that PE spectra indicate that any extra electron would be very weakly bound. The ionization energies of the neutral species are only about 5.5 eV, and there is a substantial electron repulsion term disfavoring electron addition. In contrast the first PE band of V(CO)$_6$ appears at 7.5 eV,[26] and the electrons are probably more delocalized. Additionally, electroneutrality considerations suggest that it will be much easier to form the anions with a better π acceptor such as CO.

Acknowledgment. We are grateful to Dr. J. B. Raynor for providing the ESR simulation program and to Prof. M. C. R. Symons for helpful discussions. We also acknowledge Balliol College, Oxford, for support (F.G.N.C.) and SERC for equipment.

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Note Added in Proof. It has recently proved possible to isolate the 17-electron complexes [Ti(η-C$_6$H$_6$)$_2$]$^-$ and [Ti(η-C$_6$H$_5$Me)$_2$]$^-$ as their potassium salts by reduction of the Ti(η-arene)$_2$ with potassium or KH. Their ESR spectra show proton hyperfine coupling with A^H = 4.6 G for [Ti(η-C$_6$H$_6$)$_2$]$^-$ and A^H = 4.5 G for [Ti(η-C$_6$H$_5$Me)$_2$]$^-$. These data indicate substantial increases in delocalization across the isoelectronic series [Cr(η-C$_6$H$_6$)$_2$]$^+$ (A^H = 3.5 G), V(η-C$_6$H$_6$)$_2$ (A^H = 4.1 G), and [Ti(C$_6$H$_6$)$_2$]$^-$ (A^H = 4.6 G) (Berry, A.; Green, M. L. H.; Perutz, R. N., to be submitted for publication).

Registry No. V(η-C$_6$H$_6$)$_2$, 12129-72-5; V(η-C$_6$H$_5$Me)$_2$, 12131-27-0; Nb(η-C$_6$H$_6$)$_2$, 68088-94-8; Nb(η-C$_6$D$_6$)$_2$, 86119-97-3; Nb(η-C$_6$H$_5$Me)$_2$, 68088-95-9; Nb(η-C$_6$H$_3$Me$_3$)$_2$, 68088-96-0; Ta(η-C$_6$H$_6$)$_2$, 80346-26-5; W(η-C$_6$H$_6$)$_2$, 12089-23-5; W(η-C$_6$H$_5$Me)$_2$, 52346-44-8; W(η-C$_6$H$_3$Me$_3$)$_2$, 67087-69-8; Cr(η^5-C$_5$H$_5$)(η-C$_6$H$_6$), 12093-16-2; Mo(η-C$_5$H$_5$)(η-C$_6$H$_6$), 12153-25-2; Ti(η-C$_6$H$_6$)$_2$, 52462-43-8; Ti(η-C$_6$H$_5$Me)$_2$, 55527-82-7; V(η-C$_6$H$_3$Me$_3$)$_2$$^+$, 86119-98-4.

(η^3-Allyl)dicarbonylmolybdenum(II) Complexes: Studies of Their Redox Chemistry and Solution Equilibria by Electrochemistry

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Electrochemical oxidation of the complexes (η^3-RC$_3$H$_4$)Mo(CO)$_2$(L–L)X (where R = H or CH$_3$, L–L = 2,2'-bipyridyl when X = Cl or O$_2$CCF$_3$ and L–L = Ph$_2$PCH$_2$PPh$_2$, Ph$_2$PCH$_2$CH$_2$PPh$_2$, or Ph$_2$AsCH$_2$CH$_2$AsPh$_2$ when X = Cl) in dichloromethane–0.2 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) solutions generates the ESR active 17-electron cations [(η^3-RC$_3$H$_4$)Mo(CO)$_2$(L–L)X]$^+$. Differences between the spectra of the complexes containing 2,2'-bipyridyl and the phosphine/arsine ligands can be attributed to structural differences that exist both between the neutral and the cationic species containing the N vs. P/As donors. The ionization of (η^3-RC$_3$H$_4$)Mo(CO)$_2$(NCCH$_3$)$_2$Cl in dichloromethane–0.2 M TBAH, viz., 3(η^3-RC$_3$H$_4$)Mo(CO)$_2$(NCCH$_3$)$_2$Cl $\rightleftharpoons$ [(η^3-RC$_3$H$_4$)Mo(CO)$_2$(NCCH$_3$)$_3$]$^+$ + [(η^3-RC$_3$H$_4$)$_2$Mo$_2$(CO)$_4$Cl$_3$]$^-$ + 3CH$_3$CN, can be followed by cyclic voltammetry through the characteristic electrochemical properties of the cation and anion. Whereas ionization in this solvent system is essentially complete, little ionization occurs in acetonitrile–0.1 M TBAH solutions.

