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Preparation and Characterization of Molybdenum(IV)–Alkyne Complexes Containing Bulky Aryloxide or Arenethiolate Ligands

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Complexes of the type Mo(alkyne)$(DIPP)_2Cl_2$, Mo(alkyne)$(DIPP)_3Cl$, and Mo(alkyne)$(DIPP)_4$ (DIPP = ^-O-2,6-C_6H_3-*i*-Pr_2; alkyne = EtC$\equiv$CEt or PhC$\equiv$CPh) have been prepared by adding DIPP salts to Mo(alkyne)Cl_4(ether). $Mo(C_2Ph_2)(DIPP)_4$ crystallizes in the space group $P2_12_12$ with $a = 12.464$ (3) Å, $b = 19.230$ (4) Å, $c = 12.268$ (2) Å, $V = 2940.4$ Å^3, $Z = 2$, mol wt = 983.2, and ρ(calcd) = 1.110 g cm^{-3}. It is a crowded, distorted-trigonal-bipyramidal molecule in which the alkyne is bound in an equatorial position and almost lies in the equatorial plane. It is assumed that the alkyne is bound in a similar position in the other two molecules. Steric crowding is evidenced by restricted rotation of axial DIPP ligands in Mo(alkyne)$(DIPP)_3Cl$ and Mo(alkyne)$(DIPP)_4$, but not Mo(alkyne)$(DIPP)_2Cl_2$. Complexes of the type Mo(alkyne)$(TIPT)_4$ (TIPT = ^-S-2,4,6-C_6H_2-*i*-Pr_3) have been prepared either by adding LiTIPT to Mo(alkyne)Cl_4(ether) (alkyne = MeC$\equiv$CMe or EtC$\equiv$CEt) or by adding alkyne to $Mo(TIPT)_4$ (alkyne = MeC$\equiv$CMe, EtC$\equiv$CEt, or HC$\equiv$CH). $Mo(C_2Et_2)(TIPT)_4$ crystallizes in the space group $P2_1/n$ with $a = 13.889$ (4) Å, $b = 22.475$ (5) Å, $c = 22.041$ (5) Å, $\beta = 96.97$ (2)°, $V = 6829.4$ Å^3, $Z = 4$, mol wt = 1119.9, and ρ(calcd) = 1.089 g cm^{-3}. It is a crowded trigonal-bipyramidal complex in which the 3-hexyne is bound in an axial position and is constrained to lie along the Mo–S bond of the unique equatorial thiolate ligand. The phenyl rings of the other equatorial thiolate ligands are tilted up around the other end of the 3-hexyne ligand. The three different thiolate ligands do not interconvert rapidly on the NMR time scale at 25 °C, and the rotation of the alkyne about the Mo–alkyne bond axis is restricted. The alkyne ligand in Mo(alkyne)$(TIPT)_4$ can be substituted by another (alkyne′) in a reaction that is first order in Mo and zero order in alkyne′ when the alkyne is ethyne. In contrast, the alkyne ligand in Mo(alkyne)$(DIPP)_4$ complexes cannot be replaced by another simple alkyne. Electrochemical studies show that both Mo(alkyne)$(DIPP)_4$ and Mo(alkyne)$(TIPT)_4$ complexes can be reduced in dichloromethane, the former more easily than the latter by ~0.2 V. The reduction is an irreversible EC reaction in which only 0.5 electron is consumed; the reduction products could not be identified. Anodic waves can be observed in both the DIPP and TIPT systems, but the oxidations are also irreversible.

Introduction

It is generally agreed that Mo(IV) is a dominant oxidation state of molybdenum in nitrogenase and that at least one end of dinitrogen binds to molybdenum in the process of being reduced to ammonia.[1] Therefore, studies of $MoX_4(L)$ complexes where X is an inhibitor or a substrate for nitrogenase (e.g., L = CO, RNC, RC$\equiv$CR) may be of some relevance to the question concerning how dinitrogen is reduced. Molecules in this class are extremely rare,[2] although several examples of alkyne complexes are known. Greco reported Mo(alkyne)Cl_4 complexes (alkyne = 2-butyne or diphenylacetylene) more than 10 years ago.[3a] Related five-coordinate Mo(IV) (and W(IV)) alkyne complexes have been reported more recently by Dehnicke.[3b] Most recently we discovered that alkynes would add to $Mo(TIPT)_4$ (TIPT = ^-S-2,4,6-C_6H_2-*i*-Pr_3) to give simple adducts of the type Mo(alkyne)$(TIPT)_4$.[4] Since we had shown also that W(PhC$\equiv$CPh)$(OCMe_3)_4$ can be prepared from W(PhC$\equiv$CPh)Cl_4,[3c] we felt that some Mo(alkyne)(alkoxide)$_4$ complexes should be prepared whose properties and reactions could then be compared to those of Mo(alkyne)$(TIPT)_4$ complexes. We have now completed several such syntheses. Here we report the preparation of several Mo(alkyne)X_4 complexes where X is an aryloxide or arenethiolate along with some elementary chemistry, X-ray studies, and comparative electrochemistry.

Results

Synthesis of Aryloxide Complexes. A useful starting material for preparing Mo(IV)–acetylene complexes is $Mo(C_2R_2)Cl_4$(ether) (R = Me, Et, Ph). The brown ether-free complex with R = Me or Ph was reported some time ago.[3a] We have found that the yellow-orange (R = Me, Et) to red (R = Ph) crystalline ether adducts can be prepared easily by adding the appropriate alkyne to a solution of $MoCl_4$ in diethyl ether. Unfortunately the $Mo(C_2R_2)Cl_4$(ether) complexes are thermally sensitive, a fact that we believe has prevented our obtaining satisfactory elemental analyses. However, they are nevertheless convenient starting materials, as they can be stored indefinitely as solids at −30 °C.

$Mo(C_2Et_2)Cl_4$(ether) reacts with 3 equiv of LiO-2,6-C_6H_3-*i*-Pr_2 (LiDIPP) at 25 °C in diethyl ether to yield red-orange $Mo(C_2Et_2)(DIPP)_3Cl$. The reaction passes through a purple stage, which we propose is $Mo(C_2Et_2)(DIPP)_2Cl_2$; this species can be isolated as purple crystals when only 2 equiv of LiDIPP are employed. Addition of more than 3 equiv of LiDIPP to Mo(EtC$\equiv$CEt)Cl_4(ether) does not yield $Mo(C_2Et_2)(DIPP)_4$. However, if the *potassium* salt (K(DIPP)) is added to $Mo(C_2Et_2)(DIPP)_3Cl$ in diethyl ether, then dark red $Mo(C_2Et_2)(DIPP)_4$ can be prepared. An analogous reaction employing $Mo(C_2Ph_2)Cl_4$(ether) and K(DIPP) gave $Mo(C_2Ph_2)(DIPP)_4$.

The ^1H NMR spectrum of $Mo(C_2Et_2)(DIPP)_2Cl_2$ is unexceptional. However, $Mo(C_2Et_2)(DIPP)_3Cl$ and $Mo(C_2R_2)(DIPP)_4$ complexes each exhibit ^1H NMR spectra characteristic of restricted rotation of two of the aryl rings about their C–O bonds (and presumably also their Mo–O bonds). Let us assume that all three complexes are structurally analogous, i.e., that the alkyne is bound to the metal roughly in the equatorial plane of a trigonal bipyramid as found in $Mo(C_2Ph_2)(DIPP)_4$ (see below). If we assume further that the DIPP ligands are added to the metal so as to minimize steric interactions between them, i.e. axial chlorides

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(1) (a) Coughlin, M., Ed. *Molybdenum and Molybdenum-Containing Enzymes*; Pergamon: Elmsford, NY, 1980. (b) Hardy, R. W. F., Bottomley, F., Burns, R. C., Eds. *A Treatise on Dinitrogen Fixation*; Wiley-Interscience: New York, 1979. (c) Gibson, A. H., Newton, W. F., Eds. *Current Perspectives in Nitrogen Fixation*; Elsevier: Amsterdam, 1981.

