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Synthesis, Structure, and Properties of Octahedral d^6 Bis(alkene) Complexes of Molybdenum

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$Mo(CO)_3(CH_3CN)(NN)$ obtained by treating $Mo(CO)_3(CH_3CN)_3$ with 1 equiv of bidentate nitrogen ligand (NN) reacts with excess DMFU (dimethyl fumarate) to give $Mo(CO)_2(NN)(DMFU)_2$ (NN = *o*-phenylenediamine (**1**), en (**2**), phen (**3**), and bpy (**4**)). These products are mixtures of diastereomers **a** and **b** which resulted from face selection of the two DMFU ligands for coordination to the metal center. The two diastereomers **1a** and **1b** of **1** were separated by column chromatography. The structure of compound **1a** determined by X-ray crystallography is distorted octahedral with the two DMFU ligands being trans to each other and cis to CO and PDA ligands. The two alkenes are mutually orthogonal and each eclipses a N–M–C vector. In addition, they are bound to the Mo center in a fashion with all four ester groups lying between the carbonyl and the amino groups. The absolute configuration of the olefin carbons of the DMFU ligands in **1a** is *RRRR* or *SSSS*. The geometry of **1b** is similar to that of **1a** except that different faces of the DMFU ligands (*RRSS* or *SSRR*) are coordinated to the Mo center. As a result, the four ester groups and four olefin protons are equally distributed in the four regions defined by the two intersected N–Mo–CO vectors. For product **2**, only one diastereomer having structure **a** was observed. Due to internal hydrogen bonding between the amino protons and the keto groups on the DMFU ligands, which restricts the rotation of the coordinated DMFU, **1a**, **1b**, and **2a** are all static in solution at ambient temperature. Similar to product **1**, both products **3** and **4** also are mixtures of diastereomers **a** and **b**. As indicated by the low-temperature ^1H NMR spectra, **3a** and **4a** consist of rotational isomers **I** and **II** which undergo rapid mutual exchange at ambient temperature. **3b** and **4b** exhibit fluxional behavior on the NMR time scale due to rotation of the DMFU ligands. The structure of **3b** was also determined from X-ray diffraction measurements. The results confirm the general structural features concluded from NMR data of these species. **1a** crystallizes in monoclinic space group $C2/c$ with unit cell parameters $a = 12.311(3)$ Å, $b = 11.027(3)$ Å, $c = 17.000(6)$ Å, $\beta = 99.32(2)°$, and $D_c = 1.599$ g cm^{-3} for $Z = 4$; least-squares refinement based on 2018 independent observed reflections produced a final R value 0.028. Compound **3b** belongs to triclinic space group $P\bar{1}$ with unit cell parameters $a = 9.546(2)$ Å, $b = 10.072(2)$ Å, $c = 14.886(3)$ Å, $\beta = 77.76(1)°$, and $D_c = 1.537$ g cm^{-3} for $Z = 2$; after refinement, the final R value was 0.034 on the basis of 4727 independent observed reflections.

Introduction

Coordination of an alkene to a metal center is an important step in many metal-mediated reactions such as nucleophilic[1] and electrophilic[2] additions to coordinated alkenes, olefin isomerization,[3] oligomerization,[4] and polymerization.[5] Although many bis(alkene) complexes have been reported, most have structures with two alkenes cis to each other.[6] The conformations and mechanism of alkene ligands in octahedral d^6 *trans*-bis(alkene) complexes and the related trans bis(π-ligand) have attracted considerable attention both theoretically and experimental-

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ly.[7,8] The model complexes *trans*-$MoX_4(C_2H_4)_2$ in which X = CO or PH_3 have been theoretically studied by Veillard et al.[9] They predicted that the carbon–carbon double bonds of the alkene ligands are orthogonal to each other but each eclipses a X–Mo–X vector. Although several octahedral d^6 bis(alkene) complexes *trans*-$M(C_2H_4)_2(L)_4$, with M = Cr, Mo, or W and L = PR_3 or CO, have been prepared,[10] all employed ethylene as the alkene ligand.

Our interest in d^6 trans bis(π-ligand) complexes led us to the synthesis of several molybdenum and tungsten bis(alkyne) complexes $M(CO)_2(alkyne)_2(NN)$ (NN = bpy, phen, en, etc.).[11] To extend this chemistry to other π-ligands, we explored the possibility of preparing bis(alkene) complexes of the type $M(CO)_2(alkene)_2(NN)$. Here we report the synthesis and NMR dynamic studies of *trans*-$Mo(CO)_2(NN)(DMFU)_2$ where DMFU = dimethyl fumarate. Because of the prochiral nature of the DMFU ligands, these complexes show unprecedented diastereomers and conformational isomers.

Results and Discussion

$Mo(CO)_2(DMFU)_2(PDA)$ (1). Treatment of *fac*-$Mo(CO)_3(CH_3CN)_3$ in acetonitrile with 1 equiv of *o*-phenylenediamine (PDA) at ambient temperature followed by heating at reflux in the presence of excess dimethyl fumarate gave a yellow mixture of $Mo(CO)_2(DMFU)_2(PDA)$. This product contains two isomers which were separated on a silica-gel column using dichloromethane and THF as eluents. The first isomer **1a** came out as a yellow band from the silica-gel column using dichloromethane as the eluent, whereas the second complex **1b** is polar than **1a** and required a more polar solvent such as THF or ethyl acetate as eluent. The IR (KBr) spectra of these species exhibit different carbonyl stretching frequencies at 1971 and 1902 cm^{-1} for **1a** and 1980 and 1909 cm^{-1} for **1b**, but the results of microanalysis indicate that these two species are isomers and are consistent with the chemical formula $Mo(CO)_2(DMFU)_2(PDA)$.

X-ray Structure Determination of Isomer 1a. To learn the structure of these bis(alkene) complexes, the exact conformation of the olefin ligands, and the relationship of structures with spectral data, we determined the structure of **1a** by the X-ray diffraction method. A single crystal of **1a** suitable for X-ray analysis was grown from a mixture of dichloromethane and diethyl ether. An ORTEP diagram of **1a** with atomic numbering is presented in Figure 1; its atomic coordinates are listed in Table I, and important intramolecular bond distances and bond angles are shown in Table II. These results show **1a** to be distorted octahedral with two CO groups cis to each other, but each trans to an amino group, whereas the two DMFU ligands are trans to each other and are cis to the CO and PDA ligands. The two alkenes are mutually orthogonal (90.6°), and each alkene ligand eclipses a N–M–C vector (4.4°).

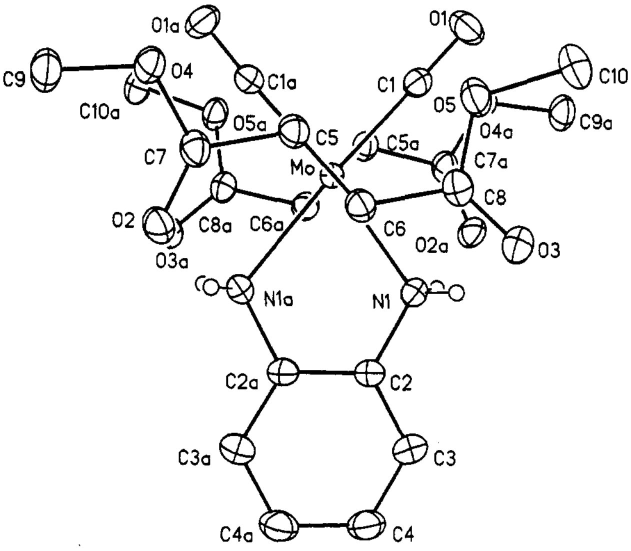
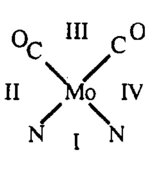


Figure 1. ORTEP diagram of **1a** with atomic numbering scheme.

