ELSEVIER

Inorganica Chimica Acta 224 (1994) 147–149

Inorganica Chimica Acta

Note

Crystal and molecular structures of [{*exo*- and *endo*-$(RO)_2P(O)$-η^5-C_6H_6}$Mn(CO)_3$]

Tae-young Lee[a], Hye-kyung Bae Yu[a], Young Keun Chung[a,*], W.A. Hallows[b], D.A. Sweigart[b]

[a] *Department of Chemistry, College of Natural Sciences, Seoul National University, Seoul 151-742, South Korea*
[b] *Department of Chemistry, Brown University, Providence, RI 02912, USA*

Received by Editor 20 December 1993; received by Publisher 20 May 1994

Abstract

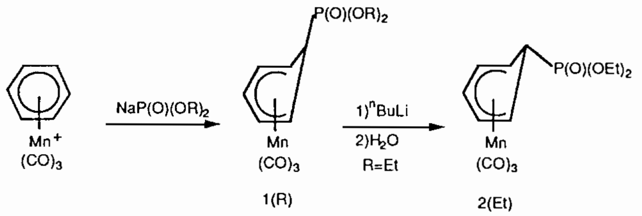
The crystal and molecular structures of [{*exo*-$(EtO)_2P(O)$-η^5-C_6H_6}$Mn(CO)_3$] (**1**) (Et) and [{*endo*-$(MeO)_2P(O)$-η^5-C_6H_6}$Mn(CO)_3$] (**2**) (Me) have been established by an X-ray structural study. Compound **1** (Et) crystallizes in the space group $P2_1/c$ with the unit cell dimensions $a = 12.839(4)$, $b = 13.982(4)$, $c = 15.188(5)$ Å, $\beta = 96.33(2)°$, $V = 2709.78(1.40)$ Å^3 and $D_{calc} = 1.59$ g/cm^3 for $Z = 4$. Refinement converged at $R = 0.0509$, $R_w = 0.0477$, based on 2721 observed reflections with intensities $I > 3\sigma(I)$. Compound **2** (Me) crystallizes in $C2/c$ with the unit cell dimensions $a = 18.466(4)$, $b = 12.377(2)$, $c = 14.267$ Å, $\beta = 92.90(1)°$, $V = 3256.67(1.02)$ Å^3 and $D_{calc} = 1.45$ g/cm^3 for $Z = 8$. Refinement converged at $R = 0.0652$, $R_w = 0.0718$, based on 2580 observed reflections with intensities $I > 3\sigma(I)$.

Keywords: Crystal structures; Manganese complexes; Carbonyl complexes; Phosphate complexes; Cyclohexadienyl complexes; *Exo* and *endo* isomers

---

1. Introduction

Several years ago we reported [1] on the use of phosphate as a nucleophile to the $[(C_6H_6)Mn(CO)_3]^+$ cation. To our knowledge there had been no reports on the use of phosphate as a nucleophile to the π-coordinated ring until we reported. Our previous communication [1] revealed that [{*exo*-$(RO)_2P(O)$-η^5-C_6H_6}$Mn(CO)_3$] (**1**) (R) on treatment with nBuLi and H_2O underwent stereospecific rearrangement to [{*endo*-$(RO)_2P(O)$-η^5-C_6H_6}$Mn(CO)_3$] (**2**) (R) (Scheme 1). In this note we describe the structural characterization of **1** (Et) and **2** (Me).



Scheme 1.

2. Experimental

Compounds $(arene)Mn(CO)_3{}^+$, **1** (Et) and **2** (Me) were synthesized as previously described [1].

Crystals suitable for X-ray diffraction were grown from a hexane solution at room temperature. A summary of the crystallographic results is presented in Table 1. All data were collected by using a Nicolet R3m/E single-crystal diffractometer, controlled by Nicolet software. Data reduction, structure determination and refinement were carried out using the SHELXTL program package. Heavy-atom positions were obtained via automated Patterson analysis and used to phase reflections for the remaining light atoms via the usual combination of structure factor, Fourier synthesis and full-matrix least-squares refinement. All refinements were performed using matrix least-squares on F, with anisotropic thermal parameters for all non-hydrogen atoms, and included idealized hydrogen coordinates as fixed atom

---

*Corresponding author.

