	Bond Di	stances		
Mo-C1	1.939(10)	Mo-Br1	2.673(1)	
Mo-C2	1.988 (10)	Mo-Br2	2.700(1)	
Mo-C3	1.982 (9)	C2-C3	1.273(11)	
Mo-P1	2.547(3)	C2-H1	1.099 (74)	
Mo-P2	2.538(3)			
Bond Angles				
C2-Mo-C3	37.40 (32)	C2-Mo-Br1	147.11 (29)	
C1-Mo-C2	71.24(40)	C3-Mo-Br1	175.41 (29)	
Br1-Mo-Br2	85.35 (4)	C2-C3-C4	134.00 (93)	
P1-Mo-P2	163.50 (10)	C3-C2-H1	139(4)	
C1-Mo-Br2	161.24(31)			

(RHNC=CNRH)X⁺¹³ complexes display a band between 500 and 570 nm assigned as a $d\pi$ - $d\pi$ transition ($\epsilon \sim 600$ M^{-1} cm⁻¹), and we have found that a low-energy visible transition with an extinction coefficient on the order of $10^2 \text{ M}^{-1} \text{ cm}^{-1}$ is characteristic of other formal 16-electron complexes including Mo(CO)₂L₂X₂,^{5,14} Mo(CO)₂- $(S_2CNR_2)_2$ ¹⁵ and $Mo(CO)(RC = CR)(S_2CNR_2)_2^{6a}$ that contain both π -acceptor and π -donor ligands in the coordination sphere.¹⁶ Addition of a seventh ligand invariably causes this band to disappear. Thus the variety of vivid blue, purple, and green colors typical of this class of compounds result from a window between high-energy absorptions and the visible $d\pi$ transition into the vacant LUMO that would be filled for related 18-electron complexes.

Both 1 and 2 exhibit reduction waves (1, -0.99 V, and 2, -1.18 V, vs. SSCE in 0.10 M n-Bu₄NClO₄, CH₃CN). No reversible oxidations were observed, but both 1 and 2 show the onset of oxidative processes near +0.87 V. The reduction of the relatively electron-rich butyne derivative 2 is 0.19 V more negative than for 1 in accord with a higher energy $d\pi$ LUMO for 2 and also comparable in magnitude to the blue shift of 0.17 V in the visible absorption in going from 1 to 2. In contrast the similarity of the oxidative processes of 1 and 2 are compatible with a $d\pi$ HOMO that is roughly independent of alkyne. The absorption and electrochemical measurements dovetail nicely here to reinforce the bonding description that has evolved for these systems. Furthermore both of these techniques offer convenient probes of the $d\pi$ interactions in other formal 16-electron complexes. We believe that experimental assessment of these bonding schemes is essential for fine tuning the reactivity of unsaturated intermediates.

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Registry No. 1, 83801-84-7; 2, 83801-85-8; Mo(CO)₂(PEt₃)₂Br₂, 25685-65-8; phenylacetylene, 536-74-3; 2-butyne, 503-17-3.

Supplementary Material Available: A table of positional and thermal parameters for 1 (2 pages). Ordering information is given on any current masthead page.

Reversible Intramolecular Isomerization of Mixed Carbonyl-Alkyl Isocyanide Complexes of Molybdenum: An Electrochemical Investigation

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Summary: Cyclic voltammetry and coulometry have been used to examine the isomerism of $Mo(CO)_2(CNC_6H_{11})_4$ and several complexes of the type Mo(CO)₂(CNR)₂(PR₃)₂ following their electrochemical oxidation. Products have been characterized by ESR and IR spectroscopy, and a possible mechanism for the isomerization is suggested.

The complexes Mo(CO)₂(CNR)₂(PR'₃)₂ and Mo(CO)₂- $(CNR)_4$ (R = CH₃, CMe₃, or C₆H₁₁ and PR'₃ = PEt₃, Pn-Pr₃, PMePh₂, or PEtPh₂), formed by the phosphineassisted elimination of allyl chloride from $(\eta^3-C_3H_5)$ - $MoCl(CO)_2(CNR)_2$, have recently been prepared in this laboratory.¹ On the basis of spectroscopic properties, these complexes were shown to have structures I and II. In subsequent studies directed at exploring the redox chemistry of these complexes, we have discovered that they undergo a rapid intramolecular isomerization to the alltrans species III and IV, respectively. Since these results have an important bearing upon studies carried out by other workers on related systems²⁻⁵ and are of relevance to problems relating to the electrochemical activation of organometallic molecules, we herein communicate preliminary details of these results.



