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Ion Cyclotron Resonance and Photoelectron Studies of the Ionization Energetics and Thermochemical Properties of $Mn(CO)_5$(benzyl). Implications for the Manganese–Manganese Bond Strength in $Mn_2(CO)_{10}$[†]

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Benzyl- and pentacarbonylmanganese radicals are not observed in the He I photoelectron spectra of $Mn(CO)_5Bz$ (Bz = $C_6H_5CH_2$) subjected to flash vacuum pyrolysis at several temperatures. Only the loss of carbon monoxide is detected, suggesting that $D[Mn(CO)_5\text{–}Bz] > D[Mn(CO)_4(Bz)\text{–}CO]$. The adiabatic IP[$Mn(CO)_5Bz$] is determined as 7.48 ± 0.03 eV. Ion cyclotron resonance experiments yield an appearance potential of benzyl ion from $Mn(CO)_5Bz$, which, combined with IP(benzyl) = 7.20 eV, gives $D[Mn(CO)_5\text{–}Bz] = 32 \pm 5$ kcal/mol. This value yields $\Delta H_f{}^\circ[Mn(CO)_5,g] = -169$ kcal/mol, IP[$Mn(CO)_5$] = 7.7 eV, and $D[(CO)_5Mn\text{–}Mn(CO)_5] = 41 \pm 9$ kcal/mol. Consideration of possible errors indicates that $D[(CO)_5Mn\text{–}Mn(CO)_5]$ can be no lower than 32 kcal/mol. This result is discussed in terms of other recent determinations of $D[(CO)_5Mn\text{–}Mn(CO)_5]$ and generally supports a higher value than some studies have yielded. The gas-phase ion chemistry of $Mn(CO)_5Bz$ is also briefly reported with attention given to processes leading to the formation of the carbene $(CO)_5Mn{=}CHC_6H_5{}^+$.

Introduction

Manganese–ligand bond dissociation energies in the complexes $Mn(CO)_5L$ have recently been examined by Conner et al.[2] and by Stevens.[3] The results in both studies are based on an estimated value for D(Mn–Mn) in $Mn_2(CO)_{10}$, 22.5 kcal/mol, which is subject to some controversy, as evidenced in Table I.

The adoption of the "low value" for D(Mn–Mn) is supported by several independent electron-impact studies involving the measurement of AP[$Mn(CO)_5{}^+$] and IP-[$Mn(CO)_5$][4-8] in addition to a van't Hoff analysis of the equilibrium between $Mn_2(CO)_{10}$ and $2Mn(CO)_5$.[8] However, as noted by Connor et al., the recent value for the adiabatic ionization potential of $Mn_2(CO)_{10}$, 7.69 ± 0.01 eV, is substantially lower than the previously accepted values, and thus it may well be that the reported AP[$Mn(CO)_5{}^+$] and IP[$Mn(CO)_5$] are also high limits.

The "high value" presented in Table I, ca. 36.8 kcal/mol, which is close to an early thermochemical estimate,[9] corresponds to the activation enthalpy for the homolytic cleavage of $Mn_2(CO)_{10}$, which has been obtained through kinetic studies in solution.[10,11] Since the recombination of the $Mn(CO)_5$ radicals is diffusion controlled and independent of the nonpolar solvent used, it is unlikely that there is a significant activation enthalpy for the reverse process and little or no contribution to the activation enthalpy from solvation effects.[11,12] It has been argued by Poe[2,11] that the "low value" for D(Mn–Mn) is "totally unreasonable". In addition, Muetterties and co-workers[13] have reported recently that a reaction between a mixture of $Mn_2(CO)_{10}$ and $Mn_2(^{13}CO)_{10}$ with ^{12}CO or ^{13}CO in octane at 120 °C gives very small amounts of $Mn_2(^{12}CO)_n(^{13}CO)_{12-n}$ with n = 4–6 compared to the abundance of products resulting from sequential exchanges (which starts with n = 1 and 11), indicating that the cleavage of Mn–Mn bonds is not significant. This suggests that the CO exchange mechanism does not involve a rate-determining Mn–Mn bond fission and that the Mn–Mn bond energy "substantially exceeds" 22.5 kcal/mol.[13] Finally, sonochemical studies by Suslick and Schubert[14] on CO replacement in $Mn_2(CO)_{10}$ by phosphines or phosphites also indicate that the very high temperatures of ultrasonic cavitation lead to carbonyl loss and not to Mn–Mn cleavage.