Introduction

Reactions of the acetonitrile and alkyl isocyanide complexes (η^3-C$_3$H$_5$)Mo(CO)$_2$(NCCH$_3$)$_2$Cl and (η^3-C$_3$H$_5$)Mo(CO)$_2$(CNR)$_2$Cl with tertiary phosphines provides a route, through the reductive elimination of allyl chloride, to molybdenum(0) complexes of the types Mo(CO)$_2$(CNR)$_4$, Mo(CO)$_2$(CNR)$_2$(PR$_3$)$_2$, and Mo(CO)$_2$(PR$_3$)$_4$.[2–4] Our recent study[5] of the reversible intramolecular isomerization of Mo(CO)$_2$(CNR)$_4$ and Mo(CO)$_2$(CNR)$_2$(PR$_3$)$_2$ following their oxidation to the corresponding 17-electron cations had led us to explore the redox properties of the synthetic precursor complexes (η^3-C$_3$H$_5$)Mo(CO)$_2$(L)$_2$Cl and (η^3-C$_3$H$_5$)Mo(CO)$_2$(L–L)Cl, where L is a monodentate donor

and L–L a chelating bidentate. In the present report, we describe the electrochemical properties of this class of complexes which not only provide insight into the electronic structure of these species but, furthermore, are of relevance to the solution equilibria which may exist in nonaqueous solvents.[6,7]

Experimental Section

Starting Materials. The (η^3-allyl)dicarbonylmolybdenum(II) complexes and closely allied derivatives were prepared by standard literature procedures[2,6,8–11] as were the two tungsten derivatives (η^3-C$_3$H$_5$)W(CO)$_2$(NCCH$_3$)$_2$Cl and (η^3-C$_3$H$_5$)W(CO)$_2$(dppe)Cl

(1) (a) University of Bath. (b) Purdue University.
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Table I. $E_{1/2}$ Values for Molybdenum(II) Complexes
of the Type (η^3-RC$_3$H$_4$)Mo(CO)$_2$(L–L)X in
Dichloromethane[a]

complex[b]	$E_{1/2}$(ox)[c]	$\Delta E_p{}^d$
(η^3-C$_3$H$_5$)Mo(CO)$_2$(bpy)Cl	+0.59	70
(η^3-2-MeC$_3$H$_4$)Mo(CO)$_2$(bpy)Cl	+0.51	70
(η^3-C$_3$H$_5$)Mo(CO)$_2$(bpy)(O$_2$CCF$_3$)	+0.65	70
(η^3-2-MeC$_3$H$_4$)Mo(CO)$_2$(bpy)(O$_2$CCF$_3$)	+0.63	75
(η^3-C$_3$H$_5$)Mo(CO)$_2$(dppm)Cl	+0.68	120
(η^3-C$_3$H$_5$)Mo(CO)$_2$(dppe)Cl	+0.68	80
(η^3-2-MeC$_3$H$_4$)Mo(CO)$_2$(dppe)Cl	+0.59	80
(η^3-C$_3$H$_5$)Mo(CO)$_2$(dpae)Cl	+0.71	90
(η^3-C$_3$H$_5$)W(CO)$_2$(dppe)Cl	+0.65	70

[a] With 0.2 M TBAH as supporting electrolyte. [b] Ligand abbreviations are as follows: bpy = 2,2'-bipyridyl, dppm = bis(diphenylphosphino)methane, dppe = 1,2-bis-(diphenylphosphino)ethane, dpae = 1,2-bis(diphenyl-arsino)ethane. [c] Volts vs. SCE with a Pt-bead working electrode. [d] In mV at a sweep rate (ν) of 200 mV/s.

(dppe = 1,2-bis(diphenylphosphino)ethane).[10,11] Tetra-n-butyl-ammonium hexafluorophosphate (TBAH) was obtained by re-acting tetra-n-butylammonium iodide with KPF$_6$ in hot water. The product was recrystallized from aqueous ethanol and dried in vacuo.

