Synthesis, Structure, and Isomerism of Octahedral Bis(maleate)molybdenum(0) Complexes

Chen-Hsing Lai, Chien-Hong Cheng,* Wen-Ch'ing Chou, and Sue-Lein Wang*

*Department of Chemistry, National Tsing Hua University,
Hsinchu, Taiwan 300, Republic of China*

Received March 30, 1993

Treatment of $Mo(CO)_3(CH_3CN)_3$ in acetonitrile with 1 equiv of *o*-phenylenediamine (PDA) and excess dimethyl maleate (DMMA) at ambient temperature gave *trans*-$Mo(CO)_2(DMMA)_2$-(PDA) (1). There are three possible conformations d-I–d-III for the two trans DMMA ligands in 1. On the basis of the chemical shifts of olefin and methyl protons, the conformation of the DMMA ligands in 1 was determined to be **d-I**. Complexes *trans*-$Mo(CO)_2(DMMA)_2(NN)$ (NN = bpy (2), phen (3)) were synthesized by treating $Mo(CO)_4(NN)$ with excess DMMA in refluxing toluene for 4 h. The conformation of these complexes in solution indicated by NMR data is **d-III**. Complexes 1–3 isomerize to the corresponding *trans*-$Mo(CO)_2(DMMA)(DMFU)(NN)$ (NN = PDA (4), bpy (5), phen (6)) and then to *trans*-$Mo(CO)_2(DMFU)_2(NN)$. There are four possible conformations e-I–e-IV of a *trans*-$Mo(CO)_2(DMMA)(DMFU)(NN)$ complex. The conformation of $Mo(CO)_2(DMMA)(DMFU)(PDA)$ (4) determined by X-ray crystallography was shown to be **e-I**. The same conformation was also observed in solution by NMR spectroscopy. Compound 4 crystallizes in monoclinic space group $P2_1/c$ with cell parameters a = 14.636(3) Å, b = 9.998(3) Å, c = 15.845(6) Å, β = 93.02(1)°, and Z = 4; R = 0.0309 and R_w = 0.0295 for 2552 independent reflections with intensity $\geq 3\sigma(I)$. The low-temperature ^1H NMR spectra of 5 and 6 show that they exist as mixtures of rotamers **e-II** and **e-III** that undergo exchange at ambient temperature. The mechanism for the isomerization of coordinated DMMA to DMFU ligand is discussed.

Introduction

The rotation mechanism and conformations of octahedral *trans*-bis(alkene) complexes of chromium, molybdenum, and tungsten have attracted considerable attention recently.[1-4] Several *trans*-bis(ethylene) complexes of the chromium family have been reported.[5-11] The structure, conformation, and dynamic NMR behavior of bis(alkene) complexes became much more complicated and interesting as the ethylene ligands were replaced by substituted alkenes. Earlier, we successfully prepared a series of bis-(alkene) complexes $Mo(CO)_2(DMFU)_2(NN)$[12] and $Mo(CO)_2(MeMI)_2(NN)$[13] (DMFU = dimethyl fumarate; MeMI = *N*-methylmaleimide; NN = bidentate nitrogen ligand). Due to the prochiral nature of DMFU, two diastereomers

a and b for the bis(DMFU) complexes arising from face selectivity of this ligand were isolated. For the bpy or phen complex, the diastereomer **a** exists as two rotamers

a-I a-II b
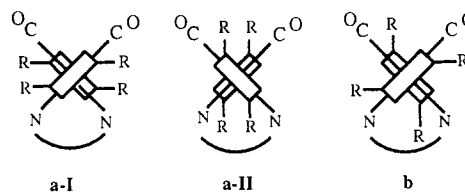
a-I and a-II in thermodynamic equilibrium in solution. Both a and b are fluxional because of the rotation of the DMFU ligands. For the bis(MeMI) complexes, there are three possible rotamers, but only c-I was observed in the solid state and c-I and c-II were detected, with the former as the major species, in solution.

c-I c-II c-III
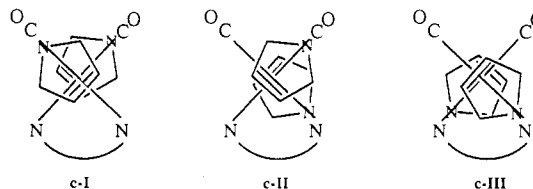
Our continued efforts to understand the structural and conformational properties of bis(alkene) complexes led us to explore the coordination chemistry of dimethyl maleate (DMMA) to the d^6 octahedral molybdenum center. Herein, we report the synthesis, characterization, and isomerization of complexes $Mo(CO)_2(DMMA)_2(NN)$ and $Mo(CO)_2(DMMA)(DMFU)(NN)$. These bis(alkene) complexes exhibit interesting conformational preferences of the DMMA and DMFU ligands that depend greatly on

(1) Bachmann, C.; Demuynck, J.; Veillard, A. *J. Am. Chem. Soc.* 1978, *100*, 2366.

(2) Marcos, E. S.; Caballol, R.; Trinquieer, G.; Bartherlat, J.-C. *J. Chem. Soc., Dalton Trans.* 1987, 2373.

(3) Alvarez, R.; Carmona, E.; Marin, J. M.; Poveda, M. L.; Gutierrez-Puebla, E.; Monge, A. *J. Am. Chem. Soc.* 1986, *108*, 2286.

(4) Chevrier, B.; Diebold, Th.; Weiss, R. *Inorg. Chim. Acta* 1976, *19*, L57.

(5) Carmona, E.; Marin, J. M.; Poveda, M. L.; Atwood, J. L.; Rogers, R. D. *J. Am. Chem. Soc.* 1983, *105*, 3014.

(6) Byrne, J. W.; Blaser, H. U.; Osborn, J. A. *J. Am. Chem. Soc.* 1975, *97*, 3871.

(7) Gregory, M. F.; Jackson, S. A.; Poliakoff, M.; Turner, J. J. *J. Chem. Soc., Chem. Commun.* 1986, 1175.

(8) Carmona, E.; Galindo, A.; Poveda, M. L.; Rogers, R. D. *Inorg. Chem.* 1985, *24*, 4033.

(9) Carmona, E.; Galindo, A.; Marin, J. M.; Gutierrez-Puebla, E.; Monge, A.; Ruiz, C. *Polyhedron* 1988, *7*, 1831.

(10) Grevels, F.-W.; Jacke, J.; Ozkar, S. *J. Am. Chem. Soc.* 1987, *109*, 7536.

(11) Hohmann, F.; Dieck, H. T.; Kruger, C.; Tsay, Y.-H. *J. Organomet. Chem.* 1979, *171*, 353.

(12) Lai, C. H.; Cheng, C. H.; Chou, W. C.; Wang, S. L. *Organometallics* 1993, *12*, 1105.