Assigning a correct value to D(Mn–Mn) is therefore not a simple task. The solution of the problem would be provided by the knowledge of a reliable value for the adiabatic ionization potential of the radical $Mn(CO)_5$ since the enthalpy of formation of the cation has been obtained by photoionization mass spectrometry studies as 9.1 ± 3.3 kcal/mol.[15] The "low" and the "high" results for D(Mn–Mn) yield IP[$Mn(CO)_5$] = 8.2 and 7.8 eV, respectively. Alternatively, D(Mn–Mn) could be evaluated through an indirect method consisting of the measurement of the appearance potential of L^+ from $Mn(CO)_5L$, affording D(Mn–L) and $\Delta H_f{}^\circ[Mn(CO)_5]$. For this method to be successful it is desirable that L be chosen such that IP(L) $\lesssim$ IP[$Mn(CO)_5$], which is essential if L is to be observed as a major fragment ion.

We have used both of the described methods in an attempt to obtain D(Mn–Mn), and the results are described

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Table I. Literature Values for D(Mn-Mn) in $Mn_2(CO)_{10}$[a]

				$Mn(CO)_5$		
year	method[b]	ref	IP[$Mn_2(CO)_{10}$]	AP	IP	D(Mn-Mn)
1960	TE	9				34 ± 13
1966	EI[c]	4		9.26 ± 0.03	8.44 ± 0.03	19 ± 1
1966	KS	10, 11				36.8
1967	EI	5	8.58	9.40	8.44[d]	22
1968	EI[e]	6		9.4	8.2	28
1970	EI	7	8.46 ± 0.03	9.40[f]	8.32[g]	25 ± 1
1970	EI[c]	8	8.42 ± 0.1	9.26 ± 0.1	8.44 ± 0.10	19 ± 3[h]
1970	E/EI	8				23 ± 3[h]
1982	TE	2	7.69 ± 0.01[i]			(22.5)
1981	PIMS	3		10.3 ± 0.1[j]	(8.1)	(22.5)

[a] Ionization and appearance potentials in eV and D(Mn-Mn) in kcal/mol. [b] TE = thermochemical estimation; EI = electron-impact mass spectrometry; KS = kinetic studies in solution; E/EI = equilibrium studies using electron-impact mass spectrometry; PIMS = photoionization mass spectrometry. [c] Pyrolysis of $Mn_2(CO)_{10}$. [d] Value quoted from ref 4. [e] Pyrolysis of $Mn(CO)_5Cl$. [f] Value quoted from ref 5. [g] Average value from ref 4 and 6. [h] Value corrected to 298 K. Authors give D(Mn-Mn) = 21 ± 3 kcal/mol at 0 K. [i] Adiabatic IP from the photoelectron spectrum of $Mn_2(CO)_{10}$. [j] AP[$Mn(CO)_5^+$] from $Mn(CO)_5H$. This value, taken with D(Mn-Mn) = 22.5 kcal/mol, leads to IP[$Mn(CO)_5$] ≈ 8.1 eV.

in this paper. The complex $Mn(CO)_5Bz$ (Bz = $CH_2C_6H_5$) was chosen for the photoelectron and mass spectrometry studies on the basis of the reported low values for the manganese-benzyl bond dissociation energy[2] and for the adiabatic IP(Bz) = 7.20 ± 0.02.[16]

Experimental Section

The complex $Mn(CO)_5Bz$ was prepared by reaction of Na[$Mn(CO)_5$] with benzyl chloride[17] and purified by sublimation.

He I photoelectron spectra were recorded on a spectrometer of standard design which has been modified to study the products of low-pressure (~10^{-2} torr) gas-phase pyrolysis. Detailed descriptions of the spectrometer and pyrolyzer have been given elsewhere.[16] Spectra were calibrated by using Xe, Ar, and CO (when it was present as a major decomposition product). Resolution was 35-40 meV fwhm as determined from the Ar peaks.

Appearance potentials were obtained by using a previously described ion cyclotron resonance mass spectrometer.[18,19] The ionization efficiency curves were recorded under the following conditions: ion source temperature, ~298 K; filament emission current, 0.2 μA; sample pressure in the ICR cell, ~10^{-7} torr. The electron energy scale was calibrated against the adiabatic ionization potential of $Mn(CO)_5Bz$ obtained from the photoelectron spectrum. This calibration was checked by comparing the measured IP[CH_3I] with the spectroscopic value of 9.538 eV.[20] Ionization and appearance potentials were determined by using the extrapolated voltage difference method.

