a regular octahedral coordination site. This strain puts the N donor in an irregular position with an unusually long Cr–N bond. With the larger Mo atom in $Mo(CO)_3(PNP)$, the distortion is likely to be even greater.

Acknowledgments. We appreciate the support of this research by the National Science Foundation through Grant No. GP-28480. We are grateful to Professor J. Espenson, Dr. H. Fritz, and D. Sellers for their assistance with the stopped-flow studies and to D. Powers for preliminary studies.

Registry No. $Mo(CO)_4[(C_6H_5)_2PNHC_5H_4N]$, 49626-24-6; $Mo(CO)_4[(C_6H_5)_2PCH_2C_5H_4N]$, 49626-25-7; $Mo(CO)_4[(C_6H_5)_2PCH_2CH_2C_5H_4N]$, 49626-26-8; $Mo(CO)_4[(C_6H_5)_2PCH_2CH_2CH_2C_5H_4N]$, 49626-27-9; $Mo(CO)_3[PNP]$, 49626-28-0; $Mo(CO)_4[PNP]$, 49626-29-1; CO, 630-08-0.

Contribution from the Department of Chemistry,
University of Georgia, Athens, Georgia 30602

Organometallic Chemistry of the Transition Metals. XXVIII. Some Novel Olefinic Manganese Carbonyl Derivatives[1,2]

R. B. KING* and M. N. ACKERMANN[3]

Received September 11, 1973

Reactions of $[HMn(CO)_4]_3$ with excesses of various olefins and acetylenes under mild conditions (boiling hexane or neohexane) give novel organomanganese carbonyl derivatives, in addition to much $Mn_2(CO)_{10}$. Thus, reaction of $[HMn(CO)_4]_3$ with 1,3-cyclohexadiene gives the cyclohexadienyl derivative $C_6H_7Mn(CO)_3$. Reaction of $[HMn(CO)_4]_3$ with cycloheptatriene gives the cycloheptadienyl derivative $C_7H_9Mn(CO)_3$. A similar reaction of $[HMn(CO)_4]_3$ with 1,3-cycloheptadiene gives a mixture of the same cycloheptadienyl derivative $C_7H_9Mn(CO)_3$ and the cycloheptenyl derivative $C_7H_{11}Mn(CO)_4$. Reaction of $[HMn(CO)_4]_3$ with cyclooctatetraene gives a mixture of yellow crystalline $C_8H_9Mn(CO)_3$ and fluxional orange crystalline $C_8H_8Mn_2(CO)_6$. Reaction of $[HMn(CO)_4]_3$ with 1,3,5-cyclooctatriene gives a mixture of yellow crystalline 1,2,3,4,5-h^5-$C_8H_{11}Mn(CO)_3$, yellow crystalline 1,2,3,5,6-h^5-$C_8H_{11}Mn(CO)_3$, and air-sensitive yellow liquid $C_8H_{11}Mn(CO)_4$. Reaction of $[HMn(CO)_4]_3$ with dimethylaminofulvene gives the orange liquid substituted cyclopentadienylmanganese tricarbonyl derivative $(CH_3)_2NCH_2C_5H_4Mn(CO)_3$. Reaction of $[HMn(CO)_4]_3$ with azulene gives the yellow crystalline bimetallic derivative $[C_{10}H_8Mn(CO)_3]_2$. Reaction of $[HMn(CO)_4]_3$ with norbornadiene gives red crystalline $C_7H_8Mn_2(CO)_7$. Reaction of $[HMn(CO)_4]_3$ with 3-hexyne results in cyclotrimerization to give the 1,2,3,4,5,6-hexaethylcyclohexadienyl derivative $(C_2H_5)_6C_6HMn(CO)_3$. However, reaction of $[HMn(CO)_4]_3$ with diphenylacetylene results in linear dimerization to give *cis,cis*-1,2,3,4-tetraphenylbutadiene.

Introduction

A major impetus to the development of transition-metal organometallic chemistry has been the preparation of compounds with unusual metal–carbon bonding by reactions of various metal carbonyls with olefins and acetylenes.[4] Notable reactions of this type include the preparations of various (diene)$Fe(CO)_3$ derivatives from 1,3-dienes and $Fe(CO)_5$[5] and the preparations of various (arene)$Cr(CO)_3$ derivatives from arenes and $Cr(CO)_6$.[6] The number of unusual organometallic structures that have been prepared by reactions of various olefins and acetylenes with simple metal carbonyls such as $M(CO)_6$ (M = Cr, Mo, and W), $M_2(CO)_{10}$ (M = Mn and Re), $Fe(CO)_5$, $Co_2(CO)_8$, and $Ni(CO)_4$ is now very large.

A significant limitation in the preparation of transition-metal organometallic compounds by reactions of olefins and acetylenes with the simple metal carbonyls $M(CO)_6$ (M = Cr, Mo, and W), $M_2(CO)_{10}$ (M = Mn and Re), and $Fe(CO)_5$ is the need for elevated temperatures (generally 100 to 150°) before displacement of carbonyl groups by olefinic ligands can take place. In the cases of some of the more temperature-sensitive olefinic metal carbonyl derivatives, the elevated temperatures required for these reactions may exceed the decomposition temperatures of the desired products. In order to circumvent this difficulty, more complex but more reactive metal carbonyl derivatives can be used in the place of the simple metal carbonyl derivatives for the reactions with olefins or acetylenes. For example, the polymetallic iron carbonyls $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ react with olefins and acetylenes under much milder conditions than $Fe(CO)_5$.[4] In general, the reactivities of these more reactive metal carbonyl derivatives depend upon the rupture of some bond weaker than the metal–carbonyl bond, such as the iron–iron bonds in $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ and the metal–ligand bonds involving ligands that are both poor σ donors and poor π acceptors in the complexes $(CH_3CN)_3M(CO)_3$ (M = Cr,[7] Mo,[7] and W)[8] and (diglyme)$Mo(CO)_3$.[9]

When this research was initiated, a similar principle had not been used for the synthesis of olefinic manganese carbonyl derivatives. The known range of olefinic manganese carbonyl derivatives was therefore limited to compounds either which could survive the relatively high temperatures (above 100°) required for reactions of $Mn_2(CO)_{10}$ with ole-

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[1] For part XXVII of this series, see R. B. King and P. N. Kapoor, *J. Organometal. Chem.*, 33, 383 (1971).

[2] Portions of this work were presented at the Sixth International Conference on Organometallic Chemistry, Amherst, Mass., August 1973.

[3] Faculty member of the Department of Chemistry, Oberlin College, Oberlin, Ohio, on sabbatical leave at the University of Georgia during the 1972–1973 academic year.

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fins or acetylenes or which could be prepared by indirect methods. Examples of olefinic manganese carbonyl derivatives which can be obtained from $Mn_2(CO)_{10}$ and an appropriate unsaturated organic compound include the pentahapto[10] pyrrolyl derivative[11] $C_4H_4NMn(CO)_3$, the cyclohexadienyl derivative[12] $C_6H_7Mn(CO)_3$ and related substituted cyclohexadienyl derivatives, and the cycloheptadienyl derivative[13] $C_7H_9Mn(CO)_3$. Numerous substituted cyclopentadienylmanganese tricarbonyls (cymantrenes)[14] have also been known for a long time. In order to expand the known range of olefinic manganese carbonyl derivatives to compounds of other types, a manganese carbonyl derivative was needed which would react with olefins and acetylenes under appreciably milder conditions than $Mn_2(CO)_{10}$.

Considerable experience with iron carbonyl chemistry[4] indicates that $Fe_3(CO)_{12}$, which has a triangle of iron atoms bonded to each other,[15] is more reactive toward olefins and acetylenes than $Fe(CO)_5$. A related compound with a triangle of manganese atoms is the trimetallic manganese carbonyl hydride[16] $[HMn(CO)_4]_3$. The idea that $[HMn(CO)_4]_3$ might be appreciably more reactive toward olefins and alkynes than $Mn_2(CO)_{10}$ received support from the reported facile reactions[17] of $[HMn(CO)_4]_3$ with certain tertiary phosphines and related ligands with rupture of the manganese triangle to give the bimetallic derivatives $[LMn(CO)_4]_2$. All of these considerations led us to investigate the reactions of $[HMn(CO)_4]_3$ with various olefins and acetylenes. Such reactions were found to yield a variety of new organomanganese carbonyl derivatives. The details of this work and the characterization of the new compounds are presented in this paper.