(13) Lai, C. H.; Cheng, C. H. *Organometallics*, in press.

the bidentate nitrogen ligand. Moreover, they are active catalysts for the isomerization of DMMA to DMFU.[14-21]

Results and Discussion

Mo(CO)₂(DMMA)₂(PDA) (1). Treatment of *fac*-Mo-(CO)₃(CH₃CN)₃ in acetonitrile with 1 equiv of *o*-phenyl-enediamine (PDA) at ambient temperature followed by addition of excess dimethyl maleate gave a yellow product Mo(CO)₂(DMMA)₂(PDA) (1). This complex was characterized by IR and NMR spectra and microanalysis. In the IR spectrum of 1, the absorption pattern with two carbonyl stretching frequencies at 1963 and 1886 cm⁻¹ is similar to that of the previously reported Mo(CO)₂-(DMFU)₂(PDA),[12] indicating a *cis*-dicarbonyl and *trans*-bis(DMMA) structure. The ¹H NMR spectrum consists of two singlets at δ 3.78 and 2.65 for the methoxy groups, two doublets at δ 3.85 and 3.69 for the olefin protons of the DMMA ligands, and a broad signal at δ 7.18 for the phenylene protons in addition to the resonances for the amino protons of the PDA ligand appearing as an AB-type pattern at δ 5.64 and 4.45. There are three possible rotational isomers **d-I**, **d-II**, and **d-III** for *trans*-Mo(CO)₂-

d-I   d-II   d-III

(DMMA)₂(PDA) based on the orthogonal-eclipsed conformational arrangement of the DMMA ligands. From the number of NMR signals observed for the methoxy and olefin protons of 1, structure **d-II** is clearly eliminated. The other two structures **d-I** and **d-III**, which both possess a C_2 symmetry axis bisecting the N–Mo–N and C–Mo–C angles, are consistent with the observed number of signals in the ¹H NMR spectra. In agreement with the proposed structure, the ¹³C NMR spectrum of this isomer shows a pair of signals for carbons of each type in the DMMA ligands and only one carbonyl carbon resonance and three aromatic carbon resonances at δ 222 and δ 138, 129, and 128, respectively. Both ¹H and ¹³C NMR spectra of this compound change insignificantly with decreasing temperature, indicating that the complex is static at ambient temperature.
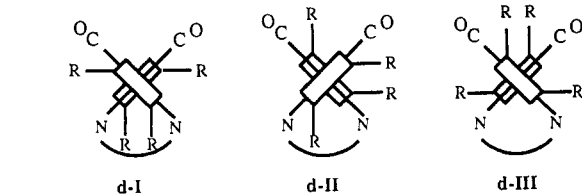
If we view 1 from the top of the plane described by MoN₂(CO)₂, the molecule may be divided into six regions (I, II, II', III, IV, and IV') by the two intersected N–Mo–CO vectors and the vector which bisects the two angles ∠N–Mo–C. The chemical shifts of methoxy and olefin protons provide useful information for the assignment of the conformation of DMMA ligands. In general, for
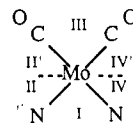
protons of the same type on the alkene ligands, the chemical shifts (ppm relative to TMS) depend greatly on the regions in which they lie and decrease in the order region III > region II' (and IV') > region II (and IV) ≫ region I.[12,13] The resonances of the protons in region I appear at a much higher field than those of the same type in other regions.[22] In view of the observed great difference, more than 1 ppm in chemical shift for the two methoxy resonances (at δ 2.65 and 3.78), and small difference of the two olefin proton signals (at δ 3.69 and 3.85) and the arrangement of the methoxy groups and olefin protons in the two possible conformations **d-I** and **d-III**, the methoxy groups are assigned to be in regions I and II' (and IV') and the olefin protons of the DMMA ligands are in regions II (and IV) and III. Thus, the conformation of 1 is expected to be **d-I**.

Mo(CO)₂(DMMA)₂(bpy) (2) and Mo(CO)₂(DMMA)₂-(phen) (3). These two complexes were obtained by treating the corresponding Mo(CO)₄(NN) (NN = bpy or phen) with excess DMMA in refluxing toluene solution. Similar to complex 1, IR spectra of these two complexes exhibit two characteristic cis carbonyl absorptions, and microanalysis data support the proposed chemical formula. Key information for the conformation of the DMMA ligands was provided by the ¹H NMR spectra of these complexes. At ambient temperature, the ¹H NMR signals for the olefin protons of 2 cannot be seen presumably due to rotation of the alkene ligands. As the temperature decreases to 243 K, the complex becomes static and all its ¹H NMR signals are clearly observed (Figure 1). There are two methoxy resonances at δ 3.73 (s) and 3.30 (s), two olefin proton resonances at δ 3.49 (d) and 1.57 (d), and four resonances in the aromatic region for the bpy ligand. Of the three possible rotamers, both **d-I** and **d-III** are consistent with the number of observed signals in the NMR spectrum. However, from the chemical shift difference of 0.43 and 1.92 ppm for the methoxy and olefin protons, respectively, rotamer **d-III** is strongly favored. The signal at δ 1.57 is assigned to the two olefin protons of DMMA lying in region I, while the other resonance at δ 3.49 is due to the olefin protons in region II'. Of the two methoxy resonances, the one at δ 3.73 is attributed to the two methoxy groups in region III, and the other at δ 3.30 is assigned to the methoxy protons in region II. The ¹³C NMR spectrum of this isomer which shows a pair of signals for the carbons of each type in the DMMA ligands and only one carbonyl carbon and five aromatic carbon resonances at 243 K also supports the proposed conformation. The observed broad signals for the olefin and methoxy protons at temperatures >263 K indicate that at least two rotamers exist in solution, but the ¹H NMR spectra in the slow-exchange limit (<243 K) shows only one measurable rotamer **d-III**. The other isomer(s), most probably **d-II**, is too low in concentration for NMR measurement at low temperature.

The ¹H NMR spectra of 3 are similar to those of complex 2. For example, the olefin proton signals which cannot be clearly seen at room temperature appear at δ 3.58 and 1.47

(14) Okuda, J.; Herberich, G. E. *Organometallics* **1987**, *6*, 2331.

(15) Fachinetti, G.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1979**, *18*, 2282.

(16) Edwards, B. H.; Rogers, R. D.; Sikora, D. J.; Atwood, J. L.; Rausch, M. D. *J. Am. Chem. Soc.* **1983**, *105*, 416.

(17) Schenck, G. O.; Koerner von Gustorf, E.; Jun, M.-J. *Tetrahedron Lett.* **1962**, 1059.

(18) Chicote, M. T.; Green, M.; Spencer, J. L.; Stone, F. G. A.; Vincente, J. *J. Organomet. Chem.* **1977**, *137*, C8.

(19) Padolik, L. L.; Ungv'ary, F.; Wojcicki, A. *J. Organomet. Chem.* **1992**, *424*, 319.

(20) Ungv'ary, F.; Wojcicki, A. *J. Am. Chem. Soc.* **1987**, *109*, 6848.

(21) Bianchini, C.; Mealli, C.; Meli, A.; Peruzzini, M.; Zanobini, F. *J. Am. Chem. Soc.* **1988**, *110*, 8725.

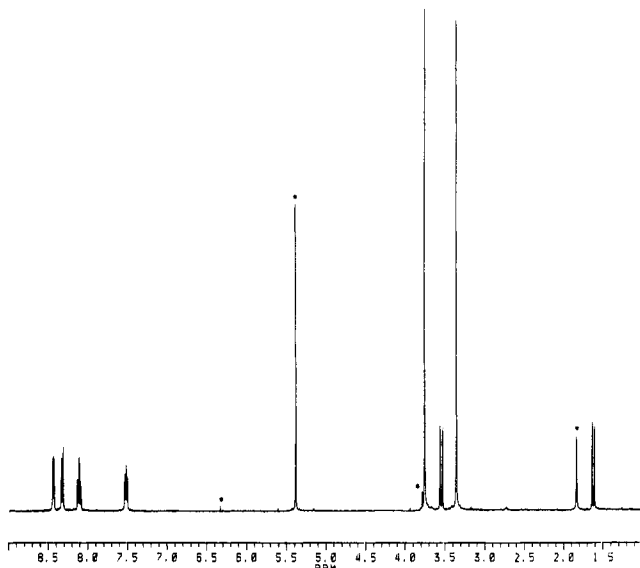(22) Mayr, A.; Dorries, A. M.; Rheingold, A. L.; Geib, S. J. *Organometallics* **1990**, *9*, 964.

