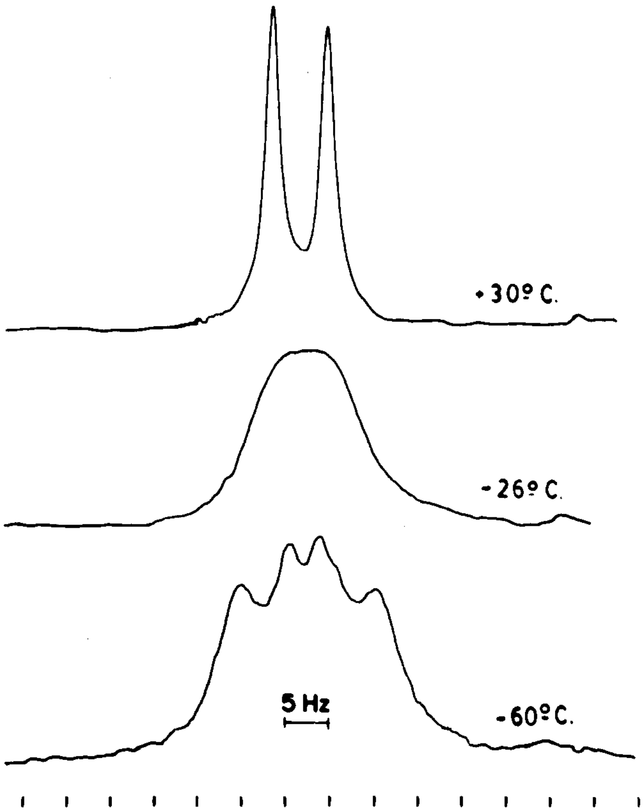
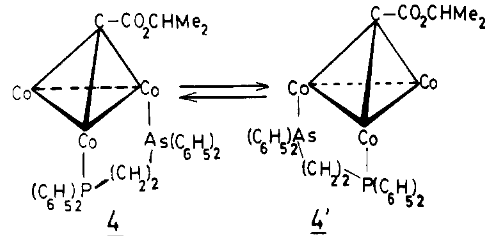


Figure 3. Temperature-dependent ^1H NMR spectrum (80 MHz) of 4 (4′) in CD_2Cl_2 (methyl region) showing interconversion of the enantiomers of 4. Carbonyls are omitted for clarity.

techniques.[16] A molecule which falls between these two extremes is (arphos)$Co_3C(CO)_7(CO_2CHMe_2)$ (4),[17] which



4 4′

again contains the diastereotopic probe. The appropriate section of the ^1H NMR spectrum is shown as Figure 3. This molecule, for which $\Delta G^{\ddagger} = 13.1 \pm 0.6$ kcal/mol for the racemization process, could utilize a mechanism involving cleavage of a Co–P or Co–As bond and migration of the dangling ligand with concomitant reorganization of the carbonyls. However, in light of the results in the M_2C_2 tetrahedral systems, it is conceivable that racemization could occur not only by ligand migration but also by direct interchange of the cluster skeletal nuclei. This and other related systems are currently under investigation using ^{59}Co NMR spectroscopy.

Acknowledgment. We thank the CNRS for financial support, Dr. C. A. Rodger, Bruker Spectrospin, Mississauga, Ontario, for the 250-MHz spectra, and Dr. R. E. Lenkinski, Southwest Ontario Regional NMR Center, Guelph, Ontario, for recording the 400-MHz spectra.

Registry No. **1**, 79816-41-4; **2**, 79839-04-6; **3**, 79816-42-5; **4**, 79816-43-6; $Co_2(CO)_8$, 10210-68-1; $(C_5H_5)_2Mo_2(CO)_6$, 12091-64-4; $Mn_2(CO)_{10}$, 10170-69-1; Cp_2Ni, 1271-28-9; $Co_3(CO)_9CCO_z$-$_i$-Pr, 36834-86-3.

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[16] Gladfelter, W. L.; Geoffroy, G. L. *Inorg. Chem.* **1980**, *19*, 2579–2585.

