Octahedral d^6 Bis(maleimide) and Bis(maleic anhydride) Complexes of Molybdenum

Chen-Hsing Lai, Chien-Hong Cheng,* Fen-Ling Liao, and Sue-Lein Wang*

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

Received May 4, 1993●

$Mo(CO)_3(CH_3CN)_3$ reacts with 2 equiv of alkene, where the alkene is maleimide (MI), *N*-phenylmaleimide (PhMI), or *N*-methylmaleimide, to give the corresponding $Mo(CO)_2(alkene)_2(CH_3CN)_2$ complex (**1a–c**, respectively) in excellent yield. Dissolution of **1** in DMSO led to the substitution of acetonitrile ligands by DMSO to form the corresponding cis bis(DMSO) complexes **2a–c**. Addition of 1 equiv of NN to **1** yields $Mo(CO)_2(alkene)_2(NN)$ (NN = en, alkene = PhMI (**3b**), MeMI (**3c**); NN = *o*-phenylenediamine, alkene = PhMI (**4b**)). Treatment of $Mo(CO)_4(NN)$, where NN = phen or bpy, with 2 equiv of alkene in refluxed acetonitrile for 2 h gave $Mo(CO)_2(alkene)_2(NN)$ (NN = phen, alkene = MI (**5a**), PhMI (**5b**); NN = bpy, alkene = MI (**6a**), PhMI (**6b**)). Treatment of $Mo(CO)_3(CH_3CN)_3$ with 2 equiv of maleic anhydride (MA) gave $Mo(CO)_2(MA)_2(CH_3CN)_2$ (**7**). The acetonitrile ligands in **7** were replaced by DMSO molecules to give complex **8** as **7** was dissolved in DMSO. Similarly, the reaction of **7** with a bidentate ligand NN (phen or bpy) gave the substituted product $Mo(CO)_2(MA)_2(NN)$ (**9** or **10**). The structures and conformations of **1b** and **7** were determined by X-ray diffraction. Both molecules adopt an octahedral geometry with mutually perpendicular trans alkene ligands and each alkene ligand eclipses a N–Mo–CO vector. Each PhMI or MA is oriented so that the central nitrogen or oxygen atom points to a carbonyl group. **1b** crystallizes in triclinic space group $P1$ with unit cell parameters $a = 10.110(3)$ Å, $b = 11.607(3)$ Å, $c = 12.278(3)$ Å, $\beta = 76.61(2)°$, and $D_c = 1.512$ g cm^{-3} for $Z = 2$; least-squares refinement based on 2839 independent observed reflections produced final R and R_w values of 0.041 and 0.038, respectively. Compound **7** belongs to orthorhombic space group *Pbcn* with unit cell parameters $a = 9.493(3)$Å, $b = 12.954(5)$Å, $c = 13.460(6)$Å, and $D_c = 1.726$ g cm^{-3} for $Z = 4$; after refinement, the final R and R_w values were 0.023 and 0.026, respectively, on the basis of 1027 independent observed reflections. There are three possible conformations for a trans bis(maleimide) or bis(maleic anhydride) complex (**I–III**). The results of X-ray and NMR studies indicate that the main conformation of complexes **1–10** is **I** both in the solid state and in solution.

Introduction

Octahedral d^6 trans bis(π-ligand) complexes are of interest both theoretically and experimentally.^{1} The mechanism of rotation, the conformation of the two trans π-ligands, and the orbital interactions between the metal center and the π-ligands have been the focus of these studies.^{2} The π-ligands that are known to form such stable complexes include dioxygen,^{3} carbon dioxide,^{4} various alkynes,^{5} and various alkenes.^{6}

Recently, we prepared a series of molybdenum and tungsten trans bis(alkyne) complexes $M(CO)_2(alkyne)_2(NN)$ (NN = bpy, phen, en, etc.).^{7} In these complexes, the two alkynes are mutually staggered, but each eclipses one of the N–M–CO vectors. For unsymmetrical alkyne complexes, conformational isomers arising from different orientations of the unsymmetrical alkyne ligands relative to the N–M–CO vectors exist in solution. Related trans bis(alkene) complexes $Mo(CO)_2(DMFU)_2(NN)$, $Mo(CO)_2(DMMA)_2(NN)$, and $Mo(CO)_2(DMFU)(DMMA)(NN)$ where DMFU = dimethyl fumarate and DMMA = dimethyl maleate have geometries^8 similar to that of the bis(alkyne) complexes. However, due to the presence of two enantiotopic faces of these substituted alkenes, various diastereomers and conformational isomers of trans bis(alkene) complexes were observed.^{9} In addition to these DMFU and DMMA complexes, we have prepared two molybdenum(0) complexes $Mo(CO)_2(MeMI)(NN)$ ((NN = bpy,

---

● Abstract published in *Advance ACS Abstracts,* November 1, 1993.

(1) (a) Bachmann, C.; Demuynck, J.; Veillard, A. *J. Am. Chem. Soc.* **1978**, *100*, 2366. (b) Byrne, J. W.; Blaser, H. U.; Osborn, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 3871. (c) Burdett, J. K.; Albright, T. A. *Inorg. Chem.* **1979**, *18*, 2112. (d) Daniel, C.; Veillard, A. *Inorg. Chem.* **1989**, *28*, 1170. (e) Hohmann, F.; Dieck, H. T.; Kruger, C.; Tsay, Y.-H. *J. Organomet. Chem.* **1979**, *171*, 353. (f) Grevels, F.-W.; Skibbe, V. *J. Chem. Soc., Chem. Commun.* **1984**, 681. (g) Stolz, I. W.; Dobson, G. R.; Sheline, R. K. *Inorg. Chem.* **1963**, *2*, 1264. (h) Grevels, F.-W.; Lindemann, M.; Benn, R.; Goddard, R.; Kruger, C. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1980**, *35*, 1298. (i) Henderson, R. A.; Oglieve, K. E. *J. Chem. Soc., Chem. Commun.* **1991**, 584. (j) Beaumont, I. R.; Begley, M. J.; Harrison, S.; Wright, A. H. *J. Chem. Soc., Chem. Commun.* **1990**, 1713. (k) Ziegler, T.; Rauk, A. *Inorg. Chem.* **1979**, *18*, 1558. (l) Weiller, B. H.; Grant, E. R. *J. Phys. Chem.* **1988**, *92*, 1458. (m) Weiller, B. H.; Grant, E. R. *J. Am. Chem. Soc.* **1987**, *109*, 1252. (n) Ito, T.; Kokubo, T.; Yamamoto, T.; Yamamoto, A.; Ikeda, S. *J. Chem. Soc., Chem. Commun.* **1974**, 136.

(2) (a) Marcos, E. S.; Caballol, R.; Trinquieer, G.; Bartherlat, J.-C. *J. Chem. Soc., Dalton Trans.* **1987**, 2373. (b) Carmona, E.; Hughes, A. K.; Munoz, M. A.; O'Hare, D. M.; Perez, F. J.; Poveda, M. L. *J. Am. Chem. Soc.* **1991**, *113*, 9210.

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

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

(5) Birdwhistll, K. R.; Tonker, T. L.; Templeton, J. L. *J. Am. Chem. Soc.* **1987**, *109*, 1401.

(6) (a) Carmona, E.; Marin, J. M.; Poveda, M. L.; Atwood, J. L.; Rogers, R. D. *J. Am. Chem. Soc.* **1983**, *105*, 3014. (b) Carmona, E.; Galindo, A.; Poveda, M. L.; Rogers, R. D. *Inorg. Chem.* **1985**, *24*, 4033. (c) Carmona, E.; Galindo, A.; Marin, J. M.; Gutierrez-Puebla, E.; Monge, A.; Ruiz, C. *Polyhedron* **1988**, *7*, 1831. (d) Gregory, M. F.; Jackson, S. A.; Poliakoff, M.; Turner, J. J. *J. Chem. Soc., Chem. Commun.* **1986**, 1175. (e) Grevels, F.-W.; Jacke, J.; Ozkar, S. *J. Am. Chem. Soc.* **1987**, *109*, 7536. (f) Hohmann, F.; Dieck, H. T.; Kruger, C.; Tsay, Y.-H. *J. Organomet. Chem.* **1979**, *171*, 353.

(7) (a) Lain, J. S.; Cheng, C. H.; Cheng, C. Y.; Wang, S. L. *J. Organomet. Chem.* **1990**, *390*, 333. (b) Lai, C. H.; Cheng, C. H.; Cheng, C. Y.; Wang, S. L. *J. Organomet. Chem.*, in press. (c) Hsiao, T. Y.; Kuo, P. L.; Lai, C. H.; Cheng, C. H.; Cheng, C. Y.; Wang, S. L. *Organometallics* **1993**, *12*, 1094.