Figure 1. ^{1}H NMR spectrum of **2** at 243 K.

at low temperatures. The chemical-shift difference between these two signals is slightly greater than that of complex **2**. Consequently, the same conformation **d-III** is also assigned to complex **3**.

It is interesting to note that various arrangements of the DMMA ligands relative to the MoC$_2$N$_2$ plane are adopted by complexes **1–3**, although the exact driving forces for the selection of these conformations are unknown at the present time. A possible reason for complex **1** to adopt structure **d-I** is the formation of two sterically favored hydrogen bonds between the amino groups and the two ester groups in regions II′ and IV′. A strong evidence for the formation of hydrogen bonds between one hydrogen in each NH$_2$ group and the keto oxygen of an ester group is the observation of two different N–H stretching frequencies at 3164 and 3285 cm^{-1} in the IR spectrum of **1** and two resonances of the amino protons of the PDA ligand that appear as an AB type pattern at δ 5.64 and 4.45. A hydrogen-bonded N–H is expected to appear at a lower stretching frequency (3164 cm^{-1}) and in a lower magnetic field (δ 5.64). Although the other structure **d-III** is also able to form hydrogen bonds between the amino groups and the two ester groups in region II, the bonding is significantly weaker than that in **I** because of the angle strain of hydrogen bonding arising from the eclipsed conformation of DMMA relative to the Mo–N vector. Unlike **1**, there is no hydrogen bonding in complexes **2** and **3**. Under these circumstances, **d-III** is expected to be the most likely conformation of these complexes because the structure avoids possible strong steric repulsion between the ester group(s) and the NN ligand.

Isomerization of Mo(CO)$_2$(DMMA)$_2$(NN). All the present three bis(DMMA) complexes **1–3** are thermally sensitive and undergo isomerization on heating to give the corresponding Mo(DMMA)(DMFU) and then to the bis(DMFU) complexes. For example, Mo(CO)$_2$(DMMA)$_2$-(PDA) (**1**) isomerized to a mixture of Mo(CO)$_2$(DMMA)-(DMFU)(PDA) and Mo(CO)$_2$(DMFU)$_2$(PDA) and then to Mo(CO)$_2$(DMFU)$_2$(PDA) after 4 h in refluxing acetonitrile. A small degree of dissociation of DMMA and DMFU ligands accompanied the isomerization reactions. Pure Mo(CO)$_2$(DMMA)(DMFU)(PDA) (**4**) was isolated from the reaction of excess DMMA and Mo(CO)$_2$(CH$_3$-

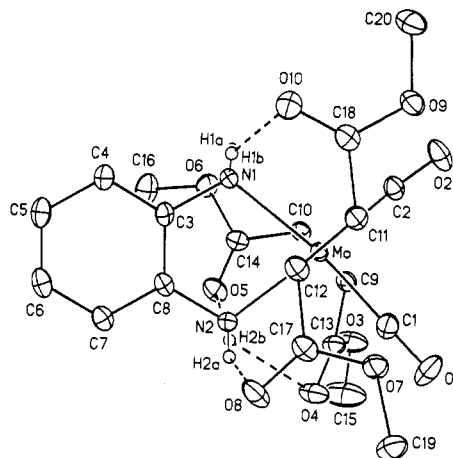**Figure 2.** ORTEP diagram of **4** with atomic numbering scheme.

CN)(PDA) in acetonitrile at 60 °C for 4 h, followed by separation on a silica gel column. Further heating led to complete isomerization and the isolation of Mo(CO)$_2$-(DMFU)$_2$(PDA). Similarly, heating of bpy and phen complexes Mo(CO)$_4$(NN) with DMMA in refluxing toluene for 6 h resulted in isolation of the corresponding Mo(CO)$_2$-(DMMA)(DMFU)(NN) (NN = bpy (**5**) and phen (**6**)). Prolonged heating at the same temperature produced the bis(DMFU) complexes Mo(CO)$_2$(DMFU)$_2$(NN).

X-ray Structure Determination of Mo(CO)$_2$(DM-MA)(DMFU)(PDA) (4). There are four possible rotational isomers **e-I–e-IV** for a Mo(CO)$_2$(DMMA)(DMFU)-(NN) complex. To know the correct conformations of
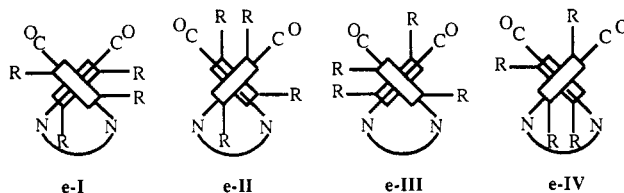
mixed (DMMA)(DMFU) complexes of molybdenum and to establish the relationship of structures with spectra data, we determined the structure of **4** by X-ray diffraction. A single crystal of **4** suitable for X-ray analysis was grown from a mixture of dichloromethane and *n*-hexane. An ORTEP diagram of **4** with atomic numbering is presented in Figure 2; the atomic coordinates are listed in Table I, and important intramolecular bond distances and bond angles are shown in Table II. The results show that complex **4** is distorted octahedral with the two CO groups cis to each other, but each trans to an amino group,[23–25] whereas the DMMA and DMFU ligands are trans to each other and are cis to the CO and PDA ligands. The two alkenes are mutually orthogonal (87.3°), and each alkene ligand eclipses a N–M–C vector (1.8 and 5.4°).

As shown in Figure 2, the DMMA and DMFU ligands are bound to the Mo in a fashion with the two ester groups of DMFU falling in regions II′ and IV and the ester groups of DMMA in regions I and IV′. Three of four keto oxygens O(4), O(5), and O(8) point to the amino group N(2). The other keto oxygen O(10) points to N(1), indicating the

(23) Lain, J. S.; Cheng, C. H.; Cheng, C. Y.; Wang, S. L. *J. Organomet. Chem.* **1990**, *390*, 333.

(24) Lai, C. H.; Cheng, C. H.; Cheng, C. Y.; Wang, S. L. *J. Organomet. Chem.*, in press.

(25) Hsiao, T. Y.; Kuo, P. L.; Lai, C. H.; Cheng, C. H.; Cheng, C. Y.; Wang, S. L. *Organometallics* **1993**, *12*, 1094.

