

JOM 23667

## Synthesis, structure, and properties of molybdenum octahedral $d^6$ bis(alkyne) complexes

C.H. Lai, C.H. Cheng, C.Y. Cheng and S.L. Wang

Department of Chemistry, National Tsing Hua University, Hsinchu 300 (Taiwan)

(Received January 22, 1993; in revised form March 12, 1993)

### Abstract

The complex  $\text{Mo}(\text{CO})_3(\text{CH}_3\text{CN})_3$  reacts with two equiv of alkyne to give  $\text{Mo}(\text{CO})_2(\text{CH}_3\text{CN})_2(\text{alkyne})_2$ . Addition of 1 equiv of NN to the latter compound yields the desired product  $\text{Mo}(\text{CO})_2(\text{NN})(\text{alkyne})_2$  (alkyne = DMAC (dimethylacetylenedicarboxylate), NN = en (1), pn (2), *o*-phenylenediamine (3), and *o*- $\text{NH}_2\text{CH}_2\text{py}$  (4); alkyne = DEAC (diethylacetylenedicarboxylate), NN = en (5), and *o*- $\text{NH}_2\text{CH}_2\text{py}$  (6); alkyne =  $\text{PhC}\equiv\text{CCO}_2\text{Et}$ , NN = bipy (7), and phen (8)). Compounds 1 and 2 may also be synthesized from the reaction of  $\text{Mo}(\text{CO})_3(\text{NN})_2$  with excess DMAC. The structure of  $\text{Mo}(\text{CO})_2(\text{en})(\text{DMAC})_2$  (1) has been determined by X-ray crystallography and refined to  $R = 0.0235$  ( $R_w = 0.0242$ ) by using 3063 independent reflections with intensity  $\geq 3\sigma(I)$ . The crystals were triclinic, space group  $P\bar{1}$ ;  $a = 8.508(2)$ ,  $b = 9.587(2)$ , and  $c = 13.214(3)$  Å;  $\alpha = 78.35(2)$ ,  $\beta = 87.98(2)$ , and  $\gamma = 78.99(2)$ ;  $Z = 2$ . The molecule adopts an octahedral geometry with the two CO groups *cis* to each other, the two DMAC ligands in *trans* positions and the remaining two sites being occupied by the nitrogen atoms of the ethylenediamine group. The orientations of the two *trans* alkyne ligands are mutually perpendicular with each DMAC ligand eclipsing a N–Mo–CO vector. All the present complexes 1–8 exhibit fluxional behavior on the NMR timescale due to the rotation of alkyne ligands around the axis through the metal center and perpendicular to the two alkyne ligands. At low temperatures, the NMR spectra of 4 and 6 reveal the presence of four different signals for each type of nuclei on the alkyne ligands. Each set of the four signals averages to only one at the fast-exchange limit. For  $\text{Mo}(\text{CO})_2(\text{phen})(\text{PhC}\equiv\text{CCO}_2\text{Et})_2$  (8), two conformational isomers A and B exist in solution arising from the different orientations of the  $\text{PhC}\equiv\text{CCO}_2\text{Et}$  ligands relative to the N–Mo–CO vectors. The possible mechanisms for the observed fluxional behavior of these complexes are discussed.

### 1. Introduction

Complexes of molybdenum and tungsten containing alkyne ligands have attracted considerable attention recently. These alkynes have been shown formally to donate two to four electrons to the metal center by way of the filled  $\pi_{||}$  and  $\pi_{\perp}$  orbitals [1]. Moreover, due to the special orbital interaction between metal and ligands, these coordinated alkynes exhibit various orientation preferences relative to any other ligand that may be on the metal center [2]. Bis(alkyne) complexes of the early transition metals are known. Examples include  $(\pi\text{-C}_5\text{H}_5)\text{M}(\text{CO})(\text{PhC}\equiv\text{CPh})_2$  ( $\text{M} = \text{V}, \text{Nb}, \text{Ta}$ ) [3],  $(\pi\text{-C}_5\text{H}_5)\text{M}(\text{RC}\equiv\text{CR})_2\text{X}$  ( $\text{M} = \text{Mo}, \text{X} = \text{Cl}, \text{R} = \text{CH}_2\text{OH}$ ) [4];  $\text{M} = \text{Mo}, \text{W}, \text{X} = \text{Cl}, \text{R} = \text{CF}_3, \text{Ph}$  [5];  $\text{M} = \text{Mo}, \text{W}, \text{X} = \text{CO}^+, \text{R} = \text{CH}_3$ ) [6],  $\text{Mo}(\text{R}^1\text{C}\equiv\text{CR}^2)_2$

$(\text{S}_2\text{CNR}_2)_2$  ( $\text{R} = \text{Me}, \text{Et}, \text{R}^1 = \text{R}^2 = \text{Ph}; \text{R}^1 = \text{H}, \text{R}^2 = \text{Ph}; \text{R}^1 = \text{Me}, \text{R}^2 = \text{Ph}$ ) [7];  $[\text{W}(\text{CO})(\text{NCMe})(\text{S}_2\text{CNC}_4\text{H}_8)(\text{MeC}\equiv\text{CMe})_2][\text{BPh}_4]$  [8] and  $[\text{W}(\text{CO})(\text{R}^1\text{C}\equiv\text{CR}^2)_2(\text{S}_2\text{CNR}_2)]$  ( $\text{R} = \text{Me}, \text{R}^1 = \text{R}^2 = \text{Me}, \text{Ph}; \text{R} = \text{Et}, \text{R}^1 = \text{R}^2 = \text{Me}, \text{Ph}$ ) [9]. Interestingly, nearly all of these compounds are in the  $d^4$  configuration and the two alkyne ligands are *cis* and approximately parallel to each other. Octahedral  $d^6$  bis(alkyne) complexes deserve particular attention in view of the presence of the repulsion between filled  $d_{\pi}$  of the complexes and  $\pi_{\perp}$  orbitals of the alkyne ligands. The effect of this repulsion on the stability of a  $d^6$  metal complex has not been fully understood. A tungsten  $d^6$  octahedral complex  $\text{W}(\text{CO})_2(\text{dppe})(\text{DMAC})_2$  was first prepared by Templeton *et al.* [10]. Recently, we reported a series of tungsten bis(alkyne) complexes of the type  $\text{W}(\text{CO})_2(\text{NN})(\text{alkyne})_2$  where NN is a bidentate nitrogen ligand [11]. Most of these complexes with asymmetric alkyne

Correspondence to: Dr. S.L. Wang.

ligands show interesting conformational isomers. Due to the rotation of alkyne ligands, these complexes are fluxional, and the rotations of alkyne ligands in these bis(alkyne) tungsten species were shown to be conrotatory. There are only two molybdenum bis(alkyne) complexes Mo(CO)<sub>2</sub>(NN)(DMAC)<sub>2</sub> (NN = bipy and phen) [12] known. To enlarge the scope of d<sup>6</sup> molybdenum bis(alkyne) complexes and to compare the mechanism of alkyne rotation and the stability of these complexes with those in the corresponding tungsten species, we further investigate the chemistry of molybdenum bis(alkyne) complexes. Here we report the results of these studies.

## 2. Experimental section

All reactions were performed under dry nitrogen and all solvents were dried by standard methods. The <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker AM-400 instrument, while infrared spectra were obtained from a Bomem MB-100 spectrometer. Structural determination was carried out on a Siemens R3m/V diffractometer.

Dimethylacetylenedicarboxylate (DMAC), diethylacetylenedicarboxylate (DEAC), ethylenediamine (en), propylenediamine (pn) (Merck), *o*-phenylenediamine, and molybdenum hexacarbonyl (Janssen), ethyl phenylpropionate, 2-aminomethylpyridine (*o*-NH<sub>2</sub>CH<sub>2</sub>py), 2,2'-bipyridine (bipy), and 1,10-phenanthroline (phen) (Aldrich) were used as purchased.

### 2.1. Synthesis of Mo(CO)<sub>2</sub>(en)(DMAC)<sub>2</sub> (1)

#### 2.1.1. Method a

Mo(CO)<sub>6</sub> (0.500 g, 1.89 mmol) in 20 ml of acetonitrile was refluxed under nitrogen for 5 h. IR monitoring of the solution indicated that all Mo(CO)<sub>6</sub> was converted to Mo(CO)<sub>3</sub>(CH<sub>3</sub>CN)<sub>3</sub>. To the solution was added DMAC (2 equiv, 0.47 ml). The solution was stirred at room temperature for 10 min. Addition of ethylenediamine (1 equiv, 0.13 ml) was followed by further stirring for 5 min at ambient temperature. Separation on a silica gel column using CH<sub>2</sub>Cl<sub>2</sub>/EA (v/v = 1/5) as the eluent led to the isolation of the desired product in 44% yield (0.41 g). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 293 K): δ 2.58 (s, 4H, CH<sub>2</sub>), 2.79 (b, 4H, NH<sub>2</sub>), 3.81 (s, 12H, OCH<sub>3</sub>). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 188 K): δ 1.63, 4.16 (NH<sub>2</sub>), 2.15, 2.80 (CH<sub>2</sub>), 3.80, 3.76 (OCH<sub>3</sub>). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 293 K): δ 42.07 (CH<sub>2</sub>), 52.45 (OCH<sub>3</sub>), 142.98 (C≡C), 168.80 (COO), 218.06 (C≡O). <sup>13</sup>C {<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 188 K): δ 42.27 (CH<sub>2</sub>), 53.46, 53.65 (OCH<sub>3</sub>), 142.04, 143.58 (C≡C), 167.04, 171.43 (COO), 218.94 (C≡O). IR (KBr): 1700s, 1682s

(ν(C=O)); 1785br (ν(C≡C)); 2010s, 1935vs (ν(C≡O)); 3325, 3280 cm<sup>-1</sup> (ν(NH<sub>2</sub>)). Anal. calcd for MoC<sub>16</sub>H<sub>20</sub>N<sub>2</sub>O<sub>10</sub>: C, 38.72; H, 4.06; N, 5.65. Found: C, 38.76; H, 4.11; N, 5.76%.

