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Conformation of the Dimethyl Maleate Ligands in a Molybdenum(0) Complex. Crystal Structure of d^6 *trans*-Bis(dimethyl maleate)-dicarbonyl-*o*-phenylenediaminemolybdenum(0)

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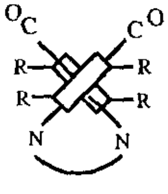
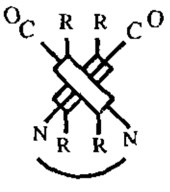
The solid-state structure of $Mo(CO)_2(DMMA)_2(PDA)$ (DMMA = dimethyl maleate, PDA = *o*-phenylenediamine) was determined by X-ray diffraction of single crystal. The complex crystallizes in the hexagonal space group P_6122 with a = 11.085(5), b = 11.085(5), c = 33.653(21) Å, γ = 120°, and Z = 6. The geometry of this bis(DMMA) complex is distorted octahedral with the two CO groups cis to each other and trans to the PDA ligand and the two DMMA ligands trans to each other and cis to the two CO ligands. The orientations of the two trans DMMA ligands are mutually perpendicular and each DMMA ligand eclipses an N-Mo-CO vector. The carbon-carbon double bond of DMMA is bonded to molybdenum unsymmetrically with the olefin carbon adjacent to a coordinated amino group closer to the metal than that adjacent to a carbonyl group. The conformation of each DMMA is that the two ester groups attached to DMMA lie in the regions described by N-Mo-C and N-Mo-N. Bond-distance calculations indicate that each keto oxygen of the ester groups in the region described by N-Mo-C forms a hydrogen bond with an amino hydrogen on the PDA ligand; this hydrogen bonding is responsible for the observed conformation of the complex. The conformation of this complex in the solid-state is in agreement with the results in solution predicted according to ^1H NMR spectral data.

INTRODUCTION

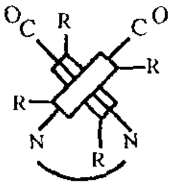
The structures, conformations, and fluxional behavior of d^6 octahedral trans bis(alkene) complexes of chromium, molybdenum, and tungsten and the mechanism of alkene rotation in these complexes have received considerable attention in recent years. While several groups reported the synthesis of simple trans bis(ethylene) complexes of the chromium family,[1,2] we successfully prepared a series of substituted bis(alkene) species of molybdenum.[3-5] The structure, conformation, and dynamic NMR behavior of substituted bis(alkene) complexes are much more complicated than those of the simple bis(ethylene) complexes. There are two diastereomers **a** and **b** isolated for the dimethyl fumarate (DMFU) complexes $Mo(CO)_2(DMFU)_2(NN)$ (NN = bidentate nitrogen ligand) arising from face selectivity of the DMFU ligands.[3] For the bpy or phen complex, the diastereomer **a** exists as two rotamers **a-I** and **a-II** in thermodynamic equilibrium in solution, while for the **a** isomer of $Mo(CO)_2(DMFU)_2(PDA)$, only the rotamer **a-I** was observed both in the solid state and in solution. Bis(MeMI), bis(PhMI), bis(MI) and bis(MA) complexes of molybdenum (PhMI = *N*-phenyl maleimide, MeMI = *N*-methyl maleimide and MA = maleic anhydride) were prepared.[4,5] Three rotamers **c-I**, **c-II**, and **c-III** are possible for these cyclic bis(alkene) complexes, but in fact only **c-I** was observed in the solid state for all these species. In solution, for bpy and phen complexes, **c-I** and **c-II** were detected with the former as the major species.



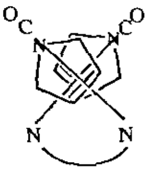
a-I



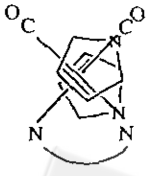
a-II



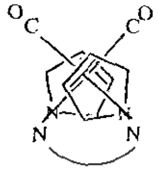
b



c-I



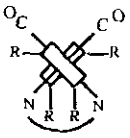
c-II



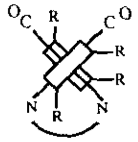
c-III

Very recently, we have reported the synthesis, and structure of complexes $Mo(CO)_2(DMMA)_2(NN)$ and $Mo(CO)_2(DMMA)(DMFU)(NN)$ where DMMA = dimethyl maleate.[6] There are three possible rotational isomers **d-I**

