and moisture-free argon atmosphere. The flask was placed in an oil bath and heated to 120 °C, where the solid liquefied, creating a yellow-green solution. The apparatus was then evacuated and back-filled with argon. The temperature was raised to 140–150 °C for 4 h with occasional evacuation and back-filling with argon. The vacuum is very important, for it removes trimethylsilanes III, IV, and V. During this time, the color of the solid changed from light yellow to pale yellow and finally to dark orange. A liquid byproduct was produced in the reaction and was determined to be a mixture of THF and hexamethyldisilane by ^{1}H NMR and mass spectroscopy. The orange solid was placed in a vacuum line trap under argon. The trap was then evacuated, and an excess of d_1-ethyl alcohol was transferred into the trap along with ethyl ether. The contents were stirred overnight to complete the hydrolysis reaction. Analysis of the mixture by GC/MS revealed four major components: $(Me_3Si)_2SiD_2$ (35%), $(Me_3Si)_3SiD$ (22%), $(Me_3Si)_4Si$ (10%), and $(Me_3Si)_3SiSi(SiMe_3)_3$ (27%). If the reaction is carried out for longer periods of time, more of the coupling product $Si_2(SiMe_3)_6$ (V) is produced at the expense of the dilithio compound. Mass spectral analysis of the deuterated product $(Me_3Si)_2SiD_2$ showed a molecular ion at 178 (10%) and a base peak at m/e 73 corresponding to Me_3Si^+; other peaks at 163 and 90 are indicative of $Me_5Si_3D_2$ and $Me_2Si_2D_2$.

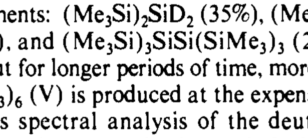
The product also derivatized with methyl iodide to give a 27% yield of bis(trimethylsilyl)dimethylsilane:[10]

$$\underset{\text{II}}{(Me_3Si)_2SiLi_2} \xrightarrow{CH_3I} \underset{27\%}{(Me_3Si)_2Si(CH_3)_2}$$

A solid sample of $(Me_3Si)_2SiLi_2$ was studied by flash vaporization mass spectroscopy using methods previously reported.[3,11] Direct observation of the parent ions for both the monomer and dimer of the new dilithiosilane revealed the parent ions

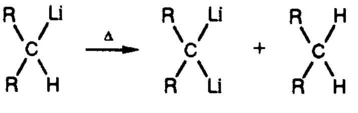
$$\underset{P_I}{[(Me_3Si)_2SiLi_2]_2^+} \qquad \underset{P_{II}}{[(Me_3Si)_2SiLi_2]^+}$$

plus $[P_I - (SiMe_3)]^+$, $(P_I - CH_3)^+$, $(P_I - H)^+$, $(P_{II} - CH_3)^+$, and $(P_{II} - H)^+$. The structure of the molecular ion of the dimer is most probably



The structures of the gas-phase monomers and dimers are under study.[12]

This reaction bears a similarity to our studies of the Kawa–Lagow modified Ziegler rearrangement[1,2] in which a disproportionation reaction takes place with proton transfer:



However, on the silicon center, the trimethylsilyl group is the moiety transferred. It is probable that species III and V are produced by thermal rearrangement of IV.

Acknowledgment. We are grateful to the National Science Foundation (CHE-9012405) and the Robert A. Welch Foundation (F-700) for support of this work.

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[10] Mass spectral analysis of octamethyltrisilane m/e: M^+ 204 (23.5) $(M - Me)^+$ 189 (16), $(M - TMS)^+$ 131 (78.9), $(M - Me - TMS)^+$ 116 (44), $[(TMS)Si]^+$ 101 (8.5), and $(TMS)^+$ 73 (100). ^{1}H NMR (ppm): 0.062, 0.075.

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[12] Work in progress in collaboration with Josef Michl and co-workers.

