Journal of Organometallic Chemistry, 205 (1981) 71—78
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

THE CRYSTAL STRUCTURE OF (η^5-C_5H_5)Mn(CO)$_2$-(η^2-NORBORNADIENE): THE ABSENCE OF A POSTULATED C—H—METAL INTERACTION IN AN 18-ELECTRON COMPLEX

PHILIP A. VELLA, MARK BENO, ARTHUR J. SCHULTZ * and JACK M. WILLIAMS *
Chemistry Division, Argonne National Laboratory, Argonne, IL 60439 (U.S.A.)

(Received July 15th, 1980)

Summary

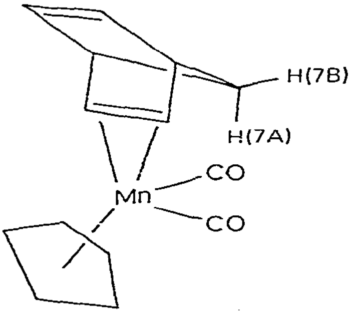
The crystal and molecular structure of (η^5-C_5H_5)Mn(CO)$_2$(η^2-C_7H_8) has been determined at 170 K using single crystal X-ray diffraction. The complex crystallizes in the orthorhombic space group *Pnma* with lattice parameters of a = 11.986(5), b = 11.171(5), c = 8.837(5) Å and Z = 4. The crystal consists of discrete molecules of (η^5-C_5H_5)Mn(CO)$_2$(η^2-C_7H_8) with a distorted tetrahedral geometry around the central Mn atom. The molecule also possesses a mirror plane which bisects the η^5-C_5H_5 ligand, the norbornadiene, and the OC—Mn—CO angle. The Mn atom is coordinated to the norbornadiene moiety in in an *exo* configuration with one olefin bond not participating in metal bonding. The metal coordinated olefinic bond is significantly longer than a corresponding non-coordinated double bond. The distance between the Mn atom and one of the bridgehead methylene hydrogen atoms on the norbornadiene ligand is 2.97-(5) Å, which is indicative of the lack of a C—H · · · metal interaction.

Introduction

The activation of C—H bonds in saturated hydrocarbons and the promotion of the hydrogen reduction of CO in methanol synthesis, methanation, and Fischer—Tropsch synthesis are properties of metal surfaces commonly utilized in industrial catalysis [1,2]. In order to characterize the intermediate steps of metal assisted C—H bond activation, there have been a number of recent reports of structural studies, often preceded by spectroscopic studies, of molecular compounds which contain unusually strong C—H—metal interactions [3—7]. The correlation of spectroscopic and structural data over a range of C—H · · · M (M = transition metal) interactions, in which the C—H and H · · · M distances vary, requires the examination not only of compounds with strong interactions, but also those in which the expected interaction is relatively weak.

In this paper we present the results of our investigation of the crystal structure of $(\eta^5\text{-}C_5H_5)Mn(CO)_2(\eta^2\text{-}C_7H_8)$ for which a short C—H · · · Mn contact had been postulated [8,9].

In 1963 Fritz and Keller [8] proposed structure I for $(\eta^5\text{-}C_5H_5)Mn(CO)_2(\eta^2\text{-}C_7H_8)$ based largely on NMR data. In particular, the large high-field shift of H(7A) (τ 9.91 ppm) was attributed to shielding from the nearby Mn atom. An X-ray structure by Granoff and Jacobson [9] in 1968 generally confirmed these predictions, although the hydrogen atoms were not located. However, based on the relative positions of the Mn and carbon atoms, they noted that H(7A) is probably "quite close" to the metal.



(I)

In order to precisely determine the position of H(7A) and thereby derive the C—H · · · M geometry, we prepared large crystals of $(\eta^5\text{-}C_5H_5)Mn(CO)_2(\eta^2\text{-}C_7H_8)$ for a neutron diffraction investigation. However, although spectroscopic and elemental analysis data were consistent with I, a preliminary X-ray determination of the unit cell was in disagreement with that reported by Granoff and Jacobson. A full X-ray study was undertaken as a means of verifying the molecular formulation of the crystals prepared in our laboratory. The results of that study, which are reported here, do not necessitate the need for neutron diffraction data to adequately answer the question which initiated this investigation.