Electrochemistry has been found to be an extremely sensitive technique for studying cis-trans isomerization in complexes of the type $Mo(CO)_4(PR_3)_2$,² $Mo(CO)_2(P-P)_2$, where P-P represents $Ph_2P(CH_2)_nPPh_2$ (n = 1, 2, or 3),³ and $Mo(CO)_4(carbene)_2$,⁴ following their oxidation to the related 17-electron monocations. On the basis of kinetic and thermodynamic measurements,²⁻⁶ these isomerizations are believed to occur via a trigonal-prismatic intermediate through a nondissociative rearrangement commonly referred to as the "Bailar twist".⁷ Although this twist mechanism can easily account for isomerization in the MX_2Y_4 systems, two separate twists are required to convert an $MX_2Y_2Z_2$ complex with one pair of trans ligands (as in I) to the all-trans isomer (III).

The electrochemical properties were investigated by cyclic voltammetry and controlled potential electrolysis.

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Table I.Voltammetric $E_{1/2}$ Values for CH_2Cl_2 Solutions
of Mixed Carbonyl-Alkyl Isocyanide Complexes of Molybdenum^a

complex	$E_{1/2}$ (I or II)	$E_{1/2}$ (III or IV)
$\begin{array}{l} Mo(CO)_{2}(CN-t-Bu)_{2}(PEt_{3})_{2} \\ Mo(CO)_{2}(CN-t-Bu)_{2}(P-n-Pr_{3})_{2} \\ Mo(CO)_{2}(CN-t-Bu)_{2}(PMePh_{2})_{2} \\ Mo(CO)_{2}(CNC_{6}H_{11})_{4} \\ [Mo(CO)_{2}(CN-t-Bu)_{2}(PMePh_{2})_{2}]^{+b} \end{array}$	-0.25 -0.26 -0.065 -0.065	-0.50 -0.51 -0.31 -0.295 -0.31

^a In volts vs. SCE at a Pt bead working electrode and 0.2 M tetra-n-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. ^b Generated chemically by using $C_7 H_7^+ PF_6^-$ as the oxidant.

CV measurements were made on degassed dichloromethane, acetonitrile, and acetone solutions containing 0.2 M tetra-n-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte at a platinum bead electrode.⁸ The redox behavior of the complexes was found to be similar in all three solvents. Voltammetric half-wave potentials (vs. SCE in CH_2Cl_2 at 22 ± 2 °C and uncorrected for junction potentials) are presented in Table I.

Figure 1a shows a CV typical of those exhibited by these complexes; a scan to positive potentials starting from 0 V reveals an irreversible oxidation at $E_{p,a} \sim +1.3 \text{ V}^9$ and two couples at negative potentials (i.e., $E_{1/2}$ values of -0.26 and -0.51 V in the case of Mo(CO)₂(CN-t-Bu)₂(P-n-Pr₃)₂) corresponding to an oxidation and a reduction, respectively. If the scan is started at a potential between these two couples and carried out in a negative direction (Figure 1b), it is observed that the species responsible for the more negative couple is not present and in fact is produced only after the first oxidation has occurred.

Bulk electrolysis carried out at potentials more positive than those corresponding to the first couple (i.e., $E_{1/2}$ (I or II) in Table I) converted the pale yellow solutions to bright orange and produced voltammograms (Figure 1c) with just one couple $(E_{1/2}(\text{III or IV}) \text{ in Table I})$. The oxidation was shown by coulometry to be a one-electron process $(n = 1 \pm 0.1)$ and the couple $E_{1/2}$ (III or IV) was characterized by values for $E_{p,a} - E_{p,c}$ of 70–90 mV and $i_{p,a}/i_{p,c}$ ratios that were close to unity for sweep rates ranging from 50 to 500 mV s⁻¹. These orange solutions could be electrochemically reduced back to the parent species (exhibiting CV's identical with Figure 1a) at potentials more negative than those listed as $E_{1/2}$ (III or IV) in Table I with little apparent decomposition as measured by peak currents.