(8) (a) Lai, C. H.; Cheng, C. H.; Chou, W. C.; Wang, S. L. *Organometallics* **1993**, *12*, 1105. (b) Lai, C. H.; Cheng, C. H.; Chou, W. C.; Wang, S. L. *Organometallics*, in press.

(9) (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.

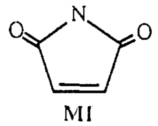
0020-1669/93/1332-5658$04.00/0

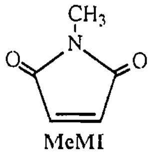
phen; MeMI = *N*-methylmaleimide).[10] The rotation of MeMI ligands in these two species was shown to be conrotatory. In the crystal structure of the bpy complex, weak interaction between the nitrogen atoms of MeMI ligands and the carbonyl groups exists. To date, only few reports on this type of interligand interactions have appeared in literature.[11]

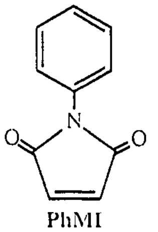
The interesting interligand interaction betweeen the carbonyl ligands and the MeMI ligands of $Mo(CO)_2(MeMI)(NN)$ prompted us to study systematically the synthesis, structure, and spectral properties of a series of trans bis(maleimide) and bis(maleic anhydride) complexes of molybdenum. The results indicate that these new bis(alkene) complexes construct one of the largest classes of metal compounds that show weak interligand interactions.

Results and Discussion

Synthesis and Spectral Properties of Trans Bis(maleimide) Complexes. Treatment of $Mo(CO)_3(CH_3CN)_3$ with maleimide (MI), *N*-phenylmaleimide (PhMI), and *N*-methylmaleimide (MeMI) led to the formation of the corresponding trans bis(alkene) complexes $Mo(CO)_2(MI)_2(CH_3CN)_2$ (**1a**), $Mo(CO)_2(PhMI)_2(CH_3CN)_2$ (**1b**), and $Mo(CO)_2(MeMI)_2(CH_3CN)_2$ (**1c**), respectively (eq 1). These complexes were characterized


MI

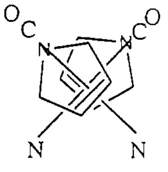

MeMI

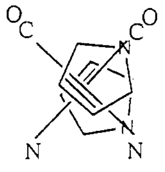

PhMI

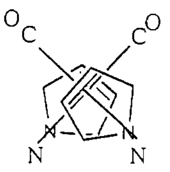
$$Mo(CO)_3(CH_3CN)_3 + 2RMI \rightarrow Mo(CO)_2(RMI)_2(CH_3CN)_2 + CH_3CN + CO \quad (1)$$

by IR and NMR spectroscopies and microanalysis. In the IR spectra, all these complexes show two C≡N absorptions at *ca.* 2300 cm^{-1}, two carbonyl absorptions at *ca.* 1980 and 1910 cm^{-1}, and two keto carbonyl absorptions at *ca.* 1725 and 1675 cm^{-1}. These IR absorption patterns are similar to those of the known $Mo(CO)_2(DMFU)_2(NN)$.[8a]

In principle, there are three possible conformational isomers, **I**–**III**, for a bis(maleimide)[9] complex with the olefins orthogonal


I


II


III

and aligned with a N–Mo–CO vector. While the IR data for these bis(maleimide) complexes do not provide information about the conformation of the maleimide ligands, the NMR spectra for these species reflect their geometries. For example, the ^1H NMR spectrum of **1a** in CD_3CN shows olefinic resonances at δ 4.06 and 3.77 at 293 K. On the basis of the observed number of resonances for the olefinic protons and the assumption of a static structure, the conformation of **1a** is either **I** or **III**. Four olefinic proton resonances would result if isomer **II** was the static conformation for **1a**. Similarly, there are two olefinic signals (in CD_3CN) at δ 4.21 and 3.99 for **1b** and at δ 4.06 and 3.77 for **1c**, suggesting that the conformation of **1b** and **1c** in acetonitrile is also either **I** or **III**. Variable-temperature studies of the NMR spectra of these acetonitrile complexes showed no significant change as temperature decreases from 298 to 183 K. This observation suggests that complexes **1a**–**c** are static in the temperature range studied or else are rotating rapidly. From the spectral data available, we are unable to definitely assign the conformation of the maleimide ligands in these complexes.

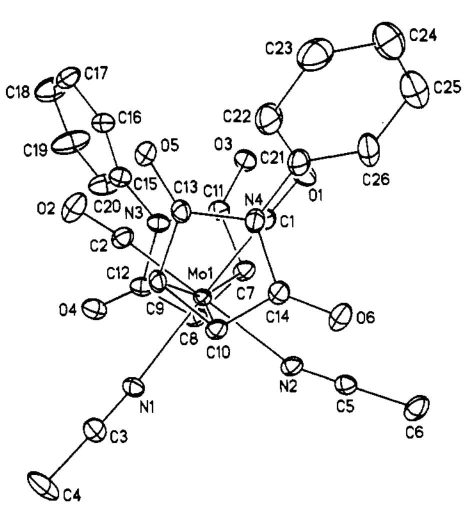


Figure 1. ORTEP diagram of **1b** with atomic numbering scheme.

Crystal Structure of $Mo(CO)_2(PhMI)_2(CH_3CN)_2$ (1b). The structure of **1b** was determined in order to learn the conformation of the PhMI ligands in the solid-state and to seek a relationship between the structure and spectral data. Crystals with sizes suitable for X-ray diffraction measurements of **1b** were grown from a mixture of acetonitrile and ether. An ORTEP diagram of this complex with atomic numbering is displayed in Figure 1; atomic coordinates are listed in Table I, and important intramolecular bond distances and bond angles are shown in Table II. As shown in Figure 1, **1b** is distorted octahedral with the two PhMI ligands trans to each other and cis to the CO and acetonitrile ligands. The two CO groups are cis to each other and trans to an acetonitrile group. The two maleimides are mutually orthogonal (96.4°), and each maleimide ligand eclipses a N–M–C vector (2.3, 8.2°). For each *N*-phenylmaleimide ligand, the olefinic carbon adjacent to a coordinated acetonitrile group is slightly closer to the metal than that adjacent to a carbonyl group (2.257 vs 2.300 Å). Competition between the π^* orbitals of carbonyl and maleimide ligands for the d_π electrons reduces the back-donation from metal to the olefinic carbon adjacent to the carbonyl group and may as a result weaken the latter metal–olefinic carbon bond. Similar results were also observed in other trans bis(alkene) complexes of molybdenum(0).[8a] It is noteworthy that both acetonitrile molecules are not linearly coordinated to the molybdenum center. The $Mo–NCCH_3$ fragments showed substantial bending at the nitrogen atoms (Mo–N(1)–C(3) = 169.3°; Mo–N(2)–C(5) = 159.3°). The cause for the observed bending is not clear. Most interestingly, each PhMI molecule lies with the nitrogen atom of the imide group pointing to one carbonyl ligand. The distances from the nitrogen atoms to carbonyl carbons (N(3)–C(2), N(4)–C(1)) are 3.028 and 2.996 Å, respectively, possibly indicating a weak bond between the carbonyl carbon and the nitrogen atom. One possible interaction is the donation of an electron lone pair on the nitrogen atom to a π^* orbital of the carbonyl group. It is also possible that the observed solid conformation simply results from reduction of steric repulsion between the PhMI ligands and other moieties in the complex. On the basis of the X-ray results for **1b** and the similarities observed for NMR patterns of complexes **1a**–**c**, we assign conformation **I** to all three of these acetonitrile complexes in the solid state and in solution.

---

[10] Lai, C. H.; Cheng, C. H. *Organometallics*, in press.

[11] (a) Liu, L. K.; Sun, C. H.; Yang, C. Z.; Wen, Y. S.; Wu, G. F.; Shih, S. Y.; Lin, K. S. *Organometallics* **1992**, *11*, 972. (b) Ball, R. G.; Burke, M. R.; Takats, J. *Organometallics* **1987**, *6*, 1918.

