neering Research council of Canada is gratefully acknowledged. B.M. thanks the Ontario Provincial Government for an International Students Scholarship. We also thank Professor J.-Y. Saillard (Université de Rennes) for helpful discussions.

Appendix

All calculations were performed via the extended Hückel method[22] with use of weighted H_{ij}'s.[23] The parameters used are taken from ref 24. The following distances were used: Mo-C(Ar) = 2.42 Å, Mo-CO = 2.0 Å, C-O = 1.14 Å, Mo-H = 1.7 Å, Mo-Cl = 2.47 Å.

Registry No. 1, 47378-46-1; 11, 125519-18-8; 12, 88077-04-7; 13, 125519-19-9; $(C_6H_6)Mo(CO)_3$, 12287-81-9; $[(C_6H_6)Mo(CO)_3H]^+$, 125519-20-2; $[(C_6H_6)Mo(CO)_3Cl]^+$, 125519-21-3.

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Steric Effects in the Oxidative-Addition Reactions of Gaseous $V(CO)_5^-$

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Received August 18, 1989

Some gas-phase reactions of the 16-electron complex $V(CO)_5^-$ are reported. The reactions of $V(CO)_5^-$, generated by dissociative electron capture from $V(CO)_6$, were performed in a Fourier transform ion cyclotron resonance mass spectrometer. $V(CO)_5^-$ reacts with $V(CO)_6$ to generate $V(CO)_6^-$ and $V_2(CO)_9^-$. $V(CO)_4^-$, also generated by dissociative electron capture from $V(CO)_6$, reacts with $V(CO)_6$ to generate $V_2(CO)_7^-$ and $V_2(CO)_8^-$. These results contrast with condensed-phase photolysis studies of $V(CO)_6^-$. The reaction of $V(CO)_5^-$ with CH_3OH generates $V(CO)_4CH_2O^-$. Labeling studies indicate a 1,2-dehydrogenation with retention of the incoming C-O group. $V(CO)_5^-$ is unreactive with larger alcohols (C_2-C_4). this difference in reactivity is ascribed to a steric effect in the reaction intermediate. A positive second derivative in a plot of the decay kinetics for $V(CO)_5^-$ consumed in the $V(CO)_5^-/CH_3OH$ reaction indicates the process is endothermic or there is an energy barrier along the reaction coordinate. These results also indicate internal excitation drives the dehydrogenation reaction.

Introduction

In recent years there has been a steady stream of work appearing on the gas-phase reactions of anionic metal complexes with neutral molecules.[1] Though the volume of work on anionic complexes is considerably smaller than for their cationic counterparts, enough work has appeared on anionic systems to reveal some general trends. This work has shown anionic systems to undergo many of the same reactions as cationic metals, including oxidative-addition/reductive-elimination,[2] ligand displacement,[3] nucleophilic displacement,[4] oxidation,[5] and clustering reactions.[6]

The clustering reactions of atomic metal anions and ligated metal anions with their parent neutral complexes have been studied by numerous groups. In particular, the reactions of the $Fe(CO)_n^-/Fe(CO)_5$ system have been heavily investigated.[6] The reactions proceed by formation of metal-metal bonds with loss of carbonyl ligands. Products from this reaction up to and including $Fe_4(CO)_n^-$ (n = 11-13) have been identified, with many of these small cluster ions analogous to those observed in the condensed-phase cluster chemistry of $Fe(CO)_5$. Other clustering systems have also been reported, including the reactions of $Cr(CO)_n^-/Cr(CO)_6$ (n = 3, 4),[7] $Ni(CO)_3^-/Ni(CO)_4$,[7] and $CpCo(CO)^-/CpCo(CO)_2$[8] (Cp = cyclopentadienyl). In this paper we report some anionic clustering reactions of the $V(CO)_6$ system.

