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ISOLATION AND X-RAY MOLECULAR STRUCTURE ANALYSIS OF $(C_6H_5O)_2\overline{P(OC_6H_4)Mn}\cdot(CO)_2\{P(OC_6H_5)_3\}_2$ FROM $R_3Sn\text{-}Mn(CO)_3\{P(OC_6H_5)_3\}_2$ ($R = CH_3$ and C_2H_5) BY PHOTOCHEMICALLY INDUCED ORTHOMETALATION REACTION

Satoru ONAKA,* Yoshinori KONDO, Nobuhiro FURUICHI, and Kōshio TORIUMI**
Department of Chemistry, Nagoya Institute of Technology, Gokiso-cho,
Showa-ku, Nagoya 466 and **Division of Applied Molecular Science,
The Institute for Molecular Science, Myodaiji, Okazaki, Aichi 444

Photochemical reactions of the title compounds afforded an air-stable colorless crystalline compound in low yield. The product was characterized as an orthometalated manganese triphenylphosphite derivative by elemental analyses and an X-ray diffraction technique. Its crystal structure is described.

Photochemical reactions of metal-metal bonded complexes have attracted considerable attention in the past decade.1,2) Of particular interest is that mixed metal cluster compounds and/or mixed metal cyclic compounds were afforded by photochemical reactions of compounds with heteronuclear metal-metal bonds between Group IV and transition metal atoms.2) These results prompted us to investigate the photochemical behaviour of tin-manganese bonded carbonyl derivatives hoping to induce the tin atom to a bridging position between two manganese atoms. In the course of our investigation on this system, however, we found that di-substituted manganese carbonyl derivatives with triphenylphosphite of the type $R_3Sn\text{-}Mn(CO)_3L_2$ ($L = P(OC_6H_5)_3$) underwent facile rupture of the tin-manganese bond. A colorless crystalline product was isolated from $(CH_3)_3Sn\text{-}Mn(CO)_3L_2$ (I) and $(C_2H_5)_3Sn\text{-}Mn(CO)_3L_2$ (II) in low yield. We now report the molecular structure of this crystalline product.

Photolysis of (I) and (II) A 1.0 g sample of (I) or (II)3) was dissolved in 50 cm^3 of benzene and photolyzed for 10 h by a Riko 100 W high pressure mercury lamp. After the solution was filtered using a fine porosity glass frit, solvent was vacuum-stripped to leave a pale brown oil. The oil was dissolved in about 5 cm^3 of benzene and was chromatographed over Florisil (60-100 mesh) with benzene as an eluent. The first yellow fraction was collected and recrystallization from benzene-petroleum ether yielded air-stable colorless crystals (X) (yield: less than 0.1 g). The IR spectrum in the ν(CO) region (1980(vs) and 1920(vs) cm^{-1} in a Nujol mull), ^1H-NMR in benzene in the region from $\delta = -10$ to 9 ppm (two broad peaks at $\delta = 7.1$ and $\delta = 6.8$ ppm with relative intensity of about 1 : 2 due to phenyl protons), and elemental analyses on C, H, and P suggested that the product (X) contained two carbonyl groups and three triphenylphosphite groups around the manganese atom. However, at this moment, molecular structure or bonding mode of triphenylphosphite groups to the manganese atom was ambiguous. As is described in a later section, an X-ray crystal structure analysis of (X) revealed the presence of an orthometalated triphenylphosphite group and the product (X) is formulated as $(C_6H_5O)_2\overline{P(OC_6H_4)Mn}(CO)_2\{P(OC_6H_5)_3\}_2$. Anal. calcd. for $C_{56}H_{44}MnO_{11}P_3$: C, 64.62; H, 4.26; P, 8.93. Found: C, 64.24; H, 3.90; P, 8.73. In these photochemical reactions, attempts were made to isolate products which should contain the tin moiety. However, the yield was quite low to carry out satisfactory characterization or the product seems to be decomposed by elution with ethanol from the Florisil column (we could not obtain any significant amount of products further with benzene and color was bleached immediately with ethanol).