Experimental Section

Microanalyses were performed by Pascher Mikroanalytisches Laboratorium, Bonn, Germany, and by the Microanalytical Laboratory at the University of Georgia, under the supervision of Mr. W. Swanson. Infrared spectra were taken in cyclohexane or *n*-hexane solutions and recorded on a Perkin-Elmer Model 621 spectrometer with grating optics. Proton nmr spectra were taken in $CDCl_3$ or C_6D_6 solutions and recorded either on a Perkin-Elmer R-20 spectrometer at 60 MHz or a Varian HA-100 spectrometer at 100 MHz. Melting points were taken in capillaries and are uncorrected. Unless otherwise specified, all yields are quoted on the basis of manganese as the limiting reagent.

The mass spectra of the monometallic olefinic manganese carbonyl derivatives were taken on the University of Georgia Perkin-Elmer Hitachi RMU-6 mass spectrometer at 70 eV. In the present work, the presence of the molecular ion and the ions formed by successive losses of carbonyl groups from the molecular ion was used as an indication of the molecular weights of the monometallic olefinic manganese carbonyl derivatives. Further details of their fragmentation patterns will be presented elsewhere since they are not relevant to this paper. The mass spectra of the bimetallic manganese carbonyl derivatives $C_8H_8Mn_2(CO)_6$ and $C_7H_8Mn_2(CO)_7$ were similarly taken on the MS-12 mass spectrometer located at Colorado State University in Fort Collins, Colo., under the supervision of Dr. B. R. Kowalski, since the solid inlet system of the University of Georgia mass spectrometer was not adequate for handling these less volatile compounds.

A nitrogen atmosphere was always provided for the following three operations: (a) carrying out reactions, (b) handling all filtered solutions of organometallic compounds, (c) filling evacuated vessels containing organometallic compounds. Alumina for chromatography (80–200 mesh) was used as received from Matheson Coleman and Bell. During the chromatography of some of the reaction mixtures, the colors of the yellow bands from some of the monometallic manganese carbonyl derivatives became so weak that they could not be unequivocally observed on the column. Hexane used for the reactions was freshly distilled under nitrogen over sodium benzophenone ketyl.

Materials. Commerical $CH_3C_5H_4Mn(CO)_3$ (Ethyl Corporation, New York, N. Y.) was converted to $Mn_2(CO)_{10}$[18] and this to $[HMn(CO)_4]_3$[17,19] by the cited published procedures. The conversion of $Mn_2(CO)_{10}$ to $[HMn(CO)_4]_3$ could be scaled up to runs starting with 20 g of $Mn_2(CO)_{10}$ and yielding 10 to 11 g (58 to 64%) of $[HMn(CO)_4]_3$.

The olefins 1,3-cyclohexadiene, cycloheptatriene, cyclooctatetraene, and norbornadiene and the acetylenes 3-hexyne and diphenylacetylene were commercial products. The olefins 1,3-cycloheptadiene,[20] 1,3,5-cyclooctatriene,[21] and 6-dimethylaminofulvene[22] were prepared by the cited published procedures.

Reaction of $[HMn(CO)_4]_3$ with 1,3-Cyclohexadiene. A mixture of 2.70 g (5.36 mmol) of $[HMn(CO)_4]_3$, 2.5 ml (2.1 g, 26.3 mmol) of 1,3-cyclohexadiene, and 350 ml of hexane was boiled under reflux for 4.5 hr. The resulting yellow solution was concentrated to ~75 ml at ~25° (35 mm) and then chromatographed on a 2 × 45 cm alumina column. A yellow band containing 1.51 g (48% yield) of $Mn_2(CO)_{10}$ was first eluted from the chromatogram with hexane. Further elution with hexane, with eventual addition of some diethyl ether to the eluting solvent, followed by evaporation of the eluate, gave a yellow oil which, upon repeated chromatography, gave after a vacuum sublimation 0.123 g (3.5% yield) of yellow crystalline $C_6H_7Mn(CO)_3$, mp 76–77° (lit.[12] mp 78°). The stoichiometry $C_6H_7Mn(CO)_3$ was confirmed by its mass spectrum.

A yellow liquid product appeared between the $Mn_2(CO)_{10}$ and the $C_6H_7Mn(CO)_3$ on the chromatogram, but this could not be obtained in sufficient quantity and purity for proper characterization.

Reaction of $[HMn(CO)_4]_3$ with Cycloheptatriene. A mixture of 1.117 g (2.32 mmol) of $[HMn(CO)_4]_3$, 2 ml (1.7 g, 18.4 mmol) of cycloheptatriene, and 100 ml of hexane was boiled under reflux for 15 hr. The solution was concentrated to ~50 ml at 25° (35 mm) and then chromatographed on a 2 × 20 cm alumina column. Elution of the chromatogram with hexane first gave a fraction which, after evaporation, yielded 0.50 g (38% yield) of $Mn_2(CO)_{10}$. Further elution of the chromatogram with hexane, containing increasing amounts of diethyl ether, followed by evaporation of the eluate, gave a viscous liquid which, after rechromatography in hexane, followed by low-temperature crystallization from hexane, gave 0.187 g (11.5% yield) of yellow $C_7H_9Mn(CO)_3$, mp 66–68° (lit.[13] mp 64–66°), identical with authentic $C_7H_9Mn(CO)_3$ prepared from $Mn_2(CO)_{10}$ and 1,3-cycloheptadiene according to the published procedure.[13] The stoichiometry $C_7H_9Mn(CO)_3$ was also confirmed by its mass spectrum.

Reaction of $[HMn(CO)_4]_3$ with 1,3-Cycloheptadiene. A mixture of 2.53 g (5.03 mmol) of $[HMn(CO)_4]_3$, 2.5 ml (2.12 g, 22.6 mmol) of 1,3-cycloheptadiene,[20] and 400 ml of hexane was boiled under reflux for 15 hr. The reaction mixture was then concentrated to ~75 ml at ~25° (35 mm) and chromatographed on a 2 × 45 cm alumina column. The following products were eluted from the chromatogram in the order indicated using pure hexane as the eluant until the final stages of the chromatography when diethyl ether, tetrahydrofuran, and acetone in succession were used:

(a) Yellow $Mn_2(CO)_{10}$ (1.31 g, 45% yield) was obtained.

(b) An air-sensitive yellow liquid which was purified further by a second chromatography in hexane followed by evaporative distillation at 25° (0.1 mm) was obtained. The infrared spectrum of this liquid in hexane solution exhibited ν(CO) frequencies at 2066 (s), 1981 (m), 1964 (vs), and 1057 (vs) cm^{-1}. The proton nmr spectrum of this liquid in C_6D_6 solution exhibited broad resonances at τ 6.1,

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8.06, and 8.86 of approximate relative intensities 3:4:4. Analytical data on this liquid were consistent with its formulation as $C_7H_{11}Mn(CO)_4$.

Anal. Calcd for $C_{11}H_{11}MnO_4$: C, 50.4; H, 4.2. Found: C, 49.3; H, 4.4).

(c) A yellow crystalline solid, after rechromatography and vacuum sublimation, gave 0.10 g (2.9% yield) of yellow crystalline $C_7H_9Mn(CO)_3$, mp 66–67° (lit.[13] mp 64–66°), identical with the product obtained from $[HMn(CO)_4]_3$ and cycloheptatriene as described above.

Reaction of $[HMn(CO)_4]_3$ with Cyclooctatetraene. A mixture of 2.42 g (4.8 mmol) of $[HMn(CO)_4]_3$, 5 ml (4.6 g, 43 mmol) of cyclooctatetraene, and 150 ml of hexane was boiled under reflux for 16 hr. The reaction mixture was then concentrated to ~75 ml at ~25° (35 mm) and chromatographed on a 2 × 45 cm alumina column. The following products were eluted from the chromatogram in the order indicated and were isolated after evaporation of the eluates.

(a) Yellow $Mn_2(CO)_{10}$ (1.40 g, 50% yield) eluted with hexane.