In a recent investigation of the reactions of iridium and rhenium carbonyl cluster ions with C_6 hydrocarbons it was observed that oxidative-addition reactions of C-H bonds require the cluster to have a vacant orbital derived from an atomic s orbital.[9] The anionic clusters that were investigated were unreactive with all hydrocarbons studied, including cyclohexadiene (which is thermodynamically unstable toward dehydrogenation), indicating initial C-H bond insertion does not occur with the anionic systems. It is generally observed that oxidative-addition pathways are rare in the gas-phase chemistry of anionic transition-metal systems. Interestingly, atomic metal cations are highly reactive toward C-H and C-C bond activation with the ligated cation systems generally less reactive toward these processes,[10,11] whereas the atomic metal anions are

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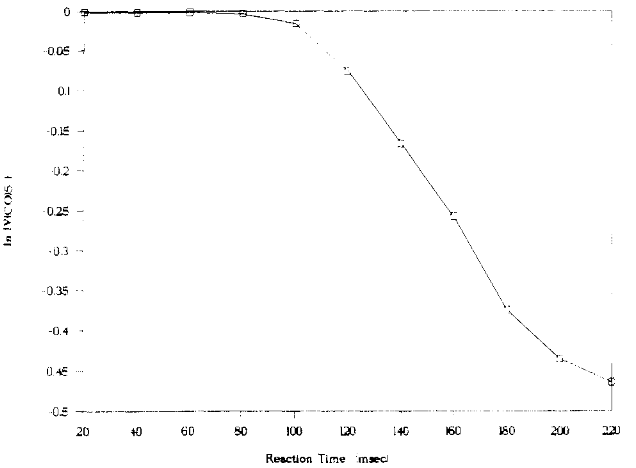


Figure 1. Temporal variation of $V(CO)_5^-$ abundance during reaction with CH_3OH.

almost completely unreactive toward oxidative addition and the ligated anionic complexes are observed to be more reactive toward C–H activation.[1]

McDonald and co-workers have investigated the reactions of many coordinatively unsaturated anionic metal complexes.[12] Recently they presented kinetic and isotopic studies of the $Mn(CO)_3^-/CH_3OH$ reaction that suggested oxidative addition of the C–H and O–H bonds in CH_3OH.[13] Lane and Squires have observed $HCr(CO)_3^-$ to activate O–H bonds in alcohols and water.[14] Finally, McElvany and Allison have shown $Cr(CO)_3^-$, $Fe(CO)_3^-$, $Co(CO)_2^-$, and $CoCONO^-$ to activate O–H and C–O bonds in alcohols.[15] All of these complexes contain 16 or less valence electrons in the metal complex, which is a requirement for oxidative-addition reactions. We decided to study the reactions of $V(CO)_5^-$ with alcohols because this is a 16-e complex that is sterically hindered. We report here on the dehydrogenation reactions of $V(CO)_5^-$ with methanol, which are proposed to proceed via initial oxidative addition of a C–H bond. This complex is not observed to react with larger (C_2–C_4) alcohols. We believe this is due to a steric effect in the intermediate complex.

Experimental Section

All experiments were performed on a Fourier transform ion cyclotron resonance mass spectrometer recently constructed in our laboratory. The trapping cell is a single chamber with solid copper plates of dimensions 2.15 in. (between trapping plates) × 0.75 in. (between excite plates) × 0.75 in. (between receive plates). The electron gun assembly is located $^3/_8$ in. from the cell. The front grid controls the electron beam energy throughout the experimental sequence, with the emission current continuously monitored by a collector behind the Re-ribbon filament. Reagent gases are admitted into the reaction chamber via three Varian variable-leak valves. The chamber is pumped by a 6-in. Alcatel diffstak diffusion pump backed by an Alcatel rough pump. The chamber pressure is monitored with a Granville-Phillips 271 ionization gauge. Base pressures in the chamber are $\sim 4 \times 10^{-9}$ Torr. The magnetic field is supplied by a Varian VHF 7200 10-in. electromagnet field regulated with a Varian V-7700 power supply assembly. The magnetic field was regulated at ~ 0.525 T for the present experiments. The trapping cell and experimental pulse sequences are controlled by a Nicolet FTMS-2000 console. A review of the principles of FT-ICR-MS can be found in ref 16.

