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THE CRYSTAL AND MOLECULAR STRUCTURE OF 1-BROMOBENZOCYMANTRENE, $(\eta^5\text{-}C_9H_6Br)Mn(CO)_3$

MICHEAL B. HONAN, JERRY L. ATWOOD *,

Department of Chemistry, University of Alabama, University, Alabama 35486 (U.S.A.)

IVAN BERNAL,

Department of Chemistry, University of Houston, Houston, Texas 77004 (U.S.A.)

and WOLFGANG A. HERRMANN

Chemisches Institut der Universität, Universitätsstrasse 31, D-8400 Regensburg 1 (Germany)

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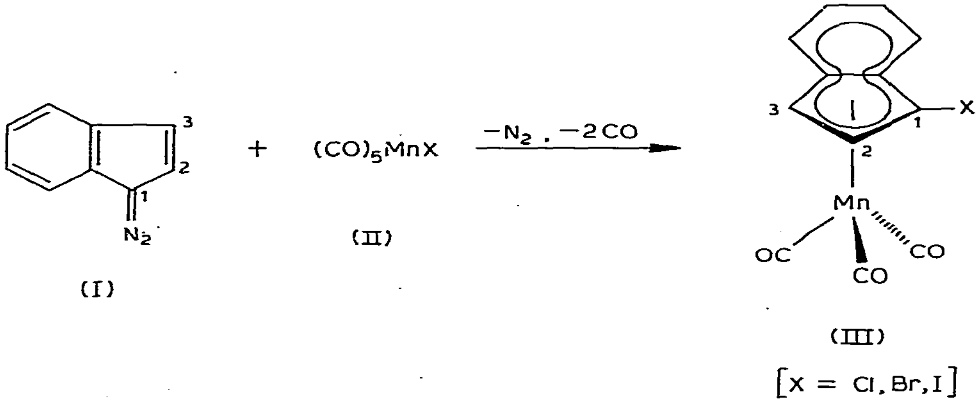
Summary

The crystal and molecular structure of tricarbonyl[1—4:9-η-(1-bromo)-indenyl]manganese (III) prepared by reaction of bromo(pentacarbonyl)manganese (II) with diazoindene (I) ("diazo method") has been determined by X-ray diffraction methods. III belongs to the monoclinic space group $P2_1/c$ with unit cell constants a 12.953(9), b 7.627(5), c 13.098(9) Å, and β 110.53(5)°. Full-matrix least-squares refinement converged with a conventional R factor of 0.052 based on 1505 observed reflections. The molecule contains an essentially planar indenyl-π-ligand which is coordinated to the manganese atom through its cyclopentadienyl-like moiety. The bromine ligand is attached to the C(1) position of the indenyl system and has only a very slight influence on the characteristics of the indenyl skeleton. The change from cyclopentadienyl (in cymantrene) to indenyl (in III) produces essentially no disturbance in the normal manganese—carbonyl linkage.

Introduction

While numerous studies of cyclopentadienyl complexes of the transition metals have been carried out, relatively few have appeared on those which contain the indenyl [2] or fluorenyl ligand [3]. Recently, first examples of haloindenyl transition metal compounds became available through an investigation of the complex chemistry of various carbocyclic diazoalkanes [4]. For example, diazoindene (I) reacts with pentacarbonyl manganese halides $(CO)_5$-