Table I. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Coefficients ($a^2 \times 10^3$) of 4

	x	y	z	U(eq)
Mo	2327(1)	1375(1)	497(1)	32(1)
O(1)	2261(3)	-509(4)	2068(3)	81(2)
O(2)	959(2)	-657(4)	-375(3)	73(1)
O(3)	241(2)	2577(4)	2319(2)	82(2)
O(4)	1743(2)	2531(4)	2574(2)	73(1)
O(5)	1409(2)	4756(3)	1200(2)	61(1)
O(6)	1104(2)	4705(3)	-208(2)	54(1)
O(7)	4234(2)	-801(3)	1372(2)	52(1)
O(8)	4704(2)	1323(3)	1553(2)	61(1)
O(9)	2676(2)	-1322(3)	-1309(2)	57(1)
O(10)	3379(2)	645(3)	-1510(2)	55(1)
N(1)	2672(2)	2775(3)	-571(2)	38(1)
N(2)	3064(2)	3094(3)	1167(2)	40(1)
C(1)	2293(3)	181(5)	1480(3)	53(2)
C(2)	1483(3)	96(5)	-89(3)	46(2)
C(3)	3180(3)	3947(4)	-271(3)	37(1)
C(4)	3465(3)	4897(4)	-835(3)	47(2)
C(5)	3943(3)	6031(4)	-535(3)	55(2)
C(6)	4134(3)	6192(5)	322(3)	53(2)
C(7)	3853(3)	5237(4)	877(3)	46(2)
C(8)	3374(3)	4107(4)	583(3)	38(1)
C(9)	1060(3)	1834(5)	1221(3)	43(2)
C(10)	1065(3)	2687(4)	508(3)	39(1)
C(11)	3237(3)	-212(4)	-113(3)	43(2)
C(12)	3800(3)	756(5)	324(3)	45(2)
C(13)	1089(3)	2365(5)	2101(3)	50(2)
C(14)	1215(3)	4131(5)	563(3)	44(2)
C(15)	133(4)	3059(9)	3157(4)	136(4)
C(16)	1262(4)	6135(5)	-237(4)	76(3)
C(17)	4297(3)	487(5)	1134(3)	45(2)
C(18)	3123(3)	-224(5)	-1041(3)	47(2)
C(19)	4625(3)	-1143(5)	2196(3)	63(2)
C(20)	2401(4)	-1374(6)	-2195(3)	82(2)

Table II. Important Bond Distances (Å) and Angles (deg) of 4

Distances

Mo–N(1)	2.273(3)	Mo–N(2)	2.264(3)
Mo–C(1)	1.964(5)	Mo–C(2)	1.975(4)
Mo–C(9)	2.278(4)	Mo–C(10)	2.266(4)
Mo–C(11)	2.316(4)	Mo–C(12)	2.275(4)
O(1)–C(1)	1.163(6)	O(2)–C(2)	1.151(6)
C(9)–C(10)	1.416(6)	C(9)–C(13)	1.490(6)
C(10)–C(14)	1.463(6)	C(11)–C(12)	1.427(6)
C(11)–C(18)	1.471(6)	C(12)–C(17)	1.465(6)

Angles

N(1)–Mo–N(2)	76.2(1)	N(1)–Mo–C(1)	168.5(2)
N(2)–Mo–C(1)	96.9(2)	N(1)–Mo–C(2)	101.9(2)
N(2)–Mo–C(2)	169.3(2)	C(1)–Mo–C(2)	86.4(2)
N(1)–Mo–C(9)	118.0(1)	N(2)–Mo–C(9)	89.5(1)
C(1)–Mo–C(9)	70.6(2)	C(2)–Mo–C(9)	82.1(2)
N(1)–Mo–C(10)	82.1(1)	N(2)–Mo–C(10)	85.7(1)
C(1)–Mo–C(10)	107.0(2)	C(2)–Mo–C(10)	83.6(2)
C(9)–Mo–C(10)	36.3(2)	N(1)–Mo–C(11)	87.5(1)
N(2)–Mo–C(11)	116.5(1)	C(1)–Mo–C(11)	87.3(2)
C(2)–Mo–C(11)	73.7(2)	C(9)–Mo–C(11)	148.2(2)
C(10)–Mo–C(11)	152.5(1)	N(1)–Mo–C(12)	80.1(1)
N(2)–Mo–C(12)	80.3(1)	C(1)–Mo–C(12)	89.6(2)
C(2)–Mo–C(12)	109.9(2)	C(9)–Mo–C(12)	156.6(2)
C(10)–Mo–C(12)	159.5(2)	C(11)–Mo–C(12)	36.2(2)
Mo–N(1)–C(3)	112.5(3)	Mo–N(2)–C(8)	112.7(3)
Mo–C(1)–O(1)	178.7(4)	Mo–C(2)–O(2)	175.0(4)
Mo–C(9)–C(10)	71.4(2)	Mo–C(9)–C(13)	124.0(3)
Mo–C(10)–C(9)	72.3(2)	Mo–C(10)–C(14)	116.9(3)
Mo–C(11)–C(12)	70.3(2)	Mo–C(11)–C(18)	112.7(3)
Mo–C(12)–C(11)	73.5(2)	Mo–C(12)–C(17)	112.0(3)
C(10)–C(9)–C(13)	122.1(4)	C(9)–C(10)–C(14)	123.6(4)
C(12)–C(11)–C(18)	121.5(4)	C(11)–C(12)–C(17)	123.2(4)

formation of hydrogen bonds between the ester groups and the amino protons. The distances 2.820, 3.074, 2.942, and 3.017 Å between O(10) and N(1), O(4) and N(2), O(5) and N(2), and O(8) and N(2), respectively, are all within the range of hydrogen-bond interaction. From the ORTEP

drawing in Figure 2 and the bond distances, it is clear that both keto oxygens O(5) and O(8) of the DMMA ligand are bound to the amino hydrogen H(2b). Hydrogen bonding is expected to be the major driving force in determining the conformation of the complex. According to this X-ray evidence, the conformation of this complex in the solid state is **e-I**. Significant variations of the bond distance from the molybdenum center to one of the olefin carbons are observed. The average distance for the DMMA (2.272 Å) is shorter than that (2.296 Å) for the DMFU ligand. In general, cis alkenes form stronger alkene–metal bonds than trans alkenes.[26] For each alkene ligand of 4, the olefin carbon adjacent to a coordinated amino group is closer to the metal than the olefin carbon adjacent to a carbonyl group. Competition between the π^* orbitals of carbonyl and alkene ligands for the d_π electrons of molybdenum(0) reduces the back-donation from metal to the olefin carbon adjacent to the carbonyl group and weakens this metal–olefin carbon bond. Similar results were observed in other *trans*-bis(alkene) complexes of molybdenum(0).[12,13] The difference in bond length between the two olefin carbon–palladium bonds for each alkene ligand is greater for DMFU than for DMMA. While the exact cause for this difference is not clear, hydrogen bonding between the ester groups and the amino protons in 4 is expected to have a significant effect on the fine adjustment of the olefin carbon–molybdenum bond distances.

Conformations of Mo(CO)₂(DMMA)(DMFU)(NN) in Solution. The ¹H NMR spectrum of 4 reveals the presence of four types of olefin and four types of methoxy protons. The resonances at δ 4.17 (d) and 2.50 (d) are assigned to the olefin protons of the DMFU ligand in regions III and I, respectively, while the resonances at δ 3.88 (d) and 3.57 (d) are attributed to the olefin protons of the DMMA ligand in regions II and III, respectively. The assignments were further verified in a proton decoupling experiment which indicates that the proton at δ 4.17 couples with that at δ 2.50. It is interesting to note that the proton resonances of DMMA and DMFU ligands in this complex are very close to the corresponding signals in complexes Mo(CO)₂(DMMA)₂(PDA) (1) (at δ 3.85 and 3.69) and one diastereomer of Mo(CO)₂(DMFU)₂(PDA) (7) with conformation **a-I** (at δ 4.11 and 2.52). The results indicate that the conformations of DMMA and DMFU ligands in 4 are similar to those of the corresponding ligands in 1 and in 7. On the basis of these assignments of the olefin protons, the conformation of complexes 4 in solution is **e-I**, the same as that in the solid state. The exact regions of the methoxy protons based on their resonances at δ 3.78, 3.75, 3.70, and 2.79 are less certain. However, it is clear that there is only one methoxy group (at δ 2.79) in region I in agreement with the conformational assignments on the basis of the olefin proton resonances. The ¹H NMR spectra of 4 do not change with temperature, indicating the complex is static at ambient temperature.

