The Protonation of $(C_6Et_6)M(CO)_3$ (M = Cr, W): A ^{13}C NMR and EHMO Investigation

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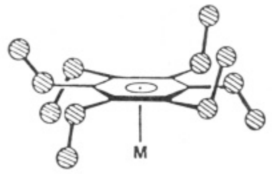
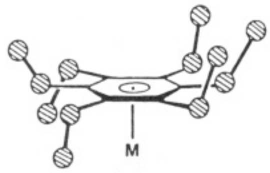
The treatment of $(C_6Et_6)M(CO)_3$ (M = Cr, W) with CF_3SO_3H in SO_2 yields a species in which the proton is directly bonded to the metal atom. In contrast to previous systems in which the $HM(CO)_3$ fragment adopted a square-based-pyramidal geometry and was fluxional, the presence of the hexaethylbenzene ligand imposes 3-fold symmetry on the molecule. The electronic structure of these complexes and also the mechanism of the fluxionality in $[(arene)M(CO)_3L]^+$ systems are examined by using the EHMO approach.

Introduction

Hexaethylbenzene (HEB) is a fascinating ligand that can exhibit remarkable conformational variability when complexed to organometallic moieties. The most favored structure (a) is the one in which the alkyl groups are oriented alternately above and below the plane of the arene ring so as to minimize steric interactions between neighboring ethyl substituents.[1] This 1,3,5-distal–2,4,6-proximal arrangement has been established crystallographically for the complexes $(HEB)Cr(CO)_3$ (**1**),[1] $(HEB)Cr(CO)_2CS$ (**2**),[2] $[(HEB)Cr(CO)_2NO]^+BF_4^-$ (**3**),[3] and $(HEB)Mo(CO)_3$ (**4**).[1] This alternating proximal–distal arrangement of methyls is also found in the closely analogous compound $(C_6Et_5COMe)Cr(CO)_3$, in which slowed rotation of the tripodal fragment on the NMR time scale has been unequivocally demonstrated.[4] When the organometallic fragment is somewhat more sterically demanding, as in $(HEB)Cr(CO)_2PMe_3$ (**5**)[5] or $[(HEB)Fe(C_5H_5)]^+PF_6^-$ (**6**),[6] the structure found in the solid state is the 1,2,3,5-distal–4,6-proximal isomer (c). Nevertheless, it is apparent from variable-temperature NMR data that in solution a number of interconverting $(HEB)ML_n$ conformers can coexist.[7] Stereoisomer e, which possesses but a single proximal ethyl group, has been observed in $(HEB)Cr(CO)_2PEt_3$ (**7**)[8] and also in $[(HEB)Fe(C_5H_5)]^+BPh_4^-$.[9] An extreme is reached in $(HEB)Cr(CO)_2PPh_3$ (**8**), for which the all-distal arrangement (h) is observed.[1] As a result of numerous NMR studies on these complexes, it has become clear that a knowledge of the particular conformation adopted in a given hexaethylbenzene complex provides a sensitive probe of the bulk and also of the symmetry of the attached organometallic fragment.



(a)



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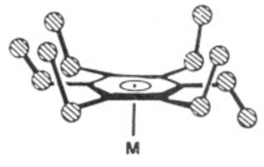

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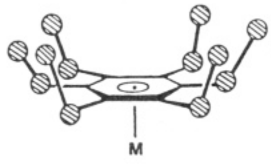
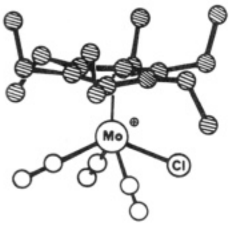


(h)

Recently, the crystal structure of $[(HEB)Mo(CO)_3Cl]^+[MoCl_6]^-$ (**9**) has been reported and the ethyls adopt the previously unknown 1,2,4,5-distal–3,6-proximal conformation (b).[10] In **9**, the $Mo(CO)_3Cl$ fragment forms



