Molecular and Crystal Structure of Hydrido(tricarbonyl)bis(triphenylphosphine)manganese(I), $HMn(CO)_3[P(C_6H_5)_3]_2$

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The crystal structure of the title compound has been determined by single crystal X-ray diffraction techniques. The compound crystallizes in the space group C2/c with unit-cell dimensions $a=23.54(1)$, $b=9.672(3)$, $c=15.941(7)$ Å, $\beta=114.90(4)°$, and $Z=4$. The manganese atom is octahedrally coordinated by two triphenylphosphines in the trans positions, three equatorial carbonyl ligands, and a hydrido hydrogen. The Mn-H bond has a normal covalent length, 1.46(8) Å. The molecule has C_2 symmetry, and Mn, O(1), C(1), and H_h are on special positions of (0, *y*, 1/4).

The crystal structure of hydrido(tricarbonyl)bis(triphenylphosphine)manganese(I), $HMn(CO)_3[P(C_6H_5)_3]_2$, has been studied in order to obtain quantitative data on the Mn–H bond and interactions of hydrido hydrogen with other ligands.

Experimental

The compound was prepared by the reaction of manganese carbonyl and triphenyl phosphine in the presence of metallic sodium in dioxane.[1] The samples used for the X-ray diffraction studies were obtained by recrystallization from a mixture of benzene-petroleum ether. A specimen, a transparent yellow rhombus, stable in the air, of dimensions *ca.* $0.2\times0.2\times0.25$ mm, was used for collection of diffraction intensity data and for measurement of the unit cell dimensions. A Rigaku automated four-circle diffractometer with Mo $K\alpha$ radiation, ($\lambda=0.71069$ Å) monochromated by a graphite crystal was used. Unit cell dimensions were calculated by a least-squares refinement of 14 reflection data obtained for $20°<2\theta<40°$.

Crystal data: $C_{39}H_{31}O_3MnP_2$, $M=664.56$, monoclinic, C2/c, $a=23.54(1)$, $b=9.672(3)$, $c=15.941(7)$ Å, $\beta=114.90(4)°$ $U=3292.1$ Å^3, $D_c=1.34$ g cm^{-3}, $D_m=1.32$ g cm^{-3}, $Z=4$, μ(Mo $K\alpha$)$=6.5$ cm^{-1}.

The diffraction intensities were measured with the 2θ-ω scan technique and 1945 independent reflections for which $|F_{abs}|\geq19$ and $|F_o|\geq3\sigma(|F_o|)$ up to $2\theta=60°$ were obtained at 23 ± 1 °C. The intensity data were corrected for the Lorenz and the polarization effects, but not for absorption. The structure was solved by the heavy atom method. The atomic parameters and the temperature factors were refined by the block-diagonal least-squares method, the function minimized being $\Sigma w(|F_o|-K|F_c|)^2$ where $w=1$ for all the reflections. The atomic scattering factors used were taken from "International Tables for X-Ray Crystallography" Vol. IV (1974).[2]

Two possible space groups, Cc and C2/c, deduced from the extinction rule (*hkl*: $h+k=2n+1$, *h*0*l*: $l=2n+1$) gave almost the same *R*-values (6.6 and 6.4%) for all the non-hydrogen atoms. However, Cc was ruled out since it gave unreasonable bond lengths and angles in the structure of phenyl groups. All the 16 independent hydrogen atoms were found as 0.35—0.52 eÅ^{-3} peaks in difference Fourier maps. The final *R*-value converged to 4.83%, all the hydrogen atoms being included in the calculation, and no peak higher than 0.26 e Å^{-3} was found in the last difference Fourier maps.

All the calculations were performed on a HITAC 8700/8800 computer at the Computer Centre of the University of Tokyo using a local version of UNICS[3] and the ORTEP[4] program.