Physical Measurements. Electrochemical measurements were made on dichloromethane and acetonitrile solutions con-taining tetra-n-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. $E_{1/2}$ values (taken as $(E_{p,a} + E_{p,c})/2$) were referenced to the saturated potassium chloride calomel electrode (SCE) at 22 ± 2 °C and were uncorrected for junction potentials. Cyclic voltammetry experiments were performed by using a BioAnalytical Systems Inc. Model CV-1A instrument in conjunction with a Hewlett-Packard Model 7035 x-y recorder. Potential control for coulometric experiments was maintained with a potentiostat purchased from BioAnalytical Systems Inc. Values of n, where n is the total number of equivalents of electrons transferred in exhaustive electrolysis at constant potentials, were calculated after the total area under current vs. time curves was measured for the complete reaction. The reactions were judged to be complete when the current had fallen below 1% of the initial value. All voltammetric measurements were made at a platinum bead electrode in solutions deaerated with a stream of dry ni-trogen. The platinum electrode was cleaned with the chromic acid and aqua regia procedures described by Adams.[12]

X-Band ESR spectra were recorded at a temperature of –160 °C with a Varian E-109 spectrometer.

Results and Discussion

Voltammetric half-wave potentials vs. SCE for di-chloromethane–0.2 M tetra-n-butylammonium hexa-fluorophosphate (TBAH) solutions of a selection of 18-electron molybdenum(II) complexes of the type (η^3-C$_3$H$_5$)Mo(CO)$_2$(L–L)Cl, where L–L represents a bidentate chelating nitrogen or phosphorus donor, and several closely related derivatives are given in Table I. These data were recorded for solutions that were ca. 10^{-3} M in complex and in all instances, the complexes exhibit a single one-electron oxidation (η^3-RC$_3$H$_4$)Mo(CO)$_2$(L–L)X → (η^3-RC$_3$H$_4$)Mo-(CO)$_2$(L–L)X$^+$ + e$^-$ (R = H or CH$_3$; X = Cl or O$_2$CCF$_3$). Representative cyclic voltammograms are shown in Figure 1.

The potential separation, ΔE_p, between the anodic and cathodic peaks was in all cases greater than 60 mV and varied with sweep rate; at ν = 200 mV/s, ΔE_p was in the range 70–90 mV. For sweep rates of between 50 and 500 mV/s, the ratio of peak currents $i_{p,c}/i_{p,a}$ was equal to unity, and the ratio $i_p/\nu^{1/2}$ was constant in accord with diffusion control. These electrochemical properties can be viewed
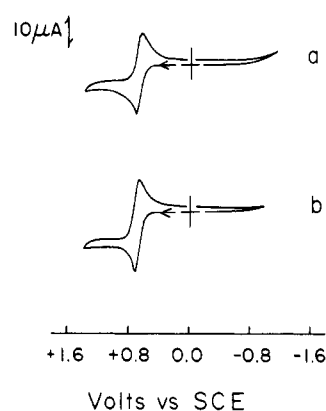

Figure 1. Cyclic voltammograms in CH$_2$Cl$_2$–0.2 M TBAH of (a) (η^3-C$_3$H$_5$)Mo(CO)$_2$(bpy)(O$_2$CCF$_3$) and (b) (η^3-C$_3$H$_5$)Mo(CO)$_2$-(dppm)Cl.

Table II. X-Band ESR Spectra of the Electrochemically
Generated Cations of the Type
[(η^3-RC$_3$H$_4$)Mo(CO)$_2$(L–L)X]$^+$

complex	g_1	g_2	g_3
(η^3-C$_3$H$_5$)Mo(CO)$_2$(bpy)Cl	2.041	2.003	1.985
(η^3-2-MeC$_3$H$_4$)Mo(CO)$_2$(bpy)Cl	2.038	2.006	1.983
(η^3-C$_3$H$_5$)Mo(CO)$_2$(bpy)(O$_2$CCF$_3$)	2.034	2.002	1.983
(η^3-2-MeC$_3$H$_4$)Mo(CO)$_2$(bpy)(O$_2$CCF$_3$)	2.031	2.000	1.982
(η^3-C$_3$H$_5$)Mo(CO)$_2$(dppm)Cl[a]	2.204	1.991	
(η^3-2-MeC$_3$H$_4$)Mo(CO)$_2$(dppe)Cl[a]	2.200	1.988	
(η^3-C$_3$H$_5$)Mo(CO)$_2$(dpae)Cl[a]	2.198	1.995	

[a] The ESR spectrum of this complex is pseudoaxial, i.e., $g_2 = g_3$.

as being in accord with quasi-reversible electron-transfer processes.[13,14] However, since we find[15] that the known reversible couples ferrocene/ferricinium and Ru-(bpy)$_3{}^{2+}$/Ru(bpy)$_3{}^{3+}$ exhibit similar electrochemical be-havior to that described above under these same experi-mental conditions, it might be concluded that these elec-tron-transfer processes approach electrochemical reversi-bility.

