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NEW SIGMA-ETHYL COMPOUNDS OF DIMOLYBDENUM AND EVIDENCE FOR DINU--ETC(U)

JUN 78 M H CHISHOLM, D A HAITKO, C A MURILLO

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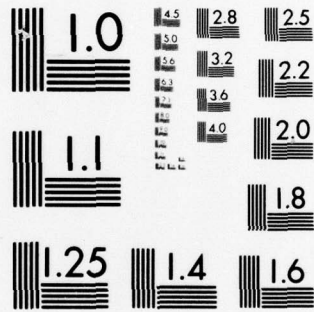
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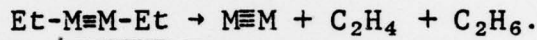
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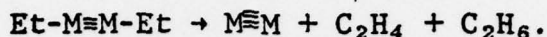
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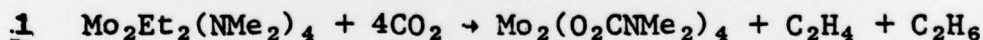
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The preparation and properties of Mo <sub>2</sub> Et <sub>2</sub> (NMe <sub>2</sub> ) <sub>4</sub> and Mo <sub>2</sub> Et(OBu <sup>t</sup> ) <sub>5</sub> are described. Reaction of the former with CO <sub>2</sub> ( $\geq$ 4 equiv) leads to Mo <sub>2</sub> (O <sub>2</sub> CNMe <sub>2</sub> ) <sub>4</sub> , C <sub>2</sub> H <sub>6</sub> and C <sub>2</sub> H <sub>4</sub> .		

New  $\sigma$ -Ethyl Compounds of Dimolybdenum ( $M\equiv M$ ) and  
Evidence for Dinuclear Reductive Elimination with a Concomitant  
Metal-Metal Triple to Quadruple Bond Transformation:

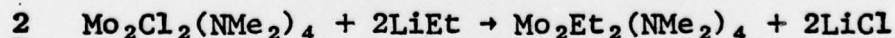


Sir:

Transition metal complexes containing  $\sigma$ -ethyl ligands are prone to thermal decomposition by an initial step involving  $\beta$ -hydrogen elimination:<sup>1</sup>  $\text{M-C}_2\text{H}_5 \rightleftharpoons \text{M-H} + \text{C}_2\text{H}_4$ . This reaction is suppressed when the metal is coordinatively saturated and attains an 18-valence shell electronic configuration.<sup>2</sup> We report here (i) the preparation of the thermally stable  $\sigma$ -ethyl dimolybdenum compounds  $\text{Mo}_2\text{Et}_2(\text{NMe}_2)_4$  and  $\text{Mo}_2\text{Et}(\text{OBu}^t)_5$ , in which the ethyl ligands are coordinated to unsaturated metal centers<sup>3</sup> and (ii) the reaction between  $\text{Mo}_2\text{Et}_2(\text{NMe}_2)_4$  and  $\text{CO}_2$  which proceeds according to eq 1 and provides a model reaction for studies of dinuclear reductive elimination.<sup>4</sup>



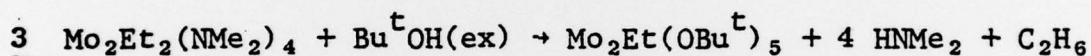
$\text{Mo}_2\text{Cl}_2(\text{NMe}_2)_4$ <sup>5</sup> reacts smoothly at  $-78^\circ\text{C}$  with  $\text{EtLi}$  (2 equiv) in hydrocarbon solvents to give the yellow, crystalline compound  $\text{Mo}_2\text{Et}_2(\text{NMe}_2)_4$  which may be obtained analytically pure<sup>6</sup> by sublimation ( $60\text{-}70^\circ\text{C}$ ,  $10^{-4}$  mmHg) in greater than 70% yield based upon eq 2.



The  $^1\text{H}$  NMR spectrum of  $\text{Mo}_2\text{Et}_2(\text{NMe}_2)_4$  obtained in toluene- $d_8$  at  $-61^\circ\text{C}$  at 270 MHz is shown in Figure 1. This corresponds to the low temperature limiting spectrum of a mixture of anti and gauche-rotamers of an ethane-like molecule  $(\text{Me}_2\text{N})_2\text{EtMo}\equiv\text{MoEt}(\text{NMe}_2)_2$ .<sup>7</sup> Note the methylene protons of the gauche rotamer (but not the anti-rotamer)

are diastereotopic and form part of an  $ABX_3$  spectrum. At  $90^\circ\text{C}$  rotation about the M-N bonds is rapid on the NMR timescale leading to the coalescence of proximal and distal N-Me signals but rotation about the  $M\equiv M$  bond (anti = gauche isomerization) is still slow. In the mass spectrometer there is a strong molecular ion  $\text{Mo}_2(\text{NMe}_2)_4\text{Et}_2^+$  ( $m/e = 430$ ) and an ion  $\text{Mo}_2(\text{NMe}_2)_4^+$  ( $m/e = 372$ ) corresponding to the loss of 2Et.

