

Alkylidyne Complexes of Molybdenum and Tungsten That Contain the [(3,4,5-C₆H₂F₃NCH₂CH₂)₂NMe]²⁻ Ligand

Frank V. Cochran and Richard R. Schrock*

Department of Chemistry, Massachusetts Institute of Technology,
Cambridge, Massachusetts 02139

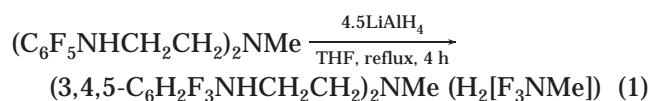
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Summary: Reduction of (C₆F₅NHCH₂CH₂)₂NMe with LiAlH₄ produces (3,4,5-C₆H₂F₃NHCH₂CH₂)₂NMe (H₂[F₃NMe]) in good yield. Reactions between H₂[F₃NMe] and MCl₄ (M = Mo, W) in the presence of NEt₃ yield pseudooctahedral paramagnetic compounds of the type [Et₃NH][F₃NMe]MCl₃. Treatment of [Et₃NH][F₃NMe]MoCl₃ with 3 equiv of Me₃CCH₂MgCl produced five-coordinate [F₃NMe]Mo(CH₂CMe₃)(CCMe₃), while treatment with 3 equiv of Me₃SiCH₂MgCl produced five-coordinate paramagnetic [F₃NMe]Mo(CH₂SiMe₃)₂. Upon heating, [F₃NMe]Mo(CH₂SiMe₃)₂ is converted into diamagnetic {[F₃NMe]Mo(CSiMe₃)₂}. Reactions between [Et₃NH][F₃NMe]WCl₃ and Me₃CCH₂MgCl or Me₃SiCH₂MgCl lead to five-coordinate diamagnetic complexes of the type [F₃NMe]W(CH₂R)(CR), where R = CMe₃, SiMe₃ respectively. X-ray studies confirmed the structures of [F₃NMe]Mo(CH₂CMe₃)(CCMe₃) and {[F₃NMe]Mo(CSiMe₃)₂}.

The chemistry of complexes that contain a triamidoamine ligand has been under investigation in our laboratories for the past few years.^{1–6} Although the focus has been on dinitrogen reduction and functionalization by Mo complexes,^{7–10} we also had the opportunity to prepare and explore Mo(IV) or W(IV) alkyl complexes.^{2,3,6} In the process we discovered an unusual α,α-dehydrogenation reaction that converts a Mo(IV) or W(IV) alkyl complex into an alkylidyne complex and molecular hydrogen. This reaction is much more facile for W than for Mo and in many cases takes place even when β-hydride elimination or abstraction processes would be plausible alternatives. We have turned to the synthesis and study of diamidoamine complexes of Mo and W, initially those that contain the [(C₆F₅NCH₂CH₂)₂NMe]²⁻ ligand,¹¹ primarily in an effort to prepare dinitrogen complexes in which the dinitrogen is more sterically accessible and therefore could be more sus-

ceptible to new modes of functionalization. Recent evidence that this is the case for V and Ta consists of reports that describe reductive cleavage of dinitrogen between two vanadium centers¹² and the reaction between dinitrogen and a tantalum hydride to give a bridging dinitrogen unit that is bound both side-on and end-on.¹³ The fact that the reaction between (C₆F₅NHCH₂CH₂)₂NMe and Mo(NMe₂)₄ led to seven-coordinate [(C₆F₄(NMe₂)NCH₂CH₂)₂NMe]MoF₂ rather than five-coordinate [(C₆F₅NCH₂CH₂)₂NMe]Mo(NMe₂)₂ suggested to us that the chemistry of complexes that contain the [(C₆F₅NCH₂CH₂)₂NMe]²⁻ ligand ultimately might be limited by undesirable nucleophilic attack on the pentafluorophenyl ring.¹¹ Here we report the synthesis and characterization of Mo and W complexes that contain the apparently more robust [(3,4,5-C₆H₂F₃NCH₂CH₂)₂NMe]²⁻ ligand and some reactions that suggest that α,α-dehydrogenation reactions can be found in environments outside of the triamidoamine platform.