The ¹H NMR spectra of 5 is temperature dependent. At ambient temperature, the signals are broad and are not useful for structural assignment. As temperature decreased, the broad signals coalesced and each split into several resonances. At 200 K, the slow-exchange limit of 5 is reached. The complicated spectrum consisted of signals in two sets corresponding to two rotational isomers **e-II** and **e-III** (Figure 3). The key to the assignments is the presence of three olefin resonances at δ 1.36, 1.57, and
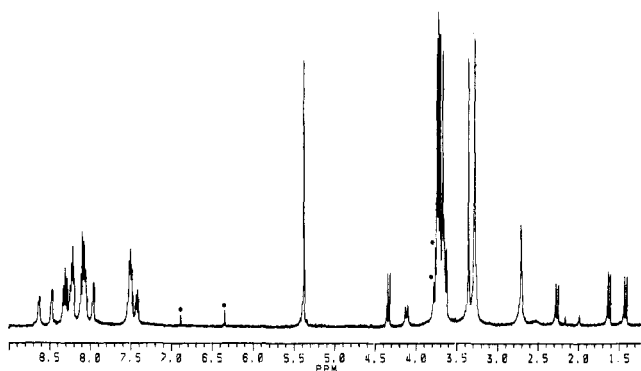
(26) Hartley, F. R. *Chem. Rev.* 1973, 73, 163.

Figure 3. ^{1}H NMR spectrum of **5** at 200 K.

2.21 and a methoxy resonance at δ 2.65. These olefin and methoxy protons all lie in region I in which the protons appear at much higher field than those of the same type in other regions. The fact of only one such methoxy resonance indicates that e-III and one of e-I and e-II are the two conformers of **5**. According to the conformations of e-I–e-IV, no methoxy resonance would appear in the range δ 3.0–2.0 for e-III, while one methoxy resonance would appear in this range for e-I or e-II. Structure e-IV is excluded as one of the conformational isomers, because its ^{1}H NMR would exhibit two upfield methoxy resonances. Of the three olefin signals, the one at δ 2.21 is assigned to a proton of DMFU, while those at δ 1.36 and 1.57 are attributed to the protons of DMMA on the basis of a close comparison of the present resonances with those of Mo-$(CO)_2(DMFU)_2(bpy)$ **(8)** and Mo$(CO)_2(DMMA)_2(bpy)$. The signals of two DMMA olefin protons at δ 1.36 and 1.57 eliminate e-I as one possible conformational isomer of **5** in view of the fact that there is one olefin proton of e-III and no olefin proton of e-I which lies in region I. The resonances at δ 4.28 and 4.06 are characteristic of the olefin protons in regions III and in region IV' of the coordinated DMFU ligands. From decoupling experiments, we established that the olefin protons corresponding to the resonances at δ 4.28 and 2.21 are on the same alkene ligand and are assigned to conformer e-III. On the basis of these analyses, only the presence of conformational isomers e-II and e-III in solution accounts for the observed ^{1}H NMR spectrum of **5** at 200 K.

Careful examination of the conformations of (DMMA)-(DMFU), bis(DMMA), and bis(DMFU) complexes reveals intriguing correlation among these species. For phenylenediamine complexes, the respective conformations of DMMA and DMFU ligands in the (DMMA)(DMFU) species are the same as those in the bis(DMMA) and in the bis(DMFU) complexes (conformation **a**). The isomerization of complex **1** to **4** formally results from a rotation by 180° of a CHCOOMe group in region I of **1** about the axis of the coordinated carbon–carbon double bond. Further rotation of the CHCOOMe group in region I or IV' of **4** leads to the formation of bis(DMFU) products **7a** and **7b** (eq 1). Similar correlation is observed for the bpy

(1)
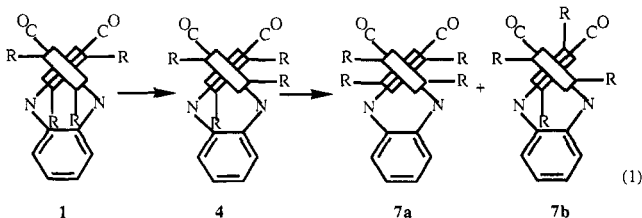
complexes; the conformations of DMMA and DMFU ligands in the mixed-ligand complex **5** are the same as those in the corresponding bis(DMMA) **2** and bis(DMFU) complexes. The rotation of one CHCOOMe of **2** in region II or III by 180° leads to the formation of complex **5** with the expected conformations, e-II and e-III (eq 2). It is interesting to note that in both **2** and **5** the DMMA ligands are arranged so that no ester group lies in region I.


(2)
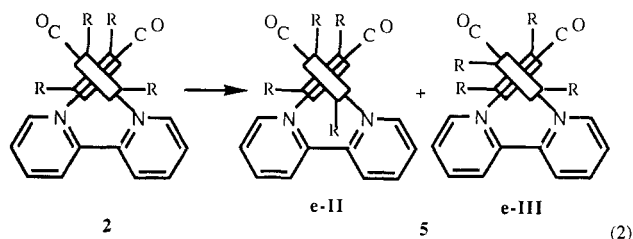
Catalytic Isomerization of Maleate to Fumarate. Dimethyl maleate isomerizes to dimethyl fumarate in the presence of bis(alkene) complexes. In a typical reaction, **2** (0.2 mmol) and DMMA (2 mmol) in toluene (20 mL) were refluxed for 5 h. All DMMA isomerized with an average rate exceeding 4.0 turnovers/h. When complex **1** or Mo$(CO)_2(DMFU)_2(en)$ was employed as the catalyst, and the isomerization reaction was carried out in refluxing CH_3CN, the reaction rates were 0.30 and 0.18 turnovers/ h, respectively. Bis(DMFU) complexes also isomerize DMMA to DMFU catalytically. Under similar conditions, the rates of isomerization in refluxing toluene were 2.51 and 0.25 for Mo$(CO)_2(DMFU)_2(bpy)$ **(8)** and Mo$(CO)_2$-$(DMFU)_2(phen)$ **(9)**, respectively. The apparently slower rate of isomerization for **9** is due to the low solubility in toluene of this species which was not entirely soluble at the concentration used for catalytic reaction. In refluxing acetonitrile in which both **8** and **9** are soluble, the isomerization rates were 0.27 and 0.25, respectively. It is noteworthy that free ethylenediamine catalyzes the isomerization of DMMA to DMFU rapidly at ambient temperature. This prevents the isolation of complexes such as Mo$(CO)_2(DMMA)_2(en)$ or Mo$(CO)_2(DMMA)(DMFU)(en)$ from the reaction of Mo$(CO)_3(en)_2$ and DMMA. In contrast, free bpy and phen do not convert DMMA to DMFU even in refluxing toluene.