MnX [X = Cl, Br, I] (II) under evolution of carbon monoxide and dinitrogen to yield the halobenzocymantrenes (η^5-C_9H_6X)$Mn(CO)_3$ (III) [5] (eq. 1), the physical properties of which resemble very much those of the parent compound (η^5-C_9H_7)$Mn(CO)_3$ [6,7]. The diazo method quoted here is the only known way to obtain haloindenyl complexes such as III, since the common precursors such as the haloindenes or their alkaline salts are not easily accessible. This is, in fact, the reason why there are only very few indenyl-π-complexes known containing ligands in the aromatic C_5-system. In compounds in which the bonding is through the five-membered ring of these moieties, the larger steric requirements have been found to produce large differences in bond lengths and angles (i.e., (η^5-C_9H_7)$_2Zr(CH_3)_2$ [8] and $Mg(C_9H_7)_2$ [9]) relative to their cyclopentadienyl analogues. Electronic effects of the indenyl ring have provided the means of resolution of crystallographic problems in dicarbonylnitrosyl complexes. (η^5-C_5H_5)$Cr(CO)_2(NO)$ [3] contains disordered carbonyl and nitrosyl groups, while (η^5-C_9H_7)$Cr(CO)_2(NO)$ [10] is ordered in a crystallographic sense. To learn more about the effects of the bromine substitution on the properties of the indenyl ligand and to prove the specific halogen transfer from the metal into the 1-position of the indenyl system, we have determined the crystal structure of 1-bromobenzocymantrene, (η^5-C_9H_6Br)$Mn(CO)_3$ (III).



(Eq. 1)

Experimental

(η^5-C_9H_6Br)$Mn(CO)_3$ (III) was prepared by reaction of bromo(pentacarbonyl)manganese (II) with freshly distilled diazoindene (I) in tetrahydrofuran solution (eq. 1) and purified by column chromatography on neutral alumina (act. I, Woelm-Pharma)/benzene and high-vacuum sublimation at 45—48°C [4] (m.p. 51°C, without decomposition; sealed capillary). Single crystals were grown by careful crystallization of III from n-pentane/diethyl ether mixtures (ca. 5/1) at +25/—35°C (temp. gradient 2°/h) using a LAUDA-Ultrakryomat K120W equipped with an automatic temperature system P250. Although slightly light-sensitive, III is fairly stable upon exposure to air and completely stable towards water. Elemental analysis of a sample used for X-ray crystallography: Found: C, 43.32; H, 1.80; Mn, 16.31; Br, 23.82. $C_{12}H_6BrMnO_3$ calcd.: C, 43.28; H, 1.82; Mn, 16.50; Br, 23.78%.

TABLE 1

CRYSTAL DATA FOR III

Mol. formula: $C_{12}H_6BrMnO_3$
Mol. wt.: 333.02
Linear abs. coeff. μ: 46.2 cm^{-1}
Calc. density: 1.82 g cm^{-3}
Max. crystal dimensions: 0.32 × 0.38 × 0.38 mm
Space group: monoclinic, $P2_1/c$
Molecules/unit cell: 4
Cell constants [a]: *a* 12.953(9), *b* 7.627(5), *c* 13.098(9) Å,
β 110.53(5)°
Cell volume: 1211.8 $Å^3$

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[a] Mo-K_α radiation, (λ 0.71069 Å). Ambient temperature of 23 ± 1°C.

Single crystals of the compound were sealed in thin-walled glass capillaries. Final lattice parameters as determined by a least-squares refinement of the angular settings of 15 reflections ($2\theta > 15°$) accurately centered on an Enraf-Nonius CAD-4 diffractometer are given in Table 1. The space group was determined uniquely as $P2_1/c$ from systematic absences: $h0l$, $l = 2n + 1$ and $0k0$, $k = 2n + 1$.

Data were collected on the diffractometer with graphite crystal monochromated Mo-K_α radiation. The diffracted intensities were collected in the standard fashion [11]. As a check on the stability of the instrument and crystal, three reflections were measured after every 50 reflections; no significant variation was noted.

One independent quadrant of data was measured out to $2\theta = 50°$. A slow scan was performed on a total of 1505 unique reflections. Since these data were scanned at a speed which would yield a net count of 4000, the calculated standard deviations were all very nearly equal. No reflection was subjected to a slow scan unless a net count of 20 was obtained in the prescan. Based on these considerations, the data set of 1505 reflections was considered observed and consisted, in the main, of those for which $I > 3\sigma(I)$. The intensities were corrected for Lorentz and polarization effects but not for absorption because of the nearly spherical shape of the crystal.

The function $w(|F_0| - |F_c|)^2$ was minimized [12]. No corrections were made for extinction. Neutral atom scattering factors were taken from the complication of Cromer and Waber [13] for Br, Mn, O, and C. The scattering by Br was corrected for the real component of anomalous dispersion using the table of Cromer and Liberman [14].