In a recent publication¹⁴ the transformation of pentafluorophenyl rings bound to nitrogen into what were proposed to be 2,4,6-C₆H₂F₃ rings with LiAlH₄ in refluxing THF was reported.¹⁵ In the belief that 2,4,6-C₆H₂F₃ rings might be less susceptible to nucleophilic attack, we attempted a similar reaction between (C₆F₅NHCH₂CH₂)₂NMe and LiAlH₄.¹⁶ We were gratified to find that (3,4,5-C₆H₂F₃NHCH₂CH₂)₂NMe was indeed formed in good yield but surprised to learn through X-ray studies of compounds described below that the product was (3,4,5-C₆H₂F₃NHCH₂CH₂)₂NMe, not (2,4,6-C₆H₂F₃NHCH₂CH₂)₂NMe (eq 1). This outcome may be the more



desirable of the two, as the reaction between H₂[F₃NMe] and Mo(NMe₂)₄ was found to yield stable five-coordinate diamagnetic [F₃NMe]Mo(NMe₂)₂ as a red-brown powder,

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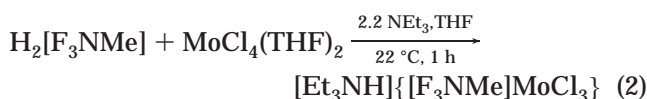
(15) We thank S. Buchler for bringing this publication to our attention.

(16) A solution of (C₆F₅NHCH₂CH₂)₂NMe (3.37 g, 7.49 mmol) in THF (20 mL) was added via syringe to LiAlH₄ (1.28 g, 33.74 mmol) in THF (30 mL) at room temperature. The reaction mixture was heated to reflux for 4 h. The reaction was quenched with water, and all volatile components were removed in vacuo. The residue was washed with 0.5 M NaOH (200 mL) and extracted twice into 200 mL of dichloromethane. The product was isolated as a thick yellow oil from the organic layers; yield 2.46 g (87%).

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in contrast to activation of the ortho fluorides in $(C_6F_5-NHCH_2CH_2)_2NMe$ upon reaction with $Mo(NMe_2)_4$.¹¹

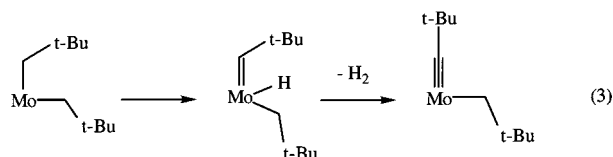
The reaction between $MoCl_4(THF)_2$, $H_2[F_3NMe]$, and NEt_3 in THF led to a paramagnetic purple product formulated as $[Et_3NH]\{[F_3NMe]MoCl_3\}$ on the basis of ^{19}F and 1H NMR spectra and elemental analysis (eq 2).



This reaction is analogous to the synthesis of $[Et_3NH]\{[(C_6F_5NCH_2CH_2)_2NMe]MoCl_3\}$;¹¹ it proceeds in good yield despite the fact that there are only three fluorides on each of the ligand aryl rings. Cation exchange with Bu_4NCl produced a more soluble tetrabutylammonium salt. The magnetic moment of $[Bu_4N]\{[F_3NMe]MoCl_3\}$ was determined by the Evans method¹⁷ as modified by Sur¹⁸ to be $3.1 \mu_B$, slightly higher than the spin-only value for two unpaired electrons ($2.83 \mu_B$).

A reaction similar to that shown in eq 2 between $WCl_4(dme)$, $H_2[F_3NMe]$, and NEt_3 in diethyl ether produced $[Et_3NH]\{[F_3NMe]WCl_3\}$. A tetrabutylammonium salt was prepared in the same manner as described above for $[Bu_4N]\{[F_3NMe]MoCl_3\}$. A measurement of the magnetic moment of $[Bu_4N]\{[F_3NMe]WCl_3\}$ by the Evans method gave $\mu_{eff} = 2.7 \mu_B$.

