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The Characterization and Crystallography of *trans*-Azulenedimanganese Hexacarbonyl

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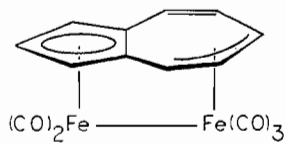
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trans-Azulenedimanganese hexacarbonyl, $trans\text{-C}_{10}\text{H}_8\text{Mn}_2(\text{CO})_6$, was prepared by the reaction of azulene and dimanganese decacarbonyl. The compound crystallizes in the triclinic space group $P\bar{1}$ (C_1 ; no. 2) with $a = 12.900 \pm 0.014 \text{ \AA}$, $b = 9.640 \pm 0.010 \text{ \AA}$, $c = 6.950 \pm 0.008 \text{ \AA}$, $\alpha = 106.49 \pm 0.10^\circ$, $\beta = 106.53 \pm 0.10^\circ$, $\gamma = 70.54 \pm 0.10^\circ$, and $Z = 2$. Observed and calculated densities are 1.75 ± 0.01 and 1.765 g cm^{-3} , respectively. A single-crystal X-ray diffraction study has been completed. Data out to $\sin \theta = 0.38$ (Mo $K\alpha$ radiation) were collected with a 0.01° -incrementing Buerger automated diffractometer, and the structure was solved by a combination of Patterson, Fourier, and least-squares refinement techniques. All atoms (including hydrogens) have been located, the final discrepancy index being $R_F = 8.12\%$ for 1683 independent, nonzero reflections. The crystal is composed of discrete molecular units of $trans\text{-C}_{10}\text{H}_8\text{Mn}_2(\text{CO})_6$, separated by normal van der Waals contacts. The molecule consists of two $\text{Mn}(\text{CO})_3$ groups bonded (with an over-all *trans* configuration) to an azulene ligand. One $\text{Mn}(\text{CO})_3$ group interacts with the atoms of the five-membered ring and participates in a π -cyclopentadienyl \rightarrow metal bond, while the other $\text{Mn}(\text{CO})_3$ group is associated with the remaining five atoms of the azulene nucleus *via* a noncyclic π -pentadienyl \rightarrow metal linkage.

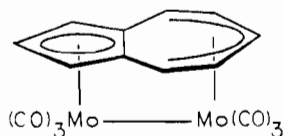
Introduction

Azulene-metal-carbonyl complexes have been known since 1958 when Burton, *et al.*, reported the preparation of $\text{AzMo}_2(\text{CO})_6$ ¹ and $\text{AzFe}_2(\text{CO})_6$.² [The mnemonic "Az" will be used throughout this paper to represent azulene or a substituted azulene.] Subsequent work led to the identification of the dimeric species $[\text{AzMn}(\text{CO})_3]_2$,³ $[\text{AzV}(\text{CO})_4]_2$,⁴ $[\text{AzMo}(\text{CO})_3\text{CH}_3]_2$,⁵ and $[\text{AzFe}(\text{CO})_2]_2$.⁶ Although a large number of possible structures for these complexes had been considered,^{1-5,7-10} the unambiguous formulation of

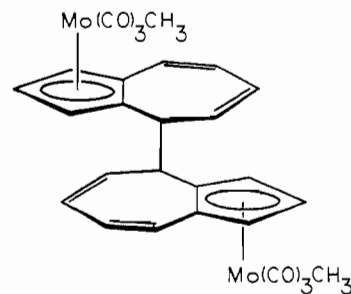
$\text{AzFe}_2(\text{CO})_6$ ^{11,12} as I and $\text{AzMo}_2(\text{CO})_6$ ¹³⁻¹⁵ as II was accomplished only by crystallographic studies. The dimeric complex $[\text{AzMo}(\text{CO})_3\text{CH}_3]_2$ has been shown^{16,17} to have structure III, in which two azulene residues are



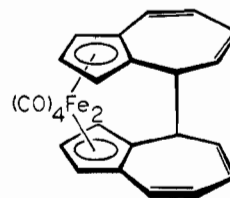
I



II



III



IV

- (1) R. Burton and G. Wilkinson, *Chem. Ind.* (London), 1205 (1958).
- (2) R. Burton, M. L. H. Green, E. W. Abel, and G. Wilkinson, *ibid.*, 1592 (1958).
- (3) R. Burton, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 4290 (1960).
- (4) E. O. Fischer, Abstracts, Organometallic Chemical Symposium, Cincinnati, Ohio, June 1963, p 66.
- (5) R. B. King and M. B. Bisnette, *Inorg. Chem.*, **4**, 475 (1965).
- (6) R. B. King, *J. Am. Chem. Soc.*, **88**, 2075 (1966).
- (7) D. A. Brown, *Chem. Ind.* (London), 126 (1959).
- (8) D. A. Brown and C. M. McMullin, *U. S. Govt. Res. Rept.*, **39**, S-4 (1964).
- (9) M. L. Maddox, S. L. Stafford, and H. D. Kaesz, *Advan. Organometal. Chem.*, **3**, 113 (1965).
- (10) M. A. Eennett, *ibid.*, **4**, 366 (1966).

linked *via* a 4-*exo*,4'-*exo* carbon-carbon bond. More recently, an investigation of the tetranuclear Az_2Fe_4

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- (13) M. R. Churchill and P. H. Bird, *Chem. Commun.*, 746 (1967).
- (14) J. S. McKechnie and I. C. Paul, *ibid.*, 747 (1967).
- (15) M. R. Churchill and P. H. Bird, *Inorg. Chem.*, **7**, 1545 (1968).
- (16) P. H. Bird and M. R. Churchill, *Chem. Commun.*, 705 (1967).
- (17) P. H. Bird and M. R. Churchill, *Inorg. Chem.*, **7**, 349 (1968).

(CO)₁₀¹⁸⁻²¹ has suggested that the dimeric [AzFe(CO)₂]₂ has structure IV, in which the two azulene nuclei are joined by a 4-*endo*,4'-*endo* carbon-carbon bond. Since the metal atoms in [AzMn(CO)₃]₂ and [AzV(CO)₄]₂ reach the appropriate inert-gas configuration without the requirement of metal-metal bond formation, it may tacitly be assumed that these molecules have structures analogous to III.

While studying the reaction of azulene with dimanganese decacarbonyl, we consistently obtained a stable material of composition AzMn₂(CO)₆, rather than the previously reported unstable [AzMn(CO)₃]₂.³ In the expectation that this new compound would further clarify the field of azulene-metal-carbonyl chemistry, we have determined its crystal and molecular structure. A preliminary account of this work has appeared previously.²²

Experimental Section

In a typical preparation, azulene (0.3 g) and dimanganese decacarbonyl (1.0 g) in ligroin (bp ~100°, 30 ml) were refluxed under nitrogen for 36 hr. The solvent was then removed under vacuum, and the remaining azulene and dimanganese decacarbonyl were sublimed from the reaction mixture. The residue was dissolved in hexane-methylene chloride and chromatographed on Florisil. The yellow band was isolated and evaporated to dryness. Recrystallization, by the slow cooling of a solution in ethylene dichloride-hexane, yielded pale yellow crystals. The complex is air stable in the solid state; solutions appear to be stable under nitrogen, but slowly decompose in the presence of air.

A mass spectral examination of the product showed the parent ion peak at *m/e* 406, corresponding to C₁₀H₈Mn₂(CO)₆⁺, along with species consistent with stepwise loss of CO—*i.e.*, C₁₀H₈Mn₂(CO)_{6-n}⁺ (*n* = 1-6).

An infrared spectrum, taken in carbon tetrachloride, showed bands typical of terminal carbonyl stretches (2031, 2016, 1966, and 1943 cm⁻¹).

Unit Cell and Space Group

Optical examination and preliminary X-ray diffraction photographs indicated that the crystals probably belonged to the triclinic system. A subsequent survey of *hk0*, *hk1*, *hk2* Weissenberg photographs and *h0l*, *h1l*, *h2l*, *0kl*, *1kl*, *2kl* precession photographs (all taken with Mo K α radiation) revealed no systematic absences nor any diffraction symmetry higher than C₁ ($\bar{1}$). The crystals were therefore assumed to be truly triclinic.

Unit cell parameters, obtained from calibrated (a_{NaCl} = 5.640 Å) precession photographs taken with Mo K α radiation ($\bar{\lambda}$ 0.7107 Å) at 24 ± 2°, are: *a* = 12.900 ± 0.014 Å, *b* = 9.640 ± 0.010 Å, *c* = 6.950 ± 0.008 Å, α = 106.49 ± 0.10°, β = 106.53 ± 0.10°, and γ = 70.54 ± 0.10°. The errors given are derived from the sum of the inaccuracies involved in measuring (from precession photographs) the positions of diffraction rows from the crystal under investigation and from the sodium chloride crystal; they are "maximum possible errors" and are therefore probably overesti-

mates. The above cell constants are those used throughout this paper. The "reduced cell," obtained by a Delaunay reduction,²³ is defined by: *a'* = [101] = 12.797 Å, *b'* = [00 $\bar{1}$] = 6.950 Å, *c'* = [$\bar{1}$ 10] = 13.283 Å, α' = 94.03°, β' = 134.17°, γ' = 104.87°.

The unit cell volume is 762.1 Å³. The observed density (ρ_{obsd} = 1.75 ± 0.01 g cm⁻³, by flotation in aqueous zinc iodide solution) is in excellent agreement with the value calculated for a molecular weight of 405.88 and *Z* = 2 (ρ_{calcd} = 1.765 g cm⁻³). Of the possible space groups (P1 and $\bar{P}1$), the latter was considered the more likely owing to its greater frequency of occurrence.^{24,25} No piezoelectric test was performed, but the successful solution of the structure (*vide infra*) confirmed that the true space group was, indeed, the centrosymmetric $\bar{P}1$ (C₁¹; no. 2).

Collection and Reduction of X-Ray Diffraction Data

Azulenemanganese hexacarbonyl crystallizes as platelike parallelepipeds with well-developed 010 faces. Two crystals were used during the collection of X-ray diffraction data. Crystal I (0.19 × 0.04 × 0.43 mm) was mounted along its extended *c* direction and crystal II (0.18 × 0.11 × 0.50 mm) was mounted along the short *b* direction. [Dimensions of the crystals refer sequentially to the *a*, *b*, *c* directions.]

Intensity data were collected with a 0.01°-incrementing Buerger automated diffractometer, using equi-inclination geometry and the customary "stationary-background, ω -scan, stationary-background" counting sequence. The apparatus, experimental technique, and general precautions have been described in a previous publication.¹⁷ Details specific to the present analysis include the following: (i) Mo K α radiation ($\bar{\lambda}$ 0.7107 Å) was used. (ii) The angle scanned (ω) is given by $\omega = [2.0 + (0.8/L)]^\circ$, where 1/*L* is the Lorentz factor.²⁶ (iii) The scan speed was 2°/min. (iv) Backgrounds (*B*₁ and *B*₂) were each counted for half the time required for the ω scan (the count associated with this scan is *C*). (v) Within a given zone, the stability of the system was monitored by remeasuring a carefully preselected check reflection after each batch of 20 reflections had been collected. [No significant variations were detected.] (vi) *I*(*hkl*), the intensity of the reflection *hkl*, was calculated as: $I(hkl) = C(hkl) - [B_1(hkl) + B_2(hkl)]$.

A total of 2142 reflections in the zones *hk0* through *hk7* were collected from crystal I, and 2092 reflections in the zones *h0l* through *h10l* were collected from crystal II. In each case this represents data complete to $\sin \theta = 0.38$, except for the few low-angle reflections ($\theta \leq 4^\circ$) which were shielded by the back-stop. [The limit $\sin \theta = 0.38$ is sufficiently high to include over

(23) "International Tables for X-Ray Crystallography," Vol. I, The Kynoch Press, Birmingham, England, 1965, pp 530-535.

(24) W. Nowacki, T. Matsumoto, and A. Edenharter, *Acta Cryst.*, **22**, 935 (1967).

(25) J. D. H. Donnay, G. Donnay, E. G. Cox, O. Kennard, and M. V. King, "Crystal Data, Determinative Tables," Monograph No. 5, 2nd ed, American Crystallographic Association, 1963.

(26) The term involving the Lorentz factor is included to allow for divergence of the X-ray beam which results in extended low-order reflections on upper level data: D. C. Phillips, *Acta Cryst.*, **7**, 746 (1954).

(18) This species had previously been reported as Az₂Fe₂(CO)₁₀¹⁸ but has recently been shown to have the composition Az₂Fe₄(CO)₁₀.¹⁹

(19) M. R. Churchill and P. H. Bird, *J. Am. Chem. Soc.*, **90**, 3241 (1968).

(20) The other presently known tetranuclear azulene-metal-carbonyl complex, AzRu₄(CO)₉, has a completely different bonding scheme.²¹

(21) M. R. Churchill and P. H. Bird, *J. Am. Chem. Soc.*, **90**, 800 (1968).

(22) P. H. Bird and M. R. Churchill, *Chem. Commun.*, 145 (1968).

TABLE I
OBSERVED AND CALCULATED STRUCTURE FACTORS FOR trans-C10H8Mn2(CO)6^2

Table with multiple columns containing numerical data for structure factors. The table is organized into several sections labeled L = -7, L = -2, L = -1, L = 0, L = 1, L = 2, L = 3, L = 4, L = 5, L = 6, L = 7, L = 8, L = 9, L = 10, L = 11, L = 12, L = 13, L = 14, L = 15, L = 16, L = 17, L = 18, L = 19, L = 20, L = 21, L = 22, L = 23, L = 24, L = 25, L = 26, L = 27, L = 28, L = 29, L = 30, L = 31, L = 32, L = 33, L = 34, L = 35, L = 36, L = 37, L = 38, L = 39, L = 40, L = 41, L = 42, L = 43, L = 44, L = 45, L = 46, L = 47, L = 48, L = 49, L = 50, L = 51, L = 52, L = 53, L = 54, L = 55, L = 56, L = 57, L = 58, L = 59, L = 60, L = 61, L = 62, L = 63, L = 64, L = 65, L = 66, L = 67, L = 68, L = 69, L = 70, L = 71, L = 72, L = 73, L = 74, L = 75, L = 76, L = 77, L = 78, L = 79, L = 80, L = 81, L = 82, L = 83, L = 84, L = 85, L = 86, L = 87, L = 88, L = 89, L = 90, L = 91, L = 92, L = 93, L = 94, L = 95, L = 96, L = 97, L = 98, L = 99, L = 100, L = 101, L = 102, L = 103, L = 104, L = 105, L = 106, L = 107, L = 108, L = 109, L = 110, L = 111, L = 112, L = 113, L = 114, L = 115, L = 116, L = 117, L = 118, L = 119, L = 120, L = 121, L = 122, L = 123, L = 124, L = 125, L = 126, L = 127, L = 128, L = 129, L = 130, L = 131, L = 132, L = 133, L = 134, L = 135, L = 136, L = 137, L = 138, L = 139, L = 140, L = 141, L = 142, L = 143, L = 144, L = 145, L = 146, L = 147, L = 148, L = 149, L = 150, L = 151, L = 152, L = 153, L = 154, L = 155, L = 156, L = 157, L = 158, L = 159, L = 160, L = 161, L = 162, L = 163, L = 164, L = 165, L = 166, L = 167, L = 168, L = 169, L = 170, L = 171, L = 172, L = 173, L = 174, L = 175, L = 176, L = 177, L = 178, L = 179, L = 180, L = 181, L = 182, L = 183, L = 184, L = 185, L = 186, L = 187, L = 188, L = 189, L = 190, L = 191, L = 192, L = 193, L = 194, L = 195, L = 196, L = 197, L = 198, L = 199, L = 200, L = 201, L = 202, L = 203, L = 204, L = 205, L = 206, L = 207, L = 208, L = 209, L = 210, L = 211, L = 212, L = 213, L = 214, L = 215, L = 216, L = 217, L = 218, L = 219, L = 220, L = 221, L = 222, L = 223, L = 224, L = 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669, L = 670, L = 671, L = 672, L = 673, L = 674, L = 675, L = 676, L = 677, L = 678, L = 679, L = 680, L = 681, L = 682, L = 683, L = 684, L = 685, L = 686, L = 687, L = 688, L = 689, L = 690, L = 691, L = 692, L = 693, L = 694, L = 695, L = 696, L = 697, L = 698, L = 699, L = 700, L = 701, L = 702, L = 703, L = 704, L = 705, L = 706, L = 707, L = 708, L = 709, L = 710, L = 711, L = 712, L = 713, L = 714, L = 715, L = 716, L = 717, L = 718, L = 719, L = 720, L = 721, L = 722, L = 723, L = 724, L = 725, L = 726, L = 727, L = 728, L = 729, L = 730, L = 731, L = 732, L = 733, L = 734, L = 735, L = 736, L = 737, L = 738, L = 739, L = 740, L = 741, L = 742, L = 743, L = 744, L = 745, L = 746, L = 747, L = 748, L = 749, L = 750, L = 751, L = 752, L = 753, L = 754, L = 755, L = 756, L = 757, L = 758, L = 759, L = 760, L = 761, L = 762, L = 763, L = 764, L = 765, L = 766, L = 767, L = 768, L = 769, L = 770, L = 771, L = 772, L = 773, L = 774, L = 775, L = 776, L = 777, L = 778, L = 779, L = 780, L = 781, L = 782, L = 783, L = 784, L = 785, L = 786, L = 787, L = 788, L = 789, L = 790, L = 791, L = 792, L = 793, L = 794, L = 795, L = 796, L = 797, L = 798, L = 799, L = 800, L = 801, L = 802, L = 803, L = 804, L = 805, L = 806, L = 807, L = 808, L = 809, L = 810, L = 811, L = 812, L = 813, L = 814, L = 815, L = 816, L = 817, L = 818, L = 819, L = 820, L = 821, L = 822, L = 823, L = 824, L = 825, L = 826, L = 827, L = 828, L = 829, L = 830, L = 831, L = 832, L = 833, L = 834, L = 835, L = 836, L = 837, L = 838, L = 839, L = 840, L = 841, L = 842, L = 843, L = 844, L = 845, L = 846, L = 847, L = 848, L = 849, L = 850, L = 851, L = 852, L = 853, L = 854, L = 855, L = 856, L = 857, L = 858, L = 859, L = 860, L = 861, L = 862, L = 863, L = 864, L = 865, L = 866, L = 867, L = 868, L = 869, L = 870, L = 871, L = 872, L = 873, L = 874, L = 875, L = 876, L = 877, L = 878, L = 879, L = 880, L = 881, L = 882, L = 883, L = 884, L = 885, L = 886, L = 887, L = 888, L = 889, L = 890, L = 891, L = 892, L = 893, L = 894, L = 895, L = 896, L = 897, L = 898, L = 899, L = 900, L = 901, L = 902, L = 903, L = 904, L = 905, L = 906, L = 907, L = 908, L = 909, L = 910, L = 911, L = 912, L = 913, L = 914, L = 915, L = 916, L = 917, L = 918, L = 919, L = 920, L = 921, L = 922, L = 923, L = 924, L = 925, L = 926, L = 927, L = 928, L = 929, L = 930, L = 931, L = 932, L = 933, L = 934, L = 935, L = 936, L = 937, L = 938, L = 939, L = 940, L = 941, L = 942, L = 943, L = 944, L = 945, L = 946, L = 947, L = 948, L = 949, L = 950, L = 951, L = 952, L = 953, L = 954, L = 955, L = 956, L = 957, L = 958, L = 959, L = 960, L = 961, L = 962, L = 963, L = 964, L = 965, L = 966, L = 967, L = 968, L = 969, L = 970, L = 971, L = 972, L = 973, L = 974, L = 975, L = 976, L = 977, L = 978, L = 979, L = 980, L = 981, L = 982, L = 983, L = 984, L = 985, L = 986, L = 987, L = 988, L = 989, L = 990, L = 991, L = 992, L = 993, L = 994, L = 995, L = 996, L = 997, L = 998, L = 999, L = 1000.

The table shows h, k, |10F0|, and |10Fc|, in blocks of constant L.

95% of the data visible on long-exposure Weissenberg films. Standard deviations assigned to reflections were: I(hkl) >= 625, sigma(hkl) = 0.1[I(hkl)]; 625 > I(hkl), sigma(hkl) = 2.5[I(hkl)]^1/2. Reflections were rejected from the analysis using two criteria: (1) I(hkl) <= 3[C(hkl) + B1(hkl) + B2(hkl)]^1/2; (2) {2|B1(hkl) - B2(hkl)| / (B1(hkl) + B2(hkl))} >= 0.5^27

All data were adjusted for Lorentz and polarization

(27) Condition 1 removes reflections that are not significantly different from zero at the 3sigma level. Condition 2 removes reflections that have a large asymmetry in background, since this has been found to be symptomatic of overlap of adjacent reflections.

effects ((LP)^-1 = 2 cos^2 mu sin gamma / (1 + cos^2 2theta)^28,29) and absorption corrections were applied^30 (mu = 17.67 cm^-1 for Mo Kalpha radiation). The resulting transmission coefficients ranged from 0.796 to 0.934 for data from crystal I (volume 0.0027 mm^3) and from 0.558 to 0.798 for data from crystal II (volume 0.0066 mm^3). The 19 zones of data were merged to a common scale by

(28) mu is the equiinclination angle, gamma is the vertical Weissenberg coordinate, and theta is the Bragg angle.

(29) C. T. Prewitt, Z. Krist., 13, 355 (1960).

(30) Using a local modification of GNABS, a Fortran general absorption program by C. W. Burnham.

a least-squares procedure which minimizes a sum of residuals linear in the logarithms of the individual scale factors.³¹ (The over-all R factor for scaling was $\sim 8\%$ based on F^2 .) The resulting 1683 independent non-zero reflections were used in calculating a Wilson plot,³² from which were obtained the approximate absolute scale factor and the over-all isotropic thermal parameter ($B = 2.81 \text{ \AA}^2$).

Elucidation and Refinement of the Structure

The coordinates of the two manganese atoms ($x_1 = 0.22$, $y_1 = 0.094$, $z_1 = 0.065$; $x_2 = 0.27$, $y_2 = -0.424$, $z_2 = -0.200$) were obtained from a three-dimensional Patterson synthesis³³ which had been sharpened such that the average intensity was independent of $\sin \theta$ and which had the origin peak removed. A three-dimensional difference-Fourier synthesis, phased by the two manganese atoms ($R_F = 0.421$),³⁴ yielded the positions of all remaining atoms other than hydrogens. Five cycles of full-matrix least-squares refinement of positional and individual thermal parameters led to convergence at $R_F = 0.123$ and $R_{wF^2} = 0.053$.³⁴ A three-dimensional difference-Fourier synthesis at this stage showed evidence of anisotropic motion for many atoms and also led to the location of the eight hydrogen atoms (H_1 through H_8) with peak heights 0.53, 0.66, 0.59, 0.48, 0.36, 0.40, 0.89, and 0.66 $e^- \text{ \AA}^{-3}$, respectively. [Peak heights on an "observed" electron density synthesis were 4.9–7.0 $e^- \text{ \AA}^{-3}$ for carbon atoms and 7.0–8.8 $e^- \text{ \AA}^{-3}$ for oxygen atoms.] A structure factor calculation, phased by all atoms, including hydrogens, had discrepancy indices $R_F = 0.119$ and $R_{wF^2} = 0.049$. Refinement was now continued using anisotropic thermal parameters (T) in the form: $T = \exp[-b_{11}h^2 - b_{22}k^2 - b_{33}l^2 - b_{12}hk - b_{13}hl - b_{23}kl]$. In order to allow refinement of all variables in a single cycle, parameters were blocked into two submatrices. Matrix I contained the scale factor plus positional and thermal parameters for Mn_1 , Mn_2 , O_1 – O_3 , C_1 – C_3 , C_9 – C_{13} ; matrix II contained all appropriate parameters for C_4 – C_8 , C_{14} – C_{17} , O_4 – O_6 . Hydrogen atoms were included in calculated positions with $B = 6.0 \text{ \AA}^2$ but were not refined. [Their positions were, however, redefined with respect to the new carbon atom positions at the end of each cycle of refinement.] Six cycles of positional and anisotropic thermal parameter refinement led to convergence at $R_F = 0.081$ and $R_{wF^2} = 0.021$. [The standard error in an observation of unit weight was 0.68.] A final difference-Fourier synthesis showed no significant features, thus confirming the correctness of the structure.

Throughout the analysis the residual $\Sigma w|F_o|^2 - |F_c|^2$ was minimized. Scattering factors for neutral manganese, oxygen, carbon, and hydrogen were taken from the compilation of Ibers.³⁵ Dispersion corrections

(31) A. D. Rae, *Acta Cryst.*, **19**, 683 (1965).

(32) A. J. C. Wilson, *Nature*, **160**, 152 (1942).

(33) All calculations were performed using CRYRM, an integrated package of crystallographic routines by R. E. Marsh and his coworkers at the California Institute of Technology.

(34) $R_F = \Sigma |F_o| - |F_c| / \Sigma |F_o|$; $R_{wF^2} = \Sigma w(|F_o|^2 - |F_c|^2)^2 / \Sigma w|F_o|^4$.

(35) "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, pp 202, 211.

are small and were ignored ($\Delta f'_{Mn} = 0.4$, $\Delta f''_{Mn} = 0.9$ electron).³⁶ Observed and calculated structure factors are shown in Table I. Final atomic positions are given in Table II. Thermal parameters are collected in Table III and the associated atomic vibration ellipsoids for nonhydrogen atoms are defined in Table IV.

TABLE II
FINAL ATOMIC COORDINATES FOR *trans*- $C_{10}H_8Mn_2(CO)_6$ ^a

	x	y	z
MN1	0.22187(12)	0.09407(14)	0.06207(22)
MN2	0.27270(12)	-0.42507(14)	-0.20329(22)
O1	0.1251(7)	0.4165(8)	0.2183(12)
O2	0.3818(6)	0.1523(9)	-0.1181(12)
O3	0.0464(6)	0.1111(8)	-0.3162(12)
O4	0.3619(7)	-0.4924(8)	0.2131(12)
O5	0.4333(7)	-0.6781(8)	-0.4151(12)
O6	0.1223(6)	-0.6225(8)	-0.3417(12)
C1	0.3614(8)	-0.0398(10)	0.2466(15)
C2	0.2727(9)	0.0372(10)	0.3592(15)
C3	0.1754(8)	-0.0113(9)	0.2518(15)
C4	0.1402(8)	-0.2210(9)	-0.0787(17)
C5	0.1289(8)	-0.2504(9)	-0.2955(17)
C6	0.2149(9)	-0.2696(10)	-0.4000(15)
C7	0.3287(9)	-0.2767(10)	-0.3032(16)
C8	0.3736(8)	-0.2522(9)	-0.0923(16)
C9	0.3173(8)	-0.1391(9)	0.0664(14)
C10	0.2045(8)	-0.1214(9)	0.0729(14)
C11	0.1625(9)	0.2905(12)	0.1641(16)
C12	0.3184(8)	0.1333(10)	-0.0476(17)
C13	0.1167(9)	0.1043(9)	-0.1695(17)
C14	0.3270(8)	-0.4697(9)	0.0503(18)
C15	0.3737(8)	-0.5782(10)	-0.3308(16)
C16	0.1823(9)	-0.5449(10)	-0.2879(15)
H1	0.4453	-0.0258	0.2901
H2	0.2785	0.1190	0.5019
H3	0.0956	0.0280	0.2982
H4	0.0973	-0.2776	-0.0260
H5	0.0477	-0.2591	-0.3896
H6	0.1924	-0.2793	-0.5639
H7	0.3877	-0.3036	-0.4009
H8	0.4565	-0.3251	-0.0496

^a Esd's appear in parentheses after each parameter. They are right-adjusted to the least significant digit of the preceding number.

TABLE III
ANISOTROPIC THERMAL PARAMETERS
($\times 10^4$) FOR *trans*- $C_{10}H_8Mn_2(CO)_6$ ^a

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
MN1	49.0(1.3)	71.4(1.9)	138.8(4.8)	-30.3(2.5)	20.7(3.8)	-26.1(4.6)
MN2	52.2(1.4)	67.3(2.5)	149.5(4.9)	-19.3(2.6)	25.4(3.8)	-16.4(4.6)
O1	172(11)	78(11)	370(32)	7(17)	136(29)	-65(28)
O2	74(8)	217(14)	367(31)	-87(17)	84(24)	160(33)
O3	91(8)	150(11)	226(25)	-96(16)	-88(22)	106(28)
O4	119(9)	181(13)	154(24)	-46(17)	0(23)	61(29)
O5	125(8)	108(10)	316(27)	25(15)	139(24)	1(27)
O6	151(8)	162(12)	95(12)	-13(17)	30(24)	16(30)
C1	68(9)	59(13)	160(31)	-82(19)	-57(27)	22(34)
C2	94(11)	108(14)	113(29)	-55(21)	64(29)	19(32)
C3	72(10)	86(13)	181(32)	-24(19)	62(28)	16(33)
C4	47(8)	71(12)	318(39)	-43(17)	36(29)	55(35)
C5	63(9)	63(12)	214(35)	-5(17)	-27(28)	2(32)
C6	79(11)	100(14)	184(33)	-32(20)	61(30)	54(34)
C7	72(10)	100(14)	205(35)	-23(19)	116(30)	1(35)
C8	49(8)	74(12)	213(33)	-5(16)	79(28)	-16(33)
C9	51(9)	52(11)	211(32)	-17(16)	-6(25)	63(30)
C10	54(8)	58(11)	179(30)	-18(16)	54(25)	-11(30)
C11	93(11)	122(17)	200(35)	-75(23)	53(31)	11(38)
C12	47(9)	92(14)	308(40)	-29(19)	15(30)	14(37)
C13	71(10)	51(12)	256(37)	-52(18)	68(31)	17(34)
C14	71(10)	66(13)	225(36)	-46(18)	12(31)	-40(35)
C15	64(10)	91(14)	214(35)	15(20)	31(29)	71(36)
C16	70(10)	100(14)	161(32)	-19(20)	24(28)	-28(34)

^a Esd's appear in parentheses after each parameter. They are right-adjusted to the least significant digit of the preceding number.

The Molecular Structure

Figure 1 shows the numbering of atoms within the molecule and also shows the 68% probability envelopes for the vibration ellipsoids. Intramolecular distances and estimated standard deviations (esd's) are given in Table V; bond angles and their esd's are shown in Table VI.

The molecule consists of two $Mn(CO)_3$ groups bonded

(36) See ref 35, p 216.

TABLE IV
ATOMIC VIBRATION ELLIPSOIDS^{a-c}
FOR *trans*-C₁₀H₈Mn₂(CO)₆

ATOM	BMAX	D.C.'S	BMED	D.C.'S	BMIN	D.C.'S
MN1	3.78(-654,-728, 790)		2.67(748,-287, 222)		1.60(116, 622, 571)	
MN2	3.98(-766,-686, 734)		2.70(641,-245, 421)		1.70(-51, 685, 489)	
O1	11.42(-985,-484, 358)		7.30(115,-363, 894)		1.90(-128, 796, 269)	
O2	7.04(3, 776, 368)		5.87(105,-499, 850)		3.60(-994,-386, 377)	
O3	7.51(-831,-92, 685)		4.49(-204,-990, 225)		2.40(517, 106, 666)	
O4	8.36(-939,-629, 408)		5.50(-326, 776, 13)		2.50(112, -41, 913)	
O5	7.68(-922,-660, 245)		5.96(75,-374, 910)		2.40(-380, 652, 334)	
O6	7.05(-454,-447, 974)		6.49(642,-907, 29)		3.40(618, 737, 225)	
C1	5.42(-850,-173, 700)		4.43(52,-880, 460)		1.50(524, 442, 547)	
C2	5.42(-979,-211, 103)		3.57(-139,-976, 328)		1.80(-141, 61, 939)	
C3	4.47(-978,-515, 269)		3.45(83,-549, 837)		2.40(-190, 658, 477)	
C4	5.69(-254,-207, 997)		2.73(811,-265, 12)		2.00(-527,-942, 79)	
C5	6.34(-798,-529, 784)		2.62(584, 67, 612)		1.80(-152, 846, 107)	
C6	4.73(-978,-420, 126)		3.18(8, 811, 595)		3.00(-209, 341, 793)	
C7	4.66(745, 114, 428)		4.05(-465,-920, 628)		2.20(-478, 376, 651)	
C8	4.29(-257,-637, 911)		3.39(837, 527, 159)		1.60(-483, 562, 380)	
C9	4.50(-702,-279, 875)		2.65(705, 326, 439)		1.50(-132, -904, 203)	
C10	3.61(-578,-616, 893)		3.21(805, 100, 337)		1.50(-132, 782, 298)	
C11	5.29(-946,-14, 154)		4.36(-301,-856, 731)		3.00(121, 517, 665)	
C12	6.27(-429,-470, 974)		2.87(311, 848, 215)		2.50(848,-163, 78)	
C13	4.55(110,-225, 919)		3.93(-956,-99, 392)		1.40(-272,-969, 40)	
C14	5.61(-707,-505, 865)		3.67(678,-260, 366)		1.60(204, 817, 320)	
C15	5.38(-896,-699, 461)		3.62(59, 183, 870)		2.10(440,-691, 175)	
C16	5.67(-809,-743, 617)		3.26(587,-435, 395)		2.10(-25, 509, 681)	

^a Direction cosines (D.C.'s) for the major, median, and minor axes of the vibration ellipsoid are defined relative to the axes of the triclinic cell. The D.C.'s have been multiplied by 1000.

^b Atomic vibration ellipsoids are presented in terms of the isotropic thermal parameter *B*, which may be related to the root-mean-square displacement $(\bar{U}^2)^{1/2}$ by $(\bar{U}^2)^{1/2} = [B/8\pi^2]^{1/2}$.

^c The 68% probability contours of these ellipsoids are illustrated in Figure 1.

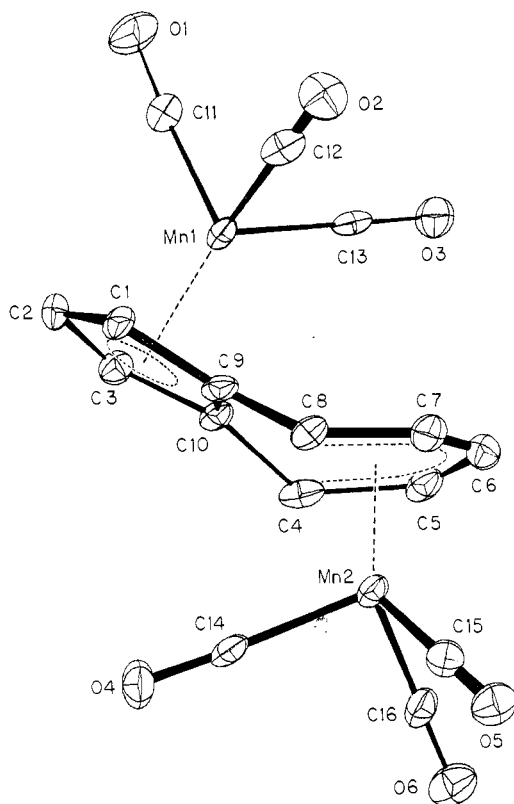


Figure 1.—Numbering of atoms within the *trans*-C₁₀H₈Mn₂(CO)₆ molecule. This diagram also shows the 68% probability contour of the ellipsoids of thermal motion. (Diagram was constructed using ORLIPS, an IBM 1620 program by P. H. Bird.)

to opposite sides of an azulene ligand (*i.e.*, the molecule has an over-all *trans* configuration). One Mn(CO)₃ is bonded symmetrically to the carbon atoms of the five-membered ring *via* a π -cyclopentadienyl \rightarrow metal linkage. The other Mn(CO)₃ group is associated with the remaining five atoms of the azulene system and participates in a noncyclic π -pentadienyl \rightarrow metal bond-

TABLE V
INTERATOMIC DISTANCES WITHIN THE
C₁₀H₈Mn₂(CO)₆ MOLECULE^{a,b}

Atoms	Dist, Å	Atoms	Dist, Å
(a) Distances from Manganese Atoms			
Mn ₁ -C ₁	2.152 (10)	Mn ₂ -C ₄	2.275 (10)
Mn ₁ -C ₂	2.151 (10)	Mn ₂ -C ₅	2.131 (10)
Mn ₁ -C ₃	2.178 (10)	Mn ₂ -C ₆	2.123 (10)
Mn ₁ -C ₁₀	2.186 (09)	Mn ₂ -C ₇	2.142 (10)
Mn ₁ -C ₉	2.178 (09)	Mn ₂ -C ₈	2.283 (09)
Mn ₁ ...C ₄	3.339 (10)	Mn ₂ ...C ₉	2.992 (09)
Mn ₁ ...C ₈	3.306 (09)	Mn ₂ ...C ₁₀	3.014 (09)
Mn ₁ -C ₁₁	1.804 (11)	Mn ₂ -C ₁₄	1.819 (10)
Mn ₁ -C ₁₂	1.814 (10)	Mn ₂ -C ₁₅	1.815 (10)
Mn ₁ -C ₁₃	1.789 (10)	Mn ₂ -C ₁₆	1.778 (10)
Mn ₁ ...O ₁	2.944 (08)	Mn ₂ ...O ₄	2.965 (08)
Mn ₁ ...O ₂	2.963 (08)	Mn ₂ ...O ₅	2.956 (08)
Mn ₁ ...O ₃	2.945 (08)	Mn ₂ ...O ₆	2.945 (08)

(b) Distances within Azulene Ligand

C ₁ -C ₂	1.445 (14)	C ₁₀ -C ₄	1.476 (13)
C ₂ -C ₃	1.417 (14)	C ₄ -C ₅	1.425 (14)
C ₃ -C ₁₀	1.437 (13)	C ₅ -C ₆	1.427 (14)
C ₁₀ -C ₉	1.419 (13)	C ₆ -C ₇	1.418 (15)
C ₉ -C ₁	1.444 (13)	C ₇ -C ₈	1.396 (14)
		C ₈ -C ₉	1.476 (13)

(c) Distances within Carbonyl Groups

C ₁₁ -O ₁	1.142 (14)	C ₁₄ -O ₄	1.147 (13)
C ₁₂ -O ₂	1.150 (13)	C ₁₅ -O ₅	1.142 (13)
C ₁₃ -O ₃	1.157 (13)	C ₁₆ -O ₆	1.167 (13)
C ₁₁ ...C ₁₂	2.625 (15)	C ₁₄ ...C ₁₅	2.718 (15)
C ₁₂ ...C ₁₃	2.580 (15)	C ₁₅ ...C ₁₆	2.475 (14)
C ₁₃ ...C ₁₁	2.552 (15)	C ₁₆ ...C ₁₄	2.640 (15)

(d) Contacts between Azulene and Carbonyl Ligands

C ₁ ...C ₁₂	2.819 (14)	C ₅ ...C ₁₆	2.701 (14)
C ₂ ...C ₁₁	2.880 (15)	C ₆ ...C ₁₆	3.151 (14)
C ₃ ...C ₁₁	3.081 (15)	C ₆ ...C ₁₅	3.077 (14)
C ₃ ...C ₁₃	3.228 (14)	C ₇ ...C ₁₅	2.728 (14)
C ₁₀ ...C ₁₃	2.865 (14)	C ₈ ...C ₁₅	3.109 (14)
C ₉ ...C ₁₃	3.258 (14)	C ₈ ...C ₁₄	2.847 (14)
C ₉ ...C ₁₂	2.956 (14)	C ₉ ...C ₁₄	3.118 (14)
C ₄ ...C ₁₄	2.916 (14)	C ₁₀ ...C ₁₄	3.179 (14)
C ₄ ...C ₁₆	2.983 (14)		

^a Esd's, shown in parentheses, are right-adjusted to the least significant digit of the preceding number. ^b Since the final refinement was carried out with blocked submatrices, the tabulated standard deviations do not include the effects of correlation between blocks and may thus be underestimated by an uncertain (but probably small) amount.

ing scheme. The donation of six electrons from the π -cyclopentadienyl anion, six electrons from the π -pentadienyl anion, and two electrons from each of the six carbonyl ligands leads to each of the d⁶ *pseudo*-octahedrally coordinated Mn(I) ions obtaining the anticipated rare gas (krypton) configuration.

The Azulene Ligand

The azulene ligand remains essentially intact, but the combination of π -cyclopentadienyl \rightarrow manganese(1) and π -pentadienyl \rightarrow manganese(2) linkages leads to a pattern of bond lengths around the azulene nucleus that differs appreciably from that observed for an uncoordinated azulene nucleus (particularly as regards the C₄-C₁₀, C₈-C₉, and C₉-C₁₀ bond lengths). Although the molecular structure of guaiazulenedimolybdenum

TABLE VI
 INTERATOMIC ANGLES WITHIN THE $C_{10}H_8Mn_2(CO)_6$ MOLECULE

Atoms	Angle, deg	Atoms	Angle, deg
(a) Angles around Manganese Atoms			
$C_1-Mn_1-C_2$	39.2 (0.4)	$C_4-Mn_2-C_5$	37.6 (0.4)
$C_2-Mn_1-C_3$	38.2 (0.4)	$C_5-Mn_2-C_6$	39.2 (0.4)
$C_3-Mn_1-C_{10}$	38.4 (0.4)	$C_6-Mn_2-C_7$	38.8 (0.4)
$C_{10}-Mn_1-C_9$	37.9 (0.3)	$C_7-Mn_2-C_8$	36.6 (0.4)
$C_9-Mn_1-C_1$	39.0 (0.4)	$C_8-Mn_2-C_4$	80.7 (0.4)
$C_{11}-Mn_1-C_{12}$	93.0 (0.5)	$C_{14}-Mn_2-C_{15}$	96.8 (0.5)
$C_{12}-Mn_1-C_{13}$	91.5 (0.5)	$C_{15}-Mn_2-C_{16}$	87.1 (0.5)
$C_{13}-Mn_1-C_{11}$	90.5 (0.5)	$C_{16}-Mn_2-C_{14}$	94.4 (0.5)
$O_1 \cdots Mn_1 \cdots O_2$	92.9 (0.2)	$O_4 \cdots Mn_2 \cdots O_5$	97.6 (0.2)
$O_2 \cdots Mn_1 \cdots O_3$	92.5 (0.2)	$O_5 \cdots Mn_2 \cdots O_6$	86.1 (0.2)
$O_3 \cdots Mn_1 \cdots O_1$	89.3 (0.2)	$O_6 \cdots Mn_2 \cdots O_4$	95.2 (0.2)
(b) Angles within Azulene Ligand			
$C_9-C_1-C_2$	107.2 (0.9)	$C_{10}-C_4-C_5$	125.1 (0.9)
$C_1-C_2-C_3$	109.1 (0.9)	$C_4-C_5-C_6$	126.0 (0.9)
$C_2-C_3-C_{10}$	106.7 (0.9)	$C_5-C_6-C_7$	124.6 (1.0)
$C_3-C_{10}-C_9$	109.9 (0.8)	$C_6-C_7-C_8$	126.6 (1.0)
$C_{10}-C_9-C_1$	107.1 (0.8)	$C_7-C_8-C_9$	125.7 (0.9)
		$C_8-C_9-C_{10}$	122.4 (0.8)
$C_1-C_9-C_8$	130.3 (0.9)	$C_9-C_{10}-C_4$	120.1 (0.8)
$C_3-C_{10}-C_4$	129.7 (0.9)		
(c) Angles within Carbonyl Groups			
$Mn_1-C_{11}-O_1$	176.0 (1.0)	$Mn_2-C_{14}-O_4$	177.3 (1.0)
$Mn_1-C_{12}-O_2$	177.3 (1.0)	$Mn_2-C_{15}-O_5$	176.7 (0.9)
$Mn_1-C_{13}-O_3$	178.0 (0.9)	$Mn_2-C_{16}-O_6$	179.3 (0.9)

hexacarbonyl (which also contains π -cyclopentadienyl and π -pentadienyl moieties) has been discussed in detail previously,¹⁵ the accuracy of the present structural analysis justifies a further consideration of carbon-carbon bond lengths around the coordinated azulene nucleus. [It should be emphasized that esd's on carbon-carbon bond lengths in the present study of $C_{10}H_8Mn_2(CO)_6$ are only 0.013–0.014 Å and are comparable to those obtained for purely organic derivatives of azulene.^{37,38} Esd's on carbon-carbon distances for guaiazulenedimolybdenum hexacarbonyl¹⁵—a complex of a second-row transition metal—are appreciably higher and range from 0.020 to 0.024 Å.] Figure 2 compares distances within the azulene nuclei of $C_{10}H_8Mn_2(CO)_6$, $(i-C_3H_7)(CH_3)_2C_{10}H_5Mo_2(CO)_6$,¹⁵ and "azulene" itself. [The values given for "azulene" are, in fact, straight averages of symmetry-related bond distances in azulene-1,3-dipropionic acid³⁷ and the azulene-sym-trinitrobenzene molecular complex.³⁸ Unsubstituted azulene is found to crystallize in a disordered manner.³⁹]

Figure 3 shows the molecule projected in the plane of the five-membered ring. Within the limits of experimental error, the five carbon atoms of the π -cyclopentadienyl ring are arranged with precise D_{5h} symmetry; individual carbon-carbon distances vary from 1.417 ± 0.014 to 1.445 ± 0.014 Å (and average 1.432 Å), bond angles range from 106.7 ± 0.9 to $109.9 \pm 0.8^\circ$ (average 108.0°), and—as shown in Table VII—the five atoms have a root-mean-square deviation of only 0.005 Å from the least-squares plane: $0.2062X -$

(37) H. L. Ammon and M. Sundaralingam, *J. Am. Chem. Soc.*, **88**, 4794 (1966).

(38) A. W. Hanson, *Acta Cryst.*, **19**, 19 (1965).

(39) J. M. Robertson, H. M. M. Shearer, G. A. Sim, and D. G. Watson, *ibid.*, **15**, 1 (1962).

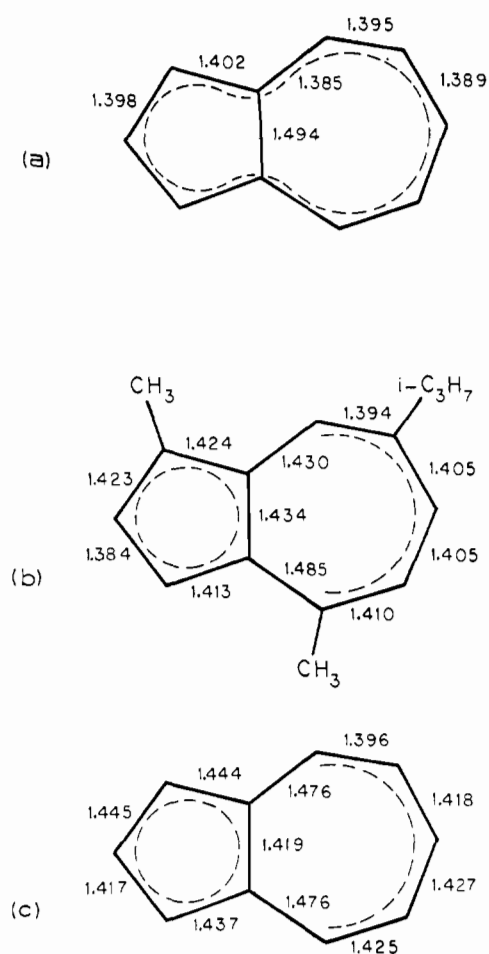


Figure 2.—Carbon-carbon bond distances in (a) uncoordinated "azulene" (see text), (b) guaiazulenedimolybdenum hexacarbonyl, and (c) azulenedimanganese hexacarbonyl.

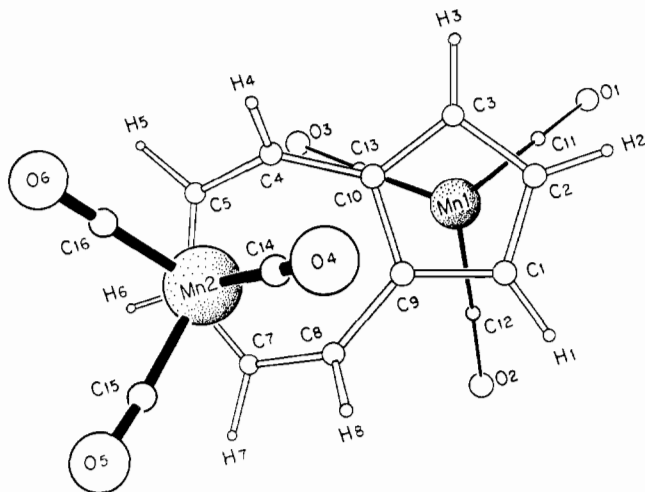


Figure 3.—The *trans*- $C_{10}H_8Mn_2(CO)_6$ molecule, projected in the plane of the five-membered ring.

$0.8330Y + 0.5132Z = 1.0925$.⁴⁰ Individual manganese-carbon distances range from 2.151 ± 0.010 Å for Mn_1-C_2 to 2.186 ± 0.009 Å for Mn_1-C_{10} . [Although none of the Mn_1-C (π -cyclopentadienyl) distances varies significantly from the mean value of 2.169 Å, it is nevertheless interesting to note that

(40) Cartesian coordinates—see footnote a, Table VII.

TABLE VII
IMPORTANT PLANES IN THE $C_{10}H_8Mn_2(CO)_6$ MOLECULE
(A) Equations of Planes^a

Plane	Atoms ^b	c_1	c_2	c_3	d
I	C ₁ , C ₂ , C ₅ , C ₉ , C ₁₀	+0.2062	-0.8330	+0.5132	+1.0925
II	C ₄ , C ₅ , C ₆ , C ₇ , C ₈	-0.2450	+0.9679	+0.0553	-1.8078
III	C ₄ , C ₈ , C ₉ , C ₁₀	+0.2129	-0.7727	+0.5979	+1.1304
IV	C ₄ , C ₅ , C ₇ , C ₈	-0.2456	+0.9686	+0.0359	-1.7934
V	C ₅ , C ₆ , C ₇	-0.2415	+0.9618	+0.1282	-1.9535
VI	C ₁₁ , C ₁₂ , C ₁₃	+0.1570	-0.8446	+0.5117	-1.8606
VII	C ₁₄ , C ₁₅ , C ₁₆	+0.2518	-0.9564	+0.1475	+4.1142

(B) Deviations from Planes

Plane I		Plane II	
C ₁	-0.001 (10)	C ₄	+0.006 (10)
C ₂	+0.005 (11)	C ₅	-0.020 (10)
C ₃	-0.006 (10)	C ₆	+0.028 (11)
C ₁₀	+0.006 (09)	C ₇	-0.021 (11)
C ₉	-0.003 (09)	C ₈	+0.007 (10)
C ₄	+0.16 (1)	C ₁	+1.57 (1)
C ₅	-0.61 (1)	C ₂	+2.04 (1)
C ₆	-1.04 (1)	C ₃	+1.61 (1)
C ₇	-0.65 (1)	C ₉	+0.80 (1)
C ₈	+0.10 (1)	C ₁₀	+0.83 (1)
Mn ₁	-1.794 (1)	Mn ₂	-1.592 (1)
C ₁₁	-2.83 (1)	C ₁₄	-2.25 (1)
C ₁₂	-2.73 (1)	C ₁₅	-2.75 (1)
C ₁₃	-2.85 (1)	C ₁₆	-2.71 (1)
O ₁	-3.55 (1)	O ₄	-2.62 (1)
O ₂	-3.28 (1)	O ₅	-3.51 (1)
O ₃	-3.52 (1)	O ₆	-3.45 (1)

Plane III		Plane IV	
C ₄	+0.004 (10)	C ₄	-0.001 (10)
C ₈	-0.004 (10)	C ₅	+0.001 (10)
C ₉	+0.008 (09)	C ₇	-0.001 (11)
C ₁₀	-0.008 (09)	C ₈	+0.001 (10)

^a Planes are defined as: $c_1X + c_2Y + c_3Z = d$, where X , Y , and Z are Cartesian coordinates which are related to the triclinic cell coordinates (x, y, z) by the transformations: $X = xa \sin \gamma + zc(\cos \beta - \cos \alpha \cos \gamma)/\sin \gamma$; $Y = yb + xa \cos \gamma + zc \cos \alpha$; $Z = zc[(1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma)/\sin^2 \gamma]^{1/2}$. ^b Planes are derived using unit weights for the atoms listed in section A of this table.

the greatest distance involves the carbon atom that is in an eclipsed configuration with respect to a carbonyl group (see Figure 3).] This portion of the structure of $C_{10}H_8Mn_2(CO)_6$ may be compared with $\pi-C_5H_5Mn(CO)_3$,⁴¹ in which Mn-C distances vary from 2.127 to 2.176 Å and average 2.151 Å. In the present complex the manganese atom lies 1.794 Å below the plane of the five-membered ring; the analogous distance is 1.80 Å in $\pi-C_5H_5Mn(CO)_3$.⁴¹

The five atoms C₄ through C₈ are bonded to Mn₂ via a π -pentadienyl-manganese linkage. Individual manganese-carbon distances vary systematically and symmetrically around the π -pentadienyl system. The "terminal" carbon atoms C₄ and C₈ are 2.275 ± 0.010 and 2.283 ± 0.009 Å from Mn₂, the "intermediate" C₅ and C₇ are 2.131 ± 0.010 and 2.142 ± 0.010 Å from Mn₂, and the "central" C₆ is 2.123 ± 0.010 Å from Mn₂. [Although similar features have been observed in hexamethylcyclohexadienylrhodium tricarbonyl^{42,43} and in guaiazulenedimolybdenum hexacarbonyl,¹⁵ the low esd's and lack of strain in the present molecule give rise to a unique opportunity for obtaining accurate parameters for a π -pentadienyl-metal linkage.] The

(41) A. F. Berndt and R. E. Marsh, *Acta Cryst.*, **16**, 118 (1963). (Bond lengths quoted from this paper are those which are not corrected for thermal motion.)

(42) P. H. Bird and M. R. Churchill, *Chem. Commun.*, 777 (1967).

(43) P. H. Bird and M. R. Churchill, unpublished work.

least-squares plane through the five atoms of the π -pentadienyl system has the equation $-0.2450X + 0.9679Y + 0.0553Z = -1.8078$,⁴⁰ but the pattern of deviations from planarity [$\delta(C_4) = +0.006 \pm 0.010$ Å, $\delta(C_8) = +0.007 \pm 0.010$ Å, $\delta(C_5) = -0.020 \pm 0.010$ Å, $\delta(C_7) = -0.021 \pm 0.011$ Å, $\delta(C_6) = +0.028 \pm 0.011$ Å] is sufficiently symmetric to lead us to believe that the ligand bends slightly about the C₅...C₇ axis. Figure 4 illustrates the various dihedral angles within the azulene ligand.

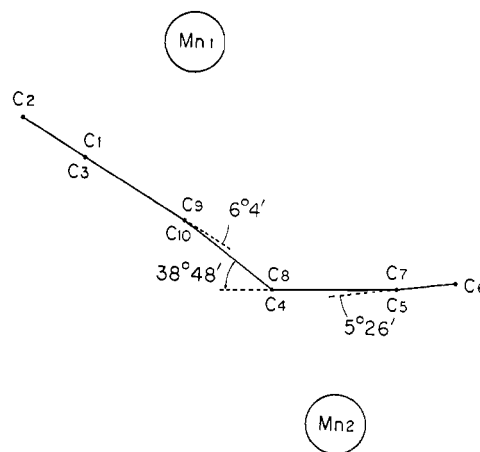


Figure 4.—Dihedral angles with the azulene ligand of $trans-C_{10}H_8Mn_2(CO)_6$.

Carbon-carbon distances around the π -pentadienyl system vary from 1.396 ± 0.014 to 1.427 ± 0.014 Å, averaging 1.417 Å. Thus, as in guaiazulenedimolybdenum hexacarbonyl, the mean carbon-carbon distance within the π -pentadienyl system is approximately 0.015 Å shorter than that within the π -cyclopentadienyl system. This may be equated¹⁵ with the π -cyclopentadienyl-metal bonding being stronger than the π -pentadienyl-metal bonding.

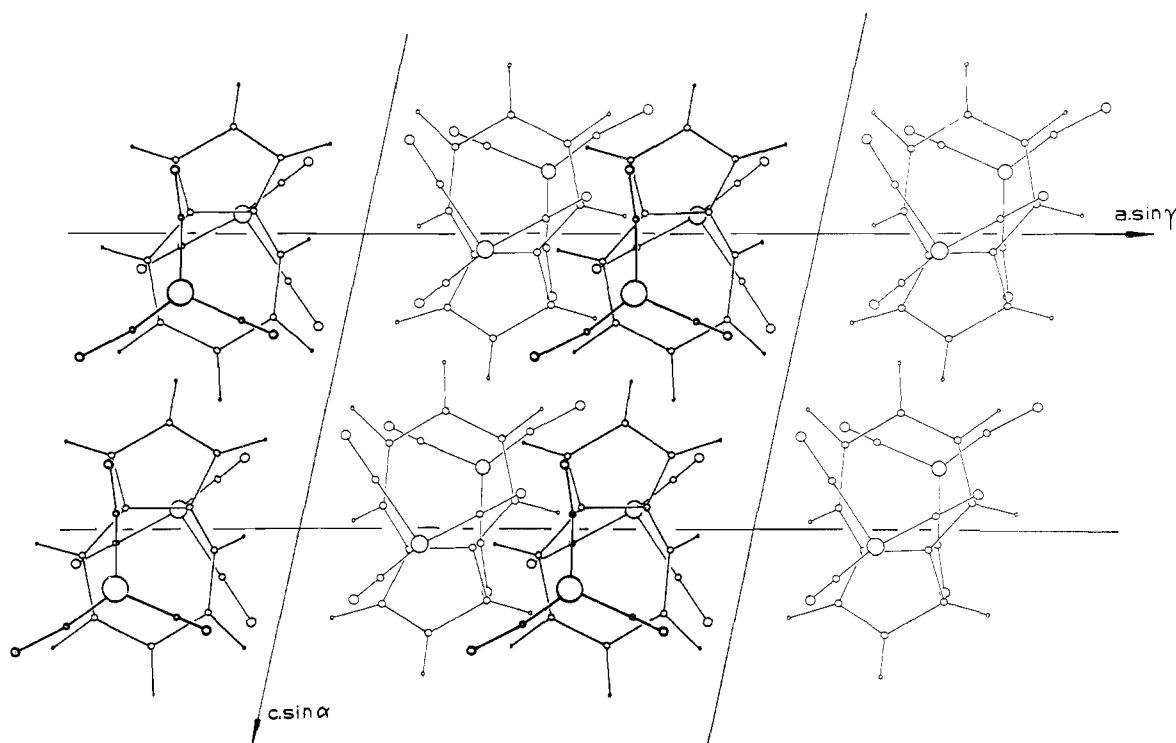
A further interesting observation is that the bonds which join the π -cyclopentadienyl and π -pentadienyl systems (*viz.*, C₄-C₁₀ = 1.476 ± 0.013 Å, C₅-C₉ = 1.476 ± 0.013 Å) are each indistinguishable from the recognized C(sp²)-C(sp²) single-bond distance of 1.465 ± 0.005 Å.⁴⁴ This would seem to indicate that there is virtually no flow of π -electron density between the π -pentadienyl and π -cyclopentadienyl systems.

The Mn(CO)₃ Groups

The Mn(CO)₃ group that is associated with the five-membered ring takes up a conformation in which one carbonyl ligand (C₁₃-O₃) lies immediately below C₁₀. Individual OC-Mn₁-CO angles vary from 90.5 ± 0.5 to $93.0 \pm 0.5^\circ$ averaging 91.7° . Variations from the mean are not significant and, indeed, are not to be expected except as a result of intermolecular forces. The dihedral angle between π -cyclopentadienyl and C₁₁, C₁₂, C₁₃ planes is close to zero ($3^\circ 7'$).

The Mn(CO)₃ group bonded to the π -pentadienyl

(44) "Tables of Interatomic Distances and Configuration in Molecules and Ions, Supplement, 1956-1959," Special Publication No. 18, The Chemical Society, London, 1965, p S15s.

Figure 5.—Packing diagram for *trans*-C₁₀H₈Mn₂(CO)₆.

system has a much less symmetric geometry. The carbonyl ligands below the π -pentadienyl ligand are orientated such that this half of the molecule (*i.e.*, the π -pentadienylmanganese tricarbonyl fragment) has approximate C₃ symmetry. The carbonyl group C₁₄-O₄ lies almost exactly between C₄ and C₈ (C₄···C₁₄ = 2.916 Å, C₈···C₁₄ = 2.847 Å) and the interligand angles are such that C₁₅-Mn₂-C₁₆ (87.1 ± 0.5°) is some 17σ less than the average value (95.6°) for the remaining two angles (C₁₄-Mn₂-C₁₅ = 96.8 ± 0.5°, C₁₄-Mn₂-C₁₆ = 94.4 ± 0.5°). [This type of distortion has previously been observed in such systems as octafluorocyclohexadieneiron tricarbonyl⁴⁵ and has been shown to be general for M(CO)₃ groups in environments of low (*i.e.*, less than C_{3v}) symmetry.⁴⁶] Finally, it should be noted that there is a dihedral angle of 11° 42' between the "plane" (*vide supra*) of the π -pentadienyl ligand and the plane defined by C₁₄···C₁₅···C₁₆.

