related systems are currently under investigation using  

could occur not only by ligand migration but the racemization process, could utilize a mechanism in-  

the carbonyls. However, in light of the results in the M2C2 D.

enantiomers of 59Co NMR spectroscopy.

were heated for 1823 h in hexane/ether: IH NMR 1.5 MHz, CDCl3 (methyl region) showing interconversion of the  

exchange at room temperature), 129.2, 129.0, 128.9 (2); IR (CHCl3, cm-1) 23.1 (NH), 22.0 (CHMe2); IR (CH2Cl2) 22.0 MHz, CD2C12 (methyl region) showing interconversion of the  

Figure 3. Temperature-dependent 'H NMR spectrum (80 MHz) of 4 (4’) in CDCl3 (methyl region) showing interconversion of the enantiomers of 4. Carbonyls are omitted for clarity.

again contains the diastereotopic probe. The appropriate techniques.16 A molecule which falls between these two extremes is (arphos)Co(CO)2(C2OCHMe2) (4),17 which

Figure 2. Diagram of approximate trigonal-bipyramid geometry, the acetylene CC vector parallel to the -N=C-Mo-C=N- axis of the trigonal bipyramid. This unusual orientation follows from the electronic structure of the complex.

Summary: Several novel acetylene complexes of Mo(II), Mo(t-BuS)(t-BuNC),(R-R’) (R, R’ = H or Ph), formally five-coordinate if the acetylene is counted as a mono-dentate ligand, are prepared from the reaction of Mo(t-BuS)(t-BuNC)2 with acetylenes. The crystal structures of two of these were determined. The metal is in an approximate trigonal-bipyramidal geometry, the acetylene CC vector parallel to the -N=C-Mo-C=N- axis of the trigonal bipyramid. This unusual orientation follows from the electronic structure of the complex.

Despite current interest in molybdenum thiolate complexes12–13 viable synthetic materials have so far been rather limited.1 The sulfur ligands in known (alkyne)molybdenum complexes, apart from Mo(S2C=CH2)2(CO)(CF3=CCF3),2 are limited to dithiocarbamate2–7 or similar chelating disulfur compounds such as R2PS2-.* The

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Registry No. 1. 79816-41-4; 2, 79839-04-6; 3, 79816-42-5; 4, 79816-43-6; Co6(CO)18 10210-68-1; (CH3)2Mo6(CO)18 12091-64-4; Mn2(CO)10 10170-69-1; Cp3Ni, 1271-28-9; Co6(CO)3CCO2-C3H5 36834-86-3.

Novel (Acetylene)molybdenum(II) Complexes,  

Masato Kamata, Toshikatsu Yoshida, and Sel Otsuka*  

Masato Kamata, Toshikatsu Yoshida, and Sel Otsuka*  

Department of Chemistry, Faculty of Engineering Science  

Tokushima University, Toyonaka, Osaka 560, Japan

Department of Chemistry, Osaka City University  

Sumiyoshi-kou, Osaka 558, Japan

Kazuyuki Tatsumi and Roald Hoffmann*  

Department of Chemistry, Cornell University  

Ithaca, New York 14853

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recently reported 16-electron Mo(II) compound, cis-Mo(t-BuS)2(t-BuNC)2,10 which is preparable virtually quantitatively from Mo(t-BuS)4,11 was found to be highly reactive toward electrophiles such as CO, NO, SO2, O2, alkynes, etc. We wish to report here the title compounds derived therefrom. These unusual five-coordinate acetylene complexes of Mo(II) show an equilibrium orientation of the acetylene ligand that illuminates several aspects of acetylene bonding.