Table I. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for **1b**

	x	y	z	U(eq)
Mo(1)	36623(6)	−8122(5)	29660(4)	290(2)
O(1)	27428(49)	16178(41)	13397(33)	595(23)
O(2)	8988(51)	−13821(49)	29810(38)	682(26)
O(3)	33508(46)	−5289(41)	−2979(30)	547(22)
O(4)	42479(48)	−41591(42)	19849(35)	582(22)
O(5)	−5180(43)	17199(37)	39137(33)	492(20)
O(6)	37091(46)	22118(41)	40691(36)	585(23)
N(1)	41762(51)	−23201(44)	43361(36)	401(22)
N(2)	57812(52)	−6155(48)	28811(35)	412(23)
N(3)	35234(51)	−23940(45)	7467(36)	431(22)
N(4)	14095(49)	23148(42)	39168(36)	382(21)
C(1)	30542(63)	7252(60)	19487(46)	413(28)
C(2)	19000(69)	−11427(59)	29290(48)	448(30)
C(3)	42372(68)	−29670(56)	51268(50)	464(30)
C(4)	43040(99)	−37924(63)	61481(57)	808(44)
C(5)	66218(67)	−1633(56)	27118(43)	396(28)
C(6)	76621(76)	4490(74)	25290(49)	658(38)
C(7)	48363(63)	−13391(58)	11610(44)	445(28)
C(8)	51006(59)	−24521(54)	18858(43)	395(26)
C(9)	18106(59)	2027(51)	44053(41)	350(25)
C(10)	31115(59)	3535(53)	44394(40)	358(26)
C(11)	38274(62)	−13058(58)	4421(44)	418(27)
C(12)	42957(60)	−31502(62)	16011(47)	435(29)
C(13)	7399(63)	14409(52)	40493(42)	362(26)
C(14)	28709(66)	16878(58)	41254(43)	393(28)
C(15)	25314(70)	−26730(58)	2568(45)	458(30)
C(16)	10867(68)	−18506(57)	3361(49)	488(30)
C(17)	1311(70)	−20897(69)	−1517(57)	604(35)
C(18)	6275(92)	−31856(80)	−6994(72)	854(47)
C(19)	21156(96)	−40004(81)	−8178(79)	1023(50)
C(20)	30559(80)	−37257(67)	−3364(65)	774(39)
C(21)	7077(71)	36243(57)	35936(53)	469(30)
C(22)	−7049(79)	42993(63)	41587(61)	633(36)
C(23)	−13848(91)	55803(77)	38348(82)	879(47)
C(24)	−6647(126)	61557(76)	30117(103)	1071(60)
C(25)	7399(115)	54779(89)	24903(80)	969(54)
C(26)	14524(81)	41884(67)	27838(62)	680(38)

Table II. Important Bond Distances and Angles of **1b**

Distances (Å)			
Mo(1)–N(1)	2.219(4)	Mo(1)–N(2)	2.223(6)
Mo(1)–C(1)	1.975(6)	Mo(1)–C(2)	1.982(8)
Mo(1)–C(7)	2.300(5)	Mo(1)–C(8)	2.257(5)
Mo(1)–C(9)	2.302(5)	Mo(1)–C(10)	2.252(6)
O(1)–C(1)	1.156(7)	O(2)–C(2)	1.141(10)
N(1)–C(3)	1.131(7)	N(2)–C(5)	1.137(10)
C(7)–C(8)	1.418(8)	C(9)–C(10)	1.407(10)
Angles (deg)			
N(1)–Mo(1)–N(2)	90.5(2)	N(1)–Mo(1)–C(1)	170.5(2)
N(2)–Mo(1)–C(1)	89.2(2)	N(1)–Mo(1)–C(2)	88.9(2)
N(2)–Mo(1)–C(2)	173.6(2)	C(1)–Mo(1)–C(2)	92.4(3)
N(1)–Mo(1)–C(7)	118.0(2)	N(2)–Mo(1)–C(7)	78.6(2)
C(1)–Mo(1)–C(7)	71.2(1)	C(2)–Mo(1)–C(7)	96.1(3)
N(1)–Mo(1)–C(8)	82.2(2)	N(2)–Mo(1)–C(8)	83.5(2)
C(1)–Mo(1)–C(8)	107.2(1)	C(2)–Mo(1)–C(8)	90.2(2)
C(7)–Mo(1)–C(8)	36.2(2)	N(1)–Mo(1)–C(9)	80.4(2)
C(2)–Mo(1)–C(9)	71.9(2)	C(1)–Mo(1)–C(9)	91.0(2)
N(2)–Mo(1)–C(10)	78.3(2)	N(1)–Mo(1)–C(10)	79.1(2)
C(2)–Mo(1)–C(10)	107.8(3)	C(9)–Mo(1)–C(10)	36.0(2)
Mo(1)–N(1)–C(3)	169.3(4)	Mo(1)–N(2)–C(5)	159.3(4)
Mo(1)–C(1)–O(1)	177.9(5)	Mo(1)–C(2)–O(2)	175.0(5)
N(1)–C(3)–C(4)	179.5(6)	N(2)–C(5)–C(6)	177.8(6)
Mo(1)–C(7)–C(8)	70.2(3)	Mo(1)–C(8)–C(7)	73.5(3)
Mo(1)–C(9)–C(10)	70.1(3)	Mo(1)–C(10)–C(9)	74.0(3)

Synthesis and Spectral Properties of $\mathrm{Mo(CO)_2(alkene)_2(DMSO)_2}$. Dissolution of $\mathrm{Mo(CO)_2(alkene)_2(CH_3CN)_2}$ in DMSO solution led immediately to the displacement of the acetonitrile ligands by DMSO molecules to form $\mathrm{Mo(CO)_2(alkene)_2(DMSO)_2}$ (eq 2).

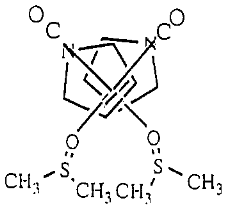
$$\mathrm{Mo(CO)_2(alkene)_2(CH_3CN)_2 + 2DMSO \rightarrow Mo(CO)_2(alkene)_2(DMSO)_2 + 2CH_3CN} \quad (2)$$

Table III. Olefinic Proton Resonances and Carbonyl Absorptions of **1–10**

compound	^{1}H NMR, ppm	IR (KBr) ν(C≡O), cm^{-1}
$\mathrm{Mo(CO)_2(MI)_2(CH_3CN)_2}$ (**1a**)	4.06, 3.77^a	1977, 1907
$\mathrm{Mo(CO)_2(PhMI)_2(CH_3CN)_2}$ (**1b**)	4.21, 3.99^a	1980, 1916
$\mathrm{Mo(CO)_2(MeMI)_2(CH_3CN)_2}$ (**1c**)	4.06, 3.77^a	1964, 1904
$\mathrm{Mo(CO)_2(MI)_2(DMSO)_2}$ (**2a**)	3.93, 3.28^b	1959, 1886
$\mathrm{Mo(CO)_2(PhMI)_2(DMSO)_2}$ (**2b**)	4.26, 3.57^b	1955, 1882
$\mathrm{Mo(CO)_2(MeMI)_2(DMSO)_2}$ (**2c**)	4.04, 3.33^b	1951, 1873
$\mathrm{Mo(CO)_2(PhMI)_2(en)}$ (**3b**)	3.91, 3.41^a	1970, 1882
$\mathrm{Mo(CO)_2(MeMI)_2(en)}$ (**3c**)	3.79, 3.26^b	1956, 1879
$\mathrm{Mo(CO)_2(PhMI)_2(PDA)}$ (**4b**)	4.30, 3.13^b	1974, 1903
$\mathrm{Mo(CO)_2(MI)_2(phen)}$ (**5a**)	4.04, 2.32^b	1955, 1890
$\mathrm{Mo(CO)_2(PhMI)_2(phen)}$ (**5b**)	4.24, 2.60^a	1967, 1891
$\mathrm{Mo(CO)_2(MeMI)_2(phen)}^d$	3.88, 2.63^c	1969, 1901
$\mathrm{Mo(CO)_2(MI)_2(bpy)}$ (**6a**)	3.93, 2.53^b	1963, 1897
$\mathrm{Mo(CO)_2(PhMI)_2(bpy)}$ (**6b**)	4.11, 2.82^a	1955, 1887
$\mathrm{Mo(CO)_2(MeMI)_2(bpy)}^d$	3.75, 3.02^c	1955, 1888
$\mathrm{Mo(CO)_2(MA)_2(CH_3CN)_2}$ (**7**)	4.46, 4.19^a	1986, 1920
$\mathrm{Mo(CO)_2(MA)_2(DMSO)_2}$ (**8**)	4.49, 3.77^b	1987, 1914
$\mathrm{Mo(CO)_2(MA)_2(phen)}$ (**9**)	4.72, 3.08^b	1999, 1927
$\mathrm{Mo(CO)_2(MA)_2(bpy)}$ (**10**)	4.59, 3.28^b	1986, 1916

^{a} In $\mathrm{CD_3CN}$. ^{b} In DMSO-d_6. ^{c} In $\mathrm{CD_2Cl_2}$. ^{d} Reference 10.