#### 2.1.2. Method b

To 1.00 g (3.68 mmol) of Mo(CO)<sub>3</sub>(en)<sub>2</sub> in 30 ml of CH<sub>3</sub>CN was added 1.60 g (11.30 mmol) of DMAC. The solution was stirred at room temperature for 10 min. Separation on a silica gel column using CH<sub>2</sub>Cl<sub>2</sub> as the eluent, collection of the desired portion, evaporation of the solvent, followed by recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/ether gave 0.61 g (33%) of the desired product as orange crystalline material.

### 2.2. Synthesis of Mo(CO)<sub>2</sub>(pn)(DMAC)<sub>2</sub> (2)

The title compound was prepared in 37% yield following a procedure similar to that (method a) for the synthesis of 1. <sup>1</sup>H NMR (*d*<sub>6</sub>-acetone, 297 K): δ 1.58 (m, 2H, CH<sub>2</sub>), 2.82 (m, 8H, CH<sub>2</sub>N, NH<sub>2</sub>), 3.80 (s, 12H, OCH<sub>3</sub>). <sup>1</sup>H NMR (*d*<sub>6</sub>-acetone, 185 K): δ 1.57 (CH<sub>2</sub>), 2.32, 4.47 (NH<sub>2</sub>), 2.76 (CH<sub>2</sub>N), 3.82, 3.77 (OCH<sub>3</sub>). <sup>13</sup>C {<sup>1</sup>H} NMR (*d*<sub>6</sub>-acetone, 297 K): δ 43.26 (CH<sub>2</sub>N), 43.10 (CH<sub>2</sub>), 52.34 (OCH<sub>3</sub>), 144.31 (C≡C), 170.05 (COO), 219.38 (CO). <sup>13</sup>C {<sup>1</sup>H} NMR (*d*<sub>6</sub>-acetone, 185 K): δ 43.00 (CH<sub>2</sub>N, CH<sub>2</sub>), δ 52.86, 52.73 (OCH<sub>3</sub>), 146.87, 141.29 (C≡C), 170.48, 169.95 (COO), and 219.93 (CO); IR (KBr) 1683s (ν(C=O)), 1780br ν(C≡C), 2008s, 1935s (ν(C≡O)), and 3323, 3275 cm<sup>-1</sup> (ν(NH<sub>2</sub>)). Anal. calcd for MoC<sub>17</sub>H<sub>22</sub>N<sub>2</sub>O<sub>10</sub>: C, 40.01; H, 4.34; N, 5.49. Found: C, 39.99; H, 4.34; N, 5.50%.

### 2.3. Synthesis of Mo(CO)<sub>2</sub>[*o*-C<sub>6</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub>](DMAC)<sub>2</sub> (3)

The title compound was prepared in 27.9% yield following a procedure similar to that (method a) for the synthesis of 1. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 3.71 (s, 12H, OCH<sub>3</sub>), 4.50 (b, 4H, NH<sub>2</sub>), and 7.12 (m, 4H, C<sub>6</sub>H<sub>4</sub>). IR (KBr): 1686s (ν(C=O)), 1793br (ν(C≡C)), 2017s, 1941s (ν(C≡O)), 3260, and 3224 cm<sup>-1</sup> (ν(NH<sub>2</sub>)).

### 2.4. Synthesis of Mo(CO)<sub>2</sub>(*o*-NH<sub>2</sub>CH<sub>2</sub>py)(DMAC)<sub>2</sub> (4)

The title compound was prepared in 42% yield following a procedure similar to that (method a) for the synthesis of 1. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 293 K): δ 3.34 (b, 2H, NH<sub>2</sub>), 3.69 (s, 12H, OCH<sub>3</sub>), 4.25 (t, *J* = 6.4 Hz, 2H, CH<sub>2</sub>), 7.17 (m, 2H, H-4, 6 of py), 7.69 (t, *J* = 7.8 Hz, 1H, H-5 of py), 8.28 (d, *J* = 5.4 Hz, 1H, H-3 of py). <sup>13</sup>C {<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 293 K): δ 48.24 (CH<sub>2</sub>), 141.21 (C≡C), 52.22 (OCH<sub>3</sub>), 158.20, 151.52, 138.21, 123.21, 121.05 (py), 168.94 (COO), 219.15, 219.01 (C≡O). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 163 K): δ 2.18 (b, 1H, NH), 3.83 (s, 3H, OCH<sub>3</sub>), 3.74 (s, 3H, OCH<sub>3</sub>), 3.62 (s, 3H, OCH<sub>3</sub>), 3.31 (s, 3H, OCH<sub>3</sub>), 4.13 (b, 2H, CH<sub>2</sub>), 4.91 (b, 1H,

NH), 7.18 (m, 2H, H-4, 6 of py), 7.69 (t,  $J = 7.3$  Hz, 1H, H-5 of py), 8.19 (d,  $J = 4.8$  Hz, 1H, H-3 of py).  $^{13}\text{C}$  { $^1\text{H}$ } NMR ( $\text{CD}_2\text{Cl}_2$ , 163 K):  $\delta$  47.69 ( $\text{CH}_2$ ), 52.35, 51.70 ( $\text{OCH}_3$ ), 143.89, 142.02, 140.98, 131.30, ( $\text{C}\equiv\text{C}$ ), 157.62, 150.32, 137.69, 123.07, 120.39 (py), 170.22, 169.62, 167.79, 165.22 (COO), 218.57, 218.30 ( $\text{C}\equiv\text{O}$ ). IR (KBr): 1684s ( $\nu(\text{C}=\text{O})$ ), 1817s ( $\nu(\text{C}\equiv\text{C})$ ), 1998s, 1929s ( $\nu(\text{C}\equiv\text{O})$ ), and 3330, 3289  $\text{cm}^{-1}$  ( $\nu(\text{NH}_2)$ ). Anal. Calcd for  $\text{MoC}_{20}\text{H}_{20}\text{N}_2\text{O}_{10}$ : C, 44.12; H, 3.68; N, 5.14. Found: C, 44.06; H, 3.68; N, 5.15%.

### 2.5. Synthesis of $\text{Mo}(\text{CO})_2(\text{en})(\text{DEAC})_2$ (5)

The title compound was prepared in 41% yield following a procedure similar to that (method a) for the synthesis of 1.  $^1\text{H}$  NMR: ( $\text{CDCl}_3$ )  $\delta$  1.27 (t,  $J = 7.1$  Hz, 12H,  $\text{CH}_3$ ), 2.53 (b, 4H,  $\text{CH}_2\text{N}$ ), 2.82 (b, 4H,  $\text{NH}_2$ ), 4.24 (q,  $J = 7.1$  Hz, 8H,  $\text{OCH}_2$ ).  $^{13}\text{C}$  { $^1\text{H}$ } NMR ( $\text{CDCl}_3$ ):  $\delta$  41.69 ( $\text{CH}_2\text{N}$ ), 14.31 ( $\text{CH}_3$ ), 61.34 ( $\text{OCH}_2$ ), 143.31 ( $\text{C}\equiv\text{C}$ ), 168.45 (COO), 217.32 (CO). IR ( $\text{CH}_2\text{Cl}_2$ ): 1781br ( $\nu(\text{C}\equiv\text{C})$ ) 1725s ( $\nu(\text{C}=\text{O})$ ), 2018s, 1952s  $\text{cm}^{-1}$  ( $\nu(\text{C}\equiv\text{O})$ ). Anal. calcd for  $\text{MoC}_{20}\text{H}_{28}\text{N}_2\text{O}_{10}$ : C, 43.48; H, 5.07; N, 5.07. Found: C, 42.44; H, 5.07; N, 4.69%.