Experimental

The preparation and purification of the title compound was carried out under an atmosphere of prepurified argon using Schlenk techniques. All solvents were dried and rigorously deoxygenated. UV irradiations were carried out using a General Electric Sunlamp. Infrared spectra were recorded on a Beckman 4260 spectrophotometer and calibrated against polystyrene. Elemental analysis was performed by Midwest Microlab Ltd., Indianapolis, IN.

Preparation of $(\eta^5\text{-}C_5H_5)Mn(CO)_2(\eta^2\text{-}C_7H_8)$

The compound was synthesized by the method of Heberhold and Fischer with certain modifications [10]. A solution of $Mn(\eta^5\text{-}C_5H_5)(CO)_3$ (0.76 g, 3.5 mmol) and C_7H_8 (3 ml, 28 mmol) in hexane (100 ml) was irradiated (UV light) for a period of 5 h. The resulting yellow-brown solution was filtered, reduced in volume to 15 ml and transferred to a sublimator where the remaining solvent was removed. Sublimation at 50°C and 0.015 mmHg for a period of 3 h removed any unreacted starting compound leaving pure $(\eta^5\text{-}C_5H_5)Mn(CO)_2(\eta^2\text{-}C_7H_8)$. IR($cm^{-1}$): ν(CO), 1972, 1912. (Found: C, 62.9; H, 4.9; O, 13.3. $C_{14}H_{13}MnO_2$ calcd.: C, 62.7; H, 4.9; O, 11.9%.)

Collection and reduction of diffraction data

A suitable crystal of approximate dimensions 0.13 × 0.15 × 0.30 mm was grown by slow evaporation of a saturated hexane solution at 0°C. The crystal was mounted on a fiber and placed in a glass capillary. Preliminary zero level Weisenberg and precession photos exhibited *mmm* symmetry with systematic absences of $hk0$, $h + k = 2n + 1$ and $0kl$, $k + l = 2n + 1$, indicating the orthorhombic space groups $Pn2_1a$ or $Pnma$. The calculated density of 1.50 g cm^{-3}, for four molecules in the unit cell, agrees quite well with the observed density of 1.49 g cm^{-3} obtained by the flotation method.

In the previous study by Granoff and Jacobson [9], the space group was determined to be $P2_1/m$ with 2 molecules per unit cell and a volume equal to one-half the value obtained in this study. Based upon their reported cell parameters, the calculated density is 1.45 g cm^3 although they report a value of 1.61 g cm^{-3}, which must be an error. These differences may be attributed to different sample recrystallization conditions since both molecular structures are equivalent within experimental error.

The crystal was transferred to a Syntex $P2_1$ diffractometer and remounted in an arbitrary orientation. The sample was cooled and maintained at 170 K throughout the alignment and data collection using a cold N_2 stream [11]. A least-squares fit of 25 accurately centered reflections led to the final unit cell parameters, which in addition to data collection and refinement parameters are given in Table 1.

Intensity data were collected out to $(\sin\theta)/\lambda = 0.70$ Å^{-1} using monochromatized Mo-K_α radiation (λ 0.71069 Å) with a variable scan rate in the θ—2θ scan mode. Five standard reflections were employed to monitor diffractometer and crystal stability which over the period of data collection decreased by 5% of their original value. No data were rejected during collection and inspection reconfirmed the systematic absences observed from films. The observed

TABLE 1

SUMMARY OF CRYSTAL AND EXPERIMENTAL DATA FOR $(\eta^5\text{-}C_5H_5)Mn(CO)_2(\eta^2\text{-}C_7H_8)$ AT 170 K

