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# Note

# A molybdenum(0) complex of bis(hydroxymethyl)phenylphosphine

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#### Abstract

The thermal reaction of hexacarbonyl molybdenum with bis(hydroxymethyl)phenylphosphine afforded the 1:1 complex  $Mo(CO)_5[PPh(CH_2OH)_2]$ . Its solution spectral behavior and solid-state structure have been determined. © 1999 Elsevier Science S.A. All rights reserved.

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# 1. Introduction

Hydroxymethylphosphines are useful precursors for a variety of important phosphorus-containing compounds including aminomethylphosphines, phosphorus heterocycles and polycycles [1]. The hydrophilic hydroxyl group can also endow the ligand and its metal complexes with enhanced water solubility in biphasic catalysis as well as radiopharmaceutical applications [2,3]. We report here on the synthesis, spectral and structural characterization of a pentacarbonyl molybdenum complex of the bis(hydroxymethyl)phenylphosphine ligand.

## 2. Experimental

The bis(hydroxymethyl)phenylphosphine ligand was prepared according to a literature method [4]. Synthetic work was performed under a nitrogen atmosphere using standard Schlenk techniques. Solvents were reagent grade and dried and distilled under nitrogen immediately before use. Elemental analyses were performed on a Perkin-Elmer 2400 elemental analyzer. Proton, <sup>13</sup>C, and <sup>31</sup>P NMR spectra were recorded on a JEOL-FX-90Q spectrometer and a Bruker AM 360 spectrometer. IR spectra were obtained as KBr pellets using a Nicolet MX-1 FT-spectrophotometer.

To a flask containing 6.48 g (381 mmol) of ligand and 10.1 g (381 mmol) of Mo(CO)<sub>6</sub> was added 45 ml of toluene. After 12 h of refluxing, the reaction mixture turned yellow. Evaporation of volatiles left a tan solid. Two portions of 50 ml of hot hexane were used to extract the residue. The extracts were combined and filtered hot through celite. Upon slow cooling, the filtrate yielded 8.97 g (221 mmol, 58%) of white crystalline complex after filtration and drying. X-ray quality crystals were obtained by recrystallization from hexane. IR (cm<sup>-1</sup>, CO) 2074, 1957, 1922. <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ ) 7.42–7.64 (m, Ph), 4.48–4.63 (ABMX,  $CH_2$ ,  ${}^2J_{HH} = 12.2$ ,  ${}^2J_{PH} = 5.2$ , and  ${}^3J_{HH} = 5.5$  Hz), and 2.86 (OH, t of t,  ${}^{3}J_{HH} = {}^{3}J_{PH} = 5.5$  Hz).  ${}^{13}C$  NMR  $(\text{CDCl}_3, \delta)$  CO: 208.8 (d,  ${}^2J_{\text{PC}} = 21.8$  Hz), 204.9 (d,  ${}^{2}J_{PC} = 8.7$  Hz); aromatics: 130.8 (d,  $J_{PC} = 9.7$  Hz), 130.4 (d,  $J_{PC} = 1.9$  Hz), 130.3 (d,  $J_{PC} = 35.0$  Hz), and 129.3 (d,  $J_{PC} = 9.0$  Hz); CH<sub>2</sub>: 64.2 (d,  $J_{PC} = 20.2$  Hz). <sup>31</sup>P NMR (CDCl<sub>3</sub>,  $\delta$ ) 27.9 (s). Anal. Calc. for C<sub>13</sub>H<sub>11</sub>MoO<sub>7</sub>P: C, 38.45; H, 2.73. Found: C, 38.61; H, 2.70%.

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Crystal data collection, and refinement parameters are given in Table 1. The structure was solved by direct methods, completed by subsequent Fourier syntheses and refined by full-matrix least-squares procedures. All non-hydrogen atoms were refined anisotropically and hydrogens were calculated and treated as idealized contributions. All software and sources of scattering factors are from the SHELXTL (5.3) library (G. Sheldrick, Siemens XRD, Madison, WI).

#### 3. Results and discussion

In refluxing toluene, hexacarbonylmolybdenum and bis(hydroxymethyl)phenylphosphine afforded a white microcrystalline product in moderate yield. Elemental analyses and IR spectroscopy suggested the formation of Mo(CO)<sub>5</sub>[PPh(CH<sub>2</sub>OH)<sub>2</sub>]. In CDCl<sub>3</sub>, the NMR spectral data were also consistent with this formulation of the product. Its <sup>31</sup>P{<sup>1</sup>H} spectrum contained a single resonance at  $\delta$  27.9. Its <sup>1</sup>H spectrum in CDCl<sub>3</sub> featured the AB portion of an ABMX pattern for the methylene protons (M = hydroxyl proton, X = phosphorus) and a triplet of triplet pattern for the hydroxyl protons. Its <sup>13</sup>C spectrum revealed an axial CO at  $\delta$  + 208.8 (<sup>2</sup>J<sub>PC</sub> = 8.7 Hz).

