonium iodide were purchased from Aldrich Chemical Co.; the last compound was recrystallized once before use.

Electrochemistry was performed with a Princeton Applied Research (PAR) Model 173 Potentiostat, Model 175 Universal Programmer, and Model 179 Digital Coulometer; cyclic voltammograms were recorded on an Omnigraphic 2000 X-Y Recorder (Houston Instruments).

A three-electrode configuration, consisting of a 3-mm^2 surface area vitreous-carbon working electrode, platinum-coil counterelectrode, and Ag/AgI reference electrode,[11] was used for all voltammetric measurements. The reference electrode system consisted of a silver wire immersed in a CH_2Cl_2 solution 0.1 M in tetra-*n*-butylammonium perchlorate, 0.05 M in tetra-*n*-butylammonium iodide, and saturated with silver iodide and allowed to equilibrate 72 h in the dark before use.[12] It was situated in one compartment of a salt bridge, separated by a fine-porosity sintered-glass frit from a 0.2 M $TBAP/CH_2Cl_2$ solution in the other compartment. This latter compartment in turn was separated by another frit from the Luggin capillary, which extended into the test solution with its tip placed as close as possible to the working electrode to minimize IR drop. The test solution and working and counterelectrodes were all contained in a thermostated

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Table I. Half-Wave or Peak Potentials for Seven-Coordinate Molybdenum(II) and Tungsten(II) Isocyanide Complexes[a]

Complex			$E_{1/2}$(ox)[b]	Ep,c(red)[c]
$[Mo(CNR)_6X]^{+n}$				
R = *t*-C_4H_9	X = Cl	n = 1	0.20	
R = *t*-C_4H_9	X = Br	n = 1	0.22	
R = *t*-C_4H_9	X = I	n = 1	0.23	-2.42
R = *t*-C_4H_9	X = CN	n = 1	0.31	
R = *t*-C_4H_9	X = $SnCl_3$	n = 1	0.72[d]	
R = *c*-C_6H_{11}	X = I	n = 1	0.21	
R = CH_3	X = I	n = 1	0.16	-2.08
R = *p*-$C_6H_4CH_3$	X = I	n = 1	0.50[e]	-1.97
R = C_6H_5	X = I	n = 1	0.53[e]	-1.79
R = *p*-C_6H_4Cl	X = I	n = 1	0.55[e]	
R = *t*-C_4H_9	X = CN-*t*-C_4H_9	n = 2	0.69	-2.12
R = *c*-C_6H_{11}	X = CN-*c*-C_6H_{11}	n = 2	0.68	
R = CH_3	X = $CNCH_3$	n = 2	0.58	-2.06
$[Mo(CNR)_4\{(CNHR)_2\}X]^{+n}$				
R = *t*-C_4H_9	X = I	n = 1	0.14	-2.38
R = *t*-C_4H_9	X = CN	n = 1	0.16	
$[Mo(CNR)_5(dppm)]^{+2}$				
R = *c*-C_6H_{11}			0.59	
$[W(CNR)_6X]^{+n}$				
R = *t*-C_4H_9	X = Cl	n = 1	0.08	
R = *t*-C_4H_9	X = Br	n = 1	0.13	
R = *t*-C_4H_9	X = I	n = 1	0.14	
R = *t*-C_4H_9	X = CN-*t*-C_4H_9	n = 2	0.58	

[a] Potentials are reported in volts (±0.02 V) vs. the ferrocene/ferrocenium couple. Measurements were made in CH_2Cl_2 with 0.2 M tetra-*n*-butylammonium perchlorate as supporting electrolyte. [b] Quasi-reversible except where noted otherwise. [c] Irreversible; $E_{p,c}$ is the peak current of the cathodic scan. See text and Figure 1 for further information about the cyclic voltammograms between −1.0 and −2.5 V. [d] Irreversible. [e] Two irreversible waves ~0.77 and 0.93 V also appeared, the nature of which was not investigated.

