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Ghosh, Shishir; Kabir, Shariff E.; Camellia, Faranza K.; Hossain, Md. Kamal; Haworth, Daniel T.; Lindeman, Sergey V.; Siddiquee, Tasneem A.; and Bennett, Dennis W., "X-ray Structure of *mer*-[Mo(CO)<sub>3</sub>(PPh<sub>3</sub>)(κ<sup>2</sup>-dppm)]" (2010). *Chemistry Faculty Research and Publications*. 549.  
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## X-ray Structure of *mer*-[Mo(CO)<sub>3</sub>(PPh<sub>3</sub>)(κ<sup>2</sup>-dppm)]

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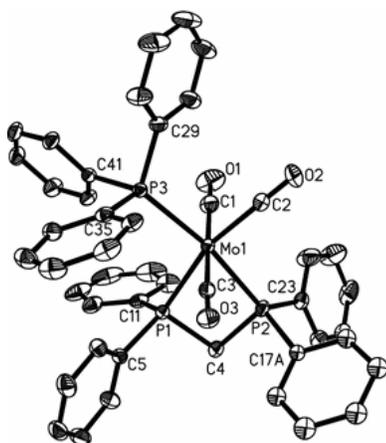
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### Abstract

Treatment of  $[\text{Mo}(\text{CO})_3(\text{NCMe})_3]$  with bis(diphenylphosphino)methane (dppm) and triphenylphosphine ( $\text{PPh}_3$ ) at  $50^\circ\text{C}$  afforded *mer*- $[\text{Mo}(\text{CO})_3(\text{PPh}_3)(\kappa^2\text{-dppm})]$  (**1**) in 55% yield which has been characterized by single crystal X-ray diffraction studies and spectroscopic measurements. Compound **1** crystallizes in the triclinic space group  $P\bar{1}$  with  $a = 10.3449(6)$ ,  $b = 11.1570(6)$ ,  $c = 17.8961(10)$  Å,  $\beta = 80.8400(10)^\circ$ ,  $Z = 2$  and  $V = 1959.8(2)$  Å<sup>3</sup>.

### Graphical Abstract

Synthesis and molecular structure of *mer*- $[\text{Mo}(\text{CO})_3(\text{PPh}_3)(\kappa^2\text{-dppm})]$  are described



### Introduction

Tertiary phosphine ligands have been playing an important role in modern organometallic chemistry [1]. These ligands are readily synthesized, and by varying the substituents on phosphorus and/or the backbone length, the electronic and steric properties of the ligands can be varied in a systematic way [2]. These ligands bind strongly to many transition metals in low oxidation states, and are commonly used to stabilize organometallic and hydride derivatives of the elements, either in isolated compounds or as intermediates in homogeneous catalysis. The number of known transition metal complexes bearing multidentate phosphines is truly immense, and many of these complexes are used in homogeneous catalysis [3–6]. Tertiary phosphine ligands in homogeneous catalysts are often modified in order to change the activity or selectivity of the catalysts.

The group 6 metals generally form six-coordinated metal complexes with a wide range of ligands including tertiary phosphines. Several synthetic routes are available for the synthesis of group 6 metal carbonyl complexes bearing tertiary phosphine ligands. For example, mono- and di-substituted metal carbonyl complexes are generally prepared by substitution reactions via a photolytic, thermolytic or chemically induced route [7]. Atwood et al. [8] synthesized a series of chromium complexes with the general formula *trans*- $[\text{Cr}(\text{CO})_4(\text{PPh}_3)\text{L}]$  ( $\text{L} = \text{PBU}_3$ ,  $\text{P}(\text{OMe})_3$ ,  $\text{P}(\text{OPPh})_3$ ) from the room temperature reaction between  $\text{Et}_4\text{N}[\text{LCr}(\text{CO})_4\text{Cl}]$  ( $\text{L} = \text{PBU}_3$ ,  $\text{P}(\text{OMe})_3$ ,  $\text{P}(\text{OPPh})_3$ ) and  $\text{PPh}_3$ , while Cotton et al. [9] has reported the preparation of *cis*- $[\text{Mo}(\text{CO})_4(\text{PR}_3)_2]$  ( $\text{R} = \text{Me}$ ,  $\text{Et}$ , *n*-Bu) from the reaction between *cis*-

