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Comparison of the X-ray Crystal Structures of Two $\text{Mo(CO)}_5(\text{Ph}_2\text{PXR})$ ($\text{R} = \text{Pri}$; $\text{X} = \text{O}$; $\text{R} = \text{C}_6\text{H}_4\text{-4-Me}$) Complexes

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Abstract

Transition metal complexes of the type $\text{Mo(CO)}_5(\text{PPh}_2\text{XR})$ ($\text{X} = \text{O}$, $\text{R} = (\text{CH}_3)$ (**1**); $\text{X} = \text{NH}$, $\text{R} = \text{C}_6\text{H}_4\text{-p-CH}_3$ (**2**)), where PPh_2 = diphenylphosphine, were synthesized in a previous study, and **2** has been recrystallized and characterized by small molecule X-ray crystallography. In this study the recrystallization of **1**, along with an analysis of the X-ray crystallographic data obtained, is presented. Complex **1** crystallizes in a $P\bar{1}$ space group and is arranged in a primitive triclinic Bravais lattice with cell dimensions $a = 12.0804(5) \text{ \AA}$, $b = 13.4548(5) \text{ \AA}$, $c = 13.5947(6) \text{ \AA}$, $\alpha = 92.405(2)^\circ$, $\beta = 99.725(3)^\circ$, $\gamma = 106.263(2)^\circ$, $Z=2$. Various bond lengths, bond angles, and torsion angles from **1** are compared to those of **2** in order to deduce steric and electronic properties of the molecules.

Keywords: molybdenum, X-ray crystallography, phosphorus-donor ligands

Introduction

Over the past 60 years, researchers have been interested in transition metal complex chemistry. This interest is sparked by the fact that a wide range of organic reactions can be catalyzed by transition metal complexes.¹ Phosphorus-donor ligands have been found to be important for use in transition metal catalysts² because these ligands affect both the activities and the selectivities of the catalysts through bonding interactions of substrates with transition metal centers. Both electronic (Lewis donor ability and hard-soft nature) and steric properties contribute to the ligand effects. The hard-soft nature of the ligand is imperative because metals that are hard acids tend to bond strongly with second row bases, while metals that are soft acids prefer third, fourth and fifth row bases.³ Overall, hard acids would prefer to bond with hard bases and soft acids to soft bases.

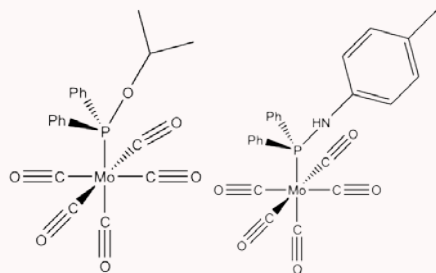


Figure 1. $\text{Mo(CO)}_5(\text{phosphorus-donor ligand})$ complexes **1** (left) and **2** (right).²

One of the best tools for characterizing the steric and electronic effects of ligands in transition metal complexes is X-ray crystallography. In this paper, we report the X-ray crystal structure of $\text{Mo(CO)}_5(\text{PPh}_2(\text{OCH}_3))$ (**1**, Figure 1 left) and compare the results to those previously obtained for $\text{Mo(CO)}_5(\text{PPh}_2(\text{NHC}_6\text{H}_4\text{-p-CH}_3))$ (**2**, Figure 1 right). The effects of the unique substituent on the phosphorus donor ligand's electronic properties are also described.

Materials and Methods

Synthesis and characterization of the complexes

Both complexes were previously prepared and the procedures for their syntheses are found in the chemical literature.⁴ Complex **1** was purified by flash chromatography through silica gel with a 1:1 dichloromethane/hexanes eluent mixture. The resultant solution was thermally recrystallized, yielding X-ray quality crystals. The crystal structure of **2** has been previously reported.²

