Molybdenum and Tungsten Complexes That Contain the Diamidoamine Ligands [(C$_6$F$_5$NCH$_2$CH$_2$)$_2$NMe]$^{2-}$, [(3,4,5-C$_6$H$_2$F$_3$NCH$_2$CH$_2$)$_2$NMe]$^{2-}$, and [(3-CF$_3$C$_6$H$_4$NCH$_2$CH$_2$)$_2$NMe]$^{2-}$

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Molybdenum and tungsten complexes have been prepared that contain three different types of diamidoamine ligands of the type [(ArNCH$_2$CH$_2$)$_2$NMe]$^{2-}$ ([ArNMe]$^{2-}$, where Ar = C$_6$F$_5$, 3,4,5-F$_3$C$_6$H$_2$, 3-CF$_3$C$_6$H$_4$). The starting materials, which are of the type [Et$_3$NH]-{[ArNMe]MCl$_3$}, are prepared from MCl$_4$ reagents and the ligand upon addition of triethylamine. X-ray studies for [Et$_3$NH]{[C$_6$F$_5$NMe]MoCl$_3$}, [Et$_3$NH]{[C$_6$F$_5$NMe]WCl$_3$}, and [Bu$_4$N]{[3-CF$_3$C$_6$H$_4$NMe]MoCl$_3$} reveal that the amido nitrogens are approximately cis to one another in a distorted-pseudooctahedral environment. Addition of various alkylating reagents to various [Et$_3$NH]{[ArNMe]MCl$_3$} species led to the formation of [C$_6$F$_5$NMe]MoMe$_2$ (**3**), [C$_6$F$_5$NMe]Mo(CH$_2$CMe$_3$)Cl (**4b**), [C$_6$F$_5$NMe]W(CH$_2$CMe$_3$)Cl (**5**), [3,4,5-F$_3$C$_6$H$_2$NMe]Mo-(CH$_2$CMe$_3$)Cl (**8**), [3,4,5-F$_3$C$_6$H$_2$NMe]Mo(CH$_2$CMe$_3$)(CCMe$_3$) (**9**), [3,4,5-F$_3$C$_6$H$_2$NMe]Mo(CH$_2$-SiMe$_3$)$_2$ (**10**), [3,4,5-F$_3$C$_6$H$_2$NMe]W(CH$_2$CMe$_3$)(CCMe$_3$) (**11a**), [3,4,5-F$_3$C$_6$H$_2$NMe]W(CH$_2$-SiMe$_3$)(CSiMe$_3$) (**11b**), [3-CF$_3$C$_6$H$_4$NMe]Mo(CH$_2$SiMe$_3$)$_2$ (**13**), [3-CF$_3$C$_6$H$_4$NMe]Mo(CH$_2$CMe$_3$)Cl (**14**), and [3-CF$_3$C$_6$H$_4$NMe]Mo(CCMe$_3$)(CH$_2$CMe$_3$) (**15**). All M^{4+} complexes are paramagnetic with magnetic moments that are expected for high-spin d^2 complexes. X-ray studies of **3**, **4b**, and **9** show them to be trigonal-bipyramidal species in which the amido nitrogens occupy equatorial positions. The alkylidyne complexes form via elimination of dihydrogen, an "α,α-dehydrogenation" reaction, as shown by measuring the dihydrogen evolved in one case.

Introduction

Transition-metal complexes that contain amido ligands have become more numerous and important in coordination chemistry and in a variety of catalytic reactions in the past decade.[1−4] Over the last several years, we have been interested in triamidoamine ligands of the type [(RNCH$_2$CH$_2$)$_3$N]$^{3-}$ or diamido−donor ligands of the type [(RNCH$_2$CH$_2$)$_2$D]$^{2-}$ (D = a donor such as O or NR′) and [H$_3$CC(2-C$_5$H$_4$N)(CH$_2$NR)$_2$]$^{2-}$.[4] Triamidoamine ligands have been employed primarily for the purpose of exploring organometallic or dinitrogen chemistry of Mo and W,[5−9] while diamido−donor ligands have been employed primarily for preparing Zr and Hf catalysts for the polymerization of ordinary olefins.[10−17] Triamidoamine ligands also have been employed in studies of

the chemistry of d^2 Mo and W alkyl complexes.[18−21] For example, molybdenum and tungsten complexes of the type [(Me$_3$SiNCH$_2$CH$_2$)$_3$N]MCH$_2$R were found to undergo α-elimination reactions that are orders of magnitude faster than β-elimination reactions and α,α-dehydrogenation reactions that convert a complex of the type [(Me$_3$SiNCH$_2$CH$_2$)$_3$N]MCH$_2$R into one of the type [(Me$_3$SiNCH$_2$CH$_2$)$_3$N]M≡CR, presumably through formation of the intermediate species [(Me$_3$SiNCH$_2$-CH$_2$)$_3$N]M(H)(CHR) followed by loss of molecular hydrogen.

We felt that Mo and W complexes containing a diamido−donor ligand could be synthesized, since in the

(1) Kempe, R. *Angew. Chem., Int. Ed.* **2000**, *39*, 469.
(2) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 428.
(3) Gade, L. H. *Chem. Commun.* **2000**, 173.
(4) Gade, L. H. *Acc. Chem. Res.* **2002**, *35*, 575.
(5) Greco, G. E.; Schrock, R. R. *Inorg. Chem.* **2001**, *40*, 3860.
(6) Yandulov, D. V.; Schrock, R. R. *Science* **2003**, *301*, 76.
(7) Yandulov, D. V.; Schrock, R. R. *J. Am. Chem. Soc.* **2002**, *124*, 6252.
(8) O'Donoghue, M. B.; Davis, W. M.; Schrock, R. R. *Inorg. Chem.* **1998**, *37*, 5149.
(9) O'Donoghue, M. B.; Davis, W. M.; Schrock, R. R.; Reiff, W. M. *Inorg. Chem.* **1999**, *38*, 243.
(10) Aizenberg, M.; Turculet, L.; Davis, W. M.; Schattenmann, F.; Schrock, R. R. *Organometallics* **1998**, *17*, 4795.
(11) Schrock, R. R.; Seidel, S. W.; Schrodi, Y.; Davis, W. M. *Organometallics* **1999**, *18*, 428.
(12) Baumann, R.; Stumpf, R.; Davis, W. M.; Liang, L.-C.; Schrock, R. *J. Am. Chem. Soc.* **1999**, *121*, 7822.
(13) Schrock, R. R.; Baumann, R.; Reid, S. M.; Goodman, J. T.; Stumpf, R.; Davis, W. M. *Organometallics* **1999**, *18*, 3649.
(14) Schrock, R. R.; Casado, A. L.; Goodman, J. T.; Liang, L.-C.; Bonitatebus, P. J., Jr.; Davis, W. M. *Organometallics* **2000**, *19*, 5325.
(15) Schrock, R. R.; Bonitatebus, P. J., Jr.; Schrodi, Y. *Organometallics* **2001**, *20*, 1056.
(16) Mehrkhodavandi, P.; Bonitatebus, P. J., Jr.; Schrock, R. R. *J. Am. Chem. Soc.* **2000**, *122*, 7841.
(17) Mehrkhodavandi, P.; Schrock, R. R. *J. Am. Chem. Soc.* **2001**, *123*, 10746.
(18) Shih, K.-Y.; Totland, K.; Seidel, S. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1994**, *116*, 12103.
(19) Seidel, S. W.; Schrock, R. R.; Davis, W. M. *Organometallics* **1998**, *17*, 1058.
(20) Schrock, R. R.; Seidel, S. W.; Mösch-Zanetti, N. C.; Dobbs, D. A.; Shih, K.-Y.; Davis, W. M. *Organometallics* **1997**, *16*, 5195.
(21) Schrock, R. R.; Seidel, S. W.; Mosch-Zanetti, N. C.; Shih, K.-Y.; O'Donoghue, M. B.; Davis, W. M.; Reiff, W. M. *J. Am. Chem. Soc.* **1997**, *119*, 11876.

process of exploring the dinitrogen chemistry of [(Me$_3$-SiNCH$_2$CH$_2$)$_3$N]Mo complexes a compound was formed as a consequence of degradation of the [(Me$_3$SiNCH$_2$-CH$_2$)$_3$N]$^{3-}$ ligand, in which a free dimethylamine arm was not coordinated to molybdenum;[8] the ligand was effectively a diamido–donor ligand. The desire to explore further the Mo or W chemistry of d^2 alkyl complexes in amido ligand environments gave rise to the work reported here, which involves diamido–donor ligands of the type [(RNCH$_2$CH$_2$)$_2$NMe]$^{2-}$, where R = C$_6$F$_5$, 3,4,5-C$_6$H$_2$F$_3$, 3-CF$_3$C$_6$H$_4$. Some of the results reported here have appeared in preliminary form[22,23] and should be compared with several analogous molybdenum complexes in which the ligand is [(3,5-Cl$_2$C$_6$H$_3$-NCH$_2$CH$_2$)$_2$NMe]$^{2-}$.[24]

Results

Synthesis and Characterization of {[F$_5$NMe]-MCl$_3$}$^-$ Species (M = Mo, W). The reaction between (H$_2$NCH$_2$CH$_2$)$_2$NH and hexafluorobenzene in the presence of K$_2$CO$_3$ in refluxing acetonitrile has been reported to give (C$_6$F$_5$NHCH$_2$CH$_2$)$_2$NH in 40% yield.[25] The yield was raised to 60% by flash-filtering a concentrated solution of the product mixture in ether through activated alumina, thereby removing monoarylated material. Approximately 18 g of pure (C$_6$F$_5$NHCH$_2$CH$_2$)$_2$NH could be obtained readily in this manner.

Replacement of the proton on the central amine nitrogen with an alkyl group was desirable in order to block formation of any complexes that contain the trianionic ligand[25] [(C$_6$F$_5$NCH$_2$CH$_2$)$_2$N]$^{3-}$ and also in order to create more steric protection near the metal. Methylation of (C$_6$F$_5$NHCH$_2$CH$_2$)$_2$NH in acetonitrile with methyl iodide in the presence of K$_2$CO$_3$ gave (C$_6$F$_5$-NHCH$_2$CH$_2$)$_2$NMe (H$_2$[F$_5$NMe]) in 63% yield on a 6–7 g scale (eq 1). After standard workup, H$_2$[F$_5$NMe] was
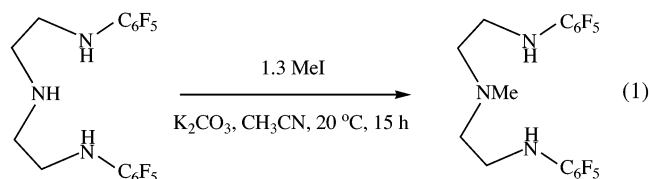
extracted into chloroform and any insoluble ammonium salt formed by double methylation at the central nitrogen was removed by filtration. A slight excess (1.3 equiv) of MeI was required in order to consume all starting material as a consequence of over-methylation of the central amine nitrogen. Methylation did not seem to work as well on a large scale. Therefore, we could not prepare H$_2$[F$_5$NMe] on a scale of more than 6–7 g at a time. Methylation of the central amine nitrogen has been employed in order to synthesize other triamines of this general type.[14,15,24]

Addition of orange MoCl$_4$(THF)$_2$ to a stirred solution of H$_2$[F$_5$NMe] dissolved in THF produced a deep red, homogeneous solution in several seconds that we believe

(22) Cochran, F. V.; Bonitatebus, P. J.; Schrock, R. R. *Organometallics* **2000**, *19*, 2414.
(23) Cochran, F. V.; Schrock, R. R. *Organometallics* **2001**, *20*, 2127.
(24) Araujo, J. P.; Wicht, D. K.; Bonitatebus, P. J., Jr.; Schrock, R. R. *Organometallics* **2001**, *20*, 5682.
(25) Schrock, R. R.; Lee, J.; Liang, L.-C.; Davis, W. M. *Inorg. Chim. Acta* **1998**, *270*, 353.

contains an adduct between H$_2$[F$_5$NMe] and MoCl$_4$. Attempts to isolate or identify this adduct were not successful. Addition of 2 equiv of NEt$_3$ caused the solution to deepen in color rapidly and an off-white precipitate of [Et$_3$NH]Cl to form. Paramagnetic [Et$_3$NH]-{[F$_5$NMe]MoCl$_3$} (**1a**) was isolated as a burgundy powder in 83% yield upon filtering the reaction mixture and adding pentane to the filtrate (eq 2). The ^{19}F NMR

1a
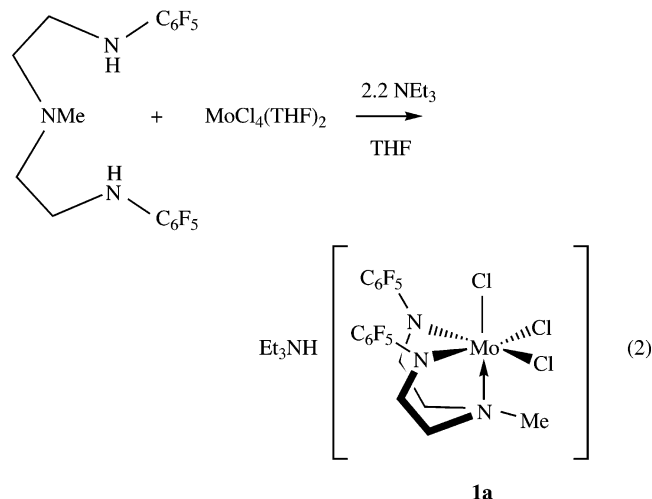
spectrum of **1a** in THF contained five resonances of equal intensity at −95.46, −119.25, −131.27, −134.95, and −169.26 ppm. Five shifted resonances are characteristic of a paramagnetic metal complex in which the pentafluorophenyl rings do not rotate rapidly on the NMR time scale.

The tetrabutylammonium analogue [Bu$_4$N]{[F$_5$NMe]-MoCl$_3$} (**1b**) was prepared in 98% yield by reacting **1a** with Bu$_4$NCl in THF (eq 3). The Et$_3$NHCl was filtered

1b
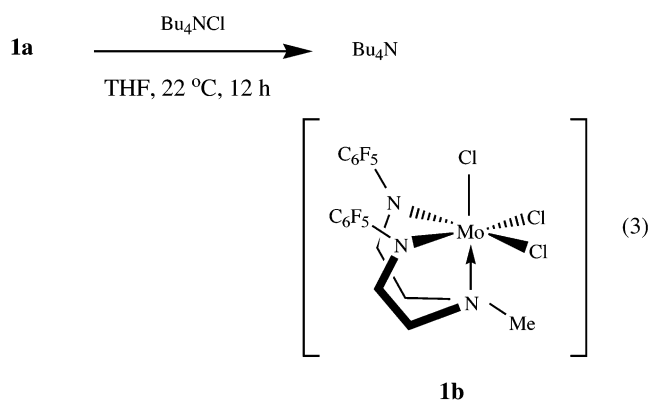
off and **1b** isolated by precipitation with pentane. Complex **1b** displayed much greater solubility in benzene and toluene than **1a**.