glass cell at 25.0 ± 0.5 °C. All test solutions, 1.0×10^{-3} M in metal complex dissolved in CH_2Cl_2 with 0.2 M TBAP as supporting electrolyte, were thoroughly deoxygenated by bubbling with dry dinitrogen. The stable reversible one-electron couple ferrocene/ferrocenium (Fc/Fc^+)[13] was run several times during the course of an experimental day to serve as a reference and to monitor the stability of the system. A "blank" was run before each sample to ensure that the solvent and supporting electrolyte were pure and that oxygen was excluded. Half-wave potentials ($E_{1/2}$), calculated from the formula $E_{1/2} = \frac{1}{2}(E_{p,a} + E_{p,c})$, where $E_{p,a}$ and $E_{p,c}$ are the anodic and cathodic peak potentials, respectively, have a precision of ~20 mV and are computed vs. the ferrocene/ferrocenium couple.[13] This procedure permits one to obtain $E_{1/2}$ values that are independent of experimental setup as long as all measurements are done in the same solvent. However, even $E_{1/2}$ values obtained in different solvents can be directly compared, provided that the Fc/Fc^+ couple is solvated in the same manner as the test compounds in a given solution.[13]

Controlled-potential coulometry experiments were performed on CH_2Cl_2 solutions with 0.01 M TBAP as supporting electrolyte. The sample compartment, containing the test solution, vitreous-carbon-rod working electrode, and Ag/Ag^+ quasi-reference electrode[14] was separated from the platinum-coil counterelectrode by an intervening 0.01 M $TBAP/CH_2Cl_2$ salt bridge. The test solution was vigorously stirred during the course of the electrolysis, and nitrogen was bubbled through all compartments. Electrolyses were performed at room temperature, with the above PAR instrumentation, and at potentials approximately 200 mV beyond the anodic peak of interest. Before each sample a "blank" was run on the solvent-supporting electrolyte solution alone to determine the background current, which was then automatically "nulled" by the PAR Model 179 Digital Coulometer's background compensation control.

Results and Discussion

Table I summarizes the half-wave or peak potentials for all compounds studied. Cyclic voltammograms of a representative group of these complexes are shown in Figure 1. All of the compounds listed in Table I are relatively easy to oxidize but difficult to reduce. The free isocyanides were found to be electroinactive over the potential ranges studied. As mentioned in the Introduction, the half-wave potentials of six of the complexes have been independently determined in CH_2Cl_2 at

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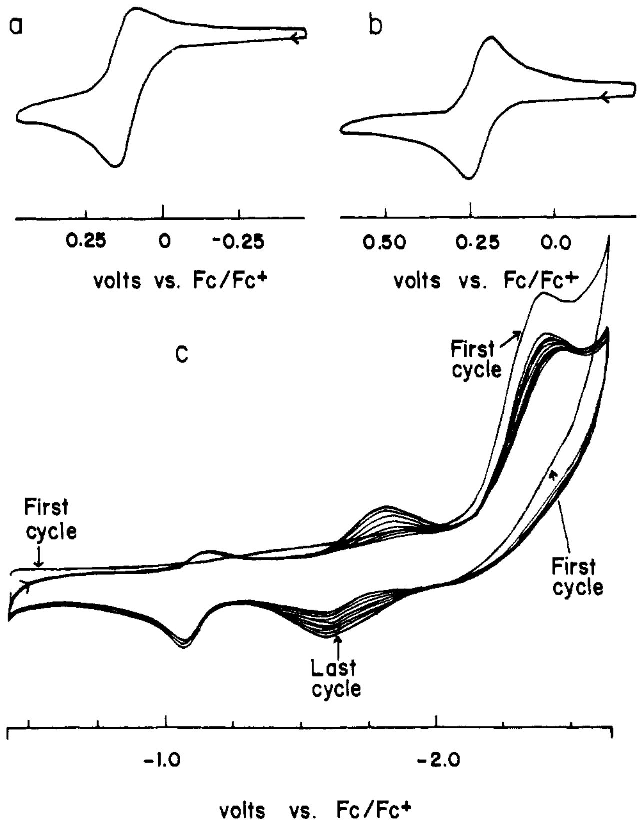