(a) Crystal parameters		(b) Data and refinement parameters	
Space group	*Pnma*	Wavelength (Mo-K_α)	0.71069 Å
a	11.986(5) Å	Independent data	1654 (2° ≤ 2θ ≤ 60°)
b	11.171(5) Å		
c	8.737(5) Å	Data with $F_0^2 > 3\sigma(F_0^2)$	1122
V	1183.3 Å^3	$R(F_0^2)$	0.032
Z	4	$R_w(F_0^2)$	0.051
ρ (calcd, 295 K)	1.50 g cm^{-3}	E	0.061
ρ (found, 295 K)	1.49 g cm^{-3}	Goodness of fit	0.71

TABLE 2

FINAL ATOMIC [a] AND THERMAL PARAMETERS [b] FOR (η^5-C_5H_5)Mn$(CO)_2$(η^2-C_7H_8)

Atom	x	y	z	U_{11} or B	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mn	0.5893(4)	0.25	0.3183(1)	0.0232(2)	0.0279(2)	0.0213(2)	0.0	0.0006(3)	0.0
C(1)	0.4647(4)	0.25	0.1330(5)	0.037(2)	0.153(6)	0.024(2)	0.0	−0.005(2)	0.0
C(2)	0.5296(4)	0.3491(3)	0.1174(3)	0.141(4)	0.051(2)	0.025(1)	0.033(2)	−0.012(2)	0.003(1)
C(3)	0.6365(3)	0.3107(3)	0.0906(3)	0.079(2)	0.117(3)	0.024(1)	−0.055(2)	0.002(1)	0.009(2)
C(4)	0.6682(2)	0.3636(2)	0.3965(3)	0.030(1)	0.036(1)	0.039(1)	0.001(1)	−0.001(1)	0.003(1)
C(5)	0.4649(2)	0.3128(2)	0.4673(2)	0.033(1)	0.033(1)	0.028(1)	0.002(1)	0.006(1)	−0.000(1)
C(6)	0.4874(2)	0.3496(2)	0.6336(3)	0.055(2)	0.039(1)	0.029(1)	−0.005(1)	0.007(2)	−0.009(1)
C(7)	0.5662(3)	0.25	0.6847(5)	0.057(2)	0.060(2)	0.025(2)	0.0	−0.007(2)	0.0
C(8)	0.3817(2)	0.3088(2)	0.7160(3)	0.061(2)	0.050(1)	0.033(2)	0.004(1)	0.018(1)	−0.004(1)
O	0.7217(2)	0.4381(1)	0.4498(2)	0.051(1)	0.045(1)	0.070(1)	−0.014(1)	−0.014(1)	−0.008(1)
H(1)	0.4009(44)	0.25	0.1559(58)	5.0					
H(2)	0.5104(30)	0.4239(32)	0.1204(35)	5.0					
H(3)	0.6999(30)	0.3515(30)	0.0885(36)	5.0					
H(5)	0.4079(30)	0.3609(26)	0.4008(35)	5.0					
H(6)	0.5107(28)	0.4359(28)	0.6533(35)	5.0					
H(7A)	0.6412(43)	0.25	0.6367(56)	5.0					
H(7B)	0.5862(41)	0.25	0.7930(58)	5.0					
H(8)	0.3288(27)	0.3584(26)	0.7395(36)	5.0					

[a] x, y, z are fractional coordinates. [b] Anisotropic temperature factors are of the form $\exp[-2\pi^2(a^{*2}U_{11}h^2 + \ldots a^*b^*U_{12}hk + \ldots)]$. Isotropic temperature factors are of the form $\exp[-B\sin^2\theta/\lambda^2]$.

TABLE 3

SELECTED INTRAMOLECULAR DISTANCES AND ANGLES FOR $(\eta^5\text{-}C_5H_5)Mn(CO)_2(\eta^2\text{-}C_7H_8)$ [a]