### 2.6. Synthesis of $\text{Mo}(\text{CO})_2(o\text{-NH}_2\text{CH}_2\text{py})(\text{DEAC})_2$ (6)

The title compound was prepared in 73% yield following a procedure similar to that (method a) for the synthesis of 1.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.22 (t,  $J = 7.0$  Hz, 12H,  $\text{CH}_3$ ), 3.51 (b, 2H,  $\text{NH}_2$ ), 4.16 (q,  $J = 7.0$  Hz, 8H,  $\text{OCH}_2$ ), 4.24 (t,  $J = 6.4$  Hz, 2H,  $\text{CH}_2\text{N}$ ), 7.17 (m, 2H, H-4,6 of py), 7.67 (t,  $J = 7.5$  Hz, 1H, H-5 of py), 8.34 (d,  $J = 5.1$  Hz, 1H, H-3 of py).  $^{13}\text{C}$  { $^1\text{H}$ } NMR ( $\text{CDCl}_3$ ):  $\delta$  14.00 ( $\text{CH}_3$ ), 48.30 ( $\text{CH}_2$ ), 141.16 ( $\text{C}\equiv\text{C}$ ), 60.85 ( $\text{OCH}_2$ ), 158.38, 151.30, 137.61, 123.28, 120.50 (py), 168.58 (COO), 218.51, 218.09 ( $\text{C}\equiv\text{O}$ ). IR ( $\text{CH}_2\text{Cl}_2$ ): 1782br ( $\nu(\text{C}\equiv\text{C})$ ), 1725s ( $\nu(\text{C}=\text{O})$ )  $\text{cm}^{-1}$ , 2019s, 1951s  $\text{cm}^{-1}$  ( $\nu(\text{C}\equiv\text{O})$ ). Anal. calcd for  $\text{MoC}_{24}\text{H}_{28}\text{N}_2\text{O}_{10}$ : C, 48.00; H, 4.67; N, 4.67. Found: C, 47.28; H, 4.93; N, 4.76%.

### 2.7. Synthesis of $\text{Mo}(\text{CO})_2(\text{bipy})(\text{PhC}\equiv\text{CCO}_2\text{Et})_2$ (7)

A mixture of 0.30 g of  $\text{Mo}(\text{CO})_4(\text{bipy})$  (0.82 mmol) and 0.43 g of ethyl phenylpropiolate (2.5 mmol) in 10 ml of toluene was refluxed for 3 h. Separation on a silica gel column using  $\text{CH}_2\text{Cl}_2/\text{EA}$  (v/v = 3/1) as the eluent, collection of the desired portion, evaporation of the solvent, followed by recrystallization from methylene chloride-hexane gave 0.11 g (20%) of the desired product as orange crystalline material.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.96 (t,  $J = 7.1$  Hz, 12H,  $\text{CH}_3$ ), 3.81 (q,  $J = 7.1$  Hz, 8H,  $\text{OCH}_2$ ), 7.12 (m, 5H, Ph), 7.25 (dd,  $J = 5.0$  Hz,  $J = 6.6$  Hz, 2H, H-4, 4' of bipy), 7.76 (dd,  $J = 7.8$  Hz,  $J = 6.6$  Hz, 2H, H-5, 5' of bipy), 7.85 (d,

$J = 7.8$  Hz, 2H, H-6, 6' of bipy), 8.62 (d,  $J = 5.0$  Hz, 2H, H-3, 3' of bipy).  $^{13}\text{C}$  { $^1\text{H}$ } NMR:  $\delta$  14.10 ( $\text{CH}_3$ ), 59.95 ( $\text{OCH}_2$ ), 136.63, 128.15, 126.64 (Ph), 129.95 ( $\equiv\text{C}-\text{Ph}$ ), 144.20 ( $\equiv\text{C}-\text{CO}_2\text{Et}$ ), 153.21, 152.42, 137.49, 125.35, 121.46 (bipy), 171.05 (COO), 224.67 ( $\text{C}\equiv\text{O}$ ). IR (KBr): 1674s ( $\nu(\text{C}=\text{O})$ ), 1784br ( $\nu(\text{C}\equiv\text{C})$ ), 1968s, 1898s  $\text{cm}^{-1}$  ( $\nu(\text{C}\equiv\text{O})$ ). Anal. calcd for  $\text{MoC}_{34}\text{H}_{28}\text{N}_2\text{O}_6$ : C, 62.20; H, 4.29; N, 4.27. Found: C, 62.15; H, 4.30; N, 4.21%.

### 2.8. Synthesis of $\text{Mo}(\text{CO})_2(\text{phen})(\text{PhC}\equiv\text{CCO}_2\text{Et})_2$ (8)

The title compound was prepared in 29% yield following a similar procedure for the synthesis of 7.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.73 (t,  $J = 7.1$  Hz, 12H,  $\text{CH}_3$ ), 3.60 (q,  $J = 7.1$  Hz, 8H,  $\text{OCH}_2$ ), 7.07 (m, 5H, Ph), 7.58 (dd,  $J = 4.9$  Hz,  $J = 8.3$  Hz, 2H, H-3,3' of phen), 7.74 (s, 2H, H-5,5' of phen), 8.25 (d,  $J = 8.3$  Hz, 2H, H-4,4' of phen), 8.93 (d,  $J = 4.9$  Hz, 2H, H-2,2' of phen).  $^{13}\text{C}$  { $^1\text{H}$ } NMR:  $\delta$  13.80 ( $\text{CH}_3$ ), 59.69 ( $\text{OCH}_2$ ), 136.50, 128.05, 127.85, 126.55 (Ph), 129.97 ( $\equiv\text{C}-\text{Ph}$ ), 144.67 ( $\equiv\text{CCO}_2\text{Et}$ ), 151.85, 144.67, 136.40, 129.55, 127.85, 124.39 (phen), 170.81 (COO), 224.72 ( $\text{C}\equiv\text{O}$ ). IR (KBr): 1671s ( $\nu(\text{C}=\text{O})$ ), 1780br ( $\nu(\text{C}\equiv\text{C})$ ), 1981s, 1910s  $\text{cm}^{-1}$  ( $\nu(\text{C}\equiv\text{O})$ ); Anal. Calcd for  $\text{MoC}_{36}\text{H}_{28}\text{N}_2\text{O}_6$ : C, 63.54; H, 4.15; N, 4.12. Found: C, 63.12; H, 4.13; N, 4.08%.

### 2.9. X-ray structure determination of $\text{Mo}(\text{CO})_2(\text{en})(\text{DMAC})_2$

A white chunk-like single crystal of dimension 0.36  $\times$  0.41  $\times$  0.55 mm was selected for X-ray analysis. Diffraction data were collected on a Siemens R3m/V diffractometer with graphite-monochromated Mo  $\text{K}\alpha$  radiation (0.7107 Å). Cell parameters were determined from the fit of 17 reflections ( $12.13 < 2\theta < 27.75^\circ$ ). There was no significant variation in intensities of three standards monitored every 50 reflections. A total of 4703 reflections was collected, but only 3063 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. Corrections for absorption were based on  $\phi$  scans of a few suitable reflections with  $\chi$  values close to  $90^\circ$  ( $T_{\text{max}}$ ,  $T_{\text{min}} = 0.811, 0.753$ ;  $\mu = 6.68 \text{ cm}^{-1}$ ). The structure was solved by direct methods and refined by full-matrix least squares based on  $F$  values. All of the non-hydrogen atoms were refined with anisotropic temperature factors. During the course of structure refinement, two of the carbon atoms, C15 and C16, showed rather large values in  $U_{22}$  (0.197 and 0.206 Å<sup>2</sup>) and the distance between them (1.36 Å) was too short to be a single bond. It appeared that C15–C16 vibrated about the b axis (twisting in the ac plane). Therefore, two sets of ethylene carbon atoms, (C15, C16) and (C15a, C16a)

TABLE 1. Summary of crystal data and data collection of compound 1.

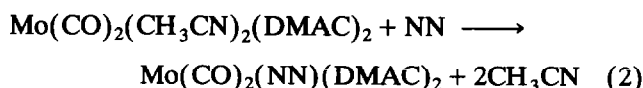
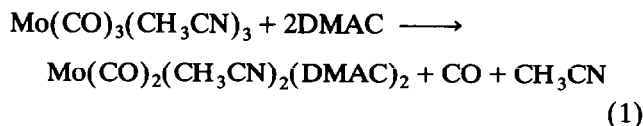
Empirical Formula	C <sub>16</sub> H <sub>20</sub> MoN <sub>2</sub> O <sub>10</sub>
Colour; Habit	White; Chunk
Crystal Size (mm)	0.36 × 0.41 × 0.55
Space Group	Triclinic; <i>P</i> $\bar{1}$
Unit Cell Dimensions	<i>a</i> = 8.508(2) Å, $\alpha$ = 78.35(2)° <i>b</i> = 9.587(2) Å, $\beta$ = 87.98(2)° <i>c</i> = 13.214(3) Å, $\gamma$ = 78.99(2)°
Volume	1036.3(4) Å <sup>3</sup>
Z	2
Formula weight	496.3
Density (calc.)	1.590 g cm <sup>-3</sup>
Absorption Coefficient	0.668 mm <sup>-1</sup>
<i>F</i> (000)	504
Diffractometer Used	Siemens R3m/V
Radiation	Mo K $\alpha$ ( $\lambda$ = 0.71073 Å)
Temperature (K)	296
2 $\theta$ Range	2.0 to 48.0°
Scan Type	$\theta/2\theta$
Scan Speed	Variable; 4.18 to 14.65°/min. in $\omega$
Scan Range ( $\omega$ )	1.00° + <i>K</i> $\alpha$ separation
Standard Reflections	3 measured every 50 reflections
Index Ranges	0 ≤ <i>h</i> ≤ 10, -11 ≤ <i>k</i> ≤ 11, -15 ≤ <i>l</i> ≤ 15
Reflections Collected	4703 (3901 ≥ 3.0 $\sigma(I)$ )
Independent Reflections	3658 (3063 ≥ 3.0 $\sigma(I)$ )
<i>T</i> <sub>min</sub> / <i>T</i> <sub>max</sub>	0.753/0.811
Weighting Scheme	$w^{-1} = \sigma^2(F) + 0.0002 F^2$
Number of Parameters refined	283
Goodness-of-Fit	1.16
Final <i>R</i> indices (obs. data)	<i>R</i> = 0.0235, <i>R</i> <sub>w</sub> = 0.0242
Largest and Mean $\Delta/\sigma$	0.002, 0.000
Data-to-Parameter Ratio	10.8:1
Largest Difference Peak/Hole	0.23/-0.20 eÅ <sup>-3</sup>

were introduced in the refinement. The two forms exist in the crystal in approximately a ratio of 60: 40%. The hydrogen atoms were calculated using ideal geometry (C–H = 0.96 Å and <H–C–H = 109.5°) and refined with fixed *U* (0.08 Å<sup>2</sup>). The final agreement factors are *R* = 0.0235, *R*<sub>w</sub> = 0.0242 with  $w = [\sigma^2(F) + 0.0002 F^2]^{-1}$ . Scattering factors were taken from ref. 13. All calculations were performed on a DEC Micro VAX II computer system using the SHELXTL, PLUS programs [14]. Crystal and general conditions of data collection and structure refinement are presented in Table 1.