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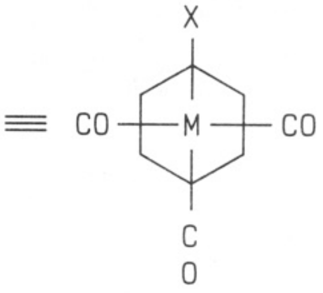
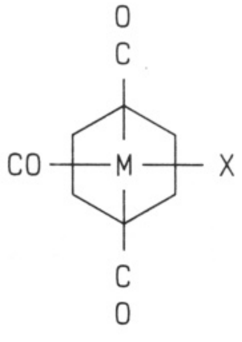


10(a)



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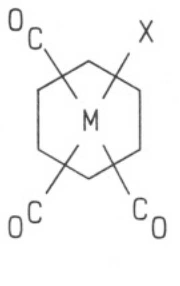

10(c)

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an approximate square-based pyramid which is oriented such that the basal ligands eclipse two bonds of the hexaethylbenzene ring, as in **10a**; in the closely analogous cation $[(C_6Me_6)W(CO)_3I]^+$, the structure of which had been described earlier,[11] the $W(CO)_3I$ moiety eclipses two ring carbons and two bonds, as in **10b**.

The conformation adopted by the ethyl substituents of the arene ligand in **9** in solution remains an open question; no variable-temperature NMR spectra have yet been reported, and indeed the presence of the paramagnetic hexachloromolybdate(V) anion would perhaps preclude such studies. In an attempt to prepare another hexaethylbenzene complex of type b that might be more amenable to an NMR investigation, we chose to protonate $(HEB)Cr(CO)_3$ (**1**).

Results and Discussion

^{13}C NMR Spectroscopic Studies. The protonation of $(arene)M(CO)_3$ systems was first described by Wilkinson et al. in 1962;[12] subsequent work established the site of attack to be at the metal atom.[13] A crucial observation was made by Olah, who noted that at −70 °C the ^{13}C NMR spectrum of protonated $(C_6H_5OMe)Cr(CO)_3$ exhibited a 2:1 pattern for the metal carbonyl resonances. This result was rationalized in terms of a C_s geometry for the $M(CO)_3H$ moiety.[14] This idea was extended by Flood, whose elegant studies on the protonation of a series of $(arene)M(CO)_2PR_3$ complexes established not only the square-based-pyramidal nature of the organometallic fragment attached to the arene but also the intramolecular character of the fluxional processes.[15] This detailed study (in conjunction with the previous work of Faller[16] on the analogous $CpML_3H$ species) was interpretable in terms of an intermediate possessing pseudo-3-fold symmetry, as in Figure 1.

Treatment of an SO_2 solution of $(HEB)Cr(CO)_3$ (**1**) with CF_3SO_3H (or a CD_2Cl_2 solution with CF_3CO_2H) at −80 °C causes an almost immediate color change from yellow to deep red. As anticipated from previous reports on the protonation of (arene)chromium tricarbonyl complexes,[12-16] the proton spectrum exhibited a singlet at δ −5.2. The carbon-13 resonances for the hexaethylbenzene ligand were also clearly resolved, showing that the methyl and ring carbon peaks had separated into pairs of equal intensity; at −100 °C the methylene carbons broadened but did not separate. However, unlike Olah's example[14] of $(C_6H_5OMe)Cr(CO)_3$, in which the ^{13}CO's split into a 2:1 pattern (at −70 °C and 25 MHz), the metal carbonyl resonance in **11** remains unsplit even at −100 °C and 125 MHz! A comparison of the ^{13}C chemical shift data for neutral (**1**) and protonated $(HEB)Cr(CO)_3$ (**11**) appears in Table I.

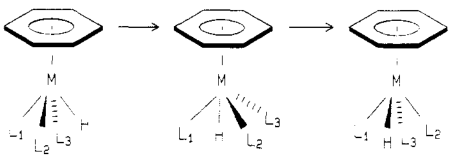

Figure 1. Proposed mechanism of fluxionality for isomers of $(arene)CrH(CO)_3^+$.