Table I. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Coefficient (Å² × 10³) of 1a

	x	*y*	*z*	*U*(eq)
Mo	5000	2471	2500	40(1)
O(1)	5509(3)	4593(3)	3731(2)	78(1)
O(2)	2268(3)	1711(3)	1346(2)	67(1)
O(3)	3979(3)	1586(3)	4362(2)	68(1)
O(4)	2079(3)	3740(3)	1273(2)	65(1)
O(5)	3315(3)	3442(3)	4011(2)	63(1)
N(1)	5559(3)	843(3)	3281(2)	51(1)
C(1)	5305(4)	3798(4)	3288(3)	54(1)
C(2)	5286(3)	−313(3)	2885(2)	49(1)
C(3)	5590(4)	−1393(4)	3271(3)	66(2)
C(4)	5307(4)	−2471(5)	2887(3)	79(2)
C(5)	3154(3)	2979(4)	2411(2)	53(1)
C(6)	3443(3)	2043(4)	2989(2)	53(1)
C(7)	2464(3)	2707(4)	1635(2)	57(2)
C(8)	3600(3)	2303(4)	3848(2)	55(2)
C(9)	1439(4)	3613(5)	487(3)	78(2)
C(10)	3604(5)	3851(5)	4827(3)	80(2)

If we view **1a** from the top of the basal plane described by $MoN_2(CO)_2$, the molecule is divided into four regions (I–IV) by the two intersected N–Mo–CO vectors.



Detailed analysis of the structure in Figure 1 reveals that the two DMFU ligands are bound to the Mo center in a fashion with all four ester groups falling in regions II and IV. In addition, the four keto oxygens O(2) and O(3a),

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Table II. Important Bond Distances (Å) and Angles (deg) of 1a

	Distances		
Mo–N(1)	2.272(3)	Mo–C(1)	1.974(4)
Mo–C(5)	2.322(4)	Mo–C(6)	2.259(4)
N(1)–C(2)	1.454(5)	O(1)–C(1)	1.156(5)
O(2)–C(7)	1.211(5)	O(3)–C(8)	1.213(5)
O(4)–C(7)	1.343(5)	O(4)–C(9)	1.443(4)
O(5)–C(8)	1.345(5)	O(5)–C(10)	1.448(5)
C(2)–C(3)	1.381(6)	C(2)–C(2A)	1.383(7)
C(3)–C(4)	1.374(7)	C(4)–C(4A)	1.409(10)
C(5)–C(6)	1.429(6)	C(5)–C(7)	1.480(5)
C(6)–C(8)	1.470(6)		
	Angles		
N(1)–Mo–C(1)	100.5(2)	N(1)–Mo–C(5)	115.4(1)
C(1)–Mo–C(5)	86.7(2)	N(1)–Mo–C(6)	79.3(1)
C(1)–Mo–C(6)	89.1(2)	C(5)–Mo–C(6)	36.3(1)
N(1)–Mo–N(1A)	75.6(2)	C(1)–Mo–N(1A)	170.5(1)
C(5)–Mo–N(1A)	87.2(1)	C(6)–Mo–N(1A)	81.7(1)
C(5)–Mo–C(1A)	72.6(2)	C(1)–Mo–C(1A)	84.6(3)
C(6)–Mo–C(5A)	155.0(1)	C(6)–Mo–C(1A)	108.9(2)
C(6)–Mo–C(6A)	155.9(2)	C(5)–Mo–C(5A)	152.1(2)
Mo–N(1)–C(2)	113.4(2)	Mo–C(1)–O(1)	177.5(4)
C(3)–C(2)–C(2A)	120.4(2)	C(2)–C(3)–C(4)	119.6(4)
C(3)–C(4)–C(4A)	120.0(3)	Mo–C(5)–C(6)	69.5(2)
Mo–C(5)–C(7)	115.1(3)	C(6)–C(5)–C(7)	120.7(4)
Mo–C(6)–C(5)	74.2(2)	Mo–C(6)–C(8)	110.0(3)
C(5)–C(6)–C(8)	121.4(4)		

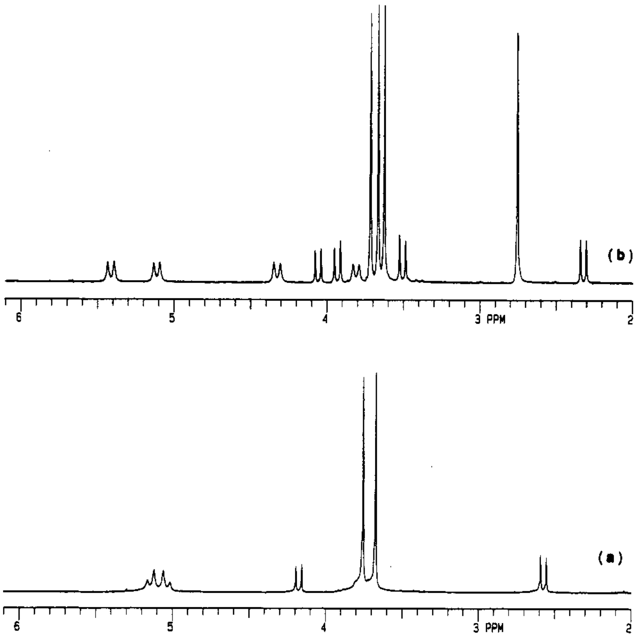
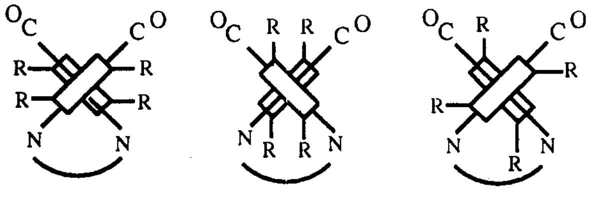


Figure 2. (a) ^{1}H NMR spectrum of **1a**. (b) ^{1}H NMR spectrum of **1b** at ambient temperature.

O(2a) and O(3) point to the two amino groups N(1a) and N(1), respectively, indicating the formation of hydrogen bonding between the ester groups and the amino ligands. The distances between O(2) and N(1a), O(3) and N(1) of 2.815 and 2.999 Å, respectively, are all within the range of hydrogen bond interaction. The hydrogen bonding appears to be the major driving force in determining the conformation of the complex. As is pointed out below, hydrogen bonding of the DMFU ligands is also important in the NMR behavior of these bis(alkene) complexes.