### 3. Results

Addition of DMAC to an acetonitrile solution of Mo(CO)<sub>3</sub>(CH<sub>3</sub>CN)<sub>3</sub> yields Mo(CO)<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>(DMAC)<sub>2</sub> (eqn. (1)). In addition to this product, a side

product Mo(CO)<sub>4</sub>(CH<sub>3</sub>CN)<sub>2</sub> presumably from the reaction of Mo(CO)<sub>3</sub>(CH<sub>3</sub>CN)<sub>3</sub> with the CO released from reaction (1) was also observed.



NN = en	1
NN = pn	2
NN = 1,2-(NH <sub>2</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	3
NN = <i>o</i> -NH <sub>2</sub> CH <sub>2</sub> py	4

Mo(CO)<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>(DMAC)<sub>2</sub> is not stable enough to be isolated. However, its presence is indicated by the observation of two new infrared carbonyl absorptions at 2021 and 1955 cm<sup>-1</sup> in the solution of reaction (1). Further addition of 1 equiv of ethylenediamine (en) to the solution followed by separation on silica gel led to the isolation of Mo(CO)<sub>2</sub>(en)(DMAC)<sub>2</sub> (1). The infrared spectrum of 1 also exhibits two characteristic *cis* carbonyl absorptions at 2008s and 1935s cm<sup>-1</sup>. In addition, there are three new bands at 1785b cm<sup>-1</sup> assigned to the coordinated C≡C triple bond and at 1700, 1682 cm<sup>-1</sup> due to the carbonyl groups of the esters. In the <sup>1</sup>H NMR spectrum of 1 at ambient temperature, the singlet at 3.81 ppm is attributed to the methoxy groups of the alkyne ligands and the resonances at 2.56 and 2.81 ppm are assigned to the methylene and amino protons of the bound ethylenediamine, respectively. In the <sup>13</sup>C NMR spectrum, the two equivalent carbonyl carbons appear at 218.1 ppm, while the carbonyl carbons of the ester groups come at 168.8 ppm. The resonances at 143.0, 52.5 and 42.1 ppm are due to the alkyne, the methoxy and the methylene carbons of the coordinated ethylenediamine, respectively. The equivalent environments for the chelating en and the *cis* dicarbonyl pattern agree with a *trans* configuration of the two DMAC ligands.

Similarly, the addition of propylenediamine (pn), *o*-phenylenediamine, and *o*-NH<sub>2</sub>CH<sub>2</sub>Py to a Mo(CO)<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>(DMAC)<sub>2</sub> solution resulted in the formation of Mo(CO)<sub>2</sub>(pn)(DMAC)<sub>2</sub> (2), Mo(CO)<sub>2</sub>[1,2-(NH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>](DMAC)<sub>2</sub> (3), and Mo(CO)<sub>2</sub>(*o*-NH<sub>2</sub>CH<sub>2</sub>py)(DMAC)<sub>2</sub> (4) respectively. Compounds 1–2 may also be synthesized from the direct reaction of DMAC with Mo(CO)<sub>3</sub>(NN)<sub>2</sub> where NN is the corresponding diamine. The species Mo(CO)<sub>3</sub>(NN)<sub>2</sub> was prepared by refluxing Mo(CO)<sub>6</sub> in CH<sub>3</sub>CN in the presence of excess diamine. The procedure for preparing bis(DEAC) complexes is similar to that for bis(DMAC) species.

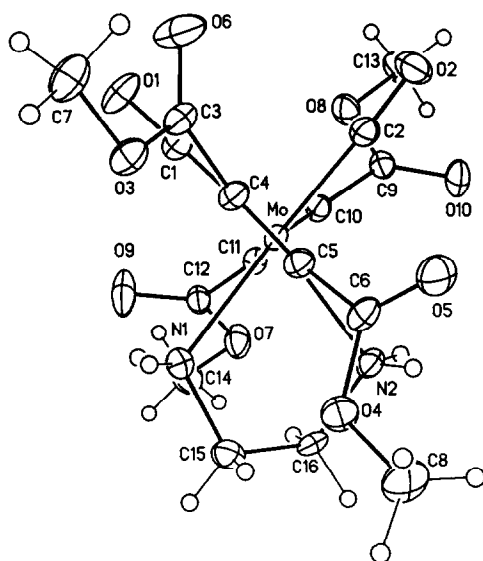


Fig. 1. ORTEP drawing of  $\text{Mo}(\text{CO})_2(\text{en})(\text{DMAC})_2$  (**1**) showing the atom-labeling scheme. The en group exhibits two stable conformations and two sets of ethylene carbons (C15, C16) and (C15a, C16a).

TABLE 2. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement coefficients

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}^a$
Mo	3739	6940	2467	33(1)
O(1)	1394(5)	6437(4)	4355(3)	83(2)
O(2)	686(4)	7904(4)	1051(3)	68(1)
O(3)	2525(4)	10907(3)	3794(2)	54(1)
O(4)	6301(4)	10115(4)	1581(3)	63(1)
O(5)	4039(4)	11109(4)	687(3)	69(1)
O(6)	485(4)	9917(5)	3470(3)	86(2)
O(7)	5918(4)	2337(4)	3077(2)	62(1)
O(8)	1314(4)	3645(4)	1863(2)	57(1)
O(9)	5063(6)	3249(4)	4444(2)	84(2)
O(10)	2510(5)	4683(4)	449(2)	63(1)
N(1)	5988(4)	6640(4)	3459(3)	48(1)
N(2)	5815(4)	6606(4)	1345(3)	43(1)
C(1)	2223(6)	6647(5)	3665(3)	50(2)
C(2)	1821(5)	7570(5)	1545(3)	45(2)
C(3)	1869(6)	9982(5)	3397(3)	49(2)
C(4)	3046(5)	9061(5)	2853(3)	42(2)
C(5)	4059(5)	9173(4)	2123(3)	40(1)
C(6)	4741(6)	10254(5)	1395(3)	45(2)
C(7)	1428(7)	11895(5)	4310(4)	67(2)
C(8)	7143(8)	11087(7)	881(5)	89(3)
C(9)	2341(5)	4422(4)	1371(3)	41(1)
C(10)	3227(5)	4979(4)	2086(3)	39(1)
C(11)	4259(5)	4604(4)	2815(3)	40(1)
C(12)	5099(5)	3351(5)	3533(3)	42(2)
C(13)	423(7)	3008(6)	1214(5)	74(2)
C(14)	6747(7)	1047(6)	3762(4)	75(2)
C(15)	7479(13)	6683(19)	2854(10)	56(5)
C(16)	7308(12)	5968(14)	1948(10)	50(4)
C(15a)	7390(17)	5995(18)	2884(12)	53(6)
C(16a)	7390(15)	6664(26)	1741(10)	53(6)

<sup>a</sup> Equivalent isotropic  $U$  defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

TABLE 3. Important bond lengths ( $\text{\AA}$ ) of compound **1**

Mo–N(1)	2.298(4)	Mo–N(2)	2.283(3)
Mo–C(1)	2.016(5)	Mo–C(2)	1.995(4)
Mo–C(4)	2.164(4)	Mo–C(5)	2.165(4)
Mo–C(10)	2.166(5)	Mo–C(11)	2.155(4)
O(1)–C(1)	1.143(6)	O(2)–C(2)	1.141(6)
C(3)–C(4)	1.472(6)	C(4)–C(5)	1.273(6)
C(5)–C(6)	1.457(6)	C(9)–C(10)	1.467(7)
C(10)–C(11)	1.275(6)	C(11)–C(12)	1.454(5)

Treatment of DEAC with  $\text{Mo}(\text{CO})_3(\text{CH}_3\text{CN})_3$  in acetonitrile generated the DEAC acetonitrile complex  $\text{Mo}(\text{CO})_2(\text{CH}_3\text{CN})_2(\text{DEAC})_2$ . The reaction of this species with chelating nitrogen ligands NN gave the corresponding products  $\text{Mo}(\text{CO})_2(\text{NN})(\text{DEAC})_2$  [NN = en (**5**), and *o*- $\text{NH}_2\text{CH}_2\text{py}$  (**6**)]. In addition to the DMAC and DEAC complexes, we also synthesize two molybdenum bis(PhCCCO<sub>2</sub>Et) compounds from direct reaction of PhCCCO<sub>2</sub>Et with  $\text{Mo}(\text{CO})_4(\text{NN})$  where NN = bipy (**7**) and phen (**8**) in refluxing  $\text{CH}_3\text{CN}$ . This method is similar to that employed for the synthesis of  $\text{Mo}(\text{CO})_2(\text{bipy})(\text{DMAC})_2$  and  $\text{Mo}(\text{CO})_2(\text{phen})(\text{DMAC})_2$ . Both elementary analysis and spectral data of these complexes support the proposed structures with two acetylenes, two carbonyls and a chelating nitrogen ligand. The detailed spectral data are presented in the Experimental section.