[Mo(CO)<sub>4</sub>(NHC<sub>5</sub>H<sub>10</sub>)<sub>2</sub>] and excess PR<sub>3</sub> (R = Me, Et, *n*-Bu) in refluxing CH<sub>2</sub>Cl<sub>2</sub>. Hor and coworkers [10–12] have also synthesized a series of [M(CO)<sub>5</sub>L] and [M(CO)<sub>4</sub>L<sub>*n*</sub>] (M = Cr, Mo, W; L = monophosphine, *n* = 2; L = diphosphine, *n* = 1) complexes by treatment of the labile complexes [M(CO)<sub>5</sub>(NCMe)] and [M(CO)<sub>4</sub>(NCMe)<sub>2</sub>] with mono- and diphosphines.

In this work we report the synthesis and the molecular structure of a mixed-phosphine complex of molybdenum synthesized by a rather unusual pathway, i.e. the reaction between [Mo(CO)<sub>3</sub>(NCMe)<sub>3</sub>], PPh<sub>3</sub> and dppm and, in addition, the study of the competitive reactivity of the phosphines.

## Experimental

All manipulations were carried out under a dry oxygen-free nitrogen atmosphere using standard Schlenk techniques unless otherwise noted. Reagent grade solvents were freshly distilled from appropriate drying agents prior to use. Infrared spectra were recorded on a Shimadzu FTIR 8101 spectrophotometer. NMR spectra were recorded on a Bruker DPX 400 instrument. Elemental analysis was performed by BCSIR Laboratories, Dhaka. Mo(CO)<sub>6</sub> was purchased from Strem Chemicals Inc. and used without further purification. Bis(diphenylphosphino)methane and triphenylphosphine were purchased from Sigma-Aldrich Chemical Company and used as received. [Mo(CO)<sub>3</sub>(NCMe)<sub>3</sub>] was prepared according to literature procedure [13]. Preparative thin layer chromatography was carried out on 1 mm plates prepared from silica gel GF254 (type 60, E. Merck) at Jahangirnagar University.

## Reaction of [Mo(CO)<sub>3</sub>(NCMe)<sub>3</sub>] with bis(diphenylphosphino)methane (dppm) and triphenylphosphine

A THF solution (20 mL) of dppm (115 mg, 0.299 mmol) and PPh<sub>3</sub> (79 mg, 0.302 mmol) was added to the solid [Mo(CO)<sub>3</sub>(NCMe)<sub>3</sub>] (90 mg, 0.297 mmol) prepared and stored in a Schlenk tube. The solution was allowed to stir at 50 °C for 5 h during which time the color of the reaction mixture changed from yellow to orange. The solvent was removed under reduced pressure and the residue was chromatographed by TLC on silica gel. Elution with hexane/acetone (4:1, v/v) developed three bands. The faster-moving band afforded *mer*-[Mo(CO)<sub>3</sub>(PPh<sub>3</sub>)(κ<sup>2</sup>-dppm)] (**1**) (136 mg, 55%) as orange crystals after recrystallization from hexane/CH<sub>2</sub>Cl<sub>2</sub> at –4 °C while the content of the other bands were too small for characterization. Spectral data for **1**: Anal. Calcd. for C<sub>46</sub>H<sub>37</sub>MoO<sub>3</sub>P<sub>3</sub>: C, 66.84; H, 4.51. Found: C, 66.98; H, 4.56%. IR (ν<sub>CO</sub>, CH<sub>2</sub>Cl<sub>2</sub>): 1967 w, 1869 vs, 1844 m cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.63 (m, 4H), 7.41 (m, 6H), 7.33 (m, 8H), 7.23–7.11 (m, 17H), 4.59 (t, *J* = 8.8 Hz, 2H); <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 56.2 (d, *J* = 72.2 Hz, 1P), 21.2 (d, *J* = 72.2 Hz, 1P), 1.7 (s, 1P); FAB mass spectrum: *m/z* 828 (M<sup>+</sup>), 800 (M<sup>+</sup> – CO), 772 (M<sup>+</sup> – 2CO), 744 (M<sup>+</sup> – 3CO).