Addition of 3 equiv of Me_3CCH_2MgCl to $[Et_3NH]\{[F_3NMe]MoCl_3\}$ in THF yielded $[F_3NMe]Mo(CH_2CMe_3)(CCMe_3)$ as an amber crystalline solid in 68% yield.¹⁹ The alkylidene carbon resonance was located at 308 ppm in the ^{13}C NMR spectrum. An X-ray diffraction study revealed the complex to be approximately a trigonal bipyramid with the neopentylidene ligand occupying an axial position trans to the amine donor (Figure 1). All bond lengths and angles are in the expected range. Note that the aryl rings contain fluorides in the 3-, 4-, and 5-positions. We hypothesize that this species arises via α,α -dehydrogenation of transient $[F_3NMe]Mo(CH_2CMe_3)_2$ (eq 3). The ease of α,α -dehydrogenation in



$[F_3NMe]Mo(CH_2CMe_3)_2$ stands in contrast to that process in isolable Mo(IV) neopentyl complexes containing the $[(Me_3SiNCH_2CH_2)_3N]^{3-}$ and $[(C_6F_5NCH_2CH_2)_3N]^{3-}$ ligands, which are converted to the corresponding neopentylidene complexes at appreciable rates only when heated.^{2,3} An unusual feature of α,α -dehydrogenation in $[F_3NMe]Mo(CH_2CMe_3)_2$ is that dihydrogen

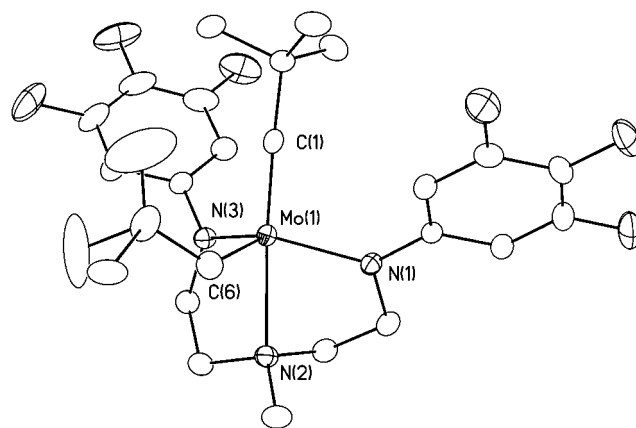


Figure 1. Thermal ellipsoid plot (30% probability level) of the structure of $[F_3NMe]Mo(CH_2CMe_3)(CCMe_3)$. Selected bond distances (Å) and angles (deg): Mo–C(1) = 1.776(3), Mo–C(6) = 2.143(3), Mo–N(1) = 2.042(2), Mo–N(2) = 2.392(2); N(1)–Mo–N(3) = 126.43(9), C(6)–Mo–N(1) = 112.67(11), C(1)–Mo–N(2) = 170.66(10), C(2)–C(1)–Mo = 173.0(2), C(7)–C(6)–Mo = 129.7(2). Crystal data: $C_{27}H_{35}F_6N_3Mo$, monoclinic, $P2_1/n$, $Z = 4$, $a = 12.5977(9)$ Å, $b = 14.7520(11)$ Å, $c = 15.0992(11)$ Å, $\beta = 98.1530(10)^\circ$, $R1 = 0.0294$, $wR2 = 0.0812$ (all data).

rather than neopentane is formed, although the immediate product upon loss of neopentane would be what is perhaps a relatively disfavored Mo(IV) neopentylidene complex. A minor byproduct isolated from this alkylation reaction (<5% yield) was $\{[F_3NMe]Mo(CH_2CMe_3)\}_2(\mu-N_2)$, as revealed in an X-ray crystallographic study. We believe that this product most likely arises via reduction of the intermediate $[F_3NMe]Mo(CH_2CMe_3)Cl$ and capture of dinitrogen by “ $[F_3NMe]Mo(CH_2CMe_3)$.” Synthesis and characterization of $\{[F_3NMe]Mo(CH_2CMe_3)\}_2(\mu-N_2)$ will be reported fully elsewhere when a more reliable and high-yield route to it is found.