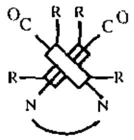
\- **d-III** for a Mo(CO)$_2$(DMMA)$_2$(NN) complex and four possible rotational isomers **e-I** - **e-IV** for a Mo(CO)$_2$(DMMA)(DMFU)(NN) complex. For *trans*-Mo(CO)$_2$(DMMA)$_2$(PDA) (PDA = *o*-phenylenediamine), the conformation of the DMMA ligands was predicted to be **d-I** in solution and for the mixed ligand complex *trans*-Mo(CO)$_2$(DMMA)(DMFU)(PDA), the conformational isomer in solution and in the solid state as determined by X-ray diffraction is **e-I**. On the other hand, when NN = bpy and phen, the conformational isomers existing in solution for bis(DMMA) complexes as evidenced by ^{1}H NMR spectra are **d-III** and for Mo(DMMA)(DMFU) species are **e-II** and **e-III**.



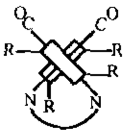
d-I



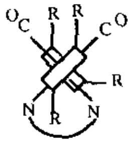
d-II



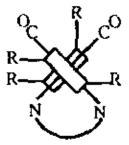
d-III



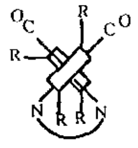
e-I



e-II



e-III



e-IV

The solid-state structures of bis(DMFU),[3] bis(MeMI)[4] and (DMFU)(DMMA)[6] complexes have been unambiguously determined by X-ray diffraction, but there is still no bis(DMMA) complex of which the solid-state structure is clearly known. In order to complete the series of solid-state structural analysis of trans bis(alkene) complexes, we investigated the crystal structure of *trans*-Mo(CO)$_2$(DMMA)$_2$(PDA) by X-ray diffraction. Herein, we report the results of this study.

Table 1. Atomic Positional Parameters for Non-hydrogen Atoms of Mo(CO)$_2$(DMMA)$_2$(PDA)

	x	y	z	B$_{iso}$/Å
Mo	0.51336(8)	0.51336	1/6	5.96(5)
N(1)	0.3000(6)	0.4039(7)	0.19510(14)	4.9(4)
C(1)	0.2110(7)	0.2630(7)	0.18063(17)	3.9(4)
C(2)	0.0765(8)	0.1819(9)	0.19494(22)	5.3(5)
C(3)	-0.0037(9)	0.0481(8)	0.18086(23)	6.7(6)
C(4)	0.6086(9)	0.5381(13)	0.2290(3)	8.9(7)
C(5)	0.5369(10)	0.5687(11)	0.2624(3)	8.5(7)
O(1)	0.6313(7)	0.6547(7)	0.28735(16)	10.9(5)
O(2)	0.4145(7)	0.5185(9)	0.26898(17)	10.4(6)
C(6)	0.5768(11)	0.6919(13)	0.3213(3)	13.5(9)
C(7)	0.5699(10)	0.4056(14)	0.21460(25)	7.4(7)
C(8)	0.4643(10)	0.2724(14)	0.2309(3)	6.8(8)
O(3)	0.4624(8)	0.1673(9)	0.21162(20)	8.3(6)
O(4)	0.3843(7)	0.2546(8)	0.25720(17)	9.4(6)
C(9)	0.3607(12)	0.0302(14)	0.2248(3)	12.3(11)
C(10)	0.5743(12)	0.7009(10)	0.18659(24)	9.5(8)
O(5)	0.6081(9)	0.8119(7)	0.19727(21)	13.8(7)

B$_{iso}$ is the mean of the principal axes of the thermal ellipsoid.