$V(CO)_5^-$ was generated via reaction 1.[17] The electrons were introduced into the trapping cell as a short spray. The electron

$$V(CO)_6 + e^- \text{ (0–8 eV)} \rightarrow V(CO)_5^- + CO \qquad (1)$$

pulse was ~15 ms in duration with an electron energy of 5–8 eV. Some of these electrons undergo direct dissociative electron capture with $V(CO)_6$. Many electrons are scattered by $V(CO)_6$ and slowed down sufficiently to be trapped in the ICR cell. The trapping voltage is maintained at −0.5 V, indicating the trapped electrons have energies at or below this value. These low-energy electrons are rapidly attached via process 1 as shown by the kinetic data in Figure 1 (see below). $V(CO)_6$ was admitted into the cell at a pressure of $\sim 1 \times 10^{-5}$ Torr with other gas pressures added to bring the total cell pressure to $\sim 5 \times 10^{-5}$ Torr as measured on the ionization gauge. $V(CO)_6$ was obtained from Alfa. $^{13}CH_3OH$ was obtained from Cambridge Isotope Laboratories; CH_3OD was obtained from MSD Isotopes. All other reagents were obtained commercially and used as supplied except for multiple freeze–pump–thaw cycles to remove noncondensable gases from liquid samples.

Results and Discussion

Clustering Reactions. Trapping $V(CO)_5^-$ with the neutral parent in the ICR cell results in ions at m/z = 219 and m/z = 354 (reactions 2 and 3). The clustering re-

$$V(CO)_5^- + V(CO)_6 \longrightarrow \begin{cases} V(CO)_6^- + V(CO)_5 & (2) \\ V_2(CO)_9^- + 2CO & (3) \end{cases}$$

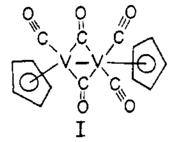
action, (3), most likely results in formation of a V–V bond with the reaction exothermicity driving loss of the carbonyl ligands. $V(CO)_4^-$ is also observed in low intensity during the initial dissociative electron attachment process. This ion also reacts with the parent neutral (reactions 4 and 5).

$$V(CO)_4^- + V(CO)_6 \longrightarrow \begin{cases} V_2(CO)_8^- + 2CO & (4) \\ V_2(CO)_7^- + 3CO & (5) \end{cases}$$

$V(CO)_4^-$ undergoes more extensive loss of carbonyl ligands (reaction 5) than does $V(CO)_5^-$. This may be due to the higher degree of coordinative unsaturation of $V(CO)_4^-$, which drives the clustering reactions with a higher exothermicity. Alternatively, reaction with $V(CO)_4^-$ may generate different structural isomers. Clustering reactions have also been observed in the condensed-phase chemistry of carbonylvanadium complexes.[18] Reaction 6 proceeds

$$2CpV(CO)_4 \xrightarrow{h\nu} Cp_2V_2(CO)_5 + 3CO \qquad (6)$$

by initial photodissociation of a CO ligand from the complex, followed by metal–metal bond formation. This product then cleaves two carbonyl ligands to generate the product, which has structure I. Clusters can be generated



I

in solution by the reaction of metal carbonyl complexes after initial reduction, as in the case of $Fe(CO)_4^-$, or by initial photodecomposition of the metal carbonyl complex to create an unsaturated species that is highly reactive. This has been observed for $Fe(CO)_5$[19] and $Ru(CO)_5$ to

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generate $Fe_2(CO)_9$ and $Ru_3(CO)_{12}$, respectively, and as in reaction 6.

