

- mada, T.; Tabusa, F. *Tetrahedron* **1990**, *46*, 256.
5. The ratio was checked by 300 MHz  $^1\text{H}$  NMR. The chemical shift for the methyl group of **5** thus prepared showed a doublet at  $\delta$  3.75 whereas the other isomer showed at  $\delta$  3.76 in 300 MHz  $^1\text{H}$  NMR.
6. Miller, D. G.; Wayner, D. D. M. *J. Org. Chem.* **1990**, *55*, 2924.
7. Tsuji, J. *Synthesis* **1984**, 369.

### Oxidation of $(\text{PPh}_3)_2(\text{CO})_2\text{Br}_2\text{Mo(II)}$ to $(\text{Ph}_3\text{P}=\text{O})_2(\text{O})_2\text{Br}_2\text{Mo(VI)}$

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Received July 30, 1994

In the course of the reaction between *trans*, *cis*, *cis*- $(\text{PPh}_3)_2(\text{CO})_2\text{Br}_2\text{Mo(II)}$ , **A**, and the primary amines in tetrahydrofuran (THF) under argon at room temperature, the continuous color change of **A** was observed. Compound **A** changed its color much more rapidly in air in various solvents even in the absence of the amines. This kind of air-sensitivity appeared to be both solvent- and temperature-dependent. We decided to investigate how the product was formed and to determine its molecular structure. Herein we report the preparation and structure of *cis*, *cis*, *trans*- $(\text{Ph}_3\text{P}=\text{O})_2(\text{O})_2\text{Br}_2\text{Mo(VI)}$ , **B**, which was formed by oxidation of **A**.

### Experimental

Unless otherwise stated, all the reactions have been performed with standard Schlenk line and cannula techniques under an argon atmosphere. Air-sensitive solids were manipulated in a glove box filled with an argon gas. Glassware was either flame-dried or oven-dried. Benzene, diethyl ether, tetrahydrofuran (THF), and hydrocarbon solvents were stirred over sodium metal and distilled under vacuum. NMR solvents ( $\text{C}_6\text{D}_6$  and  $\text{CDCl}_3$ ) were freeze-pump-thaw degassed before use and stored over zeolite 4A under argon. Triphenylphosphine ( $\text{PPh}_3$ ;  $\text{Ph}=\text{C}_6\text{H}_5$ ) was purchased from Aldrich Co. and used as received.  $(\text{PPh}_3)_2(\text{CO})_2\text{Br}_2\text{Mo(II)}$ , **A**, was prepared by the literature method.<sup>1</sup>

$^1\text{H}$  and  $^{31}\text{P}$  NMR spectra were recorded with a Hitach 1100 60-MHz spectrometer and a Varian 200-MHz spectrometer with reference to tetramethylsilane and 85%  $\text{H}_3\text{PO}_4$ , respectively. IR spectra were recorded with a Nicolet 205 FTIR spectrophotometer. Melting points were measured with a Thomas Hoover capillary melting point apparatus without calibration.

**Preparation of *cis*, *cis*, *trans*- $(\text{Ph}_3\text{P}=\text{O})_2(\text{O})_2\text{Br}_2\text{Mo(VI)}$ , **B**.** A blue slurry of **A** (0.3 g, 0.36 mmol) in 30 mL of THF was stirred for 4 h at room temperature or refluxed

**Table 1.** Crystallographic Data and Summary of Data Collection and Structure Refinement

formula	$\text{C}_{36}\text{H}_{30}\text{O}_4\text{P}_2\text{Br}_2\text{Mo}$	F(000)	1680
fw	844.30	no. of	2907
crystal system	monoclinic	unique data	
space group	$P2_1/c$	no. of reflns	2708
<i>a</i> , Å	19.097(3)	used, $I > 2\sigma(I)$	
<i>b</i> , Å	9.973(3)	no. of params	340
<i>c</i> , Å	19.201(6)	Z	4
$\beta$ , deg	111.32(2)	scan range	$3 < 2\theta < 50^\circ$
<i>V</i> , Å <sup>3</sup>	3407(2)	scan type	$\omega$ -2 $\theta$
<i>d</i> <sub>calc</sub> , g cm <sup>-3</sup>	1.646	GOF	1.124
$\mu$ , mm <sup>-1</sup>	2.863	R	0.0536
Max. in $\Delta\rho$ (e Å <sup>-3</sup> )	0.61	$wR_2^a$	0.1226