(b) A paler yellow solid eluted with 3:1 hexane–diethyl ether. This solid was purified by two low-temperature crystallizations from *n*-hexane and pentane, followed by two sublimations at 25° (0.1 mm), to give 0.225 g (6.4% yield) of pale yellow crystalline $C_8H_9Mn(CO)_3$, mp 69–71°. The infrared spectrum of this product in cyclohexane solution exhibited ν(CO) frequencies at 2028 (s), 1961 (s), and 1941 (s) cm.$^{-1}$ The proton nmr spectrum of this product in C_6D_6 solution exhibited resonances at τ 4.92 (double doublet, $J_1 = 10$ Hz, $J_2 = 8$ Hz), 5.43 (triplet, $J = 8$ Hz), 5.89 (multiplet), 7.69 (doublet of multiplets, $J_D = 20$ Hz), and 8.09 (doublet of multiplets, $J_D = 20$ Hz) of approximate relative intensities 2:1:4:1:1.

Anal. Calcd for $C_{11}H_9MnO_3$: C, 54.1; H, 3.7; Mn, 22.5; O, 19.7; mol wt 244. Found: C, 53.9; H, 3.7; Mn, 22.5; O, 19.4; mol wt 244 (mass spectrum).

(c) An orange solid eluted with diethyl ether. This solid was rechromatographed on a 2 × 20 cm alumina column. A small amount of a yellow impurity was first eluted with pure hexane. The orange compound was then eluted with hexane containing increasing amounts of diethyl ether. Slow evaporation of the hexane–diethyl ether eluate deposited 0.044 g (1.6% yield) of orange crystalline $C_8H_8Mn_2(CO)_6$, mp 165–166°. The infrared spectrum of $C_8H_8Mn_2(CO)_6$ in cyclohexane solution exhibited ν(CO) frequencies at 2044 (s), 1991 (m), 1970 (s), 1948 (w), and 1933 (s) cm^{-1}. The proton nmr spectrum of $C_8H_8Mn_2(CO)_6$ in $CDCl_3$ solution exhibited a singlet resonance at τ 5.70.

Anal. Calcd for $C_{14}H_8Mn_2O_6$: C, 44.0; H, 2.1; Mn, 28.8; O, 25.1; mol wt, 382. Found: C, 44.5; H, 2.1; Mn, 28.8; O, 25.2; mol wt, 366 (vapor pressure lowering in CH_2Cl_2 solution), 382 (mass spectrum).

Reaction of $[HMn(CO)_4]_3$ with 1,3,5-Cyclooctatriene. A mixture of 2.52 g (5.01 mmol) of $[HMn(CO)_4]_3$, 1.5 ml (~1.3 g, 13 mmol) of 1,3,5-cyclooctatriene,[21] and 150 ml of hexane was boiled under reflux for 17 hr. The reaction mixture was then concentrated to ~50 ml at ~25° (35 mm) and chromatographed on a 2 × 50 cm alumina column. The following products were eluted from the chromatogram in the order indicated.

(a) Yellow $Mn_2(CO)_{10}$ (1.46 g, 50% yield) eluted with hexane.

(b) A yellow liquid eluted with hexane. This product required further treatment as discussed below.

(c) A light yellow solid eluted with 1:10 diethyl ether–hexane. This was sublimed twice at ~25° (0.1 mm) to give 0.063 g (1.7% yield) of yellow 1,2,3,5,6-h^5-$C_8H_{11}Mn(CO)_3$, mp 107–109° (dec). An infrared spectrum of 1,2,3,5,6-h^5-$C_8H_{11}Mn(CO)_3$ in hexane solution exhibited ν(CO) frequencies at 2020 (s), 1936 (s), and 1930 (s). A proton nmr spectrum of 1,2,3,5,6-h^5-$C_8H_{11}Mn(CO)_3$ in $CDCl_3$ solution exhibited resonances at τ 5.46 (double doublet, $J_1 = 9$ Hz, $J_2 = 6$ Hz), 5.91 (multiplet), 6.05 (triplet, $J = 9$ Hz), 6.43 (broad, width at half-height 18 Hz), and 6.9–8.1 (complex very broad multiplet) of approximate relative intensities 1:1:1:1:7, respectively.

Anal. Calcd for $C_{11}H_{11}MnO_3$: C, 53.6; H, 4.5; Mn, 22.3; O, 19.5; mol wt, 246. Found: C, 53.9; H, 4.8; Mn, 21.7; O, 18.8; mol wt, 246 (mass spectrum).

The yellow liquid from the intermediate band on the original chromatogram (b above) was rechromatographed on a 2 × 50 cm alumina column in hexane solution. This chromatogram was first eluted with hexane. Evaporation of the first yellow eluates gave some more $Mn_2(CO)_{10}$, but the later hexane eluates gave a yellow liquid upon evaporation. This yellow liquid was purified by evaporative distillation at 25° (0.1 mm). An infrared spectrum of the redistilled air-sensitive yellow liquid in hexane solution exhibited ν(CO) frequencies at 2071 (s), 1990 (s), 1973 (s), and 1959 (s) cm^{-1}. A proton nmr spectrum of the yellow liquid in C_6D_6 solution exhibited resonances at τ 5.38 (broad, width at half-height 14 Hz), 5.61 (triplet, $J = 7$ Hz), 6.50 (quintet, $J = 7$ Hz), 7.59 (broad, width at half-height 15 Hz), and 8.3 (multiplet) of approximate relative intensities 2:1:2:1:~5, respectively. Analytical data on this liquid were consistent with its formulation as $C_8H_{11}Mn(CO)_4$.

Anal. Calcd for $C_{12}H_{11}MnO_4$: C, 52.6; H, 4.0. Found: C, 53.6; H, 4.2.

After removal of the liquid $C_8H_{11}Mn(CO)_4$ from the second chromatogram, this chromatogram was eluted with diethyl ether. Evaporation of this eluate gave a yellow solid which was sublimed at ~25° (0.1 mm) in a closed system to give 0.062 g (1.7% yield) of light yellow 1,2,3,4,5-h^5-$C_8H_{11}Mn(CO)_3$, mp 78–80°. The infrared spectrum of 1,2,3,4,5-h^5-$C_8H_{11}Mn(CO)_3$ in hexane solution exhibited ν(CO) frequencies at 2024 (s), 1951 (s), and 1937 (s) cm^{-1}. The proton nmr spectrum of 1,2,3,4,5-h^5-$C_8H_{11}Mn(CO)_3$ in C_6D_6 solution exhibited resonances at τ 4.81 (triplet, $J = 7$ Hz), 5.89 (double doublet, $J_1 = 9$ Hz, $J_2 = 7$ Hz), 7.30 (broad, width at half-height 21 Hz), 8.2–8.8 (complex multiplet), 9.45 (broad doublet, $J_D = 12$ Hz), and 10.43 (multiplet) of approximate relative intensities 1:2:2:4:1:1, respectively.

Anal. Calcd for $C_{11}H_{11}MnO_3$: C, 53.6; H, 4.5; Mn, 22.3; O, 19.5; mol wt, 246. Found: C, 53.6; H, 4.7; Mn, 22.1; O, 20.2; mol wt, 246 (mass spectrum).

Reaction of $[HMn(CO)_4]_3$ with Dimethylaminofulvene. A mixture of 2.5 g (5 mmol) of $[HMn(CO)_4]_3$, 1.03 g (8.45 mmol) of freshly vacuum sublimed 6-dimethylaminofulvene,[22] and 150 ml of hexane was boiled under reflux for 2.5 hr. The reaction mixture was concentrated to ~60 ml at 25° (35 mm) and then chromatographed on a 2 × 45 cm alumina column. The first yellow band of the chromatogram was eluted with hexane. Evaporation of this eluate gave 1.23 g (42% yield) of $Mn_2(CO)_{10}$. The next deep yellow band was eluted with diethyl ether. Evaporation of this eluate at ~25° (35 mm) gave a deep yellow-brown liquid. This liquid was purified further by chromatography on Florisil, using pure diethyl ether as eluent, after removal of impurities by elution with mixtures of diethyl ether and hexane. The doubly chromatographed liquid was evaporatively distilled at 35° (0.1 mm) to give ~0.5 g (~13% yield) of orange liquid $(CH_3)_2NCH_2C_5H_4Mn(CO)_3$. An infrared spectrum of $(CH_3)_2NCH_2C_5H_4Mn(CO)_3$ in cyclohexane solution exhibited ν(CO) frequencies at 2031 (s) and 1942 (vs) cm^{-1}. A proton nmr spectrum of $(CH_3)_2NCH_2C_5H_4Mn(CO)_3$ in C_6D_6 solution exhibited resonances at τ 5.87 (triplet, $J = 3$ Hz), 5.96 (triplet, $J = 3$ Hz), 7.21 (singlet), and 8.03 (singlet) of approximate relative intensities 2:2:2:6, respectively.