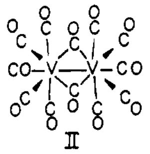
The generation of unsaturated complexes in solution does not necessarily result in metal–metal bond-forming cluster reactions. The reactions of the group VI metal carbonyls after photolysis result exclusively in solvent coordination (reaction 7). This occurs even in noncoordinating solvents such as hydrocarbons.

$$M(CO)_6 \xrightarrow{h\nu} M(CO)_5 + CO \xrightarrow{\text{solvent}} M(CO)_5(\text{solvent}) \qquad (7)$$

dinating solvents such as hydrocarbons. This type of behavior is also observed in the case of $V(CO)_6^-$, which reacts with CN^- via reaction 8 upon photolysis.[20] There is formation of a metal-bonded dimer, however, upon photochemical oxidation to generate $[V_2(CO)_8(CN)_4]^{4-}$.

$$V(CO)_6^- + CN^- \xrightarrow{h\nu} V(CO)_5CN^{2-} + CO \qquad (8)$$

This dimer is isoelectronic with the structure $V_2(CO)_{12}$. There have been a number of reports of formation of dimeric vanadium complexes during the codeposition of vanadium atoms and carbon monoxide in matrix isolation experiments.[21,22] In these experiments, $V(CO)_6$ and $V_2(CO)_{12}$ are both generated and observed by absorption spectroscopic methods. The structure determined for the dimeric complex is shown by II. The present results shown in reactions 3–5 indicate clearly that gas-phase anionic vanadium carbonyl complexes undergo clustering reactions. One other gas-phase study of the clustering reactions with $V(CO)_6$ indicated V^- readily reacts via (9–12).[23] The products from reactions 3–5 contain a large number of carbonyl ligands, and by comparison with the dimeric vanadium complexes in solution and matrix isolation studies, which both generate complexes containing two bridging ligands, reasonable structures are shown by III–V for $V_2(CO)_n^-$ (n = 7–9).



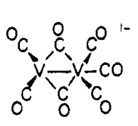
II

$$V^- + V(CO)_6 \rightarrow V(CO)_6^- + V \qquad (9)$$

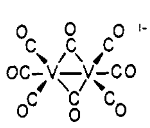
$$V^- + V(CO)_6 \rightarrow V(CO)_5^- + V + CO \qquad (10)$$

$$V^- + V(CO)_6 \rightarrow V_2(CO)_4^- + 2CO \qquad (11)$$

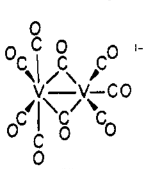
$$V^- + V(CO)_6 \rightarrow V_2(CO)_3^- + 3CO \qquad (12)$$



III



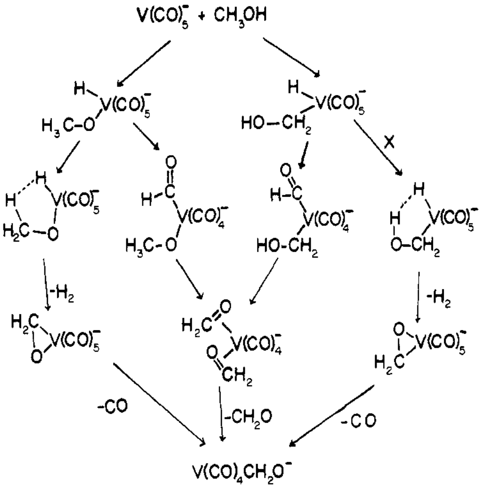
IV



V

These reactions demonstrate that gas-phase unsaturated vanadium carbonyl anions, generated by direct electron impact or via collision-induced dissociation, can readily undergo clustering reactions with the parent carbonyl complex. Thus, the solution reactions for which clustering is not observed may be due to rapid and strong coordination of ligands and not a barrier to the clustering reaction.