$$^a wR_2 = \{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2] \}^{1/2}$$

for 2 h in air to form a dark brown solution. The solution was filtered, concentrated, and layered by hexanes to give orange crystalline *cis*, *cis*, *trans*- $(\text{Ph}_3\text{P}=\text{O})_2(\text{O})_2\text{Br}_2\text{Mo(VI)}$ , **B**, (0.19 g, 63%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  8.0-6.7 (m).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  58.35. Mp (decomp): 271-273 °C. IR (Nujol): 1155 (P=O), 1115, 1065, 1052, 972 (Mo=O, sym.), 894 (Mo=O, asym., sh), 853, 725 cm<sup>-1</sup>.

**X-ray Structure Determination.** All X-ray data were collected with use of an Enraf-Nonius CAD4 automated diffractometer equipped with a Mo X-ray tube and a graphite crystal monochromator. Details on crystal and intensity data are given in Table 1. The orientation matrix and unit cell parameters were determined from 25 machine-centered reflections with  $16 < 2\theta < 24^\circ$ . Axial photographs were used to verify the unit cell choice. Intensities of three check reflections were monitored after every 1 h during data collection. Data were corrected for Lorentz and polarization effects. The intensity data were empirically corrected with  $\psi$ -scan data. All calculations were carried out on the personal computer with use of the SHELXS-86,<sup>2</sup> SHELXL-93<sup>3</sup> programs.

An orange crystal, shaped as a block, of approximate dimensions 0.2 × 0.2 × 0.3 mm, was used for crystal and intensity data collection. The unit cell parameters and systematic absences,  $0k0$  ( $k = 2n + 1$ ),  $00l$  ( $l = 2n + 1$ ), and  $h0l$  ( $l = 2n + 1$ ), unambiguously indicated  $P2_1/c$  as the space group. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically and the phenyl rings were treated as rigid groups. All hydrogen atoms were positioned geometrically and refined using a riding model. The selected bond distances and bond angles are shown in Table 2; final atomic positional parameters for non-hydrogen atoms, anisotropic thermal parameters for non-hydrogen atoms, hydrogen atom coordinates, full bond distances and bond angles, and tables of observed and calculated structure factors are available as supplementary materials.

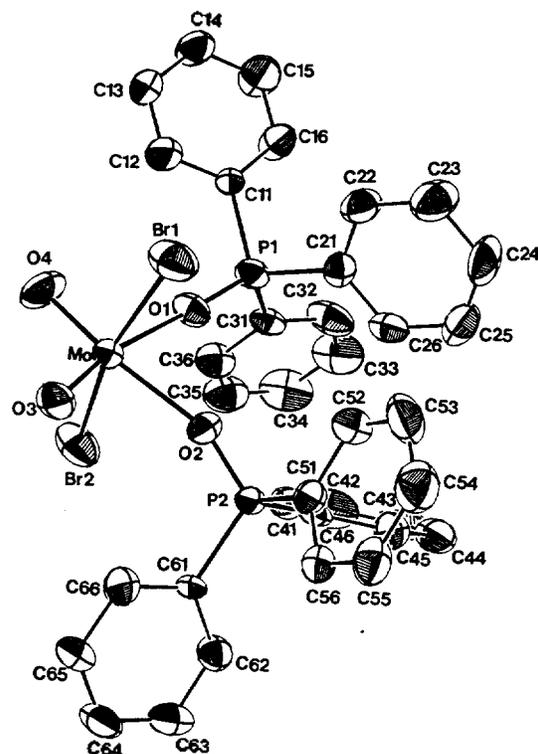
### Results and Discussion

**Formation of **B**.** A blue complex, *trans*, *cis*, *cis*- $(\text{PPh}_3)_2(\text{CO})_2\text{Br}_2\text{Mo(II)}$ , **A**, was gradually air-oxidized to form a known orange complex *cis*, *cis*, *trans*- $(\text{Ph}_3\text{P}=\text{O})_2(\text{O})_2\text{Br}_2\text{Mo(VI)}$ , **B**, in THF for 4 h at room temperature (Eq. 1). This

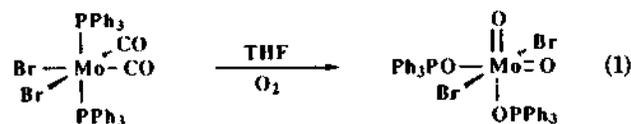
\*This paper is dedicated to professor Woon-Sun Ahn on the occasion of his retirement.

