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Oxidative Reactions of the Mo^{IV} Dialkyl Complex [{(3-$CF_3C_6H_4NCH_2CH_2)_2NMe$}Mo($CH_2SiMe_3)_2$]

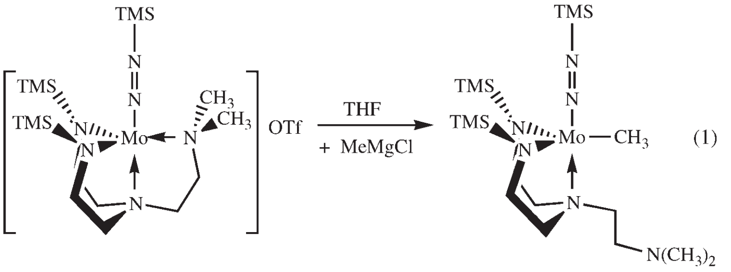
Adam S. Hock and Richard R. Schrock*[a]

Abstract: The structure of [(CF_3N_2NMe)Mo($CH_2SiMe_3)_2$] (in which $(CF_3N_2NMe)^{2-}$ is [(3-$CF_3C_6H_4NCH_2CH_2)_2NMe]^{2-}$) is approximately trigonal bipyramidal with one axial and one equatorial alkyl ligand. Heating of solutions of [(CF_3N_2NMe)Mo($CH_2SiMe_3)_2$] in [D$_6$]benzene in the presence of five equivalents of 2-butyne led to diamagnetic [(CF_3N_2NMe)Mo($CHSiMe_3$)(η^2-MeC≡CMe)], whose structure is approximately square pyramidal with the alkyne occupying the axial site. Addition of one equivalent of cyclohexene sulfide to [(CF_3N_2NMe)Mo($CH_2SiMe_3)_2$] at room temperature produced the diamagnetic, dimeric molybdenum(IV) sulfido complex, [{(CF_3N_2NMe)MoS}$_2$]. This complex is composed of two approximately trigonal bipyramidal centers, each containing one axial and one equatorial sulfur atom. Oxidation of [(CF_3N_2NMe)Mo($CH_2SiMe_3)_2$] with hexachloroethane resulted in formation of tetramethylsilane, HCl, and the sparingly soluble, red alkylidyne complex, [{(CF_3N_2NMe)Mo($CSiMe_3$)Cl}$_2$]. This complex forms a dimer through bridging chlorides. The oxidation reactions of [(CF_3N_2NMe)Mo($CH_2SiMe_3)_2$] with 2-butyne, cyclohexene sulfide, or C_2Cl_6 are all proposed to proceed by α-hydrogen abstraction in the Mo^{VI} species to yield (initially) the Mo=$CHSiMe_3$ species and tetramethylsilane.

Keywords: alkylidenes · alpha abstraction · molybdenum · oxidation · structure elucidation

Introduction

We began studying triamidoamine complexes, initially [$(Me_3SiNCH_2CH_2)_3N]^{3-}$ complexes of Group 5 and 6 metals, in the early 1990s.[1] During studies of dinitrogen functionalization by [$(Me_3SiNCH_2CH_2)_3N$]Mo complexes, a Mo^{IV} complex that contains a diamidoamine ligand was discovered [Eq. (1)].[2]



(1)

This discovery led to the synthesis of Mo and W complexes that contain [$(RNCH_2CH_2)_2NMe]^{2-}$ ligands, in which the R group is C_6F_5,[3a,c] 3,4,5-$C_6F_3H_2$,[3b,c] or 3,5-$Cl_2C_6H_3$.[3d] The desire for a fluorinated amido substituent, but one that does not contain a potentially coordinating *ortho*-aryl fluoride, provided motivation for the synthesis of the [(3,4,5-$C_6F_3H_2NCH_2CH_2)_2NMe]^{2-}$ ligand.[3b] Unfortunately, H_2[(3,4,5-$C_6F_3H_2NCH_2CH_2)_2NMe$] could not be prepared straightforwardly on a large scale. Therefore, we turned to routes that began with the readily available acid, MeN($CH_2COOH)_2$.[4] We found that H_2[(3-$CF_3C_6H_4NCH_2CH_2)_2NMe$] ($H_2$[$CF_3N_2NMe$]) could be prepared readily by employing inexpensive 3-$CF_3C_6H_4NH_2$ on a large scale. A convenient Mo starting material, (Et_3NH)[(CF_3N_2NMe)$MoCl_3$], could also be prepared simply from [$MoCl_4(thf)_2$].[3c] Addition of Me_3CCH_2MgCl to (Et_3NH)[(CF_3N_2NMe)$MoCl_3$] led to [(CF_3N_2NMe)Mo(CH_2CMe_3)Cl] and [(CF_3N_2NMe)Mo($CCMe_3$)(CH_2CMe_3)], whereas addition of Me_3SiCH_2MgCl to (Et_3NH)[(CF_3N_2NMe)$MoCl_3$] yielded [(CF_3N_2NMe)Mo($CH_2SiMe_3)_2$]. [(CF_3N_2NMe)Mo($CCMe_3$)(CH_2CMe_3)] was proposed to arise through selective loss of molecular hydrogen (α,α dehydrogenation) from unobservable [(CF_3N_2NMe)Mo($CH_2CMe_3)_2$]. α,α Dehydro-

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genation was first observed in the form of clean decomposition of the W^{IV} complex [{($Me_3SiNCH_2CH_2)_3N\}WCH_3$] to the methylidyne complex [{($Me_3SiNCH_2CH_2)_3N\}W{\equiv}CH$].[5] This process is believed to occur via an intermediate alkylidene hydride on the basis of isolation and structural characterization of the cyclopentylidene hydride complex [{($Me_3SiNCH_2CH_2)_3N\}W(CC_4H_8)(H)$].[6] The surprising feature of the reaction that produces [($CF_3N_2NMe)Mo(CCMe_3)(CH_2CMe_3)$] is that α,α dehydrogenation takes place and the neopentyl ligand is left intact. It is puzzling as to why [($CF_3N_2NMe)Mo(CH_2SiMe_3)_2$] can be isolated and does not yield [($CF_3N_2NMe)Mo(CSiMe_3)(CH_2SiMe_3)$] readily. Therefore, we became interested in exploring the reactions of [($CF_3N_2NMe)Mo(CH_2SiMe_3)_2$] in more detail, in particular, reactions that involve α abstraction or α,α dehydrogenation. The results are reported herein.