The ^{19}F NMR spectrum of **1b** in C$_6$D$_6$ (Figure 1) is similar to that of **1a** with five broad resonances of about equal intensity at −92.54, −115.76, −128.40, −133.75, and −168.07 ppm. The resonances are assigned as shown in Figure 1 on the basis of their breadth: i.e., the ortho fluorines, which are closest to the paramagnetic metal center, are the broadest. The ^{1}H NMR spectrum of complex **1b** in C$_6$D$_6$ (Figure 2) showed resonances for the ligand backbone that are shifted upfield to a degree found for the triamidoamine ligand backbone in paramagnetic d^2 complexes of molybde-
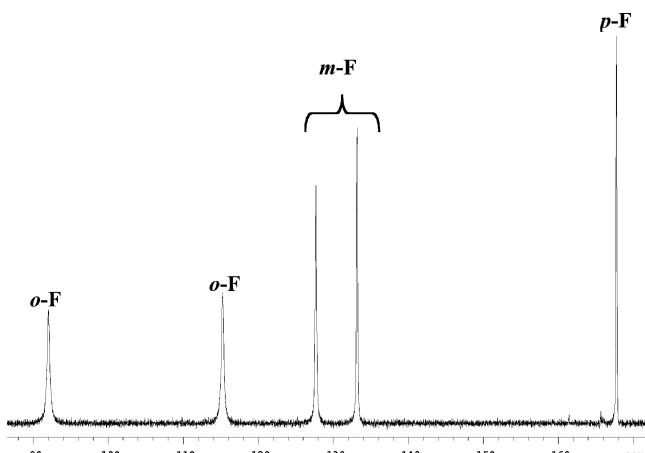
Figure 1. ^{19}F NMR spectrum (282 MHz, C_6D_6) of [Bu_4N]{[F_5NMe]$MoCl_3$}.
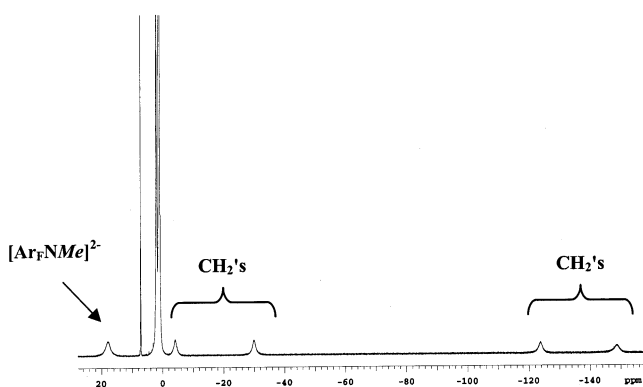
Figure 2. ^{1}H NMR spectrum (300 MHz, C_6D_6) of [Bu_4N]-{[F_5NMe]$MoCl_3$}.

num.[26] The resonances near 1 ppm are assigned to the tetrabutylammonium cation, while the resonances at −4.15, −29.98, −123.84, and −149.7 ppm are assigned to the four types of CH_2 protons in the backbone of the [F_5NMe]$^{2−}$ ligand. The resonance at 18.82 ppm is assigned to the methyl group on the central donor nitrogen. The magnetic susceptibility of **1b** in C_6D_6 at 22 °C was determined by the Evans method[27] as modified by Sur[28] to be 3.1 μ_B, which is consistent with the molybdenum having two unpaired electrons. This value is essentially identical with several other experimentally determined magnetic moments of related d^2 Mo complexes in this work.

Complex **1a** crystallized as dark red blocks from toluene solution at −30 °C in the monoclinic space group $P2_1/c$. Crystallographic data, collection parameters, and refinement parameters can be found in Table 1, while selected bond lengths (Å) and angles (deg) are listed in Table 2. The anion (Figure 3) is a distorted-octahedral species in which the [F_5NMe]$^{2−}$ ligand is bound in a facial manner. All Mo−N bond lengths and angles are similar to those in an analogous species that contains the [$(3,5-Cl_2C_6H_3NCH_2CH_2)_2NMe$]$^{2−}$ ligand.[24] The Mo−F_{ortho} distances (3.7−4.2 Å) are long enough to rule out any significant interaction between the ortho fluorides and the molybdenum, the closest approach of two ortho fluorides being 2.84 Å. Restricted rotation of the C_6F_5

(26) Greco, G. E.; Schrock, R. R. *Inorg. Chem.* **2001**, *40*, 3850.
(27) Evans, D. F. *J. Chem. Soc.* **1959**, 2003.
(28) Sur, S. K. *J. Magn. Reson.* **1989**, *82*, 169.
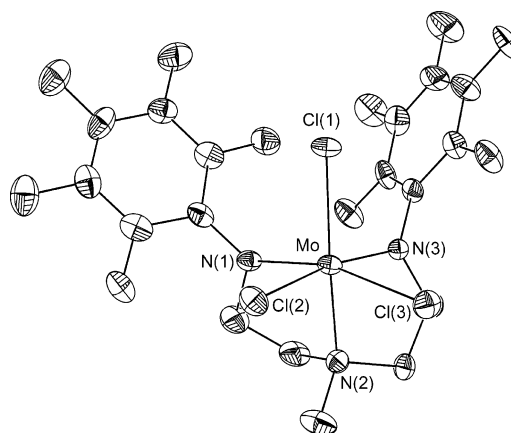
Figure 3. Thermal ellipsoid plot (35% probability level) of the anion structure of [Et_3NH]{[F_5NMe]$MoCl_3$} (**1a**). Hydrogens have been omitted for clarity.

rings on the NMR time scale can be attributed to interactions between an ortho fluoride and the apical chloride (1.3−1.4 Å away when the C_6F_5 ring is rotated, so as to lie approximately in the N(1) or N(3) plane) and between an ortho fluoride and the methylene protons next to N(1) and N(3). The cation is oriented toward a {[F_5NMe]$MoCl_3$}$^−$ ion in an adjacent asymmetric unit. The triethylammonium proton approaches the trichloride face of the octahedron. The closest contact is to the chloride trans to the N_{amine} donor at a distance of 2.27 Å.

Tungsten complexes analogous to **1a** and **1b** could be prepared from WCl_4(dme).[29] The reaction between (C_6F_5-$NHCH_2CH_2$)$_2$NMe, WCl_4(dme), and 2 equiv of NEt_3 was carried out in diethyl ether instead of THF in order to avoid formation of relatively insoluble and unreactive WCl_4(THF)$_2$. The ether was removed in vacuo, and [Et_3-NH]{[F_5NMe]WCl_3} (**2a**) was extracted into THF, from which it could be crystallized in 60% yield. Cation exchange was accomplished by salt metathesis of **2a** with Bu_4NCl in THF to give [Bu_4N]{[F_5NMe]WCl_3} (**2b**) as a light green powder in good yield. Fluorine and proton NMR spectra of **2a** and **2b** are similar to those for **1a** and **1b**, except the resonances are much sharper in the tungsten compounds as a consequence of greater spin−orbit coupling for tungsten. A magnetic moment of 2.7 μ_B was found for **2b** in C_6D_6 by the Evans method, consistent with two unpaired electrons.

Large dark green crystals of **2a** were grown from a THF solution layered with pentane. Crystallographic data, collection parameters, and refinement parameters can be found in Table 1, while selected bond lengths (Å) and angles (deg) are given in Table 2. A thermal ellipsoid plot of the anion structure is shown in Figure 4. As opposed to **1a**, the triethylammonium cation approaches the trichloride face of the pseudooctahedron with the H−Cl distances to Cl(1), Cl(2), and Cl(3) being longer (2.99, 2.73, and 2.77 Å, respectively). The core structure of the molecule is not significantly different from **1a** and warrants no discussion.

Organometallic Complexes of Molybdenum That Contain the [F_5NMe]$^{2−}$ Ligand. Addition of 3 equiv of MeMgCl to a dark red solution of [Et_3NH]{[F_5NMe]-$MoCl_3$} (**1a**) in THF resulted in a color change from dark

(29) Persson, C.; Andersson, C. *Inorg. Chim. Acta* **1993**, *203*, 235.

Table 1. Crystallographic Data, Collection Parameters, and Refinement Parameters for [Et$_3$NH]{[F$_5$NMe]MoCl$_3$} (1a), [Et$_3$NH]{[F$_5$NMe]WCl$_3$} (2a), and [Bu$_4$N]{[CF$_3$NMe]MoCl$_3$} (12b)^a

	1a^b	2a^c	12b
empirical formula	C$_{23}$H$_{27}$N$_4$Cl$_3$F$_{10}$Mo	C$_{23}$H$_{27}$N$_4$Cl$_3$F$_{10}$W	C$_{35}$H$_{55}$N$_4$MoCl$_3$F$_6$
formula wt	751.78	733.33	848.12
cryst syst	monoclinic	monoclinic	triclinic
space group	$P2_1/c$	$C2/c$	$P\bar{1}$
unit cell dimens			
a (Å)	11.811(3)	19.8048(3)	10.631(6)
b (Å)	17.123(4)	11.48880(10)	14.548(7)
c (Å)	17.325(4)	27.8998(5)	15.045(8)
α (deg)	90	90	64.132(9)
β (deg)	95.233(4)	92.8030(10)	78.308(9)
γ (deg)	90	90	85.861(11)
V (Å^3)	3489.2(13)	6340.54(16)	2049.9(18)
Z	4	8	2
calcd density (Mg/m^3)	1.605	1.759	1.374
abs coeff (mm^{-1})	0.687	3.976	0.572
$F(000)$	1700	3264	880
θ range for data collecn (deg)	1.68−19.99	2.05−22.50	1.53−22.50
index ranges	$-11 \le h \le 9, -16 \le k \le 16,$ $-16 \le l \le 14$	$-21 \le h \le 21, -12 \le k \le 9,$ $-21 \le l \le 30$	$-11 \le h \le 9, -15 \le k \le 15,$ $-16 \le l \le 16$
no. of rflns collected	10 314	11 573	8724
no. of indep rflns	3256 (R_{int} = 0.1596)	4141 (R_{int} = 0.0976)	5343 (R_{int} = 0.1326)
abs cor	empirical	none	none
no. of data/restraints/params	3256/0/429	4141/0/371	5343/0/448
goodness of fit on F^2	1.127	1.074	1.202
final R indices ($I > 2\sigma(I)$)	R1 = 0.0612, wR2 = 0.1517	R1 = 0.0403, wR2 = 0.1003	R1 = 0.0788, wR2 = 0.2201
R indices (all data)	R1 = 0.0807, wR2 = 0.1833	R1 = 0.0453, wR2 = 0.1033	R1 = 0.1038, wR2 = 0.2640
largest diff peak and hole (e Å^{-3})	0.929 and −1.350	0.787 and −1.883	1.421 and −2.591

^{a} Conditions: wavelength, 0.710 73 Å; refinement by full-matrix least squares on F^2; temperature, 183(2) K. ^{b} One molecule of toluene was present per molybdenum. ^{c} Excess electron density due to a highly disordered THF molecule was found in voids (a total of 230 electrons per unit cell). It was "removed" using the program SQUEEZE.[51]

Table 2. Selected Bond Lengths (Å) and Angles (deg) for the Anions in [Et$_3$NH][F$_5$NMe]MoCl$_3$ (1a), [Et$_3$NH]{[F$_5$NMe]WCl$_3$} (2a), and [Bu$_4$N]{[CF$_3$NMe]MoCl$_3$} (12b)

	1a	2a	12b
M−N(1)	1.991(8)	1.996(6)	2.003(8)
M−N(2)	2.216(8)	2.230(6)	2.250(8)
M−N(3)	2.019(9)	2.010(6)	1.995(9)
M−Cl(1)	2.410(3)	2.4010(18)	2.377(3)
M−Cl(2)	2.514(3)	2.4505(19)	2.446(3)
M−Cl(3)	2.480(3)	2.4845(19)	2.496(3)
N(1)−M−N(2)	77.9(3)	78.2(2)	81.0(3)
N(1)−M−N(3)	102.9(3)	100.3(2)	96.2(3)
N(1)−M−Cl(1)	94.6(2)	97.60(18)	97.3(2)
N(1)−M−Cl(2)	86.8(2)	92.13(19)	89.7(3)
N(1)−M−Cl(3)	167.8(2)	170.82(19)	169.2(3)
N(2)−M−Cl(1)	171.5(2)	174.80(18)	172.9(3)
N(2)−M−Cl(2)	87.7(2)	90.59(19)	93.2(3)
N(2)−M−Cl(3)	98.1(2)	94.54(18)	90.1(2)
Cl(1)−M−Cl(2)	96.11(9)	92.67(7)	92.29(10)
Cl(2)−M−Cl(3)	81.56(10)	82.21(7)	84.67(11)

red to green. Green paramagnetic [F$_5$NMe]MoMe$_2$ (**3**) was isolated in 50% yield (eq 4) after recrystallization

(4)

3
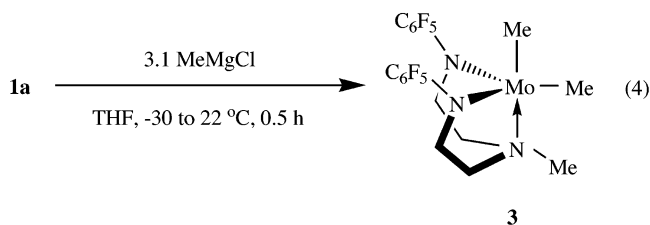
from diethyl ether and pentane. The ^{19}F and ^{1}H NMR spectra of **3** in THF are analogous to those of **1a** and other d^2 compounds in this category. As expected, resonances corresponding to the methyl groups directly bound to the metal could not be located, as a conse-
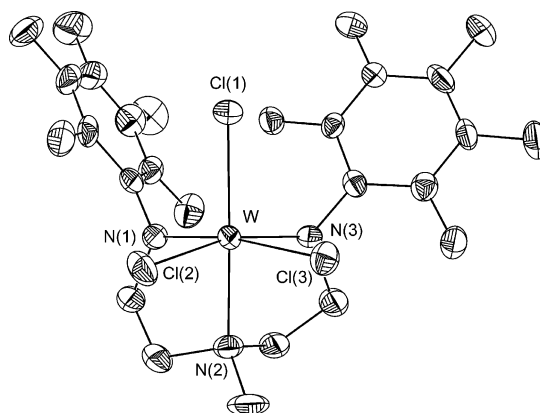
Figure 4. Thermal ellipsoid plot (35% probability level) of the anion structure of [Et$_3$NH]{[F$_5$NMe]WCl$_3$} (**2a**). Hydrogens have been omitted for clarity.

quence of the proximity of these protons to the paramagnetic metal center. The magnetic susceptibility of **3** in solution (Evans method) was found to be 3.1 μ_B.

