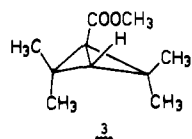


C(4) bonds of **1**, corresponding to a coupling constant of 23.06 Hz (compared with 21.0 Hz in bicyclobutane).¹² A rather small $^1J_{\text{CH}}$ (191 Hz) was also found for the C(3)-H bond in



compound **3**.¹³ The remarkably small value of $^1J_{\text{CH}}$ in **1** and **3** can be explained with an increase of the angle between the two three-membered rings, caused by the repulsion of the two *endo*-methyl groups,¹⁴ since it is known that a decrease of this angle increases $^1J_{\text{CH}}$.^{15,16} Presumably such a geometry change influences $^1J_{\text{C(1)-C(3)}}$ as well.

To exclude this undesired effect, investigations on other bicyclobutanes, in which there can be no *endo-endo* repulsions, are in progress.⁹ The results will shortly be reported.

The most striking result, however, is the fact that a ^{13}C - ^{13}C coupling constant of -17.49 Hz (using any of the coupling constant-hybridization relationships, published until now^{2,17-19}) leads to a negative s^2 and consequently to an imaginary result for the s character of the orbitals forming the C(1)-C(3) bond. As there is no physical sense in this result, it is obvious that none of the known quantitative correlations between $^1J_{\text{CC}}$ and s character can be applied to the central bond in **1**. A similar situation has been predicted for benzvalene.³ Most likely the noncontact contributions to $^1J_{\text{CC}}$, which cannot linearly be related to the product of the s characters, are of even greater importance in this bond than predicted for the corresponding bond of bicyclobutane.³

Considering this, it must be doubted that an equation of the simple form

$$^1J_{\text{CC}} = x s_{\text{A}} s_{\text{B}} - y \quad (2)$$

will be able to give satisfactory results for all types of C-C bonds even within the saturated hydrocarbons. For strained rings y in eq 2 would at least have to be >17.49 .

The calculations by Schulman et al.,²⁻⁴ predicting negative coupling constants of an absolute value <12.2 Hz for the central bond in bicyclobutanes, have proved to be correct in tendency and very useful to encourage experimental work on these exceptional coupling constants. The experimental values of -17.49 Hz in **1** (and possibly -16 Hz in 1-cyanobicyclobutane), however, differ from the calculated ones more than expected. We hope that this communication will encourage further theoretical investigations on this subject.

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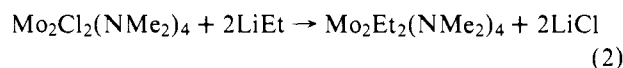
New σ -Ethyl Compounds of Dimolybdenum ($\text{M}\equiv\text{M}$) and Evidence for Dinuclear Reductive Elimination with a Concomitant Metal-Metal Triple to Quadruple Bond Transformation: $\text{Et}-\text{M}\equiv\text{M}-\text{Et} \rightarrow \text{M}\equiv\text{M} + \text{C}_2\text{H}_4 + \text{C}_2\text{H}_6$

Sir:

Transition metal complexes containing σ -ethyl ligands are prone to thermal decomposition by an initial step involving β -hydrogen elimination:¹ $\text{MC}_2\text{H}_5 \rightleftharpoons \text{MH} + \text{C}_2\text{H}_4$. This reaction is suppressed when the metal is coordinatively saturated and attains an 18-valence-shell electronic configuration.² We report here (i) the preparation of the thermally stable σ -ethyldimolybdenum 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 centers³ and (ii) the reaction between $\text{Mo}_2\text{Et}_2(\text{NMe}_2)_4$ and CO_2 which proceeds according to eq 1 and provides a model reaction for studies of dinuclear reductive elimination.⁴

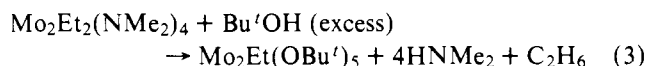


$\text{Mo}_2\text{Cl}_2(\text{NMe}_2)_4$ ⁵ reacts smoothly at -78°C with EtLi (2 equiv) in hydrocarbon solvents to give the yellow, crystalline compound $\text{Mo}_2\text{Et}_2(\text{NMe}_2)_4$ which may be obtained analytically pure⁶ by sublimation (60 - 70°C , 10^{-4} mmHg) in $>70\%$ yield based upon eq 2.