Several DMSO complexes ($\mathrm{Mo(CO)_2(MI)_2(DMSO)_2}$ (**2a**), $\mathrm{Mo(CO)_2(PhMI)_2(DMSO)_2}$ (**2b**), and $\mathrm{Mo(CO)_2(MeMI)_2(DMSO)_2}$ (**2c**)) were readily prepared according to the procedure. These complexes were characterized by IR and NMR spectroscopies. The olefinic proton signals of **2a–c** are listed in Table III. As with complexes **1a–c**, each of these DMSO species shows two olefinic proton resonances in the ^{1}H NMR spectrum. For example, the ^{1}H NMR spectrum of **2c** in DMSO-d_6 at 293 K exhibits resonances at δ 4.04, and 3.33 for the olefinic protons and signals at δ 2.70 and 2.54 for the methyl protons of MeMI and DMSO ligands, respectively. In the IR spectra, all these complexes show S–O absorptions at *ca.* 980 cm^{-1}, two carbonyl absorptions at *ca.* 1951 and 1873 cm^{-1}, and two keto absorptions at *ca.* 1723 and 1663 cm^{-1}. These carbonyl absorption patterns are similar to those of the $\mathrm{Mo(CO)_2(MI)_2(CH_3CN)_2}$ complexes but lower in frequency. Although no DMSO complex structure was determined by X-ray diffraction, the conformation of complexes **2a–c** is expected to be **I** in view of the similarity in spectral data between complexes **1** and **2**. There are two possible coordination modes, O- and S-coordinations, for a DMSO ligand.[12] For a S-coordinated DMSO, the S–O absorption appears at a wavenumber higher than 1060 cm^{-1} whereas, for an O-coordinated DMSO, the corresponding absorption is lower than 1060 cm^{-1}. The observed low S–O absorptions in the IR spectra of the present DMSO complexes suggest that all the DMSO ligands are O-coordinated.



2

Synthesis and Spectral Properties of $\mathrm{Mo(CO)_2(alkene)_2(NN)}$. Treatment of $\mathrm{Mo(CO)_2(alkene)_2(CH_3CN)_2}$ with a bidentate amine or pyridine ligand (NN) led to the formation of the corresponding bis(alkene) complexes (eq 3). Complexes **3b**, **3c**, **4b**, **5a**, **5b**, **6a**, and **6b** were thus prepared. The latter complexes (**5a**, **5b**, **6a**, and **6b**) may also be synthesized by treating Mo-

---

(12) (a) Cotton, F. A.; Francis, R. *J. Am. Chem. Soc.* **1960**, *82*, 2986. (b) Meek, D. W.; Drago, R. S.; Piper, T. S. *Inorg. Chem.* **1962**, *1*, 285. (c) Drago, R. S.; Meek, D. W. *J. Phys. Chem.* **1961**, *65*, 1446.

$$\mathrm{Mo(CO)_2(alkene)_2(CH_3CN)_2 + NN \rightarrow Mo(CO)_2(alkene)_2(NN) + 2CH_3CN} \quad (3)$$

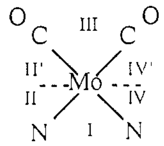
3b,c, 4b, 5a, 6a,b

alkene, NN: PhMI, en (**3b**); MeMI, en (**3c**); PhMI, PDA (**4b**); MI, phen (**5a**); MI, bpy (**6a**); PhMI, bpy (**6b**)

$(CO)_3(CH_3CN)_3$ with 1 equiv of either phen or bpy, followed by addition of the corresponding maleimide. As for the corresponding acetonitrile complexes, the IR spectrum of each species exhibits two strong carbonyl absorptions and two characteristic imide absorptions. The ^1H NMR spectrum of each complex displays two olefinic proton signals, and the ^{13}C spectrum shows two olefinic, two keto, and two carbonyl resonances. Thus, the conformation of these complexes in solution is consistent with conformation **I**.

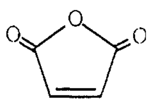
NMR Properties of Complexes 1–6. Detailed analysis of the ^1H and ^{13}C NMR spectra of **1–6** reveals interesting aspects about the conformations of these complexes. For comparison, the olefinic proton resonances of the maleimide ligands of each complex are listed in Table III. Upon coordination to the molybdenum center, dramatic upfield shifts of *ca.* 4 ppm for the olefinic protons and of 70 ppm for the olefinic carbon-13 resonances were found. The chemical shifts of the olefinic protons on the maleimides vary greatly with the NN ligands (i.e. CH_3CN, DMSO, or bidentate nitrogen ligands) on the molybdenum center. The average chemical shift (ppm) for the olefinic protons in each complex increases in the order phen < bpy < PDA < en < DMSO < acetonitrile.

If we view each complex from the top of the $MoN_2(CO)_2$ plane (the plane is $MoO_2(CO)_2$ for DMSO complexes), the molecule may be divided into six regions (I, II, II′, III, IV, and IV′) by the two N–Mo–CO vectors and the vector which bisects the two N–Mo–C angles. The proton chemical shifts depend on the region in which the protons lie and decrease in the order region III > region II′ (and IV′) > region II (and IV) ≫ region I. The correlation was established by analyzing the ^1H NMR data and structures of various bis(alkene) complexes reported previously.[7,8,10] For each pair of the olefinic signals in a complex of **1–6**, the downfield one is assigned as the protons lying in the region between the nitrogen and the carbonyl ligands (region II′ or IV′), while the upfield resonance is attributed to the proton in the region between the two nitrogen ligands (region I). It is noteworthy that the chemical shift difference between the two olefinic protons in each complex also varies greatly with the NN ligand. The chemical shift differences are *ca.* 0.5–0.7 ppm for acetonitrile, DMSO, and en but are generally greater than 1 ppm for PDA, bpy, and phen complexes. In the latter complexes, regional differences account only partly for the observed chemical shift differences of the olefinic protons. The ring currents on the aromatic rings of these bidentate ligands further lower the chemical shift of the olefinic protons in region I. If we assume that the chemical shift differences of the olefinic protons in the absence of a ring current effect are 0.5 ppm for all NN ligands (the same as that for en), the chemical shift differences arising from ring current effects are *ca.* 0.7, 0.9, and 1.1 ppm for PDA, bpy, and phen, respectively. The large chemical shift differences observed for the olefinic protons in PDA, bpy, and phen complexes provide strong evidence that the conformation of the maleimide ligands is **I**. If the conformation of the maleimides is **III**, there would be no olefinic proton in region I and the chemical shift differences of the olefinic protons should be less than 1 ppm. In addition, if the conformation of PhMI and MeMI complexes were **II** or **III**, a phenyl or methyl group attached to the nitrogen atom of the maleimide ligand would fall on top of the phen or bpy ligand. Significant upfield shifts of the phenyl and methyl protons should then be observed. Such an effect was in fact observed for the octahedral $M(CO)_2(NN)(PhCCCOOMe)_2$ complex where M = Mo or W and NN = bpy or phen.[7] Examination of the ^1H NMR spectra of $Mo(CO)_2(PhMI)_2(phen)$ (**5b**) and $Mo(CO)_2(PhMI)_2(bpy)$ (**6b**) reveals no significant ring current effect on the proton resonances of the phenyl groups, indicating that the conformation of these complexes is neither **II** nor **III**.



The proton chemical shifts of $Mo(CO)_2(PhMI)_2(bpy)$ vary with temperature significantly, although the number of signals remains the same through the temperature range 173–313 K. At 173 K in CD_2Cl_2, the ^1H NMR spectrum displays doublets at δ 4.12 and 2.44 for the olefin protons. As the temperature increases, peak broadening occurs and the signal at δ 4.12 gradually shifts upfield, while the resonance at δ 2.44 shifts downfield. These two signals appear at δ 3.97 and 2.98 at 313 K. At temperatures below 173 K, the chemical shifts of the two olefinic protons remain constant. The observed limiting spectrum may be attributed to conformational isomer **I**. Although there is no observed signal corresponding to conformational isomer **II** at 173 K, the change in the chemical shifts with temperature is due to the presence of a small unobserved amount of this isomer and the rapid rotation of PhMI ligands, leading to interconversion of both isomers **I** and **II**. The notion is supported by the observation of a small amount of isomer **II** by ^1H NMR spectroscopy at low temperature for the closely related complexes $Mo(CO)_2(MeMI)_2(bpy)$ and $Mo(CO)_2(MeMI)_2(phen)$.[10] From the X-ray and NMR results, the energy of the three conformational isomers is expected to be in the order **I** < **II** < **III**. On this basis, it is reasonable to predict that the relative population of **I** decreases with respect to **II** as temperature increases, leading to the observed shifts of the two olefinic signals with temperature. The ^1H NMR spectrum of $Mo(CO)_2(PhMI)_2(phen)$ also depends greatly on the temperature, indicating a fluxional NMR behavior of this species similar to that of $Mo(CO)_2(PhMI)_2(bpy)$. Notable is that rotation of PhMI ligands does not interconvert the olefin protons in complexes $Mo(CO)_2(MeMI)_2(bpy)$ and $Mo(CO)_2(PhMI)_2(phen)$. In contrast with this observation, the rotation of DMFU ligands in the corresponding bis(alkene) complexes leads to the interconversion of olefin protons. For all these bis(alkene) complexes, the observed fluxional NMR behavior may be rationalized on the basis of a conrotatory motion of the alkene ligands.[10]

Synthesis and Properties of Bis(maleic anhydride) Complexes. The reaction of $Mo(CO)_3(CH_3CN)_3$ with maleic anhydride (MA) in acetonitrile led to the formation of $Mo(CO)_2(MA)_2(CH_3CN)_2$ (**7**) (eq 4). Dissolution of **7** in DMSO yielded the DMSO complex **8**. Treatment of $Mo(CO)_3(CH_3CN)_3$ with phen (or bpy) followed by maleic anhydride gave the corresponding bis(anhydride)[13] species $Mo(CO)_2(MA)_2(phen)$ (**9**) or $Mo(CO)_2(MA)_2(bpy)$ (**10**). Complexes **6**, **7**, **9**, and **10** were readily separated from the reaction solutions due to the low solubility in the solvent used (acetonitrile). These anhydride complexes are slightly soluble in DMSO and



MA

$$\mathrm{Mo(CO)_3(CH_3CN)_3 + 2MA \rightarrow Mo(CO)_2(MA)_2(CH_3CN)_2 + CH_3CN + CO} \quad (4)$$

---

[13] Ungvary, F.; Gallucci, J.; Wojcicki, A. *Organometallics* **1991**, *10*, 3053.