Compound **3** crystallized from ether in the monoclinic space group $P2_1/n$. Crystallographic data, collection parameters, and refinement parameters are given in Table 3, while selected bond lengths (Å) and angles (deg) can be found in Table 4. Compound **3** was found to be approximately a trigonal bipyramid, as shown in Figure 5. The C(1)−Mo−N(2) bond angle is 171.4(2)°, while N(1)−Mo−N(3) = 123.3(2)° and C(2)−Mo−N(3) = 114.9-(2)°. The Mo−C$_{ax}$ bond length (2.269(4) Å) is significantly longer than the Mo−C$_{eq}$ bond length (2.134(6) Å). The metal−amido and metal−amine bond lengths are in the expected range.

Addition of 1 equiv of 2,6-lutidinium chloride to **3** in diethyl ether yielded light green, paramagnetic [F$_5$-NMe]MoMeCl (**4a**), which could be isolated in 47% yield

**Table 3. Crystallographic Data, Collection Parameters, and Refinement Parameters for [F$_5$NMe]MoMe$_2$ (3),
[F$_5$NMe]Mo(CH$_2$CMe$_3$)Cl (4b), and [F$_3$NMe]Mo(CH$_2$CMe$_3$)(CCMe$_3$) (9)**

|	**3**	**4b**	**9**
empirical formula	C$_{19}$H$_{17}$N$_3$F$_{10}$Mo	C$_{22}$H$_{22}$N$_3$ClF$_{10}$Mo	C$_{27}$H$_{35}$N$_3$F$_6$Mo
formula wt	573.29	649.81	611.52
cryst syst	monoclinic	orthorhombic	monoclinic
space group	$P2_1/n$	$Pna2_1$	$P2_1/n$
unit cell dimens			
a (Å)	11.7234(4)	14.8706(16)	12.5977(9)
b (Å)	12.0802(4)	10.3947(11)	14.7520(11)
c (Å)	16.2635(5)	15.9370(17)	15.0992(11)
α (deg)	90	90	90
β (deg)	110.599 (1)	90	98.1530(10)
γ (deg)	90	90	90
V (Å^3)	2156.0(1)	2463.5(5)	2777.7(4)
Z	2	4	4
calcd density (Mg/m^3)	1.769	1.752	1.462
abs coeff (mm^{-1})	0.706	0.735	0.533
F(000)	1139	1292	1256
cryst size (mm^3)	0.5 × 0.3 × 0.2	0.2 × 0.1 × 0.1	0.2 × 0.2 × 0.2
θ range for data collecn (deg)	3.74−26.58	2.34−22.50	2.66−23.28
index ranges	−13 ≤ h ≤ 12, −13 ≤ k ≤ 8, −14 ≤ l ≤ 18	−15 ≤ h ≤ 16, −16 ≤ k ≤ 11, −10 ≤ l ≤ 17	−10 ≤ h ≤ 14, −16 ≤ k ≤ 16, −16 ≤ l ≤ 16
no. of rflns collected	8595	8843	10 874
no. of indep rflns	3098 (R_{int} = 0.0395)	2838 (R_{int} = 0.0383)	3983 (R_{int} = 0.0390)
completeness to θ_{max} (%)		99.8	99.5
abs cor	empirical	none	none
max and min transmissn	0.4139 and 0.3262		
no. of data/restraints/params	3096/0/328	2838/1/340	3983/0/362
goodness of fit on F^2	1.222	1.080	0.943
final R indices ($I > 2\sigma(I)$)	R1 = 0.0457, wR2 = 0.1108	R1 = 0.0310, wR2 = 0.0769	R1 = 0.0294, wR2 = 0.0770
R indices (all data)	R1 = 0.0496, wR2 = 0.1127	R1 = 0.0409, wR2 = 0.0821	R1 = 0.0374, wR2 = 0.0812
largest diff peak and hole (e Å^{-3})	0.666 and −0.352	0.386 and −0.400	0.337 and −0.526

[a] Conditions: wavelength, 0.710 73 Å; refinement by full-matrix least squares on F^2; temperature 183(2) K.

**Table 4. Selected Bond Lengths (Å) and Angles (deg) for [F$_5$NMe]MoMe$_2$ (3), [F$_5$NMe]Mo(CH$_2$CMe$_3$)Cl (4b),
and [F$_3$NMe]Mo(CCMe$_3$)(CH$_2$CMe$_3$) (9)**

3		**4b**		**9**	
Mo−N(1)	1.970(4)	Mo−N(1)	1.974(3)	Mo−N(1)	2.042(2)
Mo−N(2)	2.325(4)	Mo−N(2)	2.254(4)	Mo−N(2)	2.392(2)
Mo−N(3)	1.957(4)	Mo−N(1A)	1.974(3)	Mo−N(3)	1.966(2)
Mo−C(1)	2.269(4)	Mo−Cl(1)	2.3847(14)	Mo−C(1)	1.776(3)
Mo−C(2)	2.134(6)	Mo−C(1)	2.141(6)	Mo−C(6)	2.143(3)
N(1)−Mo−N(2)	78.4(2)	N(1)−Mo−N(2)	79.67(10)	N(1)−Mo−N(2)	75.42(9)
N(1)−Mo−N(3)	123.3(2)	N(1)−Mo−N(1a)	126.01(19)	N(1)−Mo−N(3)	126.43(9)
N(1)−Mo−C(1)	98.9(2)	N(1)−Mo−Cl(1)	94.50(9)	N(1)−Mo−C(1)	101.19(10)
N(1)−Mo−C(2)	118.8(2)	N(1)−Mo−C(1)	114.75(10)	N(1)−Mo−C(6)	112.67(11)
N(2)−Mo−C(1)	171.4(2)	N(2)−Mo−Cl(1)	166.69(12)	N(2)−Mo−C(1)	170.66(10)
N(2)−Mo−C(2)	96.7(2)	N(2)−Mo−C(1)	90.52(19)	N(2)−Mo−C(6)	88.54(11)
C(1)−Mo−C(2)	91.7(2)	C(1)−Mo−Cl(1)	102.79(16)	C(1)−Mo−C(6)	100.78(12)
		Mo−C(1)−C(2)	130.1(4)	Mo−C(1)−C(2)	173.0(2)
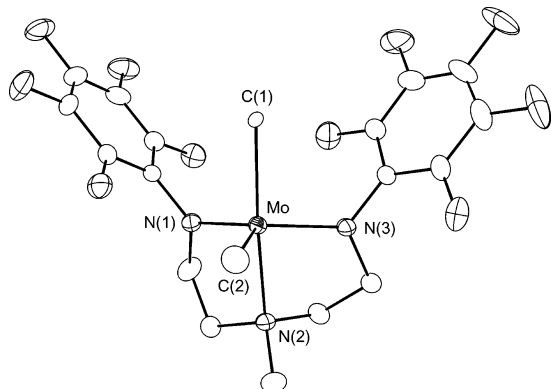
Figure 5. Thermal ellipsoid plot (30% probability level) of the structure of [F$_5$NMe]MoMe$_2$ (**3**). Hydrogens have been omitted for clarity.

(eq 5). On the basis of the structure of **3** and related molecules reported here, we believe that **4a** is likely to be a trigonal bipyramid with the two amido nitrogens
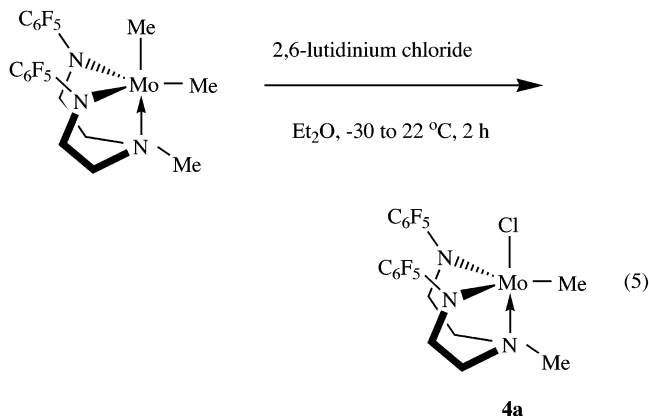
in the equatorial plane. However, we do not know whether the methyl group is in the equatorial position or the axial position. The ^{19}F NMR spectrum of **4a** in C$_6$D$_6$ is similar to those of other compounds discussed here, although the ^{1}H NMR spectrum of **4a** in C$_6$D$_6$
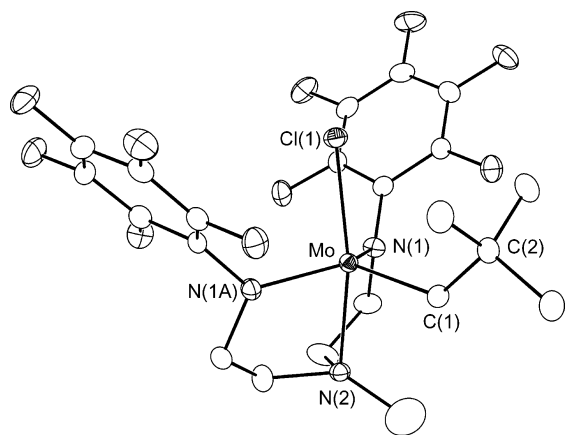
Figure 6. Thermal ellipsoid plot (30% probability level) of the structure of [F₅NMe]Mo(CH₂CMe₃)Cl (**4b**). Hydrogens have been omitted for clarity.

revealed only three very broad resonances for the ligand CH₂ and CH₃ groups at 14.3, −54.6, and −84.4 ppm. As expected, a resonance for the methyl group bound to the metal could not be located.

Addition of either 2 or 3 equiv of Me₃CCH₂MgCl to a THF solution of **1a** led to formation of deep green, paramagnetic [F₅NMe]Mo(CH₂CMe₃)Cl (**4b**), which could be isolated in 60% yield. Five resonances of approximately equal intensity were found in the ¹⁹F NMR spectrum of **4b** in CD₂Cl₂, while in the ¹H NMR spectrum in CD₂Cl₂ five broadened resonances were found at 9.5, 6.3, 3.2, −59.6, and −82.8 ppm. The most intense resonance, at 3.2 ppm, was assigned to the protons of the CMe₃ group. A resonance corresponding to the methylene protons of the neopentyl group could not be located. For **4b** in CD₂Cl₂ at room temperature μ_{eff} was found to be 3.1 μ_B (Evans method), as expected. The solubility of **4b** in common solvents other than THF was surprisingly low, which made isolation of pure material tedious and which limited the amount of **4b** that could be synthesized and purified readily.

Complex **4b** crystallized from THF in the orthorhombic space group *Pna*2₁ as dark green blocks. Crystallographic data, collection parameters, and refinement parameters are given in Table 3, while selected bond lengths (Å) and angles (deg) are listed in Table 4. As shown in Figure 6, compound **4b** is approximately a trigonal bipyramid in which the neopentyl group and the two amido nitrogens of the [F₅NMe]²⁻ ligand comprise the equatorial plane and the chloride is in the apical site trans to the amine donor. The Cl(1)−Mo−N(2) angle is only 166.69(12)°, as a consequence of steric interaction between the apical chloride and the neopentyl's *tert*-butyl group, which is forced to point toward the chloride as a consequence of steric interaction with the methyl group on the central amine donor. All bond lengths are in the expected range and are similar to those found in [(3,5-Cl₂C₆H₃NCH₂CH₂)₂NMe]Mo(CH₂-CMe₃)Cl,[24] whose structure is analogous to that of **4b**. The low solubility of **4b** and similar species remains a curiosity.

The reaction between [Et₃NH]{[F₅NMe]WCl₃} and either 2 or 3 equiv of Me₃CCH₂MgCl in THF led to green, paramagnetic [F₅NMe]W(CH₂CMe₃)Cl (**5**) in 45% yield. Complex **5** is believed to have a structure similar to that of **4b**. Like **4b**, **5** also has surprisingly low

solubility in common organic solvents other than THF. A measurement of the magnetic moment in CD₂Cl₂ by the Evans method gave a value of 2.6 μ_B for μ_{eff}, a figure that is similar to μ_{eff} for other d² W complexes reported here.

Attempts to force more than one neopentyl group to add to Mo or W to yield species analogous to **3** or neopentyl/neopentylidyne species analogous to those reported below were not successful.

Synthesis and Characterization of {[F₃NMe]-MCl₃}⁻ Species (M = Mo, W). A report that two fluorides in pentafluorophenyl rings bound to secondary amine nitrogens could be replaced upon treatment with LiAlH₄ in refluxing THF[30] prompted us to attempt a similar reaction starting with (C₆F₅NHCH₂CH₂)₂NMe. A mixture of (C₆F₅NHCH₂CH₂)₂NMe and 2 equiv of LiAlH₄ in THF was heated to reflux for 4 h. Standard workup led to the isolation of (C₆H₂F₃NHCH₂CH₂)₂NMe (H₂[F₃NMe]) as a thick yellow oil in 85% yield on a 4−5 g scale (eq 6). Replacement of two fluorine atoms on each

$$ (6) $$
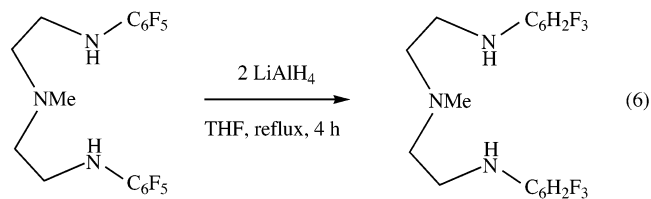
aryl ring with two hydrogen atoms was consistent with observation of a multiplet at 5.73 ppm in the ¹H NMR spectrum of (C₆H₂F₃NHCH₂CH₂)₂NMe in C₆D₆ and two resonances at −136.3 and −177.8 ppm in a 2:1 ratio in the ¹⁹F NMR spectrum in C₆D₆. X-ray crystallographic studies of complexes containing the [F₃NMe]²⁻ ligand (described later) proved that the aryl is a 3,4,5-C₆H₂F₃ ring. Formation of a 2,4,6-C₆H₂F₃ ring was proposed in the compounds in the original report.[30]

A deep red, homogeneous solution formed after several seconds when orange MoCl₄(THF)₂ was stirred into a solution of (C₆H₂F₃NHCH₂CH₂)₂NMe in THF. Subsequent addition of 2 equiv of NEt₃ caused the solution to turn dark purple and an off-white precipitate of Et₃NHCl to form. Paramagnetic [Et₃NH]{[F₃NMe]MoCl₃} (**6a**) was isolated as a dark purple powder in 87% yield by filtering the reaction mixture and precipitating the product with pentane (eq 7). The ¹⁹F NMR spectrum of

$$ (7) $$
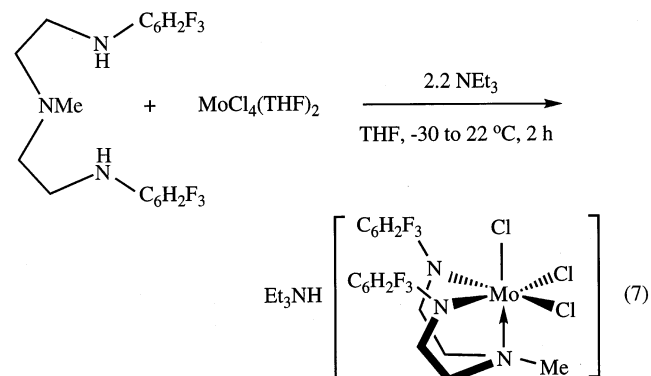
6a in THF displayed two resonances in a 2:1 ratio at

(30) Buchler, S.; Meyer, F.; Jacobi, A.; Kircher, P.; Zsolnai, L. *Z. Naturforsch.* **1999**, *54b*, 1295.