Nucleophilic Attack at C2 of Neutral (η^5-Pentadienyl)manganese Complexes: Formation of σ,η^3-Manganese Complexes

Bernard C. Roell, Jr., and Keith F. McDaniel*

Department of Chemistry, Ohio University
Athens, Ohio 45701

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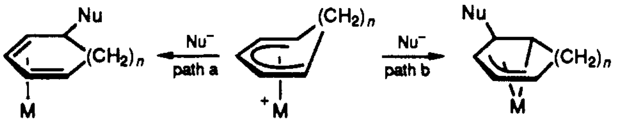
The reaction of nucleophiles with a wide variety of transition-metal π-complexes has been documented and utilized extensively in organic synthesis.[1] This literature includes many examples utilizing η^5-dienyl transition-metal complexes, mainly cationic (η^5-cyclohexadienyl)iron complexes.[2] In most cases, attack at the terminus of the π-system provides substituted η^4-diene metal complexes (eq 1, path a). The literature contains only scattered reports of this reaction with η^5-pentadienyl complexes,[2c,3] however, and a growing body of evidence indicates that the use of certain η^5-pentadienyl[4] and also η^5-cycloheptadienyl[5] systems promotes nucleophilic attack at the internal C2 position, generating σ,η^3-transition-metal complexes (eq 1, path b).[6] It has also been determined that the use of relatively soft nucleophiles and electron rich metal centers promotes reaction at the C2 position of the η^5-dienyl π-system.[4a-c,e,5a,7] Although the chemistry of σ,η^3-complexes generated by this reaction has not been explored in detail, several noteworthy reactions of these pentenediyl complexes have been reported.[5a,d,8] Our interest in the chemistry of η^5-pentadienyl and σ,η^3-transition-metal complexes led us to investigate the reaction of nucleophiles with (η^5-pentadienyl)manganese complexes. In this paper we report that the reaction of certain



(1)

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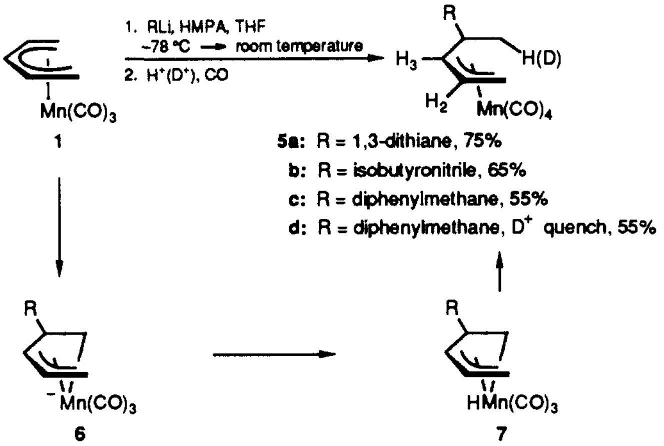
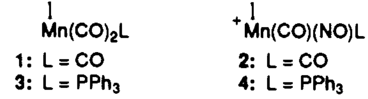
Scheme I



nucleophiles with neutral tricarbonyl(η^5-pentadienyl)manganese takes place regioselectively at C2, generating novel (σ,η^3-pentenediyl)manganese complexes.

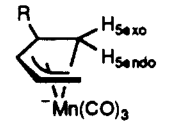
Although the reactivity of cationic (η^5-cyclohexadienyl)- and (η^5-cycloheptadienyl)manganese complexes with nucleophiles has been investigated in detail,[9] the literature contains few reports of the chemistry of the acyclic analogue.[10] Tricarbonyl(η^5-pentadienyl)manganese (**1**) is readily available by the reaction of bromomanganese pentacarbonyl with trimethyl-2,4-pentadienylstannane in refluxing tetrahydrofuran,[10a] but in our hands attempts to prepare cationic nitrosyl(dicarbonyl)(η^5-pentadienyl)manganese complex **2** (eq 2), under a variety of nitrosation conditions, were unsuccessful. Especially perplexing was the failure of this reaction under conditions used for the preparation of the analogous cationic (η^5-cyclohexadienyl)- and (η^5-cycloheptadienyl)manganese complexes.[9,11] Reaction of the triphenylphosphine-substituted (η^5-pentadienyl)manganese complex **3**[12] under typical nitrosation conditions also failed to produce the desired cationic complex **4**. In light of this difficulty, an investigation of the reactivity of the neutral complex **1** was initiated. Whereas the reactivity of cationic η^5-dienyl complexes has been thoroughly investigated, the literature contains few reports of nucleophilic attack on neutral η^5-dienyl transition-metal complexes.[13]