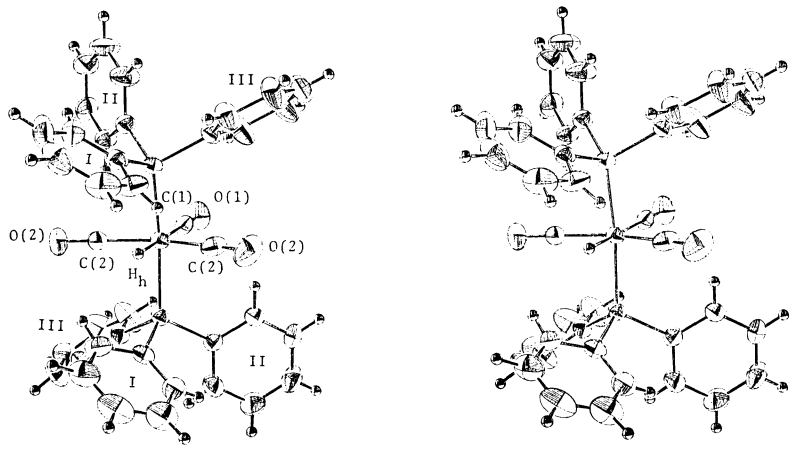

Fig. 1. Stereoscopic drawing of the molecule of $HMn(CO)_3[P(C_6H_5)_3]_2$. The non-hydrogen atoms are represented by their thermal ellipsoids with 50% probability, while the hydrogen atoms are represented by arbitrary spheres.

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TABLE 1. FINAL ATOMIC COORDINATES ($\times 10^4$) AND THERMAL FACTORS ($\times 10^3$ Å^2)

The anisotropic thermal factors are of the form:

$$\exp[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)]$$

The isotropic temperature factor is of the form $\exp[-B(\sin\theta/\lambda)^2]$.

Atom	X	Y	Z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mn	0	2034(1)	2500	29(0)	27(0)	30(0)	0	15(0)	0
P	918(1)	1823(1)	2368(1)	29(1)	29(1)	30(1)	−2(1)	15(0)	−2(1)
O(1)	0	5077(6)	2500	75(4)	34(3)	50(4)	0	19(3)	0
O(2)	648(2)	1398(5)	4496(3)	61(3)	99(4)	44(2)	1(3)	11(2)	32(2)
C(1)	0	3889(7)	2500	29(4)	36(4)	34(4)	0	7(3)	0
C(2)	400(2)	1684(6)	3730(4)	32(3)	45(3)	47(3)	5(2)	19(2)	14(3)
C(11)	1192(2)	25(5)	2505(4)	39(3)	35(3)	38(3)	4(2)	24(2)	3(2)
C(12)	1756(3)	−408(7)	3196(4)	51(4)	52(4)	42(3)	10(3)	19(3)	3(3)
C(13)	796(3)	−984(6)	1933(4)	35(3)	42(3)	74(4)	0(3)	25(3)	−5(3)
C(14)	1913(3)	−1786(7)	3310(4)	82(5)	67(5)	51(4)	31(4)	29(3)	27(3)
C(15)	967(3)	−2368(6)	2056(5)	64(4)	37(3)	94(5)	−5(3)	44(4)	−8(3)
C(16)	1520(4)	−2774(7)	2740(5)	99(5)	40(4)	85(5)	15(4)	61(4)	19(3)
C(21)	1593(2)	2802(5)	3158(3)	31(2)	39(3)	33(2)	−4(2)	12(2)	−2(2)
C(22)	2146(3)	2830(8)	3040(4)	47(3)	89(5)	50(3)	−15(4)	30(3)	−23(4)
C(23)	1572(2)	3567(6)	3881(4)	36(3)	42(3)	38(3)	−2(2)	18(2)	−6(2)
C(24)	2661(3)	3579(8)	3635(5)	40(3)	106(6)	63(4)	−22(4)	29(3)	−15(4)
C(25)	2089(3)	4312(7)	4472(4)	43(3)	56(4)	37(3)	−8(3)	7(3)	−11(3)
C(26)	2631(3)	4312(8)	4348(4)	43(3)	78(5)	46(3)	−26(3)	11(3)	−8(3)
C(31)	904(2)	2380(5)	1255(3)	35(3)	39(3)	30(2)	−5(2)	19(2)	0(2)
C(32)	992(3)	1513(6)	646(4)	69(4)	50(3)	46(3)	11(3)	33(3)	1(3)
C(33)	786(4)	3762(7)	1024(5)	117(6)	40(4)	67(4)	−1(4)	62(4)	4(3)
C(34)	965(3)	2027(8)	−188(4)	91(5)	67(4)	39(3)	12(4)	38(3)	−4(3)
C(35)	770(4)	4254(7)	200(5)	132(7)	51(4)	98(6)	29(4)	84(6)	36(4)
C(36)	847(3)	3384(7)	−408(4)	74(4)	73(5)	47(3)	13(4)	37(3)	22(3)