Results and Discussion

Although [{(3,4,5-$F_3C_6H_2NCH_2CH_2)_2NMe\}Mo(CH_2SiMe_3)_2$] and [($CF_3N_2NMe)Mo(CH_2SiMe_3)_2$] (**1**) are known species, neither had been crystallographically characterized. Therefore, we carried out an X-ray diffraction study of **1**. Diffraction-grade crystals were grown from a saturated pentane solution over the course of several months. A thermal-ellipsoid plot is shown in Figure 1; crystallographic details can be found in Table 1. The structure of **1** is approximately trigonal bipyramidal, with one axial and one equatorial alkyl ligand. The Mo−C and Mo−N bond lengths (Mo−N(1) = 1.989(3), Mo−N(2) = 2.320(2), Mo−N(3) = 1.986(2), Mo−C_{eq} = 2.104(5), Mo−C_{ax} = 2.177(3) Å) are almost identical to those in previously characterized [{($C_6F_5NCH_2CH_2)_2NMe\}$-$MoMe_2$] (Mo−N(1) = 1.970(4), Mo−N(2) = 2.325(4), Mo−N(3) = 1.957(4), Mo−C_{ax} = 2.269(4), Mo−C_{eq} = 2.134(6) Å), except that the Mo−C_{ax} bond length is about 0.1 Å longer than the Mo−C_{eq} bond length in the latter. The equatorial Mo−C(1)−Si(1) angle (127.8(3)°) is somewhat larger than the Mo−C(2)−Si(2) angle, possibly because the equatorial alkyl group is more activated toward α abstraction.

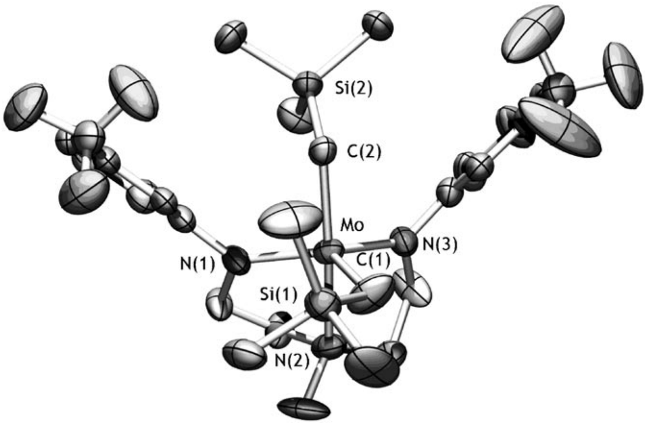

Figure 1. Structure of [($CF_3N_2NMe)Mo(CH_2SiMe_3)_2$] (**1**). Thermal ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Mo−N(1) = 1.989(3), Mo−N(2) = 2.320(2), Mo−N(3) = 1.986(2), Mo−C(1) = 2.104(5), Mo−C(2) = 2.177(3); N(2)−Mo−C(2) = 170.21(10), N(1)−Mo−N(2) = 78.22(11), N(2)−Mo−N(3) = 77.88(16), N(1)−Mo−N(3) = 128.05(18), N(1)−Mo−C(1) = 125.65(19), Mo−C(1)−Si(1) = 127.8(3), Mo−C(2)−Si(2) = 120.16(14).

Table 1. Crystal data and structure refinement for [($CF_3N_2NMe)Mo(CH_2SiMe_3)_2$] (**1**) and [($CF_3N_2NMe)Mo(CHSiMe_3)(\eta^2$-MeCCMe)] (**2**).[a]

	1	**2**
Empirical formula	$C_{27}H_{41}F_6MoN_3Si_2$	$C_{27}H_{35}F_6MoN_3Si$
Formula weight	673.75	639.61
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/n$	$Pbca$
a [Å]	9.2737(13)	19.5713(18)
b [Å]	27.439(4)	14.2824(14)
c [Å]	12.6102(17)	21.163(2)
α [°]	90	90
β [°]	99.761(4)	90
γ [°]	90	90
V [Å^3]	3162.4(8)	5915.5(10)
Z	4	8
ρ_{calcd} [$Mg\,m^{-3}$]	1.415	1.436
μ [mm^{-1}]	0.547	0.542
$F(000)$	1392	2624
θ range for collection [°]	1.48–26.49	1.92–22.50
Index ranges	$-11 \leq h \leq 11$ $0 \leq k \leq 34$ $0 \leq l \leq 15$	$-17 \leq h \leq 21$ $-12 \leq k \leq 15$ $-21 \leq l \leq 22$
Reflections collected	18206	21274
Independent reflections	6532 (R(int) = 0.0265)	3858 (R(int) = 0.0892)
Completeness to θ = 22.50° [%]	99.7	99.9
Absorption correction	empirical	empirical
Data/restraints/parameters	6532/89/500	3858/0/349
Goodness of fit on F^2	1.040	1.134
Final R indices ($I > 2\sigma(I)$)	$R1 = 0.0400$, $wR2 = 0.0873$	$R1 = 0.0776$, $wR2 = 0.1415$
R indices (all data)	$R1 = 0.0519$, $wR2 = 0.0936$	$R1 = 0.1098$, $wR2 = 0.1530$
Largest diff. peak, hole [e Å^3]	0.822, −0.792	0.675, −1.133

[a] Studies were carried out at 273(2) K with $Mo_{K\alpha}$ (0.71073 Å) radiation. The refinement method was full-matrix least squares on F^2.