Anal. Calcd for $C_{11}H_{12}MnNO_3$: C, 50.6; H, 4.6; N, 5.4; mol wt, 261. Found: C, 50.9; H, 5.1; N, 6.1; mol wt, 261 (mass spectrum).

Reaction of $[HMn(CO)_4]_3$ with Azulene. A mixture of 4.00 g (7.9 mmol) of $[HMn(CO)_4]_3$, 1.50 g (11.7 mmol) of azulene, and 400 ml of hexane was boiled under reflux for 15 hr. The reaction mixture was concentrated to ~50 ml at ~25° (35 mm) and then treated with 50 ml of dichloromethane. This solution was chromatographed on a 2 × 50 cm alumina column. Unreacted azulene and $Mn_2(CO)_{10}$ were first eluted with hexane containing up to 10% dichloromethane. The yellow band of product was then eluted with pure dichloromethane. The eluate was evaporated at ~25° (35 mm). The residue was chromatographed a second time on alumina to remove some free azulene. The yellow product from the second chromatography was purified finally by low-temperature crystallization from dichloromethane to give a total of ~0.3 g (~10% yield based on azulene) of yellow $[C_{10}H_8Mn(CO)_3]_2$, mp 152–153° (lit.[23] mp 153–154°), collected in two crops. In contrast to the monometallic $LMn(CO)_3$ derivatives, the compound $[C_{10}H_8Mn(CO)_3]_2$ did not sublime up to 120° (10^{-5} mm). The infrared spectrum of $[C_{10}H_8Mn(CO)_3]_2$ in CCl_4 solution exhibited ν(CO) frequencies at 2027 (s) and 1942 (s, br) cm^{-1} (lit.[23] 2027 (s), 1938 (s) cm^{-1}). The proton nmr spectrum of $[C_{10}H_8Mn(CO)_3]_2$ in $CDCl_3$ solution exhibited broad poorly resolved resonances at τ 3.88, 4.45, 5.36, 5.75, and 6.68 of approximate relative intensities 3:1:2:1:1, respectively.

Anal. Calcd for $C_{26}H_{16}Mn_2O_6$: C, 58.4; H, 3.0; Mn, 20.6; O, 18.0; mol wt, 534. Found: C, 58.8; H, 3.2; Mn, 21.0; O, 17.7; mol wt, 533 (vapor pressure lowering in benzene solution).

Reaction of $[HMn(CO)_4]_3$ with Norbornadiene. A mixture of 3.51 g (7.0 mmol) of $[HMn(CO)_4]_3$, 4.5 ml (4.10 g, 4.45 mmol) of redistilled norbornadiene, and 450 ml of degassed neohexane was boiled under reflux for 5 hr. The reaction mixture was then con-

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(23) R. Burton, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 4290 (1960).

centrated to ~75 ml at ~25° (35 mm) and chromatographed on a 2 × 35 cm alumina column. A yellow band of $Mn_2(CO)_{10}$ was first eluted with hexane. Evaporation of this eluate gave 1.20 g (29% yield) of $Mn_2(CO)_{10}$. Further development with hexane gave another yellow band immediately followed by a red band. These bands were eluted with hexane containing up to 10% of diethyl ether in the case of the red band. Concentration of the eluate from the red band to ~20 ml, followed by cooling overnight in a −78° bath, gave 0.328 g (8% yield) of red $C_7H_8Mn_2(CO)_7$, mp 95–97°. This product was purified by rechromatography followed by very slow sublimation at 45° (0.2 mm) (extensive decomposition) or preferably low-temperature crystallization from hexane. The infrared spectrum of $C_7H_8Mn_2(CO)_7$ in cyclohexane solution exhibited ν(CO) frequencies at 2086 (s), 2016 (s), 1982 (vs), 1969 (s), and 1939 (s) cm^{-1}. The proton nmr spectrum of $C_7H_8Mn_2(CO)_7$ in C_6D_6 solution exhibited very broad resonances at τ 5.6, 6.5, and 8.9 of approximate relative intensities 2:4:2.

Anal. Calcd for $C_{14}H_8Mn_2O_7$: C, 42.2; H, 2.0; O, 28.1; mol wt, 398. Found: C, 41.6; H, 2.1; O, 28.8; mol wt, 375 (vapor pressure lowering in C_6H_6 solution).

The eluate from the yellow band immediately preceding the red band of $C_7H_8Mn_2(CO)_7$ gave an air-sensitive yellow liquid upon evaporation at ~25° (35 mm). After rechromatography, the infrared spectrum of this liquid in cyclohexane solution exhibited ν(CO) frequencies at 2073 (m), 1976 (s), 1972 (s), and 1937 (s) cm^{-1}. The limited quantities and instability of this liquid prevented its complete purification and characterization.

Reaction of $[HMn(CO)_4]_3$ with 3-Hexyne. A mixture of 2.50 g (5.0 mmol) of $[HMn(CO)_4]_3$, 3.5 ml (2.5 g, 36 mmol) of 3-hexyne, and 350 ml of hexane was boiled under reflux for 15 hr. After concentrating the reaction mixture to ~75 ml at ~25° (35 mm), the solution was chromatographed on a 2 × 45 cm alumina column. Elution of the chromatogram with hexane first gave a yellow band of $Mn_2(CO)_{10}$ contaminated with small amounts of oily impurities. After removal of these oily impurities by a second chromatography, 1.07 g (37% yield) of $Mn_2(CO)_{10}$ was obtained. After removal of the $Mn_2(CO)_{10}$, further elution with hexane gave a yellow solution which, after evaporation at 25° (35 mm) and sublimation at 45° (0.1 mm), gave 0.046 g (0.8% yield) of yellow $(C_2H_5)_6C_6HMn(CO)_3$, mp 76–79°. The infrared spectrum of $(C_2H_5)_6C_6HMn(CO)_3$ in cyclohexane solution exhibited ν(CO) frequencies at 2002 (s), 1929 (s), and 1920 (s) cm^{-1}. The proton nmr spectrum of $(C_2H_5)_6C_6HMn(CO)_3$ in $CDCl_3$ solution exhibited resonances at τ 7.40 (triplet, J = 7.5 Hz), 7.5–8.3 (complex multiplet; at least 20 distinct peaks), 8.58 (triplet, J = 8.5 Hz), 8.66 (triplet, J = 8.5 Hz), 8.95 (triplet, J = 6 Hz), and 9.04 (triplet, J = 5 Hz) of approximate relative intensities 1:12:3:6:6:3, respectively.

Anal. Calcd for $C_{21}H_{31}MnO_3$: C, 65.3; H, 8.0; Mn, 14.2; O, 12.4; mol wt, 386. Found: C, 65.6; H, 8.0; Mn, 13.8; O, 11.8; mol wt, 400 (vapor pressure lowering of acetone solution).

Reaction of $[HMn(CO)_4]_3$ with Diphenylacetylene. A mixture of 2.52 g (5.0 mmol) of $[HMn(CO)_4]_3$, 3.45 g (19.4 mmol) of diphenylacetylene, and 250 ml of hexane was boiled under reflux for 3 hr. The dark brown solution was chromatographed on a 2 × 35 cm alumina column. Elution of the chromatogram with hexane containing increasing amounts of dichloromethane gave first $Mn_2(CO)_{10}$ and diphenylacetylene followed by various colored fractions (orange, green, and brown). Rechromatography of the highly colored fractions gave, after removal of some residual $Mn_2(CO)_{10}$, a white solid which, after crystallization from hexane, gave 0.25 g (7% yield based on diphenylacetylene) of *cis,cis*-1,2,3,4-tetraphenylbutadiene, mp 178–180° (lit.[24,25] mp 185–186°). Identification of this product as *cis,cis*-1,2,3,4-tetraphenylbutadiene was confirmed by its mass spectrum (molecular ion: observed m/e 358; expected m/e 358) and proton nmr spectrum (observed vinylic proton resonance τ 3.72 (singlet); reported[24] vinylic proton resonance τ 3.68 (singlet). Further work-up of the colored fractions did not yield products in sufficient quantities and purities for identification and characterization.