**Mechanisms for the Isomerization of Mo$(CO)_2$-$(DMMA)_2(NN)$ to Mo$(CO)_2(DMFU)_2(NN)$ and for the Catalytic Isomerization of DMMA to DMFU.** For the catalytic isomerization of dimethyl maleate to dimethyl fumarate, we propose two pathways for the isomerization from bis(DMMA) complexes to bis(DMFU) complexes. One is that free dimethyl maleate first isomerizes to dimethyl fumarate; the dimethyl fumarate in solution then replaces a coordinated dimethyl maleate in Mo$(CO)_2$-$(DMMA)_2(NN)$ to give the mixed alkene complex Mo-$(CO)_2(DMFU)(DMMA)(NN)$; further substitution of coordinated dimethyl maleate by free dimethyl fumarate leads to the formation of bis(DMFU) species. The second possible route involves direct isomerization of DMMA to DMFU on Mo$(CO)_2(DMMA)_2(NN)$ and Mo$(CO)_2(DMFU)$-$(DMMA)(NN)$ to yield the corresponding complexes Mo-$(CO)_2(DMFU)(DMMA)(NN)$ and Mo$(CO)_2(DMFU)_2$-(NN). Substitution of coordinated DMFU in the latter two species by DMMA would lead to catalytic conversion of DMMA to DMFU.

Since en rapidly catalyzes the isomerization of free DMMA to DMFU, the first mechanism is expected be the
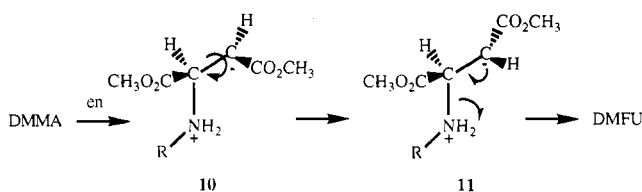
Scheme I

Scheme II
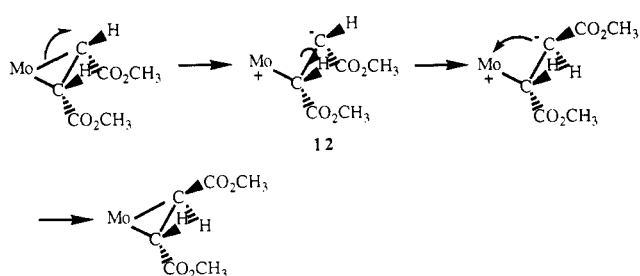
dominant pathway for isomerization of free or coordinated DMMA in the presence of free en. Amine catalyzed isomerization of maleate to fumarate is known in the literature;[27] its intimate mechanism involves the addition of amine to the carbon–carbon double bond on the maleate group to give the intermediate 10, rotation of the resulting carbon–carbon single bond in 11, and elimination of amine to yield the fumarate product (Scheme I).

As indicated in the foregoing studies, $Mo(CO)_2(DMMA)_2(NN)$ and $Mo(CO)_2(DMFU)_2(NN)$ (NN = bpy and phen) are able to catalyze the isomerization of DMMA to DMFU, although the rates are slower compared to those catalyzed by en (*vide supra*). Since bpy and phen do not catalyze the isomerization of DMMA to DMFU, the possibility that a trace of NN is responsible for the isomerization is ruled out. Thus, the isomerization occurs on the metal center and the second mechanism operates under these conditions. This mechanism is further supported by the observations that heating 2 and 5 equiv of free DMMA at refluxing toluene solution for 1 h led to the conversion of one-third of the bis(DMMA) complex 2 to the (DMMA)(DMFU) species 5, with no detectable isomerization of free DMMA to DMFU. The results of the experiment strongly suggest that isomerization first occurs on coordinated DMMA. Regarding the intimate mechanism of this metal complex catalyzed isomerization, we propose the formation of a charge separated intermediate (or transition state) 12 from a DMMA complex. This intermediate then undergoes rotation about the carbon–carbon bond and reductive elimination to give a π-coordinated DMFU species (Scheme II). In principle, this mechanism is similar to that of the amine-catalyzed reaction. Transition metal catalyzed isomerization of maleate to fumarate was reported previously, and mechanisms involving metal hydrides as active species were proposed.[28]

We have demonstrated that *trans*-bis(DMMA) complexes of molybdenum may be synthesized. The ^{1}H NMR spectral data provide key information in the assignment of the conformations of the DMMA ligands. In principle, there are three possible conformations d-I–d-III for a *trans*-bis(DMMA) complex. For the PDA complex 1 the

conformation is d-I, but for the bpy and phen complexes the stable conformation is d-III. Hydrogen bonding between the DMMA ligand and the amino group in the PDA ligand is believed to play an important role in determining the conformation. Heating the bis(DMMA) complexes led to the isolation of (DMMA)(DMFU) complexes. There are four possible conformations e-I–e-IV for a mixed (DMMA)(DMFU) complex. The stable conformation for the PDA complex 4 in both the solid state and solution is e-I. On the other hand, two conformations e-II and e-III of the bpy complex 5 exist in solution. All mixed (DMMA)(DMFU) complexes undergo further isomerization of the DMMA ligand to yield the corresponding bis(DMFU) complexes.

Experimental Section

All experiments were performed under dry nitrogen, and all solvents were purified under N_2 by standard methods. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AM-400 and Varian Gemini-300 instruments; infrared spectra were measured on a Bomem MB-100 spectrometer. Elemental analyses were performed on a Heraeus CHN-O-Rapid instrument. For X-ray structure determination a Siemens R3m/V diffractometer was used.

Dimethyl maleate, 2,2′-bipyridine, 1,10-phenanthroline, ethylenediamine (Merck), molybdenum hexacarbonyl (Strem), and 1,2-phenylenediamine (Janssen) were used as purchased. $Mo(CO)_3(CH_3CN)_3$,[29] $Mo(CO)_4(bpy)$, and $Mo(CO)_4(phen)$[30] were prepared according to reported methods.

Synthesis of $Mo(CO)_2(DMMA)_2(PDA)$ (1). To $Mo(CO)_3$-$(CH_3CN)_3$ (0.50 g, 1.65 mmol) in CH_3CN (20 mL) was added PDA (0.18 g, 1.67 mmol) to give $Mo(CO)_3(CH_3CN)(PDA)$. After removal of the solvent on a vacuum pump, dimethyl maleate (2 mL) was added to the residue. The mixture was stirred for 20 min and was then put aside for 12 h to give a yellow crystalline material in 65% yield (0.59 g). ^{1}H NMR ($CDCl_3$): δ 7.18 (b, 4 H, Ph), 5.64 (d, J = 12.6 Hz, 2 H, NH), 4.45 (d, J = 12.6 Hz, 2 H, NH), 3.85 (d, J = 11.4 Hz, 2 H, =CH), 3.78 (s, 3 H, OCH_3), 3.69 (d, J = 11.4 Hz, 2 H, =CH), 2.65 (s, 3 H, OCH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 221.69 (C≡O), 175.06, 172.43 (COO), 137.84, 128.77, 127.78 (Ph), 54.81, 48.33 (C=C), 52.19, 50.65 (OCH_3). IR (KBr): 3285, 3164 ($\nu(NH_2)$), 1963, 1886 ($\nu(C≡O)$), 1724, 1696 cm^{-1} ($\nu(COO)$). Anal. Calcd for $MoC_{20}H_{24}N_2O_{10}$: C, 43.80; H, 4.38; N, 5.11. Found: C, 43.63; H, 4.42; N, 5.12.