The ^1H NMR spectrum of $\text{Mo}_2\text{Et}_2(\text{NMe}_2)_4$ obtained in toluene- d_8 at -61°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 $(\text{Me}_2\text{N})_2\text{EtMo}\equiv\text{MoEt}(\text{NMe}_2)_2$.⁷ 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°C rotation about the $\text{M}-\text{N}$ bonds is rapid on the NMR time scale leading to the coalescence of proximal and distal N -Me signals but rotation about the $\text{M}\equiv\text{M}$ bond (anti \rightleftharpoons 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*-butyl alcohol in benzene according to eq 3.



$\text{Mo}_2\text{Et}(\text{OBu}^t)_5$ is a burgundy-red solid which sublimates with some decomposition at 60 - 70°C (10^{-4} mmHg). The ^1H NMR spectrum at low temperature (-76°C) at 270 MHz in toluene- d_8 consists of a simple triplet and quartet for the Et

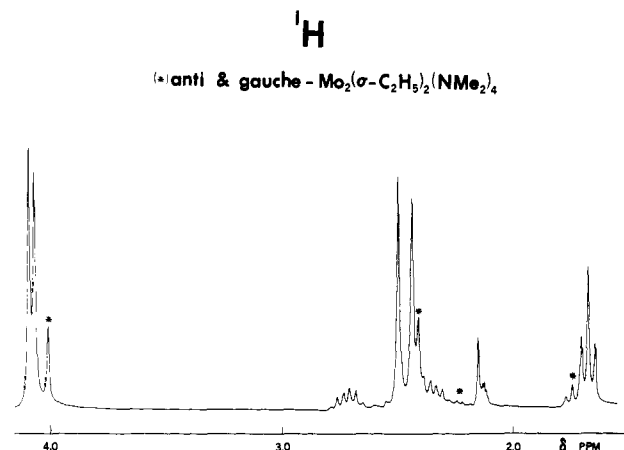


Figure 1. ^1H NMR spectrum of a mixture of anti and gauche $\text{Et}(\text{Me}_2\text{N})_2\text{Mo}\equiv\text{Mo}(\text{NMe}_2)_2$ recorded in toluene- d_8 at -61°C and 270 MHz.

ligand and two resonances in the ratio of 3:2 for the OBU' groups.⁸ This is consistent with an ethane-like molecule $(\text{Bu}'\text{O})_2(\text{Et})\text{Mo}\equiv\text{Mo}(\text{OBU}')_3$ in which rotation about the $\text{Mo}\equiv\text{Mo}$ bond is rapid on the NMR time scale.⁹

$\text{Mo}_2\text{Et}_2(\text{NMe}_2)_4$ in toluene reacts rapidly with CO_2 (≥ 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 $(\text{M}\equiv\text{M})^{10}$ on the following grounds: (i) analytical data,¹¹ (ii) infrared data,¹² 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 CD_2Cl_2 , but is sparingly soluble in pyridine.¹³

In a sealed NMR tube reaction $\text{Mo}_2\text{Et}_2(\text{NMe}_2)_4$ in toluene- d_8 was reacted with CO_2 (>4 equiv). The finely divided precipitate was centrifuged to the top of the tube and the ^1H 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.¹⁴ We conclude that the reaction between $\text{Mo}_2\text{Et}_2(\text{NMe}_2)_4$ and CO_2 proceeds stoichiometrically according to eq 1 and as such provides a model reaction for detailed studies of dinuclear reductive elimination.¹⁵ A simple intramolecular mechanism involving an initial β -hydride elimination, $\text{Et}-\text{Mo}\equiv\text{M}-\text{H} + \text{C}_2\text{H}_4$, followed by C-H reductive elimination across the $\text{Mo}\equiv\text{Mo}$ bond, $\text{Et}-\text{Mo}\equiv\text{Mo}-\text{H} \rightarrow \text{Et}-\text{H} + \text{Mo}\equiv\text{Mo}$, satisfies all our observations.