The potentials listed in Table I for the oxidation of the $M_0(CO)_2(CNR)_2(PR_3)_2$ complexes and $M_0(CO)_2(CNC_6 H_{11}$)₄ are, as expected, intermediate between those for the oxidation of neutral carbonyl complexes $Mo(CO)_4(PR_3)_2$, $Mo(CO)_4(P-P)$, and $Mo(CO)_4(carbene)_2$,²⁻⁴ on the one hand, and the much more readily oxidizable isocyanide species Mo(CNR)₂(Ph₂PCH₂CH₂PPh₂)₂,¹⁰ on the other. This trend follows from the general order of σ -donor abilities $CO < CNR < PR_3$. In any event, the $E_{1/2}$ values in Table I imply that a chemical oxidation is feasible, and such a process has been investigated by using tropylium



Figure 1. Cyclic voltammograms in 0.2 M TBAH-dichloromethane of $Mo(CO)_2(CN-t-Bu)_2(P-n-Pr_3)_2$: (a) positive scan starting at 0.0 V; (b) negative scan starting at -0.4 V (dotted line shows the second scan); (c) after controlled potential electrolysis at +0.1 V.

hexafluorophosphate as the oxidant.¹¹ Upon its addition to yellow CH₂Cl₂ solutions of the complex Mo(CO)₂(CN $t-Bu)_2(PMe_2Ph)_2$ an orange color was immediately generated. The resulting solutions gave X-band ESR spectra identical with those of the electrochemically generated cations (vide infra). Thus far the product has only been obtained as an oil that quickly decomposes, but its IR spectrum confirms that there has been a structure change. Whereas the neutral complex has two $\nu(CO)$ and two $\nu(CN)$ bands,¹ the cation has only one of each,¹² an observation that is in accord with an all-trans geometry.

The X-band ESR spectra of frozen CH₂Cl₂ solutions of the electrochemical and chemical oxidation products reveal species with approximate tetragonal symmetry possessing a single unpaired electron with $g_{\perp} > g_{\parallel}$.¹³ In the case of the $[Mo(CO)_2(CNC_6H_{11})_4]^+$ cation, this is consistent with the proposed trans structure (Figure 2a). Hyperfine splitting due to ⁹⁵Mo and ⁹⁷Mo (combined abundance 25.15%, $I = \frac{5}{2}$ accounts for the apparent asymmetry in

⁽⁸⁾ Full details of our electrochemical procedure are described else-where; see: Zietlow, T. C.; Klendworth, D. D.; Nimry, T.; Salmon, D. J.; Walton, R. A. *Inorg. Chem.* 1981, 20, 947. (9) This oxidation may correspond to the process $[Mo(CO)_2(CNR)_2-(PR_3)_2]^2 \rightarrow [Mo(CO)_2(CNR)_2(PR_3)_2]^{2+} + e$. The lack of electrochemical reversibility could follow from the structure changes that are expected to be associated with the formation of such a 16-electron species; see: Kubacek, P.; Hoffmann, R. J. Am. Chem. Soc. 1981, 103, 4320.

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⁽¹¹⁾ Solutions of $C_7H_7^+PF_6^-$ in 0.2 M TBAH-CH₂Cl₂ are characterized by a reduction at $E_{p,c} = -0.13$ V vs. SCE at $\nu = 200$ mV/s; in 0.1 M TBAH-CH₃CN the corresponding $E_{p,c}$ value is -0.19 V. (12) The IR spectrum of Mo(CO)₂(CN-t-Bu)₂(PMePh₂)₂ recorded as a Nujol mull, for example, has ν (CO) at 1855 and 1810 cm⁻¹ and ν (CN) at 2125 and 2100 cm⁻¹ (see ref 1), while for [Mo(CO)₂(CN-t-Bu)₂-(PMePh₂)₂]PF₆, ν (CO) = 1880 (s) cm⁻¹ and ν (CN) = 2130 (s) cm⁻¹ for a Nujol mull and ν (CO) = 1885 (s) cm⁻¹ and ν (CN) = 2125 cm⁻¹ for a CH₂Cl₂ solution solution.

⁽¹³⁾ Appropriate g values are as follows: $[Mo(CO)_2(CNC_6H_{11})_4]^+$, $g_{\perp} = 2.121$, $g_{\parallel} = 1.984$; $[Mo(CO)_2(CN-t-Bu)_2(PEt_3)_2]^+$, $g_{\perp} = 2.079$, $g_{\parallel} = 1.981$; $[Mo(CO)_2(CN-t-Bu)_2(PMe_2Ph)_2]^+$, $g_{\perp} = 2.076$, $g_{\parallel} = 1.976$.