In the ^{1}H NMR spectrum of **1a** at ambient temperature (Figure 2a), there are two resonances at δ 7.32 and 7.31 for the phenylene protons, two signals at δ 3.76 and 3.68 for the methoxy groups, and two doublets at δ 4.18 and 2.59 for the olefin protons of the DMFU ligands. The resonances for the amino protons of the PDA ligand appear as an AB type pattern at δ 5.15 and 5.04. The ^{13}C spectrum exhibits three phenylene, two methoxy, and two olefin resonances and two keto carbon resonances for the PDA and DMFU ligands, respectively. On the basis of the orthogonal-eclipsed conformation, three isomers **a-I**, **a-II**, and **b** are proposed for *trans*-bis(DMFU) complexes. From the observed NMR signals of **1a**, structure **b** is clearly eliminated. The other two structures **1a-I** (NN = PDA) and **1a-II**, both possessing C_2 symmetry, are consistent with the observed NMR results in the number of signals. However, in view of the observed solid-state structure of isomer **1a**, we assign conformation **a-I** to this isomer in solution. As **1a** is static at ambient temperature on the NMR time scale, **1a-I** is the only conformation existing in solution.



a-I **a-II** **b**

The other isomer **1b** which is more polar than **1a** exhibits four resonances at δ 3.72, 3.67, 3.63, and 2.76 for the methoxy groups and four resonances at δ 4.06, 3.94, 3.51, and 2.32 for the four olefin protons of the DMFU ligands (Figure 2b) in its ^{1}H NMR spectrum. The four amino protons are all magnetically inequivalent, appearing at δ 5.42, 5.12, 4.32, and 3.81. In the ^{13}C NMR spectrum, in total 20 signals are observed, indicating that all carbons in this isomer are magnetically inequivalent. On the basis of the results of these NMR studies and microanalysis, structure **b** is proposed for **1b**. In this complex, the four methyl groups and four olefin protons are equally distributed in regions I–IV. In view of the dramatic difference in the chemical shift of the amino protons and the absence of fluxional behavior at ambient temperature, it is likely that hydrogen bonds are also formed between the two ester groups in regions II and IV and two amino protons in solution. The amino protons which form hydrogen bonds with ester groups are expected to appear at lower field (δ 5.42, 5.12). We were unable to obtain crystals of **1b** for X-ray structure determination, but suitable crystals of one isomer of $Mo(CO)_2(DMFU)_2(phen)$ with a similar arrangement of the DMFU ligands have been grown and the structure has been solved from X-ray diffraction (vide infra). These results support the structural assignment of **1b**.

Dramatic upfield shifts of the olefin proton by ca. 4.3 ppm and olefin carbon-13 resonances by ca. 70 ppm of the DMFU ligands were observed upon coordination to the molybdenum(0) center.[12] In addition, the NMR signals span a range greater than 1.5 ppm for the olefin protons and 7 ppm for the ^{13}C nuclei. For example, the olefin resonances of complexes **1a** occur at δ 2.59 and 4.18. The former signal is assigned to the protons in the region between the two amino groups (region I), whereas the latter

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is attributed to the protons in the region between the two carbonyl groups (region III). The resonances at δ 4.06 and 2.32 of isomer **1b** are assigned as the olefin protons lying in regions III and I, respectively. For the other two olefin resonances at δ 3.94 and 3.51, we tend to assign the former resonance to the proton in region II and the latter to the proton in region IV of structure **b**. The former olefin proton is closer to the carbonyl group than to the amino group, and vice versa for the latter. A similar trend is observed for the methoxy resonances of the DMFU ligands. For instance, the methoxy resonances of **1b** at δ 3.72, 3.67, 3.63, and 2.76 correspond to the methoxy protons lying in regions III, IV, II, and I, respectively. For isomer **1a**, because there is no methoxy group lying between the two amino groups (region I) or two carbonyl groups (region III), the two methoxy resonances appear at δ 3.76 and 3.68, near the values observed for the methoxy groups lying in regions IV and II of **1b**. Complexes having two olefin protons lying near amino and carbonyl groups were known. The ^{1}H NMR spectra of these species showed that the olefin proton signal near the amino group appeared significantly upfield of that of the proton close to the carbonyl group.[13]

Complex $Mo(CO)_2(DMFU)_2(en)$ (2). This complex may be prepared by methods similar to those employed for complex 1. However, unlike complex 1, only one isomer was observed from the reaction of $Mo(CO)_3(CH_3CN)(en)$ with DMFU. In the ^{1}H NMR spectrum of this species, there are two methoxy resonances at δ 3.66 and 3.62 and two olefin proton resonances at δ 4.05 and 2.76. The methylene protons and amino protons appear as broad signals at δ 2.94 and 3.17, respectively. By comparison of these ^{1}H NMR data with those of **1a** ad **1b**, the olefin protons seem to be in region I (δ 2.76) and in region III (δ 4.05) and the methoxy groups of the DMFU ligands lie in regions II and IV. Hence, structure **a-I** is assigned to the complex. In agreement with the proposed structure which possesses a C_2 axis bisecting the N–Mo–N and C–Mo–C angles, the ^{13}C NMR spectrum of this isomer shows a pair of signals for carbons of each type in the DMFU ligands and only one methylene and one carbonyl carbon resonance at δ 41.7 and 219.2, respectively. The NMR spectra of this isomer do not change significantly with decreasing temperature, indicating that the complex is static at ambient temperature.

$Mo(CO)_2(DMFU)_2(phen)$ (3). The reaction of $Mo(CO)_4(phen)$ with DMFU in toluene at refluxing temperature gave a pure yellow precipitate **3a**. However, the toluene solution contains a mixture of two products **3a** and **3b** with the relative concentration ratio of 1:1.3, as determined by the ^{1}H NMR integration method. These isomers were not effectively separated by column chromatography, but they were separated by fractional crystallization from a mixture of dichloromethane and ether. They are also diastereomers arising from face selectivity of the carbon–carbon double bond of the DMFU ligands. Structural assignments of the isomers of 3 are more difficult than of 1. The ^{1}H NMR spectrum of **3b** is shown in Figure 3. Surprisingly, there is only one methoxy resonance at δ 3.17 and one olefin proton resonance at δ 3.53 in the spectrum at ambient temperature, indicating that the species is fluxional on the NMR time scale.[12] As the temperature decreased broadening of the signals occurs and the coalescence temperature is reached at 243 K. Each observed resonance at ambient temperature for a DMFU ligand starts to split into four resonances as temperature was decreased further. At 183 K, the structure became static and four singlets at δ 3.66, 3.63, 3.07, and 1.86 for the methoxy protons and also four doublets at δ 4.28, 4.00, 3.60, and 1.97 for the olefin protons with equal intensity were observed. On the basis of the results, strucuture **b** is assigned to the species. In accord with the unsymmetrical nature of structure **b**, all the carbons and protons of the phen ligand are magnetically inequivalent, even at the fast exchange regime. There were 12 signals for the phen ligand in the ^{13}C NMR spectrum at ambient temperature. In the ^{1}H NMR spectrum, the chemical shifts of the protons ortho and meta to the nitrogen atoms appear as a pair of doublets and a pair of triplets, respectively, consistent with the inequivalent nature of these phen protons.

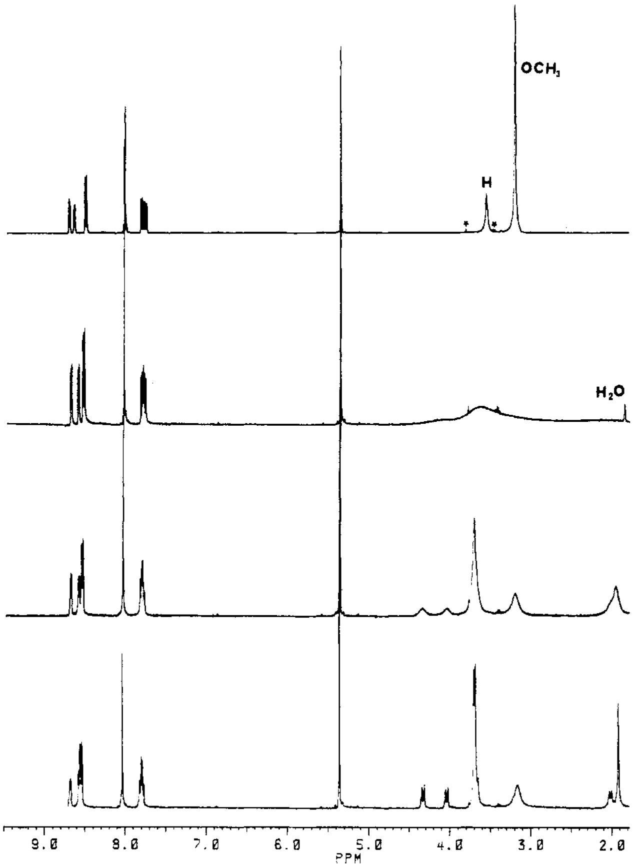

Figure 3. ^{1}H NMR spectrum of **3b** at (bottom to top) (a) 183 K, (b) 213 K, (c) 243 K, and (d) 283 K.