Hydride transfer reactions were examined by using the ICR mass spectrometer in the trapped ion mode and were identified by double-resonance techniques.

Results and Discussion

Photoelectron Studies. To achieve an adequate sample pressure, the sample and the inlet to the pyrolyzer were heated to ~70 °C. The photoelectron spectrum of $Mn(CO)_5Bz$, taken under these conditions, is shown in Figure 1. A very small amount of CO is observed, indicating the sample decomposes slightly in the inlet during the course of the experiment. The adiabatic ionization potential of $Mn(CO)_5Bz$, assigned to the first photoelectron band onset, is 7.48 ± 0.03 eV. The photoelectron band maxima for the individually resolved bands below 11 eV are 7.84 ± 0.07, 8.50 ± 0.05, 8.97 ± 0.05, and 10.02 ± 0.05 eV. The assignment of these low-energy bands is not straightforward. Comparison of the spectrum of Figure 1 with photoelectron spectra of substituted benzenes[21] and other $Mn(CO)_5R$ derivatives[22] suggests that the bands at 8.97 and 10.02 eV are due to the lowest benzyl π ionizations. There are probably three ionizations at lower energy, corresponding to the metal d orbitals with e and b_2 symmetry, as well as the a_1 metal-ligand bonding orbital (the indicated symmetries are for C_{4v} symmetry; further small splittings are expected in the e orbital due to lower symmetry in the present case).

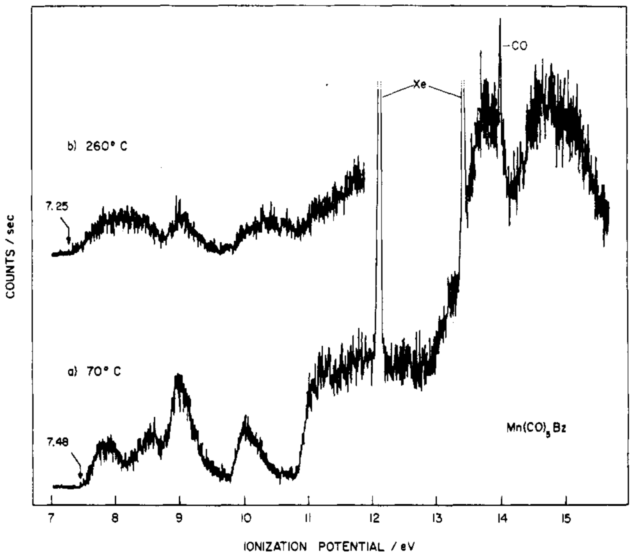

Figure 1. Photoelectron spectra of $Mn(CO)_5Bz$ with the pyrolyzer at (a) 70 °C and (b) 260 °C.

The photoelectron spectrum obtained at a pyrolyzer temperature of 200 °C has the same appearance as that obtained at 70 °C. At a pyrolyzer temperature of 225 °C, there is an increase in the intensity of the peak due to CO. With the pyrolyzer at 260 °C, in addition to detecting even more CO, noticeable changes occur in other regions of the photoelectron spectrum obtained under these conditions (Figure 1). The sharply structured first band of the benzyl radical photoelectron spectrum, with adiabatic and vertical ionization potentials coinciding at 7.20 eV,[16] is *not* evident in the spectrum. Benzyl radical is stable at the tempera-

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Table II. Major Ions Appearing in 70-eV Mass Spectrum of $Mn(CO)_5Bz$

ion	m/e	rel abund
CO^+	28	90.8
Mn^+	55	51.3
$C_5H_5^+$	65	14.3
Bz^+	91	100
$MnBz^+$	146	45.4
$Mn(CO)Bz^+$	174	12.1
$Mn(CO)_2Bz^+$	202	8.1
$Mn(CO)_3Bz^+$	230	11.7
$Mn(CO)_4Bz^+$	258	14.3
$Mn(CO)_5Bz^+$	286	5.9

tures used in this study and should not decompose to other products.