The 17-electron monocations have reasonable stability as demonstrated by controlled-potential electrolysis of solutions of the complexes that are listed in Table I. Electrochemical oxidations at potentials ~+0.2 V more positive than the $E_{1/2}$ values given in Table I led to marked color changes (from red or purple to orange in the case of the bipyridyl complexes and yellow to orange in the case of the complexes with phosphorus or arsenic donors) and the generation of paramagnetic species as evidenced by ESR spectroscopy (vide infra). The cyclic voltammograms of the resulting solutions were identical with those of the unoxidized complexes with the exception that the couple now corresponds to a reduction. This confirms that the structure remains intact following the one-electron (by coulometry) oxidation. The rereduction of these oxidized solutions at a potential of ~+0.4 V regenerates the parent neutral 18-electron complexes with very little evidence (from cyclic voltammetry) for sample decomposition.

The X-band ESR spectra of CH$_2$Cl$_2$–0.2 M TBAH so-lutions of the electrochemically generated cations (recorded at –160 °C) are in all instances well-defined and show a marked dependence upon whether the complexes contain bipyridyl or phosphine/arsine ligands. The appropriate

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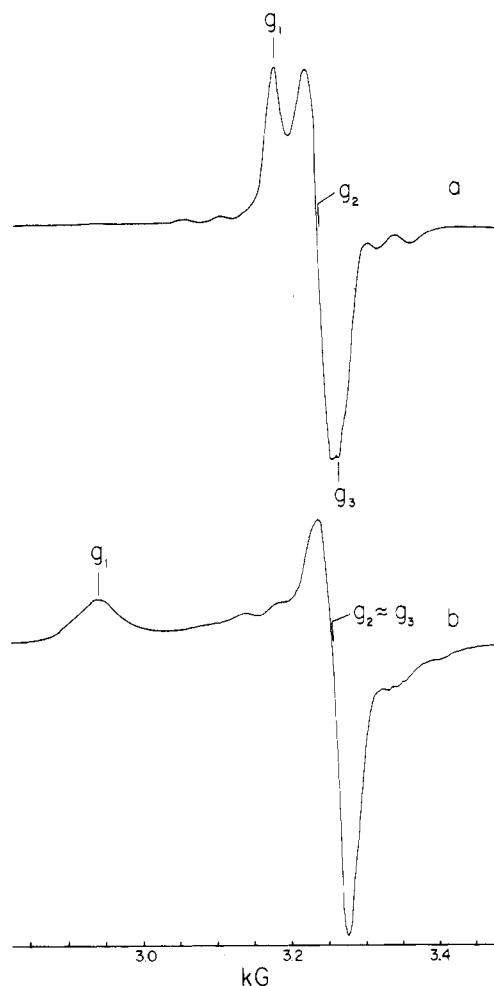(15) Zietlow, T. C.; Klendworth, D. D.; Nimry, T.; Salmon, D. J.; Walton, R. A. *Inorg. Chem.* **1981**, *20*, 947.

Figure 2. X-Band ESR spectra of frozen CH_2Cl_2–0.2 M TBAH solutions at –160 °C of (a) $[(\eta^3\text{-}C_3H_5)Mo(CO)_2(bpy)Cl]^+$ and (b) $[(\eta^3\text{-}C_3H_5)Mo(CO)_2(dppm)Cl]^+$.

g values are listed in Table II, and representative spectra are shown in Figure 2. The bipyridyl-containing 17-electron cations possess very similar ESR spectra which in turn differ from the spectra of the cations that contain the dppm, dppe, and dpae ligands. The two groups of neutral *chloride-containing* 18-electron molecules are known to possess different structures—the bipyridyl complexes have structure A, while the dppm, dppe, and dpae
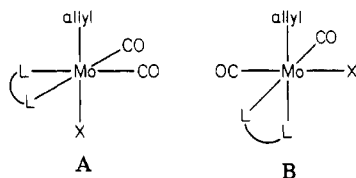

complexes are of structure type B[11]—and it is apparent that this structural difference is preserved upon oxidation in view of the reversible nature of the electrochemistry.[16]

(16) A referee has noted that a very fast rearrangement following these one-electron oxidations could lead to a reversible-looking wave if the two isomeric forms possessed very nearly the same redox potential. While this is true, it has been our experience and that of others (see ref 5 and other references cited therein) that this is not the case for other molybdenum carbonyl complexes for which a rapid, reversible intramolecular isomerization follows oxidation to formally 17-electron species. Accordingly, we feel that the electrochemical evidence strongly favors our interpretation since the alternative would require that, for each of the complexes listed in Table I, the $E_{1/2}$ values of the two isomeric forms would need to be the same. This would appear to be unlikely.

