Synthesis and Structural Characterization of Mo_2Cl_4(tetraphos-1) (tetraphos-1 = $Ph_2PCH_2CH_2P(Ph)CH_2CH_2P(Ph)CH_2CH_2PPh_2$). The First Complexes of Enantiomeric 1,2,5,8/1,2,6,7 Type

The $Mo_2X_8^{4-}$ ions have square parallelepiped structures that are almost cubic, except for a slight elongation in the direction of the Mo_2 axis. Much attention has been devoted to substitution products of these ions in which some X^- ligands (e.g., Cl^-) are replaced by neutral ligands. The most extensively studied cases are those in which four X^- ligands are replaced, thus giving neutral molecules, and the neutral ligands are phosphines or diphosphines.

For $Mo_2X_4L_4$ molecules a number of isomers are possible. These may be enumerated and designated systematically by employing a numbering scheme in which we ignore distortions from the eclipsed conformation about the Mo_2 axis and number the ligand positions as shown in Figure 1a. The following 13 isomers may then be listed, where enantiomeric pairs are bracketed together:

(1) 1,2,3,4

(2) 1,2,3,5
(3) 1,2,3,7

(4) 1,2,3,6

(5) 1,2,3,8

(6) 1,2,5,7
(7) 1,2,6,8

(8) 1,2,5,8
(9) 1,2,6,7

(10) 1,2,5,6

(11) 1,2,7,8

(12) 1,2,5,7

(13) 1,2,6,8

Few of these have yet been observed. When there are four separate monophosphines, **13**, shown in Figure 1d, was until recently the only isomer found. This may be attributed to the steric factor, whereby the four bulkiest ligands stay as far from each other as possible; positions on the same edge (either vertical or horizontal) are not both occupied. When bidentate ligands are used, it is, of course, necessary that these span edges. To do this but otherwise avoid any further occupation of adjacent positions, isomers **11** and **12** (Figure 1b,c) are formed. These are more commonly called α and β isomers of the $M_2L_4(LL)_2$ type molecule,[1,2] as shown in Figure 2. Recently in this laboratory the first example of a 1,2,7,8 (**11**) type molecule in which all ligands are monodentate was found, namely, $Mo_2(OC_6F_5)_4(PMe_3)_4$.

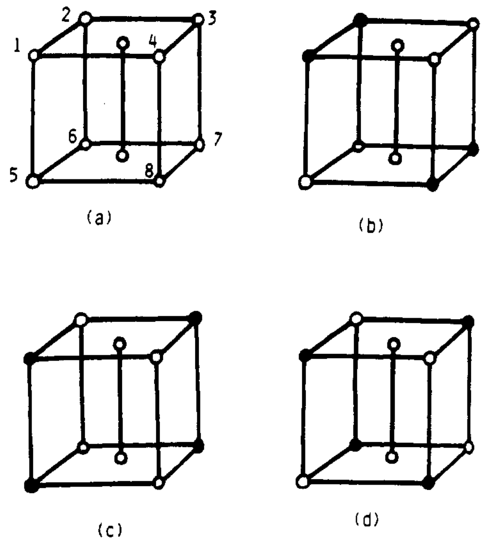

Figure 1. Cubic drawings showing the positions of the phosphorus and the halogen atoms for several types of complexes: (a) general positions; (b) 1,2,7,8-type complex; (c) 1,3,5,7-type complex; (d) 1,3,6,8-type complex. Full circles denote the positions of the phosphorus atoms.

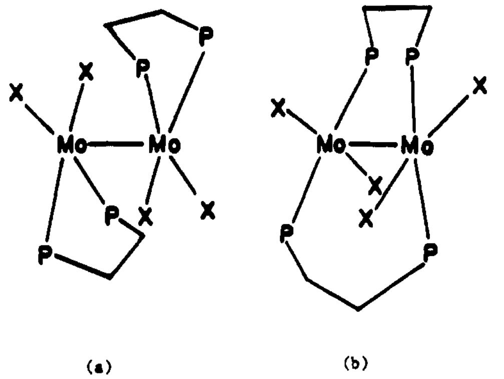

Figure 2. Schematic structures of (a) the α and (b) the β form of $Mo_2X_4(PP)_2$.