Scheme I



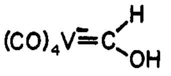
Reactions with Alcohols. $V(CO)_5^-$, generated in reaction 1, reacts with CH_3OH as in reaction 13. The neutral products may be formaldehyde or CO and H_2.

$$V(CO)_5^- + CH_3OH \rightarrow V(CO)_4CH_2O^- + (CO, H_2) \qquad (13)$$

A further discussion of possible reaction mechanisms may shed light on the actual products. Interestingly, $V(CO)_5^-$ from process 1 is unreactive with C_2–C_4 alcohols and water. Labeling studies were performed on reaction 13 in order to elucidate the mechanism. CH_3OD and $^{13}CH_3OH$ react via pathways 14 and 15. It is possible for reaction 13 to proceed by a 1,1-mechanism to generate a substituted carbene, such as structure VI.

$$V(CO)_5^- + CH_3OD \rightarrow V(CO)_4CH_2O^- + (CO, HD) \qquad (14)$$

$$V(CO)_5^- + {}^{13}CH_3OH \rightarrow V(CO)_4{}^{13}CH_2O^- + (CO, H_2) \quad >90\% \qquad (15)$$



$$(CO)_4V{=}C(H)(OH)$$

VI

Early-transition-metal *cations* such as vanadium ($D(V^+–CH_2) \approx 77$ kcal/mol)[24] are known to form strong carbene bonds. Also, steric hindrance, which is the case for the present complex, favors α-hydrogen migration. Reaction 14, however, verifies that the reaction proceeds by a 1,2-mechanism. Reaction 15 shows the incoming carbon from methanol is always retained on the metal center. The reaction indicates >90% competition because the S/N was insufficient to rule out loss of ^{13}CO beyond this level. Scheme I shows a series of possible mechanisms. They all involve initial oxidative addition of methanol bonds to the metal center. We believe this to be the most likely initial course for the reaction. If the initial step involved proton transfer, for example, one would expect to see some amont of CH_3O^- in the mass spectrum. If the initial step were displacement of CO by CH_3OH, one would expect similar displacements by larger alcohols or H_2O. We also do not observe any ligand displacement reactions in $V(CO)_5^-$ with benzene or benzaldehyde. Also, if ligand displacement were the first step in the reaction, $V(CO)_4(CH_3OH)^-$ would be expected

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as a product. Initial displacement of the ligand would result in a statistical partitioning of energy into the reaction products, and some portion of the $V(CO)_4(CH_3OH)^-$ that was generated would be thermally cold and stable toward dissociation. Also, a recent study by Allison and co-workers on the gas-phase reactions of ligated Ni^+ with aromatic compounds and of $CoCO^+$ with a variety of substituted alkanes indicates the initial weakly bound ligand is not always lost as the first step in the reaction.[25] In fact, many of the reactions of these highly unsaturated metal complexes proceed with retention of the ligand in the final product. One of the reactions reported, $Ni(CO)_2^+$ with $(C_6H_5)CH(OH)CH_3$, was reported to lose H_2 and two CO molecules as two separate steps, with loss of H_2 occurring initially followed by elimination of CO from the excited product ion. Thus, we invoke oxidative addition as the first step, in analogy to recent results on the reaction of alcohols with other anionic metal complexes.