A deep yellowish green solution of Mo(t-BuS)2(t-BuNC)2 in toluene was treated with excess acetylene (1 atm, 30 °C, 30 min) resulting in a dark solution. From this was isolated, after purification by alumina chromatography, an acetylene complex of formula Mo(t-BuS)2(t-BuNC)2(HC=CH) (1, as orange vermilion crystals, mp 90 °C dec, 63% yield). Similar reactions of Mo(t-BuS)2(t-BuNC)2 in toluene produced Mo(t-BuS)2(t-BuNC)2(PPh=CH) (2, vermilion crystals, mp 120 °C dec, 60%) and Mo(t-BuS)2(PPh=CH)3 (3, deep rose crystals,12 mp 184 °C dec, 70%), respectively.

These compounds were well characterized by IR and 1H and 13C NMR spectra and elemental analysis. The 13C signal(s) in (C6D6) of the acetylenic carbons of 1, 2, and 3 appear at δ 171.7, 184.0 (PhC=), and 171.6 (CH), and 183.4, respectively. The signal was observed around δ 200 for Mo(dtc)2(CO)(RC=CR)9 and W(dtc)2(CO)(RC=CR)13 (dtc = dialkyldithiocarbamate), where the alkyne was thought to donate four electrons to the metal center.9,13 According to the electron count formalism proposed by Hoffmann, R.; Otauka, S. J. Am. Chem. Soc. 1981, 103, 5772-5778.

Table I. Comparison of Selected Molecular Parameters of Molybdenum(II) Alkyne Complexes

<table>
<thead>
<tr>
<th>bond lengths, Å</th>
<th>angles, deg</th>
</tr>
</thead>
<tbody>
<tr>
<td>M=C</td>
<td>C=CC=C=R</td>
</tr>
<tr>
<td>Mo(τ-C5H5)2(PhC=CH)</td>
<td>2.143 (6)</td>
</tr>
<tr>
<td>Mo(t-BuS)2(t-BuNC)2(PhC=CH)</td>
<td>2.05 (1)</td>
</tr>
<tr>
<td>Mo(t-BuS)2(t-BuNC)2(HC=CH)</td>
<td>2.04 (2)</td>
</tr>
</tbody>
</table>

Figure 1. Perspective view of Mo(t-BuS)2(t-BuNC)2(HC=CH) (1). Important parameters around the alkyne ligand are listed in Table I. Other main distances (Å) are as follows: Mo—S = 2.338 (3) and 2.337 (3) for 1 and 2.338 (3) for 3; Mo—C(N) = 2.115 (16) and 2.088 (14) for 1 and 2.109 (11) and 2.154 (11) for 3.

King14 and Templeton,13 the alkyne ligand in 1–3 can be regarded as a four-electron donor. The present 13C NMR data thus indicate that the four electron donating alkyne ligands can show a range of chemical shifts considerably broader than previously thought.9 For a better understanding of these data, therefore, comparative studies based on established molecular structural parameters and molecular orbital analyses are desirable.

X-ray diffraction studies were carried out on 1 and 3. Figure 1 shows the results for molecule 1.15 Molecule 316


(12) (a) The product was recrystallized from hexane and was dried in vacuo for a few days. Anal. Calcd for C21H22N2Mo: C, 51.48; H, 8.21; N, 6.00. Found: C, 50.94; H, 8.09; N, 6.05. (b) After recrystallization from toluene/hexane mixture, the product was dried in vacuo. Anal. Calcd for C21H22N2Mo: C, 51.48; H, 8.21; N, 6.00. Found: C, 50.94; H, 8.09; N, 6.05.


(15) Single crystals of 1, [Mo(t-BuS)2(t-BuNC)2(HC=CH)]+/C8H16, were grown from hexane. They belong to space group P21/c with a = 18.672 (9) Å, b = 10.106 (3) Å, c = 17.322 (8) Å, β = 112.59 (7) Å, V (for Z = 4) = 3018 (3) Å3, and dcalc = 1.13 g cm−3 and R = 5.9% for 1684 reflections with I > 3σ(I).
was virtually isostructural. Conspicuously the CC vector is nearly parallel to the -N=C—Mo—C≡N- axis. If the alkyne is regarded as a unidentate ligand, the first coordination environment is approximately a trigonal bipyramid. The important structural parameters are compared with those of other molybdenum(II) alkyne complexes in Table 1.