X-ray data A crystal of approximate dimensions 0.26 x 0.19 x 0.07 mm was glued on the tip of a glass fiber and mounted on a Rigaku automated four circle diffractometer, AFC-5, equipped with a graphite monochromated Mo Kα radiation source ($\lambda = 0.71073$ Å). The crystal belongs to a triclinic system with unit cell dimensions $a = 10.820(3)$, $b = 25.943(3)$, $c = 10.061(2)$ Å, $\alpha = 90.61(1)$, $\beta = 115.26(1)$, $\gamma = 82.77(1)°$, $V = 2530.8(10)$ $Å^3$, and $Z = 2$. A total of 4199 independent reflections with $|F_o| > 3\sigma(|F_o|)$ were measured using a θ-2θ scan technique up to $2\theta = 50°$. The structure was solved by the standard heavy atom method and refined based on $P\bar{1}$ space group using a UNICS-III program system$^{4)}$ and a HITAC M-180 computer at the Institute for Molecular Science. The present discrepancy indices are $R = R_w = 0.069$ for 71 nonhydrogen atoms with anisotropic temperature factors.

The molecular structure and the atom numbering scheme are shown in Fig.1. Two carbonyl groups, two monodentate triphenylphosphite groups, and a bidentate triphenylphosphite group compose a distorted octahedral array about the manganese atom. Two axial $P(OPh)_3$ groups are slightly bent (the angle P_1-Mn-P_3 is 165.7(1)°) toward the benzene ring, Ph_{22}, in the chelating $P(OPh)_3$ to minimize steric repulsion with the benzene rings, Ph_{21} and Ph_{23}. The chelating phosphite is coordinated to the manganese atom through the phosphorus atom and an ortho carbon atom of one of the phenoxy groups to form a five-membered ring (Fig.1b). The manganese, phosphorus, oxygen, and six carbon atoms in the orthometalated phenyl group are almost coplanar; the greatest deviation of any of these atoms from the least-squares planes is 0.019 Å. The carbonyl carbon atoms are as much as 0.07 Å away from the least-squares plane. Although the coplanarity suggests possible π-electron delocalization over this ring, the bond lengths associated with this ring do not differ significantly from those in the monodentate triphenylphosphite groups in (X). The Mn-P$_2$ distance, 2.208(3) Å, which is quite close to those found for Mn-P$_1$ and Mn-P$_3$ lengths for monodentate P(OPh)$_3$, 2.199(6) Å as an average, is shorter than those in analogous triphenylphosphine manganese ring systems, 2.279(3)∿2.304(4) Å[5]. The result is best interpreted in terms of the increased Lewis π-acidity of the phosphite ligand compared with the phosphine ligand. The Mn-C(phenyl) distance, 2.078(8) Å, is in the range of generally found Mn-C distances, 2.001 ∿ 2.097 Å for analogous manganese triphenylphosphine derivatives.[5] The Mn-C(carbonyl) and C-O distances trans to P$_2$ are essentially identical to those trans to C$_{222}$ atom. All bond angles related to the chelate ring are smaller than normal bond angles of the relevant atoms, especially the deviation from the ideal angle of 90° is significant in the P$_2$-Mn-C$_{222}$ angle (80.0(2)°). This deviation should originate from the coplanarity of the chelate ring. Selected bond

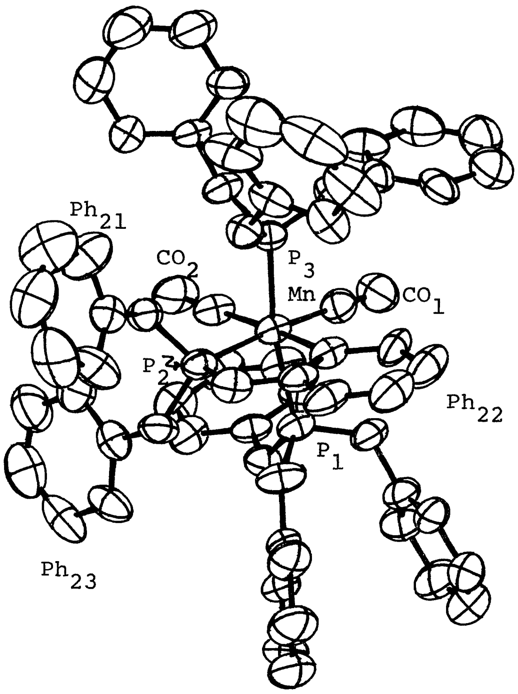

Fig. 1a. An ORTEP view of (PhO)$_2$P(OC$_6$H$_4$)Mn(CO)$_2${P(OPh)$_3$}$_2$. Thermal ellipsoids are at the 50% probability level.