Distances (Å)			
Mn—C(1)	2.141(4)	C(5)—C(5)′	1.404(4)
Mn—C(2)	2.136(3)	C(5)—C(6)	1.550(3)
Mn—C(3)	2.121(3)	C(6)—C(7)	1.528(4)
Mn—C(4)	1.773(2)	C(6)—C(8)	1.531(4)
Mn—C(5)	2.154(2)	C(8)—C(8)′	1.314(5)
Mn—C(7)	3.336(4)	C(1)—H(1)	0.79(5)
Mn—H(7A)	2.96(5)	C(2)—H(2)	0.87(3)
Mn—Cp	1.773(3)	C(3)—H(3)	0.89(3)
Mn—NBD	2.036(3)	C(5)—H(5)	1.05(3)
C(1)—C(2)	1.361(5)	C(6)—H(6)	1.02(3)
C(2)—C(3)	1.372(5)	C(7)—H(7A)	0.99(5)
C(3)—C(3)′	1.356(7)	C(7)—H(7B)	0.99(5)
C(4)—O	1.151(3)	C(8)—H(8)	0.87(3)
Angles (deg)			
C(4)—Mn—C(4)′	91.4(5)	C(2)—C(3)—C(3)′	108.2(2)
C(4)—Mn—C(5)	108.5(1)	C(5)′—C(5)—C(6)	105.4(1)
C(4)—Mn—Cp	124.1(5)	C(5)—C(6)—C(7)	101.2(2)
C(4)—Mn—NBD	95.1(5)	C(5)—C(6)—C(8)	103.2(2)
C(5)—Mn—C(5)′	38.0(1)	C(7)—C(6)—C(8)	98.9(2)
C(5)—Mn—Cp	117.4(5)	C(6)—C(7)—C(6)′	93.5(3)
Cp—Mn—NBD	119.2(5)	C(6)—C(8)—C(8)′	107.3(1)
Mn—C(4)—O	178.1(2)	C(6)—C(7)—H(7A)	116(2)
C(2)—C(1)—C(2)′	109.0(4)	C(6)—C(7)—H(7B)	116(2)
C(1)—C(2)—C(3)	107.3(3)	H(7A)—C(7)—H(7B)	101(4)

[a] Primed atoms have been transformed by $(x, 1/2 - y, z)$. Cp denotes the centroid of the cyclopentadienyl ring and NBD denotes the halfway point between C(5) and C(5)′.

intensities were corrected for Lorentz polarization, crystal decay and absorption effects, yielding 1654 independent data for structure solution and refinement.

Solution and refinement of the structure

The initial Patterson map revealed the position of the manganese atom. The space group *Pnma* was then chosen and successful structure refinement indicated that the choice was correct. The remainder of the non-hydrogen atom positional parameters were determined from a difference Fourier synthesis phased on the manganese atom coordinates [12]. Following full-matrix least-squares refinement with anisotropic temperature factors, a difference-Fourier synthesis revealed the positions of the hydrogen atoms. After introducing H-atom coordinates, five additional cycles of least-squares refinement were performed. Because the weak data appeared to be weighted too heavily, a constant was added to the e.s.d. of each reflection, which improved the overall agreement but led to a "goodness-of-fit" of less than one (see Table 1). The refinement converged to $R(F_o) = 0.032$, $R(F_o^2) = 0.051$ and $R_w(F_o^2) = 0.061$ for all 1122 unique reflections with $(F_o^2) > 3\sigma(F_o^2)$. A final difference-Fourier synthesis revealed no electron density greater than 0.7 $e\text{Å}^{-3}$ where the average value for a carbon atom was 6.3 $e\text{Å}^{-3}$. Interatomic distances and angles are

