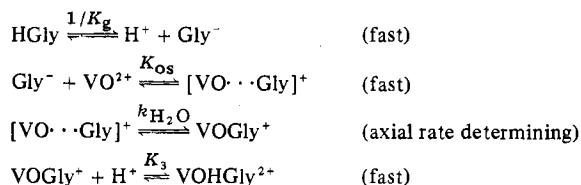


In the case of oxovanadium(IV) complexes, the intermediate species are relatively stable and their properties can be observed directly. Furthermore, the differences in lability between axially^{14,20} and equatorially coordinated species have been measured and $k_{\text{H}_2\text{O}}(\text{axial})$ and $k_{\text{H}_2\text{O}}(\text{equatorial})$ differ by at least a factor of 10^6 . Clearly, this rules out mechanisms of the type



in that the formation processes are independent of acid and the stable species in the pH region of concern is VOHGly^{2+} .

An additional mechanism recently proposed by Margerum²² also involves formation of the chelated product. This mechanism, in the case of the glycine complex, would not involve initial coordination of the carboxyl group, even though it is the more stable species thermodynamically, but initial coordination of the amino group followed by rapid chelation of the carboxyl group.

If this mechanism were valid for reactions with oxovanadium(IV), the chelation step for oxalic acid should not be observable and no difference should be observed between malonic acid and oxalic acid. Clearly this is not the case, and in each reaction, the major difference is reflected in changes in ΔS^\ddagger and not ΔH^\ddagger .

In conclusion, we have shown that the oxovanadium(IV) species is a particularly useful probe in attempting to understand the microscopic details of chelate reactions in that the monodentate oxovanadium(IV) intermediates can be observed directly because of marked differences in lability between coordination in the axial and equatorial positions.

Acknowledgment. The authors wish to express their appreciation to the Japanese Society for the Promotion of Science

and the National Science Foundation [International Science Activities, United States–Japan Cooperative Science Program] for financial support of this research.

Registry No. VOHGly^{2+} , 58281-22-4; $\text{VO}(\text{Gly})^+$, 58281-23-5.

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Synthesis and Fluxional Behavior of (η^5 -Cycloheptatrienyl)tricarbonylmanganese. Rearrangement by 1,2 Shifts

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Received September 5, 1975

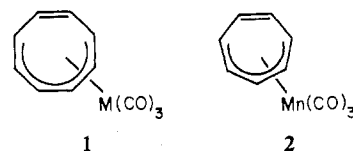
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The synthesis of the π -excessive fluxional molecule (η^5 -cycloheptatrienyl)tricarbonylmanganese by low-temperature photochemical decarbonylation of (7-cycloheptatrienyl)pentacarbonylmanganese is described. Low-temperature NMR studies confirm the structure as the expected η^5 species. Characterization of the mechanism of the fluxional rearrangement by ^{13}C NMR clearly demonstrates a 1,2 shift mechanism. The random or 1,3 shift process observed for (η^6 -cyclooctatetraene)tricarbonylmolybdenum is thus unique among characterized mononuclear ring whizzers. The existence of only a single uncomplexed bond is not sufficient to guarantee such a mechanism.

Introduction

Over the last several years a substantial number of organometallic species have been shown to display fluxional behavior involving the sequential occupation by a metal fragment of several equivalent locations around the periphery of a continuously conjugated cyclic polyolefin. Such molecules, known as "ring whizzers", have been the subject of intensive study,¹ particularly by Cotton and co-workers,² who have in several cases characterized the detailed nature of the fluxional process by NMR line shape analysis. By far the most commonly observed mechanism involves the occupation of

adjacent sites by the metal atom; i.e., the rearrangement occurs via 1,2 shifts. Recently, Cotton, Hunter, and Lahuerta³ described a study of $\text{COTM}(\text{CO})_3$ ($M = \text{Cr}, \text{Mo}, \text{W}$), **1**. In



these cases, line shape analysis shows that either a 1,3 shift or a random process (indistinguishable in the eight-membered

ring) was occurring. As pointed out by Cotton,³ this unique result suggested the possibility that the presence of only *one* uncomplexed double bond might allow a nonselective rearrangement pathway and encouraged us to carry out similar experiments on $(\eta^5\text{-cycloheptatrienyl})\text{tricarboxylmanganese}$, **2**, whose synthesis we described briefly some years ago.⁴ Here we report the results of this work, together with experimental details for the synthesis of compound **2**. The unequivocal result is that **2**, unlike **1**, rearranges by sequential 1,2 shifts.