−104.85 and −206.57 ppm, consistent with free rotation of the $C_6H_2F_3$ rings about the N−C_{ipso} bond. Complex **6a** is believed to have a structure analogous to the structures of [Et₃NH]{[F₅NMe]MoCl₃} (Figure 3) and [Et₃NH]{[(3,5-$C_6Cl_2H_3NCH_2CH_2$)₂NMe]MoCl₃}.[24]

The reaction between **6a** and tetrabutylammonium chloride in THF gave the more soluble complex [Bu₄N]-{[F₃NMe]MoCl₃} (**6b**) in 90% yield as a purple powder. The ¹⁹F NMR spectrum of **6b** in C_6D_6 displayed two resonances at −103.89 ppm and −207.48 ppm in a 2:1 ratio assigned to the meta and para fluorines of the $C_6H_2F_3$ rings on the [F₃NMe]²⁻ ligand, while the ¹H NMR spectrum of **6b** in C_6D_6 displayed resonances corresponding to the tetrabutylammonium ion at 1.64, 1.21, and 0.97 ppm. Broadened resonances corresponding to the [F₃NMe]²⁻ ligand in the ¹H NMR spectrum were found at 28.25, 6.11, −3.84, −29.67, −96.83, and −99.60 ppm. A measurement of the magnetic moment of **6b** by the Evans method[27] as modified by Sur[28] in C_6D_6 gave μ_{eff} = 3.1 μ_B.

A reaction between WCl₄(dme), H₂[F₃NMe], and 2 equiv of NEt₃ in diethyl ether produced [Et₃NH]{[F₃-NMe]WCl₃} (**7a**) in 86% yield. The more soluble tetrabutylammonium analogue [Bu₄N]{[F₃NMe]WCl₃} (**7b**) was synthesized by salt metathesis of **7a** with Bu₄NCl in THF in 78% yield. The ¹⁹F and ¹H NMR spectra of **7a** and **7b** are entirely analogous to those of **6a** and **6b**, except that the resonances for **7a** and **7b** are sharper. A measurement of the magnetic moment of **6b** by the Evans method[27] in C_6D_6 gave μ_{eff} = 2.7 μ_B, consistent with the tungsten center having two unpaired electrons.

Organometallic Complexes of Molybdenum and Tungsten That Contain the [F₃NMe]²⁻ Ligand. Attempts to prepare and isolate methyl complexes of molybdenum containing the [F₃NMe]²⁻ ligand analogous to [F₅NMe]MoMe₂ and [F₅NMe]MoMeCl were not successful. However, organometallic derivatives could be prepared that contain neopentyl and (trimethylsilyl)-methyl groups. The reaction between [Et₃NH]{[F₃NMe]-MoCl₃} and 2 equiv of Me₃CCH₂MgCl in THF led to green, paramagnetic [F₃NMe]Mo(CH₂CMe₃)Cl (**8**) in 43% yield. Like other monoalkyl complexes of this type, **8** was only sparingly soluble in common organic solvents, with the exception of THF. The structure of **8** is believed to be approximately trigonal bipyramidal with the neopentyl group in an equatorial position, on the basis of the structures of crystallographically characterized **4b** and [Ar_{Cl}NNMe]Mo(CH₂CMe₃)Cl (Ar_{Cl} = 3,5-$C_6Cl_2H_3$).[24]
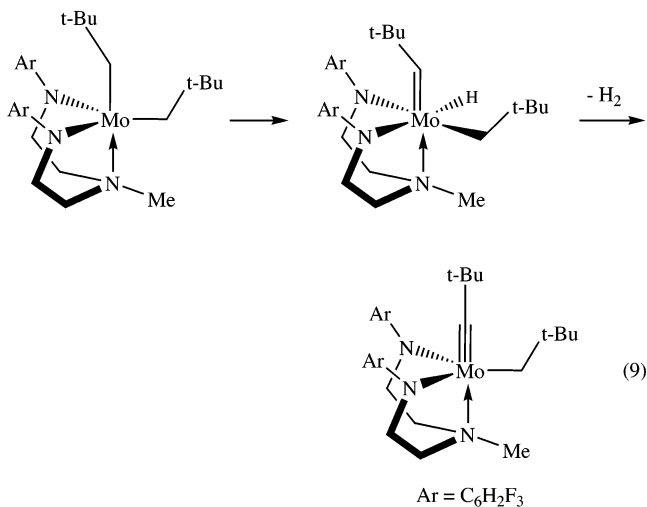
The reaction between [Et₃NH]{[F₃NMe]MoCl₃} and 3 equiv of Me₃CCH₂MgCl in THF led to diamagnetic [F₃NMe]Mo(CH₂CMe₃)(CCMe₃) (**9**) in 68% yield (eq 8). The ¹H NMR spectrum of **9** showed two singlet resonances corresponding to two distinct *tert*-butyl groups at 1.37 and 0.66 ppm. A resonance at 1.56 ppm was assigned to the CH₂ protons of the neopentyl ligand. The alkylidyne carbon resonance was located at 307.7 ppm in the ¹³C NMR spectrum in C_6D_6, which is typical for a d⁰ alkylidyne complex.[31] For comparison, the alkylidyne carbon resonance for [Ar_{Cl}NNMe]Mo(CCMe₃)(CH₂-CMe₃) was located at 309.8 ppm.[24]

Amber crystals of **9** were grown from a mixture of benzene and pentane at −30 °C. Crystallographic data,

(31) Schrock, R. R. *Chem. Rev.* **2002**, *102*, 145.
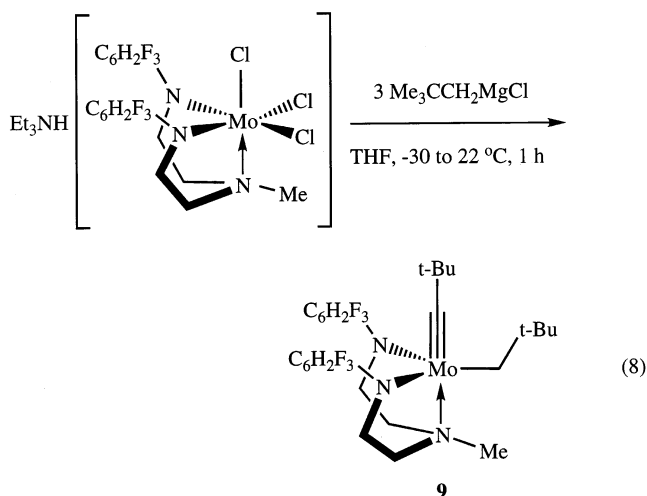
collection parameters, and refinement parameters for **9** are given in Table 3, and selected bond lengths (Å) and angles (deg) are listed in Table 4. The structure of **9** is approximately a trigonal bipyramid, with the neopentylidyne ligand occupying an axial position trans to the amine donor of the [F₃NMe]²⁻ ligand (Figure 7). The fluorides were found in the 3-, 4-, and 5-positions of the aryl rings. The two amido nitrogens of the [F₃NMe]²⁻ ligand and the neopentyl group's methylene group are found in the equatorial positions. The short Mo−C(1) bond length (1.776(3) Å) is that expected for a metal−carbon triple bond.[31] The *tert*-butyl group of the neopentyl group is turned away from the methyl group on the central amine donor, which forces the axial neopentylidyne ligand away from the axial position slightly (N(2)−Mo−C(1) = 170.66(10)°).

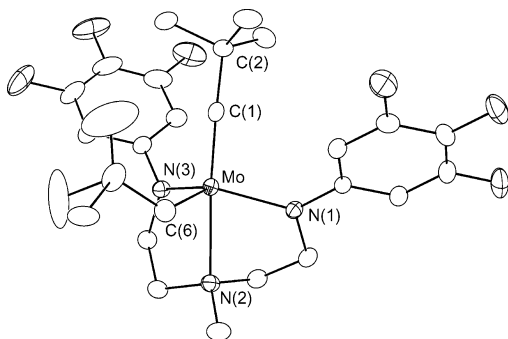We propose that the alkylidyne ligand in **9** is formed through an α,α-dehydrogenation reaction in which [F₃-NMe]Mo(CH₂CMe₃)₂ is the intermediate, as shown in eq 9.[20] This proposal is supported by the amount of

dihydrogen produced in the reaction between [Et₃NH]-{[F₃NMe]MoCl₃} and 3 equiv of Me₃CCH₂MgCl, as measured with a Toepler pump. A yield of 90% was found for the collected H₂ (mmol of H₂/mmol [of F₃NMe]-Mo(CH₂CMe₃)(CCMe₃) produced), consistent with the proposal shown in eq 9.
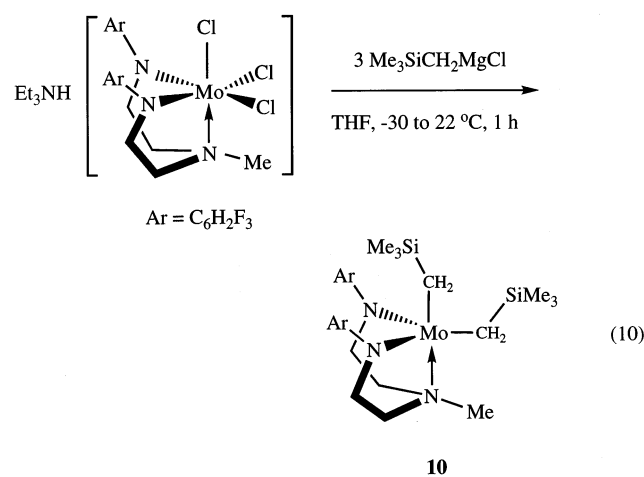
The reaction between [Et₃NH]{[F₃NMe]MoCl₃} and 3 equiv of Me₃SiCH₂MgCl in THF led to paramagnetic,

Figure 7. Thermal ellipsoid plot (30% probability level) of the structure of $[F_3NMe]Mo(CH_2CMe_3)(CCMe_3)$ (**9**). Hydrogens have been omitted for clarity.

purple $[F_3NMe]Mo(CH_2SiMe_3)_2$ (**10**) in 72% yield (eq 10). The ^{19}F NMR spectrum of **10** displayed two reso-

(10)

10

nances in a 2:1 ratio at -99.06 and -160.17 ppm, corresponding to the freely rotating $C_6H_2F_3$ rings on the $[F_3NMe]^{2-}$ ligand, while the ^1H NMR spectrum of **10** showed two broad resonances at 3.6 and 1.2 ppm, assigned to the two different Me_3Si groups. Unfortunately, no suitable crystals for X-ray diffraction could be obtained. In one instance a single crystal suitable for data collection was obtained, but the structure was revealed to be a bridging dinitrogen complex of molybdenum, $\{[F_3NMe]Mo(CH_2SiMe_3)\}_2(\mu\text{-}N_2)$, in which the dinitrogen is located in the axial position.[32] Since we could not find a method that yielded $\{[F_3NMe]Mo(CH_2\text{-}SiMe_3)\}_2(\mu\text{-}N_2)$ reproducibly in reasonable quantities, we mention it here only for informational purposes. The low solubility of the dimeric dinitrogen complex is the primary reason it was discovered and isolated.

The reaction between $[Et_3NH]\{[F_3NMe]WCl_3\}$ and 3 equiv of either Me_3CCH_2MgCl *or* Me_3SiCH_2MgCl yielded five-coordinate diamagnetic, alkylidyne complexes of the type $[F_3NMe]W(CH_2R)(CR)$ (R = CMe_3 (**11a**), $SiMe_3$ (**11b**)). The alkylidyne carbon atom resonances were located at 295.7 ppm in **11a** and 336.8 ppm in **11b** in ^{13}C NMR spectra. We assume that $[F_3NMe]W(CH_2\text{-}CMe_3)_2$ and $[F_3NMe]W(CH_2SiMe_3)_2$ are intermediates in the reactions in which **11a** and **11b** are formed. The more facile α,α-dehydrogenation in $[F_3NMe]W(CH_2\text{-}$

$SiMe_3)_2$ versus that in **10** is consistent with what has been found in W and Mo triamido/amine complexes.[18−21]

Synthesis and Characterization of Mo Complexes That Contain the $[(3\text{-}CF_3C_6H_4NCH_2CH_2)_2\text{-}NMe]^{2-}$ Ligand. One of the main limitations to the chemistry of complexes that contain the $[F_5NMe]^{2-}$ ligand, we believe, is the presence of side reactions that involve the ortho fluorides in the pentafluorophenyl group. An example of such a complication, exchange of two dimethylamido ligands on Mo with two ortho fluorides on the $[F_5NMe]^{2-}$ ligand, was presented in a preliminary communication.[22] Although complications involving ortho fluorides of course are not possible in complexes that contain the $[F_3NMe]^{2-}$ ligand, synthesis of large quantities of $H_2[F_3NMe]$ by the current route is limited. Therefore, we searched for a $H_2[(ArylNCH_2\text{-}CH_2)_2NMe]$ species that (i) could be prepared on a large scale, (ii) would react with $MoCl_4$ in the presence of triethylamine to give $[Et_3NH]\{[(ArylNCH_2CH_2)_2NMe]\text{-}MoCl_3\}$, and (iii) would lack any substituent in the ortho position. It would be most desirable if the aryl group were relatively electron withdrawing (in order to increase the acidity of the amine proton in an initial adduct) and were to contain one or more fluorides (in order to allow for ^{19}F NMR to be a viable diagnostic tool for following reactions that involve paramagnetic species). These considerations, in addition to the low cost of $3\text{-}CF_3C_6H_4NH_2$, attracted us to the $3\text{-}CF_3C_6H_4$ group.