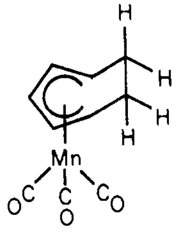
Other Reactions of $[HMn(CO)_4]_3$. Reactions of $[HMn(CO)_4]_3$ with the following unsaturated compounds, under the indicated conditions, gave $Mn_2(CO)_{10}$ as the only manganese carbonyl reaction product in quantities sufficient for identification after a chromatographic work-up procedure similar to those described above: (a) butadiene in hexane solution at 75° for 17 hr in a sealed glass reaction vessel; (b) 1,5-cyclooctadiene in boiling neohexane for 15 hr; under these conditions some of the $[HMn(CO)_4]_3$ starting material was recovered unchanged; (c) 3,3,6,6-tetramethyl-1,4-cyclohexadiene in boiling hexane for 12 hr; incidentally, the metal carbonyl derivatives $Mo(CO)_6$, $(CH_3CN)_3Mo(CO)_3$, $Fe_2(CO)_9$, $Fe_3(CO)_{12}$, and $C_5H_5Co(CO)_2$ did not form olefin complexes with 3,3,6,6-tetramethyl-1,4-cyclohexadiene under conditions[4] where these metal carbonyl derivatives form complexes with other diolefins; (d) 1,4-diphenylbutadiene in boiling hexane for 14 hr; (e) methyl vinyl ketone in boiling hexane for 18 hr; (f) dimethyl acetylenedicarboxylate in boiling hexane for 45 min.

Discussion

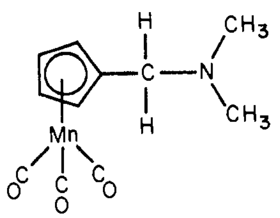
The reactions of $[HMn(CO)_4]_3$ with excesses of many olefins and acetylenes at 50–70° resulted in complete disappearance of the $[HMn(CO)_4]_3$ within a few hours.[26] The major manganese carbonyl product present in the resulting reaction mixtures was $Mn_2(CO)_{10}$. However, after removal of the $Mn_2(CO)_{10}$ by chromatography from many of such reaction mixtures, olefin manganese carbonyls of interest could be isolated by further chromatography generally in low to mediocre yields. The reactivity of $[HMn(CO)_4]_3$ relative to $Mn_2(CO)_{10}$ toward unsaturated compounds is demonstrated by the facile reaction of $[HMn(CO)_4]_3$ with cycloheptatriene under conditions (boiling hexane) where $Mn_2(CO)_{10}$ is completely inert toward cycloheptatriene.

Olefin metal carbonyls of the type (olefin)$M(CO)_3$ are generally the most stable and form most readily in reactions of metal carbonyls with unsaturated compounds.[4] In the case of manganse, the compounds of the type (olefin)$Mn(CO)_3$ with the favored 18-electron rare gas electronic configuration[27] require a neutral olefinic ligand to be a five-electron donor. Such ligands (*e.g.*, cyclopentadienyl), if considered as neutral species, have odd numbers of electrons and thus are not stable in the free state but instead arise from addition or elimination of one hydrogen atom from a stable polyolefin. The presence of potentially reactive hydrogen atoms(s) in $[HMn(CO)_4]_3$ provides a good source of the hydrogen necessary to convert a polyolefin stable in the free state to an olefinic unit capable of forming stable monometallic manganese carbonyl complexes. Thus, addition of an $HMn(CO)_n$ unit (n = 3 or 4) to a triolefin provides a potential source of stable (dienyl)$Mn(CO)_3$ derivatives.

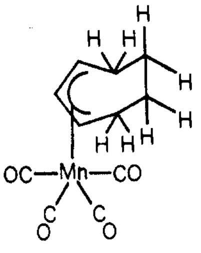
The reaction of $[HMn(CO)_4]_3$ with the triolefin cycloheptatriene gives significant quantities of the previously reported[13] cycloheptadienyl complex $C_7H_9Mn(CO)_3$ (I) and thus is an excellent example of the addition of an $HMn(CO)_n$ unit (n = 3 or 4) to a triolefin to give the corresponding (dienyl)$Mn(CO)_3$ derivative. Similarly, $[HMn(CO)_4]_3$ reacts with 6-dimethylaminofulvene to give the substituted cyclopentadienylmanganese tricarbonyl derivative $(CH_3)_2NCH_2C_5H_4Mn(CO)_3$ (II).



I



II



III

Potentially analogous to the addition of an $HMn(CO)_n$ unit (n = 3 or 4) to a triolefin to give a pentahapto (dienyl)-

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[24] H. H. Freedman, G. A. Doorakian, and W. R. Sandel, *J. Amer. Chem. Soc.*, 87, 3019 (1965).

[25] H. H. Freedman, *J. Org. Chem.*, 27, 2298 (1962).

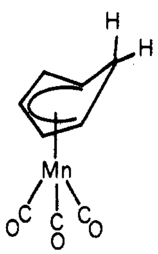
[26] The reaction times of 15 to 18 hr used for many of the reactions of $[HMn(CO)_4]_3$ were selected for convenience. The reactions are probably over within a much shorter time.

[27] R. B. King, *Advan. Chem. Ser.*, No. 62, 203 (1967).

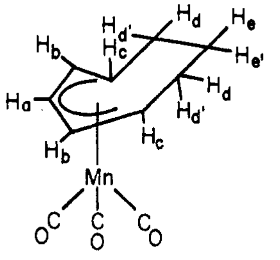
$Mn(CO)_3$ derivative is the addition of an $HMn(CO)_4$ unit to a diolefin to give a trihapto (allylic)$Mn(CO)_4$ derivative. Some evidence for the formation of (allylic)$Mn(CO)_4$ derivatives by reactions of $[HMn(CO)_4]_3$ with conjugated dienes was obtained but the thermal and oxidative instability of these (allylic)$Mn(CO)_4$ derivatives prevented their detailed characterization. The best identified product of this type was the yellow liquid $C_7H_{11}Mn(CO)_4$ obtained from $[HMn(CO)_4]_3$ and 1,3-cycloheptadiene. The infrared spectrum of $C_7H_{11}Mn(CO)_4$ in the $\nu(CO)$ region under high-resolution conditions exhibited the four-band pattern expected for a *cis*-$L_2M(CO)_4$ derivative (L_2 = the C_7H_{11} ligand) rather than the three-band pattern at somewhat lower frequencies expected for a *cis*-$L_2L'M(CO)_3$ derivative and observed for the (dienyl)$Mn(CO)_3$ derivatives. Locally performed analyses for carbon and hydrogen on $C_7H_{11}Mn(CO)_4$ supported the ratio of one C_7 ring to one $Mn(CO)_n$ unit; unfortunately, the limited stability of $C_7H_{11}Mn(CO)_4$ precluded its being shipped to laboratories equipped for more complete elemental analyses. The proton nmr spectrum of $C_7H_{11}Mn(CO)_4$ provided excellent evidence for the obvious structure III by exhibiting, of the correct relative intensities, a resonance at τ 6.1 assignable to the three π-allylic protons, a resonance at τ 8.06 assignable to the four protons of the CH_2 groups adjacent to the π-allylic system, and a resonance at τ 8.86 assignable to the four protons of the two CH_2 groups more remote from the π-allylic system.

The reaction of $[HMn(CO)_4]_3$ and 1,3-cycloheptadiene, besides giving the *trihapto*cycloheptenyl derivative C_7H_{11}-$Mn(CO)_4$ (III), also gave the *pentahapto*cycloheptadienyl derivative $C_7H_9Mn(CO)_3$ (I)[13] apparently by some type of dehydrogenation process. An analogous process occurs in the reaction of $[HMn(CO)_4]_3$ with 1,3-cyclohexadiene to give the *pentahapto*cyclohexadienyl derivative $C_6H_7Mn(CO)_3$ (IV).[12] The reaction of $[HMn(CO)_4]_3$ with 1,3-cyclohexadiene also gave small quantities of an air-sensitive yellow liquid but this could not be unequivocally identified because of its instability and the small quantities available. The reaction of $[HMn(CO)_4]_3$ with butadiene gave no identifiable manganese carbonyl product other than the ubiquitous $Mn_2(CO)_{10}$.