Volts vs SCE

Figure 3. Cyclic voltammograms of (a) $(\eta^3\text{-}C_3H_5)Mo(CO)_2\text{-}(NCCH_3)_2Cl$ in CH_2Cl_2–0.2 M TBAH, (b) $(\eta^3\text{-}C_3H_5)Mo(CO)_2\text{-}(NCCH_3)_2Cl$ in CH_3CN–0.1 M TBAH, (c) $Ph_4P[(\eta^3\text{-}C_3H_5)_2Mo_2\text{-}(CO)_4Cl_3]$ in CH_2Cl_2–0.2 M TBAH, and (d) $[(\eta^3\text{-}C_3H_5)Mo(CO)_2\text{-}(NCCH_3)_3]BF_4$ in CH_2Cl_2–0.2 M TBAH.

In the case of the two trifluoroacetate complexes $(\eta^3\text{-}RC_3H_4)Mo(CO)_2(bpy)(O_2CCF_3)$, where R = H or CH_3, their electrochemical and ESR spectral properties (Tables I and II) conform to those of the other bipyridyl-containing complexes in spite of the fact that ^{1}H NMR measurements[8] on solutions of the $\eta^3\text{-}C_3H_5$ derivative show the presence of *both* isomer A and B. Only isomer A exists in comparable solutions of the $\eta^3\text{-}2\text{-}MeC_3H_4$ complex. However, additional ^{1}H NMR spectral studies have shown[17] that the relative amount of isomer B is diminished by the addition of an excess of Bu_4NPF_6 to CD_2Cl_2 solutions of $(\eta^3\text{-}C_3H_5)Mo(CO)_2(bpy)(O_2CCF_3)$. Furthermore, the amount of B decreased relative to that of A as the concentration of complex was decreased. At the lower limits of concentration (a solution 2×10^{-2} M in complex which was also 0.2 M in supporting electrolyte) the ratio of isomer A to isomer B approached 3:1. It is apparent from the present CV and ESR spectral studies that under conditions of even lower concentration of complex ($\sim 10^{-3}$ M) but the same high concentration of supporting electrolyte only a single isomeric form is in evidence (i.e., isomer A).

In the case of the complexes $(\eta^3\text{-}RC_3H_4)Mo(CO)_2L_2Cl$, where L represents a monodentate donor, we have focused our attention upon those cases where L is *tert*-butyl isocyanide, acetonitrile, or benzonitrile. Dichloromethane solutions of $(\eta^3\text{-}C_3H_5)Mo(CO)_2(CN\text{-}t\text{-}Bu)_2Cl$ (0.2 M in TBAH) possess an oxidation at $E_{p,a} = +0.78$ V vs. SCE and a coupled reduction wave at +0.50 V. However, unlike the situation with the complexes listed in Table I, this process is neither electrochemically reversible ($\Delta E_p = 280$ mV and $i_{p,c}/i_{p,a} < 1$) nor chemically reversible. Bulk electrolysis at +1.0 V led to decomposition of the complex. Accordingly, this system was not investigated further.

The electrochemical properties of the acetonitrile and benzonitrile complexes $(\eta^3\text{-}RC_3H_4)Mo(CO)_2(NCR)_2Cl$ were strikingly different from those of any of the other complexes discussed so far. Solutions of $(\eta^3\text{-}C_3H_5)Mo(CO)_2\text{-}(NCCH_3)_2Cl$ in CH_2Cl_2–0.2 M TBAH possessed cyclic voltammograms (Figure 3a) that exhibited three couples in the potential range +1.6 to –1.6 V, each of which corresponded to a one-electron oxidation. This behavior can be contrasted to the related electrochemical properties of a solution of this complex in CH_3CN–0.1 M TBAH (Figure

(17) Brisdon, B. J., unpublished results.