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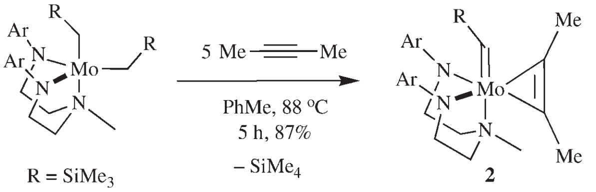
Richard R. Schrock *joined M.I.T. in 1975, where he became Full Professor in 1980 and the Frederick G. Keyes Professor of Chemistry in 1989. His interests include the inorganic and organometallic chemistry of high-oxidation-state, early metal complexes (especially those that contain an alkylidene or alkylidyne ligand), catalysis and mechanisms, the chemistry of high-oxidation-state dinitrogen complexes and catalytic dinitrogen reduction, and the controlled polymerization of olefins and acetylenes. In 2005, he shared the Nobel Prize in Chemistry with Y. Chauvin and R. H. Grubbs.*

Solutions of **1** in C_6D_6 or [D_8]toluene were heated at temperatures ranging from 60 to 100 °C and monitored periodically by ^{19}F and ^{1}H NMR spectroscopy. A complex mixture of products was observed. Numerous peaks were always found in the ^{19}F NMR spectrum of the product mixture, and no product could be isolated. Tetramethylsilane was typically observed in crude mixtures, which suggests that [(CF_3N_2NMe)Mo($CHSiMe_3$)] might have formed rather than [(CF_3N_2NMe)Mo($CSiMe_3$)(CH_2SiMe_3)] and dihydrogen. Notably, when a solution of [{(3,4,5-$F_3C_6H_2NCH_2CH_2)_2NMe$}Mo($CH_2SiMe_3)_2$] in benzene was heated to 62 °C for 24 h, diamagnetic dimeric [{(3,4,5-$F_3C_6H_2NCH_2CH_2)_2NMe$}Mo($CSiMe_3$)]$_2$ was formed in 37% yield.[3b] This complex has an unusual, essentially linear bridging alkylidyne ligand (Mo−C−Si = 177.9(6)°) and an Mo−Mo bond (Mo−Mo = 2.4152(15) Å). It was proposed that [{(3,4,5-$F_3C_6H_2NCH_2CH_2)_2NMe$}Mo($CH_2SiMe_3)_2$] loses tetramethylsilane to yield the intermediate [{(3,4,5-$F_3C_6H_2NCH_2CH_2)_2NMe$}Mo($CHSiMe_3$)], which then eliminates molecular hydrogen in a reaction that is bimolecular in Mo to yield [{(3,4,5-$F_3C_6H_2NCH_2CH_2)_2NMe$}Mo($CSiMe_3$)]$_2$.

The heating of solutions of **1** in [D_6]benzene in the presence of 5 equivalents of 2-butyne led to diamagnetic [(CF_3N_2NMe)Mo($CHSiMe_3$)(η^2-MeC≡CMe)] (**2**; [Eq. (2)]).



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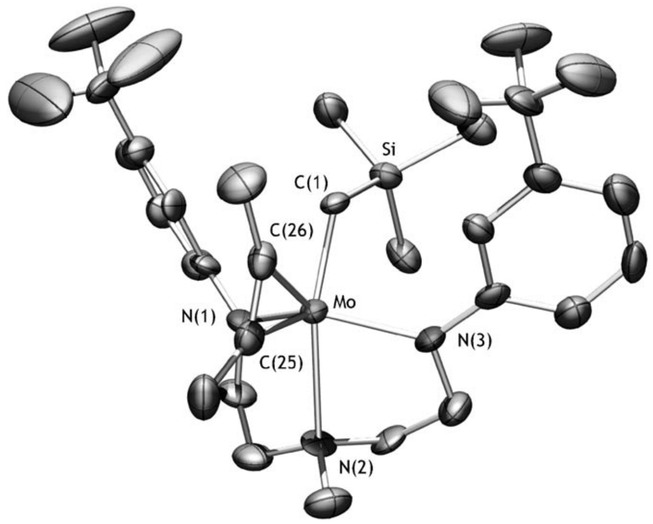
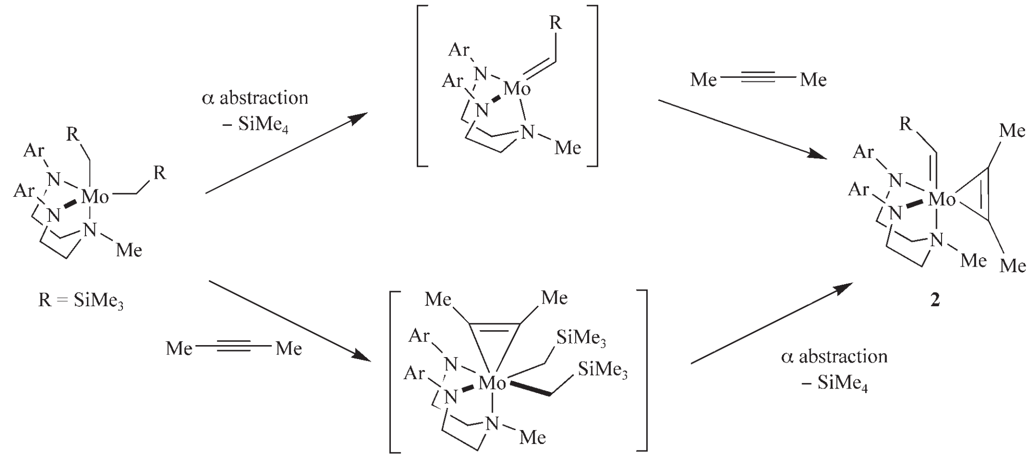


Figure 2. Structure of [(CF_3N_2NMe)Mo($CHSiMe_3$)(η^2-MeC≡CMe)] (**2**). Thermal ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Mo−C(1) = 1.959(8), Mo−N(2) = 2.375(6), Mo−N(1) = 2.057(6), Mo−N(3) = 2.035(6), Mo−C(25) = 2.052(8), Mo−C(26) = 2.031(8), C(25)−C(26) = 1.303(11); Mo−C(1)−Si(1) = 123.0(4), C(1)−Mo−N(2) = 152.7(3), N(3)−Mo−N(1) = 130.0(3), N(3)−Mo−N(2) = 76.6(2), N(1)−Mo−N(2) = 75.5(2), C(1)−Mo−N(1) = 93.2(3), C(26)−Mo−N(1) = 117.1(3).