Since few or no benzyl radicals were observed, the changes in the photoelectron spectrum observed at a pyrolysis temperature of 260 °C, besides the increase of the CO spectrum, are probably due mainly to species of composition $Mn(CO)_nBz$ (n = 2–4), particularly since changes occur in an energy region appropriate for d orbital ionizations in manganese. If the onset (7.25 eV) of the first band in the spectrum at 260 °C (Figure 1) was identified with the adiabatic ionization potential of $Mn(CO)_4Bz$, the value $D[Mn(CO)_4(Bz)–CO] \simeq 15$ kcal/mol would be obtained by taking the appearance potential of $Mn(CO)_4Bz^+$ (Table III). We believe this is too low to be assigned to the first Mn–CO bond dissociation energy. A higher value implies that $IP[Mn(CO)_4Bz] < 7.25$ eV. The absence of bands at lower energies suggests therefore that the fragment $Mn(CO)_4Bz$ is not observed in the spectra. This could be confirmed if a mass spectrometer were coupled to the photoelectron spectrometer, an arrangement which would also enable the identification of the other species formed under pyrolysis. Our instrument is not presently equipped for such studies.

While pyrolysis of $Mn(CO)_5Bz$ does not yield the desired $Mn(CO)_5$ radical, the results provide evidence that $D[Mn(CO)_4(Bz)–CO]$ is *less* than $D[Mn(CO)_5–Bz]$. An attempt[23] to obtain $Mn(CO)_5$ radicals from pyrolysis of $Mn_2(CO)_{10}$ was also unsuccessful. The free carbon monoxide spectrum was again observed, suggesting that $D(Mn–Mn) > D(Mn–CO)$. This observation is consistent with the discussion in the introduction relative to these competing processes in condensed phase studies.

Appearance Potentials of Fragment Ions. The relative intensities of the major ions formed in the 70 eV mass spectrum of $Mn(CO)_5Bz$ are presented in Table II, and the breakdown diagram is shown in Figure 2. The high intensity of the benzyl cation peak, which can be explained in terms of the low IP(Bz), contrasts with the rather small intensities of L^+ in the mass spectra of other $Mn(CO)_5L$ complexes (L = CF_3, CHF_2, CH_2F, CH_3).[24] The relative intensities of $Mn(CO)_n^+$ ions in the $Mn(CO)_5Bz$ spectrum (not shown in Table II) are very small: ~3 for n = 1–4 and ~1 for n = 5. It is of interest to note that the decrease in abundance of $MnBz^+$ above 20 eV is accompanied by an increase in Mn^+ and not Bz^+. This suggests that fragmentation of $MnBz^+$ yields mainly manganese cations, despite the fact that IP(Mn) = 7.434 eV[20] is about 0.2 eV higher than IP(Bz).

The measured appearance potentials of fragment ions are collected in Table III. As stated above, the electron energy scale was calibrated against $IP[Mn(CO)_5Bz] = 7.48 \pm 0.03$ eV and checked by measuring the ionization potential of methyl iodide. The result obtained, 9.5 ± 0.1 eV, is in good agreement with the spectroscopic value, 9.548 eV.[20] The photoelectron spectrum of $Mn(CO)_5Bz$ (Figure 1) indicates that ionic states can be populated continuously between 7.5 and 9.5 eV. Hence, it is unlikely that fragmentation thresholds in this energy region are determined spectroscopically.

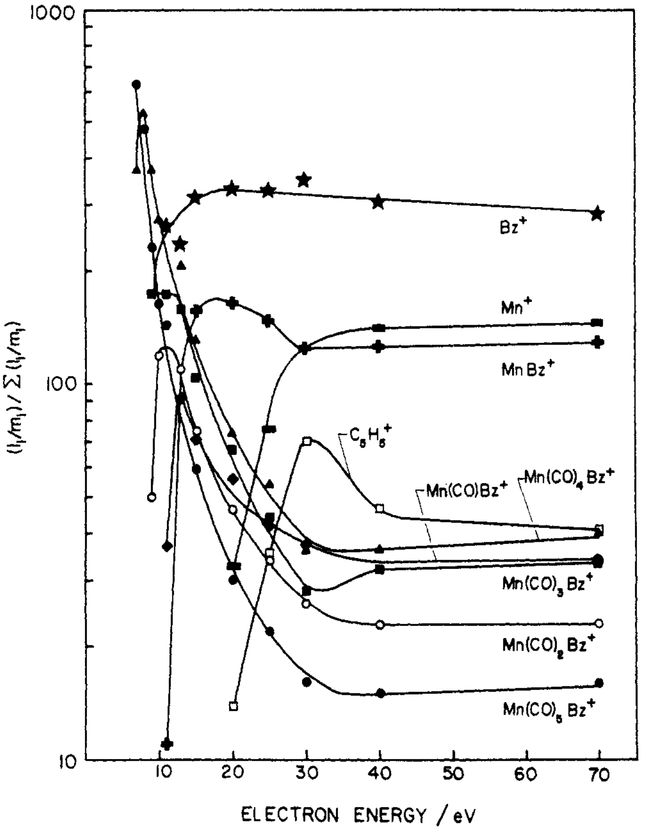

Figure 2. Breakdown diagram of $Mn(CO)_5Bz$.