The *trans* alkyne-*cis* carbonyl arrangement for **1** was further confirmed by the results of a single-crystal X-ray structure determination of the compound. An ORTEP drawing of **1** with the atomic number scheme is shown in Fig. 1. Final atomic positional parameters for non-hydrogen atoms are summarized in Table 2, and bond distances and angles are listed in Tables 3 and 4, respectively.

TABLE 4. Important bond angles ( $^\circ$ ) of compound **1**

N(1)–Mo–N(2)	75.7(1)	N(1)–Mo–C(1)	95.7(2)
N(2)–Mo–C(1)	163.1(1)	N(1)–Mo–C(2)	169.8(2)
N(2)–Mo–C(2)	103.4(2)	C(1)–Mo–C(2)	87.6(2)
N(1)–Mo–C(4)	87.2(2)	N(2)–Mo–C(4)	117.8(1)
C(1)–Mo–C(4)	75.5(2)	C(2)–Mo–C(4)	84.4(2)
N(1)–Mo–C(5)	82.5(1)	N(2)–Mo–C(5)	84.0(1)
C(1)–Mo–C(5)	109.7(2)	C(2)–Mo–C(5)	87.4(2)
C(4)–Mo–C(5)	34.2(2)	N(1)–Mo–C(10)	115.5(1)
N(2)–Mo–C(10)	83.5(1)	C(1)–Mo–C(10)	87.3(2)
C(2)–Mo–C(10)	74.2(2)	C(4)–Mo–C(10)	153.1(2)
C(5)–Mo–C(10)	154.6(1)	N(1)–Mo–C(11)	82.1(2)
N(2)–Mo–C(11)	82.0(1)	C(1)–Mo–C(11)	82.4(2)
C(2)–Mo–C(11)	107.9(2)	C(4)–Mo–C(11)	154.3(2)
C(5)–Mo–C(11)	161.3(2)	C(10)–Mo–C(11)	34.3(2)
Mo–C(1)–O(1)	177.8(4)	Mo–C(2)–O(2)	177.1(4)
Mo–C(4)–C(5)	72.9(3)	C(3)–C(4)–C(5)	140.1(4)
Mo–C(5)–C(4)	72.9(3)	C(4)–C(5)–C(6)	141.5(4)
Mo–C(10)–C(9)	143.8(3)	Mo–C(10)–C(11)	72.4(3)
C(9)–C(10)–C(11)	143.7(4)	Mo–C(11)–C(10)	73.3(3)
Mo–C(11)–C(12)	143.6(3)	C(10)–C(11)–C(12)	142.6(5)

#### 4. Discussion

The *trans* bis(alkyne) compounds 1–2 may be prepared either from  $\text{Mo}(\text{CO})_3(\text{CH}_3\text{CN})_3$  or from  $\text{Mo}(\text{CO})_3(\text{NN})_2$ . These two methods are different from the previous one for the synthesis of  $\text{Mo}(\text{CO})_2(\text{NN})(\text{DMAC})_2$  (NN = bipy and phen) which employed  $\text{Mo}(\text{CO})_4(\text{bipy})$  as the starting compound. Unlike the reaction of  $\text{Mo}(\text{CO})_6$  with bipy which readily gives pure  $\text{Mo}(\text{CO})_4(\text{bipy})$ , the reaction of  $\text{Mo}(\text{CO})_6$  with en or pn yields a mixture of *fac*- $\text{Mo}(\text{CO})_3(\text{NN})_2$  and  $\text{Mo}(\text{CO})_4(\text{NN})$  even in the early stage of the reaction. It is difficult to obtain pure  $\text{Mo}(\text{CO})_4(\text{NN})$  just by controlling the reaction time and the amount of reactants. As a result, the reaction of  $\text{Mo}(\text{CO})_6$  with en or pn in  $\text{CH}_3\text{CN}$  was carried out under refluxing conditions until all Mo species were converted to *fac*- $\text{Mo}(\text{CO})_3(\text{NN})_2$ . In the complex with NN = ethylenediamine, one of the en ligands is a bidentate, while the other is coordinated to the metal using only one of the amino groups. This structure is supported by the observation of two CO absorptions at 1889 and at 1763  $\text{cm}^{-1}$  in the IR spectrum of the complex, and by the observation of three methylene signals at  $\delta$  2.58, 2.57, and 2.56, with two broad amino signals at  $\delta$  3.02 and 2.30 (ratio 3:1).

IR monitoring of the reaction of DMAC with  $\text{Mo}(\text{CO})_3(\text{NN})_2$  or  $\text{Mo}(\text{CO})_3(\text{CH}_3\text{CN})_3$  reveals no significant concentration of mono-coordinated DMAC intermediate. Only the starting complex, the bis(alkyne) product and the side product  $\text{Mo}(\text{CO})_4(\text{NN})$  were detected during the reaction. The results suggest that only the carbonyl groups *cis* to the NN or  $\text{CH}_3\text{CN}$  may be replaced by DMAC ligands, and once a DMAC is attached to the metal centre, the carbonyl *trans* to the coordinated DMAC ligand becomes labile and further substitution by DMAC is rapid. The observed selectivity is probably due to the strong *trans* effect of DMAC which is expected to be larger than that of the CO group. While several chelating nitrogen ligands may be used to prepare the *trans* bis(alkyne) molybdenum complexes, DMAC, DEAC and  $\text{PhCCCO}_2\text{Et}$  appear to be the only alkynes that give stable complexes indicating that a strong electron-withdrawing substituent in the alkyne ligand is required to stabilize the  $d^6$  alkyne complex.

##### 4.1. Infrared properties

The average CO absorption frequencies of  $\text{Mo}(\text{CO})_2(\text{NN})(\text{DMAC})_2$  reflect the relative electron donating nature of the bidentate ligands NN. For comparison, the average CO absorption frequencies of  $\text{Mo}(\text{CO})_2(\text{NN})(\text{DMAC})_2$  (NN = en and pn,) of 1972 and 1971  $\text{cm}^{-1}$  are approximately 5, 10 and 35  $\text{cm}^{-1}$

lower than those of  $\text{Mo}(\text{CO})_2(\text{NH}_2\text{CH}_2\text{py})(\text{DMAC})_2$ ,  $\text{Mo}(\text{CO})_2(\text{bipy})(\text{DMAC})_2$  and  $\text{W}(\text{CO})_2(\text{dppe})(\text{DMAC})_2$ , respectively. The observed CO frequency increases in the order:  $\text{pn} \cong \text{en} > \text{NH}_2\text{CH}_2\text{py} > \text{bipy} \cong \text{phen} > \text{dppe}$  parallel to the order of  $\pi$ -acidity of the chelating ligand. A similar trend was also observed for the broad acetylenic  $\text{C}\equiv\text{C}$  stretching frequency. For example, the value of 1785  $\text{cm}^{-1}$  for the en and pn bis(alkyne) complexes is more than 25  $\text{cm}^{-1}$  lower than the corresponding value for the bipy complex. For the same bidentate ligands NN, the average CO absorption frequency also increases as the electron withdrawing ability of alkyne ligand increases. For  $\text{Mo}(\text{CO})_2(\text{bipy})(\text{DMAC})_2$ , the average is 1982  $\text{cm}^{-1}$ , while for  $\text{Mo}(\text{CO})_2(\text{bipy})(\text{PhCCCO}_2\text{Et})_2$  the corresponding value is 1933  $\text{cm}^{-1}$ . A close comparison of the IR data of the present molybdenum complexes with those of the corresponding tungsten complexes indicates that the acetylenic  $\text{C}\equiv\text{C}$  stretches of the former are approximately 30–40  $\text{cm}^{-1}$  higher than the corresponding values of the latter [11].

##### 4.2. Molecular structure of $\text{Mo}(\text{CO})_2(\text{en})(\text{DMAC})_2$

As shown in Fig. 1, the geometry of compound 1 is octahedral with the two CO groups *cis* to each other and the two DMAC ligands in *trans* positions. The results agree with the spectroscopic data of the compound. Interestingly, the orientation of the two *trans* alkyne ligands are mutually perpendicular and each DMAC ligand eclipses a N–Mo–CO vector. Several tungsten and molybdenum bis(alkyne) complexes were known to possess such geometry [10,11,12]. Orthogonal and eclipsed orientations of *trans*  $\pi$ -acid ligands including  $\text{CO}_2$  [15],  $\text{O}_2$  [16], and olefins [17,18] have been observed and have also been discussed theoretically [19].