An X-ray structural determination of a single-crystal, grown from hexane, confirmed the overall structure of this pentacarbonyl phosphine complex and also revealed the presence of both intra- and intermolecular hydrogen-bonding. Two independent molecules were located

Table 1 Crystallographic data

Crystal parameters	
Formula	C <sub>13</sub> H <sub>11</sub> MoO <sub>7</sub> P
Formula weight	406.13
Crystal system	triclinic
Space group	PĪ
a (Å)	10.283(2)
b (Å)	12.240(2)
c (Å)	13.316(3)
α (°)	96.03(3)
β (°)	94.90(3)
γ (°)	91.55(3)
$D_{\text{calc}}$ (g cm <sup>-3</sup> )	1.625
Temperature (K)	293
$\mu$ (Mo K $\alpha$ ) (cm <sup>-1</sup> )	9.14
Data collection	
Diffractometer	Siemens P4
Monochromator graphite	
Radiation	Mo K $\alpha$ ( $\lambda = 0.71073$ Å)
$2\theta$ Scan (°)	4.0-50.0
Independent reflections	5064
Independent observed reflections	3983
Refinement	
R(F) (%)	5.26
$R(wF^2)$ (%)	9.03
GOF	1.2



Fig. 1. Structure of one molecule of  $Mo(CO)_5[PPh(CH_2OH)_2]$  in the asymmetric unit.

in the asymmetric unit, with one of these shown in Fig. 1. The coordination geometry around both molybdenum centers approximates an octahedron with normal Mo–P bond lengths of 2.483(2) and 2.498(2) Å, respectively. Average equatorial Mo–C bonds (2.03(1) Å) are only marginally longer than the axial bonds (2.014(8) and 2.010(8) Å, respectively) in both molecules. *Cis*bond angles around the metal deviate by no more than 2.7° from orthogonality. Selected bond distances and angles are listed in Table 2.

A bifurcated hydrogen bond centered at O(7) links the two independent molecules with O(7) $\cdots$ O(7') at 2.752(7) Å while the intramolecular O(6) $\cdots$ O(7) is also at 2.718(7) Å and the O(6) $\cdots$ O(7) $\cdots$ O(7') angle is 91.3° (Fig. 2).

Table 2 Selected bond distances (Å) and angles (°)

Bond distances (Å)			
Mo(1)–C(1)	2.014(8)	Mo(1)–C(2)	2.010(9)
Mo(1)–C(3)	2.037(9)	Mo(1)–C(5)	2.041(9)
Mo(1)–C(4)	2.045(9)	Mo(1) - P(1)	2.483(2)
Mo(1')–C(1')	2.010(8)	Mo(1')–C(2')	2.031(9)
Mo(1')-C(5')	2.037(9)	Mo(1')–C(3')	2.029(10)
Mo(1')-C(4')	2.039(9)	Mo(1')-P(1')	2.498(2)
Bond angles (°)			
C(1)–Mo(1)–C(2)	89.0(3)	C(1)-Mo(1)-C(3)	92.2(3)
C(2)–Mo(1)–C(3)	88.6(3)	C(1)-Mo(1)-C(5)	90.9(3)
C(2)–Mo(1)–C(5)	93.0(3)	C(3)-Mo(1)-C(5)	176.5(3)
C(1)–Mo(1)–C(4)	90.0(3)	C(2)-Mo(1)-C(4)	177.2(3)
C(3)-Mo(1)-C(4)	88.8(3)	C(5)-Mo(1)-C(4)	89.7(3)
C(1)–Mo(1)–P(1)	179.0(2)	C(2)–Mo(1)–P(1)	90.7(2)
C(3)–Mo(1)–P(1)	88.6(2)	C(5)-Mo(1)-P(1)	88.2(2)
C(4)–Mo(1)–P(1)	90.4(2)	C(1')-Mo(1')-C(2')	88.0(3)
C(1')-Mo(1')-C(5')	90.0(3)	C(2')-Mo(1')-C(5')	91.6(3)
C(1')-Mo(1')-C(3')	91.5(3)	C(2')-Mo(1')-C(3')	88.2(3)
C(5')–Mo(1')–C(3')	178.4(3)	C(1')-Mo(1')-C4)	88.7(3)
C(2')-Mo(1')-C(4')	176.1(3)	C(5')-Mo(1')-C(4')	90.5(3)
C(3')–Mo(1')–C(4')	89.8(3)	C(1')–Mo(1')–P(1')	177.9(2)
C(2')–Mo(1')–P(1')	92.7(2)	C(5')-Mo(1')-P(1')	88.0(2)
C(3')-Mo(1')-P(1')	90.5(2)	C(4')-Mo(1')-P(1')	90.6(2)



Fig. 2. Intermolecular H-bonding linking the two molecules of  $Mo(CO)_5$ [PPh(CH<sub>2</sub>OH)<sub>2</sub>].

#### 4. Supplementary material

Tables of X-ray experimental details and crystallographic data, full atomic coordinates, anisotropic thermal parameters, and bond distances and angles have been deposited with the Cambridge Crystallographic Data Centre as CCDC No. 110872. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

## References

- (a) H. Coates, P.A.T. Hoye, Br. Patent 842 (1960) 593. (b) G. Markl, G.Y. Jin, C. Schoerner, Tetrahedron Lett. 21 (1980) 1409.
  (c) K.J. Coskran, J. G. Verkade, Inorg. Chem. 4 (1965) 1655. (d) J. Fawcett, P.A.T. Hoye, R.D.W. Kemmitt, D.J. Law, D.R. Russell, J. Chem. Soc., Dalton Trans. (1993) 2563.
- [2] See, for examples: (a) W.A. Herrmann, C.W. Kohlpaintner, Angew. Chem., Int. Ed. Engl. 32 (1993) 1524. (b) B. Cornils, W. Wiebus, Recl. Trav. Chim. Pays-Bas 115 (1996) 211. (c) B. Cornils, E. Wiebus, Chem. Tech. 25 (1995) 33.
- [3] J.S. Lewis, J. Zweit, J.L.J. Dearling, B.C. Rooney, P.J. Blower, J. Chem. Soc., Chem. Commun. (1996) 1093.
- [4] J.B. Rampal, G.D. MacDonnell, J.P. Edasery, K.D. Berlin, A. Rahman, D. van der Helm, K.M. Pietrusiewicz, J. Org. Chem. 46 (1981) 1156.