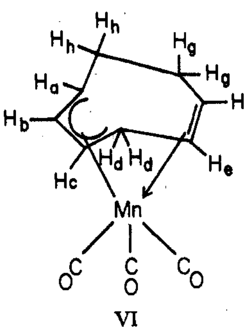
Reactions of $[HMn(CO)_4]_3$ with nonconjugated diolefins did not appear to give simple monometallic olefinic manganese carbonyl derivatives analogous to those obtained from $[HMn(CO)_4]_3$ and 1,3-cyclohexadiene or 1,3-cycloheptadiene. Reaction of $[HMn(CO)_4]_3$ with 1,5-cyclooctadiene gave a mixture containing only $Mn_2(CO)_{10}$ and unreacted $[HMn(CO)_4]_3$ as identifiable manganese carbonyl derivatives. Reaction of $[HMn(CO)_4]_3$ with norbornadiene gave, besides $Mn_2(CO)_{10}$, two other manganese carbonyl derivatives. One of these obtained in low yield was an air-sensitive yellow liquid with an infrared spectrum in the $\nu(CO)$ region similar to that found for the (allylic)$Mn(CO)_4$ derivatives but with a wider separation between the two lowest $\nu(CO)$ frequencies. This liquid could not be obtained in sufficient quantities and purity for detailed characterization. The other product obtained from $[HMn(CO)_4]_3$ and norbornadiene was a red volatile crystalline solid of stoichiometry $C_7H_8Mn_2(CO)_7$. The proton nmr spectrum of this compound was very broad but exhibited a 2:4:2 pattern of the broad nmr resonances suggesting the absence of rearrangement of the norbornadiene ligand by hydrogen migration. Speculation on the nature of $C_7H_8Mn_2(CO)_7$ appears premature until X-ray crystal structure data become available.



IV



V



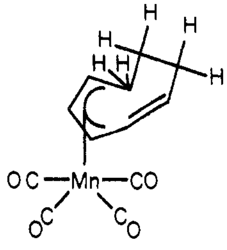
VI

The apparently exclusive formation of the 1,2,3,4,5-*pentahapto*cycloheptadienyl derivative I from the reaction of $[HMn(CO)_4]_3$ with cycloheptatriene suggests that hydrogen preferentially adds to an outside sp^2 carbon atom of a 1,3,5-triene allowing the five remaining sp^2 carbon atoms to remain as a delocalized unit. Corresponding addition of a hydrogen to an internal sp^2 carbon atom of a 1,3,5-triene would give either a 1,2,3,4,6- or a 1,2,3,5,6-*pentahapto*cycloheptadienyl derivative, neither of which was observed. The reaction of $[HMn(CO)_4]_3$ with cyclooctatriene (predominantly the 1,3,5-isomer) gave two crystalline $C_8H_{11}Mn(CO)_3$ products. The proton nmr spectrum of the $C_8H_{11}Mn(CO)_3$, mp 78–80°, supported its formulation as the 1,2,3,4,5-*pentahapto*cyclooctadienyl derivative V. The triplet at τ 4.81 can be assigned to the unique proton bonded to the center carbon atom in the system of five delocalized carbon atoms bonded to the manganese atom (H_a in V). Similarly, the nmr resonances at τ 5.89 and 7.30 can be assigned to the two pairs of protons bonded to the pairs of outer carbons in the system of five delocalized carbon atoms bonded to the manganese atom (H_b and H_c in V). The complex multiplet spread over the range τ 8.2 to 8.8 can be assigned to the four protons in the CH_2 groups adjacent to the five-carbon delocalized system (H_d and $H_{d'}$). The breadth of this resonance clearly arises from the nonequivalence of the "endo" and "exo" protons of these two CH_2 groups. The resonances at τ 9.45 and 10.43 can be assigned to the two nonequivalent protons (H_e and $H_{e'}$) on the center CH_2 group. The formation of 1,2,3,4,5-h^5-$C_8H_{11}Mn(CO)_3$ (V) from $[HMn(CO)_4]_3$ and 1,3,5-cyclooctatriene involves addition of the hydrogen atom to an outside carbon atom of the 1,3,5-triene system of 1,3,5-cyclooctatriene clearly in accord with our observations on the formation of $C_7H_9Mn(CO)_3$ (I) from $[HMn(CO)_4]_3$ and cycloheptatriene.

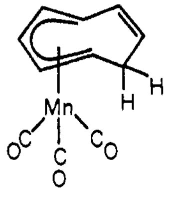
The proton nmr spectrum of the second $C_8H_{11}Mn(CO)_3$ product from $[HMn(CO)_4]_3$ and 1,3,5-cyclooctatriene of mp 107–109° covered a much narrower range than the proton nmr spectrum of 1,2,3,4,5-h^5-$C_8H_{11}Mn(CO)_3$ (V). Since a product of the stoichiometry $C_8H_{11}Mn(CO)_3$ with a monocyclic C_8H_{11} system acting as a five-electron donor cannot have any uncomplexed double bonds, the lowest field nmr resonances in any such $C_8H_{11}Mn(CO)_3$ must be assigned to complexed olefinic, π-allylic, or π-dienyl protons. The fact that the lowest field nmr resonance in $C_8H_{11}Mn(CO)_3$, mp 107–109°, corresponds to only one proton and is 0.45 ppm from the next lowest field nmr resonance suggests that $C_8H_{11}Mn(CO)_3$ must have a structure with an *odd number* of adjacent sp^2 carbon atoms (other than unity) bonded to the metal atom. The 1,2,3,5,6-pentahapto structure VI containing a π-allylic unit is therefore assigned to $C_8H_{11}Mn(CO)_3$, mp 107-109°. The lowest field proton nmr resonance (τ 5.46) is assigned to the central proton of the π-allylic unit (H_b in VI) and the two next highest proton nmr resonances at τ 5.91 and 6.05 to the two outer protons of the π-allylic unit (H_a and H_c in VI) which must be slightly nonequivalent because of the asymmetry of the C_8H_{11} ligand in VI. The resonance at τ 6.43 and a resonance in the broad τ 6.9-8.1 multiplet can be assigned to the complexed olefinic protons (H_e and H_f in VI) with the remainder of the τ 6.9-8.1 complex multiplet arising from the six protons of the three CH_2 groups, no pair of which is equivalent. The formation of a $C_8H_{11}Mn(CO)_3$ isomer of structure VI from $[HMn(CO)_4]_3$ and cyclooctatriene can arise from addition of the hydrogen atom to an outer carbon atom of the 1,3-diene unit in 1,3,6-cyclooctatriene. Since an impurity of only ~2% of the very similar 1,3,6-cyclooctatriene in the 1,3,5-cyclooctatriene used for this work could give rise to the amount of 1,2,3,5,6-$C_8H_{11}Mn(CO)_3$ actually isolated, consideration of possible processes for forming 1,2,3,5,6-$C_8H_{11}Mn(CO)_3$ (VI) from 1,3,5-cyclooctatriene does not seem justified.

The reaction between $[HMn(CO)_4]_3$ and 1,3,5-cyclooctatriene, besides giving the crystalline compounds 1,2,3,4,5-h^5-$C_8H_{11}Mn(CO)_3$ (V) and 1,2,3,5,6-h^5-$C_8H_{11}Mn(CO)_3$ (VI), also gave a small amount of an air-sensitive distillable yellow liquid. The infrared spectrum of this liquid in the ν(CO) region under high resolution conditions, like the corresponding spectrum of the cycloheptenyl derivative $C_7H_{11}Mn(CO)_3$ (III), exhibited the four ν(CO) frequencies expected for a (π-allylic)$Mn(CO)_4$ derivative. This infrared spectrum coupled with carbon and hydrogen analyses indicative of a 1:1 ratio of the C_8 ring and $Mn(CO)_n$ units demonstrates the stoichiometry $C_8H_{11}Mn(CO)_4$ for this liquid. It is tempting to formulate this liquid $C_8H_{11}Mn(CO)_4$ as the bicyclo[4.2.0]octenyl derivative expected from addition of an $HMn(CO)_n$ unit to the bicyclo[4.2.0]octadiene which is readily[28] formed by heating cyclooctatrienes, but the proton nmr spectrum of this $C_8H_{11}Mn(CO)_4$ provides no support for such a formulation. Instead, the observed proton nmr spectrum for $C_8H_{11}Mn(CO)_4$ can only be interpreted on the basis of a monocyclic structure, such as VII, containing an uncomplexed carbon-carbon double bond. The triplet at τ 5.61 looks like the central proton of an allylic group and the apparent quintet at τ 6.50 like the two slightly nonequivalent outer protons of the same π-allylic group. This leaves the broad nmr resonance at τ 5.38 for the two uncomplexed olefinic protons in VII and the resonances at τ 7.59 and 8.3 for the various saturated CH_2 groups in VII. Any interpretation of the observed proton nmr spectrum of $C_8H_{11}Mn(CO)_4$, on the basis of a bicyclic C_8H_{11} group (*e.g.*, a bicyclo[4.2.0]octenyl group), requires that the isolated $C_8H_{11}Mn(CO)_4$ be a mixture containing significant quantities of at least two different compounds, none of which can be either $C_8H_{11}Mn(CO)_3$ isomer V or VI.