The isomer **3a** from the reaction of $Mo(CO)_4(phen)$ with DMFU is also fluxional. Similarly to **3b**, the ^{1}H NMR spectrum of this species contains only one resonance at δ 3.69 for the olefin protons and one resonance as well at δ 3.18 for the methoxy protons of the DMFU ligands at ambient temperature (Figure 4). These resonances appear in the spectrum at positions near those of the isomer **3b**. A distinction between the ^{1}H NMR spectra of these two isomers is in the region of the phen ligand; there are only four proton signals for the phen ligand found for the **3a** isomer, indicating that C_2 symmetry exists. The ^{13}C NMR spectrum similarly contained six resonances corresponding to the phen carbons, one resonance assigned to the methoxy carbons, and one to olefin carbons on the DMFU ligands at ambient temperature. The results indicate that the

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[13] Mayr, A.; Dorries, A. M.; Rheingold, A. L.; Geib, S. J. *Organometallics* **1990**, *9*, 964.

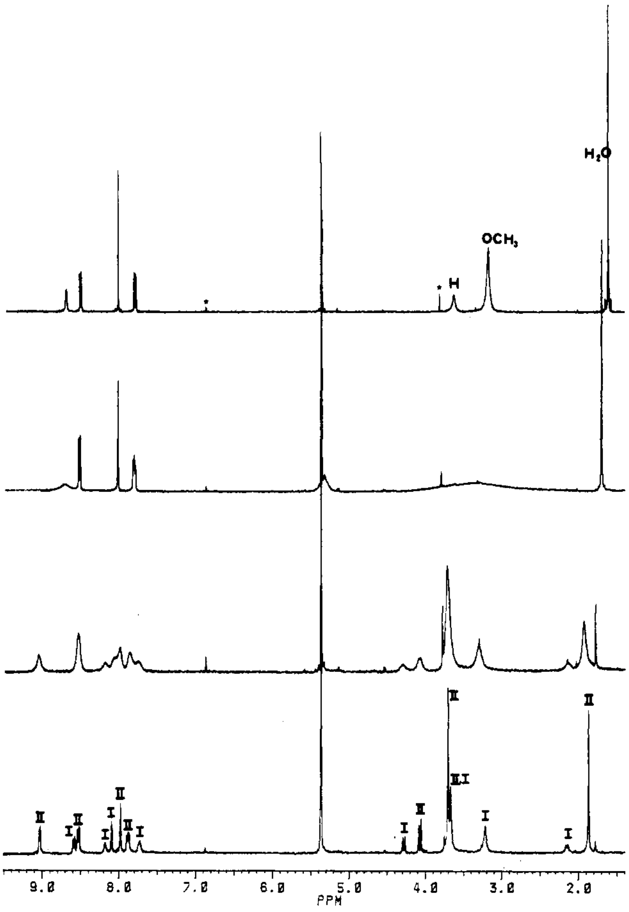

Figure 4. ^{1}H NMR spectrum of **3a** at (bottom to top) (a) 173 K, (b) 218 K, (c) 255 K, and (d) 294 K.

isomer is fluxional and that the DMFU ligands undergo rapid rotation at ambient temperature. Upon cooling, the rotational process is frozen out. The low-temperature-limiting spectrum at 183 K has two sets of two doublets for the olefin protons and two sets of two singlets for the methoxy protons of the DMFU lignads. In the region δ 9.2–7.5 for the phen protons, two sets of signals for the phen protons were observed. The spectrum clearly indicates that two conformational isomers exist in solution. The structure of the conformer having its olefin protons at δ 4.29 and 2.14 and the methoxy protons at δ 3.67 and 3.28 is proposed to be **3a-I** on the basis of the observations that one olefin signal is more upfield than the other.[13] The signal at δ 2.14 is attributed to olefin protons lying in region I, whereas the signal at δ 4.29 is due to protons lying in region III. The structure of the conformer with signals of its olefin protons at δ 4.08 and 3.69 and of the methoxy protons at δ 3.72 and 1.90 is assigned as **3a-II**. This assignment is based on the observations that no olefin signal appears at $\delta < 2.5$ ppm, but one methoxy proton signal (δ 1.90) occurs unusually upfield. As determined by integration of the NMR spectrum, the ratio of **3a-I** to **3a-II** is ca. 3:4.

$Mo(CO)_2(DMFU)_2(bpy)$ (4). The reaction of $Mo(CO)_4(bpy)$ with DMFU in toluene at refluxing temperature gave a pure yellow precipitate **4b**. Similar to the reaction of $Mo(CO)_4(phen)$ with DMFU, the toluene solution contains a mixture of two products **4a** and **4b** with the relative concentration ratio of 1:1.3. These two products are also diastereomers arising from face selectivity of the carbon–carbon double bond of the DMFU ligands. The ^{1}H NMR spectrum of the yellow precipitate **4b** exhibits a single resonance at δ 3.60 for the olefin protons, one resonance at δ 3.39 for the methoxy groups of the DMFU ligands, but six resonances for the bpy protons. These ^{1}H NMR data consist of two doublets for the ortho protons and two triplets for the meta protons of the bpy ligand. The observed NMR patterns are similar to those of the phen isomer **3b**. On the basis of these observations, structure **b** is assigned to the isomer. As indicated by the NMR spectra, the molecule is fluxional on the NMR time scale. Lowering the temperature led to broadening of the NMR signals; the coalescence temperature was 225 K. As temperature further decreased, the molecule is eventually frozen out. The low-temperature-limiting spectrum at 185 K contains four olefin proton signals at δ 4.30, 4.04, 3.56, and 2.08 and four methoxy proton signals at δ 3.67, 3.64, 3.14, and 2.64 with equal intensity. It is noteworthy that the yellow precipitates **3a** and **4b** from the reactions of DMFU with the corresponding $Mo(CO)_4(NN)$ in toluene have different arrangements of the two DMFU ligands. The other isomer **4a** with its structure similar to that of **3a** was not isolated due to the difficulty of separating it from **4b**. However, the presence of the isomer in toluene solution is indicated by the observation of a set of resonances at δ 3.67 and 3.40 for the olefin and methoxy protons in addition to the set of signals corresponding to **4b**. Evidence for the presence of **4a** is also observed in the ^{13}C NMR spectrum (see Experimental Section).

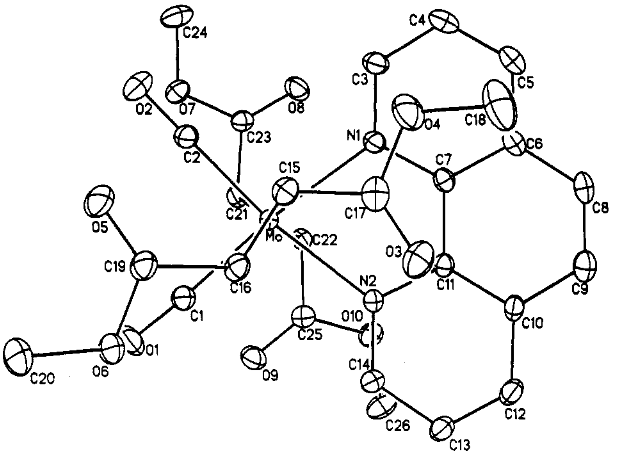

Figure 5. ORTEP diagram of **3b** with atomic numbering scheme.