Table III. Appearance Potentials of $Mn(CO)_{n-1}Bz^+$ (n = 1–5) and Bz^+ Relative to $IP[Mn(CO)_5Bz] = 7.48 \pm 0.03$ eV

ion	AP/eV[a]	ion	AP/eV[a]
$Mn(CO)_4Bz^+$	7.9 ± 0.1	$MnBz^+$	11.7 ± 0.1
$Mn(CO)_3Bz^+$	8.8 ± 0.1	Mn^+	15.2 ± 0.3
$Mn(CO)_2Bz^+$	9.3 ± 0.1	Bz^+	8.6 ± 0.2
$Mn(CO)Bz^+$	10.4 ± 0.1		

[a] Average values determined through the extrapolated voltage difference method and the vanishing current method. The largest disagreement between both methods was 0.2 eV.

The adiabatic ionization potential of benzyl radical, 7.20 ± 0.02 eV,[16] together with $AP(Bz^+)$ from Table III gives $D[Mn(CO)_5–Bz] = 32.3 \pm 5$ kcal/mol, which enables the calculation of $D(Mn–Mn)$ in $Mn_2(CO)_{10}$ through eq 1. By

$$D(Mn–Mn) = 2\Delta H_f°[Mn(CO)_5,g] - \Delta H_f°[Mn_2(CO)_{10},g] = 2D(Mn–Bz) - 2\Delta H_f°(Bz,g) + 2\Delta H_f°[Mn(CO)_4Bz,g] - \Delta H_f°[Mn_2(CO)_{10},g] \quad (1)$$

using the known enthalpies of formation for the gaseous complexes[2] and $\Delta H_f°(Bz,g) = 47.8 \pm 1.5$ kcal/mol,[25] we arrive at $\Delta H_f°[Mn(CO)_5,g] = -169$ kcal/mol and $D(Mn–Mn) = 41 \pm 9$ kcal/mol. Since the measured value for $AP[Bz^+]$ may only be an upper limit, the resulting $D(Mn–Mn)$ must also be regarded as an upper limit. However, it suggests that the assumed $D(Mn–Mn) = 22.5$

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Table IV. Manganese–Carbon Monoxide Bond Dissociation Energies in $Mn(CO)_nBz^+$ (n = 1–5)

process	D_n^+, kcal/mol
$Mn(CO)_5Bz^+ \rightarrow Mn(CO)_4Bz^+ + CO$	$D_1^+ = 10$
$Mn(CO)_4Bz^+ \rightarrow Mn(CO)_3Bz^+ + CO$	$D_2^+ = 21$
$Mn(CO)_3Bz^+ \rightarrow Mn(CO)_2Bz^+ + CO$	$D_3^+ = 12$
$Mn(CO)_2Bz^+ \rightarrow Mn(CO)Bz^+ + CO$	$D_4^+ = 25$
$Mn(CO)Bz^+ \rightarrow MnBz^+ + CO$	$D_5^+ = 30$
	av value $\bar{D}^+ = 20$

kcal/mol is actually too low. This bond energy would correspond to a value for AP(Bz^+) which is 0.4 eV below the observed threshold. Equation 1 shows that D(Mn–Mn) is quite sensitive to the accuracy of D(Mn–Bz), which in turn relies on AP(Bz^+). This appearance potential has been determined with an uncertainty of about 4.6 kcal/mol. If the lower limit D(Mn–Bz) = 27.7 kcal/mol is accepted, then D(Mn–Mn) = 31.7 kcal/mol, $\Delta H_f°[Mn(CO)_5,g] = -173.6$ kcal/mol, and IP[$Mn(CO)_5$] = 7.9 eV. Even considering the possible erros, it appears that the manganese–manganese bond strength in $Mn_2(CO)_{10}$ may be closer to the kinetic result than previously accepted by some workers. The fact that D(Mn–CO) (for loss of the first CO) in $Mn_2(CO)_{10}$ is less than D(Mn–Mn) also supports the notion that the value D(Mn–Mn) = 22.5 kcal/mol is too low since the metal–carbonyl bond dissociation energy would have to be even less. This would be somewhat surprising considering $D[Cr(CO)_5–CO]$ = 36.8 kcal/mol and $D[Fe(CO)_4–CO]$ = 41.5 kcal/mol.