Atom	X	Y	Z	B	Atom	X	Y	Z	B
H_h	0	52(9)	250	2.1(1.9)	H(24)	302(3)	353(8)	355(4)	4.9(1.9)
H(12)	202(2)	21(5)	347(3)	1.0(1.1)	H(25)	207(3)	489(7)	492(4)	3.0(1.5)
H(13)	41(2)	−77(6)	158(4)	1.4(1.2)	H(26)	296(3)	478(7)	473(4)	3.1(1.5)
H(14)	228(3)	−198(7)	377(4)	3.8(1.6)	H(32)	107(3)	53(7)	76(4)	3.8(1.7)
H(15)	67(3)	−297(7)	165(4)	3.4(1.5)	H(33)	76(3)	432(7)	144(4)	3.8(1.7)
H(16)	164(2)	−376(6)	289(4)	1.6(1.2)	H(34)	103(3)	150(7)	−56(4)	3.8(1.7)
H(22)	219(2)	236(5)	260(3)	0.7(1.0)	H(35)	66(3)	512(7)	7(4)	3.1(1.5)
H(23)	119(2)	355(5)	398(3)	1.0(1.1)	H(36)	84(3)	366(6)	−92(4)	2.5(1.4)

TABLE 2. BOND DISTANCES (STANDARD DEVIATIONS IN PARENTHESES)

Mn-P	2.267(2) Å	C(21)-C(22)	1.393(9) Å	C(11)-C(12)	1.386(7)		
Mn-C(1)	1.794(7)	C(22)-C(24)	1.389(9)	C(12)-C(14)	1.375(10)	C(31)-C(32)	1.363(9)
Mn-C(2)	1.815(5)	C(24)-C(26)	1.367(11)	C(14)-C(16)	1.373(9)	C(32)-C(34)	1.395(10)
Mn-H_h	1.46(8)	C(25)-C(26)	1.371(11)	C(15)-C(16)	1.357(9)	C(34)-C(36)	1.357(10)
		C(23)-C(25)	1.387(7)	C(13)-C(15)	1.387(8)	C(35)-C(36)	1.353(12)
C(1)-O(1)	1.150(9)	C(21)-C(23)	1.387(8)	C(11)-C(13)	1.391(7)	C(33)-C(35)	1.382(12)
C(2)-O(2)	1.143(7)					C(31)-C(33)	1.383(8)
		C(22)-H(22)	0.88(6)	C(12)-H(12)	0.85(5)		
P-C(11)	1.836(5)	C(23)-H(23)	0.96(6)	C(13)-H(13)	0.87(5)	C(32)-H(32)	0.97(7)
P-C(21)	1.823(5)	C(24)-H(24)	0.90(8)	C(14)-H(14)	0.89(6)	C(33)-H(33)	0.88(7)
P-C(31)	1.842(6)	C(25)-H(25)	0.92(7)	C(15)-H(15)	0.93(6)	C(34)-H(34)	0.84(8)
		C(26)-H(26)	0.88(6)	C(16)-H(16)	0.99(6)	C(35)-H(35)	0.88(7)
						C(36)-H(36)	0.85(7)

Results and Discussion

The atomic parameters and standard deviations are given in Table 1. The F_o-F_c Table is kept at the Office of the Chemical Society of Japan as Document No. 7825.