Crystal Structure of 3b. Analysis of the X-ray diffraction data for diastereomer **3b** of $Mo(CO)_2(DMFU)_2(phen)$ has been carried out. An ORTEP diagram of **3b** with atom numbering appears in Figure 5, while its atomic coordinates are listed in Table III and important intramolecular bond distances and bond angles are in Table IV. These X-ray results confirm the general structural features concluded from the carbonyl absorption patterns in the IR and NMR spectra of these species.

Similar to **1a**, the solid-state structure of **3b** is distorted octahedral with the two CO groups cis to each other, but trans to phen, whereas the two DMFU ligands are trans to each other and cis to the CO and the phen ligands. The two coordinated alkenes are mutually orthogonal (87.6°), and each alkene ligand eclipses a N–M–C vector (13.2°). The only apparent difference in structure between **1a** and **3b** is the arrangement of the ester groups on the DMFU ligands. In **3b** the two alkenes are coordinated to the metal center such that each ester group lies above or below one of the four regions in the MoN_2C_2 plane (vide supra). The

Table III. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficient ($Å^2 \times 10^3$) of 3b

	x	*y*	*z*	*U*(eq)
Mo	690	7526(1)	7375(1)	30(1)
O(1)	−2280(4)	7588(4)	8776(3)	62(1)
O(2)	−1128(4)	9797(3)	6067(2)	57(1)
O(3)	3712(4)	8482(4)	8265(3)	65(1)
O(4)	3978(4)	9481(4)	6792(3)	66(1)
O(5)	−1298(4)	11109(4)	7884(3)	68(1)
O(6)	−1558(4)	10023(3)	9336(2)	61(1)
O(7)	−1335(3)	7240(3)	5329(2)	47(1)
O(8)	1023(3)	6072(4)	5157(2)	52(1)
O(9)	−785(4)	4490(3)	8511(2)	56(1)
O(10)	1561(4)	3382(3)	8085(2)	52(1)
N(1)	2815(3)	7075(3)	6378(2)	35(1)
N(2)	2327(3)	6215(3)	8212(2)	33(1)
C(1)	−1177(5)	7535(4)	8275(3)	42(2)
C(2)	−479(5)	8950(5)	6550(3)	40(1)
C(3)	3085(5)	7577(5)	5481(3)	44(2)
C(4)	4449(6)	7199(5)	4921(3)	54(2)
C(5)	5575(5)	6272(5)	5276(3)	52(2)
C(6)	5343(5)	5742(5)	6226(3)	41(1)
C(7)	3948(4)	6189(4)	6747(3)	35(1)
C(8)	6452(5)	4770(5)	6667(4)	51(2)
C(9)	6208(5)	4327(5)	7579(3)	51(2)
C(10)	4810(4)	4788(4)	8136(3)	38(1)
C(11)	3679(4)	5715(4)	7728(3)	33(1)
C(12)	4501(5)	4389(5)	9101(3)	47(2)
C(13)	3160(5)	4912(5)	9591(3)	45(2)
C(14)	2081(5)	5812(4)	9126(3)	40(1)
C(15)	1610(5)	9332(4)	7522(3)	41(2)
C(16)	544(5)	9138(4)	8323(3)	41(2)
C(17)	3179(5)	9036(5)	7597(4)	50(2)
C(18)	5533(7)	9220(8)	6780(6)	94(3)
C(19)	−848(5)	10197(4)	8459(3)	46(2)
C(20)	−2944(8)	10965(8)	9543(5)	107(3)
C(21)	−394(4)	6280(4)	6674(3)	36(1)
C(22)	713(4)	5356(4)	7127(3)	36(1)
C(23)	−140(5)	6492(4)	5649(3)	38(1)
C(24)	−1173(7)	7607(6)	4336(3)	64(2)
C(25)	373(5)	4412(4)	7976(3)	40(2)
C(26)	1428(7)	2366(5)	8891(4)	66(2)

ester groups have an ordered arrangement with each keto group pointing in a clockwise direction (view from the top of Figure 5). There is a pseudo S_4 axis in the structure for the two DMFU ligands.

Table IV. Important Bond Distances (Å) and Angles (deg) of 3b

	Distances		
Mo–N(1)	2.239(3)	Mo–N(2)	2.218(3)
Mo–C(1)	1.989(4)	Mo–C(2)	1.986(4)
Mo–C(15)	2.274(5)	Mo–C(16)	2.293(5)
Mo–C(21)	2.307(5)	Mo–C(22)	2.274(4)
O(1)–C(1)	1.149(5)	O(2)–C(2)	1.153(5)
O(3)–C(17)	1.195(7)	O(4)–C(17)	1.348(6)
O(5)–C(19)	1.198(5)	O(6)–C(19)	1.342(5)
O(7)–C(23)	1.326(5)	O(8)–C(23)	1.213(5)
O(9)–C(25)	1.210(5)	O(10)–C(25)	1.343(5)
C(15)–C(16)	1.414(6)	C(15)–C(17)	1.475(7)
C(16)–C(19)	1.476(6)	C(21)–C(22)	1.418(5)
C(21)–C(23)	1.479(6)	C(22)–C(25)	1.472(5)
	Angles		
N(1)–Mo–N(2)	74.4(1)	N(1)–Mo–C(1)	168.9(2)
N(2)–Mo–C(1)	101.2(1)	N(1)–Mo–C(2)	98.7(1)
N(2)–Mo–C(2)	168.1(2)	C(1)–Mo–C(2)	87.3(2)
N(1)–Mo–C(15)	81.0(1)	N(2)–Mo–C(15)	86.3(1)
C(1)–Mo–C(15)	109.2(2)	C(2)–Mo–C(15)	83.1(2)
N(1)–Mo–C(16)	114.6(2)	N(2)–Mo–C(16)	83.8(1)
C(1)–Mo–C(16)	74.4(2)	C(2)–Mo–C(16)	90.7(2)
C(15)–Mo–C(16)	36.1(1)	N(1)–Mo–C(21)	92.5(1)
N(2)–Mo–C(21)	113.8(1)	C(1)–Mo–C(21)	79.9(2)
C(2)–Mo–C(21)	75.6(2)	C(15)–Mo–C(21)	156.5(1)
C(16)–Mo–C(21)	151.4(1)	N(1)–Mo–C(22)	80.0(1)
N(2)–Mo–C(22)	77.8(1)	C(1)–Mo–C(22)	89.1(2)
C(2)–Mo–C(22)	110.8(2)	C(15)–Mo–C(22)	157.9(1)
C(16)–Mo–C(22)	152.4(1)	C(21)–Mo–C(22)	36.1(1)
Mo–C(1)–O(1)	177.3(4)	Mo–C(2)–O(2)	178.1(4)
Mo–C(15)–C(16)	72.7(3)	Mo–C(15)–C(17)	117.4(3)
Mo–C(16)–C(19)	116.9(4)	Mo–C(16)–C(15)	71.2(3)
C(16)–C(15)–C(17)	119.9(4)	C(15)–C(16)–C(19)	119.0(3)
Mo–C(21)–C(22)	70.7(3)	Mo–C(21)–C(23)	116.5(3)
Mo–C(22)–C(25)	114.4(3)	Mo–C(22)–C(21)	73.2(3)
C(22)–C(21)–C(23)	118.5(3)	C(21)–C(22)–C(25)	122.7(4)

Structural details of **1a** and **3b** are of interest. The stronger electron-donating ability of PDA compared to phen is reflected in the longer average carbon–carbon double bonds (1.429 Å, cf. 1.416 Å) of the DMFU ligands and the shorter average Mo–CO bond lengths (1.979 Å, cf. 1.988 Å) for **1a** relative to **3b**. Significant variations in the bond distance from the molybdenum center to one of the olefin carbons are observed. For **1a**, the distances Mo–C(5) and Mo–C(6) are 2.322 and 2.259 Å, respectively, and for **3b**, the corresponding average distances are 2.307 and 2.274 Å, respectively. In both cases, the olefin carbons adjacent to coordinated amino groups are closer to the metal centers than those adjacent to carbonyl ligands. The interaction of the d_π and π^* orbitals of the carbonyl and DMFU ligands is shown below.