Figure 2. X-band ESR spectra of frozen CH_2Cl_2 solutions at -160 °C of (a) $[Mo(CO)_2(CNC_6H_{11})_4]^+$ and (b) $[Mo(CO)_2(CN-t-Bu)_2-(PMePh_2)_2]^+$.

Scheme I



the g_{\perp} signal. The hyperfine lines in the g_{\parallel} region are well resolved with A = 50 G. Figure 2b shows an ESR spectrum that is typical of the $[Mo(CO)_2(CNR)_2(PR_3)_2]^+$ cations. For the phosphine complexes, the "perpendicular" signal is broader and also more structured, but only one g value is clearly resolved. The 1:2:1 triplet in g_{\parallel} results from the interaction of the unpaired electron with two equivalent ³¹P atoms (I = 1/2).

On the basis of the ESR evidence for equivalent phosphines and IR data which suggest that the two carbonyl ligands are trans as are also the two isocyanides, the structure of $[Mo(CO)_2(CNR)_2(PR_3)_2]^+$ is concluded to be all-trans. The electrochemical and spectroscopic data for $[Mo(CO)_2(CNR)_2(PR_3)_2]^{0,1+}$ are in accord with Scheme I.

Oxidation of isomer I is followed by rapid isomerization to the all-trans cation (possessing structure III) that in turn isomerizes back to I upon its electrochemical reduction to



Figure 3. Schematic representation of two sequential twists that could convert I to III without bond breaking: C = CO; C' = CNR, and $P = PR_3$.

the neutral 18-electron species. From our studies it is clear that the order of rates is $k_1 > k_2$.¹⁴ The similarity of the electrochemical behavior in various solvents as well as the reversibility established by the coulometric experiments support the notion that the structural rearrangement is nondissociative. Figure 3 illustrates a possible mechanism for the intramolecular conversion of I to III.

Our work provides the first examples of the electrochemically induced isomerization of complexes of the type $MX_2Y_2Z_2$ that contain a $M(CO)_2$ unit, where M represents a group 6 metal. We hope to expand the scope of these investigations to include a wider range of isocyanide and phosphine ligands, in particular focusing upon the constraints imposed by chelating phosphines of the type $Ph_2P(CH_2)_nPPh_2$, since the latter will ensure that the isomerization will be different from that which has been studied so far (I \rightleftharpoons III).

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Registry No. $Mo(CO)_2(CN-t-Bu)_2(PEt_3)_2$, 80215-95-8; $Mo(CO)_2(CN-t-Bu)_2(P-n-Pr_3)_2$, 80215-96-9; $Mo(CO)_2(CN-t-Bu)_2(PMePh_2)_2$, 80215-97-0; $Mo(CO)_2(CNC_6H_{11})_4$, 80215-99-2; $[Mo(CO)_2(CN-t-Bu)_2(PMePh_2)_2]^+$, 83897-56-7; $C_7H_7^+PF_6^-$, 29663-54-5; $[Mo(CO)_2(CNC_6H_{11})_4]^+$, 83897-57-8; $[Mo(CO)_2(CN-t-Bu)_2(PMePh_2)_2]PF_6$, 83897-58-9; $[Mo(CO)_2(CN-t-Bu)_2(PEt_3)_2]^+$, 83897-59-0.

(14) Note that for the so-called cross redox reaction

$$I^+ + III \xrightarrow{\kappa_3}_{k=a} I + III^+$$

the order $k_3 > k_{-3}$ holds; for the appropriate theory see: Feldberg, S. W.; Jeftic, L. J. Phys. Chem. 1972, 76, 2439.

New Stable Dianions from the Electrochemical Reduction of Conjugated Bis(phenyltricarbonylchromium) Groups

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Summary: Bis(tricarbonylchromium) complexes of arene compounds with two conjugated phenyl rings reduce electrochemically in a two-electron fashion. The process is chemically reversible as shown by cyclic voltammetry and coulometry.

(Arene)tricarbonylchromium complexes exhibit redox properties that vary as a function of the arene ligand. When benzene or substituted benzene rings are present, reduction is a two-electron $\operatorname{process}^{1-3}$ yielding a highly