It is interesting to compare the bonding parameters of 1 with those of the known  $\text{W}(\text{CO})_2(\text{dppe})(\text{DMAC})_2$  complex [10]. Shorter  $\text{C}\equiv\text{C}$  bond length (1.27 Å *cf.* 1.30 Å) and larger bend back angle ( $142 \pm 2^\circ$  *cf.*  $137 \pm 2^\circ$ ) of 1 relative to the tungsten complex were observed indicating less back bonding in the Mo complex. In contrast to these structural results, the observed lower  $\text{C}\equiv\text{C}$  (100  $\text{cm}^{-1}$ ) and lower average  $\text{C}=\text{O}$  bond stretching frequencies of the DMAC ligands (10  $\text{cm}^{-1}$ ) in 1 relative to the corresponding values in the tungsten derivative imply greater back bonding in the Mo complex than in the W derivative. It is not yet known why the X-ray data and the IR data conflict. However, observed IR data appear to agree better with the well-established order of electron donating ability for the dppe and en ligands.

Disagreement in X-ray and spectral data between 1 and  $\text{Mo}(\text{CO})_2(\text{bipy})(\text{DMAC})_2$  was also observed. Com-

parisons of the bend back angles (142° *cf.* 143°), coordinated CO stretching frequencies (1972 *cf.* 1982 cm<sup>-1</sup>), C≡C stretching frequencies (1785 *cf.* 1810 cm<sup>-1</sup>), and <sup>13</sup>C chemical shifts of the carbon in C≡C bond (142.2 *cf.* 136.8 ppm) all indicate that en is a better electron donor than bipy. However, the C≡C bond distances of 1.27 and 1.29 Å for **1** and Mo(CO)<sub>2</sub>(bipy)(DMAC)<sub>2</sub>, respectively, clearly depart from the above trend. From these comparisons, it appears that X-ray data such as C≡C bond distances and angles are not as sensitive as other spectral data in the sense of their use to differentiate the degree of back bonding.

### 4.3. NMR properties

All the present molybdenum bis(alkyne) complexes **1–8** are fluxional in the NMR timescale resulting from the rotation of the two alkynes in each species. For complex **1**, there is only one singlet for the four methoxy groups of DMAC ligands in the NMR spectrum at room temperature. Similarly, the four methylene protons, and the four amino protons of en also exhibit only one resonance for each type of proton. Cooling causes coalescence, and each proton signal observed at room temperature is split into two resonances at 188 K. Splitting of the <sup>13</sup>C resonances of DMAC ligands was also observed at low temperature. These NMR results at low temperature are fully in agreement with the solid state structure of **1** (Fig. 1) which reveals that the two DMAC ligands are equivalent, with each DMAC having two inequivalent ends. In addition, the structure shows that the Mo metal in the complex is an asymmetric centre and the four methylene protons and the four amino protons on the en ligand are each divided into two sets of signals. For other DMAC and DEAC complexes with symmetric NN ligands, their NMR properties are similar to those of **1**.

The fluxional behaviors of complexes Mo(CO)<sub>2</sub>(*o*-NH<sub>2</sub>CH<sub>2</sub>py)(DMAC)<sub>2</sub> (**4**) and Mo(CO)<sub>2</sub>(*o*-NH<sub>2</sub>CH<sub>2</sub>py)(DEAC)<sub>2</sub> (**6**) are more complicated than that of **1**. For complex **4**, there are four methyl resonances at δ 3.83, 3.74, 3.62 and 3.31 observed in the <sup>1</sup>H NMR spectra at low temperature under slow-exchange limit (below 173 K). Similarly, there are four signals for the carbon triple bonds, four resonances for the keto esters and two resonances for the carbonyl carbons in the <sup>13</sup>C NMR spectra. These observations may be understood based on the asymmetric nature of the 2-NH<sub>2</sub>CH<sub>2</sub>py ligand. The most up-field signal is assigned to the methyl group above the pyridyl ring, while the second one corresponds to the methyl group close to the amino ligand. The methyl group near the carbonyl ligand opposite the pyridine ring is lowest in electron density and is therefore most down-field. In addition to the observation of different chemical shifts for the

methyl groups, the two amino protons give rise to two broad resonances at δ 4.92 and 2.18 and the methylene protons at δ 4.18 in the <sup>1</sup>H NMR spectrum at low temperatures. As temperature increases, the acetylene ligands rotate and the methyl and amino signals coalesce. Only one sharp single resonance at δ 3.69 for the methyl protons, a triplet at δ 4.25 for the methylene protons and a broad signal at δ 3.34 for the amino protons were observed at 293 K. Similar behavior was also observed in the <sup>13</sup>C NMR spectrum of **4**. At the slow-exchange limit regime, there are four resonances at δ 143.9, 142.0, 141.0 and 131.9 for the acetylene and at δ 170.2, 169.6, 167.8 and 165.2 for the keto carbons of the DMAC ligands, but two signals at δ 218.6 and 218.3 for the carbonyls. All these resonances coalesce as temperature increases and only one <sup>13</sup>C signal for each type of carbons was observed at ambient temperature. Similar fluxional behavior was observed for complex **6**. It is noteworthy that the two methylene protons on the DEAC ligands of this complex appear as AB type signals at slow and even fast exchange regimes.

Variable-temperature NMR studies of compound **8** have demonstrated rather complex dynamic behaviors of these molecules in solution. It appears that the species exists as a thermodynamic mixture of two rotational isomers **8-A**, **8-B**. The <sup>1</sup>H NMR spectra of the complex at various temperatures in CD<sub>2</sub>Cl<sub>2</sub> are shown in Fig. 2. At 163 K, complex **8** is static and two sets of resonances corresponding to two rotational isomers were observed. The major set of signals consisting of four resonances in the aromatic region δ 7.7–9.0 for the coordinated phen protons, a broad resonance at δ 7.39 for the phenyl group, a doublet of quartets (an AB pattern) at δ 3.15 for the methylene protons, and a broad resonance at δ 0.24 for the methyl protons on the alkyne ligands are assigned to isomer **8-A**. A strong support for the structure assignment is the observation that the ester groups of the PhCCCO<sub>2</sub>Et ligands in the tungsten complex W(CO)<sub>2</sub>(phen)(PhCCCO<sub>2</sub>Et)<sub>2</sub> prefer to stay closer to phen. Other evidence supporting the present assignment will be discussed below. The minor set of proton signals consists of a broad doublet at δ 9.04 and 8.92 (overlapping with the major signal) for H(2) and H(9), two broad doublets at δ 8.37, and 8.26 for the H(4) and H(7) of the phen ligand, three broad signals with intensity ratio of 5:3:2 at δ 7.26, 6.66, and 6.14 for the protons of the two phenyl groups, a broad signal at δ 4.23 for methylene protons and two broad signals at δ 1.29 and 0.20 for the methyl protons. The other signals of this minor set appear to hide in the major ones. The structure corresponding to this minor set is assigned as **8-B**. In this isomer, the protons such as H(2) and H(9), and H(4) and H(7) of the phen ring no longer have the same environment due to

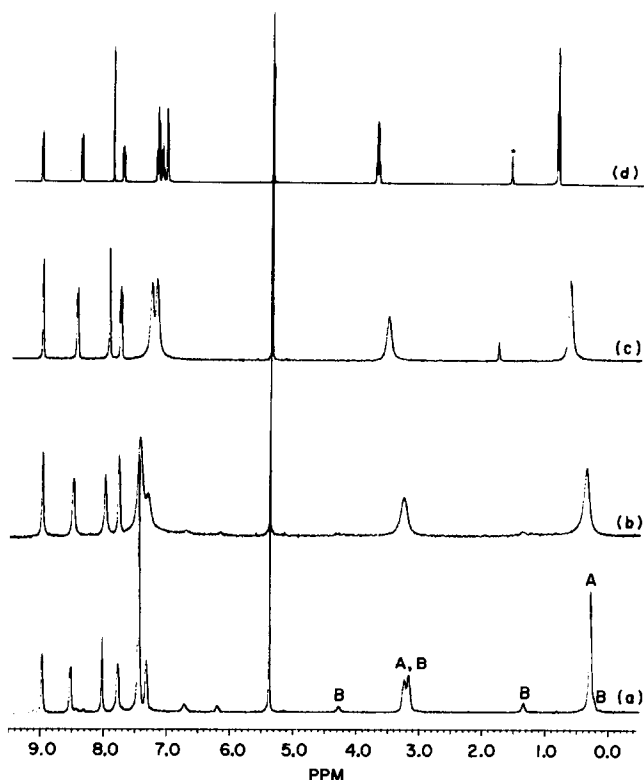
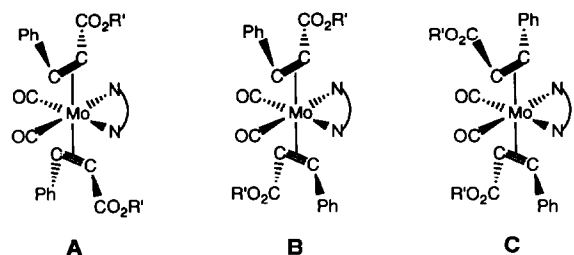


Fig. 2. The  $^1\text{H}$  NMR spectra of  $\text{Mo}(\text{CO})_2(\text{phen})(\text{PhCCCO}_2\text{Et})_2$  (**8**) in  $\text{CD}_2\text{Cl}_2$  at various temperatures: (a) 163 K; (b) 193 K; (c) 233 K; (d) 293 K.

differences in the directions of the two alkynes relative to the N–Mo–C vectors. Consequently, they appear as two separate resonances with equal intensity. From the peak intensities, the relative population of **8-A**, and **8-B** may be calculated and the values are 5 : 1 at 163 K. On the basis of the staggered and eclipsed structure of the *trans* bis(alkyne) complexes there are theoretically three rotational isomers **8-A**, **8-B**, and **8-C** for  $\text{Mo}(\text{CO})_2(\text{phen})(\text{PhCCCO}_2\text{Et})_2$ . However, in the present case, only two rotational isomers **8-A**, and **8-B** were observed. Previously, we have observed all three isomers **A**, **B**, and **C** (relative populations 19 : 5.5 : 1 at 193 K) of  $\text{W}(\text{CO})_2(\text{phen})(\text{PhCCCO}_2\text{Et})_2$  in solution [11].