$\text{Mo}_2\text{Et}_2(\text{NMe}_2)_4$  reacts rapidly at room temperature with tert-butanol in benzene according to eq 3.



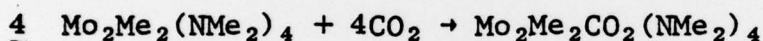
$\text{Mo}_2\text{Et}(\text{OBu}^t)_5$  is a burgundy-red solid which sublimes with some decomposition at  $60\text{-}70^\circ\text{C}$   $10^{-4}$  mmHg. The  $^1\text{H}$  NMR spectrum at low temperature ( $-76^\circ\text{C}$ ) at 270 MHz in toluene- $d_8$  consists of a simple triplet and quartet for the Et ligand and two resonances in the ratio of 3:2 for the  $\text{OBu}^t$  groups.<sup>8</sup> This is consistent with an ethane-like molecule  $(\text{Bu}^t\text{O})_2(\text{Et})\text{Mo}\equiv\text{Mo}(\text{OBu}^t)_3$  in which rotation about the  $\text{Mo}\equiv\text{Mo}$  bond is rapid on the NMR timescale.<sup>9</sup>

$\text{Mo}_2\text{Et}_2(\text{NMe}_2)_4$  in toluene reacts rapidly with  $\text{CO}_2$  ( $\geq 4$  equiv) to give a pale-yellow finely divided precipitate. This compound has not been structurally characterized but is considered to be  $\text{Mo}_2(\text{O}_2\text{CNMe}_2)_4$  and to have the dimolybdenum tetraacetate structure  $(M\equiv M)^{10}$  on the following grounds: (i) analytical data<sup>11</sup>, (ii) infrared data<sup>12</sup>, and (iii) the appearance in the mass spectrum of a very strong ion corresponding to  $\text{Mo}_2(\text{O}_2\text{CNMe}_2)_4^+$  (this is the ion of highest mass) and the doubly charged ion  $\text{Mo}_2(\text{O}_2\text{CNMe}_2)_4^{2+}$ . The compound is not appreciably soluble in hydrocarbon solvents, nor  $\text{CD}_2\text{Cl}_2$ , but is sparingly soluble in pyridine.<sup>13</sup>

In a sealed NMR tube reaction  $\text{Mo}_2\text{Et}_2(\text{NMe}_2)_4$  in toluene- $d_8$  was reacted with  $\text{CO}_2$  ( $> 4$  equiv). The finely divided precipitate was centrifuged to the top of the tube and the  $^1\text{H}$  NMR spectrum of the clear, virtually colorless solution was recorded.

The only proton signals observed corresponded to ethylene and ethane which were in the integral ratio of 4:6, respectively.<sup>14</sup> We conclude that the reaction between  $\text{Mo}_2\text{Et}_2(\text{NMe}_2)_4$  and  $\text{CO}_2$  proceeds stoichiometrically according to eq 1 and as such provides a model reaction for detailed studies of dinuclear reductive elimination.<sup>15</sup> A simple intramolecular mechanism involving an initial  $\beta$ -hydride elimination,  $\text{Et-Mo}\equiv\text{M-H} + \text{C}_2\text{H}_4$ , followed by C-H reductive elimination across the  $\text{Mo}\equiv\text{Mo}$  bond,  $\text{Et-Mo}\equiv\text{Mo-H} \rightarrow \text{Et-H} + \text{Mo}\equiv\text{Mo}$ , satisfies all our observations.

In contrast to the above we find that  $\text{Mo}_2\text{Me}_2(\text{NMe}_2)_4$  reacts with  $\text{CO}_2$  according to eq 4.



The compound  $\text{Mo}_2\text{Me}_2(\text{O}_2\text{CNMe}_2)_4$ <sup>16</sup> is of sufficient thermal stability to allow the detection of the molecular ion  $\text{Mo}_2\text{Me}_2(\text{O}_2\text{CNMe}_2)_4^+$  in the mass spectrometer. In the solid state and in solution  $\text{Mo}_2\text{Me}_2(\text{O}_2\text{CNMe}_2)_4$  is believed to share the  $\text{W}_2\text{Me}_2(\text{O}_2\text{CNEt}_2)_4$  structure<sup>17</sup> which has a planar C-W-W-C unit with a C-W-W angle equal to  $106^\circ$ .

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We thank the Office of Naval Research for support of this work and Professor D. C. Bradley, Queen Mary College, London who through the auspices of a NATO Grant kindly provided mass spectral results.