## X-ray Crystallography

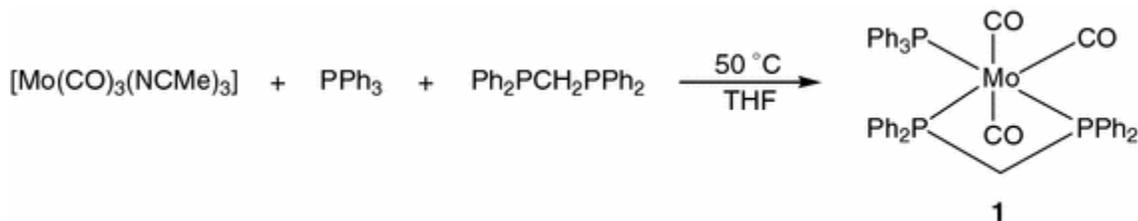
Single crystal of **1** was mounted on fiber and diffraction data were collected at low temperature (see Table 1) on Bruker AXS SMART APEX CCD diffractometers using Mo K<sub>α</sub> radiation (λ = 0.71073 Å). Data collection, indexing and initial cell refinements were all done using SMART [14] software. Data reduction was accomplished with SAINT [15] software and the SADABS program [16] was used to apply empirical absorption corrections. The structure was solved by direct methods [17] and refined by full matrix least-squares [18]. All non-hydrogen atoms were refined anisotropically and hydrogen atoms

were included using a riding model. Scattering factors were taken from International Tables for X-ray Crystallography [19]. Additional details of data collection and structure refinement are given in Table 1.

## Results and Discussion

The reaction of the labile complex  $[\text{Mo}(\text{CO})_3(\text{NCMe})_3]$  with dppm and  $\text{PPh}_3$  at  $50^\circ\text{C}$  in THF, followed by usual workup and chromatographic separation as mentioned in the “Experimental” section, resulted in the isolation of *mer*- $[\text{Mo}(\text{CO})_3(\text{PPh}_3)(\kappa^2\text{-dppm})]$  (**1**) in 55% yield (Scheme 1). The compound has been characterized by a combination of spectroscopic data and single crystal X-ray diffraction analysis.