Structure solution and refinement

The structure was solved by the application of the direct methods program MULTAN [15]. Least-squares refinement with isotropic temperature factors yielded $R_1 = \Sigma(||F_0| - |F_c||)/\Sigma|F_0| = 0.13$. Conversion to anisotropic thermal parameters and further refinement gave $R_1 = 0.052$ and $R_2 = [\Sigma w(|F_0| - |F_c|)^2/\Sigma|F_0|^2]^{1/2} = 0.055$. The weighting scheme was based on unit weights and unobserved reflections were not included. The hydrogen atoms were not

TABLE 2

FINAL FRACTIONAL COORDINATES AND THERMAL PARAMETERS[a] FOR $(\eta^5\text{-}C_9H_6Br)Mn(CO)_3$ (III)

Atom	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mn	0,7653(1)	0,7228(2)	0,5047(1)	0,0059(1)	0,0156(2)	0,0059(1)	−0,0007(1)	0,0017(1)	−0,0011(1)
Br	0,9834(1)	0,8278(2)	0,7588(1)	0,0133(1)	0,0223(2)	0,0100(1)	−0,0018(1)	−0,0032(1)	0,0007(1)
O(1)	0,5687(6)	0,6425(11)	0,3138(6)	0,0086(6)	0,0403(22)	0,0090(6)	−0,0015(10)	0,0002(5)	−0,0048(9)
O(2)	0,8664(6)	0,3902(9)	0,4798(6)	0,0100(7)	0,0203(16)	0,0147(8)	0,0028(9)	0,0035(6)	−0,0033(9)
O(3)	0,6703(8)	0,5696(10)	0,6586(6)	0,0186(10)	0,0212(19)	0,0124(8)	−0,0066(12)	0,0094(8)	−0,0009(10)
C(1)	0,8896(7)	0,8800(11)	0,6166(7)	0,0060(7)	0,0170(20)	0,0079(7)	−0,0017(9)	0,0000(6)	−0,0011(9)
C(2)	0,9159(8)	0,8534(13)	0,5219(9)	0,0064(7)	0,0197(20)	0,0112(10)	−0,0023(10)	0,0026(7)	−0,0010(11)
C(3)	0,8306(8)	0,9244(13)	0,4332(8)	0,0095(9)	0,0210(20)	0,0080(8)	−0,0035(12)	0,0044(7)	−0,0002(10)
C(4)	0,7516(8)	1,0075(11)	0,4734(7)	0,0080(8)	0,0137(16)	0,0084(8)	−0,0013(10)	0,0015(6)	0,0014(9)
C(5)	0,6525(9)	1,0998(14)	0,4232(10)	0,0083(9)	0,0187(23)	0,0147(13)	−0,0008(12)	0,0001(8)	0,0036(16)
C(6)	0,5971(10)	1,1667(16)	0,4873(14)	0,0088(10)	0,0189(24)	0,0210(18)	0,0029(13)	0,0018(12)	0,0007(18)
C(7)	0,6365(11)	1,1420(16)	0,5980(14)	0,0110(12)	0,0215(26)	0,0227(19)	0,0000(15)	0,0093(13)	−0,0059(19)
C(8)	0,7309(10)	1,0501(13)	0,6548(10)	0,0121(11)	0,0180(21)	0,0136(11)	−0,0030(13)	0,0069(9)	−0,0047(12)
C(9)	0,7917(7)	0,9799(11)	0,5899(7)	0,0075(7)	0,0139(17)	0,0078(7)	−0,0005(9)	0,0024(6)	−0,0006(9)
C(10)	0,6460(8)	0,6758(12)	0,3891(8)	0,0073(8)	0,0199(21)	0,0089(8)	0,0010(10)	0,0033(6)	−0,0004(11)
C(11)	0,8269(7)	0,5198(13)	0,4896(7)	0,0066(7)	0,0198(21)	0,0073(7)	−0,0007(10)	0,0017(6)	−0,0006(10)
C(12)	0,7073(8)	0,6268(12)	0,5996(8)	0,0098(9)	0,0146(18)	0,0092(9)	−0,0042(10)	0,0025(7)	−0,0037(10)