The variation of AP[$Mn(CO)_nBz^+$] with n follows the same general behavior observed for other transition-metal carbonyl complexes.[20,27–29] The manganese–carbonyl bond dissociation energies, obtained by using eq 2 or 3 (n = 2–5),

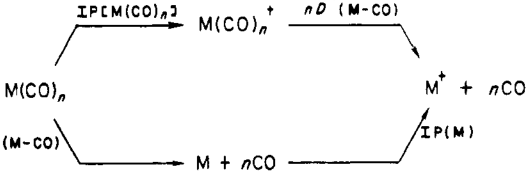
$$D_1^+ = D[Mn(CO)_4(Bz)^+CO] = AP[Mn(CO)_4Bz^+] - IP[Mn(CO)_5Bz] \quad (2)$$

$$D_n^+ = D[Mn(CO)_{5-n}(Bz)^+–CO] = AP[Mn(CO)_{5-n}Bz^+] - AP[Mn(CO)_{6-n}Bz^+] \quad (3)$$

are presented in Table IV together with the mean bond dissociation energy in the ion, $\bar{D}^+$. These results are expected to be upper limits to the true values. The thermodynamic threshold for AP(Mn^+) is calculated from literature data [2,20,30,31] as 13.3 eV. This is 1.9 eV less than the measured value (Table III). Even if there is only a small excess energy involved in each dissociation process, the additive effect of six sequential fragmentations leads to a substantial "kinetic shift" in the appearance potential of Mn^+.

The available studies on transition-metal carbonyls show that the metal carbonyl mean bond dissociation energy for the neutral complex, $\bar{D}$(M–CO), usually exceeds $\bar{D}^+$(M–CO). For example, $\bar{D}$(M–CO) – $\bar{D}^+$(M–CO) is 5 kcal/mol for $Cr(CO)_6$, 0 kcal/mol for $Fe(CO)_5$, 3 kcal/mol for $V(CO)_6$, and 4 kcal/mol for $Ni(CO)_4$.[27,29] Note that these differences are independent of the appearance potentials of $M(CO)_n^+$ ions and rely only on the adiabatic ionization potential of $M(CO)_n$ and on the ionization potential of the metal, as evidenced by Scheme I and eq 4.

Scheme I



$$\bar{D}(M–CO) - \bar{D}^+(M–CO) = \{IP[M(CO)_n] - IP(M)\}/n \quad (4)$$

The manganese–carbon monoxide *mean* bond dissciation energy in the radical $Mn(CO)_5$ is 22.5 kcal/mol [with D(Mn–Mn) = 22.5 kcal/mol] or 21.5 kcal/mol [with D(Mn–Mn) = 31.7 kcal/mol]. A considerable difference in D(Mn–Mn) has therefore a small effect on $\bar{D}$(Mn–Co). In any case, this quantity is 2–3 kcal/mol higher than $\bar{D}^+$(Mn–CO) in $Mn(CO)_5Bz^+$ which suggests, by looking at the quoted $\bar{D}$(M–CO) – $\bar{D}^+$(M–CO) results for several metal carbonyls, that $\bar{D}^+$(Mn–CO) is farily constant in different $Mn(CO)_5L^+$ complexes.

As a final point, it should be noted that we have considered the $C_7H_7^+$ fragment formed by electron impact from $Mn(CO)_5$ to have the benzyl cation structure. The tropylium ion is 4.4 kcal/mol (0.19 eV) more stable[32] and might be produced by a rearrangement process near threshold. If this is the case, then the true threshold for benzyl cation would be 0.19 eV higher and the derived bond energy $D[Mn(CO)_5–Bz]$ would be stronger by the same amount. From eq 1, D[Mn–Mn] in $Mn_2(CO)_{10}$ would be increased by 8.8 kcal/mol. Although we do not have the means to identify the structure of the $C_7H_7^+$ ion formed at threshold, rearrangement would only serve to further reinforce our conclusions regarding the strength of the $(CO)_5Mn–Mn(CO)_5$ bond.