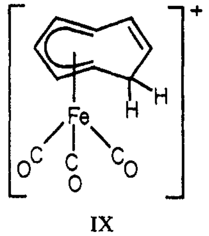
The reaction between $[HMn(CO)_4]_3$ and cyclooctatetraene gave two different manganese carbonyl derivatives besides $Mn_2(CO)_{10}$. The first product is a pale yellow solid of stoichiometry $C_8H_9Mn(CO)_3$. The obvious structure of $C_8H_9Mn(CO)_3$ with a monocyclic C_8H_9 ligand (VIII) is supported by the observed ratio from the proton nmr spectrum of 7:2 for the olefinic protons (both complexed and uncomplexed) relative to the saturated aliphatic protons. The formation of a $C_8H_9Mn(CO)_3$ of structure VIII by a reaction involving addition of hydrogen to a cyclooctatetraene unit relates to the reported observation[29] of the formation of the isoelectronic $[C_8H_9Fe(CO)_3]^+$ cation (IX) by the *low-temperature* protonation of $C_8H_8Fe(CO)_3$. The observed proton nmr spectrum of $C_8H_9Mn(CO)_3$ (VIII) is rather similar to the reported[29] proton nmr spectrum of the isoelectronic $[C_8H_9Fe(CO)_3]^+$ (IX) except for fairly large changes in the chemical shifts of the olefinic protons arising from the different charges in the two systems. The stability of $C_8H_9Mn(CO)_3$ up to at least 69° (the boiling point of hexane in which it is prepared) contrasts with the instability of the $[C_8H_9Fe(CO)_3]^+$ cation IX above about −60° where it forms bicyclic derivatives (*e.g.*, X).



VII



VIII



IX

The second product from the reaction between $[HMn(CO)_4]_3$ and cyclooctatetraene was the bimetallic derivative $C_8H_8Mn_2(CO)_6$, which was an orange air-stable crystalline solid considerably less soluble in organic solvents than the monometallic (dienyl)$Mn(CO)_3$ derivatives. The formation of $C_8H_8Mn_2(CO)_6$ from $[HMn(CO)_4]_3$ and cyclooctatetraene appears not to involve $[HMn(CO)_4]_3$ as a source of hydrogen but only as a source of reactive manganese carbonyl groups, although the possibility of a hydride intermediate $C_8H_8[Mn(CO)_3H]_2$, which under the reaction conditions is unstable with respect to $C_8H_8Mn_2(CO)_6$ and hydrogen, cannot be excluded. The proton nmr spectrum of $C_8H_8Mn_2(CO)_6$ exhibited a sharp singlet resonance from the eight cyclooctatetraene protons indicating fluxional properties[30] for $C_8H_8Mn_2(CO)_6$ similar to many known cyclooctatetraene metal carbonyl derivatives, such as the compounds $C_8H_8M(CO)_3$ (M = Cr,[31] Mo,[31,32] W,[31] Fe,[30-33] Ru,[34] and Os[35]), $C_8H_8Fe_2(CO)_5$,[36] and $(C_8H_8)_2Ru_3(CO)_4$.[37] The solubility of $C_8H_8Mn_2(CO)_6$ in suitable nmr solvents was too limited to investigate its nmr spectrum at low temperatures. The obvious structure for $C_8H_8Mn_2(CO)_6$ seems to be XI, which

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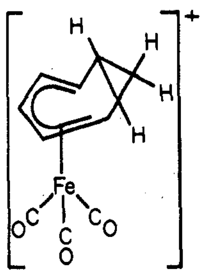

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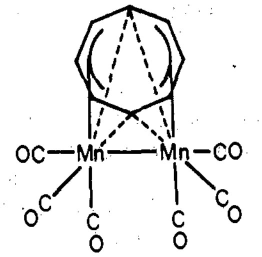
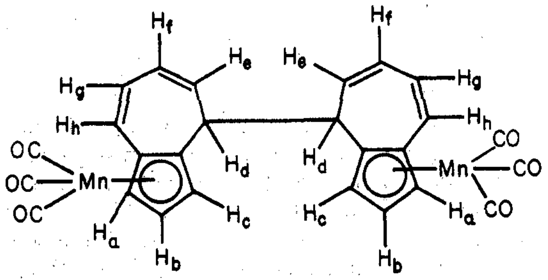


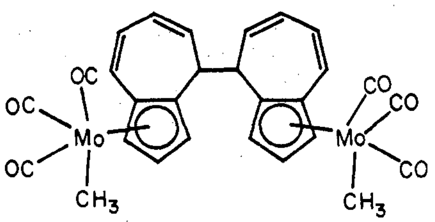
XI

is closely related to that of the similar cyclooctatetraene-iron carbonyl derivative of stoichiometry[36] $C_8H_8Fe_2(CO)_5$.

The reaction of $[HMn(CO)_4]_3$ with the fulvene $C_5H_4CH\text{-}N(CH_3)_2$ to give the cyclopentadienylmanganese tricarbonyl derivative $(CH_3)_2NCH_2C_5H_4Mn(CO)_3$ (II) by addition of hydrogen to the fulvene exocyclic double bond suggested that $[HMn(CO)_4]_3$ might react with azulene by addition to the azulene double bond exocyclic to the five-membered ring to give a substituted cyclopentadienylmanganese tricarbonyl derivative of stoichiometry $C_{10}H_9Mn(CO)_3$ with a bicyclic $C_{10}H_9$ ligand containing fused five- and seven-membered rings. However, the reaction of $[HMn(CO)_4]_3$ with azulene did not give any $C_{10}H_9Mn(CO)_3$ derivative of this type. Instead, the only manganese carbonyl derivative, other than $Mn_2(CO)_{10}$, obtained from $[HMn(CO)_4]_3$ and azulene was a yellow crystalline solid of apparent stoichiometry $[C_{10}H_8Mn(CO)_3]_2$ seemingly identical with a compound of this stoichiometry isolated in low yield by Burton, Pratt, and Wilkinson[23] from the reaction between $Mn_2(CO)_{10}$ and azulene, but whose preparation could not be reproduced by later workers.[38] We have reproduced several times the preparation of $[C_{10}H_8Mn(CO)_3]_2$ from $[HMn(CO)_4]_3$ and azulene and, therefore, feel that this preparation of $[C_{10}H_8Mn(CO)_3]_2$ is more reliable than its previously reported[23] preparation. The properties of $[C_{10}H_8Mn(CO)_3]_2$ are consistent with its previously postulated[39] similarity to other bimetallic azulene metal carbonyl complexes, such as $[C_{10}H_8Mo(CO)_3CH_3]_2$[39] and $[C_{10}H_8V(CO)_4]_2$[40], in which the five-membered ring of the azulene is bonded to the transition metal, like a pentahapto cyclopentadienyl ring, and in which coupling of the two halves does not involve metal-metal bond formation but instead formation of a carbon-carbon bond between carbon atoms in the seven-membered rings in each half. The proton nmr spectrum of $[C_{10}H_8Mn(CO)_3]_2$ in $CDCl_3$ was rather broad, but the observed resonances could be interpreted on the basis of such a structure. Thus, the resonances at τ 5.36 and 5.75 can be assigned to the three protons bonded to carbon atoms in the five-membered ring complexed with the metal atom (H_a, H_b, and H_c in XII), whereas, the resonances at τ 3.88 and 4.45 can be assigned to the four protons bonded to the carbon atoms of the two uncomplexed double bonds in the seven-membered ring (H_e, H_f, H_g, and H_h in XII). The remaining highest field proton resonance at τ 6.68 can be assigned to the proton attached to the sp^3 carbon aton in the seven-membered ring which forms a carbon-carbon single bond with the other seven-membered ring (H_d in XII). The correspondence of the higher resonance assigned to the uncomplexed olefinic protons to only one of the four uncomplexed protons suggests that only one of the hydrogen-bearing carbon atoms of the uncomplexed double bonds is adjacent to the sp^3 carbon involved in coupling of the seven-membered rings of the two halves. This supports ortho, ortho coupling of the two seven-membered rings in $[C_{10}H_8Mn(CO)_3]_2$, as in structure XII, which is completely analogous to the structure XIII found by X-ray crystallography[41] on $[CH_3Mo(CO)_3C_{10}H_8]_2$.