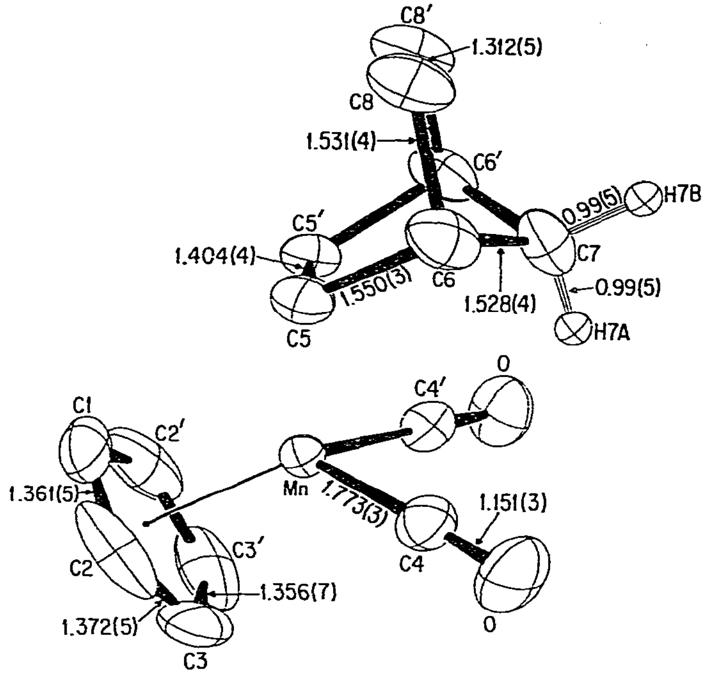


Fig. 1. The molecular structure of $(\eta^5\text{-}C_5H_5)Mn(CO)_2(\eta^2\text{-}C_7H_8)$. Except for H(7A) and H(7B), hydrogen atoms have been omitted. The thermal ellipsoids are scaled to enclose 50% probability.

listed in Table 3. Final atomic and thermal parameters are given in Table 2. A listing of observed and calculated structure factors is available. *

Results and discussion

A perspective drawing of the molecule with the atom labelling scheme is presented in Fig. 1 and a stereoscopic view is shown in Fig. 2. Important intramolecular bond distances and angles are given in Table 3.

The molecular structure obtained from this work is in agreement with that determined by Granoff and Jacobson [9], although the crystal symmetries are different. However, in both cases the molecule contains a crystallographic mirror plane which passes through Mn and C(7) and bisects the C(4)—Mn—C(4)′ angle. The geometry about the Mn atom is pseudotetrahedral if the cyclopentadiene and norbornadiene ligands are each considered to occupy a single coordination site. Since the three Cp—Mn—L angles (L = C(4), C(4)′ or NBD; see Table 2 footnote for nomenclature) are either 119.1(5)° or 124.1(5)° and the three L_1—Mn—L_2 angles are either 91.4(5)° or 95.1(5)°, the molecule can also

---

* See NAPS Document No. 03726 for 6 pages of supplementary material. Order from NAPS, c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10017. Remit in advance, in U.S. funds only. $ 5.00 for photocopies or $ 3.00 for microfiche. Outside the U.S. and Canada add postage of $ 3 for photocopy and $ 1 for microfiche.

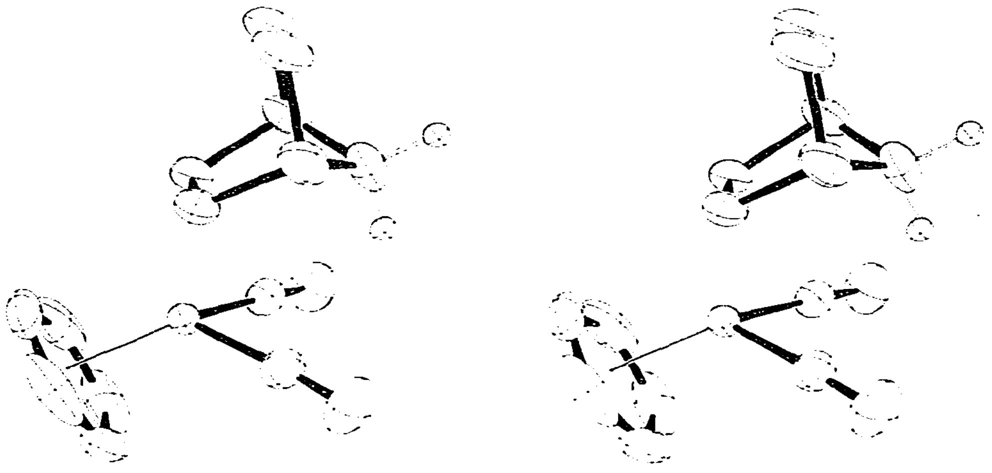


Fig. 2. Stereoscopic view of the molecular structure of $(\eta^5\text{-}C_5H_5)Mn(CO)_2(\eta^2\text{-}C_7H_8)$.

be described as a "three-legged piano stool" configuration [13] with the C_5H_5 ring as the "seat".