[17] $Co_2(CO)_8$ (5.13 g) and CCl_3CO_2-*i*-Pr (1.75 g) in 50 mL of THF were heated for 3 h at 55 °C following the standard procedures (Seyferth, D. *Adv. Organomet. Chem.* **1976**, *14*, 97) to give $Co_3(CO)_9CCO_2$-*i*-Pr (2.9 g, 37%), mp 64–65 °C. This latter compound (0.35 g) and $Ph_2P(CH_2)_2AsPh_2$ (≡arphos) (0.22 g) in 35 mL of THF were heated at 50 °C for 1.5 h to give 4 (0.38 g), mp 176 °C, as black-green crystals after chromatography and crystallization from hexane/ether: ^1H NMR (80 MHz, CD_2Cl_2) δ 1.13 (d, $J = 6.25$ Hz at +30 °C); δ 1.12, 1.00 (dd at −60 °C); ^{13}C NMR (100.577 MHz, CD_2Cl_2, 22 °C) δ 243.1 (1 C), 205 (CO's exchanging at room temperature), 182.2 (CO_2), 137.7, 132.1, 130.5, 130.2, 129.2, 129.0, 128.9 (aromatics), 68.5 (*C*HMe$_2$), 25.4 (PCH_2, d, $J_{CP} = 23$ Hz), 23.1 ($AsCH_2$), 22.0 (CH*Me*$_2$); IR (CH_2Cl_2)ν_{CO} 2056 (s), 1998 (vs), 1975 (m), 1955 (sh), 1715 (s) cm^{-1}.

Novel (Acetylene)molybdenum(II) Complexes, $Mo(t\text{-}BuS)_2(t\text{-}BuNC)_2(RC{\equiv}CR')$ (R, R′ = H or Ph)

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Summary: Several novel acetylene complexes of Mo(II), $Mo(t\text{-}BuS)_2(t\text{-}BuNC)_2(RC{\equiv}CR')$ (R, R′ = H or Ph), formally five-coordinate if the acetylene is counted as a monodentate ligand, are prepared from the reaction of $Mo(t\text{-}BuS)_2(t\text{-}BuNC)_4$ with acetylenes. The crystal structures of two of these were determined. The metal is in an 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.

Despite current interest in molybdenum thiolato complexes[1,2] viable synthetic materials have so far been rather limited.[1] The sulfur ligands in known (alkyne)molybdenum complexes, apart from $Mo(SC_6F_5)(\eta\text{-}C_5H_5)(CO)(CF_3C{\equiv}CCF_3)$,[3] are limited to dithiocarbamate[4-7] or similar chelating disulfur compounds such as $R_2PS_2^-$.[8] The

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[1] (a) Stiefel, E. I. *Prog. Inorg. Chem.* **1977**, *22*, 1–233. (b) Coucouvanis, D. *Ibid.* **1979**, *26*, 30–469. (c) Spence, J. T. In "Metal Ions in Biological Systems"; Sigel, H. Ed.; Marcel Dekker: New York, 1976; Vol. 5, pp 280–321.

[2] Newton, W. E.; Otsuka, S., Ed., "Molybdenum Chemistry of Biological Significance"; Plenum Press: New York, 1980.

[3] Howard, J. A. K.; Stanfield, R. F. D.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1976**, 246–250.

[4] Maata, E. A.; Wentworth, R. A. *Inorg. Chem.* **1979**, *18*, 524–526.

[5] Newton, W. E.; McDonald, J. W.; Corbin, J. L.; Ricard, L.; Weiss, R. *Inorg. Chem.* **1980**, *19*, 1997–2006.

[6] Ricard, L.; Martin, C., Weiss, R., XVII ICCC, Hamburg, 1976.

[7] Templeton, J. L.; Ward, B. C. *J. Am. Chem. Soc.* **1980**, *102*, 3288–3290.

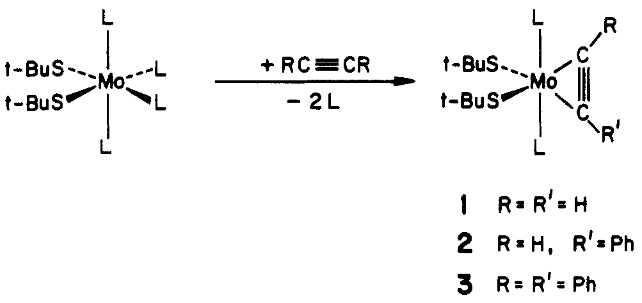
[8] McDonald, J. W.; Corbin, J. L.; Newton, W. E. *J. Am. Chem. Soc.* **1975**, *97*, 1970–1971.