The triamine $(3\text{-}CF_3C_6H_4NHCH_2CH_2)_2NMe$ ($H_2[CF_3\text{-}NMe]$) can be synthesized conveniently in three steps, the first being the known synthesis[33] of $MeN(CH_2\text{-}CO_2H)_2$ on a mole scale in good yield. Phosphite-mediated coupling[34−36] of the diacid with 3-aminobenzotrifluoride, as shown in eq 11, and the borane−dimethyl sulfide reduction of the amide,[37] as shown in eq 12, proceed smoothly in good yield. A relatively large

(11)

(12)
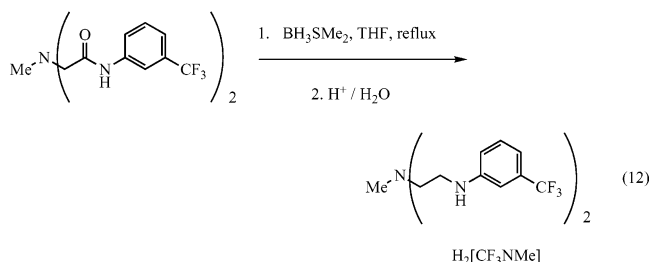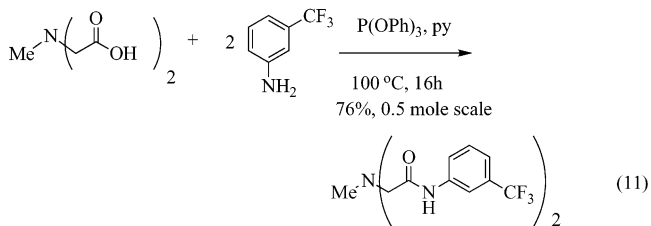
$H_2[CF_3NMe]$

quantity of $H_2[CF_3NMe]$ therefore can be obtained relatively easily.

Addition of $MoCl_4(THF)_2$ to a THF solution of $H_2[CF_3\text{-}NMe]$ followed by 2 equiv of triethylamine led to a

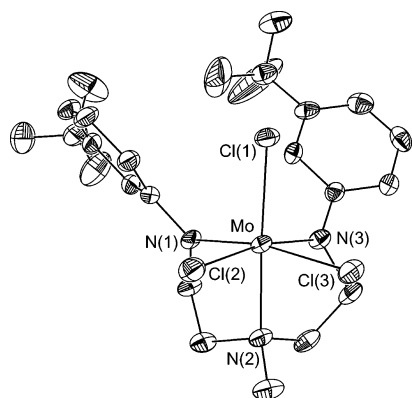(32) Cochran, F. Ph.D. Thesis, Massachusetts Institute of Technology, 2002.

(33) Berchet, G. J. *Org. Synth.* **1938**, *18*, 56.
(34) Barnes, D. J.; Chapman, R. L.; Vagg, R. S.; Watton, E. C. *J. Chem. Eng. Data* **1978**, *23*, 349.
(35) Liu, X.; Ilankumaran, P.; Guzei, I. A.; Verkade, J. G. *J. Org. Chem.* **2000**, *65*, 701.

Figure 8. Thermal ellipsoid plot (35% probability level) of the anion structure of [Bu₄N]{[CF₃NMe]MoCl₃} (**12b**). Hydrogens have been omitted for clarity.

precipitate of Et₃NHCl and a purple solution that contains [Et₃NH]{[CF₃NMe]MoCl₃} (**12a**). [Bu₄N]{[CF₃-NMe]MoCl₃} (**12b**) can be prepared using conditions analogous to those employed to prepare **1b** and **6b**. Compound **12b** also can be prepared by treating the solution of crude **12a** with excess tetrabutylammonium chloride. Both **12a** and **12b** are dark purple, paramagnetic solids analogous to compounds that have been discussed previously in this paper. Relatively sharp CF_3 resonances are observed in ^{19}F spectra at -54.5 and -54.8 ppm for **12a** and **12b**, respectively.

Complex **12b** crystallized from a THF/pentane solution -30 °C in the triclinic space group $P\bar{1}$ as dark purple plates. Crystallographic data, collection parameters, and refinement parameters can be found in Table 1, selected bond lengths (Å) and angles (deg) are listed in Table 2, and a thermal ellipsoid plot of the anion is shown in Figure 8. The structure of the {[CF₃NMe]-MoCl₃}⁻ ion is analogous to the previously characterized triethylammonium salts **1a** and **2a**; however, the weakly coordinating tetrabutylammonium cation shows no association with the anion in the solid state. A comparison of bond angles and distances of the cores of **1a**, **2a**, and **12b** reveal minimal reorganization of the anion core upon changing the metal from Mo to W or the cation from Et₃NH⁺ to Bu₄N⁺. The M−N$_{amide}$ distances are virtually the same in the three structures.

The paramagnetic dialkyl complex [CF₃NMe]Mo(CH₂-SiMe₃)₂ (**13**) can be prepared in 60% yield through addition of 3.1 equiv of ((trimethylsilyl)methyl)magnesium chloride to **12a** in THF at -78 °C. The ^{19}F resonance is observed at -55.8 ppm. Compound **13** is dark red and paramagnetic, with properties that are very similar to those of **10**. We have been unable to obtain diffraction-quality crystals of **13**. It seems likely that it is a pseudo trigonal bipyramid analogous to **3**. As was found in the case of the [F₃NMe] ligand, all attempts to synthesize a stable dimethyl species were unsuccessful.

Addition of 2 equiv of Me₃CCH₂MgCl in ether to [Et₃-NH]{[CF₃NMe]MoCl₃} in THF led to formation of dark green, paramagnetic [CF₃NMe]Mo(CH₂CMe₃)Cl (**14**), while addition of 3 equiv of Me₃CCH₂MgCl in ether to [Et₃NH]{[CF₃NMe]MoCl₃} in THF led to formation of

yellow crystalline [CF₃NMe]Mo(CCMe₃)(CH₂CMe₃) (**15**) in high yield. The alkylidyne carbon resonance was found at 307.7 ppm in **15**. Both compounds are analogous to other compounds that have been discussed here.

Discussion

Little is known about the chemistry of Mo(IV) and W(IV) diamidoamine complexes in general, and alkyl complexes in particular. We are most interested in d² alkyl complexes as a consequence of our discovery of the α,α-dehydrogenation process in d² alkyl complexes of tungsten(IV) that contain the $[(Me_3SiNCH_2CH_2)_3N]^{3-}$ ligand.[18] α,α-Dehydrogenation is an intriguing way to form d⁰ alkylidyne complexes from reduced alkyl complexes, even (in $[(Me_3SiNCH_2CH_2)_3N]W(CH_2R)$ species[21]) when the CH₂R group contains β-protons. For example, some α,α-dehydrogenation could conceivably be taking place when neopentyllithium is added to WCl₆ or MoCl₅ in ether to give complexes of the type M(C-t-Bu)(CH₂-t-Bu)₃ (in low yield), since the metal is reduced before it is alkylated under the conditions employed in the original experiments.[38] α,α-Dehydrogenation is presumed to involve formation first of an alkylidene hydride complex by α-elimination followed by an α-abstraction of the remaining alkylidene α-hydrogen by the hydride (e.g., as shown in eq 9). In $[(Me_3SiNCH_2CH_2)_3N]$-MCH₂R complexes it was shown that the α,α-dehydrogenation reaction to give $[(Me_3SiNCH_2CH_2)_3N]M\equiv CR$ complexes was most facile when R = t-Bu and M = W. In fact, the only $[(Me_3SiNCH_2CH_2)_3N]WCH_2R$ complex that could be isolated was $[(Me_3SiNCH_2CH_2)_3N]WCH_3$, since the methyl group is the least likely to undergo α-elimination or α-abstraction reactions. The only $[(Me_3SiNCH_2CH_2)_3N]MoCH_2R$ complex that could be induced to lose dihydrogen relatively cleanly was $[(Me_3SiNCH_2CH_2)_3N]MoCH_2$-t-Bu, since the neopentyl group is the most likely to undergo α-elimination or α-abstraction reactions.[39] Similar reactions of molybdenum and tungsten alkyl complexes that contain the $[(C_6F_5NCH_2CH_2)_3N]^{3-}$ ligand are known,[19] but in general the synthesis of d² alkyl complexes and α,α-dehydrogenation in $[(C_6F_5NCH_2CH_2)_3N]^{3-}$ species has been more limited in scope, perhaps as a consequence of side reactions that involve the ortho fluorides. Formation of [(arylNCH₂-CH₂)₃N]MCH₂R complexes, where the aryl group is (for example) an ordinary phenyl group,[26,40,41] has not yet been investigated.

The study of Mo and W d² alkyl complexes that contain a $[(arylNCH_2CH_2)_2NMe]^{2-}$ ligand are complicated if the amine donor remains bound to the metal, since an alkyl can reside in either an "axial" or an "equatorial" site, and since the rate of α-elimination or -abstraction could differ dramatically for an alkyl in each of these sites. On the basis of what we have seen so far in this study, it appears that an alkyl group prefers to occupy the equatorial site in an alkyl chloride complex, and α,α-dehydrogenation from the equatorial site is not facile, even for a neopentyl group bound to

(36) Ray, M.; Golombek, A.; Hendrich, M. P.; Young, V. G., Jr.; Borovik, A. S. *J. Am. Chem. Soc.* **2000**, *118*, 6084.
(37) Lane, C. F. *Chem. Rev.* **1976**, *76*, 773.

(38) Clark, D. N.; Schrock, R. R. *J. Am. Chem. Soc.* **1978**, *100*, 6774.
(39) Schrock, R. R. In *Reactions of Coordinated Ligands*; Braterman, P. R., Ed.; Plenum: New York, 1986.
(40) Greco, G. E.; Popa, A. I.; Schrock, R. R. *Organometallics* **1998**, *17*, 5591.
(41) Greco, G. E. Ph.D. Thesis, Massachusetts Institute of Technology, 2000.

W. Therefore, we suspect that it is the axial alkyl group trans to the amine donor in a dialkyl complex that is prone to α-elimination followed by α-abstraction to give a species that contains the alkylidyne in the axial position (e.g. as shown in eq 9). This is, of course, the same type of site where α,α-dehydrogenation takes place in triamidoamine complexes. Perhaps the most surprising feature of α,α-dehydrogenation reactions in diamidoamine dialkyl complexes is that reductive elimination of alkane does not compete with formation of the alkyl/alkylidyne product.

At this stage we believe that the two unpaired electrons in a dialkyl complex reside in the d_{xz} and d_{yz} orbitals (if the z axis contains the N_{amine}–M bond). However, we suspect that the first (reversible[20]) α-elimination step may take place from the singlet state, in which one of these orbitals is doubly occupied and the other is empty. The possibility that a singlet state is required adds to the complexity that surrounds reactions of this general type. The relationship between spin states and reaction rates in transition-metal chemistry has been a subject of controversy,[21,42,43] although evidence that reaction rates *can* depend on spin state, at least when a second- or third-row metal is involved, has been accumulating.[44–48] Finally, it should be noted that in very crowded complexes, e.g., dineopentyl species, the amine donor may essentially dissociate from the metal, thereby creating a pseudo *tetrahedral* species with approximately C_s symmetry, in which a singlet state may be more accessible. In short, it is premature to attempt to explain in detail how α,α-dehydrogenation takes place in complexes of the type discussed here.

In the chemistry presented here it seems that the $[F_5NMe]^{2-}$ ligand sterically protects the metal to a greater degree than either the $[F_3NMe]^{2-}$ or $[CF_3NMe]^{2-}$ ligands, as one might expect. For example, although $[F_5NMe]MoMe_2$ (3) could be prepared, no $[F_3NMe]^{2-}$ or $[CF_3NMe]^{2-}$ analogues could be prepared; we suspect that they decompose too readily bimolecularly. Only $[F_5NMe]Mo(CH_2CMe_3)Cl$ (4b) could be prepared, while all attempts to add two neopentyl groups (which would almost certainly would yield $[F_5NMe]Mo(CCMe_3)(CH_2CMe_3)$) failed, perhaps in part because of side reactions involving aryl fluorides. In contrast, $[F_3NMe]^{2-}$ and $[CF_3NMe]^{2-}$ bis((trimethylsilyl)methyl) and neopentyl neopentylidyne complexes (which arise via dineopentyl compounds) could be prepared readily. The chemistry of $[(C_6F_5NCH_2CH_2)_3N]^{3-}$ complexes of Mo and W[19] also was found to be more limited than that of $[(Me_3SiNCH_2CH_2)_3N]^{3-}$ complexes of Mo and W,[20,21] perhaps again because of steric problems and side reactions that involve attack in the pentafluorophenyl rings, as noted above. Formation of alkylidynes by α,α-dehydrogenation again appears to be more facile for tungsten than for molybdenum diamidoamine complexes reported here

and for neopentyl complexes versus (trimethylsilyl)-methyl complexes.

In a preliminary communication we reported that heating a benzene solution of $[F_3NMe]Mo(CH_2SiMe_3)_2$ at 62 °C for 24 h led to formation of $\{[F_3NMe]Mo(CSiMe_3)\}_2$ in 37% yield, a species that contains bridging alkylidyne ligands and a Mo–Mo bond. Therefore, bimolecular alternatives to intramolecular α,α-dehydrogenation in some $[(arylNCH_2CH_2)_2NMe]Mo(CH_2R)_2$ species are competitive. Now that $[CF_3NMe]^{2-}$ complexes are available in quantity, in particular, $[CF_3NMe]Mo(CH_2SiMe_3)_2$, we hope to address some of the issues surrounding the mode of decomposition of d^2 dialkyl complexes more broadly. We are especially interested in how external reagents direct decomposition pathways of dialkyl complexes. We also wish to prepare more examples of $[CF_3NMe]Mo(CH_2R)X$ species, for example, where X is an alkoxide, amide, or thiolate, to broaden our knowledge of ground-state structures and modes of decomposition of monoalkyl d^2 complexes. These studies are under way and will be reported in full in due course.