X-Ray data collection and solution

A suitable single crystal of **1** was mounted on a MiTeGen loop in immersion oil and aligned upon a Bruker SMART APEX CCD area-detector using $\text{Cu K}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$) and equipped with an Oxford Cryosystems low-temperature device. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data yielded reflections to a maximum θ angle of 66.90° (0.84 \AA resolution). All of the reported angles were greater than $2\sigma(F^2)$. The final cell constants are based upon the refinement of the XYZ-centroids of 50 reflections above $20 \sigma(I)$ with $9.079^\circ < 2\theta < 59.92^\circ$. Data were corrected for absorption effects using the numerical method (SADABS). The space groups of the crystals were assigned on the basis of systematic absences and intensity statistics. Analytical scattering factors of each compound were corrected for both $\Delta f'$ and $i\Delta f''$ components of anomalous dispersion.⁵

The structure was solved and refined using the Bruker SHELXTL Software Package. Full-matrix refinements of the positional and anisotropic thermal parameters for all non-hydrogen atoms versus F^2 were carried out. All hydrogen atoms were placed in calculated positions with the appropriate molecular geometry and $\delta(\text{C-H}) = 0.96 \text{ \AA}$. The isotropic thermal parameter of each hydrogen atom was fixed equal to 1.2 times the U_{eq} value of the atom to which it was bound.

Crystallographic data has been deposited in the Cambridge Crystallographic Database.⁵

Results

The crystal structure of **1** (Figure 2) has two molecules in the asymmetric unit, which will hereafter be referred to as molecule 1 and molecule 2. Important bond lengths for both molecules are given in Table 1, important bond angles are given in Table 2, and important torsion angles are given in Table 3. The number in parentheses to the right of the bond lengths, bond angles and torsion angles are the estimated standard deviations in the last significant digit of each number. For example, the C18-Mo1-P1-Cl2 torsion angle is listed as -111.65(15)°, meaning that the measured angle was found to be -111.65°, and has an estimated standard deviation of 0.15°. Significances in the difference between two measurements were computed using Eq. 1.⁶

$$q = \frac{(x_1 - x_2)}{\sigma_1^2 + \sigma_2^2} \tag{1}$$

In the equation above, x corresponds to the respective measurements and σ is the respective standard deviations. A difference is significant with 99% certainty when q > 2.58.

The bond lengths in Table 1 are used to compare the bonds between the molybdenum and the ligands of the two molecules within the unit cell. The bond angles in Table 2 and the torsion angles in Table 3 are used to compare the conformations of the two molecules in the asymmetric unit.

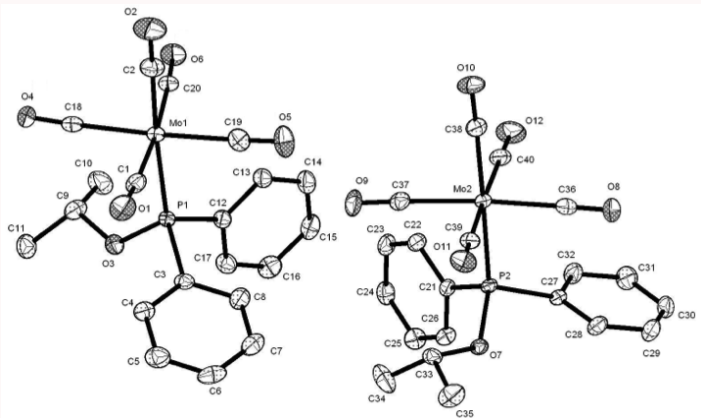


Figure 2. ORTEP drawing of **1**, showing two molecules in the asymmetric unit. Thermal ellipsoids are drawn at 30% and hydrogen atoms are omitted for clarity.

Table 1. Bond lengths (Å) of **1**.

Atom 1	Atom 2	Bond length (esd) (Å)
Mo1	C2 ^a	2.011(4)
Mo1	C1 ^b	2.060(4)
Mo1	C18 ^b	2.050(4)
Mo1	C19 ^b	2.064(4)
Mo1	C20 ^b	2.037(4)
Mo1	P1	2.5279(8)
Mo2	C36 ^b	2.057(4)
Mo2	C37 ^b	2.040(4)
Mo2	C38 ^a	2.025(3)
Mo2	C39 ^b	2.066(4)
Mo2	C40 ^b	2.066(4)
Mo2	P2	2.4982(8)

^aCarbonyl *trans* to phosphorus

^bCarbonyl *cis* to phosphorus

Table 2. Bond angles (°) of **1** as compared to those of **2**.