Average Mn-CO and C-O bond distances within the *trans*-C₁₀H₈Mn₂(CO)₆ molecule are 1.803 and 1.151 Å, as compared to values of 1.797 and 1.134 Å for π -C₅H₅Mn(CO)₃.⁴¹ It should be emphasized that, in these two molecules, the manganese-carbonyl bond distance has probably reached the minimum obtainable value. [Previous studies have shown that the Cr-CO bond distances in π -C₆H₆Cr(CO)₃⁴⁷ and π -C₆(CH₃)₆-Cr(CO)₃⁴⁸ are the same as in NH₂(CH₂)₂NH(CH₂)₂NH₂-Cr(CO)₃⁴⁹—where there is no competition between the

TABLE VIII
INTERMOLECULAR CONTACTS (≤3.3 Å)
WITHIN THE C₁₀H₈Mn₂(CO)₆ CRYSTAL

Atoms ^a	Dist, Å	Atoms ^a	Dist, Å
O ₁ ···C ₁₆ V	3.24	O ₅ ···H ₂ II	3.07
O ₁ ···O ₆ V	3.20	O ₅ ···H ₇ XII	2.88
O ₁ ···H ₈ V	3.17	O ₅ ···H ₈ XIII	3.13
O ₂ ···C ₁₅ VI	3.29	O ₆ ···C ₁₃ I	3.21
O ₂ ···O ₅ VI	3.29	O ₆ ···H ₂ II	2.79
O ₂ ···H ₁ X	2.60	O ₆ ···H ₅ IX	2.78
O ₂ ···H ₂ IV	2.58	C ₃ ···H ₆ III	3.12
O ₂ ···H ₈ X	2.88	C ₄ ···C ₃ VIII	3.20
O ₃ ···C ₅ VII	3.28	C ₅ ···H ₈ VIII	2.97
O ₃ ···O ₈ VII	3.07	C ₁₁ ···H ₄ VIII	3.25
O ₃ ···O ₆ VI	3.10	C ₁₂ ···H ₂ IV	3.00
O ₃ ···H ₃ VIII	2.65	C ₁₃ ···H ₂ VI	3.21
O ₃ ···H ₃ IV	2.76	C ₁₃ ···H ₃ VIII	3.20
O ₃ ···H ₄ VIII	3.17	C ₁₃ ···H ₄ VIII	3.17
O ₃ ···H ₅ VII	2.60	C ₁₄ ···H ₃ XIII	2.83
O ₃ ···H ₆ VII	2.96	C ₁₅ ···H ₈ XIII	3.07
O ₄ ···O ₅ III	3.30	C ₁₆ ···H ₂ II	3.14
O ₄ ···H ₆ III	2.92	H ₁ ···H ₁ XI	2.84
O ₄ ···H ₇ III	2.78	H ₃ ···H ₅ VIII	2.43
O ₄ ···H ₇ XIII	3.29	H ₃ ···H ₈ III	3.12
O ₄ ···H ₈ XIII	2.74	H ₄ ···H ₆ III	3.10
O ₅ ···H ₁ XIII	3.00		

^a Transformations are as follows: I, $x, y - 1, z$; II, $x, y - 1, z - 1$; III, $x, y, z + 1$; IV, $x, y, z - 1$; V, $x, y + 1, z + 1$; VI, $x, y + 1, z$; VII, $-x, -y, -z - 1$; VIII, $-x, -y, -z$; IX, $-x, -y - 1, -z - 1$; X, $-x + 1, -y, -z$; XI, $-x + 1, -y, -z + 1$; XII, $-x + 1, -y + 1, -z - 1$; XIII, $-x + 1, -y - 1, -z$.

carbonyl and the *trans* ligand for π -electron density. It seems reasonable to assume that the π -C₅H₅ ligand in π -C₅H₅Mn(CO)₃ will behave analogously to the π -C₆H₆ ligand in π -C₆H₆Cr(CO)₃, and we therefore conclude that the arene ligands in π -C₅H₅Mn(CO)₃ and C₁₀H₈-Mn₂(CO)₆ will not compete significantly with the (CO)₃

(45) M. R. Churchill and R. Mason, *Proc. Roy. Soc. (London)*, **A301**, 433 (1967).(46) S. F. A. Kettle, *Inorg. Chem.*, **4**, 1661 (1965).(47) M. F. Bailey and L. F. Dahl, *ibid.*, **4**, 1314 (1965).(48) M. F. Bailey and L. F. Dahl, *ibid.*, **4**, 1298 (1965).(49) F. A. Cotton and D. C. Richardson, *ibid.*, **5**, 1851 (1966).

moieties for electron density.] In keeping with this proposal, it may be noted that the mean Mn-CO bond distance in other compounds (where there is competition for π -electron density) is greater, *viz.*, 1.823 Å in $\text{Mn}_2(\text{CO})_{10}$,⁵⁰ 1.823 Å in $\text{HRe}_2\text{Mn}(\text{CO})_{14}$,⁵¹ and 1.836 Å in $\text{HMn}(\text{CO})_5$.⁵²

Discussion

The results of the present structural analysis would appear to strengthen our previously stated ideas¹⁷ on the reaction of azulene with transition metal carbonyls. If the initial reaction produces an intermediate such as V, then the present complex *trans*- $\text{C}_{10}\text{H}_8\text{Mn}_2(\text{CO})_6$ (VI) and the $[\text{C}_{10}\text{H}_8\text{Mn}(\text{CO})_3]_2$ of Burton, *et al.*³ (VII), are to be expected as products. The particular factors that favor the formation of one product rather than the other have yet to be determined, but it would seem likely that manganese-rich VI will be preferentially formed in solutions containing an excess of dimanganese decacarbonyl, while dimeric VII will form in solutions containing an excess of azulene. However, the limited stability of VII as compared to VI will complicate the over-all pattern.

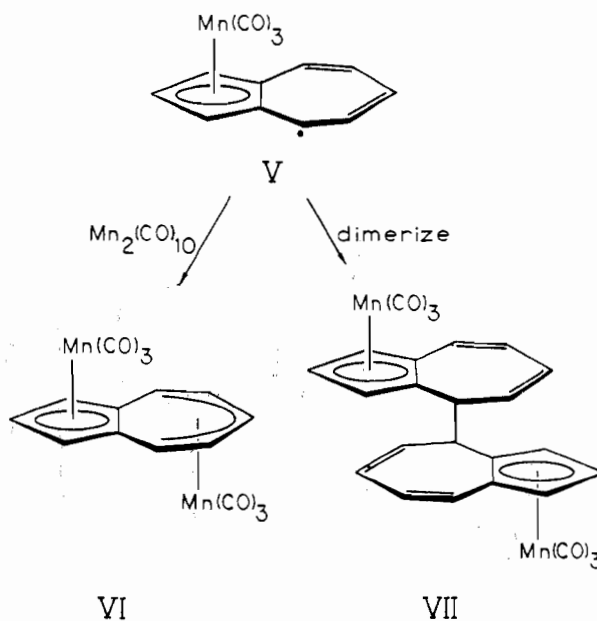
Intermolecular Contacts

Figure 5 shows the packing of molecules within the crystal lattice. Quantitative data on intermolecular interactions are collected in Table VIII. There are no

(50) L. F. Dahl and R. E. Rundle, *Acta Cryst.*, **16**, 419 (1963).

(51) M. R. Churchill and R. Bau, *Inorg. Chem.*, **6**, 2086 (1967).

(52) S. J. LaPlaca, W. C. Hamilton, and J. A. Ibers, *ibid.*, **3**, 1491 (1964).



abnormally short contacts, thus confirming that the crystal consists of a discrete molecular unit of *trans*- $\text{C}_{10}\text{H}_8\text{Mn}_2(\text{CO})_6$. Shortest contacts of each type are: carbon...hydrogen, 2.83 Å; carbon...oxygen, 3.21 Å; oxygen...oxygen, 3.07 Å; oxygen...hydrogen, 2.58 Å; hydrogen...hydrogen, 2.43 Å.

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Metal Carbonyl-Phosphorus Trifluoride Systems. VI. Manganese Pentacarbonyl Hydrides and Perfluoroalkyls

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Manganese pentacarbonyl hydride reacts with phosphorus trifluoride under the influence of uv irradiation to yield species of all possible compositions $\text{HMn}(\text{PF}_3)_z(\text{CO})_{5-z}$. The mixtures which result can be separated by gas-liquid partition chromatography yielding moderately stable, volatile liquids having properties quite similar to those of the parent. Substitution of PF_3 is also found to occur in carbonyls of the type $\text{R}_f\text{Mn}(\text{CO})_5$ where $\text{R}_f = \text{HCF}_2\text{CF}_2$, CF_3 , and CF_3CO . Geometric isomers are readily isolated for these alkylmanganese compounds but not for the hydride, even under highly efficient conditions. Very strong evidence is given for the presence of nonresolvable isomers in the various hydride compositions and the possible reasons for this nonresolvability are discussed.

Introduction

The remarkable similarity between the properties of metal carbonyl complexes and their phosphorus trifluoride substituents has been adequately demonstrated.² It was felt that a study of the substitution of phosphorus trifluoride into manganese pentacarbonyl

hydride should be undertaken in order to complement both the studies that have already been done^{2a} and a study of the $\text{HCo}(\text{CO})_4\text{-PF}_3$ system that was then in progress.

It became important to study the $\text{HMn}(\text{PF}_3)_z(\text{CO})_{5-z}$ compounds in an attempt to shed further light on the

(1) This work was submitted to the Graduate School of Florida State University for partial fulfillment of the requirements for the degree of Master of Science.

(2) (a) R. J. Clark, J. P. Hargaden, H. Haas, and R. K. Shelton, *Inorg. Chem.*, **7**, 873 (1968), and earlier references in the series; (b) Th. Kruck, *Angew. Chem. Intern. Ed. Engl.*, **6**, 53 (1967); this is an excellent review of totally substituted trifluorophosphine complexes.