The molecular geometry $HMn(CO)_3[P(C_6H_5)_3]_2$ is shown in Figs. 1 and 2, the packing in the unit cell in Fig. 4. The molecule has C_2 symmetry, Mn, O(1), C(1), and H_h lying on special positions of (0, y, 1/4). The manganese atom is octahedrally coordinated by one hydrogen (H_h), three carbonyl ligands on the equator, and two phosphorus atoms of triphenylphosphine in trans positions. However, the octahedron is deformed. The eight atoms, Mn, H_h, two C(2), two O(2), C(1), and O(1), lie exactly on a plane, $0.99790x-0.06478z+1.90852=0$, and six atoms, Mn, H_h, C(1), O(1), and two P, form another plane, $-0.08441x-0.99643z+3.4603=0$; x, y, and z, are orthogonal coordinates in Å along a, b, and c^*, respectively. These two planes are almost perpendicular to each other. The two phosphorus atoms and two carbonyl ligands bend down toward H_h to deform the octahedron, the angle Mn–C(2)–O(2) not being linear. The bond distances and angles are given in Tables 2 and 3, respectively.

The Mn–H_h distance was determined to be 1.46(8) Å. The length is quite normal as a covalent bond length as compared to the value calculated from the covalent atomic radii of manganese (1.171 Å) and hydrogen (0.30 Å).[5] Concerning the Mn–H bond length, very few data are available. In the case of $HMn(CO)_5$, the distance 1.601(16) Å was found by neutron diffraction techniques.[6] The value 1.5 Å was reported in the crystal structure determination of $HMn(CO)_3[PCH_3(C_6H_5)_2]_2$.[7]

However, this value does not seem to be refined by the least-squares method. Interactions of the hydrido

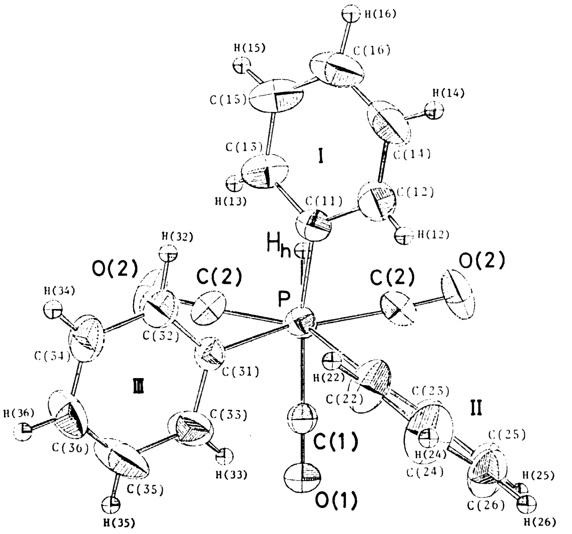

Fig. 2. Conformation of one of the triphenylphosphine ligand in the molecule of $HMn(CO)_3[P(C_6H_5)_3]_2$.

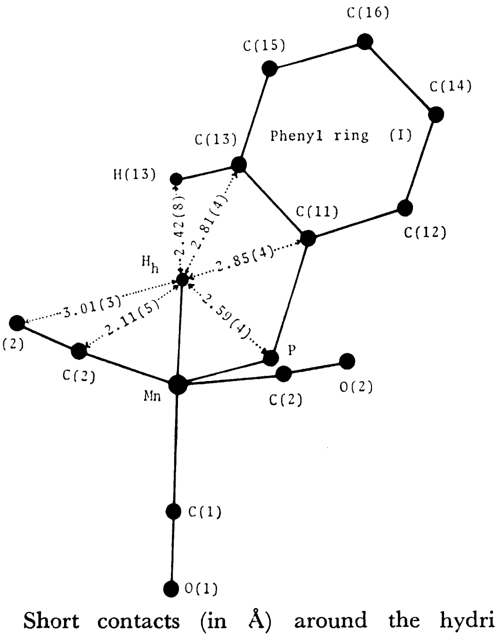

Fig. 3. Short contacts (in Å) around the hydrido hydrogen.