[a] Anisotropic thermal parameters defined by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

TABLE 3

INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR (η^5-C_9H_6Br)Mn$(CO)_3$ (III)

Mn—C(1)	2.128(9)	Br—C(1)	1.874(8)
Mn—C(2)	2.130(10)	C(1)—C(2)	1.41(1)
Mn—C(3)	2.125(8)	C(2)—C(3)	1.40(1)
Mn—C(4)	2.205(9)	C(3)—C(4)	1.45(1)
Mn—C(9)	2.222(9)	C(4)—C(9)	1.44(1)
Mn—C(10)	1.780(9)	C(9)—C(1)	1.41(1)
Mn—C(11)	1.784(10)	C(4)—C(5)	1.41(1)
Mn—C(12)	1.816(10)	C(5)—C(6)	1.38(1)
C(10)—O(1)	1.16(1)	C(6)—C(7)	1.37(1)
C(11)—O(2)	1.14(1)	C(7)—C(8)	1.38(1)
C(12)—O(3)	1.13(1)	C(8)—C(9)	1.45(1)
Cent-Mn—C(10) [a]	123.8	C(9)—C(1)—C(2)	109.5(8)
Cent—Mn—C(11)	123.9	C(1)—C(2)—C(3)	108.0(9)
Cent—Mn—C(12)	123.5	C(2)—C(3)—C(4)	108.6(9)
C(10)—Mn—C(11)	91.1(4)	C(3)—C(4)—C(9)	106.3(8)
C(10)—Mn—C(12)	93.3(5)	C(4)—C(9)—C(1)	107.4(9)
C(11)—Mn—C(12)	92.0(5)	C(9)—C(4)—C(5)	120.0(9)
Mn—C(10)—O(1)	178.8(9)	C(4)—C(5)—C(6)	118.9(9)
Mn—C(11)—O(2)	178.9(9)	C(5)—C(6)—C(7)	120.7(9)
Mn—C(12)—O(3)	179.7(9)	C(6)—C(7)—C(8)	124.8(9)
Br—C(1)—C(2)	124.7(7)	C(7)—C(8)—C(9)	115.9(9)
Br—C(1)—C(9)	124.8(8)	C(8)—C(9)—C(4)	119.7(8)

[a] Cent is defined as the centroid of the five-membered ring of the indenyl ligand.

located. The largest parameter shifts in the final cycle of refinement were less than 0.10 of their estimated standard deviation. The e.s.d. of an observation of unit weight was 0.97. The final values of the positional and thermal parameters are given in Table 2 *. The table of structure factors will be deposited as NAPS Document.

Discussion

The molecular structure and atom numbering scheme are shown in Fig. 1. As expected from the synthetic route (eq. 1), the bromine atom is attached to the C(1) position of the indenyl ring. Thus, the bromine ligand originally attached to the manganese atom of II has been transferred specifically onto the former diazo-carbon atom of the indenylidene-precursor diazoindene (I) in the course of reaction 1. A careful scrutiny of Table 3 shows that the bromine atom exerts no noticeable effect on the bonding parameters of the manganese atom.

The metal—carbon π-bond distances range from 2.125(8) to 2.224(9) Å and average 2.16(4) Å, a value only slightly longer than the 2.15(2) Å found in (η^5-C_5H_5)Mn$(CO)_3$ [16]. Both of these fall within the normal range of Mn—C(η^5) lengths from 2.13(3) Å in [(η^5-C_5H_5)Mn$(CO)_2]_2C_4H_6$ [17] to 2.18(4) Å in (C_6H_7)Mn$(CO)_3$ [18]. The π-bond lengths follow the general pattern established for indenyl systems: there are three distances closely equivalent and two which are substantially greater. In (η^5-$C_9H_7)_2$Zr$(CH_3)_2$ [7] the lengths are