In contrast to the result shown in eq 3, addition of 3 equiv of Me_3SiCH_2MgCl to a THF solution of $[Et_3NH]\{[F_3NMe]MoCl_3\}$ led to paramagnetic purple $[F_3NMe]Mo(CH_2SiMe_3)_2$. Resonances corresponding to two different trimethylsilyl proton environments were observed in the 1H NMR spectrum at 3.6 and 1.2 ppm, despite the paramagnetism of the complex ($\mu_{eff} = 3.1 \mu_B$). A bridging dinitrogen complex was isolated in low yield in this case also, as will be reported elsewhere. Heating a benzene solution of $[F_3NMe]Mo(CH_2SiMe_3)_2$ at 62 °C for 24 h caused conversion to a bright red diamagnetic product, an X-ray diffraction study of which revealed it to be $\{[F_3NMe]Mo(CSiMe_3)\}_2$ (Figure 2). This compound has only slightly different Mo–C bond lengths of 2.203(10) and 2.141(8) Å but an essentially linear alkylidene ligand (Mo(1A)–C(1)–Si(1) = 177.9(6)°). An alkylidene carbon resonance was located at 409 ppm in the ^{13}C NMR spectrum. Tungsten compounds that contain the $W_2(\mu-CSiMe_3)_2$ core were discovered in 1976,^{20,21} and a variety of studies have been published since then.^{22–29} Other examples of compounds that contain a $W_2(\mu-CR)_2$

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(19) A solution of $NpMgCl$ (0.43 mL, 2.27 M in Et_2O) was added to a solution of $[Et_3NH]\{[F_3NMe]MoCl_3\}$ (0.2 g, 0.29 mmol) in THF (10 mL) at $-30^\circ C$. After the reaction mixture was warmed to room temperature and stirred for 1 h, all volatile components were removed in vacuo. The residue was extracted into toluene (20 mL) and filtered through Celite to remove magnesium salts. The filtrate was added dropwise to a rapidly stirred volume of cold pentane (100 mL) and filtered a second time. A brown crystalline solid was isolated upon concentrating the solution to dryness; yield 0.122 g (68%). Analytically pure, amber crystals suitable for X-ray diffraction were grown from a mixture of benzene and pentane at $-30^\circ C$.

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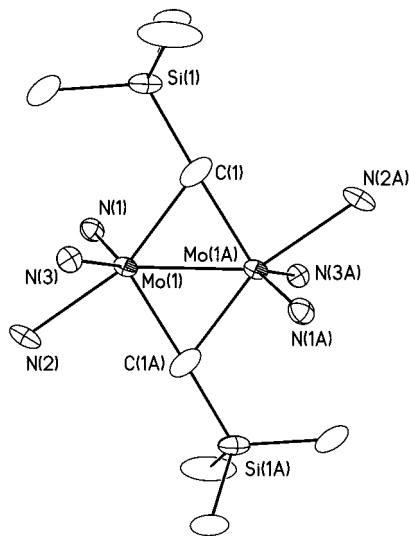
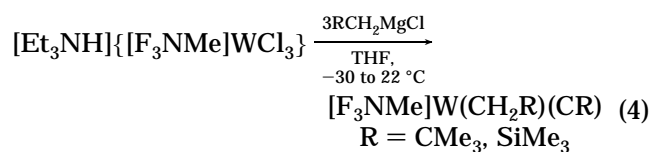


Figure 2. Thermal ellipsoid plot (30% probability level) of the structure of $\{[\text{F}_3\text{NMe}]\text{Mo}(\text{CSiMe}_3)_2\}_2$ (ligand backbone and aryl rings omitted for clarity). Selected bond distances (Å) and angles (deg): Mo(1)–C(1) = 2.203(10), Mo(1)–C(1A) = 2.141(8), Mo(1)–Mo(1A) = 2.4152(15), Mo(1)–N(1) = 2.055(7), Mo(1)–N(2) = 2.306(7), Mo(1)–N(3) = 2.093(7); N(1)–Mo(1)–N(3) = 127.3(3), C(1)–Mo–N(1) = 93.1(3), C(1A)–Mo(1)–N(1) = 109.9(3), C(1)–Mo(1)–C(1A) = 112.5(3), C(1)–Mo(1)–N(2) = 161.5(3), C(1A)–Mo(1)–N(2) = 86.0(3), Si(1)–C(1)–Mo(1) = 114.1(4), Si(1)–C(1)–Mo(1A) = 177.9(6). Crystal data: $\text{C}_{42}\text{H}_{48}\text{N}_6\text{F}_{12}\text{Si}_2\text{Mo}_2$, monoclinic, $P2_1/c$, $Z = 2$, $a = 10.818(2)$ Å, $b = 16.850(3)$ Å, $c = 14.216(2)$ Å, $\beta = 104.610(3)^\circ$, $R1 = 0.0650$, $wR2 = 0.1425$ (all data).