(2) (a) Mo(1-adamantoxy)$_4(Me_2NH)$ and related adducts have been reported by Wilkinson,[2b] while Chisholm has found that $Mo(N_2CPh_2)(OCMe_3)_4$ is a product of the reaction between $Mo_2(OCMe_3)_6$ or $Mo(OCMe_3)_4$[2c] and Ph_2CN_2.[2d] To our knowledge other simple five-coordinate adducts have not been prepared. $Mo(SCMe_3)_4$ is a rare example of a monomeric MoX_4 complex[2e] but addition of isocyanides or CO to it led to reduction of the metal.[2f,g] (b) Bochmann, M.; Wilkinson, G.; Young, G. B.; Hursthouse, M. B.; Malik, K. M. A. *J. Chem. Soc., Dalton Trans.* **1980**, 901. (c) Chisholm, M. H.; Reichert, W. W.; Thorton, P. *J. Am. Chem. Soc.* **1978**, *100*, 2744. (d) Chisholm, M. H.; Folting, K.; Huffman, J. C.; Ratermann, A. L. *Inorg. Chem.* **1984**, *23*, 2303. (e) Otsuka, S.; Kamata, M.; Hirotsu, K.; Higuchi, T. *J. Am. Chem. Soc.* **1981**, *103*, 3011. (f) Kamata, M.; Yoshida, T.; Otsuka, S. *J. Am. Chem. Soc.* **1981**, *103*, 3572. (g) Kamata, M.; Hirotsu, K.; Higuchi, T.; Tatsumi, K.; Hoffman, R.; Yoshida, T.; Otsuka, S. *J. Am. Chem. Soc.* **1981**, *103*, 5772.

(3) (a) Greco, A.; Pirinoli, F.; Dall'asta, G. *J. Organomet. Chem.* **1973**, *60*, 115. (b) Hey, F.; Weller, F.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1984**, *514*, 18; **1984**, *514*, 25 and references therein. (c) Theopold, K. H.; Holmes, S. J.; Schrock, R. R. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 1010.

(4) Roland, E.; Walborsky, E. C.; Dewan, J. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1985**, *107*, 5795.

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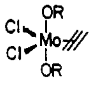
Table I. ^{13}C NMR Chemical Shifts for Acetylenic Carbon Atoms[a]

compd	δ
$Mo(C_2Et_2)(DIPP)_2Cl_2$	178.8
$Mo(C_2Et_2)(DIPP)_3Cl$	195.4, 182.2
$Mo(C_2Et_2)(DIPP)_4$	197.7
$Mo(C_2Ph_2)(DIPP)_4$	191.6
$Mo(C_2Et_2)(DMP)_4$	197.9
$Mo(C_2Me_2)(TIPT)_4$	219.2, 202.6[b]
$Mo(C_2Et_2)(TIPT)_4$	217.4, 202.8[b]

[a] Solvent was CD_2Cl_2 at 298 K, unless otherwise noted. [b] Temperature was 240 K.

substitute first, then we can propose the consistent set of structures **1**–**3**. The isopropyl groups of the two axial DIPP ligands cannot easily pass by the isopropyl groups of the equatorial DIPP ligand(s) in **2** and **3** if the phenyl rings of the equatorial DIPP ligand(s) is (are) roughly perpendicular to the equatorial plane. (See X-ray structure of Mo(PhC≡CPh)$(DIPP)_4$.) Rotation of the phenyl rings in the axial DIPP ligands in **1**, however, would not be so impeded. We believe this is the reason why restricted rotation in **1** is not observed. Other less attractive explanations are possible if we do not make the two assumptions above. For example, **2** could contain two equatorial DIPP ligands. The alkyne would then be required to be perpendicular to the equatorial plane (the two ends are inequivalent), and rotation of the phenyl rings in the *equatorial* DIPP ligands would have to be restricted. While this and other explanations involving other basic geometries or binding of the alkyne in an axial position cannot be eliminated, we prefer the above explanation until we have any evidence to the contrary.



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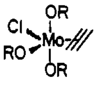

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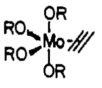

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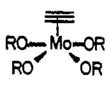

4

As an example, let us examine the ^1H NMR spectrum of $Mo(C_2Et_2)(DIPP)_3Cl$ more closely. We observe four doublet resonances, each of area 6, which we assign to four different isopropyl methyl groups in the axial DIPP ligands (where rotation of the phenyl ring is proposed to be slow), and one doublet resonance of area 12, which we assign to isopropyl methyl groups in the equatorial DIPP ligand. Three septets of area 2 each are assigned to isopropyl methine protons. The aromatic region is relatively complex. Since the two ends of the acetylene are inequivalent, it must lie in a plane of symmetry. All of these observations are consistent with a molecule of structure **2** in which the axial DIPP phenyl rings cannot rotate freely about the C–O and M–O bonds. ^{13}C NMR spectra show the number of signals in the appropriate region that one would expect on the basis of the above hypothesis. Specific assignments in any one region of the spectrum could not be confirmed, as the gated-proton-decoupled spectrum was too complex at the field strength employed (270 MHz ^1H).

The difference between the DIPP ligand and the ^-O-2,6-$C_6H_3Me_2$ (DMP) ligand in acetylene complexes of this type is marked. Addition of 4 equiv of LiDMP to $Mo(C_2Et_2)Cl_4$(ether) in diethyl ether yields red-orange $Mo(C_2Et_2)(DMP)_4$. Its ^1H NMR spectrum shows that all DMP ligands are equivalent and phenyl rings rotate freely about C–O bonds, even at −78 °C. We propose that $Mo(C_2Et_2)(DMP)_4$ has a structure of type **3** and that now not only can the axial DMP phenyl rings rotate freely but also what is perhaps a relatively more crowded tetragonal-pyramidal structure (**4**) can form and thereby interconvert axial and equatorial DMP ligands. Although it is possible that the lowest energy structure *is* **4** in this case and that there is still enough room for the phenyl rings to rotate freely, we prefer the former explanation.

The chemical shifts of the acetylene carbon atoms in several aryloxide complexes are listed in Table I. One interesting and unexpected trend is the *smaller* chemical shift for the chloride derivatives. We had expected the inductive effect of the chloride ligands to shift the acetylene carbon atom signals to lower field.

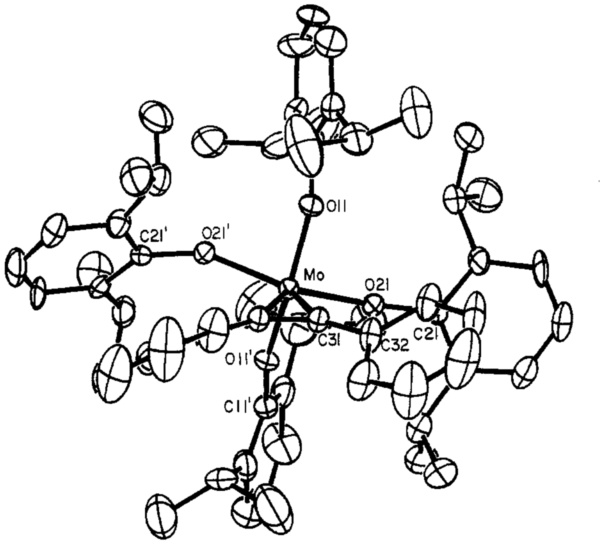

Figure 1. ORTEP diagram of $Mo(C_2Ph_2)(DIPP)_4$ (30% probability ellipsoids). Hydrogen atoms are not shown. Primed atoms are related to unprimed atoms by a crystallographically required two-fold axis passing through the midpoint of C(31)–C(31′) and Mo. A fully labeled diagram can be found in the supplementary material.

Table II. Relevant Bond Distances (Å) and Angles (deg) in Mo(PhC≡CPh)$(DIPP)_4$

Mo–O(11)	1.876 (10)	O(11)–Mo–C(31′)	104.7 (5)
Mo–O(21)	2.004 (10)	O(11)–Mo–O(11′)	158.5 (7)
Mo–C(31)	2.031 (16)	O(21)–Mo–O(21′)	143.9 (6)
C(31)–C(32)	1.449 (25)	Mo–O(11)–C(11)	160.5 (11)
C(31)–C(31′)	1.271 (28)	Mo–O(21)–C(21)	144.4 (10)
O(11)–C(11)	1.378 (22)	O(21)–Mo–C(31)	90.5 (5)
O(21)–C(21)	1.361 (18)	C(31)–Mo–C(31′)	36.5 (8)
O(11)–Mo–O(21)	89.4 (4)	C(31′)–C(31)–C(32)	139.9 (10)
O(11)–Mo–O(21′)	84.0 (4)	C(31′)–C(31)–Mo	71.8 (4)
O(11)–Mo–C(31)	95.7 (5)	Mo–C(31)–C(32)	148.2 (12)

X-ray Structure of $Mo(C_2Ph_2)(O\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)_4$. A diagram of the $Mo(C_2Ph_2)(DIPP)_4$ molecule is shown in Figure 1. A complete description of the structure solution can be found in the Experimental Section. Selected bond lengths and angles can be found in Table II.