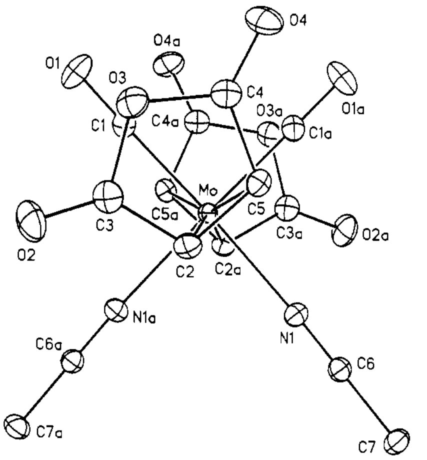


Figure 2. ORTEP diagram of 7 with atomic numbering scheme.

Table IV. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for 7

	x	*y*	*z*	*U*(eq)
Mo	0	448(1)	2500	25(1)
O(1)	920(2)	−1283(2)	1011(2)	63(1)
O(2)	3914(3)	618(2)	1500(2)	70(1)
O(3)	3323(2)	−715(2)	2477(2)	48(1)
O(4)	2527(2)	−1663(2)	3758(2)	59(1)
N(1)	−355(3)	1704(2)	3578(2)	36(1)
C(1)	608(3)	−641(3)	1560(2)	37(1)
C(2)	2264(3)	861(2)	2856(2)	36(1)
C(3)	3239(3)	325(3)	2186(2)	46(1)
C(4)	2542(3)	−854(2)	3340(2)	40(1)
C(5)	1827(3)	121(2)	3570(2)	34(1)
C(6)	−502(3)	2367(2)	4109(2)	36(1)
C(7)	−679(3)	3225(2)	4794(2)	47(1)

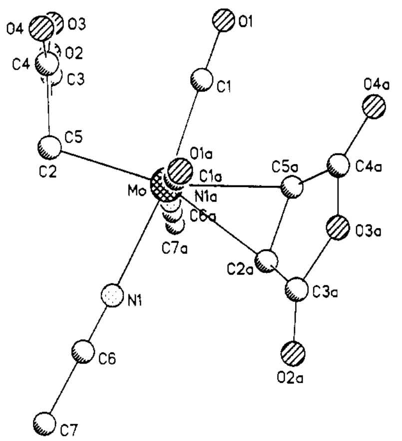


Figure 3. Different perspective view of 7 showing the bending of the central oxygen in a maleic anhydride ligand toward a carbonyl group.

Table V. Important Bond Distances and Angles of 7

	Distances (Å)		
Mo–N(1)	2.206(3)	Mo–C(1)	1.982(3)
Mo–C(2)	2.266(3)	Mo–C(5)	2.294(3)
O(1)–C(1)	1.150(4)	O(2)–C(3)	1.187(4)
O(3)–C(3)	1.405(4)	O(3)–C(4)	1.389(4)
O(4)–C(4)	1.190(4)	N(1)–C(6)	1.126(4)
C(2)–C(3)	1.467(5)	C(2)–C(5)	1.420(4)
C(4)–C(5)	1.467(4)	C(6)–C(7)	1.453(4)
	Angles (deg)		
N(1)–Mo–C(1)	171.9(1)	N(1)–Mo–C(2)	80.3(1)
C(1)–Mo–C(2)	91.5(1)	N(1)–Mo–C(5)	80.7(1)
C(1)–Mo–C(5)	92.8(1)	C(2)–Mo–C(5)	36.3(1)
N(1)–Mo–N(1A)	84.9(1)	C(1)–Mo–N(1A)	93.5(1)
C(2)–Mo–N(1A)	79.6(1)	C(5)–Mo–N(1A)	115.7(1)
C(2)–Mo–C(1A)	108.0(1)	C(1)–Mo–C(1A)	89.2(1)
C(5)–Mo–C(2A)	153.3(1)	C(5)–Mo–C(1A)	71.8(1)
C(5)–Mo–C(5A)	158.7(1)	C(2)–Mo–C(2A)	152.7(2)
Mo–C(1)–O(1)	178.0(3)	Mo–C(2)–C(3)	110.9(2)
Mo–C(2)–C(5)	72.9(2)	C(3)–C(2)–C(5)	106.3(3)
Mo–C(5)–C(2)	70.8(2)	Mo–C(5)–C(4)	112.1(2)
C(2)–C(5)–C(4)	107.6(2)	N(1)–C(6)–C(7)	179.5(3)

acetonitrile and insoluble in most other organic solvents; they were characterized by IR, NMR, and microanalysis data. For example, the IR spectrum of 7 shows two C≡N absorptions at 2321 and 2292 cm^{-1}, two carbonyl absorptions at 1986 and 1920 cm^{-1}, and two keto carbonyl absorptions at 1808 and 1744 cm^{-1}, while the ^{1}H NMR spectrum exhibits two olefinic signals of the maleic anhydride ligands at δ 4.46 and 4.19 and a methyl resonance of acetonitrile at δ 1.96. Because the two olefinic protons are close in chemical shift, we are unable to unambiguously assign the conformation of the alkene ligands in 7. However, in view of the X-ray results (*vide infra*) for complex 7, conformation **I** is strongly favored in solution. In the ^{1}H NMR spectra of **9**, two signals at δ 4.72 and 3.08, corresponding to the olefinic protons of the maleic anhydride ligands, were observed. These two signals differ by more than 1.5 ppm, indicating that the upfield olefinic proton at δ 3.08 lies in region **I**. Consequently, the conformation of complex **9** in solution is assigned as **I**. The olefinic proton resonances of **10** appear at δ 4.59 and 3.28, suggesting that the conformation of this species is also **I**.

X-ray Structure Determination of $Mo(CO)_2(MA)_2(CH_3CN)_2$ (7). The structure of 7 was determined by X-ray diffraction. A single crystal suitable for X-ray analysis was grown during a slow reaction of $Mo(CO)_3(CH_3CN)_3$ with maleic anhydride in acetonitrile at ambient temperature. An ORTEP diagram of 7 with atomic numbering is shown in Figure 2; its atomic coordinates are listed in Table IV, and important intramolecular bond distances and bond angles are shown in Table V. The results of these studies indicate that this complex is distorted octahedral with the two MA ligands trans to each other and cis to the CO and acetonitrile ligands, whereas the two CO groups are cis to each other, but each is trans to an acetonitrile group. Both acetonitrile molecules in the complex are linearly bonded to the molybdenum center (177.5°) using the lone pairs on the nitrogen atoms. The two maleic anhydrides are mutually orthogonal (85.2°), and each anhydride ligand eclipses a N–M–C vector (4.5°). Each anhydride molecule lies with the central oxygen atom pointing to a carbonyl group. The distance from the oxygen atom to the carbonyl carbon is 2.859 Å, indicating a weak bonding between the carbonyl group and the oxygen atom. The results clearly indicate that the conformation of this species is **I** in the solid state. Thus, the conformation of maleic anhydride ligands in 7 is similar to those of maleimides in complexes **1–6**. The interaction between an electron lone pair on the central oxygen atom of maleic anhydride and a π* orbital of a carbonyl group likely accounts for the weak bonding and the observed conformation. However, pure steric effects occurring between the maleic anhydride ligands and other moieties of the complex also favor the observed conformation.