	Atom 1	Atom 2	Atom 3	Bond Angle (esd) (°)
Molecule 1	P1	Mo1	C1	90.80(10)
	P1	Mo1	C2	176.35(12)
	P1	Mo1	C18	97.46(9)
	P1	Mo1	C19	88.03(11)
	P1	Mo1	C20	90.63(10)
	O3	P1	Mo1	120.78(9)
Molecule 2	C12	P1	Mo1	113.10(10)
	C3	P1	Mo1	118.47(10)
	C2	Mo1	C18	86.18(15)
	C2	Mo1	C19	88.32(16)
	P2	Mo2	C36	89.86(10)
	P2	Mo2	C37	88.08(9)
	P2	Mo2	C38	173.97(11)
	P2	Mo2	C39	96.84(9)
	P2	Mo2	C40	86.53(10)
	O7	P2	Mo2	120.27(8)
	C27	P2	Mo2	112.83(10)
	C21	P2	Mo2	117.62(9)
	C38	Mo2	C39	88.79(14)
	C38	Mo2	C40	87.90(14)

Table 3. Torsion angles (°) of **1**.

	Atom 1	Atom 2	Atom 3	Atom 4	Torsion Angle (esd) (°)
Molecule 1	C18	Mo1	P1	O3	2.28(15)
	C18	Mo1	P1	C12	-111.65(15)
	C18	Mo1	P1	C3	131.18(15)
Molecule 2	C39	Mo2	P2	O7	3.32(13)
	C39	Mo2	P2	C27	-112.01(14)
	C39	Mo2	P2	C21	130.75(14)

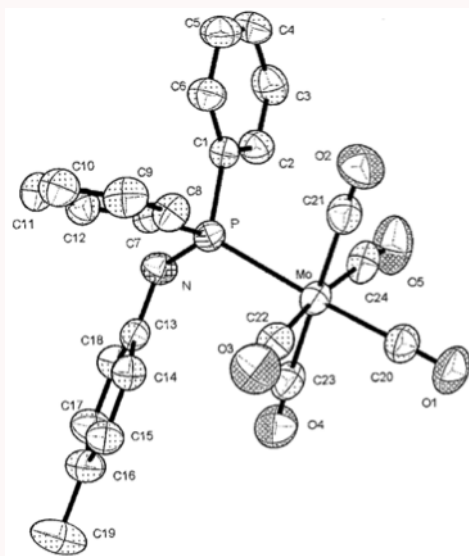


Figure 3. ORTEP drawing of the molecular structure of **2**. Thermal ellipsoids are drawn at 50% and hydrogen atoms are omitted for clarity.

Unlike the crystal structure of **1**, the previously reported crystal structure of **2** (Fig. 3) has only one molecule in the asymmetric unit. Tables 4 and 5 contain important bond lengths and angles for **2**. This data allows the effects of the different phosphorus substituents in the two compounds to be compared.

Discussion

The crystal structure of **1** (Figure 2) has two molecules in the asymmetric unit. This allows for the comparison of conformations between the two molecules, as well as the identification of common structural features. The conformations of the two molecules are also compared to those of **2**.

The coordination geometry of the molybdenum in each molecule of **1** is a distorted octahedron due to the steric effects of the large phosphorus-donor group. The two molecules of **1** exhibit similar distortions with one of the P-Mo-C_{cis} angles, defined by P1-Mo1-C18 and P2-Mo2-C39, respectively. Both of the aforementioned angles are significantly larger than the

Table 4. Bond lengths (Å) of **2**.

Atom 1	Atom 2	Bond length (esd) (Å)
Mo	C20 ^a	1.995 (4)
Mo	C21 ^b	2.034 (4)
Mo	C22 ^b	2.032 (4)
Mo	C23 ^b	2.061 (4)
Mo	C24 ^b	2.050 (4)
Mo	P	2.5274 (9)

^aCarbonyl *trans* to phosphorus

^bCarbonyl *cis* to phosphorus

Table 5. Bond Angles (°) of **2**.