Experimental Section

General Details. All experiments were conducted under dinitrogen in a Vacuum Atmospheres glovebox or using standard Schlenk techniques. Pentane was washed with HNO_3/H_2SO_4 (5/95 v/v), sodium bicarbonate, and water, stored over $CaCl_2$, sparged with nitrogen, and then passed through a column of activated alumina. Diethyl ether and toluene were sparged with N_2 and passed through a column of activated alumina. THF was distilled from purple sodium benzophenone ketyl or sparged with nitrogen and passed through two columns of activated alumina. Acetonitrile was distilled from CaH_2. Deuterated solvents were sparged with N_2 for several minutes and dried over activated 4 Å molecular sieves unless otherwise noted. All solvents, with the exception of acetonitrile, were stored in the drybox over activated 4 Å molecular sieves. Pyridine and triethylamine were distilled from CaH_2 and stored over 4 Å molecular sieves. Molecular sieves and Celite were activated and dried in vacuo ($>10^{-3}$ Torr) for 24 h at ∼180 °C.

Reported ^1H and ^{13}C NMR chemical shifts are listed as parts per million downfield from tetramethylsilane and were referenced using the residual protio solvent resonance. Unless otherwise noted, ^{13}C NMR experiments were proton decoupled. ^{19}F NMR data were referenced using C_6F_6 in $CDCl_3$ as an external standard (-163 ppm vs $CFCl_3$). Coupling constants are listed in hertz, and routine coupling constants are not reported. Spectra were obtained at ∼22 °C unless noted otherwise. Elemental analyses were performed by H. Kolbe Microanalytical Laboratory, Mülheim an der Ruhr, Germany. All Grignard reagents were titrated before use.

$MoCl_4(THF)_2$,[49,50] $WCl_4(dme)$,[29] and $MeN(CH_2CO_2H)_2$[33] were prepared according to literature procedures. Grignard reagents were prepared by standard techniques. All other chemicals were purchased from commercial suppliers and used as received.

$(C_6F_5NHCH_2CH_2)_2NMe$ ($H_2[F_5NMe]$). Methyl iodide (1.86 mL, 29.88 mmol) was added dropwise to a stirred mixture of $(C_6F_5NHCH_2CH_2)_2NH$ (10 g, 22.97 mmol) and K_2CO_3 (17.5 g, 126.62 mmol) in CH_3CN (120 mL). The mixture was stirred for 15 h, and the volatile components were removed in vacuo.

(42) Schrock, R. R.; Shih, K.-Y.; Dobbs, D.; Davis, W. M. *J. Am. Chem. Soc.* **1995**, *117*, 6609.

(43) Detrich, J. L.; Reinaud, O. M.; Rheingold, A. L.; Theopold, K. H. *J. Am. Chem. Soc.* **1995**, *117*, 11745.

(44) Jin, N.; Groves, J. T. *J. Am. Chem. Soc.* **1999**, *121*, 2923.

(45) Veige, A. S.; Slaughter, L. M.; Wolczanski, P. T.; Matsunaga, N.; Decker, S. A.; Cundari, T. R. *J. Am. Chem. Soc.* **2001**, *123*, 6419.

(46) Keogh, D. W.; Poli, R. *J. Am. Chem. Soc.* **1997**, *119*, 2516.

(47) Jensen, V. R.; Poli, R. *J. Phys. Chem. A* **2003**, *107*, 1424.

(48) Harvey, J. N.; Poli, R.; Smith, K. M. *Coord. Chem. Rev.* **2003**, *238–239*, 347.

(49) Dilworth, J. R.; Richards, R. L.; Chen, G. J.; McDonald, J. W. *Inorg. Synth.* **1980**, *20*, 119.

(50) Stoffelbach, F.; Saurenz, D.; Poli, R. *Eur. J. Inorg. Chem.* **2001**, 2699.

(51) (a) van der Sluis, P.; Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, 194–201. (b) Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C34.

The residue was then washed with water (200 mL) and extracted into ethyl acetate (200 mL). The organic layer was separated, dried over MgSO$_4$, and concentrated to dryness. The resulting solid was then extracted with CHCl$_3$ (100 mL), and the mixture was filtered in order to remove any insoluble white powder. Removal of the CHCl$_3$ in vacuo left a waxy, yellow solid: yield 6.5 g (63%); ^{1}H NMR (CDCl$_3$) δ 4.20 (br s, 2, NH), 3.41 (q, 4, CH_2), 2.65 (t, 4, CH_2), 2.29 (s, 3, NCH_3); ^{13}C NMR (CDCl$_3$) δ 139.78, 136.55, 135.10, 131.87, 124.25 (C_6F_5), 57.05 (NCH$_3$), 43.46 (CH$_2$), 41.14 (CH$_2$); ^{19}F NMR (CDCl$_3$) δ −160.48 (d, 4, F$_o$), −164.93 (t, 4, F$_m$), −172.26 (t, 2, F$_p$); HRMS (EI) calcd for C$_{17}$H$_{13}$N$_3$F$_{10}$ 449.094 98, found 449.0940.

(C$_6$H$_2$F$_3$NHCH$_2$CH$_2$)$_2$NMe (H$_2$[F$_3$NMe]). A solution of H$_2$[F$_5$NMe] (3.37 g, 7.49 mmol) in THF (20 mL) was added via syringe to LiAlH$_4$ (1.28 g, 33.74 mmol) in THF (30 mL) at room temperature. The reaction mixture was heated to reflux for 4 h, cooled to room temperature, and stirred for an additional 15 h. Water was then added dropwise until gas evolution ceased. The reaction mixture was filtered through Celite, and the precipitate was washed liberally with additional THF. Volatile components were removed from the filtrate under vacuum. The residue was extracted twice with 200 mL of dichloromethane, and the solution was washed with 0.5 M NaOH (300 mL). The organic layers were combined and dried over MgSO$_4$. All volatile components were removed in vacuo to afford a thick yellow oil: yield 4.74 g (85%); ^{1}H NMR (C$_6$D$_6$) δ 5.73 (m, 4, C$_6$H$_2$F$_3$), 3.46 (br s, 2, NH), 2.37 (q, 4, CH_2), 1.94 (t, 4, CH_2), 1.76 (s, 3, NCH_3); ^{13}C NMR (C$_6$D$_6$) δ 153.77, 151.80, 144.96, 133.83, 131.93, 96.64, 96.45 ($C_6H_2F_3$), 55.77 (NCH$_3$), 41.78 (CH$_2$), 41.35 (CH$_2$); ^{19}F NMR (C$_6$D$_6$) δ −136.00 (m, 4, F$_m$), −177.29 (m, 2, F$_p$); HRMS (EI) calcd for C$_{17}$H$_{17}$N$_3$F$_6$ 377.132 667, found 377.1319. Anal. Calcd for C$_{17}$H$_{17}$N$_3$F$_6$: C, 54.11; H, 4.54; N, 11.14. Found: C, 54.01; H, 4.43; N, 11.22.

CH$_3$N[CH$_2$CONH(3-CF$_3$C$_6$H$_4$)]$_2$. In a 2 L round-bottom flask equipped with an addition funnel, stir bar, and reflux condenser was added 74 g (0.5 mol) of methyliminodiacetic acid.[33] A 300 mL portion of anhydrous pyridine was added via cannula. To the resulting suspension was added 162.7 g (1 mol) of 3-aminobenzotrifluoride (which had been sparged with dinitrogen for 10 min) via cannula. The suspension was heated to ca. 50 °C, and 260 mL (1.06 mol) of triphenyl phosphite was added dropwise. The mixture was heated to 100 °C for 20 h. The homogeneous, bright yellow reaction mixture was cooled to room temperature, and pyridine was removed at reduced pressure. The resulting thick yellow oil was stirred with 500 mL of 5 N HCl in methanol for 1 h, and then the entire mixture was carefully added to 2 L of 2 N sodium hydroxide and extracted with 3 × 1 L of CH$_2$Cl$_2$. The extracts were combined and dried over MgSO$_4$, and the solvent was removed at reduced pressure. Crude CH$_3$N[CH$_2$CONH(3-CF$_3$C$_6$H$_4$)]$_2$ was obtained as an off-white solid. The product was recrystallized by adding an equal volume of hexanes to a concentrated THF solution and storing at ∼5 °C overnight to give a white solid that was dried in vacuo: yield 159.3 g (74%); ^{1}H NMR (300 MHz, CDCl$_3$) δ 2.55 (s 3H, CH_3N), 3.40 (s, 4H, NCH_2CONH), 7.35−7.44 (m, 4H, Ar H), 7.85 (d, 2H, Ar H), 9.22 (s, 2H, CH$_2$CONHAr); ^{19}F NMR (283 MHz, CDCl$_3$) δ −63.87 (s); HRMS (ESI) calcd for C$_{19}$H$_{17}$N$_3$O$_2$F$_6$ 434.1298 [M + H$^+$], found 434.1304 [M + H$^+$].

CH$_3$N[CH$_2$CH$_2$NH(3-CF$_3$C$_6$H$_4$)]$_2$ (H$_2$[CF$_3$NMe]). To 52.18 g of CH$_3$N[CH$_2$CONH(3-CF$_3$C$_6$H$_4$)]$_2$ (0.12 mol) in 230 mL of THF was added 62 mL (0.62 mol) of BH$_3$SMe$_2$ dropwise. The mixture was then refluxed for 6 h and cooledl to room temperature. The reaction mixture was carefully quenched with 250 mL of 5 N HCl, made alkaline with NaOH pellets, and extracted (3 × 250 mL) with methylene chloride. The extracts were combined and dried with MgSO$_4$. The mixture was filtered, and the solvent was removed at reduced pressure to yield H$_2$[CF$_3$NMe] as a colorless oil: yield 33 g (68%); ^{1}H NMR (300 MHz, C$_6$D$_6$) δ 1.77 (s, 3H, CH_3N), 1.99 (t, 4H, NCH_2CH$_2$N), 2.53 (q, NCH$_2$CH_2N), 3.73 (br s, 2H, NH), 6.3 (m, 2H, Ar H), 6.66 (s, Ar H), 6.90 (d, 2H, Ar H), 7.13 (s, 2H, Ar H);

^{13}C NMR (125 MHz, CDCl$_3$) δ 40.99 (CH_2), 41.91 (CH_2), 55.95 (NCH$_3$), 108.85, 113.77, 116.074, 124.61 (q, J_{CF} = 272.38 Hz, CF$_3$C$_6$H$_4$), 129.81, 131.62 (q, J_{CF} = 31.6 Hz, C_6H$_4$), 148.61; ^{19}F NMR (283 MHz, CDCl$_3$) δ −63.2 (s); HRMS (ESI) calcd for C$_{19}$H$_{21}$F$_6$N$_3$ 406.1712 [M + H$^+$], found 406.1715 [M + H$^+$].

[Et$_3$NH]{[F$_5$NMe]MoCl$_3$} (1a). MoCl$_4$(THF)$_2$ (2.547 g, 6.67 mmol) was added as a solid to a stirred solution of (C$_6$F$_5$-NHCH$_2$CH$_2$)$_2$NMe (3 g, 6.67 mmol) in THF (50 mL) at room temperature. The reaction mixture became nearly homogeneous after approximately 30 min. Addition of NEt$_3$ (2.0 mL, 14.35 mmol) caused a white precipitate to form and the resulting mixture was stirred for an additional 2 h. The white powder was removed by filtering the reaction mixture through Celite. The product precipitated upon dropwise addition of the THF solution to a volume (100 mL) of rapidly stirred pentane. The burgundy powder was collected on a frit, washed liberally with pentane, and dried in vacuo: yield 4.70 g (83%); ^{1}H NMR (tol-d_8) δ 1.51, 1.19 (Et_3NH); ^{19}F NMR (THF) δ −95.46, −119.25, −131.27, −134.95, −169.26. Anal. Calcd for C$_{23}$H$_{27}$N$_4$F$_{10}$Cl$_3$Mo: C, 36.75; H, 3.62; N, 7.45; Cl, 14.15. Found: C, 36.64; H, 3.54; N 7.33; Cl, 14.02.

[Bu$_4$N]{[F$_5$NMe]MoCl$_3$} (1b). Tetrabutylammonium chloride (0.203 g, 0.73 mmol) was added to a solution of [Et$_3$NH]-[(C$_6$F$_5$NCH$_2$CH$_2$)$_2$NMe]MoCl$_3$ (0.5 g, 0.67 mmol) in THF (10 mL). The mixture was stirred vigorously for 12 h and filtered through Celite. The volatile components were removed in vacuo. The residue was dissolved in toluene (20 mL), the extract was filtered, and the volume of the extract was halved by removing solvent in vacuo. Dropwise addition of the toluene solution to a rapidly stirred volume of pentane (125 mL) produced a bright red powder, which was collected on a frit, washed liberally with pentane, and dried in vacuo: yield 0.513 g (98%); ^{1}H NMR (C$_6$D$_6$) δ 18.82, 4.15, 1.84, 1.21, 0.97 (Bu_4N), −29.98, −123.84, −149.7; ^{19}F NMR (C$_6$D$_6$) δ −92.55, −115.76, −129.40, −133.74, −168.07; μ_{eff} = 3.1 μ_B (Evans method). Anal. Calcd for C$_{33}$H$_{47}$N$_4$F$_{10}$Cl$_3$Mo: C, 44.43; H, 5.31; N, 6.28; Cl, 11.92. Found: C, 44.28; H, 5.39; N, 6.16; Cl, 12.01.

[Et$_3$NH]{[F$_5$NMe]WCl$_3$} (2a). A solution of (C$_6$F$_5$NHCH$_2$-CH$_2$)$_2$NMe (1.0 g, 2.22 mmol) and NEt$_3$ (0.67 mL, 4.81 mmol) in diethyl ether (10 mL) was added to a stirred mixture of WCl$_4$(dme) (0.92 g, 2.21 mmol) and diethyl ether (10 mL) at −30 °C. The reaction mixture was warmed to room temperature and stirred for 15 h. The yellow-green precipitate was collected on a frit, washed with additional diethyl ether (10 mL), and extracted with THF (15 mL). The mixture was filtered through Celite in order to remove an off-white powder. The volatile components were removed from the extract in vacuo, and the residue was washed with diethyl ether (10 mL) and collected on a frit. The resulting material was dissolved in THF (15 mL), and the solution was filtered through Celite and added dropwise to rapidly stirred pentane (125 mL). The olive green powder produced was collected on a frit, washed liberally with pentane, and dried in vacuo: yield 1.10 g (60%); ^{1}H NMR (tol-d_8) δ 5.54 (NMe), 0.42, −0.44 (Et_3NH), −11.51, −32.43, −48.30, −75.89 (CH_2); ^{19}F NMR (THF) δ −90.96, 105.14, −133.65, −134.48, −160.62. Anal. Calcd for C$_{23}$H$_{27}$N$_4$F$_{10}$-Cl$_3$W: C, 32.90; H, 3.24; N, 6.67; Cl, 12.67. Found: C, 33.11; H, 3.21; N, 6.64; Cl, 12.58.