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b) P. J. Davidson, M. F. Lappert and R. Pearce, Acc. Chem. Res. 7, 209 (1974).  
c) R. R. Schrock and G. W. Parshall, Chem. Rev. 76, 243 (1976).
2. See, for example, the detailed studies of the thermal reaction  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)(\text{alkyl}) \rightarrow (\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{H})(\text{PPh}_3) + \text{olefin}$ :  
D. L. Reger and E. C. Culbertson, J. Am. Chem. Soc. 98, 2789 (1976).
3. In  $\text{M}_2\text{X}_6$  and  $\text{M}_2\text{X}_{6-n}\text{Y}_n$  compounds (X, Y are uninegative monodentate ligands) the metals attain only 12 valence shell electrons as a result of M-X  $\sigma$  bonds and the M-M triple bond. The metals are capable of increasing their coordination number and number of valence electrons by Lewis base association reactions e.g.,  $\text{Mo}_2(\text{OSiMe}_3)_6 + 2\text{HNMe}_2 = \text{Mo}_2(\text{OSiMe}_3)_6(\text{HNMe}_2)_2$  M. H. Chisholm, F. A. Cotton, M. W. Extine and W. W. Reichert, J. Am. Chem. Soc. 100, 153 (1978).
4. For reductive elimination in mononuclear chemistry see C. A. Tolman, Chem. Soc. Rev. 1, 357 (1972).
5. M. Akiyama, M. H. Chisholm, F. A. Cotton, M. W. Extine and C. A. Murillo, Inorg. Chem. 16, 320 (1977). Note all operations must be carried out in dry and oxygen free solvents and atmosphere.
6. Found (Calcd): C, 33.55 (33.79); H, 7.89 (8.04); N, 12.99 (13.15).
7. See the structural and dynamic behavior of the related compound  $\text{W}_2\text{Me}_2(\text{NEt}_2)_4$ : M. H. Chisholm, F. A. Cotton, M. W. Extine, M. Millar and B. R. Stults, Inorg. Chem. 15, 2244 (1976).
8. Et group:  $\delta(\text{CH}_2) = 2.98$ ,  $\delta(\text{CH}_3) = 1.78$ ,  $J_{(\text{HH})} = 7.9\text{Hz}$ .  
 $\text{OBu}^t$  groups at  $-76^\circ\text{C}$ :  $\delta = 1.60$  and  $1.56$  in the integral ratio 3:2, respectively. Chemical shifts ( $\delta$ ) given in ppm downfield from TMS.
9. Accidental magnetic degeneracy could account for the observed 3:2 spectrum (c.f. predicted low temperature limiting spectrum 2:2:1).



10. For a recent review of compounds containing M-M quadruple bonds see F. A. Cotton, Chem. Soc. Rev. 4, 27 (1975) (b) The diethylcarbamate  $\text{Cr}_2(\text{O}_2\text{CNEt}_2)_4 \cdot (\text{HNEt}_2)_2$  has recently been structurally characterized and shown to have a  $\text{Cr}\equiv\text{Cr}$  bond. M. H. Chisholm, F. A. Cotton, M. W. Extine and D. C. Rideout, Inorg. Chem., submitted for publication.
11. Found (Calcd): C, 26.23 (26.48); H, 4.25 (4.44); N, 10.09 (10.29).
12. In particular the presence of a strong absorption at  $1560\text{ cm}^{-1}$  assignable to  $\nu(\text{NCO}_2)$  of a bridging bidentate carbamate ligand. See M. H. Chisholm and M. W. Extine, J. Am. Chem. Soc. 99, 782 (1977).
13.  $^1\text{H}$  nmr data recorded at 100MHz,  $25^\circ\text{C}$  in pyridine- $d_5$ :  $\delta(\text{O}_2\text{CNMe}_2) = 2.93$  ppm relative to TMS.
14. Found by weighing the traces 38:62. Any departure from the predicted ratio, 4:6, may be due to their differing solubilities.
15. Labelling studies are planned in order to investigate (i) the reversibility of  $\beta$ -hydrogen elimination and (ii) the intra vs. intermolecular nature of the reaction.
16. Analysis Found (Calcd): C, 29.50 (29.29); H, 5.14 (5.23); N, 9.65 (9.75).
17. M. H. Chisholm, F. A. Cotton, M. W. Extine and B. R. Stults, Inorg. Chem. 16, 603 (1977).
18. Alfred P. Sloan Fellow, 1976-78.

Caption to Figure 1

$^1\text{H}$  nmr spectrum of a mixture of anti- and gauche-  
 $\text{Et}(\text{Me}_2\text{N})_2\text{Mo}\equiv\text{Mo}(\text{NMe}_2)_2$  recorded in toluene- $d_8$  at  $-61^\circ\text{C}$   
and 270MHz.

**<sup>1</sup>H**

**(\*)anti & gauche - Mo<sub>2</sub>(σ-C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>(NMe<sub>2</sub>)<sub>4</sub>**