Table I. ^{13}C NMR Data (ppm) for $(HEB)M(CO)_3$ and for the Corresponding Protonated Systems[a]

	distal Et groups			proximal Et groups			
	CH_3	CH_2	C_{Ar}	CH_3	CH_2	C_{Ar}	CO
$(HEB)Cr(CO)_3$	14.2	22.8	117.2	20.1	19.4	108.8	235.4
$(HEB)CrH(CO)_3^+$	13.5	20.5	126.1	23.1	20.5	124.8	225.2
$(HEB)W(CO)_3$	14.6	22.6	117.5	24.6	19.6	111.4	214.8
$(HEB)WH(CO)_3^+$	13.9	23.5	130.4	24.0	21.1	126.2	201.0

[a] Data for the neutral complexes were obtained in CD_2Cl_2 and those for the protonated systems in SO_2 solution.

The analogous reaction with $(HEB)W(CO)_3$ (**12**) likewise yields a ^1H resonance at δ −6.4 typical of a metal hydride environment, and the attachment of the proton to the tungsten atom is clearly indicated by the observation of tungsten satellites with $J(^{183}W–^1H)$ = 26.4 Hz. The carbon-13 spectra of **12** and of protonated $(HEB)W(CO)_3$ (**13**) are shown in Figure 2, and the striking similarities lead to the conclusion that the HEB ligand has maintained its 1,3,5-distal–2,4,6-proximal conformation in the protonated species. As with the chromium analogue **11**, the metal carbonyl resonance in **13** maintains its singlet character even at low temperature.

One could rationalize these observations either in terms of a ground-state C_{3v} geometry or by postulating interconversion of the C_s isomers in a process that is still rapid on the NMR time scale, even at low temperature; we incline to the former view for the following reasons. We note that Olah's protonation of $(C_6H_5OMe)Cr(CO)_3$ revealed a limiting 2:1 pattern for the ^{13}CO resonances at −70 °C and a field of 2.35 T (25.1 MHz for ^{13}C). Use of the Gutowsky–Holm approximation would put the minimum activation energy for carbonyl exchange in this system in the range 10–11 kcal mol^{-1}. The careful studies on $[(arene)CrH(CO)_2PR_3]^+$ systems reported by Flood[15] yield analogous exchange barriers of 12–13 kcal mol^{-1}. If we assume a similar chemical shift separation for the ^{13}CO resonances of the supposed square-pyramidal isomer of **11** as has been found in the previously mentioned $[(arene)CrL_3H]^+$ systems, then one should certainly detect a 2:1 ^{13}CO pattern for **11** at low temperature on an 11.74-T instrument (125.7 MHz for ^{13}C). However, we see no evidence for splitting of the carbonyl resonance even at −100 °C. Such a scenario would need a $C_s \rightleftarrows C_{3v}$ interconversion barrier of ~6–7 kcal mol^{-1}, which would be a reduction in $\Delta G^\ddagger$ of approximately 5 kcal mol^{-1} relative to those values already reported in comparable molecules.

The fluxional behavior of the neutral $(HEB)M(CO)_3$ molecules **1**, **4**, and **12**, where M = Cr, Mo, and W, respectively, has been described previously. At low temperature, the original singlets for the methyl, methylene, and arene ring carbons are each split into two equally intense resonances. This phenomenon is readily explicable in terms of the interconversion of proximal and distal ethyl substituents,[1,2] and the barrier to ethyl rotation in these molecules is generally ~11 kcal mol^{-1}. In the protonated system **11** (M = Cr) the analogous rotation barrier can be obtained from the coalescence behavior of the methyls and yields a value of $\Delta G^\ddagger_{224}$ = 9.8 ± 0.4 kcal mol^{-1}.

It is presumably the presence of the ethyl groups that stabilizes the C_{3v} structure of the cations **11** and **13** with respect to the normally favored C_s geometry. In order for the $M(CO)_3H$ fragment to adopt its preferred square-based-pyramidal structure, it would be necessary to generate a conformer of type b as observed in the solid state for **9**. Thus, we propose that the C_{3v} structure can become