Strong support for the interligand interaction between a maleic anhydride and a carbonyl group in complex 7 is that the oxygen atom in each maleic anhydride bends toward a carbonyl group by 4.7° (the angle between the planes defined by C(3), O(3), and C(4) and by C(3), C(2), C(5), and C(4)) (Figure 3). The anhydride ligand is expected to bend away from the carbonyl groups to avoid steric repulsion, if there is no bonding between the oxygen atoms and the carbonyl groups. The angle defined by the anhydride oxygen, the carbonyl carbon, and the metal center Mo–C(1)–O(3) is 90.6°, suggesting that the π* orbital of each carbonyl carbon is interacting with an essentially pure p orbital of the oxygen atom. The latter overlaps strongly with the other π orbitals on the maleic anhydride ring. Similar results are also observed for complex **1b** and for $Mo(CO)_2(MeMI)_2(bpy)$. The bent-over angles of the nitrogen atoms on the maleimide ligands to a carbonyl group are 1.9 and 1.0°, while the angles defined by the imide nitrogen, the carbonyl carbon, and the metal center, Mo–C–N, are 89.4 and 90.3° for **1b** and $\mathrm{Mo(CO)_2(MeMI)_2(bpy)}$, respectively.

Conclusion

We have demonstrated that a large class of trans bis(maleimide) and bis(maleic anhydride) molybdenum(0) complexes may be synthesized. All these species appear to favor conformation I in the solid state and in solution, with the nitrogen atom of the maleimide or the oxygen atom of the anhydride ligand pointing to a carbonyl group. Interligand interactions between the nitrogen atom of a maleimide ligand (or the oxygen atom of a maleic anhydride molecule) and a carbonyl group likely exist in all these complexes.

Experimental Section

All experiments were performed under dry nitrogen, and all solvents were purified under $\mathrm{N_2}$ by standard methods. The ^{1}H and ^{13}C NMR spectra were obtained on a Bruker AM-400 and a Varian Gemini 300 instrument, while infrared spectra were obtained on a Bomem MB-100 spectrometer. Elemental analyses were performed by Heraens CHN-O-Rapid. All reagents were used as obtained from commercial sources.

Maleic anhydride, maleimide, *N*-phenylmaleimide, *N*-methylmaleimide, 2,2′-bipyridine, 1,10-phenanthroline, ethylenediamine (Merck), molybdenum hexacarbonyl (Strem), and 1,2-phenylenediamine (Janssen) were used as received. $\mathrm{Mo(CO)_3(CH_3CN)_3}$[14] was prepared by heating $\mathrm{Mo(CO)_6}$ in refluxing acetonitrile for 5 h, whereas $\mathrm{Mo(CO)_4(bpy)}$ and $\mathrm{Mo(CO)_4(phen)}$ were synthesized according a method previously reported.[15]

Synthesis of $\mathrm{Mo(CO)_2(MI)_2(CH_3CN)_2}$ (1a). A mixture of $\mathrm{Mo(CO)_3(CH_3CN)_3}$ (0.500 g, 1.65 mmol) and maleimide (0.480 g, 4.95 mmol) in $\mathrm{CH_3CN}$ (20 mL) under nitrogen was refluxed for 2 h. A yellow precipitate was obtained at the end of the reaction. The precipitate was filtered off and washed with $\mathrm{CH_3CN}$ to give the desired product **1a** in 91% yield (0.64 g). ^{1}H NMR ($\mathrm{CD_3CN}$): δ 7.62 (s, 2 H, NH), 4.06 (d, J = 5.6 Hz, 2 H, $=$CH), 3.77 (d, J = 5.6 Hz, 2 H, $=$CH), 1.97 (s, 3 H, $\mathrm{CH_3}$). IR (KBr): 1977 (s), 1907 (s) ($\nu(\mathrm{C{\equiv}O})$), 1724, 1675 cm^{-1} ($\mathrm{C{=}O}$). Anal. Calcd for $\mathrm{MoC_{14}H_{12}N_4O_6 \cdot H_2O}$: C, 37.67; H, 3.14; N, 12.56. Found: C, 38.16; H, 3.05; N, 12.84.

Synthesis of $\mathrm{Mo(CO)_2(PhMI)_2(CH_3CN)_2}$ (1b). The title compound was prepared in 96% yield from $\mathrm{Mo(CO)_3(CH_3CN)_3}$ and *N*-phenylmaleimide in acetonitrile by following a procedure similar to that described for **1a**. ^{1}H NMR ($\mathrm{CD_3CN}$): δ 7.34 (m, 10 H, Ph), 4.21 (d, J = 5.7 Hz, 2 H, $=$CH), 3.99 (d, J = 5.7 Hz, 2 H, $=$CH), 1.95 (s, 6 H, $\mathrm{CH_3}$). ^{13}C{^{1}H} NMR ($\mathrm{CD_3CN}$, 294 K): δ 217.62 ($\mathrm{C{\equiv}O}$), 176.18, 176.02 ($\mathrm{C{=}O}$), 132.72, 128.27, 126.68, 126.12 (Ph), 61.05, 60.84 ($=$CH). IR (KBr): 1980 (s), 1916 (s) ($\nu(\mathrm{C{\equiv}O})$), 1734, 1684 cm^{-1} ($\nu(\mathrm{C{=}O})$). Anal. Calcd for $\mathrm{MoC_{26}H_{20}N_4O_6}$: C, 53.75; H, 3.51; N, 9.65. Found: C, 53.56; H, 3.54; N, 9.53.

Synthesis of $\mathrm{Mo(CO)_2(MeMI)_2(CH_3CN)_2}$ (1c). The title compound was prepared in 94% yield from $\mathrm{Mo(CO)_3(CH_3CN)_3}$ and *N*-methylmaleimide in acetonitrile by following a procedure similar to that described for **1a**. ^{1}H NMR ($\mathrm{CD_3CN}$): δ 4.06 (d, J = 5.7 Hz, 2 H, $=$CH), 3.77 (d, J = 5.7 Hz, 2 H, $=$CH), 2.72 (s, 6 H, $\mathrm{NCH_3}$), 1.95 (s, 6 H, $\mathrm{CH_3CN}$). ^{13}C{^{1}H} NMR ($\mathrm{CD_3CN}$): δ 219.45 ($\mathrm{C{\equiv}O}$), 178.36, 178.11 ($\mathrm{C{=}O}$), 126.41 ($\mathrm{C{\equiv}N}$), 61.90, 61.47 ($=$CH), 22.98 ($\mathrm{NCH_3}$), 1.45 ($\mathrm{CH_3CN}$). IR (KBr) 1964 (s), 1904 (s) ($\nu(\mathrm{C{\equiv}O})$), 1729, 1672 cm^{-1} ($\mathrm{C{=}O}$). Anal. Calcd for $\mathrm{MoC_{16}H_{16}N_4O_6}$: C, 42.11; H, 3.51; N, 12.27. Found: C, 41.40; H, 3.58; N, 11.93.

Synthesis of $\mathrm{Mo(CO)_2(MI)_2(DMSO)_2}$ (2a). $\mathrm{Mo(CO)_2(MI)_2(CH_3CN)_2}$ (0.2 g) was dissolved in dimethyl sulfoxide (2 mL), and the solution was left at room temperature for 1 h. Addition of methylene chloride and hexanes to the filtrate led to precipitation of orange material. The mixture was filtered, and the solid was washed with diethyl ether to give the desired product in essentially quantitative yield. ^{1}H NMR (DMSO-d_6): δ 9.71 (s, 2 H, NH), 3.93 (d, J = 5.5 Hz, 2 H, $=$CH), 3.28 (d, J = 5.5 Hz, 2 H, $=$CH), 2.53 (s, 6 H, DMSO). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 224.19 ($\mathrm{C{\equiv}O}$), 178.22 ($\mathrm{C{=}O}$), 66.40, 66.36 ($=$CH). IR (KBr): 1959 (s), 1886 (s) cm^{-1} ($\nu(\mathrm{C{\equiv}O})$), 1722, 1680 ($\nu(\mathrm{C{=}O})$).

Synthesis of $\mathrm{Mo(CO)_2(PhMI)_2(DMSO)_2}$ (2b). The title compound was prepared in quantitative yield by following a procedure similar to that described for **2a**. ^{1}H NMR (DMSO-d_6): δ 7.34 (m, 10 H, Ph), 4.26 (d, J = 5.7 Hz, 2 H, $=$CH), 3.57 (d, J = 5.7 Hz, 2 H, $=$CH), 2.54 (s, 6 H, DMSO). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 222.52 ($\mathrm{C{\equiv}O}$), 175.82, 175.71 ($\mathrm{C{=}O}$), 132.61 128.19, 126.56, 126.25 (Ph), 65.39, 65.07 ($=$CH), 1.13 ($\mathrm{CH_3}$). IR (KBr): 1955 (s), 1882 (s) ($\nu(\mathrm{C{\equiv}O})$), 1727, 1678 cm^{-1} ($\nu(\mathrm{C{=}O})$). Anal. Calcd for $\mathrm{MoC_{26}H_{26}N_2O_8S_2 \cdot H_2O}$: C, 46.43; H, 4.17; N, 4.17. Found: C, 45.77; H, 4.20; N, 4.01.