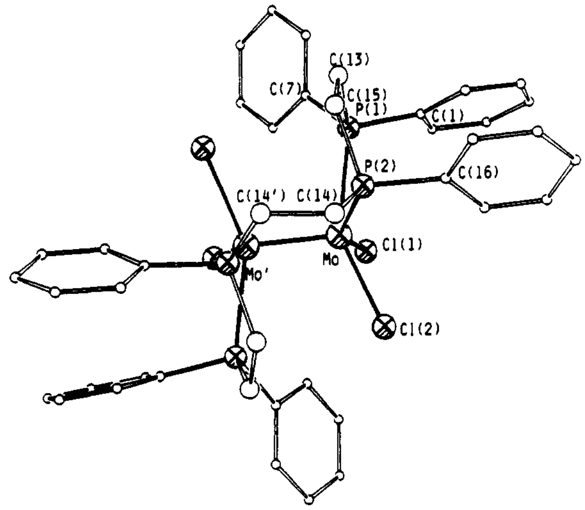

Figure 3. ORTEP drawing of Mo_2Cl_4(tetraphos-1) in its entirety. Selected bond distances (Å) and angles (deg): Mo–Mo = 2.155 (0), Mo–Cl(1) = 2.400 (1), Mo–Cl(2) = 2.430 (1), Mo–P(1) = 2.542 (1), Mo–P(2) = 2.509 (1); Mo–Mo–Cl(1) = 108.11 (3), Mo–Mo–Cl(2) = 107.53 (3), Mo–Mo–P(1) = 101.82 (3), Mo–Mo–P(2) = 101.22 (3), P(1)–Mo–P(2) = 76.67 (4), Cl(1)–Mo–Cl(2) = 94.16 (4), Cl(1)–Mo–P(1) = 85.19 (4), Cl(1)–Mo–P(2) = 148.11 (4), Cl(2)–Mo–P(1) = 149.24 (4), Cl(2)–Mo–P(2) = 88.64 (4).

None of the remaining geometrical isomers has yet been observed. It seems unlikely that any of them will be observed unless polydentate ligands are chosen to especially favor (or even require)

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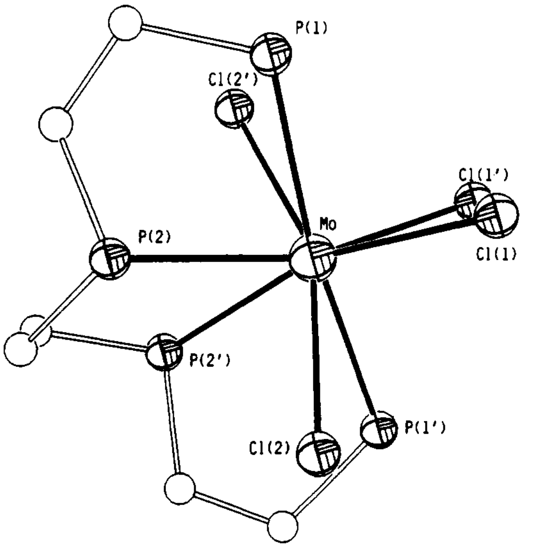

Figure 4. View looking down from the Mo–Mo bond. The phenyl groups are not shown for clarity.

such arrangements. We report here the first example of such a designed synthesis of a previously unobserved geometrical isomer, namely, the enantiomeric pair **8** and **9**.

The new complex Mo_2Cl_4(tetraphos-1) reported herein was prepared by the reaction of $K_4Mo_2Cl_8$ and the ligand, tetraphos-1, in boiling methanol.[3] The ligand sample used contained all of the possible diastereomers: the meso *R,S* form and the racemic *R,R* and *S,S* enantiomeric pair. Crystals of Mo_2Cl_4(tetraphos-1) conform to the space group *C*2/*c* with four molecules per unit cell.[4] One molecule of Mo_2Cl_4(tetraphos-1) is depicted in Figure 3. This molecule resides on a 2-fold axis that perpendicularly bisects the Mo–Mo bond, and thus the crystallographic symmetry of the molecule is C_2. Since the two central phosphorus atoms are interrelated by the C_2 axis, they must possess the same chirality, and it can be seen from Figure 3 that in the molecule shown this is *R*. Two molecules in the centrosymmetric unit cell have the *R,R* chirality and the other two possess the *S,S* chirality. Thus we have obtained a racemic *R,R* and *S,S* diastereomer, and the meso ligand has not yet been obtained in a crystalline product.