RESULTS AND DISCUSSION

Crystals of *trans*-Mo(CO)$_2$(DMMA)$_2$(PDA) suitable for X-ray analysis were grown from a mixture of CH$_2$Cl$_2$ and Et$_2$O. Interestingly, the molecules pack in a highly symmetric manner leading to a hexagonal crystal system and space group P_6122. The c axis (33.653 Å) of the unit cell is about three times as longer as the a or b axis and is exceptionally long compared to those of common molecular crystals. A molecular drawing of *trans*-Mo(CO)$_2$(DMMA)$_2$(PDA) with the atomic number scheme is shown in Fig. 1. Final atomic positional parameters for non-hydrogen atoms are summarized in Table 1, and bond distances and angles are listed in Tables 2 and 3, respectively. As shown in Fig. 1, the geometry of this bis(DMMA) compound is distorted octahedral with the two CO groups cis to each other and the two DMMA ligands in trans positions. The orientations of the two trans DMMA ligands are mutually perpendicular and each DMMA ligand eclipses a N-Mo-CO vector. Although the structure of the molybdenum center, the two cis CO ligands and the two nitrogen atoms on the PDA ligand

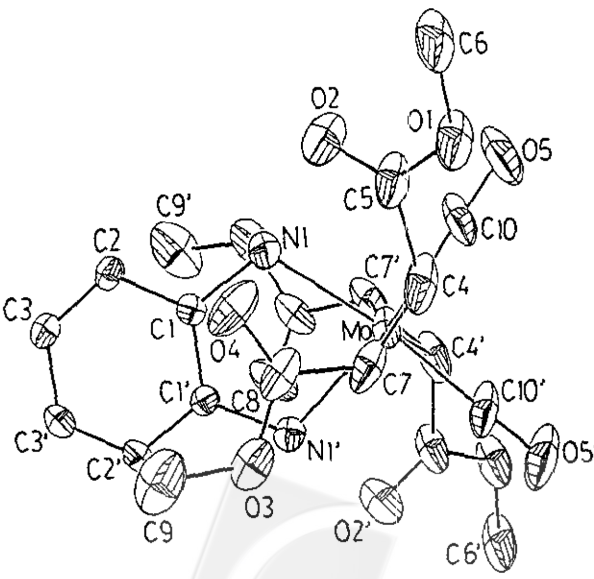


Fig. 1. Molecular structure drawing of Mo(CO)$_2$(DMMA)$_2$(PDA) showing the atom-labeling scheme.

Table 2. Bond Distances/Å of Mo(CO)$_2$(DMMA)$_2$(PDA)

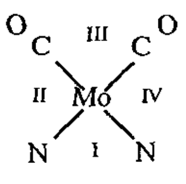
Mo-N(1)	2.261(6)	Mo-C(4)	2.304(9)
Mo-C(7)	2.274(11)	Mo-C(10)	1.955(10)
N(1)-C(1)	1.452(9)	C(1)-C(1′)	1.372(11)
C(1)-C(2)	1.286(11)	C(2)-C(3)	1.377(11)
C(3)-C(3′)	1.378(14)	C(4)-C(5)	1.509(16)
C(4)-C(7)	1.395(19)	C(5)-O(1)	1.308(10)
C(5)-O(2)	1.202(12)	O(1)-C(6)	1.444(12)
C(7)-C(8)	1.456(16)	C(8)-O(3)	1.325(16)
C(8)-O(4)	1.198(12)	O(3)-C(9)	1.437(15)
C(10)-O(5)	1.150(12)		

Table 3. Bond Angles/deg of Mo(CO)$_2$(DMMA)$_2$(PDA)

N(1)-Mo-N(1′)	75.38(22)	N(1)-Mo-C(4)	88.4(3)
N(1)-Mo-C(4′)	119.0(4)	N(1)-Mo-C(7)	84.7(3)
N(1)-Mo-C(7′)	84.0(3)	N(1)-Mo-C(10)	97.9(4)
N(1)-Mo-C(10′)	167.6(4)	C(4)-Mo-C(4′)	146.4(4)
C(4)-Mo-C(7)	35.5(5)	C(4)-Mo-C(7′)	152.4(4)
C(4)-Mo-C(10)	70.6(5)	C(4)-Mo-C(10′)	85.8(3)
C(7)-Mo-C(7′)	165.7(4)	C(7)-Mo-C(10)	106.0(4)
C(7)-Mo-C(10′)	84.3(4)	C(10)-Mo-C(10′)	90.5(5)
Mo-N(1)-C(1)	113.6(4)	Mo-C(4)-C(5)	116.3(7)
Mo-C(4)-C(7)	71.1(5)	Mo-C(7)-C(4)	73.4(6)
Mo-C(7)-C(8)	120.4(6)	Mo-C(10)-O(5)	177.8(10)

may be viewed as being square planar, the angles < N(1)-Mo-N(1′), < N(1)-Mo-C(10), < N(1′)-Mo-C(10′) and < C(10)-Mo-C(10′) that form the plane are 75.4°, 97.9°, 97.9°, and 90.5°, respectively varying significantly with the ligands.