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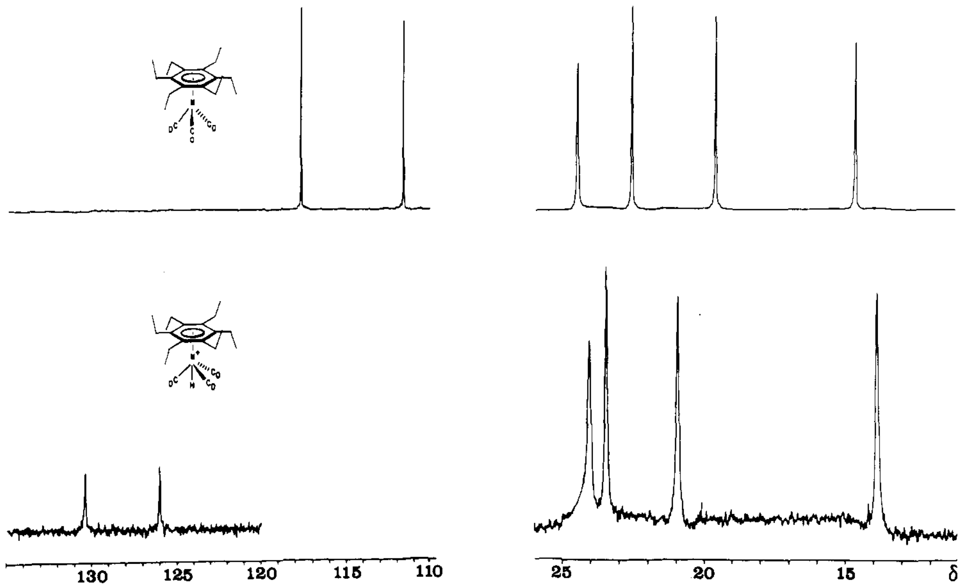

Figure 2. ^{13}C NMR spectra (125.7 MHz) of $(HEB)W(CO)_3$ and of its protonated analogue (spectra recorded at –70 °C).

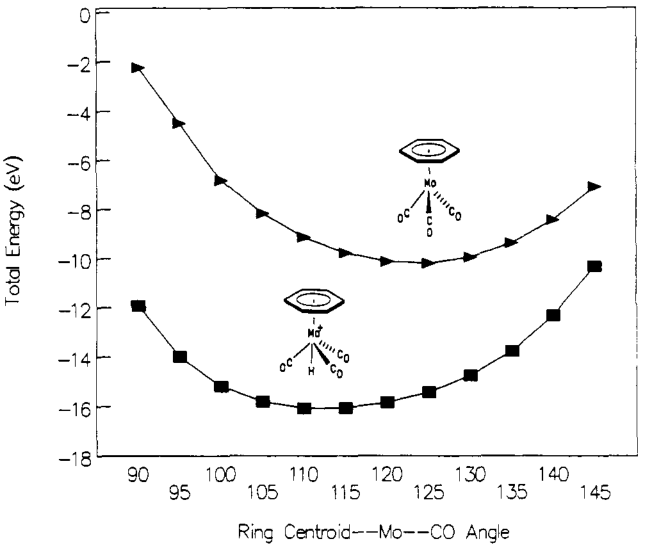

Figure 3. Plots of total energy (EHMO) versus the ring centroid-Mo-CO angle showing the minimum-energy conformations.

competitive with the square-based-pyramidal geometry when the arene imposes serious steric constraints. Subsequently, we carried out extended Hückel molecular orbital calculations on $[(C_6H_6)Mo(CO)_3E]^+$, where E = H and Cl, to try to gain an understanding of the electronic and steric factors involved.

EHMO Calculations. Molecules of the type (arene)-$M(CO)_3$ have been extensively studied by using the EHMO approach, and the general electronic features have been elucidated.[17] In Figure 3 we show the effect on the total energy of the system of varying the angle made by the carbon monoxide ligands with the 3-fold axis of the molecule. It is clear that placing the three CO's coplanar with the metal atom ($\theta = 90°$) is strongly disfavored. Not surprisingly, attempts to push the tripodal ligands too close together raise the energy of the system. The minimum-energy geometry is found when $\theta \approx 125°$, and this can be rationalized on the basis of the alignment of the nodal planes of the π^* orbitals of the carbonyl ligands with that of the d_{z^2} orbital on molybdenum. It is apparent that this optimum overlap will occur for $\theta = 125.3°$, since the nodal plane of the d_{z^2} orbital lies at 54.7° to the C_3 axis. (In fact, the $M(CO)_3$ moiety effectively retains its octahedral parentage and the back-donation from the metal to the CO's occurs via the remnants of the original t_{2g} set.[18]) Clearly, as the carbonyls are bent back toward the metal, this back-donation from metal d_{z^2} into π^* on the carbonyls is greatly diminished; indeed, when $\theta = 90°$ the overlap should be rigorously zero by symmetry. However, concomitant with the decrease in θ we observe that the HOMO, which was initially an almost pure d_{z^2} orbital, steadily mixes with s and p_z, resulting in a hybrid that "squeezes" the electron density away from the arene ring and along the C_3 axis, as depicted in Figure 4. In essence, the electrons that were previously delocalized onto the CO ligands are now concentrated on the metal; the net results are a raising of the energy of the HOMO and a decreased positive charge on molybdenum. The resulting structure could be described as a trigonal bipyramid with an axial lone pair—a situation that would appear to be ideal for the approach of a proton along the 3-fold axis. As shown in Figures 3 and 4, a compromise is reached between the development of a hybrid orbital suitable for attachment to the proton and the need to delocalize electron density via back-donation from the metal to the carbonyls. For the protonated system the situation is optimal when $\theta \approx 110°$ but the energy surface is rather flat, suggesting that