XII



XIII

The interesting olefinic manganese carbonyl derivatives obtained from reactions between olefins with several double bonds and $[HMn(CO)_4]_3$ made of interest similar reactions of acetylenes with $[HMn(CO)_4]_3$. Reaction of 3-hexyne (diethylacetylene) with $[HMn(CO)_4]_3$ gave a low yield (~1%) of a volatile yellow crystalline solid of stoichiometry $C_{18}H_{31}Mn(CO)_3$ (*i.e.*, (hexyne)$_3$HMn(CO)$_3$). The proton nmr spectrum of this compound supported its formulation as the 1,2,3,4,5,6-hexaethylcyclohexadienyl derivative XIV. The CH_2 resonances of the six ethyl groups exhibited a broad and complex resonance at τ 7.5–8.3, but this region also contained a clear triplet, centered at τ 7.40, which can be assigned to the unique proton on the sp^3 carbon atom of the cyclohexadienyl ring which is split by the CH_2 moiety of the ethyl group attached to the same carbon atom. The methyl resonances were four distinct ~1:2:1 triplets in the τ 8.5 to 9.1 region with an approximate relative intensity pattern 1:2:2:1. This is in perfect agreement with the numbers of equivalent and nonequivalent ethyl groups required for structure XIV. The cyclotrimerization of acetylenes with metal carbonyls and related systems to form benzene derivatives is well established,[42] but the incorporation of a hydrogen atom during such cyclotrimerization to give a cyclohexadienyl derivative as found for the reaction between 3-hexyne and $[HMn(CO)_4]_3$ is unprecedented.

The reaction of $[HMn(CO)_4]_3$ with diphenylacetylene yielded mixtures giving chromatograms with highly colored bands, in addition to the usual yellow band of $Mn_2(CO)_{10}$. However, none of these bands yielded any organomanganese carbonyl derivatives in quantities sufficient for identification. Instead, this reaction gave a white crystalline hydrocarbon indicated by its mass spectrum to have the stoichiometry $C_{28}H_{22}$. The melting point and proton nmr spectrum of this hydrocarbon indicated it to be the reported[24,25] *cis,cis*-1,2,3,4-tetraphenylbutadiene (XV). This indicates that one

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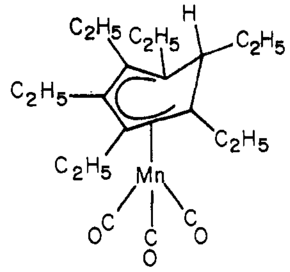
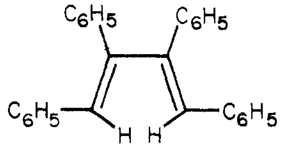


XIV



XV

process which diphenylacetylene undergoes upon its reaction with $[HMn(CO)_4]_3$ is linear dimerization accompanied by hydrogen addition; this reaction resembles the dimerization of diphenylacetylene with alkali metals.[43] The formation of the cis,cis isomer of 1,2,3,4-tetraphenylbutadiene upon reaction of diphenylacetylene with $[HMn(CO)_4]_3$ is consistent with an unstable manganacyclopentadiene or 1,2-dimanganacyclohexadiene derivative as an intermediate.

Acknowledgment. We are indebted to the National Science Foundation for partial support of this work under Grant GP-31347X, to Oberlin College for a research status appointment to Dr. M. N. Ackermann during his sabbatical leave, to Professor Bruce R. Kowalski of the Colorado State University, Fort Collins, Colo., for help with some of the mass spectra of the bimetallic manganese carbonyl derivatives, and to the Badische Anilin-und Sodafabrik, Ludwigshafen, Germany, for generous research samples of cyclooctatetraene.

Registry No. I, 32798-86-0; II, 49626-33-7; III, 49626-34-8; IV, 12108-14-4; V, 49626-35-9; VI, 49626-36-0; VII, 49626-37-1; VIII, 49626-38-2; XI, 49626-39-3; XII, 49664-76-8; XIV, 49784-17-0; XV, 1608-10-2; $C_7H_8Mn_2(CO)_7$, 50270-79-6; $[HMn(CO)_4]_3$, 18444-56-9; 1,3-cyclohexadiene, 592-57-4; cycloheptatriene, 544-25-2; 1,3-cycloheptadiene, 4054-38-0; cyclooctatetraene, 629-20-9; 1,3,5-cyclooctatriene, 1871-52-9; 1,3,6-cyclooctatriene, 3725-30-2; 6-(dimethylamino)fulvene, 4477-03-6; azulene, 275-51-4; norbornadiene, 121-46-0; 3-hexyne, 928-49-4; diphenylacetylene, 501-65-5.

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Contribution from the Department of Chemistry,
Worcester Polytechnic Institute, Worcester, Massachusetts 01609

Relative Energies of the Cubic $t_{2g}(\pi^*)$ Orbitals in Some Mixed-Ligand Complexes of Iron(II)

P. B. MERRITHEW,* J. J. GUERRERA, and A. J. MODESTINO

Received June 26, 1973

The temperature dependence of the quadrupole splitting of $Fe(isoq)_4X_2$ ($X^- = I^-, Br^-, Cl^-$), $Fe(py)_4X_2$ ($X^- = Br^-, OCN^-, N_3^-$), and $Fe(1,10\text{-phen})_2X_2$ ($X^- = Br^-, Cl^-, SCN^-$) was obtained in the range 77–300°. These data and those obtained earlier on $Fe(py)_4X_2$ ($X^- = I^-, Cl^-, SCN^-$) were analyzed in order to determine the splitting of the cubic $t_{2g}(\pi^*)$ orbitals. The axial splitting in these compounds was found to be less than 800 cm^{-1}. The relative energy of the $e_g(\pi^*)$ orbital in the series FeL_4X_2 (L = pyridine, isoquinoline) follows the order $I^- \leqslant Br^- \leqslant Cl^-$. Analysis of the $Fe(1,10\text{-phen})_2X_2$ ($X^- = Br^-, Cl^-, SCN^-$) data suggests a trigonal distortion from octahedral symmetry.

The relative energies of the cubic $t_{2g}(\pi^*)$ orbitals in mixed-ligand complexes have been previously investigated by Mossbauer spectroscopy.[1,2] In these treatments of the quadrupole splitting data, assumptions were made regarding the sign and the magnitude of the temperature-independent or "lattice" contributions to the quadrupole splitting. Burbridge, *et al.*,[1] assumed that the "lattice" contributions could be calculated from a crystal field model. The large quadrupole splittings observed for some iron(II) low-spin compounds[3] suggest that this is generally not a good assumption. Merrithew, *et al.*,[2] assumed that the "lattice" contributions were relatively small and that the signs of the electric field gradient tensor components could be predicted on the basis of the formal charge on the ligands. The latter assumption has been shown to be unjustified.[4] We have undertaken a more rigorous investigation of the quadrupole splitting of a series of mixed-ligand complexes to define more accurately the effect of the halogens and pseudohalogens on the energy of the cubic $t_{2g}(\pi^*)$ orbitals.

Experimental Section

Preparation of Complexes. $Fe(py)_4Br_2$ (py = pyridine) and $Fe(py)_4(OCN)_2$ were prepared by the methods of Golding, *et al.*[5] $Fe(isoq)_4Cl_2$ (isoq = isoquinoline), $Fe(isoq)_4Br_2$, and $Fe(isoq)_4I_2$ were prepared by the methods of Goodgame, *et al.*[6] $Fe(phen)_2Cl_2$ (phen = 1,10-phenanthroline), $Fe(phen)_2Br_2$, and $Fe(phen)_2(SCN)_2$ were prepared by the methods of Madeja and Konig.[7]

$Fe(py)_4(N_3)_2$ was prepared in a manner similar to the cyanate and recrystallized from pyridine. The compound decomposes slowly with the evolution of pyridine. *Anal.* Calcd for $Fe(py)_4(N_3)_2$: C, 52.63; H, 4.39; N, 30.70. Found: C, 50.42; H, 4.27; N, 29.59.

Mossbauer Spectra. The Mossbauer spectrometer and associated cryostat have been described previously.[8] The temperature was measured with a copper-constantan thermocouple and controlled to within 2° of the indicated temperature. The spectra were fitted with

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