$Mo(C_2Ph_2)(DIPP)_4$ is roughly a trigonal bipyramid with a relatively large O_{eq}–Mo–O_{eq} angle (143.9 (6)°) and an O_{ax}–Mo–O_{ax} angle (158.5 (7)°) significantly less than 180°. Diphenylacetylene is bound in an equatorial position with Mo–C distances of 2.031 (16) Å; it is only slightly twisted out of the equatorial plane. The molecule contains a crystallographically required two-fold axis that passes through the midpoint of the C(31)C(31′) bond and through the metal. The C–C bond length in the alkyne is relatively short (1.271 (28) Å) and the phenyl rings are not bent back from the C–C axis to any unusual degree (~40°). Therefore, we cannot say that this alkyne is in any way different from a vast number of alkynes bound to many metals in many different oxidation states.[5] In particular, there is no basis for saying that diphenylacetylene is reduced to any significant extent and the metal consequently oxidized.

The axial and equatorial DIPP ligands differ rather markedly. The axial Mo–O bonds are shorter (1.876 (10) vs. 2.004 (10) Å) and the Mo–O–C bond angles larger (160.5 (11) vs. 144.4 (10)°) than those in the equatorial ligand set. If these values reflect only electronic differences between axial and equatorial Mo–ligand bonding, then we would be tempted to say that the axial DIPP ligand is donating more π-electron density to the metal than the equatorial DIPP ligand. Rehybridization of the oxygen atoms alone (to sp^2 or sp) would result in a shorter Mo–O bond and larger

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(5) (a) Otsuka, S.; Nakamura, A. *Adv. Organomet. Chem.* **1976**, *14*, 245. (b) Ittel, S. D.; Ibers, J. A. *Adv. Organomet. Chem.* **1976**, *14*, 33.

Mo–O–C angle without any donation of π-electron density to the metal. We prefer the more popular view that a shorter Mo–O bond and larger Mo–O–C angle are indicative of a greater degree of π bonding between the metal and oxygen in an early-transition-metal alkoxide complex.[6]

The structural results support the notion that the phenyl rings in the axial set of DIPP ligands cannot rotate freely. The phenyl rings in the equatorial DIPP ligands are oriented roughly perpendicular to the equatorial plane so as to place isopropyl groups above and below the equatorial plane. The O(21)–Mo–O(21′) angle (143.9 (6)°) is surprisingly large, but not because of any obvious significant steric interaction between the equatorial phenoxide ligands. However, there probably would be some significant steric interaction between them, and between the equatorial phenoxide isopropyl groups and the acetylene's phenyl rings, were both phenyl rings in the equatorial DIPP ligands turned so as to lie roughly in, rather than perpendicular to, the equatorial plane. The phenyl rings of the axial DIPP ligands therefore must be oriented so as to place the isopropyl groups in the "holes" above and below the equatorial plane and between the isopropyl groups of the equatorial DIPP ligands. As long as only one equatorial DIPP phenyl ring at one time can rotate so as to lie roughly in the equatorial plane, then the axial DIPP phenyl rings will be "locked" in the configuration shown. However, if the structure of the $Mo(C_2Et_2)(DIPP)_3Cl$ complex is analogous to that of $Mo(PhC{\equiv}CPh)(DIPP)_4$, it is not obvious why the phenyl ring in the axial ligand should not be able to rotate when the phenyl ring of the single equatorial DIPP ligand turns so as to lie (roughly) in the equatorial plane. Perhaps the steric problems encountered in a concerted "cogwheel" action in both $Mo(C_2R_2)(DIPP)_3Cl$ and $Mo(C_2R_2)(DIPP)_4$ alone prevent rotation of the axial DIPP phenyl ring from being nearly as rapid as that of the equatorial DIPP phenyl ring.

Finally, the results of the structure study also suggest that it would be easy for the DMP ligands in isostructural trigonal-bipyramidal $Mo(EtC{\equiv}CEt)(DMP)_4$ to exchange via the tetragonal-pyramidal **4** since the trigonal bipyramid already is distorted part of the way toward a tetragonal pyramid.

Synthesis of Arenethiolate Complexes. Red complexes of the type $Mo(C_2R_2)(TIPT)_4$ (TIPT = ^{-}S-2,4,6-C_6H_2-*i*-Pr_3; R = Me or Et) can be prepared by adding 4 equiv of LiTIPT to $Mo(C_2R_2)Cl_4$(ether) in diethyl ether. They also can be prepared quantitatively by adding the acetylene to $Mo(TIPT)_4$.[4] This latter method allowed us to prepare the parent complex, $Mo(C_2H_2)(TIPT)_4$, at –78 °C in ~40% yield.

The ^1H NMR spectra of all three complexes at room temperatures are complex. In the aromatic region three aryl proton singlet resonances in a ratio of 4:2:2 are observed along with four methine multiplets in the ratio of 4:4:2:2 or three in a ratio of 6:4:2. The region between 1.0 and 1.5 ppm contains a large number of relatively sharp signals, among which signals for the Me or Et groups of the alkyne ligand cannot be discerned. However, we can see the acetylenic proton in the 25 °C ^1H NMR spectrum of $Mo(C_2H_2)(TIPT)_4$ at 9.5 ppm as a sharp singlet. All ^1H NMR spectra change somewhat in the temperature range 240–330 K, but not in a readily explained fashion. The 9.5 ppm signal for the ethyne ligand remains sharp down to 240 K.

The acetylenic carbon atom resonances in the Mo(alkyne)-$(TIPT)_4$ complexes cannot be observed at room temperature. At 240 K two acetylenic carbon atom resonances can be observed at 219.2 and 202.6 ppm in $Mo(C_2Me_2)(TIPT)_4$ and at 217.4 and 202.8 ppm in $Mo(C_2Et_2)(TIPT)_4$. These chemical shifts are not dramatically different from those of acetylenic carbon atoms in DIPP complexes (Table I). Apparently, the inequivalent acetylenic carbon atoms are interconverting by rapid rotation about the Mo–alkyne bond at room temperature. The averaging process clearly does not consist of loss of the alkyne to give $Mo(TIPT)_4$ at a rate that is *rapid* on the NMR time scale, since this type of exchange is observable on the *chemical* time scale (see later). So far we have not been able to observe a ^{13}C NMR resonance for the acetylenic carbon atom in $Mo(C_2H_2)(TIPT)_4$ in the temperature range 240–330 K. Since we observe the expected TIPT signals for both $Mo(TIPT)_4$ and $Mo(C_2H_2)(TIPT)_4$ in a ^1H NMR spectrum of a mixture of the two at 25 °C, the ethyne ligand cannot be coming off at a rate comparable to the NMR time scale, a process that conceivably could produce the observed result. We believe that the ethyne ligand is rotating significantly more rapidly in $Mo(C_2H_2)(TIPT)_4$ than in $Mo(RC{\equiv}CR)(TIPT)_4$ (R = Me or Et) at a given temperature. The circumstances must be such that the rotation is not slow enough on the NMR time scale at 240 K to see sharp, separate resonances for the two carbon atoms at the concentration that is possible at this temperature. Unfortunately, at room temperature or above in dichloromethane-d_2 $Mo(C_2H_2)(TIPT)_4$ decomposes during the time required to accumulate sufficient data.

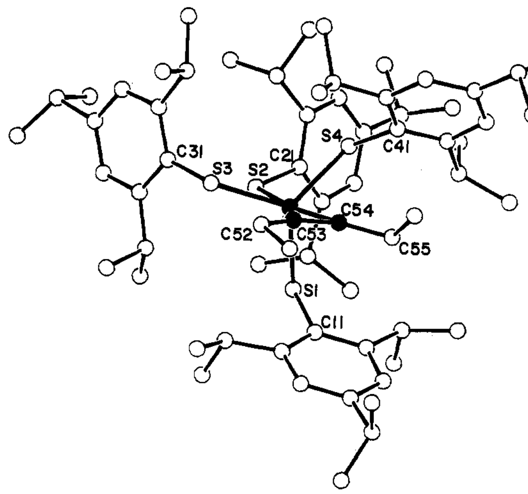

Figure 2. Diagram of $Mo(C_2Et_2)(TIPT)_4$ in which, for clarity, the atoms are shown as spheres of arbitrary radius. A fully labeled diagram can be found in the supplementary material.