**Table 2.** Selected Bond Distances (Å) and Bond Angles (deg)

Mo-Br1	2.541(2)	Mo-Br2	2.554(2)
Mo-O1	2.173(6)	Mo-O2	2.158(6)
Mo-O3	1.682(6)	Mo-O4	1.725(6)
P1-O1	1.493(6)	P1-C11	1.805(7)
P1-C21	1.814(6)	P1-C31	1.817(6)
P2-O2	1.505(6)	P2-C41	1.812(6)
P2-C51	1.798(7)	P2-C61	1.803(6)
Bond Angles			
Br2-Mo-Br1	167.2(1)	P1-O1-Mo	166.6(4)
P2-O2-Mo	160.8(4)	O1-Mo-Br1	83.8(2)
O1-Mo-Br2	86.5(2)	O2-Mo-Br1	85.9(2)
O2-Mo-Br2	83.8(2)	O2-Mo-O1	77.4(2)
O3-Mo-Br1	93.0(2)	O3-Mo-Br2	94.6(2)
O3-Mo-O1	167.5(3)	O3-Mo-O2	90.3(3)
O4-Mo-Br1	96.4(2)	O4-Mo-Br2	92.2(3)
O4-Mo-O1	91.1(3)	O4-Mo-O2	168.0(3)
O4-Mo-O3	101.3(3)	C11-P1-O1	108.7(4)
C21-P1-O1	115.2(4)	C21-P1-C11	107.5(3)
C31-P1-O1	110.6(3)	C31-P1-C11	108.5(3)
C31-P1-C21	106.1(3)	C41-P2-O2	112.6(3)
C51-P2-O2	110.9(3)	C51-P2-C41	107.8(3)
C61-P2-O2	111.4(3)	C61-P2-C41	107.1(3)
C61-P2-C51	106.7(3)		

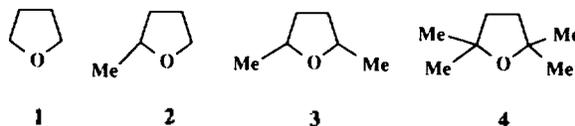
**Figure 1.** ORTEP drawing of **B** showing the atom-labeling scheme and 50% probability thermal ellipsoids

reaction was accelerated in the refluxing THF and completed for less than 2 h. The compound **B** was originally prepared from the reaction between molybdc acid and triphenylphosphine oxide in HBr.<sup>4</sup> The crystal structure of **B** (*vide infra*) indicates the ligand rearrangement of the two Br atoms, oxidation of triphenyl phosphine to triphenyl phosphine oxide, and replacement of the CO ligands by the oxide ligands. The oxidation state of the Mo metal also changed from +2 to +6. In the presence of excess phosphine (10-fold excess), we obtained the product whose melting point is quite different from that of **B** (259 vs 272 °C).



An IR absorption band at 1156 cm<sup>-1</sup> is assigned to a P=O stretching, which usually range between 1200 and 1130 cm<sup>-1</sup> for the coordinated OPPh<sub>3</sub> for a variety of metals.<sup>5</sup> **B** exhibits two Mo=O stretching bands at 972 (symmetric), 894 (asymmetric, sh), which were originally reported as 944 and 903 cm<sup>-1</sup>.<sup>4</sup> The phosphine oxides are prepared by oxidation of the corresponding phosphines. For the most part, H<sub>2</sub>O<sub>2</sub><sup>6</sup> has been used as the oxidizing agent and some milder reagents such as SO<sub>3</sub> and SO<sub>2</sub>Cl have also been reported.<sup>7</sup> The phosphine oxide complexes are usually prepared from the direct reaction between a metal salt and the ligand in a nonaqueous solvent such as alcohol, acetone or halogenated hydrocarbon, selected according to the solubility of the metal salt.<sup>5</sup> In all the structurally characterized complexes the phosphine oxide ligands are coordinated to a central metal through the oxygen atom.