3b), where the single couple at $E_{1/2}$ = +0.62 V (ΔE_p = 90 mV at ν = 200 mV/s and $i_{p,c}/i_{p,a}$ = 1) is typical of that which characterizes other *undissociated* mononuclear derivatives of the type (η^3-C_3H_5)Mo(CO)$_2$(L)$_2$Cl (see Table I). The explanation for the much more complex behavior of (η^3-C_3H_5)Mo(CO)$_2$(NCCH$_3$)$_2$Cl in dichloromethane lies in the existence of the equilibrium 3(η^3-C_3H_5)Mo(CO)$_2$-(NCCH$_3$)$_2$Cl $\rightleftharpoons$ [(η^3-C_3H_5)Mo(CO)$_2$(NCCH$_3$)$_3$]$^+$ + [(η^3-C_3H_5)$_2$Mo$_2$(CO)$_4$Cl$_3$]$^-$ + 3CH$_3$CN, which previous ^{1}H NMR and IR spectral studies have shown[6] can occur in certain solvents (including CHCl$_3$ and CH$_3$CN). That this is also the case in dichloromethane is demonstrated in the present work, where the couples at $E_{1/2}$ = +1.10, +0.96, and +0.58V (Figure 3a) can be attributed to [(η^3-C_3H_5)Mo(CO)$_2$-(NCCH$_3$)$_3$]$^+$ and [(η^3-C_3H_5)$_2$Mo$_2$(CO)$_4$Cl$_3$]$^-$, through comparison with the cyclic voltammograms of CH$_2$Cl$_2$–0.2 M TBAH solutions of authentic salts of these ions (see Figure 3c,d). Note that the $E_{1/2}$ value of +0.62 V (Figure 3b) for an acetonitrile solution of unionized (η^3-C_3H_5)Mo(CO)$_2$-(NCCH$_3$)$_2$Cl is almost coincident with one of the couples of [(η^3-C_3H_5)$_2$Mo$_2$(CO)$_4$Cl$_3$]$^-$ (i.e., that at $E_{1/2}$ = +0.58 V, Figure 3c). Although an $E_{1/2}$ value of approximately +0.6 V would also be expected for unionized (η^3-C_3H_5)Mo-(CO)$_2$(NCCH$_3$)$_2$Cl in CH$_2$Cl$_2$–0.2 M TBAH, the cyclic voltammogram shown in Figure 3a is, on the basis of peak currents, in accord with almost complete ionization to [(η^3-C_3H_5)Mo(CO)$_2$(NCCH$_3$)$_3$]$^+$[(η^3-C_3H_5)$_2$Mo$_2$(CO)$_4$Cl$_3$]$^-$; i.e., the currents associated with the three couples are the same. For the cation and anion, the electron-transfer processes are quasi-reversible as seen by $i_{p,c}/i_{p,a}$ ratios of unity and ΔE_p values of 70 mV (for both couples of the anion) and 130 mV (for the cation). Thus, under our experimental conditions, ionization is essentially complete in CH$_2$Cl$_2$–0.2 M TBAH but negligible in CH$_3$CN–0.1 M TBAH.[18] Furthermore, it is clear that cyclic voltammetry constitutes a valuable alternative means of monitoring this and related equilibria (vide infra). Solutions of (η^3-C_3H_5)Mo(CO)$_2$(NCCH$_3$)$_2$Cl in CH$_3$CN–0.1 M TBAH changed from yellow to pale yellow upon electrolysis at +0.75 V. The cyclic voltammogram of the resulting solution confirmed that the structural integrity of the complex had been preserved although the formation of a *small* amount of [(η^3-C_3H_5)Mo(CO)$_2$(NCCH$_3$)$_3$]$^+$ was signaled by the appearance of a couple at +1.10 V.

The X-band ESR spectra (recorded at –160 °C) of oxidized solutions (+0.75 V) of (η^3-C_3H_5)Mo(CO)$_2$-(NCCH$_3$)$_2$Cl (Figure 4a) and Ph$_4$P[(η^3-C_3H_5)$_2$Mo$_2$-(CO)$_4$Cl$_3$][19] in CH$_2$Cl$_2$–0.2 M TBAH are identical, thereby supporting the notion that complete ionization has occurred. As we have mentioned above, (η^3-C_3H_5)Mo-(CO)$_2$(NCCH$_3$)$_2$Cl is essentially undissociated in CH$_3$CN–0.1 M TBAH based upon cyclic voltammetry measurements. In accord with this, we find that the ESR spectrum of this solution (following oxidation at +0.75V) is, as shown in Figure 4b, different from that of the solution of (η^3-C_3H_5)Mo(CO)$_2$(NCCH$_3$)$_2$Cl in CH$_2$Cl$_2$–0.2 M TBAH, both with regard to g values and the appearance of hyperfine structure due to interaction with the coordinated nitrogen (I = 1) of the acetonitrile molecules. Related hyperfine structure is also seen in the ESR of the 2,2'-bipyridyl
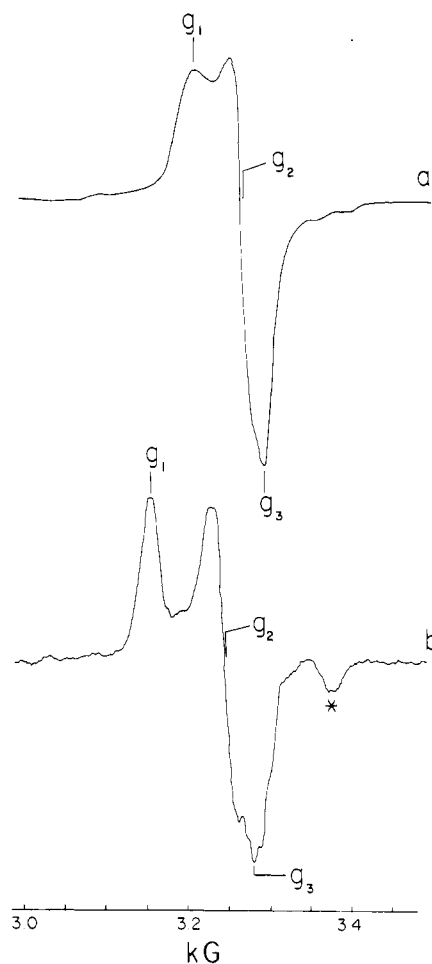