In the proton NMR spectrum, the pattern of methylene backbone resonances is typical of C_S-symmetric diamidoamine complexes. Only one alkyne carbon resonance was found at 195.3 ppm in the ^{13}C NMR spectrum, a chemical shift that is typical of an alkyne behaving as a four-electron donor.[7] Only one alkyne methyl resonance was found at 2.98 ppm, consistent with the ^{13}C NMR spectroscopic results. These data suggest that the alkyne rotates readily on the NMR timescale. The alkylidene carbon resonance was found at 305 ppm with a $J_{C,H}$ value of 131 Hz, whereas the alkylidene proton resonance was found at 15.12 ppm. The $J_{C,H}$ value of 131 Hz is approximately halfway between values typical for a *syn* alkylidene (120 Hz) and an *anti* alkylidene (140 Hz) in high-oxidation-state imido alkylidene complexes.[8] Therefore, we cannot assign the alkylidene configuration with certainty on the basis of the $J_{C,H}$ value alone.

Crystals of **2** were obtained from a concentrated solution in toluene over a period of several days. The crystallographic details can be found in Table 1, and a thermal-ellipsoid drawing is shown in Figure 2. The Mo−C_{alkyne} (2.031(8) and 2.052(8) Å) and C(25)−C(26) bond lengths (1.303(11) Å) are consistent with the assignment of the alkyne as a four-electron donor. The alkylidene ligand lies in the Mo–C(25)–C(26) plane, and the Si substituent points away from the alkyne (*anti* configuration). The distance between the alkyne and alkylidene carbon atoms (2.59 Å) is well outside the bonding distance. The overall structure is closer to a square pyramid than a trigonal bipyramid with the alkyne occupying the axial site. The molybdenum atom sits slightly beyond the basal plane, with an N(2)−Mo−C(1) angle of 152.7(3)° and a somewhat more acute N(3)−Mo−N(1) angle of 130.0(3)°, presumably to maximize overlap between the amide π orbitals and molybdenum. If we view the alkyne as a four-electron donor analogous to an imido ligand, [(CF_3N_2NMe)Mo($CHSiMe_3$)(η^2-MeC≡CMe)] is isoelectronic with the base adduct of an imido *anti*-alkylidene complex, for which numerous structures have been published.[9,10] [(CF_3N_2NMe)Mo($CHSiMe_3$)(η^2-MeC≡CMe)] appears to be the first "Mo^{VI}" complex with both an alkylidene and alkyne group in the coordination sphere of molybdenum, although two "W^{VI}" examples are known in the literature.[11,12] As the 2-butyne ligand in **1** is not "locked" on the NMR timescale, its orientation must be dictated by interligand interactions and related effects in the solid state. In the tungsten compounds noted above,[11,12] the alkyne is oriented in a more-random fashion.

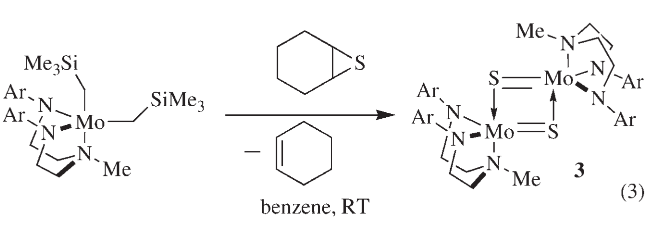
Two of the simplest possible mechanisms for formation of **2** are shown in Scheme 1. In the first mechanism, α abstraction generates [(CF_3N_2NMe)Mo($CHSiMe_3$)], which is then trapped by the alkyne. In the second mechanism, the alkyne coordinates to the electron-deficient molybdenum center first, effectively "oxidizing" it to molybdenum(VI). This six-



Scheme 1. Two simple possible mechanisms for the formation of **2**.

coordinate (assuming the amine donor remains bound during the course of the reaction) or five-coordinate species (if the amine donor is not bound) then undergoes α abstraction to yield the observed product. We favor the mechanism in which the alkyne attacks the metal for several reasons. First, a related alkyne dialkyl compound, $[W\{(OC_6H_3R)_2O\}(\eta^2\text{-PhC}{\equiv}\text{CPh})R_2]$ ($R = CH_2SiMe_3$), was reported to form an observable alkylidene species upon heating.[13] Second, the reaction of $[(CF_3N_2NMe)Mo(CH_2SiMe_3)_2]$ with PhC≡CMe is considerably slower ($t_{1/2} \approx 7$ h) than the reaction with 2-butyne ($t_{1/2} \approx 3$ h). An alkylidene resonance was observed at 15.2 ppm for hypothetical $[(CF_3N_2NMe)Mo(CHSiMe_3)(\eta^2\text{-PhC}{\equiv}\text{CMe})]$, but this product could not be isolated. Finally, the reaction between diphenylacetylene and $[(CF_3N_2NMe)Mo(CH_2SiMe_3)_2]$ is very slow, and no tractable product could be identified. Attempts to perform kinetic studies of the rate of formation of $[(CF_3N_2NMe)Mo(CHSiMe_3)(\eta^2\text{-MeC}{\equiv}\text{CMe})]$ were not successful as a consequence of alkyne polymerization by an unknown mechanism.

We then turned to other possible methods of oxidation. Addition of one equivalent of cyclohexene sulfide to $[(CF_3N_2NMe)Mo(CH_2SiMe_3)_2]$ at room temperature produced the diamagnetic, dimeric molybdenum(IV) sulfido complex, $[\{(CF_3N_2NMe)MoS\}_2]$, in good yield (**3**; [Eq. (3)]).



(3)

This species is almost entirely insoluble in common solvents, although ^{1}H NMR spectroscopic data can be obtained in a mixture of dichloromethane and diethyl ether.

Diffraction-grade crystals of **3** were obtained through addition of cyclohexene sulfide to a solution of $[(CF_3N_2NMe)Mo(CH_2SiMe_3)_2]$ followed by storage of the mixture shielded from mechanical agitation for 15 h. Compound **3** crystallized as long black needles in the space group $P2_1/c$. The crystallographic parameters can be found in Table 2, and a thermal-ellipsoid drawing is shown in Figure 3. Compound **3** is a dimer composed of two approximately trigonal bipyramidal monomers, each containing one axial and one equatorial sulfur atom. The $Mo{-}S_{eq}$ bond (2.2531(12) Å) is slightly shorter than the $Mo{-}S_{ax}$ bond (2.3393(12) Å), which is consistent with the greater multiple-bond character of the $Mo{-}S_{eq}$ bond. Any significant Mo–Mo interaction is doubtful as the Mo···Mo distance is 2.7077(8) Å. The selected bond lengths and angles listed in the caption of Figure 3 are typical for this family of five-coordinate trigonal biyramidal molybdenum complexes.