Competition for the d_π electrons between the π^* orbitals of carbonyl and DMFU ligand appears to reduce the back-donation from the metal to the olefin carbon adjacent to the carbonyl group and as a result weakens the latter metal–olefin carbon bond. It is interesting to note that the average difference in bond length of the two metal–olefin carbon bonds for the same DMFU is larger in **1a** (0.063 Å) than in **3b** (0.033 Å). This bond-length difference is expected to increase as the difference of π-acidity of the carbonyl and the trans nitrogen ligand increases. Both nitrogens of the PDA ligand in **1a** are sp^3 hybridized and essentially have no π-acidity, but the two nitrogens of the phen ligand in **3b** are sp^2 hybridized and substantial π-acidity is expected. Consequently, the difference of π-acidity between the carbonyl and the trans nitrogen ligand is smaller in **3b** than in **1a**. The distances of carbon–carbon double bonds of the DMFU ligands in **1a** and **3b** are within the established range for electron-withdrawing olefins coordinated to low-valent metal centers and are close to the value (1.42(1) Å) observed for $Co(CH_3CN)_2(DEFU)_2$,[14] where DEFU = diethyl fumarate, but are slightly longer than that (1.39(1) Å) for $Ni(CH_3CN)(DEFU)_2$.[15]

Face Selectivity of the DMFU Ligands. Due to the prochiral character[16] of DMFU, there are two enantiotopic

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[14] Agnes, G.; Bassi, I. W.; Benedicenti, C.; Intrito, R.; Calcaterra, M.; Santini, C. *J. Organomet. Chem.* **1977**, *129*, 401.

[15] Bassi, I. W.; Calcaterra, M. *J. Organomet. Chem.* **1976**, *110*, 129.

[16] (a) Bodner, G. S.; Fernandez, J. M.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 4082. (b) Bodner, G. S.; Peng, T.-S.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1990**, *9*, 1191. (c) Consiglio, G.; Morandini, F. *J. Organomet. Chem.* **1986**, *310*, C66. (d) Consiglio, G.; Pregosin, P.; Morandini, F. *J. Organomet. Chem.* **1986**, *308*, 345. (e) Begum, M. K.; Chu, K.-H.; Coolbaugh, T. S.; Rosenblum, M.; Zhu, X.-Y. *J. Am. Chem. Soc.* **1989**, *111*, 5252. (f) Chang, T. C. T.; Coolbaugh, T. S.; Foxman, B. M.; Rosenblum, M.; Simms, N.; Stockman, C. *Organometallics* **1987**, *6*, 2394. (g) Peng, T.-S.; Gladysz, J. A. *J. Am. Chem. Soc.* **1992**, *114*, 4174. (h) Paiaro, G.; Panunzi, A. *J. Am. Chem. Soc.* **1964**, *86*, 5148.

faces of the carbon–carbon double bond for coordination to the molybdenum center. For isomers with structure **a**, both DMFU ligands are bound to the metal by employing the same face, resulting in *RRRR* or *SSSS* configuration of the carbons on the olefin double bond. In contrast, the two trans alkenes in the isomers with structure **b** use different double-bond faces as they are coordinated to the molybdenum center; the carbon configurations of the two olefin double bonds are either *RRSS* or *SSRR*. In the reaction of $Mo(CO)_4(NN)$ (NN = PDA, phen, and bpy) with DMFU, both diastereomers **a** and **b** were detected. However, for NN = en, the reaction of $Mo(CO)_3(en)(CH_3CN)$ with DMFU gave only the $R^*R^*R^*R^*$ (indicating a racemic mixture of *RRRR* and *SSSS*) isomer **2a**. These observations indicate that the nonplanar en ligand strongly favors $R^*R^*R^*R^*$ coordination of the two DMFU ligands. Significant steric repulsion between the methylene groups of en and one methoxy group of DMFU ligand is expected for an $R^*R^*S^*S^*$ configuration.

The present complexes also may be prepared by treating complex $Mo(CO)_3(CH_3CN)_3$ with 2 equiv of DMFU to give $Mo(CO)_2(CH_3CN)_2(DMFU)_2$ followed by addition of 1 equiv of chelating ligand such as PDA, phen, or bpy to $Mo(CO)_2(CH_3CN)_2(DMFU)_2$ at ambient temperature. This process led to substitution of two acetonitrile ligands in the latter species by the chelate nitrogen ligand and to formation of the corresponding diastereomers **a** and **b**. The ratio of the resulting diastereomers **a** and **b** (1.2:1) appeared independent of the chelate nitrogen ligand employed. The results indicate that the ratio **a**:**b** was determined in the reaction of $Mo(CO)_3(CH_3CN)_3$ with DMFU and no dissociation of the DMFU ligands occurred during the substitution reactions.

In the presence of free DMFU, conversion of isomer **a** to **b** and vice versa occurred readily at the refluxing temperatures of toluene, acetonitrile, and 2-methoxy diethyl ether. Equilibrium between isomers **a** and **b** was eventually reached. For example, **4b** and 1 equiv of free DMFU in toluene was heated at refluxing temperature of 1 h, **4a** was detected, and the ratio of **4a** to **4b** was 1:2. There was no significant change of the ratio on further heating, indicating that the two isomers reached equilibrium at that temperature.

Conclusion

We demonstrated that *trans*-bis(DMFU) complexes of molybdenum may be synthesized. Due to the prochiral character of the DMFU ligands, two diastereomers **a** and **b** exist for each chelating NN (PDA, bpy, and phen) ligand. In most cases, the two isomers were separated by column chromatography or fractional crystallization. For the bpy and phen complexes, both isomers **a** and **b** were fluxional due to fast rotation of the two DMFU ligands on the NMR time scale. In the NMR spectra of **a** at low temperatures, two conformations **a-I** and **a-II** were observed. On the other hand, for PDA and en complexes, all the structures appear static at ambient temperature because of formation of hydrogen bonding between the keto group of the DMFU ligands and the amino protons. These hydrogen bonds, presumably, restrict the rotation of the DMFU ligands. From the available variable-temperature NMR data, we were unable to determine unambiguously the mechanism for the alkene rotation in the bpy and phen complexes. In the closely related octahedral *trans*-bis(CO_2)[17] and *trans*-bis(alkyne) complexes,[11c] the mechanism for CO_2 and alkyne rotation has been carefully determined and the results indicate that the two trans CO_2 or alkyne ligands in each complex rotate synchronously in the same direction. In view of these two closely related precedents, we favor a similar process for the rotation of DMFU ligands in complexes **3** and **4**.

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 Bruker AM-400 and Varian Gemini-300 instruments; infrared spectra were measured on a Bomem MB-100 spectrometer. Elemental analysis were performed by Heraeus CHN-O-RAPID. All reagents were used as obtained from commercial sources. For X-ray structure determination a Siemens R3m/V diffractometer was used.

Dimethyl fumarate, 2,2′-bipyridine, 1,10-phenanthroline, ethylenediamine (Merck), molybdenum hexacarbonyl (Strem), and 1,2-phenylenediamine (Janssen) were used as received. $Mo(CO)_3(CH_3CN)_3$,[18] $Mo(CO)_4(bpy)$, and $Mo(CO)_4(phen)$[19] were prepared according to reported methods.

Synthesis of $Mo(CO)_2(PDA)(DMFU)_2$ (1). To $Mo(CO)_3(CH_3CN)_3$ (0.50 g, 1.65 mmol) in acetonitrile (20 mL) was added *o*-phenylenediamine (0.18 g, 1.65 mmol). The solution was stirred at room temperature for 0.5 h. Addition of dimethyl fumarate (0.95 g, 6.60 mmol) was followed by refluxing for 2 h. On cooling to room temperature, the solvent was removed on a rotory evaporator and the residue was separated on a silica-gel column. A yellow fraction was collected using methylene chloride as eluent. Evaporation of the solvent gave **1a** as a yellow powder in 32% yield. Further elution with a mixture of CH_2Cl_2 and ethyl acetate (v/v = 1/1) afforded **1b** also as a yellow powder in 32% yield. Spectral data for **1a**: ^1H NMR ($CDCl_3$) δ 7.32 (d, J = 5.2 Hz, 2 H, Ph), 7.31 (d, J = 5.2 Hz, 2 H, Ph), 5.15 (d, J = 12.4 Hz, 2 H, NH_2), 5.04 (d, J = 12.4 Hz, 2 H, NH_2), 4.18 (d, J = 11.4 Hz, 2 H, $=C-H$), 3.76 (s, 6 H, OCH_3), 3.68 (s, 6 H, OCH_3), 2.59 (d, J = 11.4 Hz, 2 H, $=C-H$); $^{13}C\{^1H\}$ NMR δ 219.63 ($C\equiv O$), 178.09, 174.86 (COO), 137.08, 128.63, 128.43 (Ph), 56.53, 52.10 ($C=C$), 50.96 (OCH_3); IR (KBr) 3280, 3238 ($\nu(NH_2)$), 1971 (s), 1902 (s) ($\nu(C\equiv O)$), 1673 cm^{-1} (ν(COO)). Anal. Calcd for $MoC_{20}H_{16}N_2O_{10}$: C, 43.81; H, 4.38; N, 5.11. Found: C, 43.44; H, 4.37; N, 5.08. Spectral data for **1b**: ^1H NMR ($CDCl_3$) δ 7.18 (m, Ph), 5.42 (d, J = 12.9 Hz, 1 H, NH), 5.12 (d, J = 12.0 Hz, 1 H, NH), 4.32 (d, J = 12.9 Hz, 1 H, NH), 3.81 (d, J = 12.0 Hz, 1 H, NH), 4.06 (d, J = 11.4 Hz, 1 H, $=CH$), 3.94 (d, J = 12.0 Hz, 1 H, $=CH$), 3.51 (d, J = 12.0 Hz, 1 H, $=CH$), 2.32 (d, J = 11.4 Hz, 1 H, $=CH$), 3.72 (s, 3 H OCH_3), 3.67 (s, 3 H, OCH_3), 3.63 (s, 3 H, OCH_3), 2.76 (s, 3 H, OCH_3); $^{13}C\{^1H\}$ NMR δ 220.43, 219.42 ($C\equiv O$), 178.57, 174.54, 174.61, 174.42 (COO), 137.80, 136.13, 128.98, 128.52, 128.26, 128.07 (Ph), 57.16, 56.06, 50.73, 50.42 ($C=C$), 52.14, 51.40, 51.33, 51.19 (OCH_3); IR (KBr) 1980 (s), 1909 (s) ($\nu(C\equiv O)$), 1681 cm^{-1} (ν(COO)). Anal. Calcd for $MoC_{20}H_{16}N_2O_{10}$: C, 43.81; H, 4.38; N, 5.11. Found: C, 43.61; H, 4.45; N, 5.12.

Synthesis of $Mo(CO)_2(en)(DMFU)_2$ (2). The title compound was prepared in 66.0% yield by following a procedure similar to that described for 1. ^1H NMR ($CDCl_3$): δ 4.05 (d, J = 11.2 Hz, 2 H, $=CH$), 2.76 (d, J = 11.2 Hz, 2 H, $=CH$), 3.66 (s, 6 H, OCH_3), 3.62 (s, 6 H, OCH_3), 3.17 (b, 4 H, NH_2), 2.94 (s, 4 H, CH_2). $^{13}C\{^1H\}$ NMR: δ 219.24 ($C\equiv O$), 177.55, 174.36 (COO), 52.17, 57.03 ($C=C$), 50.99 (OCH_3), 41.75 (CH_2). IR (KBr): 3318, 3234 ($\nu(NH_2)$), 1966 (s), 1892 (s) ($\nu(C\equiv O)$), 1680 cm^{-1} (ν(COO)). Anal. Calcd for $MoC_{16}H_{24}N_2O_{10}$: C, 38.41; H, 4.80; N, 5.60. Found: C, 38.44; H, 4.89; N, 5.62.

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Synthesis of Mo(CO)$_2$(phen) (DMFU)$_2$ (3). A mixture of Mo(CO)$_4$(phen) (0.30 g, 0.77 mmol) and dimethyl fumarate (0.45 g, 3.09 mmol) in toluene (20 mL) was heated at reflux for 4 h. During this period, precipitation was observed. The precipitate was filtered and washed with diethyl ether to give isomer **3a** as a yellow material in 81% yield. The filtrate was evacuated to remove the solvent and was passed through a silica-gel column using CH$_2$Cl$_2$/THF as eluent. Collection of the desired yellow band followed by solvent removal gave a mixture of **3a** and **3b** in a 1:1.2 ratio. Fractional crystallization of the mixture in dichloromethane and diethyl ether led to isolation of pure **3b**. The total yield of **3** was 91%. Isomer **3a**: ^{1}H NMR (CDCl$_3$) δ 8.71 (d, J = 4.5 Hz, 2 H, H(2,9) of phen), 8.42 (d, J = 8.2 Hz, 2 H, H(4,7) of phen), 7.94 (s, 2 H, H(5,6) of phen), 7.76 (dd, J = 4.5 Hz, J = 8.2 Hz, 2 H, H(3,8) of phen), 3.69, (s, 4 H, =CH), 3.18 (s, 12 H, OCH$_3$); ^{13}C{^{1}H} NMR (CDCl$_3$) δ 221.84 (C≡O), 174.28 (COO), 153.90, 144.63, 136.98, 130.06, 127.36, 124.68 (phen), 58.54 (C=C), 50.76 (OCH$_3$); IR (KBr) 1972 (s), 1898 (s) (ν(C≡O)), 1695 cm^{-1} (ν(COO)). Anal. Calcd for MoC$_{26}$H$_{24}$N$_2$O$_{10}$: C, 50.33; H, 3.90; N, 4.52. Found: C, 49.86; H, 3.91; N, 4.54. Isomer **3b**: ^{1}H NMR (CDCl$_3$) δ 8.72 (d, J = 4.5 Hz, 1 H, H(2) of phen), 8.67 (d, J = 4.5 Hz, 1 H, H(9) of phen), 8.44 (d, J = 8.1 Hz, 2 H, H(4,7) of phen), 7.95 (s, 2 H, H(5,6) of phen), 7.76 (m, 2 H, H(3,8) of phen), 3.53 (s, 4 H, =CH), 3.17 (s, 12 H, OCH$_3$); ^{13}C{^{1}H} NMR (CDCl$_3$) δ 223.15, 221.25 (C≡O), 174.21 (COO), 155.82, 153.00, 145.57, 144.70, 137.39, 137.27, 130.43, 130.37, 127.99, 127.44, 125.45, 124.44 (phen), 59.57 (C=C), 51.07 (OCH$_3$); IR (KBr) 1970 (s), 1897 (s) (ν(C≡O)), 1696 cm^{-1} (ν(COO)). Anal. Calcd for MoC$_{26}$H$_{24}$N$_2$O$_{10}$: C, 50.33; H, 3.90; N, 4.52. Found: C, 49.89; H, 3.93; N, 4.51.