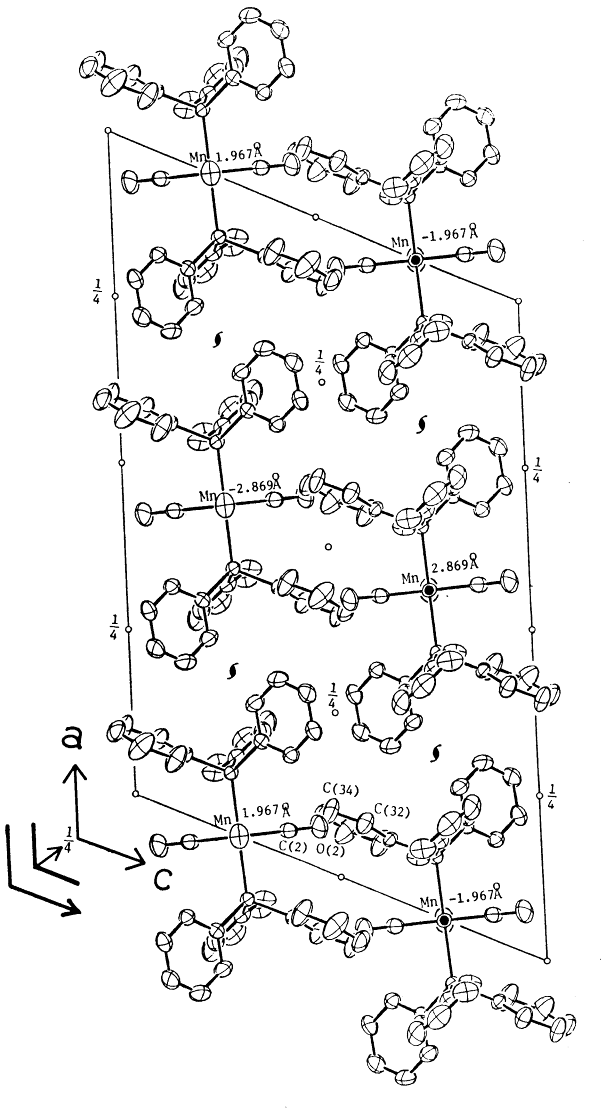

Fig. 4. Projection of the crystal structure along the b axis. The y coordinates (Å) of the Mn atoms are indicated.

TABLE 3. BOND ANGLES (STANDARD DEVIATIONS IN PARENTHESES)

H_h - Mn - C(1)	180 (3)°	Mn - C(2) - O(2)	176.8 (5)	C(21) - C(23) - C(25)	120.9 (5)
H_h - Mn - C(2)	79 (3)	P - C(11) - C(12)	123.5 (4)	C(22) - C(24) - C(26)	120.2 (7)
P - Mn - P	169.66(8)	P - C(11) - C(13)	118.8 (4)	C(23) - C(25) - C(26)	120.4 (6)
P - Mn - C(1)	95.2 (3)	P - C(11) - C(16)	175.1 (3)	C(24) - C(26) - C(25)	119.8 (6)
P - Mn - C(2)	90.1 (2)	C(12) - C(11) - C(13)	117.6 (5)	P - C(31) - C(32)	124.1 (5)
Mn - P - C(11)	112.1 (2)	C(11) - C(12) - C(14)	120.8 (5)	P - C(31) - C(33)	117.4 (5)
Mn - P - C(21)	118.5 (2)	C(12) - C(14) - C(16)	121.2 (6)	C(32) - C(31) - C(33)	118.6 (6)
Mn - P - C(31)	115.6 (2)	C(13) - C(15) - C(16)	121.0 (6)	C(31) - C(32) - C(34)	120.0 (6)
C(11) - P - C(21)	104.5 (2)	P - C(21) - C(22)	120.6 (5)°	C(31) - C(33) - C(35)	120.5 (8)
C(11) - P - C(31)	104.7 (3)	P - C(21) - C(23)	121.7 (4)	C(32) - C(34) - C(36)	120.9 (7)
C(21) - P - C(31)	99.8 (2)	C(22) - C(21) - C(23)	117.7 (5)	C(33) - C(35) - C(36)	120.6 (7)
Mn - C(1) - O(1)	179.9 (7)	C(21) - C(22) - C(24)	121.0 (6)	C(34) - C(36) - C(35)	119.4 (7)

TABLE 4. BEST PLANES OF THREE PHENYL GROUPS EXPRESSED BY THE FORMULAE, $Ax+By+Cz+D=0$, AND DEVIATIONS OF CARBON ATOMS FROM THE PLANES. x, y, AND z ARE ORTHOGONAL COORDINATES IN Å ALONG a, b, AND c^*