Gas-Phase Ion Chemistry of $Mn(CO)_5Bz$. Although it is not produced by electron impact, the metal carbene ion $Mn(CO)_5CHPh^+$ is formed in abundance in the ICR cell at longer reaction times (10–130 ms) by reaction 5, as

$$Mn^+ + Mn(CO)_5Bz \rightarrow Mn(CO)_5CHPh^+ + MnH \quad (5)$$

demonstrated by double-resonance techniques, indicating that $D[Mn(CO)_5CHPh^+–H^-]$ is lower than $D(Mn^+–H^-)$ = 196 kcal/mol.[15] This contrasts with the fact that reaction 6 was not observed in similar experiments. In this case

$$Mn^+ + Mn(CO)_5CH_3 \rightarrow Mn(CO)_5CH_2^+ + MnH \quad (6)$$

$D[Mn(CO)_5CH_2^+–H^-]$ = 221 kcal/mol[15] is higher than the hydride affinity of manganese ion. The resonance stabilization of the phenyl carbene must be responsible for its greater stability as compared with methylene carbene.

Attempts to observe reactions 7 or 8, where $Mn(CO)_5CH_2^+$ and $Mn(CO)_5CHF^+$ were produced by fluorine or hydride abstraction from $Mn(CO)_5CH_2F$, were not successful even at long delay times (1 s), despite the fact that reaction 7 is exothermic by at least 25 kcal/mol.[32] Steric effects may account for the fact that these reactions are too slow to be observed.

$$Mn(CO)_5CH_2^+ + Mn(CO)_5Bz \rightarrow Mn(CO)_5CHPh^+ + Mn(CO)_5CH_3 \quad (7)$$

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(32) The heats of formation of benzyl and tropylium cations are 214.0 ± 1.5 and 209.6 ± 2.0 kcal/mol, respectively. The latter value is calculated by using ΔH_f(tropyl radical) = 64.8 kcal/mol[25] and IP(tropyl radical) = 6.28 eV, from: Koenig, T.; Snell, W.; Chang, J. C. *Tetrahedron Lett.* **1976**, *50*, 4569.

$$Mn(CO)_5CHF^+ + Mn(CO)_5Bz \rightarrow Mn(CO)_5CHPh^+ + Mn(CO)_5CH_2F \quad (8)$$

Mixtures of $Mn(CO)_5Bz$ and D_2 did not show evidence for H/D exchange in any of the fragment ions. Only the deuterated species $Mn(CO)_n(Bz)(D)^+$ were observed (n = 0-4). The proton affinity of the complex was not measured.

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Registry No. $Mn(CO)_5Bz$, 14049-86-6; $[(CO)_5Mn-Mn(CO)_5]$, 10170-69-1.

Preparative and Reaction Chemistry of the Bimetallic μ-Formate and μ-Acetate Complexes $[(\eta\text{-}C_5H_5)(CO)_2Fe]_2O_2CR^+PF_6^-$

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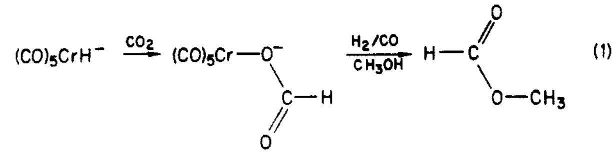
Unidentate η^1-*O* Fp–O_2CR and bimetallic μ-(η^1-*O,O'*) $Fp_2(O_2CR)^+PF_6^-$ carboxylate complexes (R = H, CH_3) have been synthesized and characterized [Fp = (η^5-C_5H_5)$(CO)_2Fe$]. Even though only a formate or acetate ligand bridges the Fp centers, these Fp_2 μ-carboxylate salts do not dissociate in even polar solvents. Nucleophilic hydride donors and other nucleophiles (I^-, PPh_3) cleave these bimetallic salts via direct displacement at an iron center. No evidence was found, using labeling studies, for hydride addition to the μ-(η^1-*O,O'*)-formate bridge and transience of a μ-(η^1-*O,O'*)-methylenedioxy ligand, Fp–OCH_2O–Fp.

Introduction

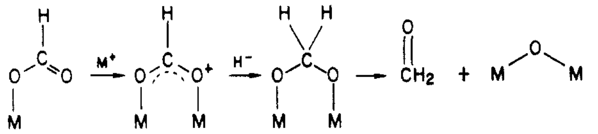
The reduction of carbon dioxide that is suitably ligated to a transition organometallic complex offers an alternative and potentially unique source of C_1 ligands. Most studies to date have elaborated on transforming a metal hydride complex plus CO_2 into coordinated formate.[1] In one set of studies by Darensbourg and co-workers, anionic group 6 metal pentacarbonyl formates—prepared by this procedure—further functioned as catalysts in converting CO_2 (in methanol) to methyl formate (eq 1).[2] Examples



$$(CO)_5CrH^- \xrightarrow{CO_2} (CO)_5Cr{-}O{-}C(H){=}O^- \xrightarrow[CH_3OH]{H_2/CO} H{-}C(=O){-}O{-}CH_3 \quad (1)$$

also abound in the heterogeneous catalysis literature for hydrogenating carbon dioxide (as opposed to CO_2-derived CO) to methanol or to methane—possibly involving formate intermediates.[1] Given these developments it is surprising that information on reducing formate ligated to transition organometallic complexes is generally lacking.