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

	bond lengths, Å		angles, deg	
	M-C	C≡C	C≡C-R	ref
$\mathrm{Mo}(\eta\text{-}C_5H_5)_2(\mathrm{PhC{\equiv}CPh})$	2.143 (6) 2.144 (6)	1.269 (7)		17
$\mathrm{Mo}(t\text{-BuS})_2(t\text{-BuNC})_2(\mathrm{PhC{\equiv}CPh})$	2.05 (1) 2.06 (1)	1.28 (2)	139 (1) 140 (1)	this work
$\mathrm{Mo(EtDTC)_2(CO)(PhC{\equiv}CPh)}$	2.026 (2) 2.042 (3)	1.313 (4)	140.30 (32) 140.35 (32)	6, 18
$\mathrm{Mo(TPP)(PhC{\equiv}CPh)}$	1.983 (4) 1.965 (4)	1.324 (5)	136.4 (4) 145.4 (4)	17
$\mathrm{Mo}(t\text{-BuS})_2(t\text{-BuNC})_2(\mathrm{HC{\equiv}CH})$	2.04 (2) 2.05 (2)	1.28 (2)	143 (2) 152 (2)	this work
$\mathrm{W(EtDTC)_2(CO)(HC{\equiv}CH)}$	2.015 (9) 2.038 (8)	1.29 (1)	130.2 (6.2) 136.1 (4.4)	19

recently reported 16-electron Mo(II) compound, *cis*-Mo(t-BuS)$_2$(t-BuNC)$_4$,[9,10] which is preparable virtually quantitatively from Mo(t-BuS)$_4$,[11] was found to be highly reactive toward electrophiles such as CO, NO, SO_2, O_2, 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)$_4$ 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,[12a] mp 120 °C dec, 63% yield). Similar reactions of Mo(t-BuS)$_2$(t-BuNC)$_4$ with an excess of PhC≡CH and PhC≡CPh (50 °C, in toluene) produced Mo(t-BuS)$_2$(t-BuNC)$_2$(PhC≡CH) (**2**, vermilion crystals, mp 90 °C dec, 60%) and Mo(t-BuS)$_2$(t-BuNC)$_2$(PhC≡CPh) (**3**, deep rose crystals,[12b] mp 184 °C dec, 70%), respectively.



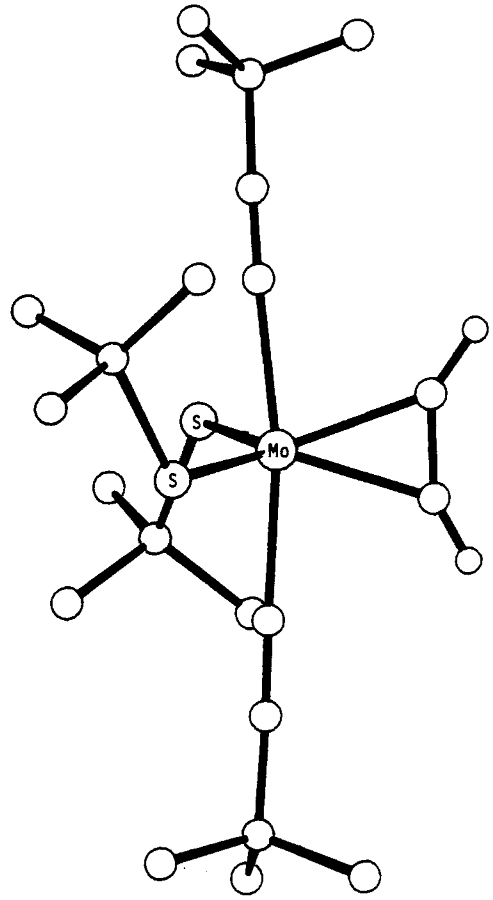


Figure 1. Perspective view of Mo(t-BuS)$_2$(t-BuNC)$_2$(HC≡CH) (**1**). Important parameters around the alkyne ligand are listed in Table I. Other main distances (Å) are as follows: Mo—S = 2.321 (3) and 2.329 (4) for **1** and 2.338 (3) and 2.337 (3) for **3**; Mo—C(N) = 2.115 (16) and 2.088 (14) for **1** and 2.109 (11) and 2.154 (11) for **3**.