Figure 1. Cyclic voltammograms in CH_2Cl_2 of 0.2 M $(Bu_4N)(ClO_4)$ solutions: (a) oxidation of 1 mM $[Mo(CN\text{-}t\text{-}C_4H_9)_4((CNH\text{-}t\text{-}C_4H_9)_2)I](BF_4)$, scan rate 100 mV s^{-1}; (b) oxidation of 1 mM $[Mo(CN\text{-}t\text{-}C_4H_9)_6Br](PF_6)$, scan rate 100 mV s^{-1}; (c) reduction of 1 mM $[Mo(CN\text{-}t\text{-}C_4H_9)_6I](BF_4)$ in THF and 0.2 M $Li(ClO_4)$ containing 50 μL of H_2O, scan rate 100 mV s^{-1}, showing multiple scans.

22 °C[7-9] with saturated potassium chloride calomel as the reference electrode (SCE). The two sets of $E_{1/2}$ values exhibit a good linear dependence described by eq 1. We have also

$$E_{1/2}(\mathrm{SCE}) = E_{1/2}(\mathrm{Fc/Fc^+}) + 0.45\ \mathrm{V} \qquad (1)$$

measured the potential of the Fc/Fc+ couple in THF relative to SCE (1 N KCl at 25 °C) and find its potential to be 0.455 V (uncorrected for junction potentials). Since the saturated and 1 N KCl calomel electrode potentials differ by +0.039 V,[15] the relationship between $E_{1/2}$ values referred to the SCE and Fc/Fc+ couple in THF should be that described by eq 2, in agreement with eq 1.

$$E_{1/2}(\mathrm{SCE}) = E_{1/2}(\mathrm{Fc/Fc^+}) + 0.42\ \mathrm{V} \qquad (2)$$

Oxidations. Compounds containing alkyl isocyanide ligands gave well-defined oxidation waves to form the seven-coordinate M(III) cations. The only exception was the complex $[Mo(SnCl_3)(CN\text{-}t\text{-}C_4H_9)_6](PF_6)$, which exhibited irreversible redox behavior and underwent color changes during the experiment. Aryl isocyanide complexes exhibited a single, well-defined oxidation wave followed by two irreversible oxidation waves.

The first oxidation step of the alkyl and aryl isocyanide complexes satisfied the criteria for a diffusion-controlled quasi-reversible one-electron oxidation process.[16-18] For scan rates (v) between 50 and 500 mV/s, the anodic to cathodic peak current ratio $i_{p,a}/i_{p,c}$ was approximately 1 and the ratio

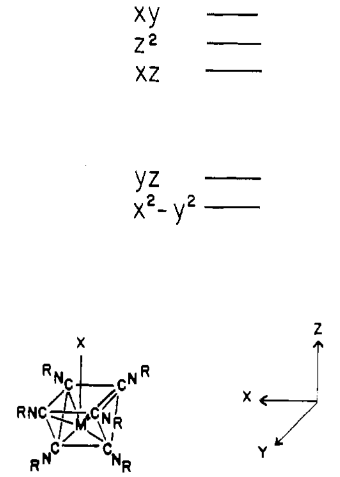

Figure 2. Coordinate system and approximate metal d-orbital energies for C_{2v} capped trigonal-prismatic $[M(CNR)_6X]^+$ cations.

$i_p/v^{1/2}$ was constant. The separation between the anodic and cathodic peaks, ΔE_p, ranged from 60 to 100 mV. Controlled-potential coulometry of $[M(CN\text{-}t\text{-}C_4H_9)_7](PF_6)_2$ (M = Mo and W) and $[Mo(CN\text{-}t\text{-}C_4H_9)_6I]BF_4$, carried out at potentials 200 mV anodic of the first oxidation peaks, was consistent with a one-electron (1.1 ± 0.2 mol of electrons/mol of complex) oxidation, but no stable products were isolated.