Phenyl ring	*A*	*B*	*C*	*D*
(I)	0.77429	0.09698	−0.62535	1.39021
(II)	−0.08213	0.79778	−0.59732	0.69332
(III)	−0.87985	−0.18445	−0.43799	2.35041

Phenyl ring	(I)	(II)	(III)
C-1	−0.0010 Å	−0.0058 Å	0.0000 Å
C-2	−0.0007	0.0040	−0.0025
C-3	0.0029	0.0037	0.0070
C-4	−0.0023	0.0009	−0.0018
C-5	−0.0021	0.0010	−0.0115
C-6	0.0032	−0.0036	0.0089

hydrogen with the surrounding atoms are discussed below.

The atom C(1) which is in the position trans to H_h is nearer to the manganese atom than the two other carbon atoms C(2) in *cis* positions, the C(1)–O(1) bond being shorter than C(2)–O(2). As shown in Fig. 2, three carbon atoms, C(11), C(21), and C(31), attached to the phosphorus do not form an equilateral triangle. The conformation of the triphenylphosphine ligand looks like a propeller with three blades having different pitches. The angles between the $Mn(CO)_3H$ plane and the three phenyl rings, (I), (II), and (III), are 35.6, 92.5, and 148°, respectively.

The phenyl ring (I) is nearest to H_h, having hardly any van der Waals contact with any carbonyl or other ligand. The bond angle Mn–P–C(11) (Table 3) is the smallest among the corresponding angles of three phenyl groups, the phosphorus atom P being bent towards H_h. Moreover, (I) is also declined to the same direction by 5°, the angle between the plane of the phenyl ring (I) and the P–C(11) vector being 175°. The phenyl group (II) seems to be balanced between carbon atoms of two carbonyl ligands, the distances C(1)–C(23) and C(2)–C(23) being 3.43 and 3.23 Å, respectively. In the case of the phenyl ring (III), a fairly short distance of 3.15 Å is found between C(31) and C(2), and an oxygen atom of the neighbor molecule O(2) is close to H(32) with the distance of 2.61 Å. These interactions might have stabilized the phenyl group (III) at the present position.

Figure 3 shows the interatomic distances from the hydrido hydrogen to the surrounding atoms. The distance to H(13) agrees with the sum of the van der Waals radii of two hydrogen atoms. The H_h–C(11) and H_h–C(13) distances are understood as the sum of the half thickness of an aromatic ring and the van der Waals radius of hydrogen atom. The two C(2) atoms of carbonyl groups and the two phosphorus atoms of triphenylphosphine ligands are found close to H_h, the distances being 2.11 and 2.59 Å, respectively. Such short contacts have been reported also in $HMn(CO)_5$⁶⁾ and $HMn(CO)_3[PCH_3(C_6H_5)_2]_2$.⁷⁾ The short contacts shown in Fig. 3 might give rise to the stability of the present hydrido complex.

The equations of the best planes for the three aromatic rings and deviations of each carbon atoms from these planes are given in Table 4. The average of all the C–C bonds is 1.378(13) Å and that of the C–H bonds 0.90(5) Å. The C–C–C angles are 120° within 1.2°. It is worthwhile to note that C(33), C(35), and C(36) having the largest deviations from the best plane (III) for an unknown reason have also the largest temperature factors (Fig. 2). Van der Waals contacts were found between O(2)···H(32) [2.61(7) Å] and H(25)···H(12) [2.54(10) Å]; there is no other intermolecular distance smaller than 2.7 Å. The crystal volume per each triphenylphosphine molecule is 411.6 Å³. This volume is near 418 Å³ of $Os(CO)_3[P(C_6H_5)_3]_2$⁸⁾, 423 Å³ of $Mn(NO)(CO)_2[P(C_6H_5)_3]_2$⁹⁾ and $Ir(CO)Cl(SO_2)[P(C_6H_5)_3]_2$,¹⁰⁾ and 404 Å³ of $ReNCl_2[P(C_6H_5)_3]_2$.¹¹⁾ Triphenylphosphine itself has a molecular volume of 364 Å³ in its crystals, the ligand occupying about 90% of the space in the solid of the present complex.

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