The angle < N(1)-Mo-N(1′) between the two N-Mo vectors is the smallest due to the inherent rigid arrangement of atoms in the chelating PDA ligand and the relatively long N-Mo bond. There are three bis(alkene) complexes with PDA as chelating ligand of which the solid-state structures have been determined by X-ray diffraction. In all these complexes, the angles < N-Mo-N are nearly the same (75.7 ± 0.3°) reflecting the rigid nature of the PDA ligand. In contrast, the angle formed by the two Mo-CO vectors is relatively flexible. For the present complex *trans*-Mo(CO)$_2$(DMMA)$_2$(PDA), the value is 90.5°, while for complexes *trans*-Mo(CO)$_2$(DMFU)$_2$(PDA) **(a-I)**,[3] *trans*-Mo(CO)$_2$(DMFU)(DMMA)(PDA) **(e-I)**,[4] *trans*-Mo(CO)$_2$-(DMFU)$_2$(phen) **(b)**[3] and *trans*-Mo(CO)$_2$(PhMI)$_2$(CH$_3$CN)$_2$ **(c-I)**[5] the corresponding values are 84.6, 86.4, 87.3, and 92.4°, respectively (Table 4). The angle < C-Mo-C depends sensitively on the conformation of the two trans alkene ligands. If we view a bis(alkene) complex from the top of the MoN$_2$(CO)$_2$ plane, we divide the molecule into four regions (I - IV) by the two intersecting N-Mo-CO vectors. For *trans*-Mo(CO)$_2$(DMFU)$_2$(PDA) **(a-I)**, the four ester groups of the two DMFU all lie in region II, and IV. The repulsion between the substituents on the DMFU ligands and the carbonyl ligands pushes the two carbonyl groups closer resulting in a smaller < C-Mo-C. For *trans*-Mo(CO)$_2$(DMFU)-(DMMA)(PDA) **(e-I)**, or *trans*-Mo(CO)$_2$(DMFU)$_2$(phen) **(b)**, there are only three and two ester groups in region II and IV leading to a larger C-Mo-C angle than that of *trans*-Mo(CO)$_2$(DMFU)$_2$(PDA) **(a-I)**. For complex *trans*-Mo(CO)$_2$(PhMI)$_2$(CH$_3$CN)$_2$ **(c-I)**, the two PhMI ligands almost equally lie in regions II and III or IV and III. Unlike in complex *trans*-Mo(CO)$_2$(DMMA)$_2$(PDA), the repulsion between the PhMI ligands and the carbonyl groups does not effectively push the two carbonyl ligands to closer positions. As a result, the OC-Mo-CO angle is the largest among these bis(alkene) complexes.



Because of the presence of a C$_2$ axis bisecting the angle < N(1)-Mo-N(1′) and passing the molybdenum center, the two angles < N(1)-Mo-C(10) and < N(1′)-Mo-C(10′) in complex *trans*-Mo(CO)$_2$(DMMA)$_2$(PDA) are equal. These are the only angles exceeding 90° in the MoN$_2$(CO)$_2$ plane. The repulsion between the ester groups on DMMA and the carbonyl ligands resulting in a small value of < C-Mo-C and the small rigid N(1)-Mo-N(1′) angle likely explain the observed large values of < N(1)-Mo-C(10), and < N(1′)-Mo-C(10′). As shown in Fig. 2, slight bending of the oxygen atoms in the two carbonyl groups to each other is observed. Again, the repulsion between the ester groups on DMMA ligands and the carbonyl groups is likely responsible for this fine structural feature. For all bis(alkene) species, the N-Mo-C angles are generally the largest of the four angles in the plane MoN$_2$(CO)$_2$. Furthermore, the smaller is the C-Mo-C angle in a bis(alkene) complex, the larger is the N-Mo-C angle. For example, < C-Mo-C and < N-Mo-C in *trans*-Mo(CO)$_2$(DMMA)$_2$(PDA) are 90.5° and 97.9°, while the corresponding values in *trans*-Mo(CO)$_2$(DMFU)$_2$(PDA) are 84.6° and 100.5°, respectively. The angles in the MoN$_2$(CO)$_2$ plane of several molybdenum bis(alkene) complexes are compared in Table 4.