Table III. Relevant Bond Distances (Å) and Angles (deg) in $Mo(EtC{\equiv}CEt)(TIPT)_4$

Mo–S(1)	2.341 (2)	S(1)–Mo–C(53)	100.0 (2)
Mo–S(2)	2.431 (2)	S(2)–Mo–C(53)	160.4 (2)
Mo–S(3)	2.355 (2)	S(3)–Mo–C(53)	74.9 (2)
Mo–S(4)	2.332 (2)	S(4)–Mo–C(53)	110.5 (2)
Mo–C(53)	2.080 (8)	S(1)–Mo–C(54)	92.2 (2)
Mo–C(54)	2.072 (8)	S(2)–Mo–C(54)	163.4 (2)
C(53)–C(54)	1.284 (11)	S(3)–Mo–C(54)	110.1 (2)
S(2)–C(21)	1.786 (7)	S(4)–Mo–C(54)	86.2 (2)
S(1)–C(11)	1.797 (8)	C(53)–Mo–C(54)	36.0 (3)
S(1)–Mo–S(2)	85.5 (1)	C(53)–C(54)–Mo	72.3 (5)
S(1)–Mo–S(3)	114.4 (1)	C(54)–C(53)–Mo	71.7 (5)
S(2)–Mo–S(3)	85.6 (1)	C(52)–C(53)–C(54)	145.8 (9)
S(1)–Mo–S(4)	122.5 (1)	Mo–S(1)–C(11)	112.8 (3)
S(2)–Mo–S(4)	81.3 (1)	Mo–S(2)–C(21)	117.4 (3)
S(3)–Mo–S(4)	119.9 (1)	Mo–S(3)–C(31)	116.4 (3)
		Mo–S(4)–C(41)	119.4 (3)

X-ray Structure of $Mo(C_2Et_2)(S$-2,4,6-C_6H_2-*i*-$Pr_3)_4$. A drawing of the $Mo(C_2Et_2)(TIPT)_4$ molecule is shown in Figure 2. A complete description of the structure solution can be found in the Experimental Section. Selected bond lengths and angles can be found in Table III.

$Mo(C_2Et_2)(TIPT)_4$ is a distorted trigonal bipyramid containing three equatorial thiolate ligands, one axial thiolate ligand, and the C_2Et_2 ligand in an axial position such that the C≡C bond is roughly parallel to the Mo–S(3) bond. Two of the equatorial thiolate ligands' phenyl rings are turned up around one end of the hexyne ligand while the phenyl ring of the third equatorial thiolate ligand is pointed in the opposite direction, away from the other end of the hexyne ligand. The phenyl ring of the axial thiolate ligand is pointed away from the phenyl ring of the unique equatorial thiolate ring. Although the Mo–S–C angles do not

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(6) (a) Durfee, L. D.; Latesky, S. L.; Rothwell, I. P.; Huffman, J. C.; Folting, K. *Inorg. Chem.* **1985**, *24*, 4569 and references therein. (b) Chisholm, M. H. *Polyhedron* **1983**, *2*, 681 and references therein.

vary significantly (113–119°), the axial Mo–S (Mo–S(2)) bond length is nearly 0.1 Å *longer* than the equatorial Mo–S bond lengths (cf. the shorter $Mo–O_{ax}$ vs. $Mo–O_{eq}$ bond lengths in $Mo(C_2Ph_2)(DIPP)_4$). It is worth noting that the shorter Mo–O (or S) bonds are found when the alkoxide or thiolate ligands are bound in positions orthogonal to that where acetylene is bound.

Structural features of the 3-hexyne ligand in $Mo(C_2Et_2)(TIPT)_4$ are again unremarkable, quite similar to the structural features of the diphenylacetylene ligand in $Mo(C_2Ph_2)(DIPP)_4$. The only potentially significant difference between the acetylene in $Mo(C_2Et_2)(TIPT)_4$ and that in $Mo(C_2Ph_2)(DIPP)_4$ is that the Mo–C bond lengths border on being shorter in $Mo(C_2Ph_2)(DIPP)_4$ (2.031 (16) Å), but the standard deviation is too great to state this with any degree of certainty.

These structural results suggest that in a low-temperature limiting NMR spectrum the acetylene is "locked" in the position found in $Mo(C_2Et_2)(TIPT)_4$. Therefore the four TIPT ligands also are likely to be locked in their observed positions on the NMR time scale at low temperature. At a temperature where the acetylene is beginning to rotate at a rate on the order of the NMR time scale, the rate of rotation about the C–S bonds and the Mo–S bonds probably increases, perhaps in a manner concerted with alkyne ligand rotation. Yet even at 330 K the ^1H NMR spectra of $Mo(C_2R_2)(TIPT)_4$ complexes are not markedly simplified, a fact that suggests that perhaps rotation of the alkyne ligand is *not* contingent upon interconversion of different equatorial thiolate ligands; i.e., the relative orientations of the thiolate ligands remains much the same.

Alkyne Exchange Reactions. One of our original reasons for preparing $Mo(C_2R_2)(DIPP)_4$ complexes was to explore alkyne ligand lability and in particular the possibility that the C_2R_2 ligand (especially C_2Ph_2) might be lost to give as yet unknown $Mo(DIPP)_4$. ($W(DIPP)_4$ is known,[7] and we have been unable so far to prepare analogous molybdenum species.) Since we suspected that an equilibrium between $Mo(C_2R_2)(DIPP)_4$ and $Mo(DIPP)_4$ might lie too far to the left to allow $Mo(DIPP)_4$ to be isolated, we chose to test for alkyne exchange. We found that $Mo(C_2Me_2)(DIPP)_4$ is *not* formed when 2-butyne is added to $Mo(C_2Et_2)(DIPP)_4$ in pentane at 25 °C. Likewise, no $Mo(C_2Et_2)(DIPP)_4$ is formed when $Mo(C_2Ph_2)(DIPP)_4$ is heated to 80 °C in the presence of an excess of 3-hexyne in C_6D_6. Since the $Mo(C_2R_2)(DIPP)_4$ complexes in the above experiments also do not decompose to any noticeable extent (by ^1H NMR employing an internal standard), we conclude that the alkynes are not lost from the $Mo(C_2R_2)(DIPP)_4$ complexes under these relatively mild conditions.

In contrast, it is relatively easy to exchange the alkyne ligand in $Mo(C_2R_2)(TIPT)_4$ complexes. For example, when $Mo(C_2Et_2)(TIPT)_4$ is recrystallized in the presence of 2-butyne, $Mo(C_2Me_2)(TIPT)_4$ is isolated, while the reverse experiment yields $Mo(C_2Et_2)(TIPT)_4$ from $Mo(C_2Me_2)(TIPT)_4$. Both 2-butyne and 3-hexyne will replace ethyne in $Mo(C_2H_2)(TIPT)_4$, the liberated ethyne being polymerized to a black polymer, which we presume to be polyacetylene. 2-Butyne or 3-hexyne cannot be displaced by ethyne, however, probably in part because ethyne is polymerized so rapidly at a temperature where exchange is rapid enough to be observed. No significant amount of metal complex is consumed during the acetylene polymerization process. The mechanism of polymerization is not known.

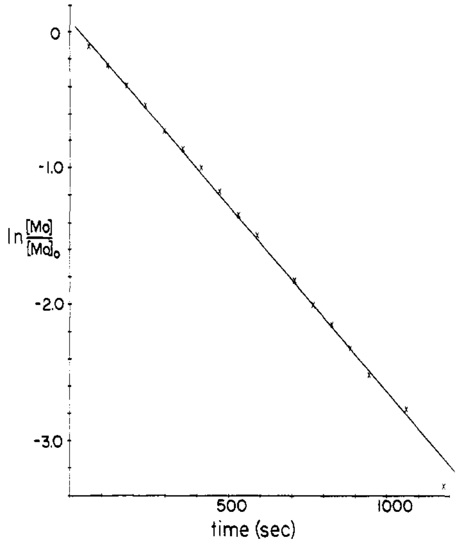

Figure 3. First-order plot for the disappearance of $Mo(C_2H_2)(TIPT)_4$ in toluene-d_8 in the presence of 2 equiv of added EtC≡CEt at 268 K (run 1 in Table IV).

Table IV. Rates of Reaction of $Mo(C_2H_2)(TIPT)_4$ with 3-Hexyne To Give $Mo(C_2Et_2)(TIPT)_4$[a]

[Mo], M	equiv of 3-hexyne	10^3 *k*, s^{-1}	*T*, K
0.046	2	2.77 (4)	268
0.046	10	3.44 (16)	268
0.046	20	3.02 (7)	268
0.046	10	3.99 (6)	270
0.023	10	4.00 (25)	270
0.0046	10	3.94 (16)	270
0.046	10	7.11 (8) × 10^{-2}	243
0.046	10	0.765 (13)	258

[a] An Eyring plot of the appropriate data yielded $\Delta H^\ddagger$ = 17.63 kcal/mol, $\Delta S^\ddagger$ = −6.33 eu, and $\Delta G^\ddagger$ = 19.32 kcal/mol; overly precise figures are given in order to facilitate calculation of *k* at any *T*.