(2)

It was discovered, in fact, that the reaction of **1** with nucleophiles in tetrahydrofuran and hexamethylphosphoric triamide (HMPA), followed by quenching with either trifluoroacetic acid or saturated aqueous ammonium chloride solution in the presence of carbon monoxide, provided (π-allyl)manganese complexes **5**[14] in 50–75% yield (Scheme I). Formation of the anti isomer was confirmed by the observation of ^{1}H nuclear magnetic resonance coupling constants of approximately 7–9 Hz between protons H_2 and H_3.[15] When the reaction is run without HMPA, the yields are approximately 10–20% lower, and acid quenching of the reaction mixture without the addition of carbon monoxide lowers the overall yield by approximately 10%. It appears that nucleophilic attack takes place regiospecifically at the internal C2 position of the π-system, generating the novel anionic σ,η^3-manganese complex **6**. Reaction of **6** with acid then generates manganese hydride **7**, which undergoes reductive elimination followed by addition of carbon monoxide to form π-allyl complex **5**. Quenching of anion **6** (R = Ph_2CH) with deuterated trifluoroacetic acid provides π-allyl complex **5e**, in which the methyl group contains a deuterium atom.

Further proof for attack at C2 and formation of σ,η^3-complex **6** was obtained from the ^{1}H nuclear magnetic resonance spectrum collected during the reaction of 2-lithio-1,3-dithiane with complex **1** in tetrahydrofuran-d_8. This spectrum contains a triplet (J = 8.3 Hz) at −2.21 ppm, a highly shielded signal which is characteristic for the endo proton (H_{5endo}) attached to the carbon σ-bonded to the metal in σ,η^3-transition-metal complexes.[4a,b,e] In addition, the signal for the exo proton (H_{5exo}) appears as a triplet (J = 9.5 Hz) at −0.40 ppm, and the carbon-13 signal for this carbon comes at 0.82 ppm.



6a: R = 1,3-dithiane

Nucleophilic attack at the internal C2 position of the neutral (η^5-pentadienyl)manganese complex **1**, in preference to attack at the terminus of the π-system as is reported with cationic (η^5-dienyl)manganese complexes, bears a striking resemblance to the reactivity of neutral and cationic η^4-diene transition-metal complexes. For example, Semmelhack and Herndon[16] have demonstrated that the reaction of a variety of nucleophiles with neutral η^4-diene iron complexes provides anionic σ,η^2-iron complexes, the result of attack at C2 of the η^4-diene complex. On the other hand, the reaction of nucleophiles with cationic η^4-diene cobalt complexes takes place solely at the terminus of the π-system.[17] Molecular orbital calculations also predict that attack should take place at the internal position with neutral η^4-diene complexes whereas nucleophilic attack at the terminus of the π-system is favored with cationic η^4-diene complexes.[18] Similar calculations are planned for the comparison of neutral and cationic η^5-pentadienyl complexes.

The preparation of σ,η^3-manganese complexes via regiospecific nucleophilic attack at the internal C2 position of neutral (η^5-pentadienyl)manganese complexes has thus been demonstrated, and the scope and generality of this reaction, as well as the reactivity of neutral (η^5-cyclohexadienyl)- and (η^5-cycloheptadienyl)manganese complexes with nucleophiles, is currently under investigation. Preliminary results indicate that significant differences in reactivity exist between the η^5-pentadienyl, η^5-cyclohexadienyl, and η^5-cycloheptadienyl complexes. The reactivity of anionic σ,η^3-manganese complexes is also being explored in these laboratories, and results will be reported shortly.