Atom 1	Atom 2	Atom 3	Bond Angle (esd) (°)
P	Mo	C20 ^a	177.71 (10)
P	Mo	C21 ^b	86.82 (10)
P	Mo	C22 ^b	93.60 (10)
P	Mo	C23 ^b	92.76 (9)
P	Mo	C24 ^b	92.01 (10)
N	P	Mo	118.13 (9)
C1	P	Mo	113.41 (11)
C7	P	Mo	118.64 (10)

^aCarbonyl *trans* to phosphorus

^bCarbonyl *cis* to phosphorus

expected angle of 90°, while the other three P-Mo-C_{cis} angles in each molecule are slightly smaller than the ideal angle of 90°. The P-Mo-C_{trans} angle is also significantly smaller than the expected angle of 180° (molecule 1: 176.35(12)°; molecule 2: 173.97(11)°).

To fully understand the distortions in the two molecules of **1**, the torsion angles from the carbonyl most closely aligned with one of the three phosphorus substituents were compared (Table 3). These are very similar for the two molecules and indicate that the isopropoxy group and the most distorted *cis* carbonyl group are eclipsed. The steric repulsion between these groups must be high and may give rise to the larger than expected P-Mo-C_{cis} bond angles.

The steric interactions between the isopropoxy group and the most distorted *cis* carbonyl can result in other distortions. The C_{cis}-Mo-C_{trans} angle is smaller than 90° (molecule 1: C2-Mo1-C18, 86.18(15)°; molecule 2: C38-Mo2-C39, 88.79(14)°), and the C_{cis}-Mo-C_{trans} angle to the *cis* carbonyl opposite the most distorted *cis* carbonyl is also smaller than 90° (molecule

1: C2-Mo1-C19, 88.32(16)°; molecule 2: C38-Mo2-C40, 87.90(14)°). This distortion can be envisioned as a tilting of the Mo(CO)₅ group away from the isopropoxy substituent of the phosphorus and a simultaneous compression of the *cis* carbonyls toward the *trans* carbonyl.

The distortion in coordination geometry in **1** is different from that in **2**. Three of the P-Mo-C_{cis} angles in **2** are significantly larger than 90°, while only one of these angles in **1** is significantly larger than 90°. However, the magnitudes of these distortions in **2** are not as large as those in **1**. This comparison suggests that the primary distortion in **2** is a compression of the *cis* carbonyls toward the *trans* carbonyl and that there is less tilting of the phosphorus ligand relative to the plane formed by the *cis* carbonyls.

The second interesting aspect of structures of the molecules of **1** is the correlation between the molybdenum-carbonyl ligand bonding and the Mo-C bond lengths. The Mo-C_{trans} bonds are shorter than all of the Mo-C_{cis} bonds (Table 1). More precisely, in molecule 1, the difference between the Mo-C_{trans} bond length (Mo1-C2, 2.011(4) Å) is significantly shorter than the average of the Mo-C_{cis} bonds (average Mo-C_{cis}, 2.053(8) Å), using equation 1. Likewise, the difference between the Mo-C_{trans} bond length in molecule 2 (Mo2-C38, 2.025(3) Å) the Mo-C_{cis} bonds (average Mo-C_{cis}, 2.049(7) Å) is also significant. This is consistent with bonding theories for Mo(CO)₅(phosphorus ligand) complexes, which predict that there should be more π -backbonding from the molybdenum to the *trans* carbonyl than from the molybdenum to the *cis* carbonyl,⁷ resulting in a higher bond order and a shorter bond distance.³

A significant difference between the Mo-C_{trans} (Mo-C20, 1.995(4) Å) and the average of Mo-C_{cis} bonds (average Mo-C_{cis}, 2.044(8) Å) is also observed in **2**. However, both of these distances are shorter than those in either of the molecules in **1**. This suggests that there is more π -backbonding in **2** than in **1**. This is consistent with the isopropoxy substituent in **1** being more electron-withdrawing than is the *p*-tolylamido group in **2**, which makes the phosphorus ligand in **1** a poorer Lewis base than the ligand in **2**.

Conclusions

The comparison of the crystal structures of **1** and **2** has shown that the phosphorus ligands in these complexes have different electron-donor and steric properties. The ligand in **2** is a better electron donor, but does not appear to be as sterically demanding. Since both steric and electronic effects are important in determining the activity of catalysts containing such ligands, it might be expected that catalysts containing the two ligands might exhibit differences in activity and/or selectivity.

Acknowledgements

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