We are interested in establishing coordinated ligand transformations and reaction conditions for reducing ligated formate to formaldehyde (or to methanol). Equation 2 illustrates, as a working hypothesis, one such set of reactions that uses a bimetallic μ-(η^1-*O,O'*)-formate complex 1 as the C_1-template. Its reduction could afford a μ-methylenedioxy system 2[3,4] that subsequently either extrudes formaldehyde or eliminates the starting formate complex $M(O_2CH)$ and metal hydride MH. As possible precedent for the former pathway (eq 2) the reaction between



$$M{-}O{-}C(H){=}O \xrightarrow{M^+} [M{-}O{\cdots}C(H){\cdots}O{-}M]^+ \xrightarrow{H^-} M{-}O{-}CH_2{-}O{-}M \rightarrow O{=}CH_2 + M{-}O{-}M \quad (2)$$

1 2

Cp_2ClZrH and CO_2 has been reported by Floriani and co-workers[5] to give $(Cp_2ClZr)_2O$ and formaldehyde. The general problem, however, remains: Carboxylate ligands even as their μ-carboxylate complexes 1 are well established,[6] but their reductive chemistry remains to be developed. With this impetus we now report (1) preparation of examples of symmetrical, bridging μ-(η^1-*O,O'*)-carboxylate compounds 1 from the known Cp-

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[1] (a) Eisenberg, R.; Hendrickson, D. E. *Adv. Catal.* **1979**, *28*, 79. (b) Sneeden, R. P. A. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1982, Vol. 8, Chapter 50.4. (c) Ito, T.; Yamamoto, A. In "Organic and Bio-organic Chemistry of Carbon Dioxide"; Inoue, S., Yamazaki, N., Eds.; Wiley: New York, 1982; Chapter 3. (d) Darensbourg, D. J.; Kudaroski, R. A. *Adv. Organomet. Chem.* **1983**, *22*, 129. (e) Behr, A. In "Catalysis in C_1 Chemistry"; Keim, W., Ed.; D. Reidel Publishers: Boston, 1983; pp 169–219.

[2] Darensbourg, D. J.; Rokicki, A.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **1981**, *103*, 3223. Darensbourg, D. J.; Rokicki, A. *Organometallics* **1982**, *1*, 1685. Darensbourg, D. J.; Ovalles, C. *J. Am. Chem. Soc.* **1984**, *106*, 3750.

[3] A methylenedioxy complex results when formaldehyde forms its μ-(η^1-*O,O'*) acetyl molybdate on polyoxomolybdate. Day, V. W.; Fredrich, M. F.; Klemperer, W. G.; Liu, R.-S. *J. Am. Chem. Soc.* **1979**, *101*, 491. Examples of complexes containing methylenedithio ligands are more common; and in a future publication we will present the reaction chemistry of the fully characterized $FpSCH_2SFp$. Menard, K.; Cutler, A. manuscript in preparation.

[4] R. S. Sapienza, W. A. Slegeir, and co-workers have discussed the possible role of similar dioxymethylene species during heterogeneous catalysis of CO_2 methanation: Sapienza, R. S.; Sansone, M. J.; Spaulding, L. D.; Lynch, J. F. In "Fundamental Research in Homogeneous Catalysis"; Tsutsui, M., Ed.; Plenum Press: New York, 1979; Vol. 3. We thank Richard Sapienza (Brookhaven National Laboratories) for helpful correspondence on this matter.

[5] Fachinetti, G.; Floriani, C.; Roselli, A.; Pucci, S. *J. Chem. Soc., Chem. Commun.* **1978**, 269. It is worth emphasizing that this reaction differs from that of CO and Cp_2ClZrH; here an η^2-formaldehyde complex bridging two Zr centers results. Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1983**, *105*, 1690. Kropp, K.; Skibbe, V.; Erker, G.; Kruger, C. *Ibid.* **1983**, *105*, 3353 and references cited.

[6] Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980; p 170. Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley-Interscience: New York, 1982.

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