An important question is whether alkyne exchange is uni- or bimolecular. We thought it would be more likely to be unimolecular, given the crowded coordination environment found in $Mo(C_2Et_2)(TIPT)_4$. The disappearance of the acetylenic proton signal in $Mo(C_2H_2)(TIPT)_4$ was followed in the presence of excess 3-hexyne under a variety of conditons. The liberated acetylene was polymerized, but again little metal was consumed as a result of that process. The rate of disappearance of $Mo(C_2H_2)(TIPT)_4$ was found to be first order (Figure 3) and *k* invariant over a 10-fold range of concentrations (Table IV). Therefore, it must be true that $Mo(C_2H_2)(TIPT)_4$ loses ethyne on the chemical time scale to give intermediate $Mo(TIPT)_4$. Note again that this exchange is not fast enough to observe on the NMR time scale, as unshifted TIPT signals can be seen for both $Mo(C_2H_2)(TIPT)_4$ and $Mo(TIPT)_4$ in C_6D_6 at 25 °C. We assume that $Mo(C_2R_2)(TIPT)_4$ complexes lose 2-butyne or 3-hexyne in a first-order manner also.

The sign for $\Delta S^\ddagger$ is somewhat surprising given the fact that ethyne is lost from Mo(ethyne)$(TIPT)_4$ in the rate-limiting step, but the magnitude is not large. We can propose that the coordination environment becomes more highly ordered (probably more crowded) in the transition state and that ethyne probably is still bound to the metal, although perhaps a good deal more weakly, in the transition state.

Acetylenes can be replaced in $Mo(C_2R_2)(TIPT)_4$ complexes by other donor ligands. For example, when $Mo(C_2H_2)(TIPT)_4$ is recrystallized from ether in the presence of acetonitrile, paramagnetic $Mo(CH_3CN)(TIPT)_4$[4] is produced. We do not know whether this and related reactions are zero order in the new ligand. It is quite possible that more basic, end-on-bonded ligands will displace an acetylene via six-coordinate $Mo(C_2R_2)(TIPT)_4(L)$.

It is interesting to note that although it was not possible to exchange alkyne ligands in phenoxide complexes, it is possible to displace the acetylene with other, relatively weak ligands. For example, $Mo(C_2Et_2)(DIPP)_4$ will react slowly with 10–15 equiv of propionitrile in ether. After 5 days approximately 50% of the 3-hexyne can be vacuum transferred and quantitated by GLC. Although we have not been able to characterize the resulting product (or products), this result suggests that an alkyne can be displaced in phenoxide complexes by donor ligands. Acetylenes themselves are not sufficiently good donor ligands to replace a bound acetylene nor are they likely to enter the coordination sphere as easily as a nitrile.

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Table V. Results of Cyclic Voltammetry Studies[a]

compd	"$E_{1/2}$"(redn),[b] V	$E_{p,a(1)}$, V	$E_{p,a(2)}$, V
$Mo(C_2Et_2)(DIPP)_2Cl_2$	–0.50 (105)	...	...
$Mo(C_2Et_2)(DIPP)_3Cl$	–0.855 (150)	+1.10	...
$Mo(C_2Et_2)(DIPP)_4$	–1.02 (110)	+0.73	+0.92
$Mo(C_2Me_2)(TIPT)_4$	–1.20		
$Mo(C_2Et_2)(TIPT)_4$	–1.20		

[a] In dichloromethane containing 0.1M $NBu_4^+PF_6^-$ vs. Ag/Ag^+ in acetonitrile. Sweep rates ~ 100 mV s^{-1}. $Mo(C_2H_2)(TIPT)_4$ is too unstable in dichloromethane to be included in a study of this type. [b] Anodic and cathodic peak separations are shown in parentheses. The quotation marks are present since the reduction is only apparently reversible chemically (see text).

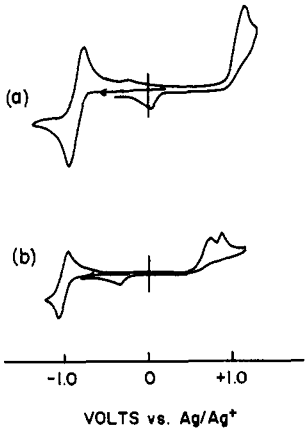

Figure 4. Cyclic voltammograms of $Mo(C_2Et_2)(DIPP)_3Cl$ (a) and $Mo(C_2Et_2)(DIPP)_4$ (b) in CH_2Cl_2 (0.1 M $NBu_4^+BF_4^-$) vs. Ag/Ag^+ in CH_3CN.

Electrochemical Studies. Both DIPP and TIPT acetylene complexes can be reduced in dichloromethane in an *apparently* chemically reversible manner (Table V, Figure 4). A plot of the peak cathodic current vs. the square root of the scan rate was linear in each case. The cathodic/anodic peak separations were in the range 100–150 mV for sweep rates of ~100 mV s^{-1}, but the ratio of $i_{p,a}/i_{p,c}$ was not strictly 1 in each case. "$E_{1/2}$" (redn) for the DIPP complexes varies in the manner one would expect if one assumes that the metal is progressively more electron poor in complexes containing chloride ligands and thereby more easily reduced.

We examined the reduction of several $Mo(C_2R_2)X_4$ complexes (X = DIPP or TIPT) in more detail. The reduction of $Mo(C_2Et_2)(DIPP)_4$ at –1.2 V under dinitrogen was shown to consume 0.50 (5) electron, both by bulk electrolysis and by comparison with ferrocenium reduction. The resulting solution was nearly colorless and did not contain any species that are electrochemically active in the range –1.5 to +2.0 V. Exactly the same results were obtained in experiments employing $Mo(C_2Et_2)(TIPT)_4$. Therefore we conclude that the initial 1e reduction product is not stable under the reaction conditions and furthermore that it, or some product of its decomposition, reacts stoichiometrically with the starting acetylene complex.

One or more anodic waves can be observed. However, it is clear that these oxidations are irreversible (Figure 4); no reduction of the initial oxidation product can be observed in the cathodic sweep by using normal sweep rates. New peaks can be observed in the return cathodic sweep that were not present in the initial cathodic sweep, as expected if the initial oxidation product decomposes rapidly to one or more electrochemically active species.

It is interesting to find that the TIPT complexes are more difficult to reduce than the analogous DIPP complexes. That would be expected if one were to assume that the TIPT ligand places more electron density on the metal atom than the DIPP ligand (through the σ and *perhaps* also π systems), making addition of an electron more difficult. But even if the Mo(alkyne)$(DIPP)_4$ and Mo(alkyne)$(TIPT)_4$ complexes were isostructural, there is no reason to expect that the reductions necessarily would be analogous, since the LUMO in Mo(alkyne)$(DIPP)_4$ need not be the same as that in Mo(alkyne)$(TIPT)_4$. Therefore, we can conclude only in the loosest sense that the DIPP complexes are more reduceable than the TIPT complexes.

Table VI. Comparison of Mo–C and C–C Bond Lengths in Mo(IV)–Alkyne Complexes

compd	dist, Å		ref
	C–C	Mo–C	
$Mo(EtC{\equiv}CEt)(TIPT)_4$	1.284 (11)	2.080 (8) 2.072 (8)	*a*
$Mo(PhC{\equiv}CPh)(DIPP)_4$	1.271 (28)	2.031 (16)	*a*
$Mo(\eta^5\text{-}C_5H_5)(O)(CF_3C{\equiv}CCF_3)(SC_6F_5)$	1.298 (6)	2.017 (5) 2.051 (5)	8d
$Mo(Ntol)(MeO_2CC{\equiv}CCO_2Me)(S_2CNEt_2)_2$	1.264 (6)	2.107 (4) 2.134 (4)	8c
$Mo(O)(tolC(O)C{\equiv}CC(O)tol)(S_2CNMe_2)_2$	1.267 (6)	2.122 (4) 2.119 (4)	8b

[a] This work.