In contrast to the above we find that $\text{Mo}_2\text{Me}_2(\text{NMe}_2)_4$ reacts with CO_2 according to eq 4.



The compound $\text{Mo}_2\text{Me}_2(\text{O}_2\text{CNMe}_2)_4^{16}$ 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 $\text{W}_2\text{Me}_2(\text{O}_2\text{CNEt}_2)_4$ structure¹⁷ which has a planar $\text{C}-\text{W}\equiv\text{W}-\text{C}$ unit with a $\text{C}-\text{W}-\text{W}$ angle equal to 106° .

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- Found (calcd): C, 33.55 (33.79); H, 7.89 (8.04); N, 12.99 (13.15).
- 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).
- Et group: $\delta(\text{CH}_2)$ 2.98, $\delta(\text{CH}_3)$ 1.78 ($J_{\text{HH}} = 7.9$ Hz). OBU' groups at -76°C : δ 1.60 and 1.56 in the integral ratio 3:2, respectively. Chemical shifts (δ) are given in parts per million downfield from Me_4Si .
- Accidental magnetic degeneracy could account for the observed 3:2 spectrum (cf. predicted low-temperature limiting spectrum, 2:2:1).
- For a recent review of compounds containing M-N quadruple bonds, see F. A. Cotton, *Chem. Soc. Rev.*, **4**, 27 (1975). (b) The diethyl carbamate $\text{Cr}_2(\text{O}_2\text{CNEt}_2)_4(\text{HNtEt})_2$ has recently been structurally characterized and shown to have a Cr-Cr quadruple bond: M. H. Chisholm, F. A. Cotton, M. W. Extine, and D. C. Rideout, *Inorg. Chem.*, submitted for publication.
- Found (calcd): C, 26.23 (26.48); H, 4.25 (4.44); N, 10.09 (10.29).
- In particular the presence of a strong absorption at 1560 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).
- ^1H NMR data recorded at 100 MHz, 25°C in pyridine- d_5 : $\delta(\text{O}_2\text{CNMe}_2)$ 2.93 ppm relative to Me_4Si .
- Found by weighing the traces 38-62. Any departure from the predicted ratio, 4:6, may be due to their differing solubilities or due to the inherent experimental error of weighing the cut traces.
- Labeling studies are planned in order to investigate (i) the reversibility of β -hydrogen elimination and (ii) the intra- vs. intermolecular nature of the reaction.
- Found (calcd): C, 29.50 (29.29); H, 5.14 (5.23); N, 9.65 (9.75).
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Stereoselective Total Synthesis of Racemic Kalafungin and Nanaomycin A

Sir:

Kalafungin (**1**)¹ and nanaomycins A (**2**)² and D (**1**)³ are members of the naphthoquinone class of antibiotics, which also includes frenolicin⁴ and griseusins A and B.⁵ These natural products are potent antimicrobial agents, and the nanaomycins, in particular, have been shown⁵ to be extremely active against mycoplasmas. In a recent publication,⁶ Moore pointed out that these compounds have potential antineoplastic activity, as bioreduction may transform them into biskalafungin agents functioning similarly to the currently useful drug, mitomycin.⁷ We wish to report the first total synthesis of kalafungin and of nanaomycins A and D.⁸

2-Allyl-5-methoxynaphthoquinone⁹ was reduced with sodium hydrosulfite and alkylated with dimethyl sulfate and potassium hydroxide giving 2-allyl-1,4,5-trimethoxynaphthalene (**3**) (mp $37.5-39^\circ\text{C}$)¹⁰ in 70% yield (Scheme I). Osmium tetroxide-potassium chlorate¹¹ converted the allyl derivative into the corresponding diol, which was readily cleaved by periodate to give the aldehyde (**4**) (mp $80.5-92^\circ\text{C}$)¹⁰ in 80% overall yield. Titanium tetrachloride catalyzed reaction¹² of ketene ethyl *tert*-butyldimethylsilyl acetal with aldehyde **4** provided the hydroxy ester **5** in 50% yield. Oxidation of the dimethyl ether of the quinol was accomplished using ceric