This first step will generate a seven-coordinate vanadium complex. This is quite reasonable in light of the numerous seven-coordinate vanadium complexes that have been isolated.[26] In fact, early studies of seven-coordinate first-row complexes were dominated by the chemistry of vanadium. The first step can result from oxidative addition of either a C–H or an O–H bond in methanol, both of which have been previously observed (addition of a C–O bond, while quite reasonable, would not be productive on the reaction pathway to bimolecular products). Addition of the O–H bond might be expected on the basis of the very strong oxygen bond strengths that have been reported for the early transition metals,[1] including V^-. However, on the basis of steric arguments we believe the initial step to be addition of the C–H bond. A comparison of the initial bond-inserted products shows the C–H pathway to be more sensitive to crowding of the metal center by substitution of alkyl groups for $H^\bullet$ at the carbon center, whereas the O–H-inserted structure should feel much less of an influence. Since methanol is observed to be the only reactive alcohol, we believe this is due to steric considerations. The dehydrogenation of methanol requires 18 kcal/mol,[27] whereas the dehydrogenation of ethanol to acetaldehyde only requires 14.9 kcal/mol and dehydrogenation of propanol to propanal only requires 10 kcal/mol; thus, energetic considerations should favor reaction with the larger alcohols. The O–H bond strengths in the alcohols used in the present study are all very close (104–105 kcal/mol), which suggests this is not a cause for the differences in reactivity. The formation of the C–H-inserted intermediate should be most sensitive to additional alkyl groups. Also, H_2O is observed to be unreactive with $V(CO)_5^-$, though this may be due to the fact that the O–H bond in H_2O ($\sim$119 kcal/mol) is stronger than the O–H bond in CH_3OH ($\sim$104 kcal/mol). Finally, the electronic saturation around $V(H)(OCH_3)(CO)_5^-$ would drastically reduce the effect of multiple V–O bonding and thus decrease the oxophilicity of the V center in the present complex.

Recent work has focused on steric effects in gas-phase ion–molecule reactions of metal complexes and the role these effects play in changing the course of reactions.[25] This was most clearly exemplified in the halide abstraction reactions of NiL^+ (L = PF_3, CO, Cp) with $PhCH_2X$ (X = Br, Cl). Ni^+ and $NiPF_3^+$ react with both compounds, while the reaction of $NiCO^+$ with $PhCH_2Cl$ is endothermic. However, $NiCp^+$ reacts with $PhCH_2Cl$ and not with the energetically more favorable $PhCH_2Br$. This is due to steric blocking of the $PhCH_2–(NiCp^+)–Br$ intermediate. The less bulky Cl can form the necessary C–Cl-inserted intermediate complex.

The next step in the reaction cannot involve a β-$H^\bullet$ migration, which is so prevalent in gas-phase dehydrogenation mechanisms,[1,10,11] as this would result in formation of a 19-electron metal center. Migration of the metal-bound hydrogen to one of the carbonyl groups is possible. This would be followed by another hydrogen migration from the oxygen (possibly via the metal center) to generate a bis(formaldehyde)vanadium complex. This pathway is unlikely, given the fact that there is no scrambling of the ^{13}C from the incoming methanol, as would be expected from the bis(formaldehyde)vanadium carbonyl anion. It is unreasonable to expect the formaldehyde generated from the incoming group to be bound more strongly than the leaving formaldehyde (i.e. axial vs equatorial) at these high temperatures because all ligands should be continuously scrambling.

Pathway X in Scheme I shows an alternative mechanism that we feel is the most plausible, given the present evidence. It involves concerted loss of H_2 from a cyclic intermediate formed from the initial bond-inserted product. This would generate an internally excited $V(CO)_5CH_2O^-$ complex that decomposes by loss of CO. This would indicate $D(V(CO)_4CH_2O^-–CO) < D(V(CO)_5^-–CH_2O)$.

Figure 1 shows a plot of the parent ion intensity from reaction 13 as a function of time. The S shape of the decay curve for $V(CO)_5^-$ can be attributed to two factors. The first portion of the decay is due to stray electrons in the cell remaining after the initial spray of electrons. These electrons are not detected due to their high cyclotron frequency (e^- cyclotron frequencies are on the order of gigahertz at the present magnetic field values). The electrons are lost due to dissociative capture by $V(CO)_6$. This results in continuous production of $V(CO)_5^-$ during the beginning of the reaction period. The electrons react much faster than the ions do. The latter portion of the decay curve has a positive second derivative. This is because the initially formed $V(CO)_5^-$ is internally excited. It is not highly kinetically excited because the dissociating CO takes away most (87%) of the kinetic energy (based on momentum conservation after dissociation). This internally excited $V(CO)_5^-$ reacts faster than does the thermalized $V(CO)_5^-$ (the ions reacting during the latter portion of the reaction period). This indicates the reaction is slightly endothermic or there is an energetic barrier along the reaction coordinate. If there is a barrier along the reaction pathway, it may be associated with the sterically hindered seven-coordinate transition state. These results also show that internal excitation can drive the dehydrogenation reaction, which does not occur at thermal energies.