Synthesis of $Mo(CO)_2(DMMA)_2(bpy)$ (2). To $Mo(CO)_4$-(bpy) (0.70 g, 1.92 mmol) in toluene (10 mL) was added dimethyl maleate (2 mL). The solution was refluxed for 4 h to yield an orange precipitate. Collection of the precipitate and recrystallization from CH_2Cl_2/THF gave the desired orange crystals in 56% yield (0.64 g). The solution consists of a mixture of Mo-$(CO)_2(DMFU)(DMMA)(bpy)$ and $Mo(CO)_2(DMMA)_2(bpy)$. ^{1}H NMR of 2 ($CDCl_3$, 294 K): δ 8.55 (br, 2 H, H-3,3′ of bpy), 8.22 (d, J = 8.1 Hz, 2 H, H-6,6′ of bpy), 8.03 (dd, J = 8.1 Hz, J = 6.7 Hz, 2 H, H-5,5′ of bpy), 7.47 (dd, J = 6.7 Hz, J = 4.5 Hz, 2 H, H-4,4′ of bpy), 3.75 (s, 6 H, OCH_3), 3.42 (br, 8 H, OCH_3, =CH), 1.72 (br, 2 H, =CH). ^{1}H NMR (CD_2Cl_2, 243 K): δ 8.55 (br, 2 H, H-3,3′ of bpy), 8.25 (d, J = 8.1 Hz, 2 H, H-6,6′ of bpy), 8.04 (dd, J = 8.1 Hz, J = 6.6 Hz, 2 H, H-5,5′ of bpy), 7.48 (dd, J = 6.6 Hz, J = 4.5 Hz, 2 H, H-4,4′ of bpy), 3.73 (s, 6 H, OCH_3), 3.49 (d, J = 11.4 Hz, 2 H, =CH), 3.30 (s, 6 H, OCH_3), 1.57 (d, J = 11.4 Hz, 2 H, =CH). ^{13}C{^{1}H} NMR ($CDCl_3$, 294 K): δ 223.55 (C≡O), 172.74, 172.60 (COO), 153.56, 153.36, 138.46, 126.06, 122.90 (bpy), 61.78, 61.67 (C=C), 51.68, 50.72 (OCH_3). IR (KBr): 1967, 1891 ($\nu(C≡O)$), 1738, 1692 cm^{-1} ($\nu(COO)$). Anal. Calcd for $MoC_{24}H_{24}N_2O_{10}$: C, 48.33; H, 4.06; N, 4.71. Found: C, 48.18; H, 4.07; N, 4.69.

(27) Milovskaya, E. B.; Sokolova, O. V.; Erusalimskii. *Zh. Obshch. Khim.* **1962**, *32*, 621.
(28) Manuel, T. A. *J. Org. Chem.* **1962**, *27*, 3941.

(29) Tate, O. P.; Knipple, W. R.; Augl, J. M. *Inorg. Chem.* **1962**, *1*, 433.
(30) Stiddard, M. H. B. *J. Chem. Soc.* **1962**, 4712.

Synthesis of Mo(CO)₂(DMMA)₂(phen) (3). The title compound was prepared in 73% yield by following a procedure similar to that described for 2. ¹H NMR (CDCl₃, 294 K): δ 8.91, 8.79 (br, H-4,7 of phen), 8.48, 8.46 (br, H-2,9 of phen), 8.00, 7.98 (br, H-5,6 of phen), 7.78 (m, H-4,7 of phen), 3.74, 3.52, 2.87 (16 H, OCH₃, ═CH). ¹H NMR (CDCl₃, 233 K): δ 8.74 (d, *J* = 4.4 Hz, 2 H, H-4,7 of phen), 8.55 (d, *J* = 8.2 Hz, 2 H, H-2,9 of phen), 8.06 (s, 2 H, H-5,6 of phen), 7.78 (dd, *J* = 8.2 Hz, *J* = 5.2 Hz, 2 H, H-4,7 of phen), 3.69 (s, 6 H, OCH₃), 3.26 (s, 6 H, OCH₃), 3.58 (d, *J* = 11.4 Hz, 2 H, ═CH), 1.47 (d, 2 H, 11.4 Hz, ═CH). ¹³C{¹H} NMR (CDCl₃, 233 K): δ 222.78 (C═O), 172.55, 172.33 (COO), 152.44, 143.86, 137.62, 130.19, 127.79, 124.64 (phen), 61.77, 58.38 (C═C), 52.40, 51.03 (OCH₃). IR (KBr): 1974, 1899 (ν(C═O)), 1734, 1698 cm⁻¹ (ν(COO)). Anal. Calcd for MoC₂₈H₂₄N₂O₁₀: C, 50.33; H, 3.90; N, 4.52. Found: C, 49.75; H, 3.85; N, 4.55.

Synthesis of Mo(CO)₂(DMMA)(DMFU)(PDA) (4). To Mo(CO)₃(CH₃CN)₃ (0.50 g, 1.65 mmol) in CH₃CN (20 mL) was added PDA (0.18 g, 1.65 mmol) to give Mo(CO)₃(CH₃CN)(PDA). Addition of excess dimethyl maleate (2 mL) was followed by stirring of the solution at 60 °C for 4 h. The solvent was then removed on a rotary evaporator, and the residue was separated on a silica gel column. The column was first eluted with CH₂Cl₂ to give a yellow band consisting of Mo(CO)₂(DMFU)₂(PDA). Further elution of the column with a mixture of CH₂Cl₂ and EA (v/v = 1/1) afforded the crude product Mo(CO)₂(DMMA)-(DMFU)(PDA). Evaporation of the solvent, followed by recrystallization from CH₂Cl₂/hexane gave the desired yellow crystalline product in 53% yield (0.48 g). ¹H NMR (CDCl₃): 7.23 (m, 4 H, Ph), 5.43 (d, *J* = 12.9 Hz, 1 H, NH), 5.34 (d, *J* = 12.6 Hz, 1 H, NH), 4.66 (d, *J* = 12.9 Hz, 1 H, NH), 4.39 (d, *J* = 12.6 Hz, 1 H, NH), 4.17 (d, *J* = 11.4 Hz, 1 H, ═CH), 3.88 (d, *J* = 11.4 Hz, 1 H, ═CH), 3.57 (d, *J* = 11.4 Hz, 1 H, ═CH), 2.50 (d, *J* = 11.4 Hz, 1 H, ═CH), 3.78 (s, 3 H, OCH₃), 3.75 (s, 3 H, OCH₃), 3.70 (s, 3 H, OCH₃), 2.79 (s, 3 H, OCH₃). ¹³C{¹H} NMR (CDCl₃): δ 221.549, 219.411 (C═O), 178.50, 174.18, 174.16, 172.05 (COO), 138.19, 136.49, 129.10, 128.38, 127.91, 127.85 (Ph), 55.84, 50.44, 49.23 (C═C), 52.03, 51.13, 50.87, 52.07 (OCH₃). IR (KBr): 3294, 3261, 3192, 3157 (ν(NH₂)), 1970 (s), 1898 (s) (ν(C═O)), 1713, 1664 cm⁻¹ (ν(COO)). Anal. Calcd for MoC₂₀H₁₆N₂O₁₀: C, 43.80; H, 4.38; N, 5.11. Found: C, 43.66; H, 4.43; N, 5.06.