SSDI 0020-1693(94)04010-S

Table 1
Crystal data, data collection and refinements of the structures for [{*endo*-$(MeO)_2P(O)$-η^5-C_6H_6}$Mn(CO)_3$] and [{*exo*-$(EtO)_2P(O)$-η^5-C_6H_6}$Mn(CO)_3$]

Formula	$C_{11}H_{12}O_6PMn$	$C_{13}H_{16}O_6PMn$
Space group	$P2_1/c$	C_2/c
a (Å)	12.839(4)	18.466(4)
b (Å)	13.982(4)	12.377(2)
c (Å)	15.188(5)	14.267(2)
β (°)	96.33(2)	92.90(1)
V (Å^3)	2709.78(1.40)	3256.67(1.02)
Z	4	8
D_{calc} (g cm^{-3})	1.59	1.45
μ (cm^{-1})	10.68	8.95
Radiation source, λ (Å)	Mo Kα, 0.71069	Mo Kα, 0.71069
Scan method	θ–2θ	θ–2θ
Range data collection (°)	$3.5° < 2\theta < 45$	$3.5° < 2\theta < 50$
Total no. observations	4068	3256
No. unique data $I > 3\sigma(I)$	2721	2580
No. parameters refined	361	190
GOF	1.811	1.813
$R = (\Sigma F_o - F_c)/\Sigma F_o$	0.0509	0.0652
$R_w = ((\Sigma F_o - F_c)^2/(\Sigma F_o^2))^{1/2}$	0.0477	0.0718

Table 2
Selected bond lengths (Å) and angles (°) for **1** (Et) and **2** (Me)

1 (Et)			
C(1)–O(1)	1.137(8)	C(1)–Mn	1.798(7)
C(5)–Mn	2.216(6)	C(6)–Mn	2.131(6)
C(7)–Mn	2.132(6)	C(4)–C(5)	1.510(7)
C(5)–C(6)	1.368(6)	C(6)–C(7)	1.426(7)
C(4)–P	1.815(5)	P–O(5)	1.456(5)
Mn–C(1)–O(1)	177.9(5)	C(5)–C(4)–C(9)	103.4(3)
C(4)–P–O(5)	114.3(2)	C(5)–C(6)–C(7)	120.6(4)
2 (Me)			
C(9)–O(4)	1.144(7)	C(9)–Mn(1)	1.794(6)
C(3)–Mn(1)	2.134(5)	C(4)–Mn(1)	2.128(5)
C(1)–C(2)	1.501(7)	C(2)–C(3)	1.407(7)
C(3)–C(4)	1.410(7)	C(1)–P(1)	1.803(5)
P(1)–O(1)	1.452(4)	P(1)–O(2)	1.557(4)
Mn(1)–C(9)–O(4)	175.4(5)	C(2)–C(1)–C(6)	103.6(4)
C(1)–P(1)–O(1)	113.0(2)	C(2)–C(3)–C(4)	119.3(5)

contributors. Selected bond lengths and angles for **1** (Et) and **2** (Me) are given in Table 2.

3. Results and discussion

Compound **1** (Et) was prepared by the reaction of $(C_6H_6)Mn(CO)_3{}^+$ with $NaP(O)(OEt)_2$ (generated in situ) in THF at room temperature. Crystals of **1** (Et) suitable for X-ray analysis were grown in a hexane solution of **1** (Et) at room temperature. Compound **2** (Me) was prepared by the reaction of **1** (Me) with nBuLi, and followed by quenching with H_2O. Single crystals of **2** (Me) for X-ray analysis were grown in a hexane solution of **2** (Me) at room temperature.

The geometry of **1** (Et) showing the atomic numbering scheme used is depicted in Fig. 1. The X-ray structure of **1** (Et) confirms that the $P(O)(OEt)_2$ is positioned *exo* as expected. The coordination sphere around the manganese atom in **1** (Et) is essentially that of a piano stool, as in $CpMn(CO)_3$ [2]. The dienyl carbon atoms, C(5), C(6), C(7), C(8) and C(9) define a plane (maximum deviation 0.014 Å). The cyclohexadienyl ring is folded about C(5)–C(9) with a dihedral angle of 38.0°, which is larger than 36.5° in $[\eta^5\text{-}PhC_6H_6]Mn(CO)_3$ [3]. The metal–carbon distances in the cyclohexadienyl ring show a pattern in which the metal atom is significantly closer to the delocalized carbon set (C(6), C(7) and C(8)) than to the two terminal carbon atoms, C(5) and C(9) [4]. This slipping of the Mn atom may be interpreted as maximization of the interaction of the Mn with π-electron density of the delocalized ring system. Similar slipping distortion from regular η^5-coordination has been seen in cyclopentadienyl- and indenyl–metal complexes [5]. The manganese atom is located 1.678 Å below the plane of the dienyl ring. The bond distances of P=O and P–O (1.456 and av. 1.570 Å, respectively) of **1** (Et) are similar to those (1.449 and 1.558 Å, respectively) of organic compounds [6], but are shorter than those (av. 1.486 and av. 1.608 Å, respectively) of $CpFe(CO)_2P(O)(OEt)_2$ [7]. The longer bond distances in $CpFe(CO)_2P(O)(OEt)_2$ would be ascribed to the π-interaction between Fe and phosphorus atoms. The electron in the P=O bond flows into the iron d orbital through presumably a phosphorus d orbital. However, there are no π-interactions between C(sp^3) and phosphorus atoms in **1** (Et).

As for **2** (Me), there are two crystallographically independent molecules in the asymmetric unit and two asymmetric units per cell ($Z = 4$). An ORTEP drawing of the two molecules with atom labels is shown in Fig. 2. The structures of the two crystallographically independent molecules (molecules 1 and 2) are basically identical. The only difference is the orientation of the

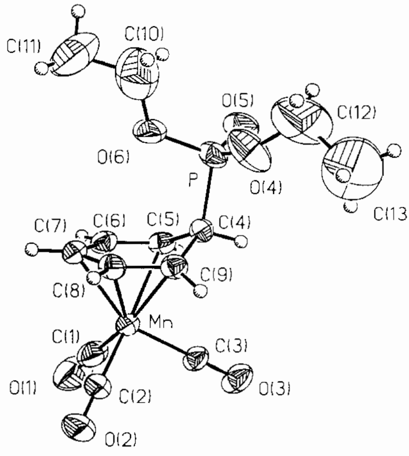


Fig. 1. ORTEP drawing of **1** (Et) with the atom labeling scheme.

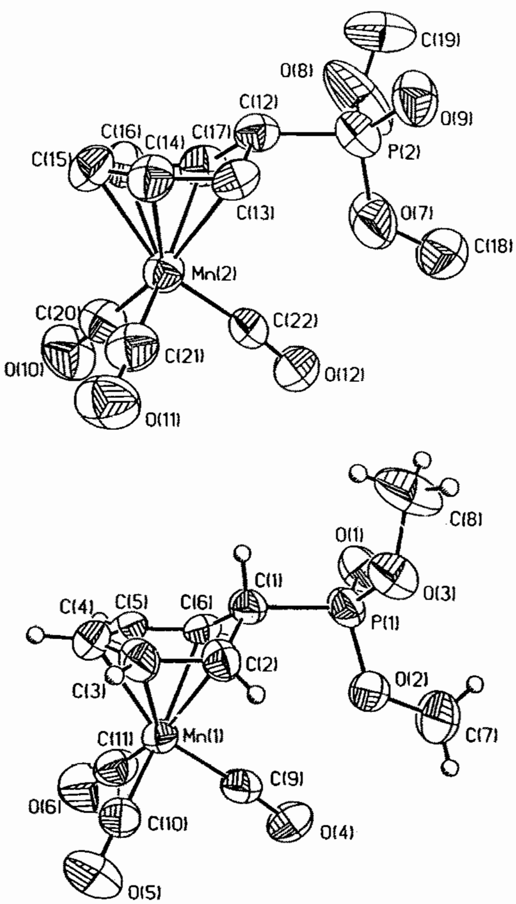


Fig. 2. ORTEP drawing of the two crystallographically independent molecules in the asymmetric unit of **2** (Me) showing the atom labeling scheme.

P=O group. The molecules are well separated by normal van der Waals distances in the crystal. The coordination sphere around the manganese atom in **2** (Me) is essentially that of a piano stool, as in $CpMn(CO)_3$ [2]. The dienyl carbon atoms define planes (maximum deviation 0.028 Å). The dihedral angles between the dienyl ring and the plane containing the sp^3 carbon takes on a value of av. 46.0°. The dihedral angle is larger than the values of 43° in $C_6H_7Mn(CO)_3$ [8], 39° in dicarbonyl-3-[π-(2-cyclohexadienyl)]-σ-propenoyliron [9], 41° in tricarbonyl {bis(ethoxycarbonyl)-methyl}cyclohexadienylmanganese [10], and are similar to the value of approximately 45° in structures of three substituted 1,2-dihydropyridinechromium tricarbonyl complexes [11], but are smaller than the value of 50° in $C_6Me_6HRe(CO)_3$ [12].

The metal–carbon distances in the cyclohexadienyl ring show the pattern as in **1** (Et). The manganese atom is located av. 1.690 Å below the plane of the dienyl ring. The bond distances of P=O and P–O (av. 1.450 and av. 1.540 Å, respectively) of **2** (Me) are similar to P=O and P–O (1.456 and av. 1.570 Å, respectively) of **1** (Et), but are shorter than those (av. 1.486 and av. 1.608 Å, respectively) of $CpFe(CO)_2P(O)(OEt)_2$ [6].

4. Supplementary material

Atomic coordinates and temperature factors, complete bond distances and angles, final fractional coordinates, and anisotropic thermal factors, hydrogen coordinates, and torsion angles for **1** (Et) and **2** (Me) are available from the authors upon request.

Acknowledgements

This work was financially supported by the Ministry of Education of Korea through the Basic Science Research Institute Program. H.K.B.Y. is grateful to the BSRI (93-313) for a fellowship.

References

[1] H.K. Bae, I.N. Jung and Y.K. Chung, *J. Organomet. Chem., 317* (1986) C1; Y.K. Chung, H.K. Bae and I.N. Jung, *Bull. Korean Chem. Soc., 9* (1988) 349.
[2] A.F. Berndt and R.E. Marsh, *Acta Crystallogr., 16* (1963) 118.
[3] S.D. Ittel, J.F. Whitney, Y.K. Chung, P.G. Williard and D.A. Sweigart, *Organometallics, 7* (1988) 1323.
[4] Y.-A. Lee, Y.K. Chung, Y. Kim, J.H. Jeong, G. Chung and D. Lee, *Organometallics, 10* (1991) 3707.
[5] D.E. Smith and A.J. Welch, *Organometallics, 5* (1986) 760; M. Mlekuz, P. Bougeard, B.G. Sayer, M.J. McGlinchey, C.A. Rodger, M.R. Churchill, J.W. Ziller, S.-K. Kang and T.A. Albright, *Organometallics, 5* (1986) 1656; N.E. Bunel, L. Valle, N.L. Jones, P.J. Carroll, C. Barra, M. Gonalez, N. Munoz, G. Visconti, A. Aizman and M. Manriquez, *J. Am. Chem. Soc., 110* (1988) 6596.
[6] F.H. Allen, O. Kennard, D.G. Watson, L. Brammer and A.G. Orpen, *J. Chem. Soc., Perkin Trans. II,* (1987) S1.
[7] H. Nakazawa, K. Morimasa, Y. Kushi and H. Yoneda, *Organometallics, 7* (1988) 458.
[8] M.R. Churchill and S. Scholer, *Inorg. Chem., 8* (1969) 1950.
[9] P.J. Van Vuuren, R.J. Fletterick, J. Meinwald and R.E. Hughes, *J. Chem. Soc., Chem. Commun.,* (1970) 883; *J. Am. Chem. Soc., 93* (1971) 4394.
[10] A. Mawby, P.J.C. Walker and R.J. Mawby, *J. Organomet. Chem., 55* (1973) C39.
[11] G. Hutter and O.S. Mills, *Chem. Ber., 105* (1972) 3924; C.A. Bear, W.R. Cullen, J.P. Kutney, V.E. Ridaura, J. Trotter and A. Zanarotti, *J. Am. Chem. Soc., 95* (1973) 3058.
[12] P.H. Bird and M.R. Churchill, *J. Chem. Soc., Chem. Commun.,* (1967) 777.