The norbornadiene ligand is *dihapto*-coordinated to the Mn atom with one of its two olefinic bonds. In the previous structure determination, the coordinated and uncoordinated olefin bond lengths (1.397(13) and 1.360(22) Å, respectively) differ by less than 2 e.s.d.'s. In the present work, the C(5)—C(5)′ bond distance is 0.092(6) Å longer than the C(8)—C(8)′ distance due to metal to ligand back donation into the olefinic π^* orbital [14].

The observed Mn—H(7A) distance of 2.97(5) Å is long and is not indicative of a C—H · · · M bonding interaction. By comparison, the copper norbonadiene complex, $[Cu(dien)(C_7H_{10})]^+$ [15], apparently contains a Cu—H distance of 2.01(15) Å (based on an X-ray diffraction study) which is in the range of other short aliphatic C—H · · · M interactions, such as 2.15 [3] and 1.93 Å [4] in two molybdenum pyrazolylborate complexes (X-ray) and 1.874(3) Å in an cyclooctenyliron complex (neutron) [6]. It is interesting to note that the latter three compounds formally contain 16 electrons and only attain 18 electron configurations if the two electrons in the C—H bond are included. In contrast, the Mn and Cu norbornadiene complexes are 18 electron systems and it is therefore plausible that the close Cu · · · H contact is due to steric factors which are absent in the Mn complex. Other examples of steric crowding in 18 electron complexes leading to C—H · · · M interactions are found in a series of alkylidenetantalum compounds prepared by Schrock and coworkers [16].

Acknowledgment

Research of Argonne National Laboratory is performed under the auspices of the Division of Basic Energy Sciences of the U.S. Department of Energy.

References

1 E.L. Muetterties, Science, 196 (1977) 839.
2 G.W. Parshall, Acc. Chem. Res., 8 (1975) 113.
3 F.A. Cotton, T. LaCour and A.G. Stanislowski, J. Amer. Chem. Soc., 96 (1974) 754.
4 F.A. Cotton and V.W. Day, J. Chem. Soc. Chem. Commun., (1974) 415.
5 A.J. Schultz, J.M. Williams, R.R. Schrock, G.A. Rupprecht and J.D. Fellmann, J. Amer. Chem. Soc., 101 (1979) 1593.
6 R.K. Brown, J.M. Williams, A.J. Schultz, G.D. Stucky, S.D. Ittel and R.L. Harlow, J. Amer. Chem. Soc., 102 (1980) 981.
7 M.A. Beno, J.M. Williams, M. Tachikawa and E.L. Muetterties, J. Am. Chem. Soc., 102 (1980) 4542.
8 H.P. Fritz and H.J. Keller, Chem. Ber., 96 (1963) 1676.
9 B. Granoff, R.A. Jacobson, Inorg. Chem., 7 (1968) 2328.
10 E.O. Fischer and M. Herberbold, Experienta, Suppl., 9 (1964) 259.
11 C.E. Strouse, Rev. Sci. Instrum., 47 (1976) 871.
12 Details of data reduction and structure refinement and programs used have been reported previously; see P.L. Johnson, A.J. Schultz, A.E. Underhill, D.M. Watkins, D.J. Wood and J.M. Williams, Inorg. Chem., 17 (1978) 839.
13 M.R. Churchill and W.J. Youngs, Inorg. Chem., 18 (1979) 171.
14 S.D. Ittel and J.A. Ibers, Advan. Organometal. Chem., 14 (1976) 33.
15 M. Pasquoli, C. Floriani, A. Gaetani-Manfredotti and A. Chiesi-Villa, J. Amer. Chem. Soc., 100 (1978) 4918.
16 R.R. Schrock, Acc. Chem. Res., 12 (1979) 98.