Figure 4. X-Band ESR spectra of oxidized solutions (+0.75 V) of (η^3-C_3H_5)Mo(CO)$_2$(NCCH$_3$)$_2$Cl: (a) in frozen CH$_2$Cl$_2$–0.2 M TBAH at –160 °C (g_1 = 2.031, g_2 = 1.994, g_3 = 1.976); (b) in frozen CH$_3$CN–0.1 M TBAH at –160 °C (g_1 = 2.062, g_2 = 2.003, g_3 = 1.979). In spectrum *b*, the peak marked with an asterisk is due to a trace of MoO^{3+} impurity.

complexes discussed previously (see Table II and Figure 2a), and this is, perhaps, in accord with a close similarity in structure (i.e., structure A). Such a structural formulation for this acetonitrile complex has been proposed previously by tom Dieck and Friedel.[20]

Related cyclic voltammetric and ESR spectral studies on the 2-methylallyl derivative (η^3-2-MeC$_3$H$_4$)Mo(CO)$_2$-(NCCH$_3$)$_2$Cl and the benzonitrile complex (η^3-C_3H_5)Mo-(CO)$_2$(NCPh)$_2$Cl show that in CH$_2$Cl$_2$–0.2 M TBAH and CH$_3$CN–0.1 M TBAH, their behavior is very similar to that observed for (η^3-C_3H_5)Mo(CO)$_2$(NCCH$_3$)$_2$Cl (vide supra). For example, the cyclic voltammogram of a CH$_2$Cl$_2$–0.2 M TBAH solution of (η^3-2-MeC$_3$H$_4$)Mo(CO)$_2$(NCCH$_3$)$_2$Cl exhibits couples at +1.02 V ([(η^3-2-MeC$_3$H$_4$)Mo(CO)$_2$-(NCCH$_3$)$_3$]$^+$) and +0.85 and +0.48 V ([(η^3-2-MeC$_3$H$_4$)$_2$Mo$_2$(CO)$_4$Cl$_3$]$^-$) arising from essentially complete ionization of this complex. Controlled potential electrolysis at +0.7 V produced a green-yellow solution whose X-band ESR spectrum (at –160 °C) was almost identical with that shown in Figure 4a for the analogous allyl complex. In CH$_3$CN–0.1 M TBAH, a single couple at $E_{1/2}$ = +0.52 V (ΔE_p = 70 mV at ν = 200 mV/s) characterized the unionized complex (η^3-2-MeC$_3$H$_4$)Mo(CO)$_2$(NCCH$_3$)$_2$Cl.

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(18) This conclusion should be contrasted with that stemming from ^{1}H NMR studies of CH$_3$CN solutions (not containing supporting electrolyte) which show[6] that ionic dissociation is appreciable. Clearly, the experimental conditions are critical in determining the extent to which ionization occurs.

(19) Whereas the one-electron oxidized species (η^3-C_3H_5)$_2$Mo$_2$(CO)$_4$Cl$_3$ is ESR active, oxidation beyond the second oxidation (+0.96V) generates a red-brown solution which at –160 °C displays no ESR signal. Presumably, the resulting species [(η^3-C_3H_5)$_2$Mo$_2$(CO)$_4$Cl$_3$]$^+$ contains a Mo–Mo bond and is diamagnetic.