Among the complexes containing *tert*-butyl isocyanide ligands bound to molybdenum, the half-wave potential was found to increase in the order $[Mo(CNR)_4((CNHR)_2)I]^+ < [Mo(CNR)_6X]^+$ (X = halide) $< [Mo(CNR)_6CN]^+ < [Mo(CNR)_7]^{2+} < [Mo(CNR)_6(SnCl_3)]^+$. This trend is explained by considering the ligand interactions that influence the energy of the HOMO. The d-orbital splitting pattern and the coordinate system for a capped trigonal prismatic seven-coordinate complex are given in Figure 2. The choice of the capped trigonal prism (CTP) reference geometry is arbitrary but inconsequential because the general energy level pattern for all seven-coordinate geometries consists of a set of three high-energy orbitals and a set of two lower energy orbitals.[19] Slight changes in relative energies of the orbitals within each set do not influence the interpretations. Moreover, the CTP is a solid-state coordination geometry commonly found in these compounds.[20] In a d^4 complex, the highest energy filled metal orbitals are the d_{yz} and $d_{x^2-y^2}$ and these are directed between the ligands. The energy of the d_{yz} (HOMO) orbital is strongly affected by the π-acceptor/donating properties of the ligands. π-acceptor ligands will lower the energy, increasing the potential required to remove an electron from the complex. The half-wave potential is decreased by π donors because they will increase the energy of the d_{yz} orbital. The value of the half-wave potential correlates very well with the increasing π-acceptor ability of the ligand X in the $[Mo(CN\text{-}t\text{-}C_4H_9)_6X]^{n+}$ cations and follows the order halide $< CN^- <$ CNR $< SnCl_3^-$. The greater charge of dicationic $[Mo(CNR)_7]^{2+}$ species compared to the other, monocationic complexes also helps to account for their relatively high half-wave potentials (Table I).

Two examples of the $[Mo(CN\text{-}t\text{-}C_4H_9)_4((CNH\text{-}t\text{-}C_4H_9)_2)X]^+$ cations have been studied (X = I, CN). The half-wave potential of $[Mo(CN\text{-}t\text{-}C_4H_9)_4((CHN\text{-}t\text{-}C_4H_9)_2)I]^+$ is 0.09 V less anodic than that of $[Mo(CN\text{-}t\text{-}C_4H_9)_6I]^+$, suggesting that the bis(alkylamino)acetylene ligand is a considerably poorer π acid than two isocyanide ligands. The

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half-wave potentials of the two coupled ligand cations exhibit the same trend as a function of the acidity of the unique ligand X as the $[Mo(CNR)_6X]^+$ cations. The difference is not as large, however.

The half-wave potential for the halide complexes $[Mo(CN\text{-}t\text{-}C_4H_9)_6X]^+$ becomes more anodic in the sequence Cl < Br < I. This trend has been observed in the redox properties of other transition-metal halides but has not been rationalized.[9,21] The alkyl isocyanide complexes $[Mo(CNR)_6I]^+$ and $[Mo(CNR)_7]^{2+}$ ($R = CH_3$, $c\text{-}C_6H_{11}$, $t\text{-}C_4H_9$) have half-wave potentials which become more positive in the sequence $R = CH_3 < c\text{-}C_6H_{11} < t\text{-}C_4H_9$. The reverse trend in half-wave potentials was observed in the first one-electron oxidation of the molybdenum(0) isocyanide species $Mo(CNR)_2(dppe)_2$, but the second and third oxidations, corresponding to Mo(I) → Mo(II) and Mo(II) → Mo(III), respectively, paralleled the trend we observe.[22]