The molecular structure of 2 was deduced from NMR data in (C₆D₆) to be analogous to those of 1 and 3: H NMR δ 1.08 (s), 1.28 (s, (CH₃)₃CS), 1.67 (s, (CH₂)₁CS), 10.40 (s, =CH). ¹³C NMR δ 29.73, 30.26 (CH₂(CN)), 56.15 ((CH₂)ₓ(CHC), 34.91 ((CH₂)₁(CHC), 44.97 ((CH₂)₁(CS), 183.98 (Ph=C=C)). The two inequivalent H and ¹³C signals of the two axial t-BuNC ligands do not equilibrate up to 100 °C, implying stereochemical rigidity.

A bonding description of a model compound for 1–3, Mo(HS)₂(HNC)₂(PhC=CH), can be conveniently constructed from the acetylene π orbitals and the ML₄ fragment. The bent acetylene orbitals are given in 4. Note the switch in the b orbital labels depending on whether the acetylenes are parallel or perpendicular to the HN—Albright, T. A.; Hoffmann, R.; Thibeault, J. C.; Thorn, D. L. J. Am. Chem. Soc. 1978, 100, 1318-1320.

Table II. Some Individual Orbital Populations (electrons) in Three (Acetylenic)molybdenum(II) Complexes

<table>
<thead>
<tr>
<th></th>
<th>Mo- (porphyrin)- (HNC)- (HC=CH)</th>
<th>Mo(η- C,H,)-(HC=CH)</th>
<th>Mo(η- C,H,)-(HNC)- (HC=CH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>0.162</td>
<td>0.082</td>
<td>0.014</td>
</tr>
<tr>
<td>7</td>
<td>1.757</td>
<td>1.704</td>
<td>1.772</td>
</tr>
<tr>
<td>8</td>
<td>4.436</td>
<td>4.147</td>
<td>4.380</td>
</tr>
</tbody>
</table>

The observed trend in Mo-C and C=C distances (Table I) suggests that the order of alkyne-metal contributions of various MO interactions. For example, the equatorial thiolate ligands in 1–3 push up the dₓz level relative to that of the pseudo C₄₀ complex, Mo(TPP)-(PhC≡CPh), leading to a reduced b₂ (γ–½π*) interaction as reflected in the π₂ population. The axial isocyanide ligands in 1–3 push down the dₓz, resulting in a reduced b₂ interaction. This situation should also affect the magnetic resonances of alkyne ligands. The observed divergence of acetylenic ¹³C resonances of 1–3 from the tenet proposed by Templeton reflects the complexity of their origin.
A question pertinent here may be as follows: can the acetylene ligand in 3, having the least population compared to other two, act as an electrophile? The alkyne–Mo bond in 1 or 3 was suprisingly inert toward acid hydrolysis. When 3 was treated with an excess of anhydrous HCl in CH₂Cl₂, a very small amount (~3%) of stilbene (a 1:1 cis/trans mixture) was obtained; together with a trace amount of free PhC≡CPh. Similar treatment of 3 with CF₃COOH in C₆H₆ gave a comparable result. In contrast, when 3 was treated with NaBH₄ in aqueous THF (THF/H₂O = 1:4), a 1:1 mixture of trans- and cis-stilbene was obtained in 98% yield. Thus, electrophilicity of the coordinated alkynes is apparent. The origin of this electronic property of alkyne ligands and the nature of their bonding are rather complex, as we have seen above. The electrophilic behavior of the coordinated acetylene ligand, perhaps enhanced by the π₂⁻bonding interaction, is unprecedented in complexes with low oxidation states.

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Registy No. 1, 79803-04-6; 2, 79803-05-7; 3, 79681-75-7; Mo(t-BuS)₃(t-BuNC)₄, 77993-55-6.