The proposed mechanism for the formation of **3** is shown in Scheme 2. Cyclohexene (>90 % of theoretical), tetramethylsilane (80 % of theoretical), and 1,2-bis(trimethylsilyl)ethylene (80 % of theoretical) were all observed in solutions of the reaction mixtures in [D$_6$]benzene, consistent with the mechanism shown. We propose that a sulfur atom first transfers to $[(CF_3N_2NMe)Mo(CH_2SiMe_3)_2]$ to yield the intermediate $[(CF_3N_2NMe)Mo(CH_2SiMe_3)_2(S)]$, a species that is now crowded enough to eliminate tetramethylsilane intramolecularly and give $[(CF_3N_2NMe)Mo(S)(CHSiMe_3)]$. Five-coordinate $[(CF_3N_2NMe)Mo(S)(CHSiMe_3)]$ is isoelectronic with the two-electron donor adduct of an $[Mo(NR)(CHR)(OR)_2]$ complex, a type of species that we have been studying for some years. Oxo alkylidene complexes are rare (only tungsten examples are known[14]), especially those with fewer than 18 electrons, and we could find no example of a high-oxidation-state sulfido alkylidene complex.[8,15] Molybdenum(VI) and tungsten(VI) imido alkylidene complexes are known to decompose through bimolecular coupling of alkylidene ligands when the metal is not sufficiently protected sterically.[16] The paucity of oxo alkylidene complexes and the lack of any example of a sulfido alkylidene complex

Table 2. Crystal data and structure refinement for $[\{(CF_3N_2NMe)MoS\}_2]$ (**3**) and $[\{(CF_3N_2NMe)Mo(CSiMe_3)Cl\}_2]$ (**4**).[a]

	3	**4**
Empirical formula	$C_{19}H_{19}F_6MoN_3S$	$C_{23}H_{28}ClF_6MoN_3Si$
Formula weight	531.37	1239.93
T [K]	194(2)	193(2)
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a [Å]	11.1169(11)	12.4041(8)
b [Å]	10.7861(11)	16.8435(10)
c [Å]	17.2515(17)	13.8243(8)
α [°]	90	90
β [°]	93.558(2)	113.2950(10)
γ [°]	90	90
V [Å^3]	2064.6(4)	2652.8(3)
Z	4	2
ρ_{calcd} [Mg m^{-3}]	1.710	1.552
μ [mm^{-1}]	0.800	0.699
$F(000)$	1064	1256
θ range for collection [°]	1.18–22.50	1.79–25.00
Index ranges	$-9 \leq h \leq 11$	$-14 \leq h \leq 14$
	$-11 \leq k \leq 11$	$-20 \leq k \leq 19$
	$-18 \leq l \leq 18$	$-16 \leq l \leq 8$
Reflections collected	8705	14117
Independent reflections	5403 (R-(int) = 0.0801)	4677 (R-(int) = 0.0349)
Completeness to $\theta = 22.50°$ [%]	99.9	100.0
Absorption correction	empirical	empirical
Data/restraints/parameters	5403/0/544	4677/0/317
Goodness of fit on F^2	1.057	1.055
Final R indices ($I > 2\sigma(I)$)	$R1 = 0.0521$, $wR2 = 0.1215$	$R1 = 0.0356$, $wR2 = 0.0920$
R indices (all data)	$R1 = 0.0640$, $wR2 = 0.1270$	$R1 = 0.0420$, $wR2 = 0.0947$
Largest diff. peak, hole [e Å^{-3}]	1.155, −0.827	1.065, −0.719

[a] Studies were carried out with $Mo_{K\alpha}$ ($\lambda = 0.71073$ Å) radiation. The refinement method was full-matrix least squares on F^2.

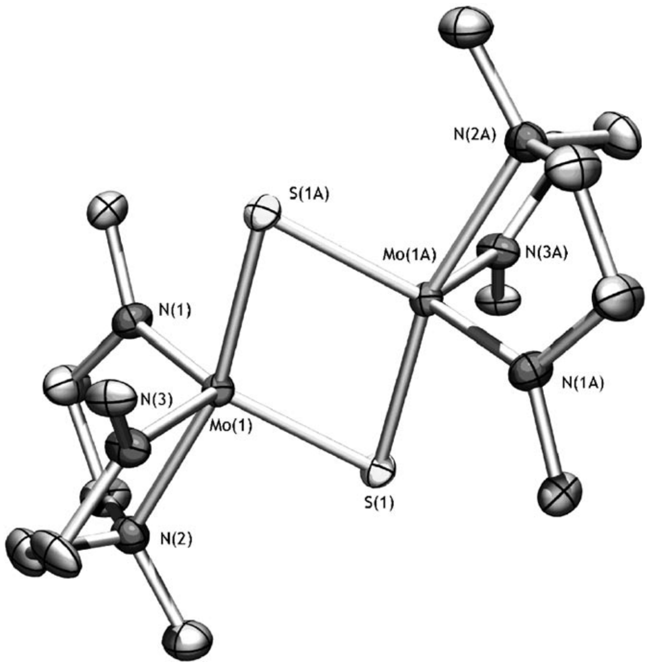
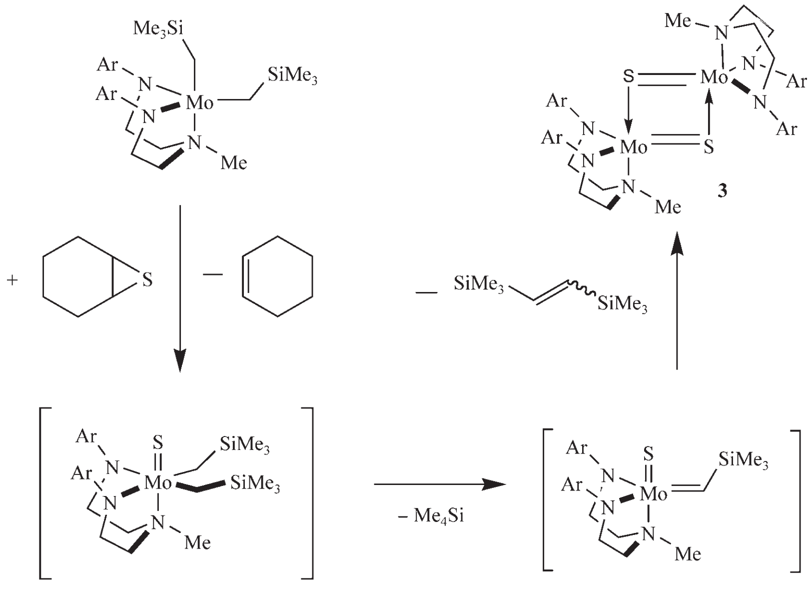