Experimental Section

General Data. All reactions involving organometallic species were carried out under an atmosphere of dry nitrogen. Saturated hydrocarbon solvents were purified by stirring with concentrated H_2SO_4 and then distillation from KOH pellets. Benzene, tetrahydrofuran (THF), and diethyl ether were distilled under N_2 from benzophenone-sodium mixtures. In the case of benzene, this treatment resulted in distillation from a suspension of benzophenone ketyl, whereas the ethers were distilled from purple solutions of benzophenone dianion. The variable-temperature proton NMR studies were carried out on a Varian A-60A spectrometer; ^{13}C NMR work was carried out on a Bruker WH-270 instrument operating in the FT mode. Temperature readings were calibrated by means of a thermocouple contained in an NMR tube inserted directly into the probe. The line shapes shown in Figure 2 were produced by a program written by T.H.W. based on equations developed by C. S. Johnson⁵ and executed on the Madison Area Computing Center's Univac 1110 computer.

(7-Cycloheptatrienylacyl)pentacarbonylmanganese, 4. The preparation of 7-cycloheptatrienylacyl chloride **3** was carried out according to the method of Dewar and Pettit.⁶ A solution of the acid chloride (5.5 g, 36 mmol) in 20 ml of THF was added dropwise to sodium pentacarbonylmanganate (36 mmol dissolved in 180 ml of THF, prepared from $\text{Mn}_2(\text{CO})_{10}$ and sodium amalgam by the method of King⁷). The mixture was stirred at room temperature for 45 min, and then the volume of the solution reduced to about 25 ml by evaporation under reduced pressure. The residue was diluted with about 1 l. of water and extracted with hexane. The hexane layer was dried (MgSO_4), filtered, and evaporated under reduced pressure to yield a yellow solid. This material was triturated with 400 ml of hexane and filtered, and the filtrate was cooled to -78°C . The metal acyl precipitated as a pale yellow solid: 7.6 g (67%); mp 83°C dec; ir (pentane) 2115, 2050, 2005 cm^{-1} (MCO), 1652 cm^{-1} (acyl CO); NMR (benzene- d_6) δ 6.30 (m, 2 H, $\text{H}_{3,4}$), 6.18 (m, 2 H, $\text{H}_{2,5}$), 4.96 (m, 2 H, $\text{H}_{1,6}$), 2.79 (t, $J = 7$ Hz, 1 H, H_7). Anal. ($\text{C}_{13}\text{H}_7\text{O}_6\text{Mn}$) H, Mn; C: calcd, 49.71; found, 49.25.

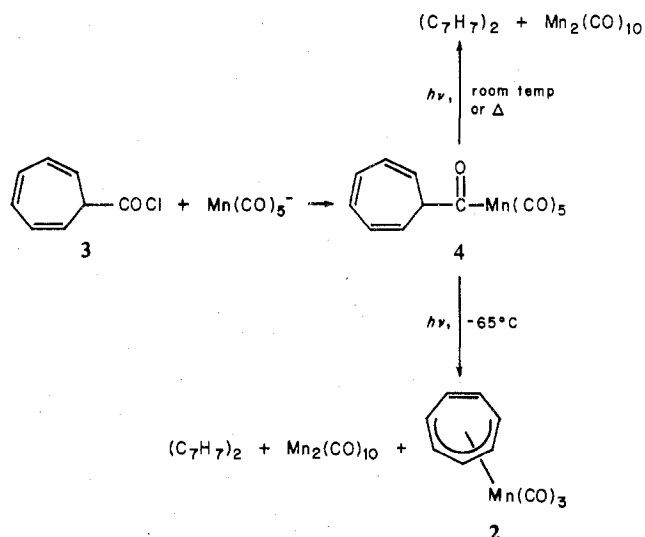
Reaction of $\text{NaMn}(\text{CO})_5$ with $\text{C}_7\text{H}_7\text{BF}_4$. Cycloheptatrienyl tetrafluoroborate, 295 mg (5 mmol), was dissolved in 5 ml of THF. The solution was cooled to -78°C and a THF solution containing 5 mmol of $\text{NaMn}(\text{CO})_5$ was added via syringe. In successive trials, the resulting solution either was allowed to warm gradually to room temperature or was subjected to photolysis at -60°C for 4 h prior to warming. In either case, evaporation of the THF and examination of the residue by NMR and ir spectra or thin-layer chromatography (TLC) showed no identifiable products other than $\text{Mn}_2(\text{CO})_{10}$ and ditropyl.