Supplementary Material Available: Listing of structural parameters for Mo(t-BuS)₃(t-BuNC)₄(HC≡CH)₁/₂C₆H₆ and Mo(t-BuS)₃(t-BuNC)(PhC≡CPh) (10 pages). Ordering information is given on any current masthead page.


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**Book Reviews**


This book is actually Volume 12 of the well-known *Topics in Stereochemistry* series and is similar in appearance and format to previous volumes in that series. In contrast to past practices, however, the issue is edited by an inorganic chemist and is devoted entirely to inorganic and organometallic chemistry. The result is a good book, of six reviews written by recognized masters of the fields discussed. I wonder about the title of volume, however; the addition of the words “Inorganic and Organometallic” to the title of the series somehow implies that just plain stereochemistry has only to do with the structures of carbon compounds.

The first article, by T. E. Sloan of Chemical Abstracts Service, deals with “Stereochemical Nomenclature and Notation in Inorganic Chemistry”. Included are a history of the development of stereochemical nomenclature, which will appeal to most chemists with interests in structures of compounds, and a critical discussion of current practices and (exceedingly complicated) conventions for describing the stereochemistry of inorganic and organometallic compounds. In contrast to the structural simplicity of compounds of carbon, most of the other elements in the periodic table exhibit a bewildering variety of coordination numbers and stereochemistries. Hence it is clear that the day is long past when a majority of inorganic chemists will be fluent in the nomenclature of their discipline.

The second article, “Stereochemistry of Reactions of Transition Metal–Carbon Sigma Bonds”, is by T. C. Flood. It is a very long (more than 260 references) and comprehensive account of what is known about the stereochemistry of all important reactions which make or break transition-metal–carbon σ bonds. In addition, the author has not hesitated to make pertinent, critical comments on some of the work reported, and his review should be a standard reference work for mechanisms of reactions of transition-metal alkyl compounds for the next few years.

In contrast, the article by B. Bosnich and M. D. Fryzuk, “Asymmetric Synthesis Mediated by Transition Metal Complexes”, makes no attempt to be comprehensive. The emphasis is almost entirely on reactions catalyzed by or via organometallic compounds, and enzyme and model enzyme systems are almost ignored. Furthermore, even for those reactions discussed, the authors eschew actually surveying the literature; in several cases, this has already been done. The strength of this article lies rather in its critical assessment of the finer points of the diastereotropic “tuning” which occurs in the diastereomeric transition states of asymmetric transformations and which results in observed enantiomeric excesses. This approach, unusual in a review article, may well induce more ideas for research in the field than would a more traditional survey of the literature.

The fourth article, by R. D. Feltham and J. H. Enemark, is entitled “Structures of Metal Nitrosoxyls”, and is a comprehensive survey of X-ray crystal structure data on nitrosoyl complexes. Aside from detailed discussion of the significance of variations in metal-N-O bond angles, there is really little pertaining to stereochemistry per se. Thus the article seems rather out of place, although it will hold great appeal to aficionados.

“The Stereochemistry of Germanium and Tin Compounds”, by M. Gielen, is the only main-group contribution to the volume. Particular emphasis is placed on tetrahedral molecules chiral at the metal and on the nature of the five-coordinate intermediates formed during reactions of such compounds. Fluxional six-coordinate compounds are also discussed.

The final review, “Stereochemistry of Transition Metal Carbonyl Clusters”, is by B. F. C. Johnson and R. E. Benfield. The very complex structures found for clusters are considered in the light of various theories such as the 18-electron rule, Wade’s rules, molecular orbital theory, and, finally, some original ideas by the authors, themselves. It is difficult to judge, inasmuch as the field of cluster chemistry is still growing rapidly, whether this review is to be taken as essentially a progress report or whether it will be regarded in time as being definitive. What cannot be denied, however, is that the authors have provided a solid bit of scholarship. All of the articles discuss aspects of organometallic chemistry; those by Sloan, Flood, Bosnich and Fryzuk, and Gielen should appeal to organic chemists having catholic interests.

M. C. Baird, Queen’s University, Kingston, Ontario