[Bu$_4$N]{[F$_5$NMe]WCl$_3$} (2b). Tetrabutylammonium chloride (0.182 g, 0.65 mmol) was added to a solution of [Et$_3$NH]-{[(C$_6$F$_5$NCH$_2$CH$_2$)$_2$NMe]WCl$_3$} (0.45 g, 0.54 mmol) in THF (10 mL). The mixture was stirred vigorously for 12 h and filtered through Celite. The volatile components were removed from the filtrate in vacuo, and the residue was dissolved in toluene (20 mL). The mixture was filtered, and the volume was reduced by half in vacuo. The toluene solution was added to rapidly stirred pentane (125 mL) to yield a light green powder, which was collected on a frit, washed liberally with pentane, and dried in vacuo: yield 0.476 g (91%); ^{1}H NMR (C$_6$D$_6$) δ 2.66 (NMe), 0.69, 0.16, −0.42 (Bu_4N), −11.04, −32.48, −45.80, −72.53 (CH_2); ^{19}F NMR (C$_6$D$_6$) δ −88.34, −102.82, −130.99,

−132.28, −158.76; μ_{eff} = 2.7 μ_B (Evans method). Anal. Calcd for $C_{33}H_{47}N_4F_{10}Cl_3W$: C, 40.45; H, 4.83; N, 5.72; Cl, 10.85. Found: C, 40.34; H, 4.97; N, 5.64; Cl, 10.93.

[F$_5$NMe]MoMe$_2$ (3). A solution of MeMgCl (0.94 mL, 3.2 M in THF) was added to a solution of [Et$_3$NH]{[(C$_6$F$_5$NCH$_2$-CH$_2$)$_2$NMe]MoCl$_3$} (0.75 g, 1.01 mmol) in THF (20 mL) at −30 °C. The reaction mixture immediately turned dark green and was warmed to room temperature while it was stirred. After 30 min, the solution was concentrated to dryness in vacuo. The residue was extracted into ether (20 mL), and 1,4-dioxane (0.28 mL) was added. The mixture was stirred for 10 min and filtered through Celite. The filtrate was added dropwise to a rapidly stirred volume of pentane (100 mL). A small amount of brown solid was filtered off. The filtrate was concentrated to approximately 15 mL to produce green crystalline material, which was collected, washed with pentane, and dried in vacuo: yield 0.29 g (50%). An analytically pure sample was obtained by recrystallization of the crude product from a diethyl ether solution layered with pentane at −30 °C: ^{1}H NMR (C$_6$D$_6$) δ 26.79 (N*Me*), 10.82, 5.15, −51.59, −81.94 (CH$_2$); ^{19}F NMR (THF) δ −57.25, −72.97, −105.98, −147.40, −148.99; μ_{eff} = 3.1 μ_B (Evans method). Anal. Calcd for $C_{19}H_{17}N_3F_{10}Mo$: C, 39.81; H, 2.99; N, 7.33. Found: C, 39.66; H, 3.09; N, 7.38.

[F$_5$NMe]MoMeCl (4a). 2,6-Lutidinium chloride (86 mg, 0.60 mmol) was added to a solution of [(C$_6$F$_5$NCH$_2$CH$_2$)$_2$NMe]-MoMe$_2$ (0.312 g, 0.54 mmol) in diethyl ether (18 mL) at −30 °C. The reaction mixture was stirred for 2 h. Tan solids were filtered off, and the volatile components were removed in vacuo. The residue was dissolved in minimal diethyl ether, and the solution was layered with pentane and chilled to −30 °C overnight. The resulting blue-green crystals were collected and dried in vacuo: yield 0.151 g (47%). An analytically pure sample was recrystallized from a solution of diethyl ether layered with pentane at −30 °C: ^{1}H NMR (tol-*d*$_8$) δ 14.26, −54.59, −84.36; ^{19}F NMR (Et$_2$O) δ −86.61, −104.10, −105.13, −141.87, −159.39. Anal. Calcd for $C_{18}H_{14}N_3F_{10}ClMo$: C, 36.41; H, 2.38; N, 7.08; Cl, 5.97. Found: C, 36.52; H, 2.32; N, 7.04; Cl, 5.91.

[F$_5$NMe]Mo(CH$_2$CMe$_3$)Cl (4b). A solution of Me$_3$CCH$_2$-MgCl (0.28 mL, 2.07 M in THF) was added to a solution of [Et$_3$NH]{[(C$_6$F$_5$NCH$_2$CH$_2$)$_2$NMe]MoCl$_3$} (0.2 g, 0.11 mmol) in THF (20 mL) at −30 °C. The reaction mixture immediately turned dark green and was warmed to room temperature while it was stirred. After 30 min, the solution was concentrated to dryness in vacuo and the residue extracted into 30 mL of toluene. 1,4-Dioxane (0.05 mL) was added, followed by stirring for an additional 20 min. The mixture was filtered through Celite and the filtrate added dropwise to cold, stirred pentane (100 mL). The bright green, crystalline precipitate was collected on a frit, washed liberally with pentane, and dried in vacuo: yield 92 mg (60%); ^{1}H NMR (CD$_2$Cl$_2$) δ 9.5, 6.3, 3.2 (C*Me*$_3$), −59.6–82.8; ^{19}F NMR (CD$_2$Cl$_2$) δ −88.67, −98.05, −104.90, −138.46, −160.10. Anal. Calcd for $C_{22}H_{22}N_3F_{10}ClMo$: C, 40.66; H, 3.41; N, 6.47; Cl, 5.46. Found: C, 40.63; H, 3.54; N, 6.40; Cl, 5.56.

[F$_5$NMe]W(CH$_2$CMe$_3$)Cl (5). A solution of Me$_3$CCH$_2$MgCl (0.29 mL, 2.07 M in THF) was added to a solution of [Et$_3$NH]-{[(C$_6$F$_5$NCH$_2$CH$_2$)$_2$NMe]WCl$_3$} (0.2 g, 0.24 mmol) in THF (20 mL) at −30 °C. The reaction mixture immediately turned dark green and was warmed to room temperature while it was stirred. After 30 min, the solution was concentrated to dryness in vacuo and the residue extracted into 30 mL of toluene. 1,4-Dioxane (0.05 mL) was added, followed by stirring for an additional 20 min. The mixture was filtered through Celite and the filtrate added dropwise to cold, stirred pentane (75 mL). The green precipitate was collected on a frit, washed liberally with pentane, and dried in vacuo: yield 80 mg (45%); ^{1}H NMR (CD$_2$Cl$_2$) δ 10.51 (C*Me*$_3$), −5.07, −8.95, −34.45, −58.23; ^{19}F NMR (CD$_2$Cl$_2$) δ −88.67, −98.05, −104.90, −138.46, −160.10. Anal. Calcd for $C_{22}H_{22}N_3F_{10}ClW$: C, 35.82; H, 3.01; N, 5.70; Cl, 4.81. Found: C, 36.04; H, 3.11; N, 5.59; Cl, 4.72.

[Et$_3$NH]{[F$_3$NMe]MoCl$_3$} (6a). MoCl$_4$(THF)$_2$ (2.02 g, 5.30 mmol) was added as a solid to a stirred solution of H$_2$[F$_3$NMe] (2 g, 5.30 mmol) in THF (40 mL) at room temperature. The reaction mixture became nearly homogeneous and deep red after approximately 10 min. Addition of NEt$_3$ (1.63 mL, 11.69 mmol) caused a white precipitate to form. The resulting purple reaction mixture was stirred for 1 h, and the white powder was removed by filtering the reaction mixture through Celite. The product precipitated upon dropwise addition of the THF solution to rapidly stirred, cold pentane (150 mL). The dark purple powder was collected on a frit, washed liberally with pentane, and dried in vacuo: yield 3.15 g (87%); ^{1}H NMR (C$_6$D$_6$) δ 1.38, 1.12 (*Et$_3$*NH); ^{19}F NMR (C$_6$D$_6$) δ −104.85, −206.57. Anal. Calcd for $C_{23}H_{31}N_4Cl_3F_6Mo$: C, 40.64; H, 4.60; N, 8.24; Cl, 15.65. Found: C, 40.72; H, 4.55; N, 8.21; Cl, 15.57.

[Bu$_4$N]{[F$_3$NMe]MoCl$_3$} (6b). Tetrabutylammonium chloride (0.25 g, 0.90 mmol) was added to a solution of [Et$_3$NH]-{[F$_3$NMe]MoCl$_3$} (0.5 g, 0.74 mmol) in THF (10 mL). The mixture was stirred vigorously for 20 h and filtered through Celite. The volatile components were removed in vacuo. The residue was dissolved in toluene (20 mL), and the toluene solution was filtered and added dropwise to a rapidly stirred volume of cold pentane (100 mL). The purple powder was collected on a frit, washed liberally with pentane, and dried in vacuo: yield 0.54 g (90%); ^{1}H NMR (C$_6$D$_6$) δ 28.26, 6.11, 1.64, 1.21, 0.97 (*Bu$_4$*N), −3.84, −29.67, −96.83, −99.60; ^{19}F NMR (C$_6$D$_6$) δ −103.89 (4, F$_m$), −207.48 (2, F$_p$); μ_{eff} = 3.1 μ_B (Evans method). Anal. Calcd for $C_{33}H_{51}N_4Cl_3F_6Mo$: C, 48.33; H, 6.27; N, 6.83; Cl, 12.97. Found: C, 48.35; H, 6.35; N, 6.69; Cl, 12.85.

[Et$_3$NH]{[F$_3$NMe]WCl$_3$} (7a). WCl$_4$(dme) (1.0 g, 2.1 mmol) was added to a solution of H$_2$[F$_3$NMe] (0.79 g, 2.1 mmol) and NEt$_3$ (0.64 mL, 4.6 mmol) in diethyl ether (30 mL) at room temperature. The reaction mixture was stirred for 15 h. The mixture was taken to dryness in vacuo, and the residue was extracted with THF (15 mL). The resulting solution was filtered through Celite, and the filtrate was added dropwise to rapidly stirred, cold pentane (75 mL). The dark orange powder produced was collected on a frit, washed liberally with pentane, and dried in vacuo: yield 1.39 g (86%); ^{1}H NMR (C$_6$D$_6$) δ 28.70, 0.04, 0.15 (*Et$_3$*NH), −1.33 (*Et$_3$*NH), −4.27 (Et$_3$N*H*), −15.26, −32.03, −38.77, −45.91; ^{19}F NMR (C$_6$D$_6$) δ −108.34, −177.86. Anal. Calcd for $C_{23}H_{31}N_4Cl_3F_6W$: C, 35.98; H, 4.07; N, 7.30; Cl, 13.85. Found: C, 36.08; H, 3.92; N, 7.21; Cl, 13.76.

[Bu$_4$N]{[F$_3$NMe]WCl$_3$} (7b). Tetrabutylammonium chloride (0.12 g, 0.42 mmol) was added to a solution of [Et$_3$NH]-{[F$_3$NMe]WCl$_3$} (0.30 g, 0.38 mmol) in THF (5 mL). The mixture was stirred vigorously for 14 h and filtered through Celite. The volatile components were removed from the filtrate in vacuo, and the residue was dissolved in toluene (15 mL). The mixture was filtered, and the toluene solution was added to rapidly stirred, cold pentane (75 mL) to yield a bright orange powder, which was collected on a frit, washed liberally with pentane, and dried in vacuo: yield 0.27 g (78%); ^{1}H NMR (C$_6$D$_6$) δ 28.74, 0.65 (*Bu$_4$*N), 0.44 (*Bu$_4$*N), −0.44 (*Bu$_4$*N), −0.61 (*Bu$_4$*N), −2.55, −13.88, −27.46, −39.21, −39.86; ^{19}F NMR (C$_6$D$_6$) δ −107.83 (m, 4, F$_m$), −179.38 (m, 2, F$_p$). μ_{eff} = 2.7 μ_B (Evans method). Anal. Calcd for $C_{33}H_{51}N_4Cl_3F_6W$: C, 43.65; H, 5.66; N, 6.17; Cl, 11.71. Found: C, 43.78; H, 5.72; N, 6.06; Cl, 11.63.

[F$_3$NMe]Mo(CH$_2$CMe$_3$)Cl (8). A solution of Me$_3$CCH$_2$MgCl (0.4 mL, 1.75 M in Et$_2$O) was added to a solution of [Et$_3$NH]-{[F$_3$NMe]MoCl$_3$} (0.2 g, 0.29 mmol) in THF (7.5 mL) at −30 °C. The reaction mixture was warmed to room temperature while it was stirred for 1 h. The reaction mixture was then added to cold, stirred pentane (100 mL), and the precipitate produced was collected on a frit, washed liberally with additional pentane, and dried in vacuo. The gray-brown solid was then added to Et$_2$O (10 mL), and 1,4-dioxane (0.055 mL) was added followed by stirring for 5 min. The solid was collected

on a frit and washed with additional Et$_2$O. The solid was transferred to a 20 mL vial, extracted three times with CH$_2$Cl$_2$ (20 mL), and filtered. The combined filtrates were concentrated in vacuo until a green precipitate began to form. The solution was then added dropwise to rapidly stirred pentane (100 mL), and the green powder produced was collected on a frit, washed liberally with additional pentane, and dried in vacuo: yield 73 mg (43%); ^{19}F NMR (THF) δ −107.20 (4, F$_m$), −164.96 (2, F$_p$). Anal. Calcd for C$_{22}$H$_{26}$N$_3$F$_6$ClMo: C, 45.73; H, 4.54; N, 7.27; Cl, 6.14. Found: C, 45.66; H, 4.56; N, 7.17; Cl, 6.19.