Conclusion

The anions produced from dissociative electron capture by $V(CO)_6$, $V(CO)_5^-$, and $V(CO)_4^-$ are observed to undergo clustering reactions with $V(CO)_6$. These reactions differ from those observed between $V(CO)_6$ and unsaturated vanadium carbonyl anions produced by photolysis in solution. $V(CO)_5^-$ reacts with methanol but is unreactive with larger alcohols. The difference in reactivities is due to steric efects in the first intermediate complex of the

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reaction. Labeling studies indicate the reaction proceeds by a 1,2-dehydrogenation mechanism in which the incoming C–O bond is retained in the final product. Kinetic data suggest the reaction with methanol is driven by excess internal excitation in $V(CO)_5^-$.

Acknowledgment is made to Bell Laboratories for an equipment donation.

Registry No. $V(CO)_6$, 14024-00-1; $V(CO)_5^-$, 53221-58-2; CH_3OH, 67-56-1.

Synthesis and Properties of (η^5-6,6-Dimethylcyclohexadienyl)molybdenum ((dmCh)MoL_n) Complexes. X-ray Structure of [(dmCh)$(CO)_2$Mo$]_2$

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Received August 18, 1989

The ancillary character of the 6,6-dimethylcyclohexadienyl ligand (dmCh) was examined via the syntheses of various (dmCh)MoL_n derivatives. Treatment of (diglyme)Mo$(CO)_3$ with K(dmCh) afforded [K(diglyme)$_n$][dmCh)Mo$(CO)_3$] (**1**, 85%), which was converted to (dmCh)Mo$(CO)_3$I (**2**) by I_2 in low yield. The addition of HgI_2 to 2.0 equiv of **1** produced [(dmCh)Mo$(CO)_3]_2$Hg (**3**, 77%); iodination of **3** generated **2** in 65% yield. Photolysis of **3** provided the dimer, [(dmCh)Mo$(CO)_3]_2$ (**4**), which was most conveniently prepared via $[Cp_2Fe]PF_6$ oxidation of **1** (57%). Thermolysis of **4** yielded a triply bonded dimer, [(dmCh)Mo$(CO)_2]_2$ (**5**, 80%), that contains a 2.508-Å $Mo\equiv Mo$ bond and two semibridging carbonyls. Crystal data for **5**: Cu Kα, triclinic, $P\bar{1}$, $a = 9.654$ (1) Å, $b = 8.658$ (1) Å, $c = 12.608$ (2) Å, $\alpha = 93.44$ (1)°, $\beta = 104.80$ (1)°, $\gamma = 100.79$ (1)°, $Z = 2$, $T = 23$ °C, $R = 0.049$, $R_w = 0.036$, 2518 reflections ($|F_o| \geq 3\sigma(F_o)$). Anion **1** ($E_a = +0.14$ V) and singly bonded dimer **4** ($E_c = -0.60$ V) were observed to be electrochemically coupled via either an ECE or an ECC process; **5** displayed a reversible reduction at −1.10 V. Diazald reacted with **1** to form (dmCh)Mo$(CO)_2$NO (**6**, 46%); exposure of **6** to PPh_3 and PMe_3 resulted in the synthesis of (dmCh)Mo(PPh_3)(NO)CO (**7**) and (dmCh)Mo(PMe_3)(NO)CO (**9**) in modest yield, the latter via (η^1-dmCh)Mo$(PMe_3)_2(CO)_2$NO (**8**). The characteristics of these complexes, as compared with cyclopentadienyl congeners, are consistent with an assessment of dmCh as a strong-field ligand.