These compounds were well characterized by IR and ^1H and ^{13}C NMR spectra and elemental analysis. The ^{13}C signal(s) in (C_6D_6) 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 King[14] and Templeton,[9,13] the alkyne ligand in **1**–**3** can be regarded as a four-electron donor. The present ^{13}C 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 understainding 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 **3**[16]

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(9) Kamata, M.; Yoshida, T.; Otsuka, S.; Hirotsu, K.; Higuchi, T. *J. Am. Chem. Soc.* **1981**, *103*, 3572–3574.

(10) Kamata, M.; Hirotsu, K.; Higuchi, T.; Tatsumi, K.; Yoshida, T.; Hoffmann, R.; Otsuka, S. *J. Am. Chem. Soc.* **1981**, *103*, 5772–5778.

(11) Otsuka, S.; Kamata, M.; Hirotsu, K.; Higuchi, T. *J. Am. Chem. Soc.* **1981**, *103*, 3011–3014.

(12) (a) The product was recrystalized from hexane and was dried in vacuo for a few days. Anal. Calcd for $C_{20}H_{38}N_2S_2Mo$: C, 51.48; H, 8.21; N, 6.00. Found: C, 50.94; H, 8.09; N, 6.05. (b) After recrystalization from toluene/hexane mixture, the product was dried in vacuo. Anal. Calcd for $C_{32}H_{46}N_2S_2Mo$: C, 62.11, H, 7.51; N, 4.55. Found: C, 61.86; H, 7.51; N, 4.55.

(13) Ward, B. C.; Templeton, J. L. *J. Am. Chem. Soc.* **1980**, *102*, 1532–1538.

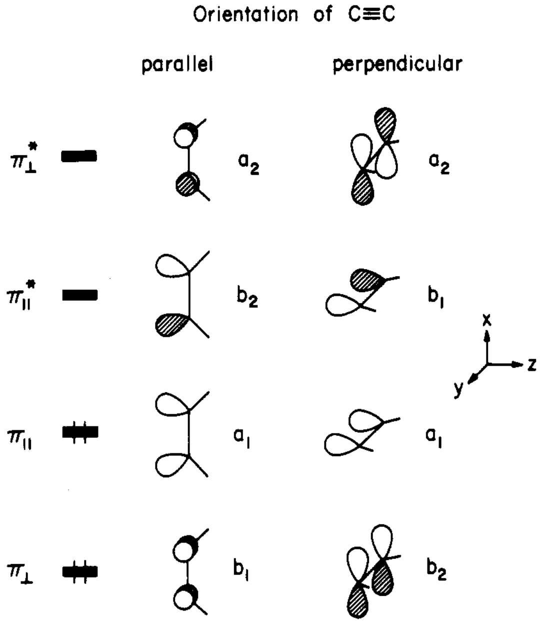
(14) King, R. B. *Inorg. Chem.* **1968**, *7*, 1044–1046.

(15) Single crystals of **1**, [Mo(t-BuS)$_2$(t-BuNC)$_2$(HC≡CH)]$\cdot{}^1/_2C_6H_{12}$, were grown from hexane. They belong to space group $P2_1/a$ with a = 18.672 (9) Å, b = 10.105 (3) Å, c = 17.322 (8) Å, β = 112.58 (7)Å, V (for Z = 4) = 3018 (3) Å^3, and d_{calcd} = 1.12 g cm^{-3} and R = 5.9% for 1684 reflections with $I > 3\sigma(I)$.

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 I.