Figure 3. Structure of $[\{(CF_3N_2NMe)MoS\}_2]$ (**3**). Thermal ellipsoids are drawn at the 50% probability level. Only the *ipso*-carbon atoms of the aryl rings are shown, and hydrogen atoms are omitted for clarity. The atoms labeled A were generated through crystallographic symmetry. Selected bond lengths (Å) and angles (°): Mo(1)−S(1) = 2.2531(12), Mo(1)−S(1A) = 2.3393(12), Mo(1)−N(1) = 1.972(4), Mo(1)−N(2) = 2.2531(12), Mo(1)−N(3) = 1.984(4); N(2)−Mo(1)−S(1) = 87.80(11), N(2)−Mo(1)−S(1A) = 164.33(11), N(1)−Mo(1)−N(2) = 78.19(15), N(1)−Mo(1)−N(3) = 115.75(17), N(2)−Mo(1)−N(3) = 79.48(15), Mo(1)−Mo(1A) = 2.7077(8), N(1)−Mo(1)−S(1) = 118.08(12), N(3)−Mo(1)−S(1) = 120.27(12).

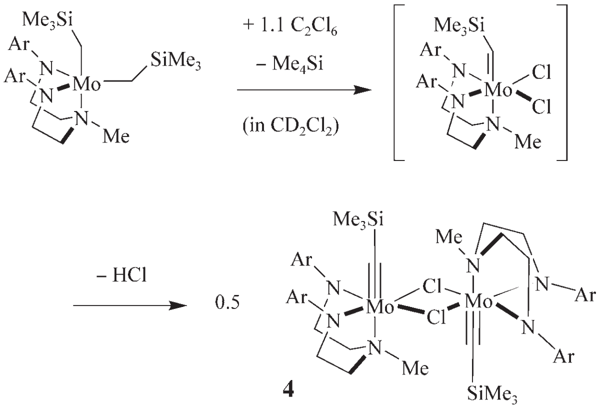
may be attributed not only to a lack of steric protection around the metal, but possibly some assistance in bimolecular decomposition as a consequence of the oxo or sulfido ligand binding to a second metal atom. In short, it would not be surprising if 16-electron $[(CF_3N_2NMe)Mo(S)(CHSiMe_3)]$ were to decompose readily in a bimolecular fashion to give $Me_3SiCH{=}CHSiMe_3$, as we propose.

Oxidation of **1** by pyridine-*N*-oxide, a common oxygen-transfer reagent,[17] proceeded rapidly in thawing benzene or cold (−40 °C) diethyl ether to yield an unstable blue product. Evidence of α abstraction consists of observation of tetramethylsilane in crude product mixtures. Unfortunately, the nature of the final metal-containing product could not be determined.



Scheme 2. Proposed mechanism for the formation of **3**.

Hexachloroethane is a potential oxidant (a mild source of chlorine).[18] Addition of 1.1 equivalents of C_2Cl_6 to **1** resulted in formation of tetramethylsilane, HCl, and the sparingly soluble, red alkylidyne complex (**4**; Scheme 3). The yield was close to 100 % when Et_3N was present to capture the HCl; when no external base was added, the yield of **4** was modest.



Scheme 3. Proposed mechanism for the formation of **4**.

Compound **4** crystallizes in the monoclinic space group $P2_1/c$. The crystallographic parameters can be found in Table 2, and a thermal-ellipsoid drawing as well as bond lengths and angles are shown in Figure 4. The dimer is formed through bridging chlorides with approximately equal Mo–Cl bond lengths. The overall geometry around each metal is best described as octahedral. The Mo–C(1) bond length (1.762(4) Å) and Mo–C(1)–Si angle (172.27(19)°) are typical for a high-oxidation-state alkylidyne species.[9b] The C(1)–Mo–N(2) angle deviates from linearity by 12.3° as a consequence of steric pressure between the methyl group of the amine donor and the trimethylsilyl group in the other half of the dimer.

The simplest mechanism for the formation of **4** (Scheme 3) involves transfer of two chlorine atoms to Mo to give $[(CF_3N_2NMe)Mo(CH_2SiMe_3)_2Cl_2]$ followed by loss of tetramethylsilane to yield $[(CF_3N_2NMe)Mo(CHSiMe_3)Cl_2]$. Loss of HCl from $[(CF_3N_2NMe)Mo(CHSiMe_3)Cl_2]$ in the presence of base is plausible as deprotonation of alkylidenes in d^0 species is a known method of forming alkylidynes.[19] Although the mechanism in Scheme 3 is sensible, several variations might be imagined, including those that involve chlorine radicals. Notably, no Me_3SiCH_2Cl was observed as a product of this reaction.

Simple Lewis bases do not react readily with **1**. For example, **1** did not react readily with trimethylphosphine, either in solution or neat. Extended heating of solutions of **1** that contain PMe_3 produced complex mixtures, according to their ^{19}F and ^{31}P NMR spectra. Compound **1** did not react at room temperature with neat benzonitrile or acetonitrile; heating of solutions of **1** in $[D_6]$benzene in the presence of benzonitrile or acetonitrile resulted in intractable mixtures.