Preparation of $\text{C}_7\text{H}_7\text{Mn}(\text{CO})_3$ (2**).** The metal acyl **4** (990 mg, 3.15 mmol), was dissolved in 60 ml of deoxygenated acetone and irradiated at -68°C while immersed in a methanol bath circulated through a coil immersed in dry ice-acetone. After the acyl had been consumed (ir and TLC), the mixture was evaporated to dryness under reduced pressure and triturated with benzene. The benzene-soluble portion was concentrated and subjected to preparative thick-layer chromatography on silica gel. The plate was developed several times with hexane until the yellow band of $\text{Mn}_2(\text{CO})_{10}$ and the orange band of **2** were well separated. Material extracted from the plate was finally sublimed at 35°C (0.04 Torr) to yield 73 mg (11%) of bright orange solid: mp 64°C , ir (CS₂) 2025, 1951, 1930 cm^{-1} (MCO); NMR, see text; λ_{max} (EtOH) 307 (ϵ 4500, sh), 262 nm (ϵ 10400). Anal. ($\text{C}_{10}\text{H}_7\text{O}_3\text{Mn}$) C, H, Mn.

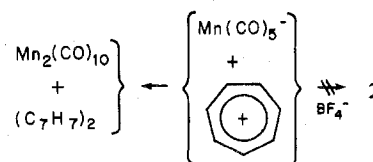
Results

Synthesis of **2.** Several attempts at the direct combination of tropylium ion and manganese pentacarbonyl anion, even at low temperature in the presence of light, failed to give any detectable quantities of **2**. The only products isolated from

Scheme I



these experiments were dimanganese decacarbonyl and ditropyl, presumably resulting from electron transfer and subsequent coupling of the fragments.



However, an indirect route, via decarbonylation at low temperature of the metal acyl species **4**, ultimately proved to be successful (Scheme I). The acid chloride **3** was allowed to react with manganese pentacarbonyl anion in THF to yield the white crystalline acyl derivative **4**. This species was characterized by its NMR spectrum, which showed a pattern of resonances typical of the C_7H_7 ring (see Experimental Section), the presence of a metal-acyl stretch in the ir spectrum at 1652 cm^{-1} , and metal carbonyl bands at 2115, 2050, and 2005 cm^{-1} with a pattern of intensities similar to other manganese pentacarbonyl derivatives. Photolysis of this material in solution at room temperature or thermolysis under a variety of conditions led to the exclusive formation of ditropyl and $\text{Mn}_2(\text{CO})_{10}$. However, photochemical decarbonylation at -68°C led to a product mixture from which pure **2** could be isolated in 11% yield after careful chromatography and fractional sublimation. The characterization of **2** is based on an acceptable elemental analysis, ir data, which showed three bands due to metal-carbonyl stretches at 2025, 1951, and 1930 cm^{-1} (compared to 2015, 1945, and 1931 cm^{-1} for $(\eta^5\text{-cycloheptadienyl})\text{tricarboxylmanganese}$ ⁸), and, finally and most characteristically, its NMR spectrum.

NMR Studies. The ^1H NMR spectrum of **2** at probe temperature (ca. 35°C) is a broad singlet. As the temperature is lowered, this signal broadens further and then splits up into a pattern consistent with the η^5 structure expected for cycloheptatrienylmanganese tricarboxyl. The assignments and temperature dependence are indicated in Figure 1. A noteworthy feature of the low temperature spectrum is the small coupling constant between the resonance due to $\text{H}_{6,7}$ at δ 4.70 and that due to $\text{H}_{1,5}$ at δ 3.53. This observation indicates that the dihedral angle between these protons is large and thus that the uncomplexed olefin is bent substantially away from the metal, in a manner consistent with other similar compounds such as cyclooctatetraeneiron tricarboxyl⁹ and the molybdenum complex **1**.¹⁰ At high temperatures, a single resonance is observed, indicating that the molecule is in fact fluxional and that the fluxional process results in mutual

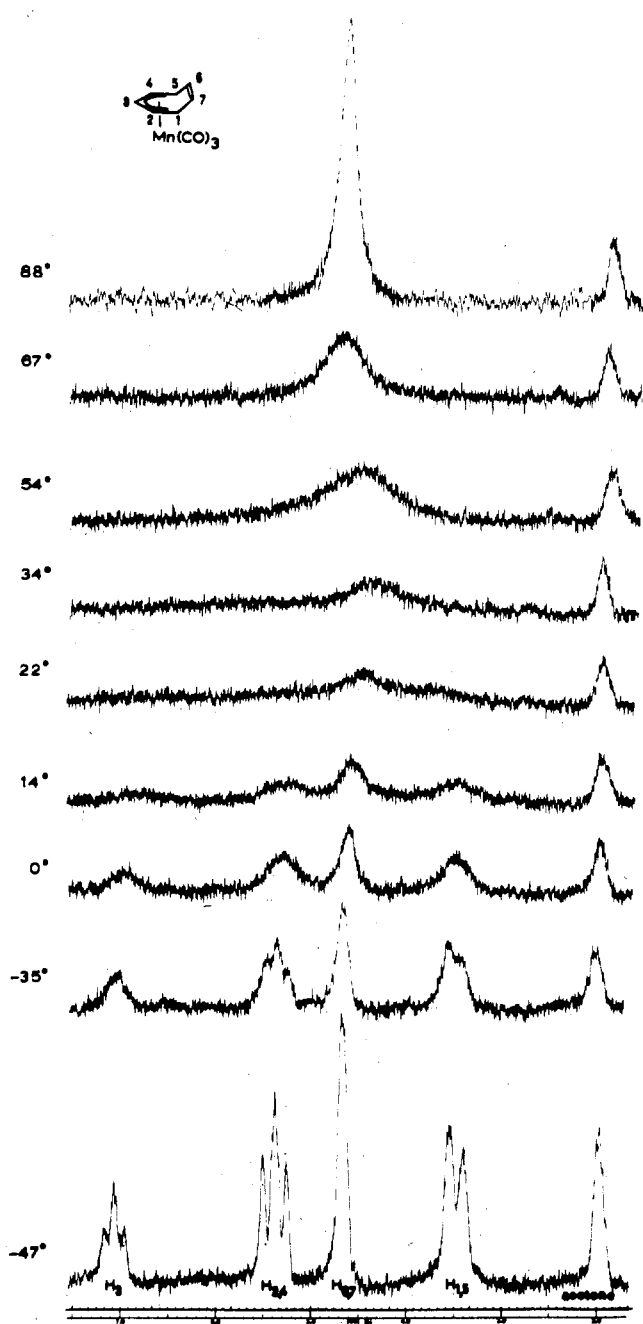


Figure 1. ^1H NMR spectrum at 60 MHz of $(\text{C}_7\text{H}_7)\text{Mn}(\text{CO})_3$, **2**, at various temperatures; solvent is acetone- d_6 .

exchange of all of the protons on the ring.

Because of important spin-coupling effects, the mechanism of the rearrangement was impossible to establish unambiguously on the basis of the proton spectrum. The absence of coupling in the natural-abundance, proton-decoupled carbon-13 spectrum makes the line shapes subject to simple theoretical analysis. The proton-decoupled ^{13}C NMR spectrum of **2** at temperatures below 0°C consists of four lines at 129.7, 107.4, 98.0, and 77.1 ppm downfield from TMS. No resonance around 200 ppm for the carbonyl carbons could be discerned, due probably to a combination of relaxation time and quadrupolar coupling effects. As the temperature is raised, again the lines broaden (reversibly) but, as shown in Figure 2, not at equal rates. Thus the line at 129.7 ppm remains substantially sharper than the others throughout the temperature range shown. This type of behavior is expected only for some kind of selective rearrangement pathway; for a random pathway, all of the lines of relative intensity 2 will

Table I. ^{13}C NMR Shifts^a and ^{13}C -H coupling Constants for Some η^5 Manganese Complexes

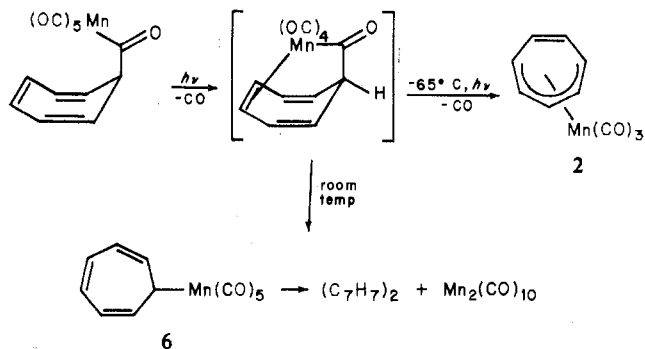
R	$C_{1,5}$ ($J^{13}\text{C-H}^b$)	$C_{2,4}$ ($J^{13}\text{C-H}^b$)	C_3 ($J^{13}\text{C-H}^b$)
c	75 (175)	75 (175)	75 (175)
$-\text{CH}_2$ - ^d	50.1 (168)	98.0 (168)	79.7 (177)
$-(\text{CH}_2)_2$ - ^e	80.2 (164)	99.7 (155)	91.2 (168)
$-\text{CH}=\text{CH}$ - ^f (2)	77.1 (154)	107.4 (166)	98.0 (171)

^a Ppm downfield from TMS, acetone- d_6 . ^b Hz. ^c $\text{CpMn}(\text{CO})_3$; ref 12. ^d C_6 : 24.2 ppm, $J^{13}\text{C-H} = 135$ Hz. ^e C_6, C_7 : 32.3 ppm, $J^{13}\text{C-H} = 129$ Hz. ^f C_6, C_7 : 129.7 ppm, $J^{13}\text{C-H} = 162$ Hz.

collapse at the same rate. The conclusion as to which selective pathway is followed depends on a correct assignment of the spectrum, which we believe can be unambiguously accomplished by comparison to other similar species (see Table I). Particularly noteworthy is the absence of a resonance near 130 ppm in the spectrum of $(\eta^5\text{-cycloheptadienyl})\text{tricarbonylmanganese}$. Since the peak at 129.7 ppm in **2** is in the region expected for a normal substituted olefinic carbon,¹¹ we believe that this peak is due to C_6 and C_7 . The relative sharpness of this peak in the intermediate-exchange region therefore implies a 1,2 shift mechanism, since this pathway results in a longer lifetime for the uncomplexed carbons than for the others. The left-hand side of Figure 2 shows line shapes calculated on the basis of this mechanism. From these data, the free energy of activation (300 K) is calculated to be about 14 kcal/mol for the fluxional process.

Discussion

Synthesis. We believe that a reasonable explanation for the success of our route to **2** involves the intermediate formation of a chelated acyl intermediate (**5**). At room temperature, this species decomposes rapidly to the σ -cycloheptatrienyl complex **6**. Homolytic dissociation of this species and re-



combination of the fragments lead to the observed dimeric products. On the other hand, at low temperature, the lifetime of species **5** is sufficiently long that it absorbs a second photon and eventually gives rise to **2**. Any route to **2** proceeding through the σ -alkyl **6** is likely to fail since this carbon-metal bond is probably very weak. The carbon-carbon bond strength in ditropyl has been estimated to be about 38 kcal/mol,¹³ implying a stabilization energy for tropyli radical of about 25 kcal/mol. While relevant bond strengths for Mn-C bonds have not been determined, it does not seem unreasonable to suggest that the manganese-carbon bond in **6** may have a bond energy of 20 kcal/mol or even less.

Fluxional Behavior. As discussed above, $\text{C}_7\text{H}_7\text{Mn}(\text{CO})_3$, **2**, is a fluxional molecule, rearranging via a series of 1,2 shifts (eq 1). Since the proton line shapes of **2** and the isoelectronic $\text{C}_7\text{H}_7\text{Fe}(\text{CO})_3^+$ are similar, we believe that the same mechanism applies in this case as well. The coalescence temperatures for the two species differ substantially, however,

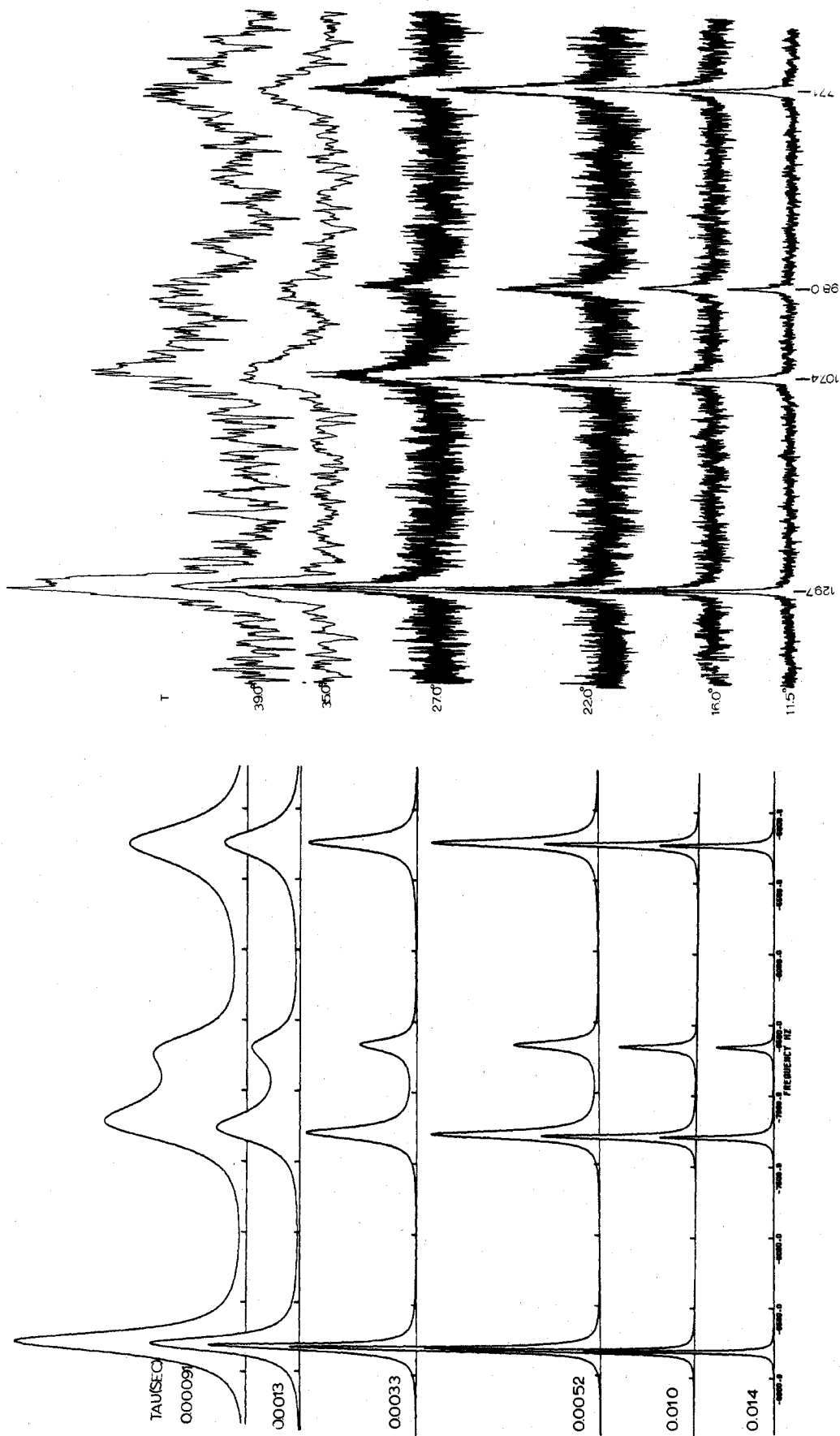
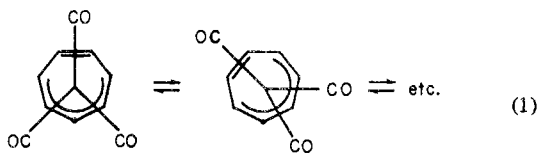
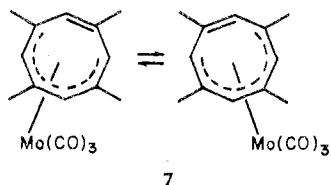


Figure 2. ^{13}C NMR spectrum at 67.923 MHz of $(\text{C}_7\text{H}_7)\text{Mn}(\text{CO})_3$ at various temperatures, compared to line shapes calculated on the assumption of a 1,2 shift mechanism, for various values of the preexchanged lifetime τ .

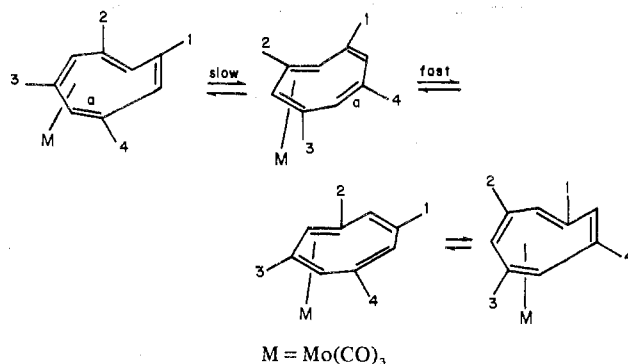


the iron compound rearranging at $-60\text{ }^{\circ}\text{C}$ at about the same rate that the manganese species does at $+20\text{ }^{\circ}\text{C}$. Assuming that the same preexponential factor applies to both species, we estimate that the activation energy for the iron compound is about 11 kcal/mol, or 4 kcal/mol less than that of the Mn compound. We have previously⁴ correlated this difference with the difference in back-bonding to the ring in the two cases. Molecular orbital calculations¹⁴ by the Fenske-Hall method¹⁵ confirm this difference: the total Mulliken population of the acceptor orbital in the two cases is 0.28091 (Mn) vs. 0.13340 (Fe). The possible result of this population difference is that the C_7 ring looks more like a tropylium ion in the iron compound, whereas the ring in **2** appears to be more like a cycloheptatrienyl anion. The decreased barrier to migration may therefore result from an increase in the aromaticity of the transition state for bond shifting in $C_7H_7Fe(CO)_3^+$ as compared to that of **2**. This argument predicts that, in ring whizzers containing a seven-membered ring, an increase in positive charge on the metal will result in an increase in the rearrangement rate. In cyclooctatetraene complexes, however, the neutral species should have the minimum rate of rearrangement; either electron-withdrawing or electron-donating metals should accelerate the reaction, other factors being equal.

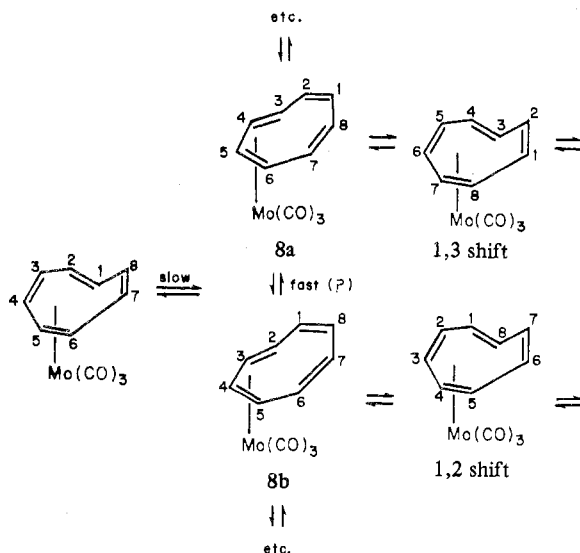
The characterization of the fluxional behavior of **2** leaves $COTMo(CO)_3$ as the only mononuclear ring whizzer for which it is necessary to postulate a rearrangement pathway other than via 1,2 shifts. Even in this species, there is a close balance between the 1,2 shift and whatever process occurs in **1**, since the closely related tetramethyl complex **7** has been shown to



undergo the 1,2 shift shown.^{3,16} We believe that a strong argument can be made that $COTMo(CO)_3$, in contrast to most ring whizzers, rearranges by a dissociative pathway, i.e., through a 16-electron species rather than through the 20-electron molecule proposed by Cotton.³ The proposed pathway is shown in Scheme II. This scheme could lead either to a specific 1,3 shift, if the η^4 intermediate **8** undergoes fluxional rearrangement slowly relative to collapse, or to a random shift if this rearrangement is rapid. These processes are not distinguishable by Cotton's experiment. Olefin complexes of group 6 metals are of very limited stability; e.g., the dissociation energy of (*cis*-butene) $W(CO)_5$ may be estimated to be ≤ 10 kcal/mol.¹⁷ Since bonds to molybdenum are generally even weaker (mean binding energy for CO in $Mo(CO)_6$ is 35.9 kcal/mol vs. 42.1 for $W(CO)_6$ ¹⁸), an activation energy of about 15 kcal/mol for a dissociative rearrangement as shown in Scheme II does not seem at all unreasonable. (The value of 15 kcal/mol is used because the rates of rearrangement of **1** and **2** are quite similar. A value of 5.8 kcal/mol for the rearrangement of **1** has been estimated by King,¹⁹ but the corresponding preexponential factor ($4.5 \times 10^5\text{ s}^{-1}$) seems much too low for a unimolecular process.) The mechanism of Scheme II could also apply to the tetramethyl derivative **7**, if (a) there is a preference for cleaving only the more weakly bound¹⁰ olefinic linkage (bond a) and (b) in the second step only clockwise rotation of the ring relative to the metal is



Scheme II



allowed (for the enantiomer shown). Both of these preferences can be explained on the basis of steric interactions between the methyl groups and the $M(CO)_3$ fragment. The high-temperature averaging process¹⁶ then involves the intervention of some collection of higher energy bond cleavages and/or rotations, which eventually lead to total scrambling.²⁰

In conclusion, we have shown that the cycloheptatrienyl-manganese species **2** rearranges by a 1,2 shift mechanism and thus that a 20-electron intermediate is not formed in this case. Further, we propose a plausible alternative to the mechanism of Cotton, Hunter, and Lahuerta³ for the rearrangement of $COTM(CO)_3$, **1**, which also provides an explanation for their experimental observations and which predicts that a specific 1,3 shift is at least possible for these complexes. Verification of this prediction would provide substantial evidence for the kind of dechelation mechanism proposed in Scheme II, but until such evidence is available, both the 16- and 20-electron intermediates must be regarded as speculative.

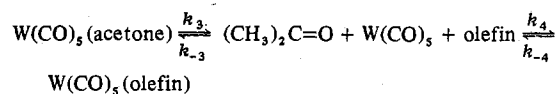
Acknowledgment. We wish to acknowledge the National Science Foundation (Grant GP 16358) and the Research Committee of the University of Wisconsin for partial support of this work. The 270-MHz NMR spectrometer was obtained with a Departmental Instrument Grant from the National Science Foundation.

Registry No. **4**, 36618-88-9; **2**, 53011-14-6.

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Now the overall equilibrium constant is 21 for olefin = 1-pentene, the ratio $k_{-3}/k_4 \approx 0.6$, and the activation energy for acetone loss is 7 kcal/mol. These numbers imply that the activation energy for olefin loss is certainly less than 10 kcal/mol.

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Organonitrogen Derivatives of Metal Carbonyls.