Synthesis of Mo(CO)$_2$(bpy)(DMFU)$_2$ (4). A mixture of Mo(CO)$_4$(bpy) (0.30 g, 0.82 mmol) and dimethyl fumarate (0.47 g, 3.30 mmol) in toluene (20 mL) was heated at reflux for 4 h. During this period, precipitation occurred. The precipitate was filtered and washed with diethyl ether to give isomer **4b** in 71% yield. The filtrate was evacuated to remove the solvent and was passed through a silica-gel column using CH$_2$Cl$_2$/THF as eluent. Collection of the desired yellow band followed by solvent removal gave a mixture of **4a** and **4b** in a 1:1.3 ratio. The total yield of **4** was 84%. Spectral data for **4a**: ^{1}H NMR (CDCl$_3$) δ 8.35 (d, J = 5.7 Hz, 2 H, H(2,9) of bpy), 8.12 (d, J = 7.8 Hz, 2 H, H(5,6) of bpy), 7.97 (dd, J = 8.1 Hz, J = 6.3 Hz, 2 H, H(4,7) of bpy), 7.43 (dd, J = 5.7 Hz, J = 6.3 Hz, 2 H, H(3,8) of bpy), 3.67 (4 H, =CH), 3.40 (12 H, OCH$_3$); ^{13}C{^{1}H} NMR (CDCl$_3$) δ 221.71 (C≡O), 174.25 (COO), 153.87, 153.33, 137.88, 125.61, 121.90 (bpy), 59.94 (C=C), 51.02 (OCH$_3$). Spectral data for **4b**: ^{1}H NMR (CDCl$_3$) δ 8.38 (d, J = 5.3 Hz, 1 H, H(2) of bpy), 8.32 (d, J = 5.3 Hz, 1 H, H(9) of bpy), 8.14 (d, J = 8.1 Hz, 2 H, H(5,6) of bpy), 7.97 (dd, J = 8.1 Hz, J = 6.3 Hz, 2 H, H(4,7) of bpy), 7.46 (dd, J = 6.3 Hz, J = 5.3 Hz, 1 H, H(3) of bpy), 7.39 (dd, J = 6.3 Hz, J = 5.3 Hz, 1 H, H(8) of bpy), 3.60 (s, 4 H, =CH), 3.39 (s, 12 H, OCH$_3$); ^{13}C{^{1}H} NMR (CDCl$_3$) δ 222.10, 221.25 (C≡O), 174.20 (COO), 155.90, 154.19, 153.72, 152.96, 138.33, 126.63, 125.18, 122.50, 122.38 (bpy), 60.31 (C=C), 51.31 (OCH$_3$); IR (KBr) 1963 (s), 1889 (s) (ν(C≡O)), 1699 cm^{-1} (ν(COO)). Anal. Calcd for MoC$_{24}$H$_{24}$N$_2$O$_{10}$: C, 48.33; H, 4.06; N, 4.71. Found: C, 48.11; H, 4.61; N, 4.06.

X-ray Structure Determination of Mo(CO)$_2$(DMFU)$_2$(PDA) (1a). An orange crystal of dimensions 0.20 × 0.24 × 0.30 mm^3 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 as listed in Table V were determined from the fit of 15 reflections ($8.85 \leq 2\theta \leq 26.35°$). The other parameters of this data collection are presented in Table V. No significant variation in intensities of three standards monitored every 50 reflections occurred. A total of 2765 reflections were collected, but only 1370 unique reflections with $I \geq 3\sigma(I)$ 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° ($T_{\min}$, $T_{\max}$ = 0.706, 0.780; μ = 6.16 cm^{-1}). Systematic absences were (hkl, $h + k = 2n + 1$; $h0l$: h, $l = 2n + 1$). 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 and C–H–C = 109.4° and fixed at a U value 0.08 Å^2. The final residuals for variables and independent reflections with $I \geq 3\sigma(I)$ were R = 0.0276 and R_w = 0.0363. The final difference Fourier map had no peak greater than 1.05 e Å^{-3}. The final positional parameters were determined with final refinements of the structure with Rogers' η value.[20] Scattering factors were taken from ref 21. All calculations were performed on a Micro VAX II computer system using SHELXTL-Plus programs.

Table V. Summary of Crystal Data and Intensity Collection of 1a and 3b

compd	MoC$_{20}$H$_{24}$N$_2$O$_{10}$ (**1a**)	MoC$_{26}$H$_{24}$N$_2$O$_{10}$ (**3b**)
fw	548.4	620.4
cryst size (mm^3)	0.20 × 0.24 × 0.30	0.42 × 0.32 × 0.10
space group	$C2/c$; monoclinic	$P\bar{1}$; triclinic
unit cell dimens		
a, Å	12.311(3)	9.546(2)
b, Å	11.027(3)	10.072(2)
c, Å	17.000(6)	14.886(3)
β, deg	99.32(2)	77.76(1)
vol, Å^3	2277.3(11)	1340(2)
Z	4	2
density (calc), g cm^{-3}	1.599	1.537
abs coeff, mm^{-1}	0.616	0.533
F(000)	1120	632
temperature	296	296
2θ range, deg	2.5–50.0	2.5–50.0
scan type	$\theta/2\theta$	$\theta/2\theta$
scan speed (in ω), deg/min	2.93–14.65	2.93–14.65
scan range (ω), deg	1.00 + Kα separation	1.00 + Kα separation
index ranges	$-14 \leq h \leq 14$, $0 \leq k \leq 11$, $0 \leq l \leq 19$	$-10 \leq h \leq 11$, $-11 \leq k \leq 11$, $0 \leq l \leq 17$
no. of reflns collcd	2765 (1646 > 3.0$\sigma(I)$)	5360 (4321 > 3.0$\sigma(I)$)
no. of ind reflns	2018 (1370 > 3.0$\sigma(I)$)	4727 (3698 > 3.0$\sigma(I)$)
R	0.0276	0.0343
R_w	0.0363	0.0395
goodness-of-fit	1.04	0.64

X-ray Structure Determination of Mo(CO)$_2$(DMFU)$_2$(phen) (3b). An orange crystal of dimensions 0.10 × 0.32 × 0.42 mm^3 was selected for X-ray diffraction. Procedures similar to those for complex **1a** were employed for data collection and structural refinement of **3b**. Important crystallographic data are presented in Table V.

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Supplementary Material Available: Tables of atomic positional parameters, complete bond distances and angles, thermal parameters, and calculated hydrogen positions for **1a** and for **3b** (8 pages). Ordering information is given on any current masthead page.

OM920694N

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