The air-oxidation reactivity appeared to be solvent-dependent. The oxidation reaction was solved down in benzene (for 4 h in the refluxing benzene). In order to check the role of solvent in the coordination sphere of the metal, the reaction was carried out in a series of methyl-substituted tetrahydrofurans (**1-4**) that have similar dielectric constants but vary widely in donor ability.<sup>8</sup> The reaction, followed by UV and TLC, had been completed for 4 h in **1** and 12 h in **2**. But the reaction had produced the several untraceable species for 36 h in **3** and never reacted for even 10 days in **4**. The above observed variations seem to be consistent with the relative nucleophilicities of these solvents and therefore the solvent may play a certain role in stabilizing the intermediate in the oxidation reaction. It seems to be likely that the phosphine ligand in **A** dissociates first, oxidizes to phosphine oxide by oxygen in air, and binds back to the central metal.



**Molecular structure of B.** Because an X-ray crystallography is the only way to give an evidence for the formation of **B**, and because the structure of **B** was more accurately determined in this experiment, some important data of an X-ray crystal structure such as an ORTEP drawing and the selected bond distances and bond angles are presented. The molecular structure with the atomic numbering scheme is shown in Figure 1. The coordination sphere of **B** can be

described as a distorted octahedron, with the four oxygen atoms sitting on the equatorial plane and the two bromine atoms occupying the axial sites. The four oxygen atoms and a Mo metal are essentially coplanar with the mean deviation of 0.04 Å. The two phosphine oxide ligands are mutually *cis* to each other, two bromide ligands are *trans*, and two oxide ligands are *cis*.

The bond distances and bond angles in **B** are essentially the same as those<sup>4</sup> previously determined, within the experimental errors. For instance, the average Mo-O (terminal oxo) bond distance is 2.168(6) Å in this experiment and 2.18(1) Å in Butcher's experiment. It is known that the bond distance (1.483(2) Å) of P-O in the free O=PPh<sub>3</sub><sup>9</sup> is usually lengthened by about 0.02 Å when coordinated to the metal.

Several conclusions can be drawn from the above observations. Complex **A** is highly air-sensitive in solution. In tetrahydrofuran the complex **A** is air-oxidized to form **B**. The rate of oxidation for **A** seems to be both solvent- and temperature-dependent. The existence of OPPh<sub>3</sub> in the complex **B** maybe results from the fact that PPh<sub>3</sub> in the complex **A** dissociates from the coordination sphere of Mo, transforms to a corresponding phosphine oxide (OPPh<sub>3</sub>) through air-oxidation, and binds back to Mo.

**Acknowledgment.** This work is based on research sponsored by the Korea Ministry of Education under grant BSRI-94-3420.

**Supplementary Material Available.** Tables of final atomic positional parameters for nonhydrogen atoms, bond distances and bond angles, anisotropic thermal parameters, positional parameters for hydrogen atoms (6 pages); listings of observed and calculated structure factors (7 pages) are available from one of authors (S. W. L.).

### References

1. Colton, R.; Tomkins, I. B. *Aust. J. Chem.* 1966, 19, 1519.
2. Sheldrick, G. M. *Acta Cryst.* 1990, A46, 467.
3. Sheldrick, G. M. University of Gottingen, 1993.
4. Bucher, R. J.; Penfold, B. R.; Sinn, E. *J. Chem. Soc. Dalton Trans.* 1979, 668.
5. Goggin, P. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Eds.; Pergamon Press: New York, 1987, Vol. 2, Chapter 15.8, pp 497-501.
6. (a) Copley, D. B.; Fairbrother, F.; Miller, J. R. *Proc. Chem. Soc.* 1964, 300. (b) Berlin, K. D.; Burtler, G. B. *J. Org. Chem.* 1961, 26, 2637.
7. Olah, G. A.; Gupta, B. G. B.; Garcia-Luna, A.; Narang, S. C. *J. Org. Chem.* 1983, 48, 1760.
8. Atwood, J. D. *Inorganic and Organometallic Reaction Mechanisms*; Brooks/Cole Publishing Company: Monterey, U. S. A., 1982; p 140.
9. Ruban, G.; Zabel, V. *Cryst. Struct. Commun.* 1976, 5, 671.