In the  $^1\text{H}$  NMR spectra of **8** at low temperatures, unusual shifts up-field were observed for the ethyl resonances of **A** and for one of the ethyl resonances of **B**. The resonances of the two ethyl groups in **8-A** appear at  $\delta$  0.24 ( $\text{CH}_3$ ) and 3.15 ( $\text{CH}_2$ ), of one ethyl group in **8-B** at  $\delta$  0.20 ( $\text{CH}_3$ ) and 3.15 ( $\text{CH}_2$ ), while the other ethyl group in **8-B** appears at  $\delta$  1.29 and 4.22 for the  $\text{CH}_3$  and  $\text{CH}_2$ , respectively. Differences of more than 1 ppm in chemical shift were observed for the methyl resonances and for the methylene resonances. All those ethyl protons in the up-field regions are for the  $\text{PhCCCOOEt}$  ligands which lie along the N–Mo–C vector in a direction with the ester groups located right above or below the phen ring and are thus markedly affected by the ring current. The ring current of the phen ligand also greatly affects the proton chemical shift of the phenyl groups on the  $\text{PhCCCOOEt}$  ligands. For comparison, the proton resonances of the phenyl groups of **8-A** which are not affected by the ring current of phen appear at  $\delta$  7.39, while the proton resonances of one phenyl ring of **8-B** lying above the phen ligand shift to  $\delta$  6.66 (3H) and 6.14 (2H) and the resonance of the other phenyl ring near one carbonyl group appears at  $\delta$  7.26 (5H). Analysis of the  $^1\text{H}$  NMR data of the DMAC complexes  $\text{Mo}(\text{CO})_2(\text{NN})(\text{DMAC})_2$  (NN = phen, bipy,  $\text{NH}_2\text{CH}_2\text{py}$ ,  $o\text{-(NH}_2)_2\text{C}_6\text{H}_4$ , en, and pn) also reveals the differing degree of the ring current effect on the chemical shift of the methyl groups. At ambient temperature, due to the rapid rotation of DMAC ligands, only one methyl resonance is observed for each species and these resonances appear at  $\delta$  3.39, 3.47, 3.69, 3.71, 3.81 and 3.80 for NN = phen, bipy,  $o\text{-NH}_2\text{CH}_2\text{py}$ ,  $o\text{-(NH}_2)_2\text{C}_6\text{H}_4$ , en, and pn, respectively. In the absence of ring current, we expect the methyl chemical shift of the en complex to appear at a slightly higher field than that of the phen complex due to the greater electron donating ability of the en ligand compared to phen, but this is small relative to the ring current effect. As a result, the chemical shift of the methyl protons in a DMAC complex may be viewed as a measure of the ring-current effect. As expected, this effect as indicated by the observed chemical shift of the methyl protons decreases in the order: phen > bipy >  $\text{NH}_2\text{CH}_2\text{py} \approx o\text{-(NH}_2)_2\text{C}_6\text{H}_4 > \text{en} \approx \text{pn}$ .

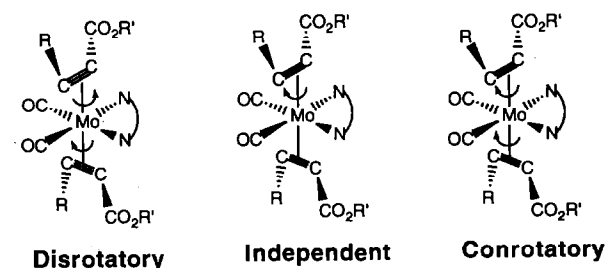
Another way to examine the ring-current effect is to compare the chemical shift difference of the methyl groups in the same DMAC complexes at low temperature. For all  $\text{Mo}(\text{CO})_2(\text{NN})(\text{DMAC})_2$  complexes, the methyl protons closer to the carbonyl groups appear at  $\delta \sim 3.8$  regardless of the NN ligands. On the other hand, the chemical shifts of the methyl protons near the NN ligand vary greatly with the type of NN due to the differing degree of ring-current effect. For exam-



ple, the two resonances of the methyl groups in the en complex are at  $\delta$  3.80 and 3.76 with a chemical shift difference of 0.04 ppm, while the two resonances of the methyl groups in the phen complex appear at  $\delta$  3.85 and 2.97 with a chemical shift difference of 0.88 ppm. For other DMAC complexes, the differences are between 0.04 and 0.88 ppm.

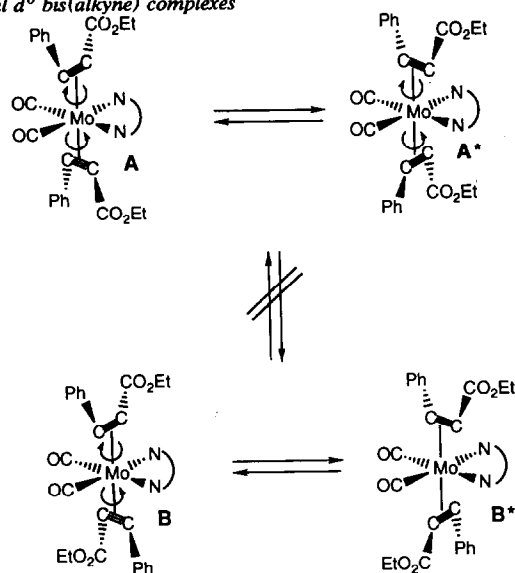
#### 4.4. Mechanism of alkyne rotation

Under the conditions for dynamic NMR investigations, no ligand exchange reaction is observed between external alkynes and the coordinated alkyne ligands. Thus, it appears that an intermolecular process involving dissociation-association of alkynes is ruled out as an explanation for the dynamic behavior of the present bis(alkyne) complexes. Thus, the intramolecular rotation of alkyne ligands around the axis through the metal center and perpendicular to the two alkyne ligands is likely to be responsible for the observed dynamic behavior. There are three possible processes: (i) disrotatory motion of the two coordinated alkynes; (ii) independent rotation of the alkyne ligands; (iii) conrotatory motion of the two coordinated alkynes.



Disrotatory motion of the two alkyne ligands in complex 1 would account for the interconversion of the enantiomeric structures and the interchange of the AB type protons on the en ligand, but fails to explain the facile interconversion of A and B observed in the variable-temperature <sup>1</sup>H NMR spectra of Mo(CO)<sub>2</sub>(phen)(PhC≡CCO<sub>2</sub>Et)<sub>2</sub> (**8**) (Scheme 1). Based on the observation, this mechanism is eliminated.

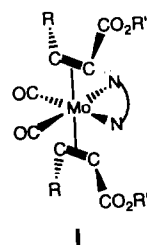
There are two possible mechanisms (ii) and (ii') for independent rotation of the alkyne ligand. Mechanism (ii) assumes an independent rotation through 180° of one alkyne ligand with the other remaining at the same conformation. Application of this mechanism to Mo(CO)<sub>2</sub>(phen)(PhC≡CCO<sub>2</sub>Et)<sub>2</sub> (**8**) successfully accounts for interconversion of the rotational isomers A and B. Furthermore, the mechanism also predicts that the enantiomeric structures do not interchange for complex 6 and this prediction is consistent with the observations of variable-temperature NMR spectra of this complex. However, it fails to explain the equivalence of the four methyl groups on the two DMAC



Scheme 1. Alkyne rotation in complexes 7 and 8 by disrotatory mechanism showing that conformers A and B are not interconvertible; \* denote enantiomeric structures.

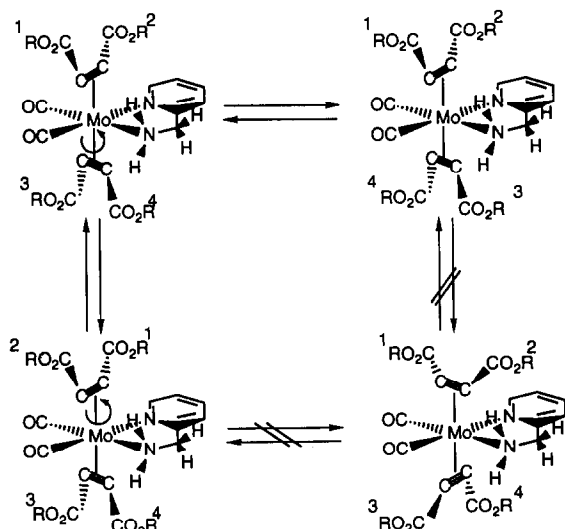
ligands of complex 4 and the equivalence of the four ethyl groups of complex 6 in the fast-exchange limit (Scheme 2) and can therefore be discarded on this basis.