Discussion

The list of Mo(IV)–acetylene complexes is a short one. Besides the compounds reported here, the only others that we know of are the tetrahalide complexes mentioned earlier[3a,b] (these probably are not monomers[3b]), compounds of the type Mo(alkyne)$(O)(S_2CNR_2)_2$,[8a,b] $Mo(Ntol)(MeO_2CC{\equiv}CCO_2Me)(S_2CNEt_2)_2$,[8c] and $Mo(\eta\text{-}C_5H_5)(O)(CF_3C{\equiv}CCF_3)(SC_6F_5)$.[8d] The only Mo(IV) complex of acetylene itself other than $Mo(C_2H_2)(TIPT)_4$ is $Mo(O)(C_2H_2)(S_2CNEt_2)_2$;[8b] it could not be isolated in pure form, however, because the equilibrium constant for its formation is only ~20 M^{-1}. A comparison of Mo–C and C–C bond lengths in Mo(IV)–alkyne complexes (Table VI) shows that although C–C bond lengths cannot be said to differ to any significant extent, the Mo–C bond lengths in the dithiocarbamate complexes are significantly longer than the others, as one would expect in six-coordinate complexes in which the alkyne appears to be relatively labile.

The arrangement of the four TIPT ligands in $Mo(C_2Et_2)(TIPT)_4$ also has been observed in $Ru(S\text{-}2,3,5,6\text{-}C_6Me_4H)_4(CH_3CN)$[9a] and $Re(S\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)_4(NO)$.[9b] In each case the metal–S_{ax} bond length is 0.15–0.20 Å longer than the metal–S_{eq} bond lengths. The "two up, one down" arrangement of equatorial bulky thiolate ligands also has been observed in $Mo(TIPT)_3(NH_3)(NO)$[9c] and $[Mo(TIPT)_3(CO)_2]^-$.[9d] The "two up, one down" arrangement of equatorial ligands is probably the best compromise of steric interactions among those equatorial ligands. In $[WCl(SC_6H_5)_4(NO)]^-$, for example, *all three* equatorial ligands are bent up around the NO ligand.[9c] The fact that an axial bulky thiolate ligand is turned away from the unique equatorial ligand that is bent toward it also makes sense. To our knowledge there are no examples of structurally characterized complexes of the type $M(SR)_4(L)$ or $M(SR)_3(L)(L')$ in which three SR ligands do not occupy the equatorial positions.

Interestingly, the only other example of an $Mo(OR)_4(L)$ complex other than that reported here that has been structurally characterized has a geometry that overall is quite similar to that of $Mo(PhC{\equiv}CPh)(TIPT)_4$. $Mo(1\text{-adamantoxy})_4(Me_2NH)$[2b] is roughly a trigonal bipyramid with two of the equatorial adamantoxy ligands pointed up around the dimethylamine ligand

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[Mo–O–C = 141.7 (2) and 136.8 (2)°], the third equatorial adamantoxy ligand pointed away from the dimethylamine ligand [Mo–O–C = 137.8 (2)°], and the axial adamantoxy ligand bent away from the equatorial ligand that is bent toward it [Mo–O–C = 140.3 (2)°]. The Mo–O bond lengths do not differ significanty [$Mo-O_{ax}$ = 1.963 (2) Å; $Mo-O_{eq}$ = 1.897 (2), 1.916 (2), and 1.888 (3) Å]. Why the structure of $Mo(1\text{-adamantoxy})_4(Me_2NH)$ is not analogous to that of $Mo(PhC\equiv CPh)(DIPP)_4$ is not clear, unless we turn to the obvious fact that $PhC\equiv CPh$ is a better π-bonding ligand than Me_2NH and therefore propose that π-bonding ligands in $Mo(OR)_4L$ complexes bind more strongly in equatorial positions. Although there is little data to back up this proposal, it is worth pointing out that the structure of $W(CHCMe_3)(OCH_2CMe_3)_4$, although it was not specifically so stated,[10] probably is similar to that of other members of this general class of alkylidene complexes,[10,11] a trigonal bipyramid with the neopentylidene ligand lying in the equatorial plane. But the structure of $Mo(EtC\equiv CEt)(TIPT)_4$ reveals that equatorial binding of an acetylene in $M(alkyne)X_4$ complexes is not a general phenomenon. We can only say at this stage that $Mo(EtC\equiv CEt)(TIPT)_4$ contains the 3-hexyne ligand bound in an axial position because the structure is no longer determined by the position at which the acetylene binds but by an as yet ill-defined and ultimately overriding set of electronic and/or steric requirements dictated by thiolate ligand binding. As mentioned above, thiolate ligands, at least in five-coordinate TBP molecules whose structures are known at this time, occupy equatorial positions.

The single most obvious and oft-quoted difference between and alkoxide ligand and an analogous thiolate ligand, as far as how each affects the reactivity at the metal center in analogous complexes, is that a thiolate ligand is more electron donating. We believe that property alone may be the reason why the acetylene is lost from $Mo(acet)(TIPT)_4$ complexes, but not from $Mo(acet)(DIPP)_4$ complexes. This point of view is somewhat peculiar since one could equally well argue that the acetylene is more strongly held by π-back-bonding from the more "electron-rich" metal in the TIPT complexes. But in the chemistry of complexes in which Mo or W is in a high oxidation state, viewing the metal as an acid has been more useful. For example, we recently prepared alkylidyne complexes of the type $W(CR)(TIPT)_3$.[12] Although analogous $W(CR)(DIPP)_3$ complexes react immediately with acetylenes to give isolable cyclotungstabutadiene complexes that break up again slowly (acetylene metathesis),[13] the TIPT complexes do not react with acetylenes. Although we cannot eliminate the role of steric factors entirely (see below), the evidence points toward the conclusion that the $W(CR)(TIPT)_3$ complexes simply are poorer acids toward an acetylene, making the reasonable assumption that the acetylene must interact to some extent with the metal before the WC_3 ring forms.

A second possible reason why an acetylene is more labile in TIPT complexes is that the TIPT ligand creates a slightly more crowded coordination sphere. Although metal–sulfur bonds are significantly longer than metal–oxygen bonds, the M–S–C angles are invariably considerably sharper than M–O–C angles in analogous complexes (here 110–120 vs. 140–160°). A greater steric pressure toward loss of an acetylene would reinforce the trend toward more facile loss of the acetylene for electronic reasons. Subtle steric differences between TIPT and DIPP ligands may be even more difficult to quantitate than electronic differences.

We were somewhat surprised by the results of the electrochemical studies in that there did not appear to be any gross differences between tetrakis complexes of TIPT and DIPP. Both reduced in an apparently chemically reversible fashion at about the same potential, but one which upon closer examination turned out to be a chemically irreversible reduction consuming 0.5 electron. Both were oxidized in what are more obviously irreversible reactions.

We have come to the conclusion in this study that the structural and reactivity differences between simple TIPT- and DIPP-Mo(alkyne) complexes, as far as we have explored them, are not enormous. However, what differences there are could prove to be of crucial importance in finely balanced analogous systems. So far we can probably generalize and state that donor ligands are going to be more labile in thiolate complexes than in analogous alkoxide complexes, although it is not yet clear whether steric or electronic factors predominant, if either. We will be looking for other ways of probing the reactions of simple analogous thiolate and alkoxide complexes in order to magnify and clarify subtle differences between them.

Experimental Section

All operations were performed under a nitrogen atmosphere in a Vacuum Atmospheres drybox. $MoCl_4$ was prepared by the literature method.[14] Hex-3-yne and but-2-yne were degassed and passed through alumina prior to use. Stabilizer was removed from ethyne. Electrochemical measurements were made with a Princeton Applied Research Model 173 potentiostat/galvanostat and Model 175 universal programmer, in conjunction with a Houston Instruments RE-0089 X-Y recorder. Voltammetry experiments were performed in the drybox on dichloromethane solutions containing 0.1 M $n\text{-}Bu_4NBF_4$ as supporting electrolyte. $E_{1/2}$ values are referenced to Ag/Ag^+ and are uncorrected for junction potentials.

Preparations. $Mo(C_2R_2)Cl_4(ether)$. $MoCl_4$ (2.0 g, 8.4 mmol) was slowly added to ~30 mL of diethyl ether to give orange crystals of what we believe to be $MoCl_4(ether)_2$; ~3 equiv of alkyne was then added, and the mixture was stirred 12–16 h. The yellow-orange (R = Et) or red (R = Ph) product was then filtered off and dried in vacuo; the yields are ~80%.