The least positive half-wave potential of the aryl isocyanide complexes $[Mo(CNAr)_6I]^+$ ($Ar = p\text{-}C_6H_4CH_3$, C_6H_5, $p\text{-}C_6H_4Cl$) is approximately 0.25 V more anodic than that of the alkyl complexes $[Mo(CNR)_6I]^+$ ($R = CH_3$, $c\text{-}C_6H_{11}$, or $t\text{-}C_4H_9$) and increases as a function of the electronegativity of the para substituent. This behavior is expected because aryl isocyanides are better π acids than alkyl isocyanides and their π acidity increases as a function of the para substituent in the order $Cl > H > CH_3$. The aryl isocyanide complexes also undergo two additional, irreversible oxidations. Although the nature of these waves was not investigated further, they may be associated with coordinated iodide ions in the Mo(III) complex.[21] In this regard it is noteworthy that the $[Mo(CNAr)_7]^{2+}$ cations do not exhibit these additional waves.[9]

In all cases studied the tungsten analogues of the molybdenum complexes exhibited the same trends in redox behavior, although the former are easier to oxidize by 0.09–0.12 V.

Reductions. Since adjacent alkyl isocyanide ligands in $[M(CNR)_6X]^+$ (M = Mo, W, generally Mo; $CNR = CN\text{-}t\text{-}C_4H_9$, $CN\text{-}c\text{-}C_6H_{11}$, generally $CN\text{-}t\text{-}C_4H_9$; X = Cl, Br, I, CN) may be coupled reductively to form complexes $[M(CNR)_4((CNHR)_2)X]^+$ containing a coordinated bis(alkylamino)acetylene ligand,[3-6] the reduction of some of the cations in CH_2Cl_2 and in THF/H_2O solutions were investigated. Studies carried out in the protic solvent THF/H_2O were based on the rationale that a source of protons was necessary at some point in the reductive coupling reactions since the product contains two more hydrogen atoms than the starting material. Experiments in THF/H_2O produced cyclic voltammograms identical with those obtained in CH_2Cl_2, however, and in no case was there any evidence for the formation of $[M(CNR)_4((CNHR)_2)X]^+$.

An irreversible reduction wave appears in the cyclic voltammograms of the molybdenum complexes near the low potential limit of the solvent (Table I). As shown in Figure 1 for the $[Mo(CN\text{-}t\text{-}C_4H_9)_6I]^+$ cation, the best studied example, two new species eventually appear on the reverse and subsequent sweeps at more positive potentials. The irreversible reduction wave at $E_{p,c} = -2.42$ V probably corresponds to the formation of $Mo(CN\text{-}t\text{-}C_4H_9)_6$. Reoxidation of this complex at $E_{1/2} \sim -1.16$ V and, eventually, also at -1.75 V would account for the new waves observed. Similar behavior occurs following the two-electron irreversible reduction of the $[Mo(CNPh)_7]^{2+}$, $[Mo(CNPh)_5(PEtPh_2)_2]^{2+}$, and $[Mo(CNPh)_5(dppe)]^{2+}$ cations.[9] The redox couple at -1.75 V is not always observed in the CV's of the other complexes studied. The cathodic peak positions of these complexes depend on scan speed, indicating that they are coupled to a chemical reaction. Further experiments, including controlled potential coulometry, would be required to establish firmly the identity of these species.

If one assumes that the irreversible reduction wave observed in the cations $[Mo(CNR)_6I]^+$ (R = alkyl, aryl) and $[Mo(CNR)_7]^{2+}$ (R = alkyl) is the Mo(II) → Mo(0) reduction, then the trend in the half-wave potentials (Table I) correlates well with the σ-donating ability of the ligands in the coordination sphere. This behavior is precisely that expected since the empty d orbitals (which accept the electrons) are σ antibonding with respect to ligands.