Another independent rotation of alkyne ligands involves the rotation by 90° of a coordinated alkyne to give an intermediate I, followed by an independent rotation of one alkyne by



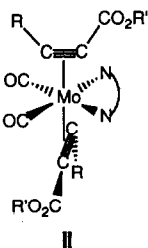
90°. A detailed analysis of this mechanism indicated that this rotational process leads to fluxional behavior equivalent to that from a combination of mechanisms (i) and (ii). It accounts for the equivalency of the four methyl groups on the two DMAC ligands of complex 4 and the equivalency of the four ethyl groups of complex 6 in the fast-exchange limit. In addition it also explains the interconversion of the rotational isomers A and B in Mo(CO)<sub>2</sub>(phen)(PhC≡CCO<sub>2</sub>Et)<sub>2</sub> (**8**).

For the mechanism of conrotatory motion (mechanism (iii)), the two *trans* alkynes rotate synchronously in the same direction and thus remain mutually orthogonal during rotation. A transition state or an interme-

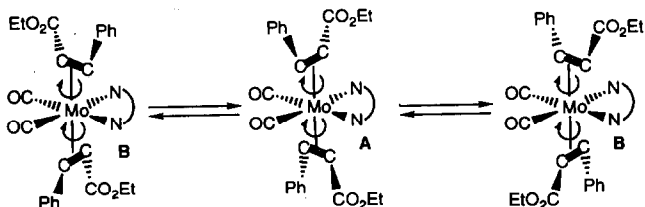


Scheme 2. Independent rotation of alkyne ligands by  $180^\circ$  in **4** and **6** indicating no site exchange between the two alkynes.

diate such as **II** is involved in this intramolecular process.



The process explains the interconversion of the rotational isomers **8-A** and **8-B** (Scheme 3). This process clearly demonstrates that the four different methyl resonances of the DMAC ligands in **4** and the methylene and methyl resonances in **6** in the slow-exchange limit would each average to a single resonance in the fast-exchange limit, as we observed. At the moment, it appears that both independent rotation of alkyne by  $90^\circ$  and conrotatory motion of alkyne ligands account for all the variable-temperature NMR results observed. We are unable to distinguish between these two mechanisms from the experimental data available. However,



Scheme 3. Conrotatory motion of the alkynes in  $\text{Mo}(\text{CO})_2(\text{phen})(\text{PhC}\equiv\text{CCO}_2\text{Et})_2$  (**8**).

in view of the fact that in the closely related bis(alkyne) complexes of tungsten [11] and the bis(carbon dioxide) complexes of molybdenum [20], the rotation of these ligands all follow a conrotatory mechanism, we tend to favor conrotatory motion of alkyne ligands to account for the observed dynamic NMR behavior of the present (bis(alkyne) complexes of molybdenum.

## 5. Conclusion

We have demonstrated that a series of molybdenum(0) complexes having a bidentate nitrogen ligand (en, pn,  $\text{NH}_2\text{CH}_2\text{py}$ , bipy or phen) and two *trans* alkynes (DMAC, DEAC, or  $\text{PhC}\equiv\text{CCO}_2\text{Et}$ ) may be synthesized in addition to the previous reported  $\text{Mo}(\text{CO})_2(\text{NN})_2(\text{DMAC})_2$  where  $\text{NN} = \text{bipy}$  and phen. These molybdenum complexes appear to be less stable than the corresponding tungsten species. In these complexes, the two *trans* alkyne ligands are perpendicular to each other with each alkyne eclipsing a N–Mo–CO vector. For complex **8**, conformational isomers **A**, and **B** were observed. Ring current of the  $\text{NH}_2\text{CH}_2\text{py}$ , bipy, or phen ligand has shown significant effects on the chemical shifts of the alkyne substituents lying above or below the pyridine rings. This effect is important in the assignment of alkyne conformations. All these molybdenum(0) bis(alkyne) complexes are fluxional on the NMR time scale due to the rotation of the alkyne ligands. Of the three rotational processes proposed to account for the NMR dynamic behavior, independent rotation of one alkyne ligand by  $90^\circ$  and conrotatory motion of the two alkynes together account for the observations.

## 6. Supplementary material available

Tables of bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates for **1** (5 pages); a listing of observed and calculated structure factors for **1** (14 pages).

## Acknowledgment

We thank the National Science Council of the Republic of China (NSC81-0208-M-007-72) for support of this work.

## References

- (a) E.M. Armstrong, P.K. Baker and M.G.B. Drew, *Organometallics*, **7** (1988) 319; (b) P.K. Baker, E.M. Armstrong and M.G.B. Drew, *Inorg. Chem.*, **27** (1988) 2287; (c) J.L. Templeton and B.C. Ward, *J. Am. Chem. Soc.*, **102** (1980) 3288; (d) B.C. Ward and J.L. Templeton, *J. Am. Chem. Soc.*, **102** (1980) 1532; (e) P.B. Winston, S.J.N. Burgmayer and J.L. Templeton, *Organometallics*, **2** (1983) 167.

- 2 (a) D.L. Wink and B.T. Creagan, *Organometallics*, **9** (1990) 328; (b) K. Tatsumi, R. Hoffman and J.L. Templeton, *Inorg. Chem.*, **21** (1982) 466; (c) A. Bouayad, M. Dartiguenave, M.-J. Menu, Y. Dartiguenave, F. Belanger-Gariepy and A.L. Beauchamp, *Organometallics*, **8** (1989) 629; (d) D.L. Wink and B.T. Creagan, *J. Am. Chem. Soc.*, **112** (1990) 8585.
- 3 A.I. Nesmeyanov, A.I. Gusev, A.A. Pasynskii, K.N. Amisimov, N.E. Kolobova and Yu.T. Struchkov, *J. Chem. Soc., D*, (1969) 277.
- 4 J.W. Faller, H.H. Murray, *J. Organomet. Chem.*, **172** (1979) 171.
- 5 J.L. Davidson, M. Green, F.G.A. Stone and A.J. Welch, *J. Chem. Soc., Dalton Trans.*, (1976) 738.
- 6 P.L. Watson and R.G. Bergman, *J. Am. Chem. Soc.*, **102** (1980) 2698.
- 7 R.S. Herrick and J.L. Templeton, *Organometallics*, **1** (1982) 842.
- 8 P.K. Baker, M.G.B. Drew and K.R. Flower, *J. Organomet. Chem.*, **391** (1990) C12.
- 9 E.M. Armstrong, P.K. Baker, K.R. Flower and M.G.B. Drew, *J. Chem. Soc., Dalton Trans.*, (1990) 1535.
- 10 K.R. Birdwhistle, T.L. Tonker and J.L. Templeton, *J. Am. Chem. Soc.*, **109** (1987) 1401.
- 11 T.Y. Hsiao, P.L. Kuo, C.H. Lai, C.H. Cheng, C.Y. Cheng and S.L. Wang, *Organometallics*, **12** (1993) 1094.
- 12 J.S. Lain, C.H. Cheng, C.Y. Cheng and S.L. Wang, *J. Organomet. Chem.*, **390** (1990) 330.
- 13 *International Tables for X-ray Crystallography, Vol. IV*, Kynoch Press, Birmingham, (present distributor Kluwer Academic Publishers, Dordrecht), 1974.
- 14 G.M. Sheldrick, *SHELXTL PLUS User Manual*, Nicolet XRD Corporation, Madison, WI, 1986.
- 15 R. Alvarez, E. Carmona, J.M. Marin, M.L. Poveda, E. Gutierrez-Puebla and A. Monge, *J. Am. Chem. Soc.*, **108** (1986) 2286.
- 16 B. Chevrier, Th. Diebold and R. Weiss, *Inorg. Chim. Acta*, **19** (1976) L57.
- 17 C.H. Lai, C.H. Cheng, W.C. Chou and S.L. Wang, *Organometallics*, **12** (1993) 1105.
- 18 (a) E. Carmona, J.M. Marin, M.L. Poveda, J.L. Atwood and R.D. Rogers, *J. Am. Chem. Soc.*, **105** (1983) 3014; (b) E. Carmona, A. Galindo, M.L. Poveda and R.D. Rogers, *Inorg. Chem.*, **24** (1985) 4033; (c) E. Carmona, A. Galindo, J.M. Marin, E. Gutierrez-Puebla, A. Monge and C. Ruiz, *Polyhedron*, **7** (1988) 1831; (d) F.-W. Grevels, J. Jacke and S. Ozkar, *J. Am. Chem. Soc.*, **109** (1987) 7536; (e) M.F. Gregory, S.A. Jackson, M. Poliakoff and J.J. Turner, *J. Chem. Soc., Chem. Commun.*, (1986) 1175.cs
- 19 (a) C. Bachman, J. Demuyne and A. Veillard, *J. Am. Chem. Soc.*, **100** (1978) 2366; (b) E.S. Marcos, R. Caballol, G. Trinquier and J.-C. Barthelat, *J. Chem. Soc., Dalton Trans.*, (1987) 2373.
- 20 E. Carmona, A.K. Hughes, M.A. Munoz, D.M. O'Hare, F.J. Perez and M.L. Poveda, *J. Am. Chem. Soc.*, **113** (1991) 9210.