Acknowledgment. The support of this research by the Robert A. Welch Foundation (F-042) and the Petroleum Research Fund of the American Chemical Society (PRF-4534-AC1) is gratefully acknowledged. The authors are also grateful for advice from Drs. Ben A. Shoulders and Clifford Becker concerning the low-temperature nmr and visible spectra techniques.

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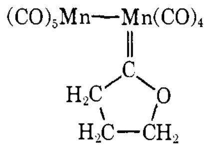
Received April 17, 1971

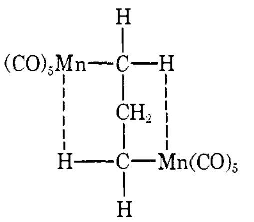
Metal–Carbene Complexes from the Reaction of Methylpentacarbonylmanganese(I) wth Sodium Pentacarbonylmanganate(−I)

Sir:

In 1963 King reported that the reaction of NaMn(CO)$_5$ with either 1,3-dibromopropane or 4-chlorobutyryl chloride gave a compound with the empirical formula $Mn_2(CO)_{10}(CH_2)_3$.[1] This compound has recently been shown to be the cyclic metal–carbene complex **1**[2] and not structure **2** as originally proposed by King. We now wish to report a new reaction which clarifies the mechanism of formation of **1** from 1,3-dibromopropane.



1



2

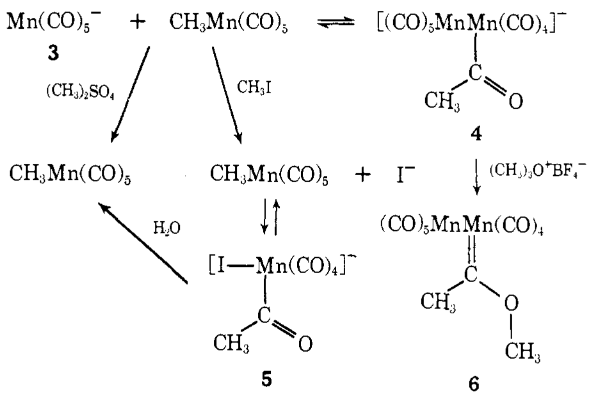
The reaction of nucleophiles such as phosphines,[3] amines,[3] carbon monoxide,[4] and iodide ion[5] with $CH_3Mn(CO)_5$ to give substituted acetyltetracarbonylmanganese complexes is well known. Here we report that the nucleophilic anion $Mn(CO)_5^-$ (**3**) reacts with $CH_3Mn(CO)_5$ in tetrahydrofuran (THF) to give the dinuclear acetylmanganese anion **4**. Furthermore, we have established this reaction to be a rapid equilibrium process.

The nmr spectrum of a solution prepared from 0.27 mmol each of NaMn(CO)$_5$ and $CH_3Mn(CO)_5$ in 0.50 ml of THF consists of a singlet at τ 10.10 due to $CH_3Mn(CO)_5$ and a new singlet at τ 7.19 which we attribute to the dinuclear acetylmanganese anion **4** in addition to the THF resonances. The relative intensities of the two singlets change upon dilution; the ratio of the area of the peak at τ 7.19 due to the adduct **4** to the area of the $CH_3Mn(CO)_5$ peak at τ 10.10 changes from 1.45 to 1.08 when the sample volume is increased from 0.50 to 1.20 ml. The equilibrium has thus been shifted to $CH_3Mn(CO)_5$ by dilution, as expected from the law of mass action. A marked change in the relative intensities of the two singlets also occurs upon heating: at 40°, the ratio of the intensity of the peak due to **4** to the intensity of the $CH_3Mn(CO)_5$ peak is 1.45; at 71°, the ratio decreases to 1.03. These changes are reversible below 90° where irreversible line broadening occurs caused by thermal decomposition.

The infrared spectrum of this equilibrium mixture run at nmr concentrations (0.55 *M*) contains a carbonyl stretch at 1560 cm^{-1} which compares well with the 1566-cm^{-1} band reported for the iodoacetylpentacarbonylmanganese anion **5**. At concentrations sufficiently low to resolve the metal carbonyls, the equilibrium concentration of the dinuclear acetylmanganese anion **4** is so low that it cannot be observed.

The equilibrium has also been shifted by chemical means as shown in Scheme I. Addition of a fourfold excess of dimethyl sulfate to the equilibrium mixture described above resulted in the disappearance of the peak at τ 7.19 corresponding to the adduct **5** in less than 30 sec; comparison of the increased $CH_3Mn(CO)_5$ peak area at τ 10.10 with the area of the methyl singlet of a known amount of *p*-di-*tert*-butylbenzene internal standard indicated the quantitative formation of $CH_3Mn(CO)_5$. Addition of methyl iodide to the equilibrium mixture also resulted in rapid disappearance of the acetyl peak at τ 7.19 and an increase in the $CH_3Mn(CO)_5$ peak at τ 10.10. The iodide ion produced in this reaction further reacted with $CH_3Mn(CO)_5$ to produce a resonance at τ 7.13 corresponding to iodoacetyltetracarbonylmanganese anion **4**, which has been previously isolated as its lithium salt.[5] The iodo compound **5** readily decomposes upon addition of water to give $CH_3Mn(CO)_5$. Addition of sodium iodide to $CH_3Mn(CO)_5$ in THF produced the iodo compound **5** with a sharp singlet at τ 7.13. Neither dimethyl sulfate nor methyl iodide gave any O-alkylation of **4**.

Scheme I



The acyl anion **4** can be alkylated on oxygen with trimethyloxonium fluoroborate to give the corresponding methylmethoxycarbene complex **6**, previously prepared by Fischer and Offhaus.[6] In a typical reaction, $CH_3Mn(CO)_5$ (0.50 g, 2.4 mmol) and NaMn(CO)$_5$ (4.3 ml, 0.55 *M*, 2.4 mmol) in 30 ml of THF were stirred for 5 min at room temperature. Solvent was evaporated under aspirator vacuum to give an orange oil which was dissolved in oxygen-free water and treated with trimethyloxonium fluoroborate until the solution became acidic. The material obtained from pentane extraction of the aqueous solution was sub-

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[1] R. B. King, *J. Amer. Chem. Soc.*, **85**, 1922 (1963).

[2] C. P. Casey *Chem. Commun.*, 1220 (1971).

[3] C. S. Kraihanzel and P. K. Maples, *Inorg. Chem.*, **7**, 1806 (1968).

[4] K. Noack and F. Calderazzo, *J. Organometal. Chem.*, **10**, 101 (1967).

[5] F. Calderazzo and K. Noack, *ibid.*, **4**, 250 (1965).

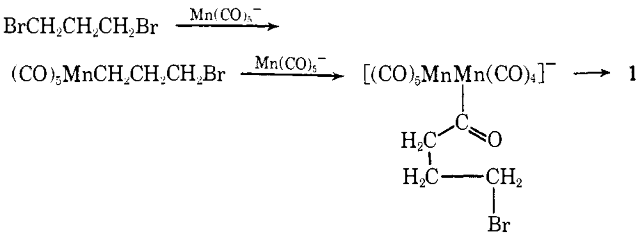
[6] E. O. Fischer and E. Offhaus, *Chem. Ber.*, **102**, 2549 (1969).

limed at 25° (40 mm) in a closed system to give $CH_3Mn(CO)_5$ (0.24 g 48% recovery). The residue from this sublimation was chromatographed on silica gel with pentane–benzene to give a small amount of $Mn_2(CO)_{10}$ and a slower moving orange solid further purified by sublimation at 50° (0.01 mm), identified as the methylmethoxycarbene complex **6** (0.24 g, 24% yield, mp 78–81°, lit.[6] mp 81°). Compound **6** was identical in physical and spectral properties with an authentic sample of the methylmethoxycarbene complex prepared according to Fischer's procedures.[6]

In contrast to Fischer's facile isolation of mononuclear acyl anions as their tetralkylammonium salts,[7] our attempts to isolate the acetyl anion **4** led to the formation of $(CH_3)_4N^+Mn(CO)_5^-$ and $CH_3Mn(CO)_5$.

The formation of the cyclic metal carbene complex **1** from 1,3-dibromopropane and $NaMn(CO)_5$ can now be rationalized according to the reaction sequence presented in Scheme II. The key step in the sequence is the attack of $Mn(CO)_5^-$ on an intermediate alkylmanganese compound to give a dinuclear acylmanganese anion similar to the adduct **4** obtained above. The dinuclear acylmanganese anion is trapped by intramolecular alkylation of the acyl oxygen atom by the alkyl bromide functionality.

Scheme II



We are presently investigating the generality of this new reaction and its potential in the synthesis of other dinuclear metal–carbene complexes.

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[7] E. O. Fischer and A. Maasbol, *Chem. Ber.*, 100, 2445 (1967).

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Received May 6, 1971

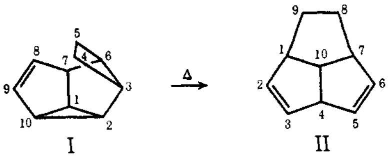
Orientation of Substituents in the Photochemical 1,3 Addition of Benzene to Cyclobutene

Sir:

The first report by Wilzbach and Kaplan[1a] on the photochemical 1,3 addition of benzene to olefins has been followed by a number of others[1–5] which have demonstrated the generality of this reaction with respect to a variety of linear and cyclic olefins. While it is known[1b] that the excited state of benzene that takes part in this reaction is the singlet ($^1B_{2u}$) state or a structure derived from it, its geometry is a matter for speculation. Two observations which are pertinent to this problem are: (i) the addition is a concerted reaction,[1a] and (ii) the 1,2 and 1,4 additions of benzene to olefins may also occur from the same precursor since, in a given system, the relative quantum yields of 1,2 and 1,4 additions to the 1,3 addition are invariant with experimental conditions.[1d,5]

We report here data on the modes of photochemical 1,3 addition of toluene and the three xylenes to cyclobutene. These results seem to provide a clue to the structure of the excited state of the benzene when it undergoes 1,3 addition.

The choice of cyclobutene as the olefin was advantageous for three reasons: first, the addition proceeded with as high a quantum yield as between benzene and cyclobutene and with the same chemical yield (~20%).[5] Secondly, it was possible to establish that the stereochemistry of the adducts was 3,6 endo (in structure I) in all cases because all of them underwent the (2′-vinylcyclopropyl)cyclobutane rearrangement (reaction 1)[6] to give derivatives of tricyclo[5.2.1.0^{7,10}]deca-2,5-diene (II). Thirdly, the location of the methyl groups in these structures was, for the most part, readily done merely by noting the chemical shifts of these protons in the nmr spectra of the photoadducts and their thermally rearranged products.[7] A cross-check was provided by the number of olefinic protons that were missing from these spectra when compared to the spectra of I or II. To illustrate, the 3,6-endo adduct obtained from *o*-xylene could have one of six structures according to the positions of the two methyl groups. Since the product had two olefinic protons, and neither of its methyl groups was located on a double bond, the substituent groups can only be (in structure I) at positions 10,2 or 2,1 or 1,7. Based on these three probable structures, pyrolysis of this adduct can give one of three tricyclic products in which the methyl groups would be (in structure II) at positions 3,5 (two olefinic protons–two allylic methyls) or 4,5 (three olefinic protons–one allylic methyl) or 4,10 (four olefinic protons–no allylic methyl). The product actually corresponded to the second one.



(1)

A unique structure assignment based on these data alone was not possible in every instance. The structures of the adducts from *p*-xylene, toluene, and one of the adducts from *m*-xylene could be narrowed down to two possibilities. The final choice was based on the following consideration. In the nmr spectra of all five of the adducts that were obtained in this work, it was noticed that the absorption at *ca.* δ 3.1 due to a proton originating from the benzene ring was missing.

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[1] (a) K. E. Wilzbach and L. Kaplan, *J. Amer. Chem. Soc.*, **88**, 2066 (1966); (b) K. E. Wilzbach, A. L. Harkness, and L. Kaplan, *ibid.*, **90**, 1116 (1968); (c) L. Kaplan and K. E. Wilzbach, *ibid.*, **90**, 3291 (1968); (d) K. E. Wilzbach and L. Kaplan, *ibid.*, **93**, 2073 (1971). The author wishes to thank Drs. Wilzbach and Kaplan for sending him a preprint of this communication.

[2] (a) D. Bryce-Smith, A. Gilbert, and B. H. Orger, *Chem. Commun.*, 512 (1966); (b) D. Bryce-Smith and H. C. Longuet-Higgins, *ibid.*, 593 (1966); (c) D. Bryce-Smith, *Pure Appl. Chem.*, **16**, 47 (1968); (d) D. Bryce-Smith, *Chem. Commun.*, 806 (1969).

[3] (a) K. Koltzenburg and K. Kraft, *Tetrahedron Lett.*, 389 (1966); (b) K. Draft, Doctoral Dissertation, University of Bonn, 1968.

[4] A. Morikawa, S. Brownstein, and R. J. Cvetanovic, *J. Amer. Chem. Soc.*, **92**, 1471 (1970).

[5] R. Srinivasan, *IBM J. Res. Develop.*, **15**, 34 (1971).

[6] R. Srinivasan, *J. Amer. Chem. Soc.*, **92**, 7542 (1970).

[7] We judge it unlikely that free-radical migrations of methyl groups will occur in the course of these thermal rearrangements.