IX. Novel Products from Reactions of Aminoalkynes with Metal Carbonyls¹

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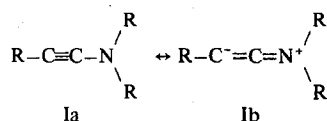
Received November 13, 1975

AIC50824J

Reaction of $(C_2H_5)_2NC\equiv N(C_2H_5)_2$ with $Fe(CO)_5$ or $Fe_3(CO)_{12}$ gives a mixture of yellow $[(C_2H_5)_2N]_2C_2Fe_2(CO)_6$ and the orange cyclopentadienone complex $[(C_2H_5)_2N]_4C_4COFe(CO)_3$. Reaction of $C_6H_5C\equiv N(CH_3)_2$ with $Fe(CO)_5$ in boiling octane gives orange $C_6H_5C_2N(CH_3)_2Fe_2(CO)_6$. Reaction of $CH_3C\equiv N(C_2H_5)_2$ with $Fe(CO)_5$ gives the orange cyclopentadienone complex $[(C_2H_5)_2N]_2(CH_3)_2C_4COFe(CO)_3$. Reaction of $HC\equiv N(CH_3)_2$ with $Fe_3(CO)_{12}$ gives the orange tricarbonylferrole-iron tricarbonyl complex $[(CH_3)_2N]_2C_4H_2Fe_2(CO)_6$. Ultraviolet irradiation of the aminoalkynes $RC\equiv N(C_2H_5)_2$ ($R = CH_3$ or $N(C_2H_5)_2$) with $Mn_2(CO)_{10}$ in tetrahydrofuran gives the orange complexes $[RC_2N(C_2H_5)_2]Mn_2(CO)_8$. Ultraviolet irradiation of $(C_2H_5)_2NC\equiv N(C_2H_5)_2$ with $W(CO)_6$ in tetrahydrofuran gives orange crystalline $[(C_2H_5)_2N]_4C_4W(CO)_4$, indicated by its proton and carbon-13 NMR spectra not to be a cyclobutadiene-tungsten tetracarbonyl derivative but instead a derivative with much lower symmetry. Reactions of $(C_2H_5)_2NC\equiv N(C_2H_5)_2$ with $C_5H_5M(CO)_2$ ($M = Co$ and Rh) give the black trimetallic derivatives $(C_5H_5)_3M_3C_2[N(C_2H_5)_2]_2$ in which the carbon-carbon triple bond of the diaminoalkyne has been broken to form a trigonal-bipyramidal M_3C_2 cluster with the two carbon atoms at the apices. The structures of these observed products can be rationalized by three alternative pathways for reactions of aminoalkynes with metal carbonyls: (1) oligomerization reactions involving only the carbon-carbon triple bond similar to those of other alkynes; (2) reactions of the aminoalkyne in its keteneimmonium ylide form leading to products containing $\eta^3\text{-CCN}$ ligands with bonding of the original amino nitrogen as well as the original triple-bond carbons to the transition metal; (3) complete cleavage of the aminoalkyne carbon-carbon triple bond to give metal complexes built from aminocarbene units.

Introduction

Reactions of alkynes with metal carbonyls have led to numerous interesting organometallic derivatives including substituted cyclobutadiene, cyclopentadienone, metallacyclopentadiene, metallacyclohexadienone, benzene, tropone, and more complex metallocyclic derivatives as well as complexes containing monoligand monometallic, biligand bimetallic, or biligand monometallic alkyne ligands^{3,4} including derivatives with metal-metal multiple bonds.⁵⁻⁷ This variety of unusual and interesting products obtained from metal carbonyls and alkynes made of interest a comparable study of reactions of metal carbonyls with aminoalkynes.⁸ The possibility for strong $p\pi\text{-}p\pi$ bonding between the amino nitrogen and the adjacent sp carbon in aminoalkynes makes dipolar resonance structures of the type Ib significant in determining the chemistry of



aminoalkynes. The reduction of the effective bond order of the carbon-carbon triple bond by keteneimmonium ylide

resonance structures of the type Ib and the resulting increased negative charge on one of the carbon atoms should make the reactivity of aminoalkynes toward metal carbonyls considerably different from that of simple alkynes.

This paper describes a survey of some reactions of aminoalkynes with metal carbonyls. Some cyclopentadienone and metallacyclopentadiene derivatives were obtained from aminoalkynes and $Fe(CO)_5$ or $C_5H_5Rh(CO)_2$ in which only the carbon-carbon triple bond of the aminoalkyne interacts with the transition metal system completely analogous to well-established^{3,4} reactions of alkynes without amino substituents. However, other reactions of aminoalkynes with iron, manganese, and tungsten carbonyls gave products in which the adjacent carbon-carbon triple bond and amino group of the aminoalkyne interact simultaneously with the metal atom to form new metal complexes of types not previously encountered in either alkyne^{3,4} or amine⁹ metal carbonyl derivatives. The most unusual reactions of aminoalkynes with metal carbonyls were the reactions of the diaminoalkyne $(C_2H_5)_2NC\equiv N(C_2H_5)_2$ with $C_5H_5M(CO)_2$ ($M = Co$ and Rh) to give the trimetallic derivatives $(C_5H_5)_3M_3C_2[N(C_2H_5)_2]_2$ in which the carbon-carbon triple bond of the diaminoalkyne has undergone complete rupture to form a trigonal-bipyramidal cage with