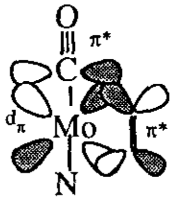
The orthogonal arrangement of the two DMMA ligands in *trans*-Mo(CO)$_2$(DMMA)$_2$(PDA) allows the π^* orbitals of DMMA ligands to overlap with the filled d_{xz} and d_{yz} orbitals on the metal center. Although the conformation of a DMMA ligand eclipsing a N-Mo-CO vector would lead to

Table 4. Comparison of the OC-Mo-CO, OC-Mo-N and N-Mo-N Angles/deg on the MoC_2N_2 Plane of Various Bis(alkene) Complexes

Complexes	OC-Mo-CO	OC-Mo-N	N-Mo-N
$Mo(CO)_2(DMMA)_2(PDA)$	90.5	97.9	75.38
$Mo(CO)_2(DMMA)(DMFU)(PDA)$	86.4	101.9, 96.9	76.2
$Mo(CO)_2(DMFU)_2(PDA)$ (a-I)	84.6	100.5	75.6
$Mo(CO)_2(DMFU)_2(phen)$ (b)	87.3	98.7, 101.2	74.4
$Mo(CO)_2(MeMI)_2(bpy)$	89.9	98.7	73.2
$Mo(CO)_2(PhMI)_2(CH_3CN)_2$	92.4	88.9, 89.2	90.5
$Mo(CO)_2(MA)_2(CH_3CN)_2$	89.2	93.5	84.9

stronger repulsion among the ligands, this arrangement is energetically more favorable. According to this geometry, the filled π orbital of DMMA meets the empty $d_{x^2-y^2}$ orbital showing little repulsion between these orbitals. On the other hand, a staggered conformation is expected to exhibit weaker steric repulsion, but the filled π orbital of DMMA and d_{xy} orbital of molybdenum would lead to strong four-electron repulsion. Orthogonal and eclipsed conformational preference appear general for trans bis(alkene) molybdenum(0) complexes and are also observed in a number of complexes containing trans π-acid ligands including CO_2,[7] O_2,[8] and alkynes.[9-11]

The carbon-carbon double bond of each DMMA ligand in this bis(DMMA) complex is bonded to molybdenum unsymmetrically. The olefin carbon adjacent to a coordinated amino group is closer to the metal than that adjacent to a carbonyl group. The interaction of d_π, and π* orbitals of carbonyl and DMMA ligand is shown below. Competition for the d_π electrons between the π* orbitals of carbonyl and DMMA ligand greatly reduce the back donation from the metal to the olefin carbon adjacent to the carbonyl group. Due to the absence of low-energy π* orbitals in an amino group, the π* orbital of the olefin carbon near the amino li-