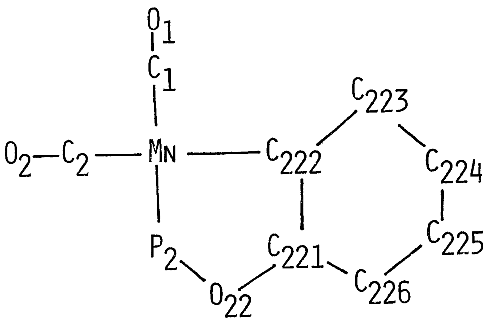

Fig. 1b. A schematic drawing of the least-squares plane together with the atom numbering sequence.

lengths and angles are listed in Table 1.

Orthometalation is now a widely recognized phenomenon for PPh_3 and/or $P(OPh)_3$ metal derivatives.$^{6)}$ Although papers dealing with an orthometalation by thermal cleavage of the C-H bond in an aromatic ring are copious,$^{6)}$ only a few examples of photochemically induced orthometalation have been reported.$^{7)}$ This paper presents another example of an orthometalation by photochemical activation of an aromatic C-H bond. We have further attempted photochemical reactions of $X(CH_3)_2Sn\text{-}Mn(CO)_3L_2$ (X = Cl and Br) hoping to obtain insight into the mechanism of photochemically induced orthometalation for (I) and (II). The primary reaction product was $XMn(CO)_3L_2$. On the basis of this result, photochemical reactions of $CH_3Mn(CO)_3L_2$ (III) which we presumed as an intermediate of the photochemical reaction of (I) were examined in benzene and (X) was produced in better yield than that of (I). The result suggests that the orthometalation reaction of (I) proceeds via (III) or via the same photochemically generated intermediate as that of (III). The detail of the photochemical reaction of (III) will appear in a subsequent paper.

$Mn\text{-}P_1$: 2.193(3)Å $Mn\text{-}P_2$:2.208(3)Å
$Mn\text{-}P_3$: 2.204(3)Å $Mn\text{-}C_1$:1.805(9)Å
$Mn\text{-}C_2$: 1.799(9)Å $C_1\text{-}O_1$:1.140(11)Å
$C_2\text{-}O_2$: 1.155(11)Å $P_2\text{-}O_{22}$:1.597(6)Å
P-O(average): 1.611(15) Å
$O_{22}\text{-}C_{221}$:1.414(10)Å
Ph-O (average): 1.423(11) Å
C-C in Ph_{22}(average):1.413(15)Å

$P_1\text{-}Mn\text{-}P_3$:165.7(1)° $P_1\text{-}Mn\text{-}P_2$:90.5(1)°
$P_2\text{-}Mn\text{-}P_3$:90.6(1)° $P_2\text{-}Mn\text{-}C_{222}$:80.0(2)°
$Mn\text{-}P_2\text{-}O_{22}$:109.5(2)°
$P_2\text{-}O_{22}\text{-}C_{221}$:113.5(5)°
$O_{22}\text{-}C_{221}\text{-}C_{222}$:119.5(7)°
$Mn\text{-}C_{222}\text{-}C_{221}$:117.5(6)°
$Mn\text{-}C_1\text{-}O_1$:175.1(8)° $Mn\text{-}C_2\text{-}O_2$:176.8(8)°
$C_1\text{-}Mn\text{-}C_2$:94.3(3)° $P_2\text{-}Mn\text{-}C_1$:174.0(3)°
$P_2\text{-}Mn\text{-}C_2$:91.3(3)° $C_1\text{-}Mn\text{-}C_{222}$:94.5(4)°
$C_2\text{-}Mn\text{-}C_{222}$:171.0(4)°

Table 1. Selected bond lengths and bond angles

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