Acknowledgment. This work was funded in part by the Ohio University Research Committee. The help of Dr. Cathy Sultany in obtaining 400-MHz NMR spectra is greatly appreciated. High-resolution mass spectral determinations were performed by the Midwest Center for Mass Spectrometry, a National Science

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Foundation Regional Instrumentation Facility (Grant No. CHE 8211164).

Supplementary Material Available: Experimental details and spectral and analytical data for the formation of π-allyl complexes **5** (3 pages). Ordering information is given on any current masthead page.

Cs^+-Induced Dehydration Reaction in $Cs[methanol]_N^+$ Cluster Ions

Jeffrey A. Draves and James M. Lisy*,†

Department of Chemistry, University of Illinois
Urbana, Illinois 61801

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We report the observation of an alkali ion induced dehydration reaction in cluster ions $Cs[CH_3OH]_N^+$ and $Cs[CD_3OD]_N^+$. This gas-phase reaction differs in two respects from similar reactions reported in protonated methanol clusters.[1,2] First, the energy needed for the reaction is obtained via collision–solvation of a Cs^+ with methanol, and second, Cs^+ acts as the charge center. The observation of this reaction suggests the possibility of a catalytic effect.

The ion clusters are formed by merging Cs^+ from a thermionic filament with neutral methanol clusters from a molecular beam expansion in an apparatus described elsewhere.[3] The mass spectrum of the clusters is shown in Figure 1A. Two progressions are observed; the first is due to $Cs[CH_3OH]_N^+$, and the second which occurs 18 amu higher has the form $Cs[CH_3OH]_N[H_2O]^+$. These cluster ions bearing water may be formed (I) in the expansion, requiring the presence of water in the methanol, (II) as a result of reaction 1 where the water is coming from background water vapor

$$Cs[CH_3OH]_N^+ + H_2O \rightarrow Cs[CH_3OH]_{N-M}[H_2O]^+ + M(CH_3OH) \quad (1)$$

and (III) as the result of reaction 2, an intracluster reaction.

$$Cs[CH_3OH]_N^+ \rightarrow Cs[CH_3OH]_{N-M}[H_2O]^+ + CH_3OCH_3 + (M-2)(CH_3OH) \quad (2)$$

We believe that mechanism III is the most likely for the following reasons. The methanol used contains only trace amounts (0.05%) of H_2O. The cluster distribution of $Cs[CH_3OH]_N[H_2O]^+$ from expansions of methanol solution with 20% water was observed to have a maximum intensity for $N = 6$ and decreased for higher mixed clusters. This is consistent with the results of Stace,[4] who found that 1% solutions of methanol in water exhibited their most intense methanol–water peak for the subunit ratio 1:1 followed by decreasing intensities of the 1:2, 1:3, etc. ratios. Thus, a small percentage of water in methanol would be expected to have its most intense mixed cluster peak at a small cluster size and larger mixed cluster peaks would be found with decreasing intensity. This is *not* observed, as Figure 1A clearly shows the intensity of the mixed cluster peak increasing with cluster size. We may therefore discount mechanism I.