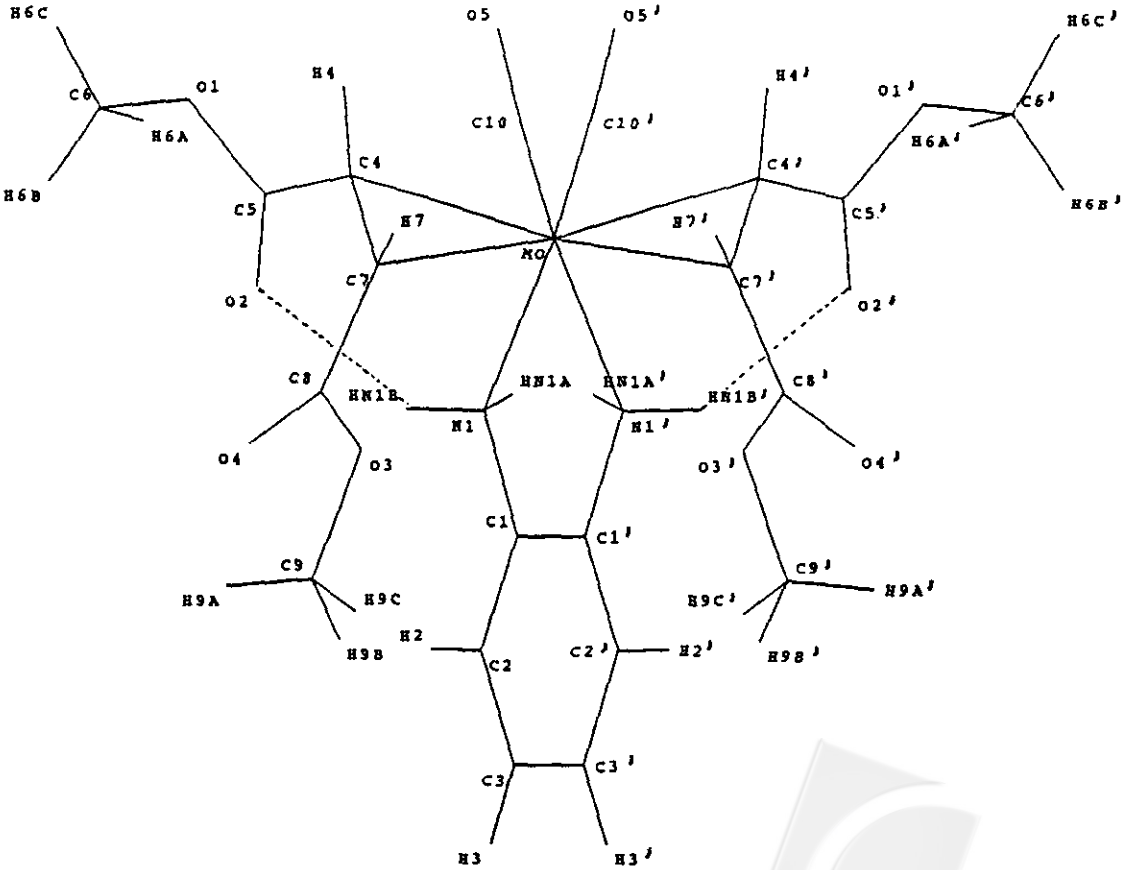


Fig. 2. Another view of the molecular structure of $Mo(CO)_2(DMMA)_2(PDA)$ showing the interligand hydrogen bonding.

gand does not compete with other ligand orbitals for the d_π electrons on the metal. As a result, the metal-olefin carbon bond adjacent to the carbonyl group is weaker than that near the amino ligand. The distance of carbon-carbon double bonds (1.395 Å) of the DMMA ligands is within the established range for electron-withdrawing olefins coordinated to low-valent metal centers and is slightly shorter than the value (1.416 Å) observed for *trans*-$Mo(CO)_2$(DMFU)(DMMA)(PDA).[4]

The conformation of the present bis(DMMA) complex in the solid state agrees with the results in solution according to ^1H NMR spectral data. In regard to the driving force for the conformational arrangement both in the solid state and in solution, the distances between O2 and HN1B and between O2′ and HN1B′ in the complex show the existence of hydrogen bonding between the keto oxygens (O2) of the ester groups in regions II and IV and the hydrogens on the amino group of the PDA ligand (Fig. 2). Hence, we conclude that the formation of intramolecular hydrogen bonds in *trans*-$Mo(CO)_2(DMMA)_2$(PDA) is the driving force for the observed conformation. For *trans*-$Mo(CO)_2(DMMA)_2$(bpy) and *trans*-$Mo(CO)_2(DMMA)_2$(phen), there is no interligand hydrogen bonding. In these complexes, the stable conformation of DMMA ligands is determined by the steric repulsion between ligands and the conformation shown in **d-III** is the most stable, because in this structure no ester group lies on the chelating bpy or phen so avoiding the strong repulsion between these groups. For the PDA complex, the repulsion between the ester group and the PDA ligand is overcome by the formation of hydrogen bonds.