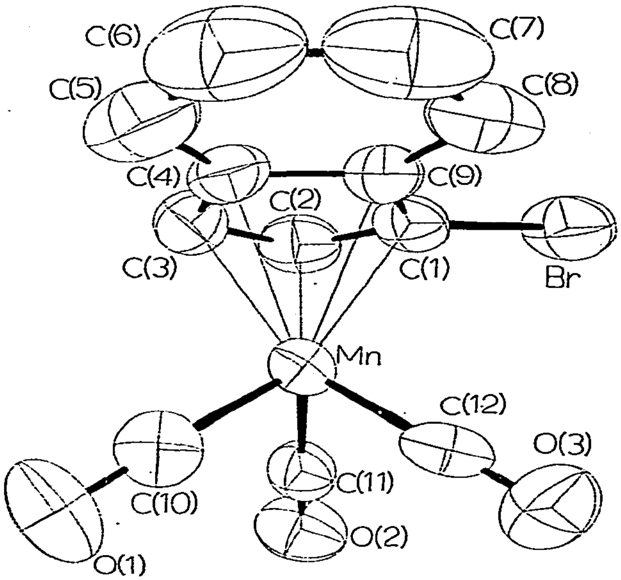
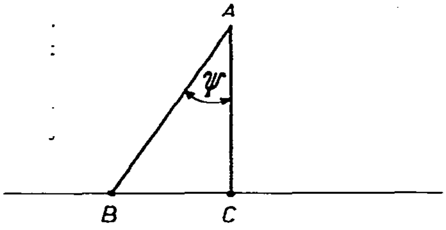


Fig. 1. Molecular structure and atom labeling scheme with the atoms represented by their 50% probability ellipsoids for thermal motion.

2.505(5), 2.502(6), 2.513(5), 2.600(5), and 2.622(5) Å, while for (η^5-C_9H_7)Cr-$(CO)_2(NO)$ [10] one finds 2.197(6), 2.177(6), 2.186(5), 2.289(4), and 2.301(5) Å. It therefore appears that the mechanism of distortion involves a translation of the metal atom parallel to the plane of the indenyl ring. A measure of this effect is the "angle slip", ψ, shown below. *A* is the metal atom position, *B* is the centroid of the five-membered ring and *C* is the intersection of the perpendicular from *A* to the plane of the ring. In (η^5-C_9H_6Br)$Mn(CO)_3$, ψ is 2.8°, *AC* 1.789 Å, and *AB* 1.791 Å.



The metal—carbon distances to the carbonyl ligands range from 1.780(9) to 1.816(10) Å and average 1.793(17) Å. This is almost identical with the 1.797(11) Å average observed in (η^5-C_5H_5)$Mn(CO)_3$ [16] and falls well within the normal range for related compounds: 1.771(7) Å in [η^4-(5-*exo*-CH_3-C_5H_5)]-Mn(CO)(NO)[$P(C_6H_5)_3$] [19] to 1.83(1) Å in [(η^5-C_5H_5)$Mn(CO)_2$]$_2C_4H_6$ [17]. The Mn—C—O bond angles are nearly 180° in both (η^5-C_9H_6Br)$Mn(CO)_3$ and (η^5-C_5H_5)$Mn(CO)_3$. It thus appears that the influence of the bromine atom on the indenyl ring is slight and that the change from cyclopentadienyl to indenyl produces essentially no disturbance in the normal manganese carbonyl linkage. These crystallographic results obtained for the crytalline state are in excellent