We may confirm mechanism III by using CD_3OD to solvate the Cs^+. Products of reaction 2 occurring in clusters of the form $Cs[CD_3OD]_N^+$ will be $Cs[CD_3OD]_{N-2}[D_2O]^+$ and CD_3OCD_3. Figure 1B shows the results of this test. The peak between $Cs[CD_3OD]_{19}^+$ and $Cs[CD_3OD]_{20}^+$ is now 20 amu higher than that for $Cs[CD_3OD]_{19}^+$ and is due to $Cs[CD_3OD]_{19}[D_2O]^+$. Thus, it appears clear that the reaction is indeed occurring as a result of mechanism III. Mechanism II is also eliminated by this test since it is highly unlikely that D_2O is being picked up from background vapor. The value of M in reaction 2 cannot be determined with our current apparatus. For protonated methanol clusters, a value of $M = 3$ was observed.[1]

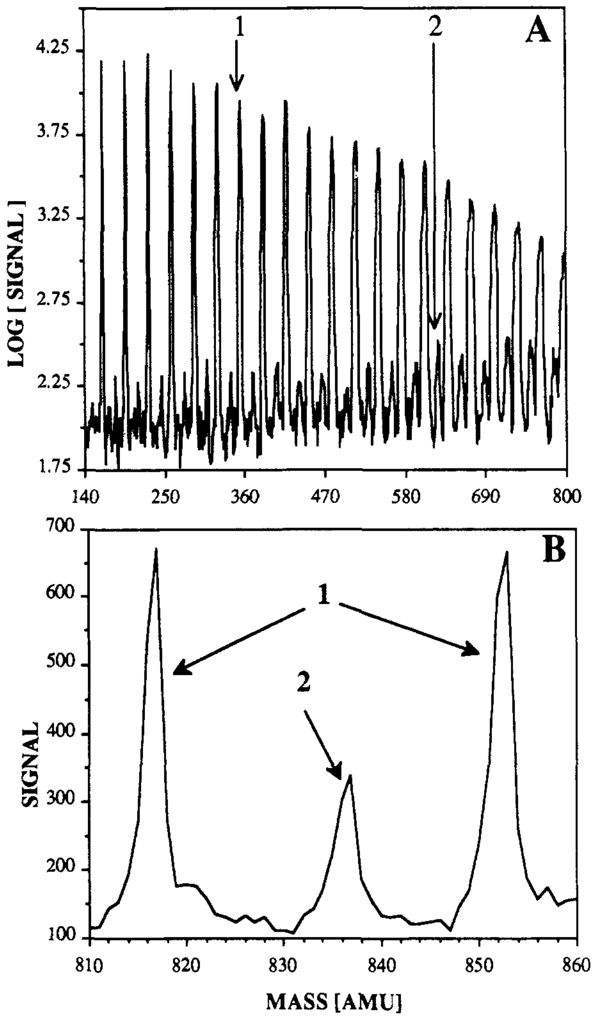

Figure 1. Mass spectrum of $Cs[CH_3OH]_N^+$ (A) and $Cs[CD_3OD]_N^+$ (B). Part A shows the mass spectrum of $Cs[CH_3OH]_N^+$, progression 1, for N = 1 to 21. Progression 2 indicates a cluster of the form $Cs[CH_3OH]_N[H_2O]^+$. Part B shows the mass spectrum of $Cs[CD_3OD]_N^+$. The peaks labeled 1 are the clusters $Cs[CD_3OD]_N^+$, N = 19, 20. The peak labeled 2 is the cluster $Cs[CD_3OD]_{19}[D_2O]^+$.

The gas-phase reaction between $CH_3OH_2^+$ and CH_3OH to produce $(CH_3)_2OH^+$ and H_2O is exoergic ($\Delta G° = -13.26$ kcal/mol[5]) but has a considerable activation energy of 26.5 kcal/mol.[6] The gas-phase reaction of two methanols to form dimethyl ether and water is slightly exoergic ($\Delta G° = -4.56$ kcal/mol[5]) but with an activation barrier that is comparable if not larger than the protonated case. The energy to overcome this barrier is apparently supplied from the collision and solvation of the Cs^+ ion. All of the Cs^+ produced via thermionic emission are in the ground ($^1S_0$) electronic state since the lowest lying excited state (^3P) is 13.4 eV above ground.[7] Thus electronic excitation

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[*] Author to whom correspondence should be addressed.

[†] Alfred P. Sloan Fellow.

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