CONCLUSION

The conformation of the two DMMA ligands in $Mo(CO)_2(DMMA)_2$(PDA) is **d-I** with one ester group of each DMMA lying in the region N-Mo-C and the other in the region N-Mo-N. Intramolecular (interligand) hydrogen bonding between the amino hydrogens and the keto oxygens of the ester group in region N-Mo-C appears to be the driving force in determining the conformation of the DMMA ligand. Although in the bis(alkene) complexes of molybdenum(0) the two trans alkenes are all orthogonal to each other and each eclipses a N-Mo-C vector, the conformation arrangement of these alkene ligands vary greatly with the alkenes and with the chelating nitrogen ligands. Secondary interactions such as hydrogen bonding, interligand interaction[5] and steric repulsion are the main factors determining the alkene conformation.

EXPERIMENTAL SECTION

All experiments were performed under dry nitrogen and all solvents were purified under N_2 by standard methods. ^1H and ^{13}C NMR spectra were recorded on Varian Gemini-300 instruments; infrared spectra were measured on a Bomem MB-100 spectrometer.

Dimethyl maleate, molybdenum hexacarbonyl (Strem), *o*-phenylenediamine (Janssen) were used as purchased. $Mo(CO)_3(CH_3CN)_3$, and *trans*-$Mo(CO)_2(DMMA)_2$(PDA) were prepared according to reported methods.[6] Crystals of $Mo(CO)_2(DMMA)_2$(PDA) suitable for X-ray analysis were grown from a mixture of CH_2Cl_2 and Et_2O.

X-ray Structure Determination of $Mo(CO)_2(DMMA)_2$(PDA)

An orange crystal of dimensions 0.30 × 0.30 × 0.40 mm^3 was selected for X-ray diffraction measurements. Crystal data were collected on an Enraf-Nonius CAD4 dif-

Table 5. Summary of Crystal Data and Data Collection of $Mo(CO)_2(DMMA)_2$(PDA)

Empirical formula	$C_{20}H_{24}MoN_2O_{10}$
Cryst size/mm^3	0.30 × 0.30 × 0.40
Space group	Hexagonal; P_6122
Unit cell dimensions	
a/Å	11.085(5)
b/Å	11.085(5)
c/Å	33.653(21)
γ/deg	120
Volume/$Å^3$	3581(3)
Z	6
Formula weight/g	548.35
Density (calc)/g cm^{-3}	1.526
Abs coeff/mm^{-1}	1.08
F(000)	1967.21
Diffractometer used	Nonius
Radiation	Mo K_α ($\lambda = 0.70930$ Å)
Temp/K	296
2θ range/deg	2.5 - 49.8
Scan mode	θ/2θ
Scan speed/deg min^{-1}	16.48/2 - 16.48/10
Index ranges	$0 \leq h \leq 11, 0 \leq k \leq 6, 0 \leq l \leq 39$
No. of reflns collected	1333 ($758 \geq 2.0\ \sigma(I)$)
No. of uniq reflns	1333
T_{min}/T_{max}	0.964/0.998
Weighting scheme	
Number of parameters refined	151
Goodness of fit	1.31
Final R indices (obs data)	R = 0.031, R_w = 0.028
Largest Δ/σ	0.177
Data-to-param ratio	10.3 : 1
Largest diff peak/hole/e$Å^{-3}$	+0.19/-0.24

fractometer equipped with a graphite-monochromated Mo source (K_α radiation, 0.7093 Å). Summary of crystal data and data collection as listed in Table 5 were determined from the fit of 24 reflections ($18.50 \le 2\theta \le 23.26°$). A total of 1333 reflections were collected, but only 758 unique reflections with $I \ge 2\sigma(I)$ were used for structure solution and refinement. These data were corrected for absorption, Lorentz and polarization effects. Correction for absorption was based on ϕ scans of a few suitable reflections with χ values near 90° (T_{min}, T_{max} = 0.964, 0.998; μ = 1.08 cm^{-1}). The structure was solved using the Patterson-superposition technique and refined by a full-matrix least-squares method based on F values. The final residuals for variables and independent reflections with $I \ge 2\sigma(I)$ were $R = 0.031$, $R_w = 0.028$. The final difference Fourier map had no peak nor hole greater than 0.19 or -0.24 e $Å^{-3}$, respectively. Atomic scattering factors were taken from International Tables for X-ray Crystallography.[12] Crystallographic computations were carried out on a MicroVax III computer using the NRCC-SDP-VAX structure determination package.[13]

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Key Words

Bis(alkene) complex; Molybdenum; Dimethyl maleate; Crystal structure.

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