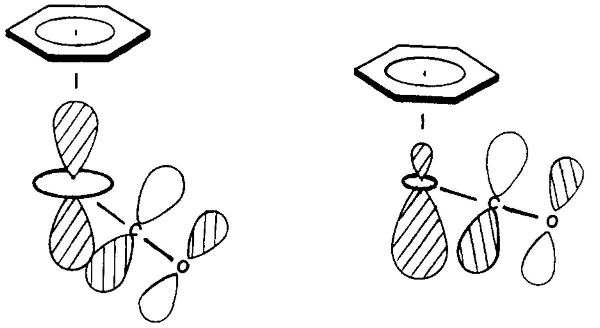

Figure 4. Frontier orbitals of a metal carbonyl fragment of $(C_6H_6)Mo(CO)_3$ showing how the pure d_{z^2} orbital (at $\theta = 125°$) is distorted along the 3-fold axis at $\theta = 105°$.

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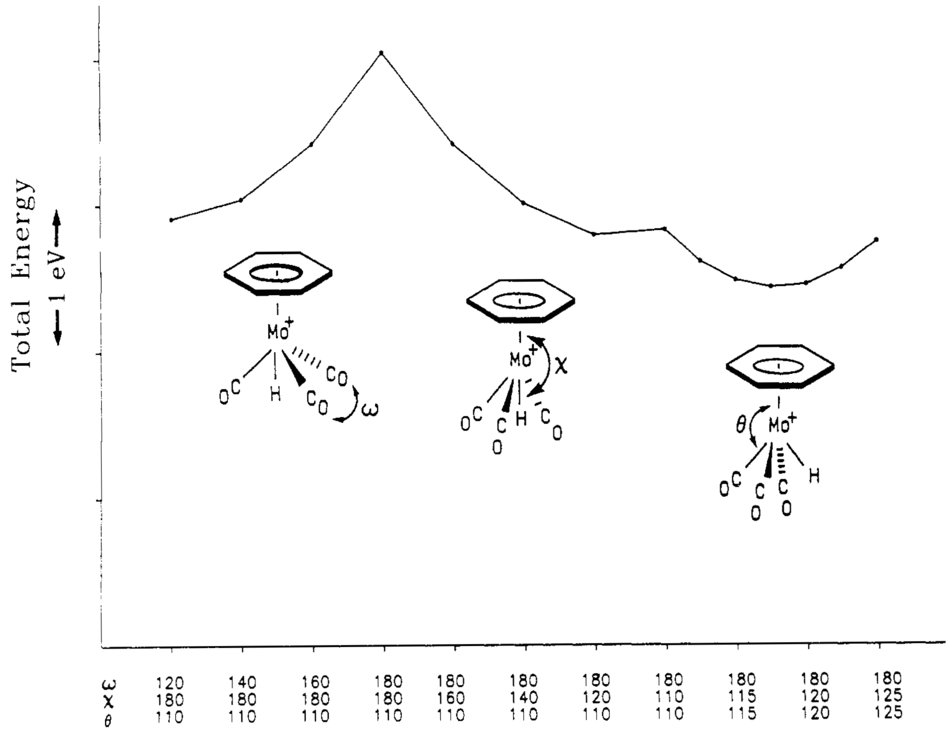

Figure 5. Energy profile of an idealized reaction path that interconverts the C_{3v} and square-pyramidal isomers of $[(C_6H_6)MoH(CO)_3]^+$.

considerable conformational mobility is possible.