Synthesis of $\mathrm{Mo(CO)_2(MeMI)_2(DMSO)_2}$ (2c). The title compound was prepared in quantitative yield by following a procedure similar to that described for **2a**. ^{1}H NMR (DMSO-d_6): δ 4.04 (d, J = 5.7 Hz, 2 H, $=$CH), 3.33 (d, J = 5.7 Hz, 2 H, $=$CH), 2.70 (s, 6 H, $\mathrm{NCH_3}$), 2.54 (s, 6 H, DMSO). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 222.81 ($\mathrm{C{\equiv}O}$), 176.93, 176.77 ($\mathrm{C{=}O}$), 64.90, 64.64 ($=$CH), 22.58 ($\mathrm{NCH_3}$). IR (KBr): 1951 (s), 1873 (s) ($\nu(\mathrm{C{\equiv}O})$), 1723, 1663 cm^{-1} ($\mathrm{C{=}O}$). Anal. Calcd for $\mathrm{MoC_{16}H_{22}N_2O_8S_2 \cdot H_2O}$: C, 35.04; H, 4.38; N, 5.11. Found: C, 35.50; H, 4.20; N, 5.11.

Synthesis of $\mathrm{Mo(CO)_2(PhMI)_2(en)}$ (3b). The title compound was prepared from $\mathrm{Mo(CO)_2(CH_3CN)_2(PhMI)_2}$ and 1 equiv of ethylenediamine in acetonitrile. The yellow material, precipitated directly from the solution, was filtered off and washed with diethyl ether to give the desired product in 95% yield. ^{1}H NMR ($\mathrm{CD_3CN}$): δ 7.39 (m, Ph), 3.91 (d, J = 6.0 Hz, $=$CH), 3.41 (d, J = 6.0 Hz, $=$CH), 3.32 (br, 2 H, NH), 2.83 (br, 2 H, NH), 3.26 (br, 2 H, $\mathrm{CH_2}$), 2.95 (br, 2 H, $\mathrm{CH_2}$). ^{13}C{^{1}H} NMR ($\mathrm{CD_3CN}$): δ 219.82 ($\mathrm{C{\equiv}O}$), 176.96, 176.75 ($\mathrm{C{=}O}$), 132.72, 128.27, 126.62, 126.31 (Ph), 57.90, 57.52 ($\mathrm{C{=}C}$), 42.09 ($\mathrm{CH_2}$). IR (KBr): 3268, 3177 ($\nu(\mathrm{NH_2})$), 1970, 1882 ($\nu(\mathrm{C{\equiv}O})$), 1727, 1670 cm^{-1} ($\nu(\mathrm{C{=}O})$). Anal. Calcd for $\mathrm{MoC_{24}H_{22}N_4O_6 \cdot H_2O}$: C, 50.00; H, 4.17; N, 9.72. Found: C, 49.06; H, 4.44; N, 10.63.

Synthesis of $\mathrm{Mo(CO)_2(MeMI)_2(en)}$ (3c). The title compound was prepared in 87% yield by following a procedure similar to that described for **3b**. ^{1}H NMR (DMSO-d_6): δ 3.79 (d, J = 5.5 Hz, 2 H, $=$CH), 3.26 (d, J = 5.6 Hz, 2 H, $=$CH), 2.66 (s, 6 H, $\mathrm{CH_3}$). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 219.98 ($\mathrm{C{\equiv}O}$), 178.05, 177.77 ($\mathrm{C{=}O}$), 57.46 ($=$CH), 41.92 ($\mathrm{CH_2}$), 22.60 ($\mathrm{CH_3}$). IR (KBr): 1956, 1879 ($\nu(\mathrm{C{\equiv}O})$), 1719, 1667 cm^{-1} ($\nu(\mathrm{C{=}O})$). Anal. Calcd for $\mathrm{MoC_{14}H_{18}N_4O_6}$: C, 38.70; H, 4.15; N, 12.89. Found: C, 38.69; H, 4.67; N, 12.34.

Synthesis of $\mathrm{Mo(CO)_2(PhMI)_2(PDA)}$ (4b). The title compound was prepared in 96% yield by following a procedure similar to that described for **3b**. ^{1}H NMR (DMSO-d_6): δ 7.4 (m, Ph), 5.47 (d, J = 13.8 Hz, 2 H, NH), 5.04 (d, J = 13.8 Hz, 2 H, NH), 4.30 (d, J = 5.9 Hz, 2 H, $=$CH), 3.13 (d, J = 5.9 Hz, 2 H, $=$CH). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 220.16 ($\mathrm{C{\equiv}O}$), 177.36, 176.89 ($\mathrm{C{=}O}$), 138.15, 129.90, 127.19 (PDA), 134.02, 128.85, 126.49, 127.02 (Ph), 59.84, 59.57 ($=$CH). IR (KBr): 3433, 3218 ($\nu(\mathrm{NH_2})$), 1974, 1903 ($\nu(\mathrm{C{\equiv}O})$), 1726, 1675 cm^{-1} ($\nu(\mathrm{C{=}O})$).

Synthesis of $\mathrm{Mo(CO)_2(MI)_2(phen)}$ (5a). A mixture of $\mathrm{Mo(CO)_4(phen)}$ (0.300 g, 0.773 mmol) and maleimide (0.188 g, 1.93 mmol) in acetonitrile (20 mL) was refluxed for 2 h. As the solution was cooled, precipitation of orange material occurred. The precipitate was collected and washed with diethyl ether to afford the desired product **5a** (0.39 g) in 97% yield. ^{1}H NMR (DMSO-d_6): δ 9.70 (s, 2 H, NH), 8.87 (d, J = 5.1 Hz, 2 H, H-2,9 of phen), 8.85 (d, J = 8.2 Hz, 2 H, H-4,7 of phen), 8.27 (s, 2 H, H-5,6 of phen), 7.99 (dd, J = 5.1 Hz, J = 8.2 Hz, 2 H, H-3,8 of phen), 4.04 (br, 2 H, $=$CH), 2.32 (br, 2 H, $=$CH). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 222.03 ($\mathrm{C{\equiv}O}$), 178.40, 177.48 ($\mathrm{C{=}O}$), 152.93, 143.11, 138.55, 130.50, 127.74, 125.62 (phen), 63.84, 61.52 ($=$CH). IR (KBr): 1955, 1890 ($\nu(\mathrm{C{\equiv}O})$), 1721, 1681 cm^{-1} ($\nu(\mathrm{C{=}O})$). Anal. Calcd for $\mathrm{MoC_{22}H_{14}N_4O_6 \cdot H_2O}$: C, 48.53; H, 2.94; N, 10.29. Found: C, 48.18; H, 2.85; N, 10.13.

Synthesis of $\mathrm{Mo(CO)_2(PhMI)_2(phen)}$ (5b). The title compound was prepared in 91% yield by following a procedure similar to that described for **5a**. ^{1}H NMR ($\mathrm{CD_3CN}$): δ 8.98 (d, J = 5.1 Hz, 2 H, H-2,9 of phen), 8.75 (d, J = 8.1 Hz, 2 H, H-4,7 of phen), 8.21 (s, 2 H, H-5,6 of phen), 7.93 (dd, J = 5.1 Hz, J = 8.1 Hz, 2 H, H-3,8 of phen), 7.37 (m, Ph), 4.24 (d, J = 5.4 Hz, $=$CH), 2.60 (d, J = 5.4 Hz, $=$CH). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 219.80 ($\mathrm{C{\equiv}O}$), 176.06, 175.09 ($\mathrm{C{=}O}$), 153.37 143.20, 138.90, 130.73, 127.90, 125.78 (phen), 132.37, 128.14, 126.49, 125.92 (Ph), 62.99, 60.58 ($=$CH). IR (KBr): 1967, 1891 ($\nu(\mathrm{C{\equiv}O})$), 1732, 1675 cm^{-1} ($\nu(\mathrm{C{=}O})$). Anal. Calcd for $\mathrm{MoC_{34}H_{22}N_4O_6}$: C, 60.18; H, 3.27; N, 8.26. Found: C, 59.72; H, 3.35; N, 8.46.

Synthesis of $\mathrm{Mo(CO)_2(MI)_2(bpy)}$ (6a). A mixture $\mathrm{Mo(CO)_4(bpy)}$ (0.300 g, 0.824 mmol) and maleimide (0.200 g, 2.06 mmol) in 20 mL of acetonitrile was refluxed for 2 h. As the solution was cooled, precipitation of yellow material occurred. The precipitate was collected and washed with diethyl ether to afford the desired product **6a** (0.38 g) in 92% yield. ^{1}H NMR (DMSO-d_6): δ 9.67 (br, 2 H, NH), 8.68 (br, 2 H, H-3,3′ of bpy), 8.42 (br, 2 H, H-6,6′ of bpy), 8.22 (br, 2 H, H-5,5′ of bpy), 7.64 (br, 2 H, H-4,4′ of bpy), 3.93 (br, 2 H, $=$CH), 2.53 (br,

---

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

2 H, =CH). $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ 221.81 (C≡O), 178.10, 177.30 (C=O), 152.56, 152.23, 139.32, 126.85, 124.18 (bpy), 64.26, 61.52 (=CH). IR (KBr): 1963, 1897 (ν(C≡O)), 1722, 1682 (ν(C=O)). Anal. Calcd for $MoC_{20}H_{14}N_4O_6{\cdot}H_2O$: C, 46.15; H, 3.08; N, 10.77. Found: C, 45.87; H, 3.07; N, 10.37.