The molecular structure of **2** was deduced from NMR data in (C_6D_6) to be analogous to those of **1** and **3**: ^1H NMR δ 1.08 (s), 1.28 (s, $(CH_3)_3CNC$), 1.67 (s, $(CH_3)CS$), 10.40 (s, ≡CH); ^{13}C NMR δ 29.73, 30.26 ($(CH_3)_3CNC$), 56.15 ($(CH_3)_3CHC$), 34.91 ($(CH_3)_3CS$), 44.97 ($(CH_3)_3CS$), 183.98 (PhC≡), 171.62 (≡CH). The two inequivalent ^1H and ^{13}C 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**, $Mo(HS)_2(HNC)_2(HC{\equiv}CH)$, can be conveniently constructed from the acetylene π orbitals and the ML_4 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-C—Mo—CNH axis.

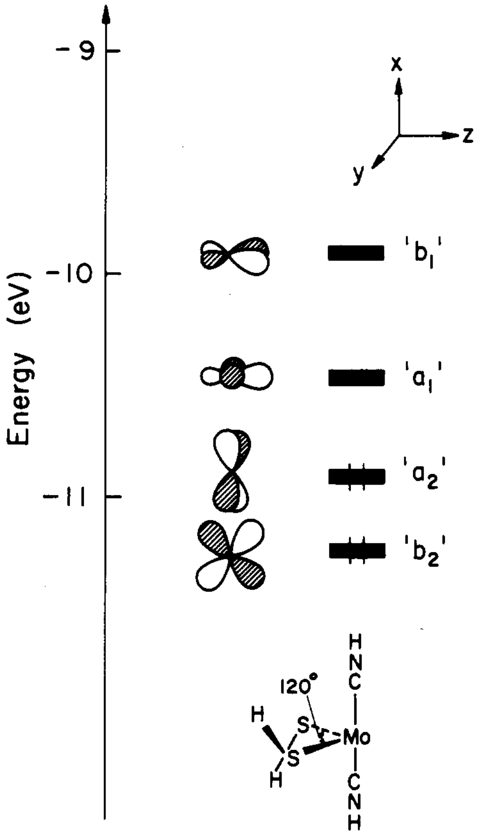


4

The $Mo(HS)_2(HNC)_2$ orbitals, **5**, are typical of an ML_4 fragment.[20] Above the remnant of an octahedral t_{2g} set (a_1, a_2, b_2) there lie out-of-phase b_1 and in-phase combinations of hybrids. In a d^4 low-spin complex what one wants to achieve is a maximal splitting of the t_{2g} set in a pattern of two below one. Juxtaposition of **4** and **5** clearly shows that this is best achieved in the observed acetylene orientation, C≡C "upright" or parallel to HNC—Mo—C-NH. Here $\pi_\parallel^*$ and $\pi_\perp^*$ stabilize b_2 and a_2 orbitals, and $\pi_\parallel$ is stabilized by the t_{2g} a_1 orbital, pushing that orbital up. The optimal two below one splitting is obtained. In the alternative in-plane or parallel orientation no such optimal two electron bonding pattern is possible.

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

	6 Mo-(porphyrin)-(HC≡CH)	**7** $Mo(HS)_2$-$(HNC)_2$-(HC≡CH)	**8** Mo(η-C_5H_5)-(HC≡CH)
$\pi_\perp^*$	0.106	0.082	0.014
$\pi_\parallel^*$	0.803	0.584	0.740
$\pi_\parallel$	1.775	1.704	1.772
$\pi_\perp$	1.752	1.777	1.854
Σ	4.436	4.147	4.380



5

In Table II some specific orbital populations of three model tolane complexes are compared. These are Mo(porphyrin)(HC≡CH) (**6**, a model for Mo(TPP)(PhC≡CPh)), $Mo(HS)_2(HNC)_2(HC{\equiv}CH)$ (**7**, a model for **1–3**), and $Mo(\eta\text{-}C_5H_5)_2(HC{\equiv}CH)$ (**8**, a model for $Mo(\eta\text{-}C_5H_5)_2(PhC{\equiv}CPh)$). The $\pi_\parallel^*$ population decreases in the order **6** > **8** > **7**, while that of $\pi_\perp$ increases in the order **6** < **7** < **8**. The observed trend in Mo-C and C≡C distances (Table I) suggests that the order of alkyne–metal bond strength is **8** < **7** < **6**. Thus the strength of acetylene bonding appears to be a reflection of composite contributions of various MO interactions. For example, the equatorial thiolato ligands in **1–3** push up the d_{yz} level relative to that of the pseudo C_{4v} complex, Mo(TPP)(PhC≡CPh), leading to a reduced b_1 (yz–$\pi_\perp$) interaction as reflected in the $\pi_\perp$ population. The axial isocyanide ligands in **1–3** push down the d_{xz} resulting in a reduced b_2 interaction. This situation should also affect the magnetic resonances of alkyne ligands. The observed divergence of acetylenic ^{13}C resonances of **1–3** from the tenet proposed by Templeton reflects the complexity of their origin.