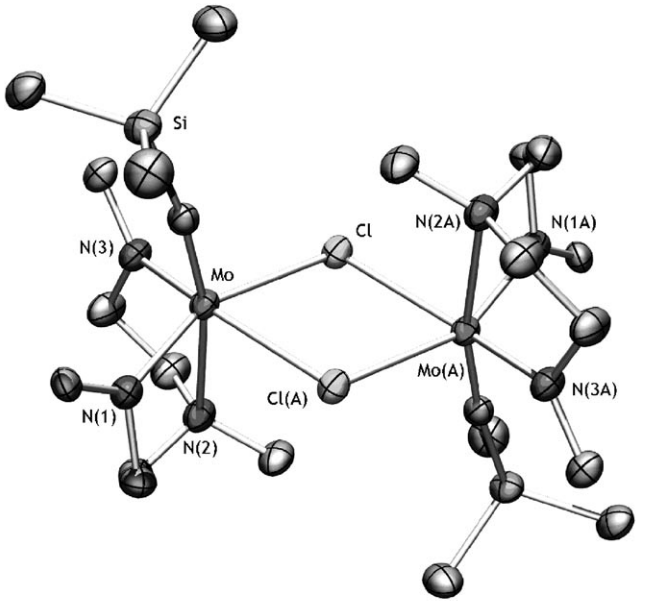


Figure 4. Structure of $[\{(CF_3N_2NMe)Mo(CSiMe_3)Cl\}_2]$ (**4**). Thermal ellipsoids are drawn at the 50 % probability level. Only the *ipso*-carbon atoms of the aryl rings are shown, and hydrogen atoms are omitted for clarity. The atoms labeled A were generated through crystallographic symmetry. Selected bond lengths (Å) and angles (°): Mo–C(1) = 1.762(4), Mo–Cl = 2.5975(10), Mo–Cl(A) = 2.5695(10), Mo–N(1) = 1.985(3), Mo–N(2) = 2.455(3), Mo–N(3) = 1.998(3); Mo–C(1)–Si = 172.27(19), C(1)–Mo–N(2) = 167.73(14), N(1)–Mo–N(2) = 76.68(12), N(1)–Mo–N(3) = 104.41(13), N(2)–Mo–N(3) = 77.28(11), Cl–Mo–N(2) = 88.33(8), Cl(A)–Mo–N(2) = 87.26(8); Mo···Mo(A) = 4.100.

Conclusions

There is no evidence for loss of dihydrogen from **1** to give $[(CF_3N_2NMe)Mo(CSiMe_3)(CH_2SiMe_3)]$ (α,α dehydrogenation), a type of reaction that was proposed to yield $[(CF_3N_2NMe)Mo(CCMe_3)(CH_2CMe_3)]$ from unobservable $[(CF_3N_2NMe)Mo(CH_2CMe_3)_2]$, and $[\{(3,4,5\text{-}C_6F_3H_2NCH_2CH_2)_2NMe\}W(CSiMe_3)(CH_2SiMe_3)]$ from unobservable $[\{(3,4,5\text{-}C_6F_3H_2NCH_2CH_2)_2NMe\}W(CH_2SiMe_3)_2]$.[3c] However, **1** can undergo α abstraction to yield the Mo=$CHSiMe_3$ species and tetramethylsilane when oxidized by two electrons with 2-butyne, cyclohexene sulfide, or C_2Cl_6. The results obtained herein complement those obtained in the last few years for first-row metals for which oxidation of a metal alkyl was shown to be a useful method for synthesizing metal–carbon double or triple bonds.[20] Formation of $[\{(CF_3N_2NMe)MoS\}_2]$ via hypothetical $[(CF_3N_2NMe)Mo(CHSiMe_3)(S)]$ is good evidence that bimolecular decomposition of non-octahedral high-oxidation-state sulfido alkylidene species, such as oxo alkylidene species, will probably continue to be difficult to prevent.

Experimental Section

General

All reactions were performed with standard Schlenk techniques or in a Vacuum Atmospheres glove box under an atmosphere of dry nitrogen, unless otherwise noted. Pentane, diethyl ether, and benzene were purged with nitrogen and then passed through a column of activated alumina. THF was predried over potassium hydroxide, purged with N_2, and passed through two columns of activated alumina. All solvents were stored over 4-Å molecular sieves in a nitrogen-filled glove box. NMR spectra were recorded on a Varian Mercury 300, Unity 300, or INOVA 500 spectrometer and referenced to the residual proton resonances (^{1}H) or to external C_6F_6 at −163.0 ppm (^{19}F). Compound **1** was prepared as reported.[3c] Pyridine-*N*-oxide (Alfa Aesar) was sublimed under dynamic vacuum onto a 0 °C probe prior to use. All other reagents were obtained from commercial suppliers and used as received unless otherwise noted. Celite and 4-Å molecular sieves were dried in full vacuum at greater than 180 °C for at least 18 h.

Syntheses

In our initial report,[3c] the calculated and found values for [(CF_3N_2NMe)Mo(Cl)(CH_2CMe_3)], **1**, and (Bu_4N)[(CF_3NMe)MoCl_3] were accidentally reversed. The correct elemental analysis data are as follows:

[(CF_3N_2NMe)Mo(Cl)CH_2CMe_3]: calcd (%) for $C_{24}H_{30}N_3F_6$ClMo: C 47.58, H 4.99, N 6.94; found: C 47.64, H 5.11, N 6.58.

[(CF_3N_2NMe)Mo($CH_2SiMe_3)_2$]: calcd (%) for $C_{27}H_{41}N_3F_6Si_2$Mo: C 48.13, H 6.13, N 6.24; found: C 47.88, H 6.06, N 6.14.

(Bu_4N)[(CF_3NMe)MoCl_3]: calcd (%) for $C_{35}H_{55}N_4F_6Cl_3$Mo: C 49.57, H 6.54, N 6.61, Cl 12.54; found: C 49.66, H 6.51, N 6.48, Cl 12.61.