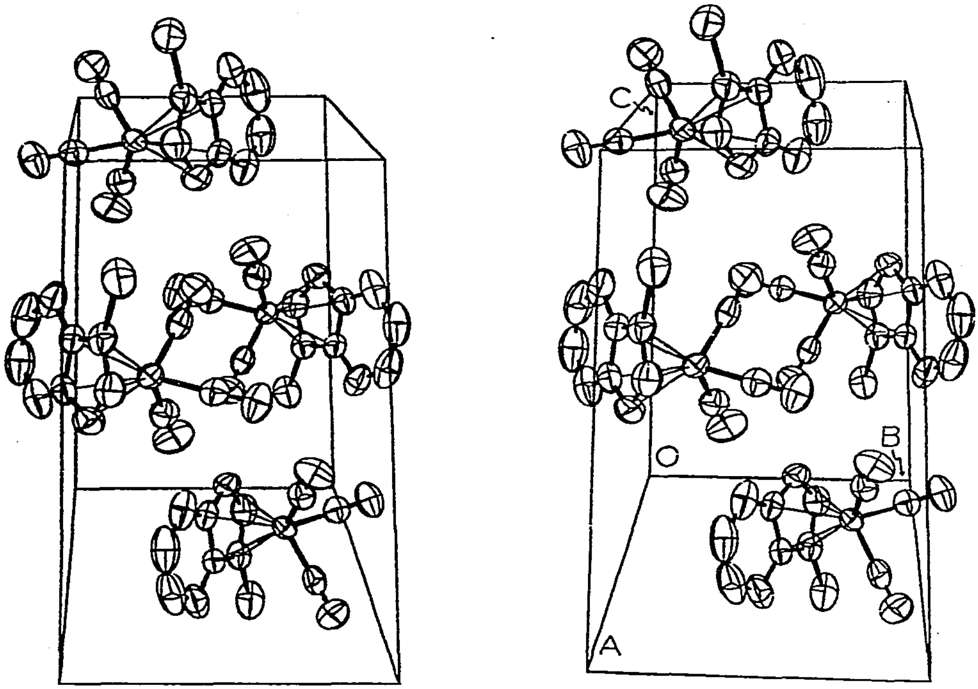


Fig. 2. Stereoscopic view of the unit cell packing in (η^5-C_9H_6Br)Mn(CO)$_3$.

agreement with the solution IR data (Table 4): they prove that the increasing electronegativity of the halogen ligands within the series I < Br < Cl does not affect the carbonyl stretching frequencies of (η^5-C_9H_6X)Mn(CO)$_3$ [X = Cl, Br, I] and that there is only an insignificant change in the spectrum of the halogen-free parent compound (η^5-C_9H_7)Mn(CO)$_3$. In contrast, there is a significant effect on the IR spectra by introducing halogen substituents into the corresponding cyclopentadienyl complex (η^5-C_5H_5)Mn(CO)$_3$ [20] and other comparable systems such as (η^5-C_5H_5)Fe(CO)$_2$(σ-C_3F_7) [20—22]. Apparently, the π-electron system of the indenyl ligand is able to provide a complete compen-

TABLE 4

INFRARED [a] AND ^{1}H NMR DATA [b] OF (η^5-C_9H_6X)Mn(CO)$_3$

X	ν(CO)-frequencies (cm^{-1})			^{1}H NMR data	
	(A_1)	(A_1)	(E)	τH(2,3)	τH(5—8)
H [5,6]	2025	1958	1950	[c]	—
Cl	2024	1961	1954	4.47 [d]	*m* 2.3—2.9
Br	2024	1962	1953	4.47 [d]	*m* 2.3—2.9
I	2024	1961	1953	4.47 [e]	*m* 2.3—2.9

[a] Beckmann IR-Spectrometer 4240 with data system 4060-A; all bands are very intense. Reproducibility: ±1/cm. Solvent: n-pentane. [b] Varian T-60 Spectrometer; acetone-d_6-solutions; τ-values [ppm] referenced on internal TMS; +33°C; intensity ratios: H(2,3)/H(5—8) 1/2. [c] Not comparable because of the additional Cl-proton. [d] AB pattern. [e] Pseudo-singlet.

sation for the electronic effects due to different halogen ligands in the metal-bonded C_5-moiety. This interpretation is also in agreement with the ^1H NMR spectra of $(\eta^6\text{-}C_9H_6X)Mn(CO)_3$ [X = Cl, Br, I]: there is not the slightest effect of the different halogen substituents on the chemical shifts of the protons (Table 4). From these findings we conclude that, besides the close similarity of the physical properties of these four compounds, they also should behave identically with respect to their chemical reactivity, as far as the indenyl—manganese bond and the tricarbonylmanganese system are concerned.

The unit cell packing shown in Fig. 2 is typical of a molecular compound of this kind.

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