Introduction

The recently explored pentadienyl (pd) ligand[1-4] has drawn substantial interest as an alternative to the ubiquitous cyclopentadienyl (Cp) fragment,[5] primarily due to its ability to stabilize low-valent early metals.[6-8] An investigation into the feasibility of cyclohexadienyl ligation[8] was initiated in an effort to design an ancillary ligand with characteristics similar to pentadienyl. A series of sandwich complexes, $(dmCh)_2M$ (M = Ti, V, Cr, Fe), containing 6,6-dimethylcyclohexadienyl (dmCh = η^5-6,6-$Me_2C_6H_5$) exhibited properties intermediate between related Cp- and pd-containing species.[9] A substantial amount of the strong-field bonding common to the "wrap-around", acyclic, pentadienyl ligand[2] is transposed to the more rigid dmCh, while the combined steric effects of methyl substituents and the six-membered ring inhibit undesirable ligand reactivity. To further examine the ancillary character of dmCh, a series of (dmCh)MoL_n complexes analogous to those derived from CpMo$(CO)_3$ (Mp)[10] were prepared and studied. Reported herein are the results of this investigation.

Table I. Comparative CO (NO) IR Data (cm^{-1})[a] for (dienyl)MoL_n Complexes (dmCh = η^5-6,6-$Me_2C_6H_5$, Cp = η^5-C_5H_5, Cp* = η^5-C_5Me_5)

(dienyl)MoL_n	dmCh	Cp/other
[(dienyl)Mo$(CO)_3$]K	**1**:[b] 1890, 1790, 1745	1898, 1790, 1750[c,12]
(dienyl)Mo$(CO)_3$I	**2**:[b] 2015, 1959, 1948	2040, 1970, 1955[d,13]
[(dienyl)Mo$(CO)_3]_2$Hg	**3**:[e] 1990, 1968, 1914, 1880	1998, 1971, 1917, 1908, 1890[f,12]
[(dienyl)Mo$(CO)_3]_2$	**4**:[d] 1950, 1900	1960, 1915[g,14] Cp*: 1940, 1907[g,14] indenyl: 2020 (vw), 1958, 1910[h,15]
[(dienyl)Mo$(CO)_2]_2$	**5**:[d] 1945, 1886	1889, 1859[g,14] Cp*: 1874, 1846[d,14] indenyl: 1893, 1858[h,15]
(dienyl)Mo$(CO)_2$NO	**6**:[d] 2017, 1957, (1678)	2016, 1936, (1674)[e,16]
(dienyl)Mo(PPh_3)(NO)(CO)	**7**:[e] 1930, (1616)	1906, (1617)[e,16]
(dienyl)Mo(PMe_3)(NO)(CO)	**9**:[d] 1933, (1625)	1901, (1610)[c,17]

[a] Bands are medium to strong. Solvents/media: [b] Nujol; [c] THF; [d] cyclohexane; [e] benzene; [f] toluene; [g] octane; [h] CH_2Cl_2.

Results and Discussion

Synthesis and Characterization. All members of the (dmCh)MoL_n class of half-sandwich complexes were ultimately derived from [K(diglyme)$_n$][(dmCh)Mo$(CO)_3$] (**1**), prepared from treatment of (diglyme)Mo$(CO)_3$[11] with K(dmCh)[9] at −78 °C in THF according to eq 1. Precip-

$$\text{(diglyme)Mo(CO)}_3 + \text{K(dmCh)} \xrightarrow[-78\ °\text{C}]{\text{THF}} \underset{\mathbf{1}}{[\text{K(diglyme)}_n][\text{(dmCh)Mo(CO)}_3]} \quad (1)$$

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0276-7333/90/2309-1097$02.50/0