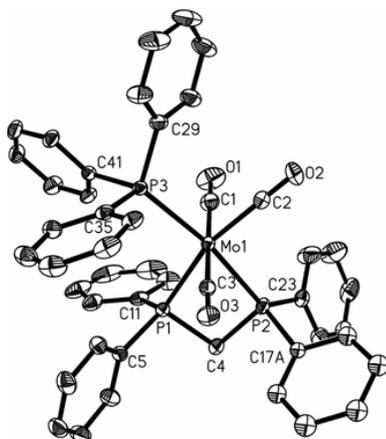
Scheme 1



### Synthesis of *mer*- $[\text{Mo}(\text{CO})_3(\text{PPh}_3)(\kappa^2\text{-dppm})]$ (**1**)

The solid-state molecular structure of **1** is depicted in Fig. 1, crystallographic data are summarized in Table 1, and selected bond distances and angles are collected in Table 2. The molecule contains a single molybdenum atom ligated by three carbonyl groups, a  $\text{PPh}_3$  and a chelating dppm ligand. The molybdenum atom adopts distorted octahedral coordination geometry with three carbonyl ligands in *meridional* arrangement. The distortion from octahedral arrangement is evident from the short chelate angle  $\{\text{P}(2)\text{--Mo}(1)\text{--P}(1) 68.347(15)^\circ\}$  which is quite similar to that observed in  $[\text{Mo}(\text{CO})_4(\kappa^2\text{-dppm})]$   $\{67.3(0.1)^\circ\}$  [20]. Except the short chelate angle the greatest deviation from the octahedral geometry at the metal center is in the  $\text{C}(1)\text{--Mo}(1)\text{--P}(2)$  angle of  $84.68(5)^\circ$ , and the two carbonyls lie *cis* to one another  $\{\text{C}(2)\text{--Mo}(1)\text{--C}(1) 87.83(3)^\circ\}$ . An interesting feature of the molecule is the different molybdenum–phosphorus bond distances  $\{\text{Mo}(1)\text{--P}(1) 2.5225(4) \text{ \AA}$  and  $\text{Mo}(1)\text{--P}(2) 2.4379(5) \text{ \AA}\}$  for the dppm ligand compared to almost equal molybdenum–phosphorus distances in  $[\text{Mo}(\text{CO})_4(\kappa^2\text{-dpppe})]$  {dpppe = bis(diphenylphosphino)pentane}  $\{2.478(2) \text{ and } 2.488(2) \text{ \AA}\}$  [21] and  $[\text{Mo}(\text{CO})_4(\kappa^2\text{-dpph})]$  {dpph = bis(diphenylphosphino)hexane}  $\{2.470(2) \text{ and } 2.468(2) \text{ \AA}\}$  [22]. The molybdenum–phosphorus bond *trans* to  $\text{PPh}_3$  ligand is  $0.08 \text{ \AA}$  shorter than the *cis* molybdenum–phosphorus bond. The molybdenum–phosphorus distance involving the  $\text{PPh}_3$  ligand  $\{\text{Mo}(1)\text{--P}(3) 2.4901(4) \text{ \AA}\}$  is comparable to that found in *trans*- $[\text{Mo}(\text{CO})_4(\text{PPh}_3)_2]$   $\{2.500(1) \text{ \AA}\}$  [23]. The *trans* Mo–C distances  $\{\text{Mo}(1)\text{--C}(1) 2.0143(19) \text{ \AA}$  and  $\text{Mo}(1)\text{--C}(3) 2.0345(17) \text{ \AA}\}$  are somewhat larger than the other Mo–C distance  $\{1.9786(18) \text{ \AA}\}$ . As a consequence the  $\text{C}(2)\text{--O}(2)$  distance  $\{1.154(2) \text{ \AA}\}$  is longer than the *trans* C–O distances  $\{1.147(2) \text{ \AA}\}$ . The *trans* angles about molybdenum in **1** span a wide range  $\{164.33(5)^\circ\text{--}178.47(7)^\circ\}$  compared to those observed in  $[\text{Mo}(\text{CO})_4\text{L}_2]$  complexes  $\{165.6(0.4)^\circ\text{--}167.9(0.5)^\circ\}$  in  $[\text{Mo}(\text{CO})_4(\kappa^2\text{-dppm})]$  [20];  $173.2(2)^\circ\text{--}177.5(2)^\circ$  in  $[\text{Mo}(\text{CO})_4(\text{PMe}_3)_2]$  [9];  $172.1(1)^\circ\text{--}176.4(2)^\circ$  in  $[\text{Mo}(\text{CO})_4(\text{PEt}_3)_2]$  [9].

Fig. 1



X-ray structure of **1** showing the atom labeling scheme used. The hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 50% probability level

The spectroscopic data of **1** are consistent with the solid-state structure. The presence of only one strong absorption band in the carbonyl region of the infrared spectrum indicates a *mer*-configuration [24]. In addition to aromatic resonances for the phenyl protons for both phosphines, the  $^1\text{H}$  NMR spectrum shows a triplet at  $\delta$  4.59 ( $J = 8.8$  Hz) assigned to the methylene protons of the dppm ligand. The coupling of the phosphorus atoms of  $\text{PPh}_3$  and dppm ligand is not observed in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum. The spectrum displays two doublets at  $\delta$  56.2 ( $J = 72.2$  Hz), and 21.2 ( $J = 72.2$  Hz) and a singlet at  $\delta$  1.7 in a relative intensity of 1:1:1 due to the phosphorus atoms of the dppm and  $\text{PPh}_3$  ligand, respectively. The FAB mass spectrum exhibits a parent molecular ion at  $m/z$  828 and fragmentation ions due to the successive loss of three carbonyls which also supports the solid-state structure.

## Supplementary Material

Crystallographic data for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Center as supplementary publication number 293492 (space group  $P-1$ ). Copies of this information can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge, CB2 1 EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

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## Acknowledgments

Financial support of this work by the University Grants Commission of Bangladesh is gratefully acknowledged.