We know from the experiments of Flood[15] and of Faller[16] that in molecules containing arenes which impose no steric problems the favored structure has the square-based-pyramidal geometry and the C_{3v} isomer is merely a way-point during the fluxional process. Figure 5 depicts the energy changes along a somewhat arbitrary reaction path that opens up one OC–Mo–CO bond angle, ω, from 120 to 180° and allows the hydride ligand to move into its preferred location by reducing the centroid–Mo–H angle, χ, from 180 to 110°. Finally, when the energy of the square-based-pyramidal structure is allowed to minimize, the centroid–Mo–CO angle, θ, is found to be $\sim$117°.

As described above, the orientation of the $M(CO)_3X$ fragment with respect to the arene ring is different in $[(C_6Et_6)Mo(CO)_3Cl]^+$ and in $[(C_6Me_6)W(CO)_3I]^+$; in the former case the molecule is found to have structure **10a**, while the latter adopts **10b**.[10,11] In order to see whether there is any electronic preference, we carried out EHMO calculations on the model system $[(C_6H_6)Mo(CO)_3Cl]^+$ in the orientations **10a**, **10b**, and **10c**. The result is that **10b** is favored over **10a**, while **10c** is the least favored of all; however, the differences are so small ($\sim$0.1 eV) that the rotational barrier would not be detectable by NMR line-broadening techniques. Presumably, the HEB complex adopts structure **10a** to minimize the interactions with the ethyl substituents. One can also profitably use the EHMO approach to compare molecules with structures as in **10** to an isomer in which the chloride is bonded to molybdenum along the 3-fold axis. Not surprisingly, the relatively large chlorine atom raises the energy markedly (by $\sim$0.4 eV) and indeed the minimized centroid–Mo–CO angle is now $\sim$105°. Apparently the disadvantages of placing a chlorine along the 3-fold axis of $(HEB)Mo(CO)_3$ are more severe than those encountered by rotating an ethyl group out of the way and allowing the $Mo(CO)_3Cl$ unit to adopt its preferred square-pyramidal geometry.

Before concluding, we note that in 1971 Green reported the treatment of $(C_6H_6)Mo(PPh_3)_3$ with CF_3CO_2H and observed that the high-field proton exhibited equivalent coupling constants to all three phosphorus nuclei, even at −96 °C. At that time he chose to interpret this result in terms of a square-based-pyramidal structure in which the phosphorus nuclei positioned cis and trans to the metal-bonded hydrogen were undergoing rapid fluxional exchange.[19] However, in light of the present results and considering the bulky nature of the three phosphine ligands, one might prefer to assign a C_{3v} structure to the molecule analogous to the situation encountered for $(HEB)M(CO)_3$ complexes described herein.

In summary, therefore, we suggest that the protonation of $(HEB)M(CO)_3$ yields a cation in which the added hydrogen atom is directly bonded to the metal atom and is positioned along the 3-fold axis of the molecule. In effect, one has trapped the transition state (or intermediate) proposed by Flood[15] for the fluxional process that interconverts the cis and trans carbonyl ligands in $[(arene)M(CO)_3H]^+$ systems, where the metal resides in a square-based-pyramidal environment. EHMO calculations suggest that this situation will only arise when the attacking electrophile has minimal steric requirements.

Experimental Section

^1H and ^{13}C NMR spectra were acquired by using a Bruker AM 500 spectrometer operating at 500 and 125.7 MHz, respectively.

$(HEB)W(CO)_3$ and $(HEB)Cr(CO)_3$ were each prepared as previously described.[20,21] Each sample was taken in an NMR tube and cooled in a dry ice/acetone bath. A few drops of CF_3SO_3H were slowly added, and the sample was degassed on a vacuum line. SO_2 was transferred into the NMR tube, which was then sealed. The initially yellow solutions turned orange-red on protonation.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. Financial support from the Natural Sciences and Engi-

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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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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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