$Mo(C_2Et_2)(DIPP)_2Cl_2$. $Mo(C_2Et_2)Cl_4(ether)$ (0.50 g, 1.27 mmol) was added to a solution of LiDIPP(ether) (0.70 g, 2.70 mmol) in diethyl ether at −40 °C. The solution turned dark purple and was allowed to warm to room temperature. The ether was removed in vacuo, and the residue was extracted with ~125 mL of pentane. The pentane solution was kept at −40 °C overnight to yield 0.53 g of purple crystals of $Mo(C_2Et_2)(DIPP)_2Cl_2$ in two crops (69% yield): ^1H NMR (CD_2Cl_2) δ 7.08 (s, 3 H), 3.83 (q, J = 7.3 Hz, 4 H), 2.95 (br, 4 H), 1.56 (t, J = 7.4 Hz, 6 H), 1.21 (d, J = 6.8 Hz, 24 H); ^{13}C NMR (CD_2Cl_2, 240 K) δ 178.8 (C_{acet}), 162.5 (C_{ipso}), 139.7, 126.5, 123.5, 28.1, 26.0, 23.5, 22.3, 14.5. Anal. Calcd for $MoC_{30}H_{44}O_2Cl_2$: C, 59.69; H, 7.36. Found: C, 60.25; H, 7.42.

$Mo(C_2Et_2)(DIPP)_3Cl$. A solution of $LiDIPP\cdot Et_2O$ (15.3 mmol) was prepared in 40 mL of ether and cooled to −40 °C. $Mo(C_2Et_2)Cl_4(ether)$ (2.0 g, 5.1 mmol) was then added and the mixture warmed to room temperature and stirred for 1.5 h during which time an intense red-orange color developed. The solution was filtered through Celite and the solvent removed in vacuo. The resulting solid was extracted with pentane, and the solution was filtered. The dark red filtrate was cooled at −40 °C to give dark red, almost black crystals, a total of 2.08 g in two crops (yield 55%): ^1H NMR (C_6D_6) δ 7.2–6.9 (m, 9 H, aryl H), 4.12 (sept, 2 H, $CHMe_2$), 3.69 (q, 2 H, CH_2CH_3), 3.38 (sept, 2 H, $CHMe_2$), 2.80 (q, 2 H, CH_2CH_3), 2.40 (sept, 2 H, $CHMe_2$), 1.62 (d, 6 H, $CHMe_2$), 1.44 (d, 6 H, $CHMe_2$), 1.18 (t, 3 H, CH_2CH_3), 1.06 (d, 6 H, $CHMe_2$), 1.00 (d, 12 H, $CHMe_2$), 0.97 (d, 6 H, $CHMe_2$), 0.93 (t, 3 H, CH_2CH_3); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 195.4 (C_{acet}), 182.2 (C_{acet}), 162.5 (C_{ipso}), 161.4 (C_{ipso}), 139.9, 139.7, 139.2, 125.3, 124.2, 124.0, 123.5, 123.2, 29.1, 28.1, 27.0, 26.6, 25.0, 24.9, 24.5, 24.3, 23.6, 22.4, 15.0, 14.3. Anal. Calcd for $MoC_{42}H_{61}O_3Cl$: C, 67.68; H, 8.25. Found: C, 67.44; H, 8.02.

$Mo(C_2Et_2)(DIPP)_4$. K(DIPP) (0.48 g, 2.2 mmol) was added to a solution of $Mo(C_2Et_2)(DIPP)_3Cl$ (1.50 g, 2.0 mmol) in 50 mL of diethyl ether. After 15 h the reaction mixture was filtered, and the volume was reduced in vacuo to a few milliliters. Several milliliters of acetonitrile were added, and the solution was held at −40 °C overnight. Dark red crystals of $Mo(C_2Et_2)(DIPP)_4$ were collected the next day (0.95 g, 51% yield). $Mo(C_2Et_2)(DIPP)_4$ appears to decompose slowly in the presence of acetonitrile so only the first crop of product is pure: ^1H NMR (C_6D_6) δ 7.13–6.85 (m, 12 H, aryl H), 4.26 (sept, 2 H, $CHMe_2$), 3.17 (sept, 4 H, $CHMe_2$), 2.99 (q, 4 H, CH_2CH_3), 2.48 (sept, 2 H, $CHMe_2$), 1.54 (d, 12 H, $CHMe_2$), 0.99 (d, 12 H, $CHMe_2$), 0.98 (t, 6 H, CH_2CH_3), 0.88 (d, 24 H, $CHMe_2$); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 197.7 (C_{acet}), 163.4 (C_{ipso}), 162.3 (C_{ipso}), 138.5, 138.1, 137.6, 124.6, 124.0, 123.7, 123.4, 121.2, 29.5,

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27.2, 26.6, 25.8, 24.6, 24.2, 24.0, 14.8.

$Mo(C_2Ph_2)(DIPP)_4$. This complex was prepared in 24% yield in a manner analogous to that used to prepare $Mo(C_2Et_2)(DIPP)_4$: ^1H NMR (C_6D_6) δ 7.5 (m, 4 H, aryl H), 8.8–7.1 (m, 16 H, aryl H), 4.4 (sept, 2 H, $CHMe_2$), 3.2 (m, 6 H, $CHMe_2$), 1.52 (d, 12 H, $CHMe_2$), 0.93 (d, 12 H, $CHMe_2$), 0.86 (d, 12 H, $CHMe_2$), 0.51 (d, 12 H, $CHMe_2$); ^{13}C NMR (C_6D_6) δ 191.6 (C_{acet}), 163.2 (C_{ipso}), 162.9 (C_{ipso}), 138.3, 137.9, 137.1, 131.8, 124.9, 124.4, 124.0, 122.1, 100.4, 93.1, 95.4, 29.8, 26.7, 26.3, 23.6, 22.7. Anal. Calcd for $MoC_{62}H_{78}O_4$: C, 75.74; H, 8.00. Found: C, 75.66; H, 8.23.

$Mo(C_2Et_2)(DMP)_4$. $Mo(C_2Et_2)Cl_4$(ether) (0.50 g, 1.27 mmol) was added to a cold (−40 °C) ether solution of LiDMP (0.65 g, 5.07 mmol). The solution turned purple and then red. The reaction mixture was warmed to room temperature, stirred for 1.5 h, and filtered. The ether was removed from the filtrate in vacuo, the dark red residue was extracted with minimal pentane, and the mixture was filtered. After 16 h at −40 °C, the filtrate had deposited dark red crystals (0.25 g in three crops, 30% yield): ^1H NMR (C_6D_6) δ 6.91 (d, 8 H, H_{meta}), 6.75 (t, 4 H_{para}), 2.82 (q, 4 H, CH_2CH_3), 2.08 (s, 24 H, $C_6H_3Me_2$), 0.86 (t, 6 H, CH_2CH_3); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 197.9 (C_{acet}), 165.2 (C_{ipso}), 128.7 (C_{meta}), 127.1 (C_{ortho}), 121.7 (C_{para}), 24.3 (t, CH_2CH_3), 17.9 (q, $C_6H_3Me_2$), 14.1 (q, CH_2CH_3). Anal. Calcd for $MoC_{38}H_{46}O_4$: C, 68.87; H, 7.00. Found: C, 68.94; H, 6.95.

$Mo(alkyne)(TIPT)_4$. Method A. The alkyne (~20% excess) was added to a pentane solution of $Mo(TIPT)_4$ (0.50 g, 0.5 mmol) that had been cooled to −30 °C. The solution turned from a dark brown color to red almost immediately. The solution was allowed to warm to room temperature. After 0.5 h the reaction mixture was filtered through Celite, and the solvent was removed from the filtrate in vacuo. The residue was recrystallized from a minimum amount of pentane at −40 °C. The procedure when the alkyne is ethyne is given below.

Method B. LiTIPT (2.0 mmol) was added as a solid in small portions to a partially dissolved sample of $Mo(alkyne)Cl_4$(ether) (0.5 mmol) in ether at −30 °C. The reaction mixture was warmed to room temperature and stirred. The mixture was filtered, and the solvent was removed from the filtrate in vacuo. The dark residue was recrystallized from a minimum amount of pentane at −40 °C.