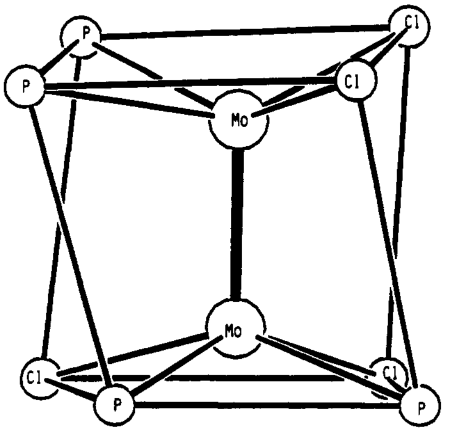

Figure 5. Drawing showing the central atoms of Mo_2Cl_4(tetraphos-1) in a distorted cube.

It can also be seen from Figure 3 that two types of coordination, bridging and chelating, can be seen in this molecule. Each has been found for the complexes of the type $Mo_2Cl_4(PP)_2$ but separately, namely, in the chelating form α-$Mo_2Cl_4(dppe)_2$ and the bridging form β-$Mo_2Cl_4(dppe)_2$.[1e,f]

Figure 4 shows a view of the inner part of Mo_2Cl_4(tetraphos-1) looking down the Mo–Mo bond. This molecule shows different torsional angles and a Λ configuration for the central portion. The torsion angle P(2)–Mo–Mo–P(2′), 31.6°, is similar to the average torsional angle of the complex β-$Mo_2Cl_4(dppe)_2$, which is 30.5°. The other three torsional angles are 18.1, 18.1, and 6.2°, respectively. The average torsional angles for Mo_2Cl_4(tetraphos-1) is thus about 18°. The average torsional of α-$Mo_2Cl_4(dppe)_2$ was found to be 0°. The Mo–Mo distance of Mo_2Cl_4(tetraphos-1) is 2.155 (0) Å, which is shorter than that of β-$Mo_2Cl_4(dppe)_2$ (2.183 (3) Å) and longer than that of α-$Mo_2Cl_4(dppe)_2$ (2.140 (2) Å). These distances are consistent with the theoretical expectation that the Mo–Mo bond distance should vary according to cos 2χ, where χ is the average of the four smallest torsional angles about the Mo–Mo quadruple bond.[1a] The mean Mo–Cl and Mo–P distances of Mo_2Cl_4(tetraphos-1) are 2.415 (2) and 2.526 (2) Å, respectively. These distances were 2.385 (7) and 2.579 (8) Å in β-$Mo_2Cl_4(dppe)_2$ and 2.423 (1) and 2.548 (2) Å in α-$Mo_2Cl_4(dppe)_2$, respectively.

As stated earlier for notational purposes, the $M_2X_4L_4$ units are treated as ideal square parallelepipeds. In most cases, there are significant distortions, and the present case provides a good example. This is emphasized by the skeletal view of the inner core shown in Figure 5.

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Supplementary Material Available: Complete tables of crystal data, positional and isotropic equivalent thermal parameters, anisotropic thermal parameters, bond distances, and bond angles (8 pages); a listing of observed and calculated structure factors (17 pages). Ordering information is given on any current masthead page.

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(3) $K_4Mo_2Cl_8$ (0.1 g, 0.158 mmol) and tetraphos-1 (0.212 g, 0.316 mmol) were placed in a flask equipped with a reflux condenser. Methanol (15 mL) was then added. This mixture was refluxed for 15 h to yield a brown solution and a brown solid. The solid was filtered off, washed with methanol and ether, and then dried under reduced pressure. Yield: 0.11 g (64%). UV–vis: 405, 475 and 720 nm in CH_2Cl_2 solvent. Crystals suitable for X-ray diffraction measurement were obtained by hexane-induced crystallization from a dichloromethane solution.

(4) Crystal data: space group *C*2/*c*, $a = 19.527$ (6) Å, $b = 18.210$ (2) Å, $c = 13.241$ (2) Å, $\beta = 104.85$ (2)°, $V = 4551$ (2) Å^3, $Z = 4$. The diffraction data were collected on a Enraf-Nonius CAD-4 diffractometer at 20 ± 1 °C which was equipped with graphite-monochromated Mo Kα ($\lambda_\alpha = 0.71037$ Å) radiation. Routine 2θ–ω data collection was used to scan a possible 4394 data points in the range of $4° < 2\theta < 50°$. The Patterson methods program in SHELXS-86[5] led to the locations of the positions of the molybdenum atoms. The remaining atoms were found in a series of alternating difference Fourier maps and least-squares refinements. Anisotropic thermal parameters were used for all the atoms. The final residuals of the refinement were $R = 0.0390$, $R_w = 0.0580$.

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