core are rare.³⁰ To our knowledge there is no published example of a compound that contains the $\text{Mo}_2(\mu\text{-CR})_2$ core or any compound that contains a $\text{W}_2(\mu\text{-CSiMe}_3)_2$ core in which the $\text{W}(1)\text{-C-Si}$ and $\text{W}(2)\text{-C-Si}$ angles are not approximately equal. Therefore, at this stage we do not know whether the linear form of the $\mu\text{-CSiMe}_3$ ligands found in $\{[\text{F}_3\text{NMe}]\text{Mo}(\text{CSiMe}_3)_2\}_2$ is a characteristic of $\text{Mo}_2(\mu\text{-CR})_2$ compounds or a feature of $\text{M}_2(\mu\text{-CR})_2$ compounds ($\text{M} = \text{Mo}, \text{W}$) that contain a diamido/donor ligand. The different modes of decomposition of $[\text{F}_3\text{NMe}]\text{Mo}(\text{CH}_2\text{SiMe}_3)_2$ and the proposed intermediate $[\text{F}_3\text{NMe}]\text{Mo}(\text{CH}_2\text{CMe}_3)_2$ are striking.

Treatment of $[\text{Et}_3\text{NH}]\{[\text{F}_3\text{NMe}]\text{WCl}_3\}$ with 3 equiv of either $\text{Me}_3\text{CCH}_2\text{MgCl}$ or $\text{Me}_3\text{SiCH}_2\text{MgCl}$ yielded five-coordinate diamagnetic alkylidyne complexes of the type $[\text{F}_3\text{NMe}]\text{W}(\text{CH}_2\text{R})(\text{CR})$ ($\text{R} = \text{CMe}_3$ or SiMe_3 , eq 4). The



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alkylidyne carbon atom resonances were located at 296 ppm in the neopentylidyne complex and 337 ppm in the (trimethylsilyl)methylidyne complex. Apparently the α,α -dehydrogenation reaction, which is known to be much faster for W than Mo in triamidoamine alkyl complexes,^{2,6} becomes the dominant reaction pathway in both $[\text{F}_3\text{NMe}]\text{W}(\text{CH}_2\text{CMe}_3)_2$ and $[\text{F}_3\text{NMe}]\text{W}(\text{CH}_2\text{SiMe}_3)_2$.

We conclude that the $[(3,4,5\text{-C}_6\text{H}_2\text{F}_3\text{NCH}_2\text{CH}_2)_2\text{-NMe}]^{2-}$ ligand has significant potential in terms of developing the chemistry of middle oxidation states of Mo and W, because starting materials can be prepared readily and because the $[(3,4,5\text{-C}_6\text{H}_2\text{F}_3\text{NCH}_2\text{CH}_2)_2\text{-NMe}]^{2-}$ ligand appears to be less susceptible to nucleophilic attack than the pentafluorophenyl ring in the $[(\text{C}_6\text{F}_5\text{NCH}_2\text{CH}_2)_2\text{NMe}]^{2-}$ ligand. We are interested in elucidating the mechanisms of the organometallic reactions reported here and determining to what extent chemistry at the α -carbon can be distinguished from chemistry at the β -carbon in alkyls that contain β -protons. We also are interested in developing high-yield routes to species that contain bound dinitrogen in order to further explore the chemistry of $[(3,4,5\text{-C}_6\text{H}_2\text{F}_3\text{NCH}_2\text{CH}_2)_2\text{-NMe}]^{2-}$ complexes with respect to dinitrogen fixation. Although a variety of complexes that contain "diamido/donor" ligands have been reported by other laboratories,^{12,31–47} those reported in this work and in a previous communication¹¹ appear to be the only ones so far that contain Mo or W.

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Supporting Information Available: Text giving experimental details, labeled ORTEP diagrams, and tables of crystal data and structure refinement details, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters for $[\text{F}_3\text{NMe}]\text{Mo}(\text{CH}_2\text{CMe}_3)(\text{CCMe}_3)$ and $[\text{F}_3\text{NMe}]\text{Mo}(\text{CSiMe}_3)_2$. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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