$Mo(C_2Et_2)(TIPT)_4$. Yield was ~50% by either method A or B: ^1H NMR (C_6D_6) δ 7.35 (s, 2 H, aryl H), 7.21 (s, 2 H, aryl H), 6.92 (s, 4 H, aryl H), 3.9 (m, 4 H, $CHMe_2$), 3.54 (m, 2 H, $CHMe_2$), 2.91 (m, 4 H, $CHMe_2$), 2.71 (m, 2 H, $CHMe_2$), 1.67 (d, 6 H, $CHMe_2$), 1.52 (d, 6 H, $CHMe_2$), 1.1–1.5 (complex, ~70 protons); $^{13}C\{^1H\}$ NMR (toluene-d_8, 243 K) δ 217.4 (C_{acet}), 202.8 (C_{acet}), 150.6, 149.5, 149.4, 149.3, 148.7, 148.1, 147.9, 144.2, 143.4, 139.4, 137.5, 121.4, 121.0, 119.6, 35.2, 35.1, 34.9, 34.8, 32.7, 32.5, 32.4, 32.1, 31.9, 29.8, 27.6, 26.5, 25.9, 25.7, 25.0, 24.9, 24.7, 24.4, 23.0, 22.9, 22.6, 22.1, 15.4, 14.5, 13.7; IR (Nujol) 1751 cm^{-1} (ν_{CC}). Anal. Calcd for $MoC_{66}H_{102}S_4$: C, 70.8; H, 9.18; S, 11.45. Found: C, 69.99; H, 9.40; S, 11.02.

$Mo(C_2Me_2)(TIPT)_4$. Yield was ~50% by either method: ^1H NMR (C_6D_6) δ 7.36 (s, 2 H, aryl H), 7.22 (s, 2 H, aryl H), 6.91 (s, 4 H, aryl H), 3.92 (m, 4 H, $CHMe_2$), 3.54 (m, 2 H, $CHMe_2$), 2.65–2.00 (m, 6 H, $CHMe_2$), 1.67 (d, 6 H, $CHMe_2$), 1.51 (d, 6 H, $CHMe_2$), 1.32–0.96 (complex, ~70 protons); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 230 K) δ 219.2 (C_{acet}), 202.6 (C_{acet}), 150.1, 149.2, 148.8, 148.2, 147.3, 147.2, 143.1, 143.0, 138.7, 121.3, 120.8, 120.4, 119.0, 65.9, 34.6, 34.3, 32.1, 31.7, 31.3, 25.7, 25.2, 25.0, 24.1, 24.0, 23.9, 23.0, 22.0, 21.9, 21.5, 19.3, 17.7, 15.3; IR (Nujol) 1742 cm^{-1} (ν_{CC}). Anal. Calcd for $MoC_{64}H_{98}S_4$: C, 70.41; H, 9.05; S, 11.75. Found: C, 71.09; H, 9.56; S, 10.80.

$Mo(C_2H_2)(TIPT)_4$. A septum-stoppered 100-mL Schlenk flask containing a solution of $Mo(TIPT)_4$ (0.50 g, 0.5 mmol) in 25 mL of pentane was cooled to −78 °C and ethyne passed over the cold solution. The color changed from brown to deep red immediately. After 3 min, the excess ethyne and all solvent were removed in vacuo. The residue was dissolved in a minimal amount of pentane, and the mixture was filtered. The volume of the filtrate was reduced to a few milliliters, and the solution was cooled to −40 °C to give red crystals after a few hours (40% yield): ^1H NMR (C_6D_6) δ 9.5 (s, 2 H, C_2H_2), 7.0–7.3 (m, 8 H, aryl H), 4.1 (m, 2 H, $CHMe_2$), 3.5 (m, 4 H, $CHMe_2$), 3.2 (m, 2 H, $CHMe_2$), 2.8 (m, 4 H, $CHMe_2$), 1.0–1.6 (complex, ~72 protons); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 230 K) δ 153.4, 153.0, 149.5, 149.0, 148.7, 146.9, 144.0, 142.2, 140.7, 126.4, 125.4, 122.5, 122.3, 121.9, 121.6, 121.1, 120.6, 34.7, 34.5, 34.4, 33.1, 32.4, 31.8, 25.6, 25.2, 24.8, 24.2, 24.1, 23.6, 22.2, 21.6; IR (Nujol) 1758 cm^{-1} (ν_{CC}). Anal. Calcd for $MoC_{64}H_{94}S_4$: C, 70.00; H, 8.93. Found: C, 69.90; H, 8.99.

Kinetic Studies. A 0.046 M stock solution of $Mo(ethyne)(TIPT)_4$ and mesitylene in toluene-d_8 was prepared. NMR tubes were charged with appropriate aliquots of the stock solution and diluted with additional toluene-d_8 to provide a 0.5 mL solution. The solutions were frozen and appropriate aliquots of hex-3-yne added. The samples were thawed just prior to use and placed in the probe of the Bruker 250 instrument maintained at the desired temperature. The disappearance of the resonance for the ethyne protons at 9.5 ppm was monitored relative to the resonance for the ring protons of mesitylene. The individual results are listed in Table IV; the first run (through greater than 4 half-lives) is plotted in Figure 3.

Electrochemical Studies. Stock dichloromethane solutions of 0.013 M ferrocene, 0.013 M molybdenum complex, and 0.1 M NBu_4BF_4 were prepared. 0.3 mL of the ferrocene solution was added to 5 mL of the electrolyte solution and a cyclic voltammogram obtained over a 0.3-V potential range at a scan rate of 100 mV/s. A second sample was prepared in exactly the same manner as for the ferrocene sample. A cyclic voltammogram was obtained over a 0.3-V potential range at a scan rate of 100 mV/s. The amount of current was obtained by cutting out each cyclic voltammogram and weighing the peak.

X-ray Structure of $Mo(C_2Ph_2)(DIPP)_4$. $Mo(C_2Ph_2)(DIPP)_4$ crystallizes in the space group $P2_12_12$ with $a = 12.464\ (3)$ Å, $b = 19.230\ (4)$ Å, $c = 12.268\ (2)$ Å, $V = 2940.4$ Å^3, $Z = 2$, mol wt = 983.2, ρ(calcd) = 1.110 g cm^{-3}, and $\mu = 2.3\ cm^{-1}$ (no absorption correction applied). Data were collected on an Enraf-Nonius CAD4F-11 κ-geometry diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Data collection, reduction, and refinement procedures have been described elsewhere.[15] A total of 2911 reflections $(+h,+k,+l)$ were collected in the range $3° \leqslant 2\theta \leqslant 50°$ with 1801 having $I_o > 2\sigma(I_o)$ being used in the structure refinement, which was by full-matrix least-squares techniques (306 variables) using SHELX-76. Final $R_1 = 0.076$ and $R_2 = 0.096$. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions (C–H = 0.95 Å) and constrained to ride on their respective carbon atoms. A final difference-fourier map showed no significant features. The position of the Mo atom was obtained from a Patterson map. Some difficulty was encountered in assigning the lighter ligand atoms since the heavy atom lies on a two-fold axis. This problem was overcome by using the program DIRDIF.[16] Refinement of the other hand of the molecule produced slightly higher R values.

A drawing of the molecule can be found in Figure 1, and selected bond lengths and angles can be found in Table II. Final coordinates, thermal parameters, structure factors, and a drawing of the structure in which all atoms are numbered can be found in the supplementary material.

X-ray Structure of $Mo(C_2Et_2)(TIPT)_4$. $Mo(C_2Et_2)(TIPT)_4$ crystallizes in the space group $P2_1/n$ with $a = 13.889\ (4)$ Å, $b = 22.475\ (5)$ Å, $c = 22.041\ (5)$ Å, $\beta = 96.97\ (2)°$, $V = 6829.4$ Å^3, $Z = 4$, mol wt = 1119.9, ρ(calcd) = 1.089 g cm^{-3}, and $\mu = 3.1\ cm^{-1}$. A semiempirical absorption correction was applied. X-ray data were collected at −65 °C on an Enraf-Nonius CAD4F-11 diffractometer, which was equipped with a liquid-nitrogen low-temperature device and used Mo Kα radiation. Data collection, reduction, and refinement procedures have been described elsewhere.[15] A total of 15643 reflections $(+h,+k,\pm l)$ were collected in the range $3° \leqslant 2\theta \leqslant 55°$ with the 9455 having $I_0 > 2\sigma(I_0)$ being used in the structure refinement, which was by full-matrix least-squares techniques (319 variables) using SHELX-76. Final $R_1 = 0.088$ and $R_2 = 0.108$. Hydrogen atoms were placed in calculated positions (C–H = 0.95 Å) and constrained to ride on their respective carbon atoms. Only the Mo and S atoms were refined anisotropically. The final difference-Fourier map showed no chemically significant features.

A diagram of the molecule can be found in Figure 2 and selected bond lengths and angles can be found in Table III. Final coordinates, thermal parameters, structure factors and a completely labeled structure are supplied as Supplementary Material.

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Supplementary Material Available: For both structure determinations, tables of final differences and thermal parameters and figures showing fully labeled structures (6 pages); tables of observed and calculated structure factors (64 pages). Ordering information is given on any current masthead page.

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