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(16) Single crystals of **3** [$Mo(t\text{-}BuS)_2(t\text{-}BuNC)_2(PhC{\equiv}CPh)$], were grown from a toluene/hexane mixture (2:1). They belong to space group $P2_1/c$ with a = 16.982 (9) Å, b = 17.378 (8) Å, c = 12.013 (6)Å, β = 96.59 (4)Å, V (for Z = 4) = 3522 (3) Å, and d_{calcd} = 1.17 g cm^{-3} and R = 6.2% for 2694 reflections with $I > 1.96\sigma(I)$.

(17) De Cian, A.; Colin, J.; Schappacher, M.; Ricard, L.; Weiss, R. *J. Am. Chem. Soc.* **1981**, *103*, 1850–1851.

(18) Private communication, we are indebted to Professor R. Weiss for supplying us with the X-ray diffraction results prior to publication.

(19) Ricard, L.; Weiss, R.; Newton, W. E.; Chen, G. J.-J.; McDonald, J. W. *J. Am. Chem. Soc.* **1978**, *100*, 1318–1320.

(20) For the ML_4 fragment orbitals see: (a) Elian, M.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 1058–1076. (b) Burdett, J. K. *J. Chem. Soc., Faraday Trans.* **1974**, *70*, 1599–1613. (c) Mingos, D. M. P. *J. Chem. Soc., Dalton Trans.* **1977**, 602–610; *Adv. Organomet. Chem.* **1977**, *15*, 1–51. (d) Albright, T. A.; Hoffmann, R.; Thibeault, J. C.; Thorn, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 3801–3812.

(21) For further details see: Tatsumi, K.; Hoffmann, R.; Templeton, J. L. *Inorg. Chem.*, in press.

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 CH_2Cl_2, a very small amount ($\sim 3\%$) of stilbene (a 1:1 cis/trans mixture) was obtained; together with a trace amount of free $PhC\equiv CPh$. Similar treatment of **3** with CF_3COOH in C_6H_6 gave a comparable result. In contrast, when **3** was treated with $NaBH_4$ in aqueous THF ($THF/H_2O = 1:4$), 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 $\pi_\perp$-bonding interaction,[9,13,22] is unprecedented in complexes with low oxidation states.

Acknowledgment. We are grateful for financial support for this research to the Ministry of Education, Science and Culture (Japan) through the Grant-in-Aid for Special Project Research, "Biomimetic Chemistry", and to the National Science Foundation (USA) through Research Grant CHE 7828048.

Registry No. **1**, 79803-04-6; **2**, 79803-05-7; **3**, 79681-75-7; $Mo(t\text{-}BuS)_2(t\text{-}BuNC)_4$, 77593-55-6.

Supplementary Material Available: Listing of structural parameters for $Mo(t\text{-}BuS)_2(t\text{-}BuNC)_2(HC\equiv CH)\cdot{}^1/_2C_6H_{14}$ and $Mo(t\text{-}BuS)_2(t\text{-}BuNC)_2(PhC\equiv CPh)$ (10 pages). Ordering information is given on any current masthead page.

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(22) Otsuka, S.; Nakamura, A. *Adv. Organomet. Chem.* **1976**, *14*, 245–279.

Book Reviews

Topics in Inorganic and Organometallic Stereochemistry. Edited by G. Geoffroy. John Wiley and Sons, New York. 1981. x + 352 pages. $60.00.

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 diastereotopic "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 Nitrosyls", and is a comprehensive survey of X-ray crystal structure data on nitrosyl 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 afficionados.

"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. G. 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.

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