Synthesis of Mo(CO)₂(DMMA)(DMFU)(bpy) (5). To Mo(CO)₄(bpy) (0.50 g, 1.37 mmol) in toluene (10 mL) was added dimethyl maleate (1.5 mL). The solution was refluxed for 6 h. Orange material containing both Mo(CO)₂(DMMA)(DMFU)-(bpy) and Mo(CO)₂(DMFU)₂(bpy) gradually precipitated during this refluxing period. Collection of the orange solid, followed by fractional crystallization in CH₂Cl₂/Et₂O afforded the desired orange crystalline material 5 in 73% yield (0.60 g). The bis-(DMFU) complex remained in the solution. ¹H NMR (CD₂Cl₂, 294 K): δ 8.37 (d, *J* = 4.4 Hz, 2 H, H-3,3′ of bpy), 8.20 (d, *J* = 7.9 Hz, 2 H, H-6,6′ of bpy), 8.01 (m, 2 H, H-5,5′ of bpy), 7.44 (m, 2 H, H-4,4′ of bpy), 3.97, 3.66, 3.52, 3.50, 3.03 (16 H, OCH₃, ═CH). ¹³C{¹H} NMR (CDCl₃, 294 K): δ 222.41, 221.63 (C═O), 174.47, 173.24, 172.08, 171.93 (COO), 154.14, 152.70, 137.93, 125.98, 125.21, 122.18 (bpy), 62.12, 61.08 (C═C), 51.44, 50.66 (OCH₃). IR (KBr): 1973, 1896 (ν(C═O)), 1730, 1694 cm⁻¹ (ν(COO)). Anal. Calcd for MoC₂₄H₂₄N₂O₁₀: C, 48.33; H, 4.06; N, 4.71. Found: C, 47.93; H, 4.04; N, 4.71.

Synthesis of Mo(CO)₂(DMMA)(DMFU)(phen) (6). The title compound was prepared in 93% yield following a procedure similar to that described for 5. ¹H NMR (CD₂Cl₂, 294 K): δ 8.91, 8.77 (br, H-4,7 of phen), 8.50 (H-2,9 of phen), 7.99 (H-5,7 of phen), 7.78 (m, H-4,7 of phen), 4.05, 3.68, 3.62, 3.48, 3.19, 2.77 (16 H, OCH₃, ═CH). ¹³C{¹H} NMR (CD₂Cl₂, 294 K): δ 222.49, 221.72 (C═O), 174.50, 173.18, 172.32, 172.13, 171.99 (COO), 154.13, 152.69, 144.49, 144.34, 144.17, 137.23, 137.08, 137.03, 130.23, 130.08, 130.03, 129.70, 127.48, 127.31, 124.76, 124.59, 124.20 (phen), 61.52 (C═C), 51.80, 51.30, 50.81, 50.24 (OCH₃). IR (KBr): 1978, 1892 (ν(C═O)), 1728, 1692 (ν(COO)). Anal. Calcd for MoC₂₀H₁₆N₂O₁₀: C, 50.33; H, 3.90; N, 4.52. Found: C, 49.77; H, 3.90; N, 4.59.

Table III. Summary of Crystal Data and Intensity Collection of 4

empirical formula	MOC₂₀H₂₄N₂O₁₀
fw	548.4
cryst size, mm³	0.44 × 0.35 × 0.32
space group	*P*2₁/*c*; monoclinic
unit cell dimens	
a, Å	14.636(3)
b, Å	9.998(3)
c, Å	15.845(6)
β, deg	93.02(1)
vol, Å³	2315.5(7)
Z	4
density (calc), g cm⁻³	1.567
abs coeff, mm⁻¹	0.606
F(000)	1120
temp, K	296
2θ range, deg	2.5–50.0
scan type	θ/2θ
scan speed, deg min⁻¹	variable; 2.93–14.65 in ω
scan range (ω), deg	1.00 plus Kα separation
index ranges	$-17 \le h \le 17, 0 \le k \le 11$, $0 \le l \le 17$
no. of reflns collcd	4781 (3008 > 3.0σ(I))
no. of indep reflns	4092 (2552 > 3.0σ(*I*))
final *R* indices (obs data)	*R* = 0.0309, *R*ᵥ = 0.0295
goodness of fit	1.08
largest diff peak/hole, e Å⁻³	+0.26/−0.27

Synthesis of Mo(CO)₂(DMFU)₂(PDA) (7). To Mo(CO)₃-(CH₃CN)₃ (0.30 g, 0.99 mmol) in CH₃CN (20 mL) was added PDA (0.11 g, 0.99 mmol) to give Mo(CO)₃(CH₃CN)(PDA). Addition of dimethyl maleate (0.57 g, 3.96 mmol) to the solution was followed by stirring at refluxing temperature for 4 h. The solvent was removed, and the residue was separated on a silica gel column using methylene chloride as eluent to give 7a. Further elution with a mixture of methylene chloride and ethyl acetate afforded 7b. The total yield was 43% yield (0.27 g). The ratio of 7a to 7b was similar to that from direct reaction of Mo(CO)₃-(CH₃CN)(PDA) with DMFU.

Synthesis of Mo(CO)₂(DMFU)₂(bpy) (8). To Mo(CO)₄-(bpy) (0.20 g, 0.55 mmol) in 20 mL of toluene was added dimethyl maleate (0.32 g, 2.22 mmol). The solution was refluxed for 8 h. During the period of reflux, a yellow precipitate appeared. The precipitate was filtered out and washed with diethyl ether to give isomer 8b in 52% yield. The filtrate was evacuated to remove the solvent, and the residue was passed through a silica gel column using CH₂Cl₂/THF as eluent. Collection of the desired yellow band followed by solvent removal gave a mixture of 8a and 8b in the ratio 1:1.3. The total yield of 8 was 89% (0.29 g).

Synthesis of Mo(CO)₂(DMFU)₂(phen) (9). To Mo(CO)₄-(phen) (0.20 g, 0.52 mmol) in toluene (20 mL) was added dimethyl maleate (0.30 g, 2.06 mmol). The solution was refluxed for 8 h. The precipitate formed during this period was filtered out and washed with diethyl ether to give isomer 9a as a yellow material in 84% yield. The filtrate was evacuated to remove the solvent, and the residue was passed through a silica gel column using CH₂Cl₂/THF as the eluent. Collection of the desired yellow band followed by solvent removal gave a mixture of 9a and 9b in the ratio 1:1.7. The total yield of 9 was 90%.

X-ray Structure Determination of Mo(CO)₂(DMMA)-(DMFU)(PDA) (4). An orange crystal of dimensions 0.44 × 0.35 × 0.32 mm³ was selected for X-ray diffraction. Data were collected on a Siemens R3m/V diffractometer equipped with a graphite-monochromated Mo source (Kα radiation, 0.7107 Å). Cell parameters were determined from the fit of 15 reflections (10.53 ≤ 2θ ≤ 26.28°). The important parameters of this data collection are presented in Table III. No significant variation in intensities of three standards monitored every 50 reflections occurred. A total of 4781 reflections were collected, but only 2552 unique reflections with *I* ≥ 3σ(*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 = 0.779, 0.856; μ = 6.06 cm⁻¹). Systematic

absences were ($h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$). The structure was solved using the Patterson-superposition technique and refined by a full-matrix least-squares method based on F values. All non-hydrogen atoms were refined anisotropically and hydrogen atoms included in the refinement were calculated with C–H = 0.96 Å, C–C–H = 109.4°, and a U value of 0.08 Å². The final residuals for variables and independent reflections with $I \geq 3\sigma(I)$ were $R = 0.0330$, $R_w = 0.0325$. The final difference Fourier map had no peak greater than 0.47 e Å⁻³. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). All calculations were performed on a Micro VAX II computer system using SHELXTL-Plus programs.

Supplementary Material Available: Tables of complete bond distances and angles, thermal parameters and calculated hydrogen positions for 4 (4 pages). Ordering information is given on any current masthead page.

OM930206R