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Studies of Molybdenum Compounds. 4. Synthesis and Structure of Dibenzyl(2,2'-bipyridyl)dioxomolybdenum(VI)

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Dibenzyl(2,2'-bipyridyl)dioxomolybdenum(VI), synthesized by the reaction of benzylmagnesium chloride with dioxodibromo(2,2'-bipyridyl)molybdenum(VI), crystallizes in the orthorhombic space group $P2_12_12_1$ with a = 9.961 (3) Å, b = 12.862 (2) Å, and c = 16.156 (5) Å with Z = 4. Its structure was resolved by Patterson and Fourier methods. The three-dimensional X-ray data were measured with the θ–2θ scan technique with a scintillation detector. The structure was refined by full-matrix least-squares calculations to give $R(F_o)$ = 0.067 and $R_w(F_o)$ = 0.104 for 1582 unique observations above 2σ. The structure of the Mo(O)$_2$(bpy) moiety is coplanar as in other complexes of this type. However, the Mo–N bonds are shorter, the C–Mo–C bond angle of 155.5° is wider, and the Mo–C bonds of 2.25 (2) Å are longer than in the corresponding dimethyl or dineopentyl derivatives. Although indefinitely stable at room temperature in the solid state, the complex exhibits a tendency to decompose with Mo–C bond cleavage in solution under aerobic conditions. This is attributed to the occurrence of spontaneous Mo–C bond cleavage reactions induced by thermal motions of the coordinated bpy ligand.

Introduction

In previous papers of this series[1,2] we described the synthesis and structure of two new dialkyl derivatives of dioxomolybdenum(VI) of composition R$_2$Mo(O)$_2$(bpy) (bpy = 2,2'-bipyridyl), with R = CH$_3$ (**1**) and CH$_2$C(CH$_3$)$_3$ (**2**), respectively. Because of the steric demands of the neo-

R = —CH$_3$ **1**

—CH$_2$C(CH$_3$)$_3$ **2**

—CH$_2$C$_6$H$_5$ **3**

pentyl groups in **2** the C–Mo–C bond angle decreased and the Mo–C bond length increased as compared to **1**. We have sence prepared dibenzyl(2,2'-bipyridyl)dioxo-molybdenum, **3**, to study both electronic and steric effects on Mo–C bond labilization in complexes of this type. Complex **3** was found to be less stable thermally (mp 155
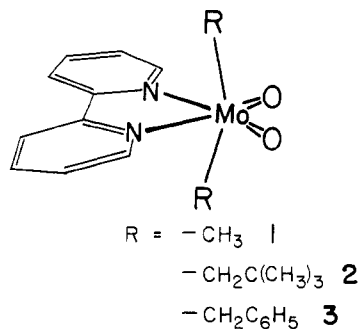
°C dec) than the corresponding alkyl derivatives and exhibits sensitivity to O$_2$ in solution. Complex **3** also has an unusual ^{1}H NMR spectrum, suggesting an interaction of the benzyl phenyl moieties with the coordinated bpy ligand. This unique structural feature was confirmed by the X-ray crystallographic structure determination to be described in the following.

Experimental Section

Reagents and Chemicals. All reagents and chemicals obtained from commercial sources were of analytical or reagent grade purity and were used without further purification. Tetrahydrofuran (Mallinckrodt) was dried over potassium and distilled immediately prior to use. The argon was of 99.998% purity and was dried by passage over KOH pellets. Mo(O)$_2$Br$_2$(bpy) was prepared according to Hull and Stiddard.[3]

Synthesis of Mo(O)$_2$(CH$_2$C$_6$H$_5$)$_2$(bpy), 3. Benzylmagnesium chloride was prepared in tetrahydrofuran by using 30 cm^3 (0.25 mol) of freshly distilled benzyl chloride diluted to 200 cm^3 with THF added dropwise to 12 g (0.5 mol) of Mg in 300 cm^3 of THF. The addition was done over 5 h under an atmosphere of nitrogen and at 0 °C. The resulting Grignard reagent was 0.4 M. A stirred suspension of 7 g of Mo(O)$_2$Br$_2$(bpy) in 100 cm^3 of dry THF and under an atmosphere of nitrogen was cooled to –10 °C in a dry ice/acetone/water bath. To this suspension, 80 cm^3 of the 0.4 M benzylmagnesium chloride was added dropwise. The Grignard was added in 1 h, and the reaction was kept cold for another 2 h after which it was allowed to warm to room temperature. The entire solution was added to 1 L of water and stirred. An orange

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