2: [(CF_3N_2NMe)Mo($CH_2SiMe_3)_2$] (135.5 mg, 0.20 mmol) was dissolved in toluene (1 mL) in a glass bomb equipped with a teflon sealed joint. 2-Butyne (80 μL, 1 mmol, 5 equiv) was dissolved in toluene (1 mL) and added to the bomb, and the bomb was sealed and heated to 88 °C for 5 h. The reaction mixture was then filtered through celite, which was washed with toluene (≈3 mL). The volatiles were removed from the filtrate in vacuo, and the residue was recrystallized from pentane at −40 °C to give **2** as yellow blocks (110 mg, 86 %). ^{1}H NMR (C_6D_6, 500 MHz): $\delta = 15.12$ (s, H, C*H*SiMe$_3$), 7.03–6.96 (m, 2H, Ar), 6.91–6.86 (m, 4H, Ar), 6.27 (s, 2H, Ar), 3.70–3.60 (m, 2H, backbone), 3.02–2.9 (m, 4H, backbone; overlapped with MeC≡CMe), 2.98 (s, 6H, MeC≡CMe; overlapped with backbone), 2.49 (s, 3H, NMe), 2.37–2.27 (m, 2H, backbone), −0.50 ppm (s, 9H, $SiMe_3$); ^{13}C NMR (C_6D_6, 125 MHz): $\delta = 305.0$ (d, $J_{C,H} = 131$ Hz, Mo*C*HR), 195.3 (Me*C*CMe), 160.7, 149.3, 127.7, 120.3, 119.2, 116.1, 55.7, 53.4, 48.7, 16.5, 2.4 ppm (MoCHSi*Me*$_3$); the CF_3 carbon resonance was obscured by solvent; ^{19}F (C_6D_6, 283 MHz): $\delta = -62.6$ ppm (s); elemental analysis: calcd (%) for $C_{27}H_{35}N_3F_6$MoSi: C 50.70, H 5.52, N 6.57; found: C 50.75, H 5.75, N 6.31.

3: Cyclohexene sulfide (50 mg) was added to **1** (76 mg) in benzene (1 mL). The resulting solution was placed away from vibration for 15 h. Large black needles of **3** formed and were filtered off, washed with pentane, and dried in vacuo (42 mg, 70 %). ^{1}H NMR (CD_2Cl_2/diethyl ether = 1:1, 500 MHz): $\delta = 7.12$ (t, 2H, Ar-H), 7.01 (d, 2H, Ar-H), 6.18 (s, 2H, Ar-H), 4.00 (s, 3H, NMe), 4.05–3.93 (m, 2H, backbone; overlapped with NMe), 3.82–3.74 (m, 2H, backbone), 3.71–3.61 (m, 2H, backbone), 3.61–3.45 ppm (m, 2H, backbone); ^{19}F NMR (C_6D_6, 283 MHz): $\delta = -62.1$ ppm; elemental analysis: calcd (%) for $C_{38}H_{38}N_6F_{12}Mo_2S_2$: C 42.95, H 3.60, N 7.91; found: C 43.11, H 3.75, N 7.76.

4: C_2Cl_6 (45.8 mg, 0.19 mmol, 1.1 equiv) was added to a solution of **1** (118.5 mg, 0.18 mmol) in pentane (3 mL). Five drops of benzene were added, and the mixture was shaken gently to dissolve all components. The solution was allowed to stand at room temperature for 12 h, and all volatile components were removed in vacuo. The resulting red solid was washed with pentane (3 mL) and dried in vacuo to give **4** (67 mg, 61 %). The complex is sparingly soluble in common organic solvents. ^{1}H NMR (CD_2Cl_2, 500 MHz): $\delta = 7.60$–7.46 (m, 2H, Ar), 7.44–7.23 (m, 4H, Ar), 7.26–7.18 (m, 2H, Ar), 4.18–4.00 (m, 2H, backbone), 3.98–3.79 (m, 2H, backbone), 3.11–2.92 (m, 2H, backbone), 2.87–2.73 (m, 2H, backbone), 2.61 (s, 3H, NMe), −0.63 ppm (s, 9H, $SiMe_3$); elemental analysis (consistently low in carbon and variable for reasons unknown): typical analysis: calcd (%) for $C_{46}H_{56}Cl_2F_{12}Mo_2N_6Si_2$: C 44.56, H 4.55, N 6.78; found: C 41.76, H 4.93, N 6.30. When the reaction was carried out in a sealed 5-mm NMR tube (17.0 mg of **1** and 6.5 mg of C_2Cl_6 in CD_2Cl_2), the proton NMR spectrum (500 MHz) showed the presence of **4**, H_2(CF_3N_2NMe) (free ligand), and Me_4Si. No Me_3SiCH_2Cl was observed.

X-ray Structural Studies

Low-temperature X-ray diffraction data were collected on a Siemens Platform three-circle diffractometer coupled to a Bruker-AXS SMART Apex CCD detector with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), with ϕ and ω scans performed. Structures were solved by direct methods by using SHELXS[21]and refined against F^2 on all data by full-matrix least squares with SHELXL-97.[22] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included into the model at geometrically calculated positions and refined by using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the *U* value of the atoms they are linked to (1.5 times for methyl groups). Crystal and structural refinement data are listed in Tables 1 and 2.

The structure of **1** was found to be disordered in several ways. The trifluoromethyl groups of the diamidoamine ligand were both disordered in two orientations. The backbone of the diamidoamine ligand is disordered in the pseudo-Δ and Λ conformations about the metal. Furthermore, the equatorial CH_2SiMe_3 ligand is disordered with slightly different Mo−C−Si angles. The disorder was refined by constraining the total occupancy of the two parts to unity and with restraints on thermal parameters. No restraints on bond angles were employed. It was found that the minor alkyl component has a slightly longer Mo−C bond and a corresponding slightly more acute Mo−C−Si angle (2.226(8) Å and 122.6(4)°, respectively) than the major component. This disorder appears to result from steric pressure between the diamidoamine methyl group and the alkyl ligand; however, the two occurrences of disorder were refined independently. Preliminary examination of data for a second crystal of **1** at lower temperature (100 K) also showed a similar disorder pattern.

The ligand trifluoromethyl groups were also disordered in **3**. The disorder was refined with restraints on the thermal parameters and by constraining the total occupancy of the two parts to unity.

CCDC-04062, -03119, 03234, and 03215 (**1**–**4**, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data request/cif.

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