Synthesis of $Mo(CO)_2(PhMI)_2(bpy)$ (6b). The title compound was prepared in 90% yield by following a procedure similar to that described for **6a**. ^1H NMR (CD_3CN): δ 8.56 (d, J = 6.0 Hz, 2 H, H-3,3′ of bpy), 8.48 (d, J = 8.3 Hz, 2 H, H-6,6′ of bpy), 8.19 (dd, J = 4.8 Hz, J = 8.3 Hz, 2 H, H-5,5′ of bpy), 7.58 (dd, J = 4.8 Hz, J = 6.0 Hz, 2 H, H-4,4′ of bpy), 7.35 (m, 5 H, Ph), 4.11 (d, J = 6.0 Hz, 2 H, =CH), 2.82 (d, J = 6.0 Hz, 2 H, =CH). $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ 220.35 (C≡O), 176.21, 175.36 (C=O), 153.17, 153.05, 140.07, 127.51, 124.94 (bpy), 132.73, 128.53, 126.88, 126.29 (Ph), 63.81, 60.99 (=CH). IR (KBr): 1955, 1887 (ν(C≡O)), 1724, 1664 cm^{-1} (ν(C=O)). Anal. Calcd for $MoC_{32}H_{22}N_4O_6$: C, 58.72; H, 3.39; N, 8.57. Found: C, 58.36; H, 3.43; N, 8.57.

Synthesis of $Mo(CO)_2(MA)_2(CH_3CN)_2$ (7). A mixture of $Mo(CO)_3(CH_3CN)_3$ (0.500 g, 1.65 mmol) and maleic anhydride (0.485 g, 4.95 mmol) in CH_3CN (20 mL) under nitrogen was refluxed for 2 h. A yellow precipitate was obtained at the end of the reaction. The precipitate was filtered off and washed with CH_3CN to give the desired product **7** in 88% yield (0.60 g). Crystals suitable for X-ray structure determination were obtained by allowing a mixture of $Mo(CO)_3(CH_3CN)_3$ and maleic anhydride in acetonitrile to stand at ambient temperature for 4 days. ^1H NMR (CD_3CN): δ 4.46 (d, J = 5.2 Hz, 2 H, =CH), 4.19 (d, J = 5.2 Hz, 2 H, =CH), 1.96 (s, 6 H, CH_3CN). IR (KBr): 1986 (s), 1920 (s) (ν(C≡O)), 1808, 1744 cm^{-1} (ν(C=O)). Anal. Calcd for $MoC_{14}H_{10}N_2O_8$: C, 39.09; H, 2.34; N, 6.51. Found: C, 38.84; H, 2.35; N, 6.57.

Synthesis of $Mo(CO)_2(MA)_2(DMSO)_2$ (8). $Mo(CO)_2(MA)_2(CH_3CN)_2$ (0.200 g) was dissolved in dimethyl sulfoxide (2 mL), and the solution was left at room temperature for 2 days. Addition of methylene chloride and hexanes to the solution led to precipitation of orange material. The mixture was filtered, and the solid was washed with diethyl ether to give the desired product in essentially quantitative yield. ^1H NMR (DMSO-d_6): δ 4.49 (d, J = 5.0 Hz, 2 H, =CH), 3.77 (b, 2 H, =CH), 2.54 (s, 6 H, DMSO). $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ 221.15 (C≡O), 172.04, 171.50 (C=O), 64.68, 64.65 (=CH). IR (KBr): 1987 (s), 1914 (s) (ν(C≡O)), 1810, 1745 cm^{-1} (ν(C=O)).

Synthesis of $Mo(CO)_2(MA)_2(phen)$ (9). The title compound was prepared in 97% yield by following a procedure similar to that described for **5a**. ^1H NMR (DMSO-d_6): δ 8.94 (br, 4 H, H-2,4,7,9 of phen), 8.31 (br, 2 H, H-5,6 of phen), 8.06 (br, 2 H, H-3,8 of phen), 4.72 (br, 2 H, =CH), 3.08 (br, 2 H, =CH). $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ 218.84 (C≡O), 172.12, 170.92 (C=O), 153.30, 143.32, 139.31, 130.86, 127.92, 125.80 (phen), 62.47, 60.22 (=CH). IR (KBr): 1999, 1927 (ν(C≡O)), 1803, 1735 cm^{-1} (ν(C=O)). Anal. Calcd for $MoC_{22}H_{12}N_2O_8$: C, 50.04; H, 2.29; N, 5.30. Found: C, 48.80; H, 2.48; N, 5.45.

Synthesis of $Mo(CO)_2(MA)_2(bpy)$ (10). The title compound was prepared in 90% yield by following a procedure similar to that described for **6a**. ^1H NMR (DMSO-d_6): δ 8.73 (d, J = 8.3 Hz, 2 H, H-6,6′ of bpy), 8.47 (d, J = 5.0 Hz, 2 H, H-3,3′ of bpy), 8.29 (dd, J = 6.8 Hz, J = 8.3 Hz, 2 H, H-5,5′ of bpy), 7.70 (dd, J = 6.8 Hz, J = 5.0 Hz, 2 H, H-4,4′ of bpy), 4.59 (br, 2 H, =CH), 3.28 (br, 2 H, =CH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 218.73 (C≡O), 171.90, 170.83 (C=O), 152.95, 152.56, 140.01, 127.20, 124.79 (bpy), 62.78, 60.26 (C=C). IR (KBr): 1986 (s), 1916 (s) (ν(C≡O)), 1804, 1738 cm^{-1} (ν(C=O)). Anal. Calcd for $MoC_{20}H_{12}N_2O_4$: C, 47.66; H, 2.40; N, 5.56. Found: C, 47.81; H, 3.14; N, 5.02.

Table VI. Crystal Data for **1b** and **7**

chem formula	$MoC_{26}H_{20}N_4O_6$ (**1b**)	$MoC_{14}H_{10}N_2O_8$ (**7**)
fw	548.4	430.2
space group	$P1$; triclinic	$Pbcn$; orthorhombic
a, Å	10.110(3)	9.493(3)
b, Å	11.607(3)	12.954(5)
c, Å	12.278(3)	13.460(6)
β, deg	76.61(2)	
V, Å^3	1275.0(6)	1655.2(11)
Z	2	4
ρ(calc), g cm^{-3}	1.512	1.726
μ, cm^{-1}	5.46	8.15
T, °C	24	24
R^a	0.0414	0.0228
$R_w{}^b$	0.0380	0.0263

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

X-ray Structure Determination of $Mo(CO)_2(PhMI)_2(CH_3CN)_2$ (1b). An orange crystal of dimensions 0.20 × 0.12 × 0.09 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 were determined from the fit of 15 reflections ($9.99 \le 2\theta \le 19.08°$). The important parameters of this data collection are presented in Table VI. No significant variation in intensities of three standards monitored every 50 reflections occurred. A total of 5087 reflections were collected, but only 2839 unique reflections with $I \ge 3\sigma(I)$ were used for structure solution and refinement. These data were corrected for absorption, Lorentz, and polarization effects. Correction for absorption was based on ψ scans of a few suitable reflections with χ values near 90° (T_{min}, T_{max} = 0.671, 0.815; μ = 5.46 cm^{-1}). The structure was solved by direct methods 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–C–H = 109.4° and fixed at a U value 0.08 Å^2. The final residuals for variables and independent reflections with $I \ge 3\sigma(I)$ were R = 0.0414 and R_w = 0.0380. The final positional parameters were determined with final refinements of the structure with Rogers' η value.[16] Scattering factors were taken from ref 17. All calculations were performed on a Micro VAX II computer system using SHELXTL-Plus programs.

X-ray Structure Determination of $Mo(CO)_2(MA)_2(CH_3CN)_2$ (7). An orange crystal of dimensions 0.66 × 0.48 × 0.38 mm^3 was selected for X-ray diffraction. Procedures similar to those for complex **1b** were employed for data collection and structure refinement of **7**. Important crystallographic data are presented in Table VI.

Acknowledgment. We thank the National Science Council of the Republic of China (Grant NSC 81-0228-M-007-72) for support of this research.

Supplementary Material Available: Tables of crystal data and data collection parameters, complete bond distances and angles, thermal parameters, and calculated hydrogen positions for **1b** and **7** (8 pages). Ordering information is given on any current masthead page.

---

(16) Roger, D. *Acta Crystallogr.* **1981**, *A37*, 734.

(17) Atomic scattering factors were obtained from the following: *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV.