Journal of Organometallic Chemistry, 262 (1984) C43—C45
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

AN UNSYMMETRICAL HYDROGEN BRIDGE IN *cis*-TETRACARBONYLHYDROGENBIS(DIPHENYLPHOSPHINITO-*P*)MANGANESE(I) $(CO)_4Mn[(P(C_6H_5)_2O)_2H]$

R. FAWZI, W. HILLER, I.-P. LORENZ*, J. MOHYLA and C. ZEIHER

Institute for Inorganic Chemistry of the University, Auf der Morgenstelle 18, D-7400 Tübingen (F.R.G.)

(Received October 31st, 1983)

Summary

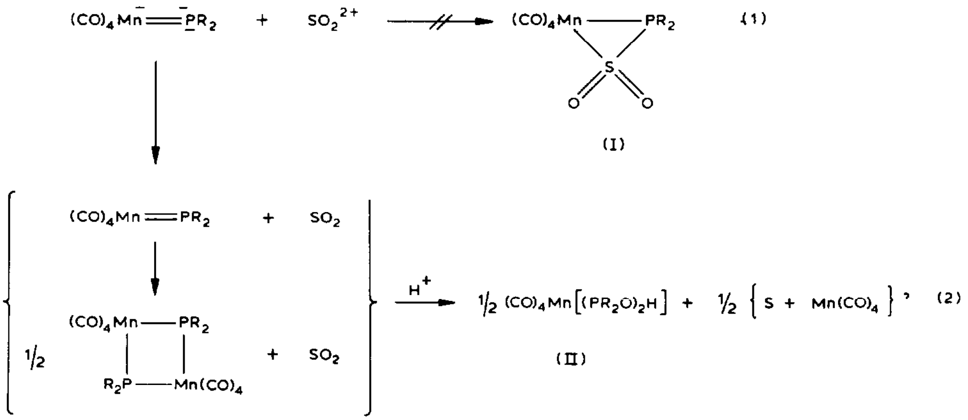
$Na_2[(CO)_4MnP(C_6H_5)_2]$ reacts with SO_2Cl_2 in ether to form the neutral complex $(CO)_4Mn[(P(C_6H_5)_2O)_2H]$, which crystallizes in the orthorhombic space group $P2_12_12_1$ with $Z = 4$ and contains a nearly planar six membered ring Mn—P(1)—O(5)—H—O(6)—P(2) with an unsymmetrical hydrogen bridge. The complex reacts with $N(C_2H_5)_3$ to give the corresponding salt.

Sulfonamides are well-known and important substances. Their phosphorus analogues, however, are unknown because of the extreme instability of the atomic combination $R'_2P—S(O)_2R$. In attempts to find suitable methods of preparation for these compounds we have treated metal-coordinated phosphanes with the corresponding sulfonyl derivatives [1], e.g. the bifunctional dianion $[(CO)_4MnP(C_6H_5)_2]^{2-}$ with SO_2Cl_2 in ether.

In the light of the report of the reaction of $[(CO)_4MnP(C_6H_5)_2]^{2-}$ with geminal dichlorides to give phosphamanganacyclopropanes [2] we expected the formation of the mono- or di-meric complex $[(CO)_4MnP(C_6H_5)_2S(O)_2]_n$ (n = 1, 2) (I) with the intact sulfonyl and phosphido function (eq. 1). Instead, the orange tetracarbonylhydrogenbis(diphenylphosphinito-*P*)manganese(I) (II), was isolated from the mixture of products in the filtrate*. In addition to simple substitution, complicated redox reactions must also take place as represented in eq. 2. Analogues of these postulated intermediates are known [3], and the hydrogen atom can be derived from the solvent:

**Editorial note.* We are advised that the IUPAC nomenclature for II would be *cis*-tetracarbonyl-(hydrogendiphenylphosphinito-*P*)(diphenylphosphinito-*P*)manganese(I), but the author wishes to emphasize the presence of the intramolecular hydrogen bond.

0022-328X/84/$03.00



Compound II is air-stable, but sensitive to moisture and can be transformed by triethylamine to the salt $[N(C_2H_5)_3H][(CO)_4Mn(PR_2O)_2]$. Thus by analogy with similar tetracoordinated VIIIA-metal complexes [4] we can expect replacement of the proton in II by Lewis acids or transition metal ions.

An X-ray structure determination [5] of the neutral complex II shows that four carbonyl and two phosphinite ligands are bound in *cis*-position to the octahedral coordinated manganese atom (Fig. 1). The two phosphorus—oxygen double bonds are elongated with 155 pm. The two oxygen atoms are linked together by an unsymmetrical hydrogen bridge, which was unexpected in view of the very short O—O distance of 241 pm in this highly symmetrical molecule [6]*. The maximum deviation from the least squares plane in the nearly planar six-membered ring Mn—P(1)—O(5)—H—O(6)—P(2) is 12 pm (*P*2). This and the unsymmetrical hydrogen bridge differentiates II from the noble metal complexes with the same ligand [4].

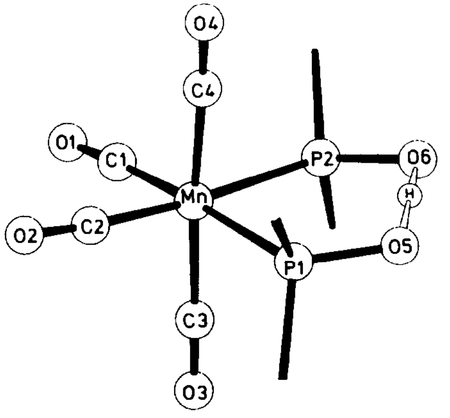


Fig. 1. The molecular structure of $(CO)_4Mn[(P(C_6H_5)_2O)_2H]$ (II). The phenyl groups have been omitted for clarity. Distances in pm: Mn—C(1) 181.9(5), Mn—C(2) 183.0(5), Mn—C(3) 186.3(5), Mn—C(4) 184.9(5), Mn—P(1) 235.5(1), Mn—P(2) 234.2(1), P(1)—O(5) 155.1(3), P(2)—O(6) 155.1(3), O(5)—H 135(6), O(6)—H 106(6). Bond angles: P(1)—Mn—P(2) 92.08(5), Mn—P—O 114.6(1), O(5)—H—O(6) 177(5)°.

---

*The hydrogen atom in the bridge was located by means of a difference Fourier map, and was included in the final least squares refinement. No other alternative minimum in the vicinity of O(5) appeared in the final difference Fourier map.

The IR spectra are characterized by 4 ν(CO) absorptions at 2076m, 2005vs, 2001sh and 1971 s cm^{-1} (in CCl_4, C_{2v}-pseudosymmetry: A_1+B_1+A_1+B_2), the P=O valence mode at 1026 cm^{-1} (in KBr) is in agreement with the expected value; because of the hydrogen bridge no ν(OH) bands are observed above 2000 cm^{-1}. We could not detect a signal for the acidic hydrogen in the ^{1}H NMR spectrum, but in the ^{31}P NMR spectrum a singlet appears at δ 137.6 ppm (in $CHCl_3$), indicating that a symmetrical hydrogen bridge is present in the liquid state.

A variety of transition metal complexes containing this six-membered ring have been hitherto obtained, either by addition of phosphinites to suitable metal complexes, or by solvolysis of coordinated P—X bonds (X = halogen, alkoxy etc.) [4, 7]. In our case, for the first time, the ring system has been built up by oxidation of phosphido ligands. Furthermore, compound II may be useful for model investigations of hydrogen bridge bonding because of its symmetrical arrangement and the absence of intermolecular O—H—O bonds*.

Acknowledgement. We are grateful to the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support.

References

1 I.-P. Lorenz, J.K. Thekumparampil and C. Zeiher, Inorg. Chim. Acta B, 79 (1983) 197.
2 E. Lindner, K.A. Starz, H.-J. Eberle and W. Hiller, Chem. Ber., 116 (1983) 1209.
3 cf. M. Luksza, S. Himmel, W. Malisch, Angew. Chem. Int. Ed., 22 (1983) 416; B. Klingert and H. Werner, J. Organomet. Chem., 252 (1983) C47.
4 D.M. Roundhill, R.P. Sperline and W.B. Beaulieu, Coord. Chem. Rev., 26 (1978) 263, cit. lit.
5 Crystal data of $(CO)_4Mn[(P(C_6H_5)_2O)_2H]$ (II): a 976, b 1372, c 1946 pm, orthorhombic in $P2_12_12_1$, $Z = 4$, $R = 0.035$ (3331 reflections with $I > 3\sigma(I)$).
6 M. Ichikawa, Acta Crystallogr., B, 34 (1978) 2074.
7 U. Schubert, R. Werner, L. Zinner and H. Werner, J. Organomet. Chem., 253 (1983) 363.

---

*Tables of atomic positional parameters, bond lengths and angles for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain). Any request should be accompanied by a full literature citation for this communication.