Correlations with the Reductive Coupling of Isocyanide Ligands. The irreversible electrochemical reductions observed for the $[M(CNR)_6X]^+$ cations offer no insights into the mechanism of the chemically induced reductive coupling to form $[M(CNR)_4((CNHR)_2)X]^+$ complexes. It is noteworthy, however, that those complexes that undergo reductive coupling (X = Cl, Br, I, CN)[6] are the ones having the least positive half-wave potentials (Table I). The complex $[Mo(CN\text{-}t\text{-}C_4H_9)_6(SnCl_3)]^+$ does not exhibit the reductive coupling at all. Instead, the molybdenum–trichlorostannate bond is cleaved and the $[Mo(CN\text{-}t\text{-}C_4H_9)_7]^{2+}$ cation is isolated in good yield.[23] Attempts to couple reductively the $[Mo(CN\text{-}t\text{-}C_4H_9)_7]^{2+}$ cation produced only $[Mo(CN\text{-}t\text{-}C_4H_9)_4((CNH\text{-}t\text{-}C_4H_9)_2)(CN)]^+$, in which dealkylation of one of the coordinated *tert*-butyl isocyanide ligands occurred.[5] Similarly, products containing coordinated bis(arylamino)acetylene have never been isolated in the reaction of $[Mo(CNAr)_6X]^+$ cations with zinc.[6] Thus it appears that complexes with half-wave potentials below ~0.3 V are efficiently reductively coupled whereas alternative chemical reduction processes occur for complexes having half-wave potentials above 0.5 V. The only apparent exception is $[Mo(CN\text{-}t\text{-}C_4H_9)_7]^{2+}$, but it is likely that the dealkylation product, $[Mo(CN\text{-}t\text{-}C_4H_9)_6(CN)]^+$, is the actual complex reductively coupled.

These results suggest that the more electron-rich, as measured by ease of oxidation, metal center favors the reductive coupling reaction. Electronic as well as steric[3,6] factors are therefore important determinants in whether the reductive coupling reaction will take place. Electrochemical studies should be useful in guiding us to other high-coordinate molecules where reductive coupling of adjacent ligands to form molecules with new carbon–carbon bonds can be achieved.

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Registry No. $[Mo(CN\text{-}t\text{-}C_4H_9)_6Cl]^+$, 80907-64-8; $[Mo(CN\text{-}t\text{-}C_4H_9)_6Br]^+$, 80907-65-9; $[Mo(CN\text{-}t\text{-}C_4H_9)_6I]^+$, 79516-87-3; $[Mo(CN\text{-}t\text{-}C_4H_9)_6CN]^+$, 78656-69-6; $[Mo(CN\text{-}t\text{-}C_4H_9)_6SnCl_3]^+$, 79466-97-0; $[Mo(CN\text{-}c\text{-}C_6H_{11})_6I]^+$, 80952-01-8; $[Mo(CNCH_3)_6I]^+$, 79466-84-5; $[Mo(CN\text{-}p\text{-}C_6H_4CH_3)_6I]^+$, 79466-92-5; $[Mo(CNC_6H_5)_6I]^+$, 79721-62-3; $[Mo(CN\text{-}p\text{-}C_6H_4Cl)_6I]^+$, 79466-90-3; $[Mo(CN\text{-}t\text{-}C_4H_9)_7]^{2+}$, 48078-09-7; $[Mo(CN\text{-}c\text{-}C_6H_{11})_7]^{2+}$, 72155-81-8; $[Mo(CNCH_3)_7]^{2+}$, 80952-02-9; $[Mo(CN\text{-}t\text{-}C_4H_9)_4\{(CNH\text{-}t\text{-}C_4H_9)_2\}I]^+$, 75878-72-7; $[Mo(CN\text{-}t\text{-}C_4H_9)_4\{(CNH\text{-}t\text{-}C_4H_9)_2\}CN]^+$, 78891-50-6; $[Mo(CN\text{-}c\text{-}C_6H_{11})_5(dppm)]^{2+}$, 74096-44-9; $[W(CN\text{-}t\text{-}C_4H_9)_6Cl]^+$, 80907-66-0; $[W(CN\text{-}t\text{-}C_4H_9)_6Br]^+$, 80907-67-1; $[W(CN\text{-}t\text{-}C_4H_9)_6I]^+$, 80907-68-2; $[W(CN\text{-}t\text{-}C_4H_9)_7]^{2+}$, 66687-56-7.

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