[F$_3$NMe]Mo(CH$_2$CMe$_3$)(CCMe$_3$) (9). A solution of Me$_3$CCH$_2$MgCl (0.43 mL, 2.27 M in Et$_2$O) was added to a solution of [Et$_3$NH]{[F$_3$NMe]MoCl$_3$} (0.2 g, 0.29 mmol) in THF (10 mL) at −30 °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 1,4-dioxane (0.135 mL) was added. The mixture was stirred for 10 min and filtered through Celite. The filtrate was added dropwise to a rapidly stirred volume of cold pentane (100 mL). A small amount of dark brown precipitate was filtered off, and the filtrate was concentrated to dryness to leave a brown crystalline solid: 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 °C: ^{1}H NMR (C$_6$D$_6$) δ 6.63 (m, 4, C$_6$H$_2$F$_3$), 3.08 (t, 4, CH$_2$), 2.13 (m, 2, CH$_2$), 1.94 (s, 3, NCH$_3$), 1.91 (m, 2, CH$_2$), 1.56 (s, 2, CH$_2$), 1.37 (s, 9, C(CH$_3$)$_3$), 0.66 (s, 9, C(CH$_3$)$_3$); ^{13}C NMR (C$_6$D$_6$) δ 307.74 (CCMe$_3$), 160.28, 152.60, 149.31, 138.79, 135.55, 109.11 (C$_6$H$_2$F$_3$), 72.74, 59.44, 55.59, 51.42, 44.49, 36.00, 35.90, 30.56; ^{19}F NMR (C$_6$D$_6$) δ −138.46 (m, 4, F$_m$), −170.87 (m, 2, F$_p$). Anal. Calcd for C$_{27}$H$_{35}$N$_3$F$_6$Mo: C, 53.03; H, 5.77; N, 6.87. Found: C, 52.94; H, 5.78; N, 6.83.

[F$_3$NMe]Mo(CH$_2$SiMe$_3$)$_2$ (10). A solution of Me$_3$SiCH$_2$MgCl (1.94 mL, 1.0 M in Et$_2$O) was added to a solution of [Et$_3$NH]{[F$_3$NMe]MoCl$_3$} (0.4 g, 0.59 mmol) in THF (20 mL) at −30 °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 1,4-dioxane (0.19 mL) was added. The mixture was stirred for 10 min and filtered through Celite. The filtrate was added dropwise to a rapidly stirred volume of cold pentane (120 mL) and filtered a second time to remove a small amount of gray precipitate. All volatile components were removed in vacuo to leave a purple, crystalline powder: yield 0.27 g (72%); ^{1}H NMR (C$_6$D$_6$) δ 21.29, 13.93, 3.58 (Si(CH$_3$)$_3$), 1.16 (Si(CH$_3$)$_3$), −40.28, −62.26; ^{19}F NMR (C$_6$D$_6$) δ −99.06 (m, 4, F$_m$), −160.17 (m, 2, F$_p$); μ_{eff} = 3.1 μ_B (Evans method). Anal. Calcd for C$_{25}$H$_{37}$N$_3$F$_6$Si$_2$Mo: C, 46.50; H, 5.78; N, 6.51. Found: C, 46.38; H, 5.71; N, 6.54.

[F$_3$NMe]W(CH$_2$CMe$_3$)(CCMe$_3$) (11a). A solution of Me$_3$CCH$_2$MgCl (0.33 mL, 1.3 M in Et$_2$O) was added to a solution of [Et$_3$NH]{[F$_3$NMe]WCl$_3$} (0.1 g, 0.13 mmol) in THF (8 mL) at −30 °C. After the reaction mixture was warmed to room temperature and stirred for 4 h, all volatile components were removed in vacuo. The residue was extracted into toluene (6 mL), and 1,4-dioxane (0.036 mL) was added. The mixture was stirred for 10 min and filtered through Celite. The filtrate was concentrated to dryness in vacuo to leave a tan powder: yield 75 mg (82%). An analytically pure sample was recrystallized from a mixture of diethyl ether and pentane at −30 °C: ^{1}H NMR (CD$_2$Cl$_2$) δ 6.75 (m, 4, C$_6$H$_2$F$_3$), 3.85 (m, 2, CH$_2$), 3.79 (m, 2, CH$_2$), 3.02 (m, 2, CH$_2$), 2.78 (m, 2, CH$_2$), 2.69 (s, 3, NCH$_3$), 1.22 (s, 9, C(CH$_3$)$_3$), 1.21 (s, 2, CH$_2$), 0.44 (s, 9, C(CH$_3$)$_3$); ^{13}C NMR (CD$_2$Cl$_2$) δ 295.71 (CCMe$_3$), 160.74, 151.68, 149.23, 138.30, 135.87, 109.94 (C$_6$H$_2$F$_3$), 76.55, 59.63, 54.54, 49.52, 44.72, 35.27, 34.73, 31.65; ^{19}F NMR (CD$_2$Cl$_2$) δ −139.15 (m, 4, F$_m$), −171.42 (m, 2, F$_p$). Anal. Calcd for C$_{27}$H$_{35}$N$_3$F$_6$W: C, 46.37; H, 5.04; N, 6.01. Found: C, 46.43; H, 5.09; N, 5.95.

[F$_3$NMe]W(CH$_2$SiMe$_3$)(CSiMe$_3$) (11b). A solution of Me$_3$SiCH$_2$MgCl (0.71 mL, 1.0 M in Et$_2$O) was added to a solution

of [Et$_3$NH]{[F$_3$NMe]WCl$_3$} (91 mg, 0.12 mmol) in THF (10 mL) at −30 °C. After the reaction mixture was warmed to room temperature and stirred for 1 h, all volatile components were removed in vacuo. The light brown residue was extracted into toluene (5 mL), and 0.07 mL of 1,4-dioxane was added. After it was stirred for an additional 10 min, the solution was filtered throuh Celite and the filtrate added dropwise to a stirred volume of cold pentane (50 mL). The pentane was removed in vacuo to leave a brown oil, which was redissolved in a minimal amount of pentane and cooled to −30 °C to produce analytically pure, amber crystals: yield 45 mg (52%); ^{1}H NMR (C$_6$D$_6$) δ 6.80 (m, 4, C$_6$H$_2$F$_3$), 3.08 (m, 4, CH$_2$), 2.00 (m, 2, CH$_2$), 1.88 (s, 3, NCH$_3$), 1.76 (m, 2, CH$_2$), 1.04 (s, 2, CH$_2$), 0.24 (s, 9, Si(CH$_3$)$_3$), 0.36 (s, 9 Si(CH$_3$)$_3$); ^{13}C NMR δ 336.84 (CCMe$_3$), 161.36, 152.20, 148.89, 138.81, 135.50, 109.00 (C$_6$H$_2$F$_3$), 58.13, 55.63, 47.40, 44.47, 4.44, 2.08; ^{19}F NMR (C$_6$D$_6$) δ −137.50 (m, 4, F$_m$), −170.19 (m, 2, F$_p$). Anal. Calcd for C$_{25}$H$_{35}$N$_3$F$_6$Si$_2$W: C, 41.04; H, 4.82; N, 5.74. Found: C, 40.93; H, 4.88; N, 5.84.

[Et$_3$NH]{[CF$_3$NMe]MoCl$_3$} (12a). MoCl$_4$(THF)$_2$ (2.79 g, 0.78 mmol) was added in several portions to a stirred solution of H$_2$[CF$_3$NMe] (3.14 g, 0.78 mmol) in 50 mL of THF. The solution was stirred for 30 min at room temperature, upon which the solution turned red. Et$_3$N (2.28 mL, 1.63 mmol) in 5 mL of THF was then added dropwise via pipet, and the solution was stirred for 2 h at room temperature. The volatile components were removed in vacuo, and the residue was extracted with 100 mL of THF, the extract was filtered through Celite, and the Celite was washed with 3 × 50 mL of THF. The product is crystallized by adding 2 volumes of pentane to a concentrated THF solution and storing at −40 °C overnight. The deep purple solid was collected on a frit, washed with 50 mL of pentane, and dried in vacuo: yield 4.57 g, 83%; ^{1}H NMR (C$_6$D$_6$) δ 19.4 (s, 3, NMe), 6.21, 1.54, 1.16, 0.97, −24.9, −30.8, −97.7, −103.7; ^{19}F NMR (C$_6$D$_6$) δ −54.5 (s).

[Bu$_4$N]{[CF$_3$NMe]MoCl$_3$} (12b). A 2.63 g amount of H$_2$[CF$_3$NMe] (6.5 mmol) and 2.49 g of MoCl$_4$(Et$_2$O)$_2$ (6.5 mmol) were combined in 80 mL of THF and stirred for 30 min. A 2.0 mL portion of triethylamine (14.3 mmol) in 4 mL of THF was added dropwise via pipet and the mixture stirred for 1 h. The purple solution was filtered through Celite and washed with 2 × 40 mL of THF. A 1.98 g amount of tetrabutylammonium chloride (7.1 mmol) was added as a solid to the solution, and the mixture was stirred vigorously for 15 h. The solution was then stripped to a dark purple solid and extracted with 200 mL of toluene, and the extract was filtered through Celite, which was washed with 3 × 40 mL of additional toluene. [Bu$_4$N]{[CF$_3$NMe]MoCl$_3$} was isolated as a purple powder by concentration of the solution and addition of pentane followed by storage at −40 °C. The purple solid was dried thoroughly in vacu: yield 4.18 g (76%); ^{1}H NMR (C$_6$D$_6$, 500 MHz) δ 28.16, 25.95, 19.37 (s, 3, NMe), 6.29, 4.67, 1.1 (NBu), 1.0 (NBu), 0.87 (NBu), 0.78(NBu), −2.33, −30.9, −99.4, −105.4; ^{19}F NMR (C$_6$D$_6$) δ −54.8. Anal. Calcd for C$_{35}$H$_{55}$N$_4$F$_6$Cl$_3$Mo: C, 49.66; H, 6.51; N, 6.48; Cl, 12.61. Found: C, 49.57; H, 6.54; N, 6.61; Cl, 12.54.

[CF$_3$NMe]Mo(CH$_2$SiMe$_3$)$_2$ (13). A 3.036 g amount (4.3 mmol) of [Et$_3$NH]{[CF$_3$NMe]MoCl$_3$} was dissolved in 25 mL of THF and chilled to −78 °C. To the purple solution was added a solution of ((trimethylsilyl)methyl)magnesium chloride (16.7 mL, 0.8 M in Et$_2$O, 13.3 mmol, 3.1 equiv) with stirring. The solution turned dark green over 4 h, and the color darkened to deep red as the reaction mixture was naturally warmed to room temperature. After 15 h all volatile components were removed, and the residue was extracted into pentane, the extract was filtered through Celite, and the Celite was washed with pentane until the washings were colorless. The solution was concentrated to ca. 30 mL and filtered through Celite a second time. The solution was concentrated to 15 mL and stored at −40 °C for 2 days, affording dark blocks of crystalline [CF$_3$NMe]Mo(CH$_2$SiMe$_3$)$_2$, which were dried in vacuo: yield 1.6 g (55%). A second crop yielded an additional 180 mg of

product, for a total yield of 62%. The complex has also been synthesized in the same fashion and in similar yield from [Bu$_4$N][{[CF$_3$NMe]MoCl$_3$}] and 2.1 equiv of alkylmagnesium reagent. ^{1}H NMR (C$_6$D$_6$): δ 15.8, 13.25 (s, 3, N*Me*), 11.68, 10.9, 5.43, 3.8, 3.5 (br s,9, Si*Me$_3$*), 1.3, 1.2 (br s, 9, Si*Me$_3$*), −46.3, −60.1. ^{19}F NMR (C$_6$D$_6$): δ −55.8. Anal. Calcd for C$_{27}$H$_{41}$N$_3$F$_6$-Si$_2$Mo: C, 47.88; H, 6.06; N, 6.14. Found: C, 48.13; H, 6.13; N, 6.24.

[CF$_3$NMe]Mo(CH$_2$CMe$_3$)Cl (14). A sample of **12a** (140 mg, 0.2 mmol) was dissolved in 12 mL of THF, and the solution was chilled to −30 °C. A solution of neopentylmagnesium chloride (0.21 mL, 2.1 M in Et$_2$O, 0.44 mmol, 2.2 equiv) was then added. After the reaction mixture was stirred for 30 min, the color changed to dark green. All volatile components were removed in vacuo, and the residue was taken up in a minimum of diethyl ether. 1,4-Dioxane was added, the solution was filtered through Celite, and the Celite was washed with 4 mL of ether. The filtrate was concentrated in vacuo, and pentane was added. After 18 h at 30 °C, dark green crystals were isolated, rinsed with a minimum of pentane, and dried in vacuo: yield 98 mg (89%); ^{1}H NMR (C$_6$D$_6$) δ 15.67, 13.5 (br s, 3, N*Me*), 4.33 (2, s) 3.93 (br s, 9, CH$_2$C*Me$_3$*), −51 (br s, 2), −88 (br s, 2); ^{19}F NMR (C$_6$D$_6$) δ −59.8. Anal. Calcd for C$_{24}$H$_{30}$N$_3$F$_6$-ClMo: C, 47.64; H, 5.11; N, 6.58. Found: C, 47.58; H, 4.99; N, 6.94.

[CF$_3$NMe]Mo(CCMe$_3$)(CH$_2$CMe$_3$) (15). [Et$_3$NH]{[CF$_3$NMe]-MoCl$_3$} (220 mg, 0.31 mmol) was dissolved in 25 mL of THF, and the solution was chilled to −30 °C. To the purple, cold solution was added 0.55 mL of neopentylmagnesium chloride in ether (1.76 M, 0.96 mmol) with stirring. After 2 h all volatiles were removed from the dark yellow solution. The residue was extracted into toluene, and 1,4-dioxane was added. The mixture was stirred for 20 min and filtered through Celite, and the Celite was washed with toluene until the washings were clear (∼25 mL). The toluene was removed in vacuo to leave a brown solid. This was taken up in a minimum of ether, and pentane was added. Storage of the solution at −30 °C for 3 days afforded yellow crystalline [CF$_3$NMe]Mo(CCMe$_3$)(CH$_2$-CMe$_3$): yield 126 mg (63%); ^{1}H NMR (C$_6$D$_6$) δ 7.47 (s, 2, C$_6$H$_4$), 7.14 (d, 2, C$_6$H$_4$), 7.02−6.94 (m, 4, C$_6$H$_4$), 3.34 (m, 2, C*H$_2$*), 3.25 (m, 2, C*H$_2$*), 2.27 (m, 2, C*H$_2$*), 2.04 (m, 2, C*H$_2$*), 2.03 (s, 3, N*Me*), 1.64 (s, 2, C*H$_2$*CMe$_3$), 1.47, (s, 9, CC*Me$_3$*), 0.52 (s, 9, CC*Me$_3$*); ^{13}C (tol-*d$_8$*) δ 307.7 (Mo*C*CMe$_3$), 165.3, 137.7, 130.8 (J_{CF} = 31.6 Hz), 125.58, 125.1 (J_{CF} = 272.6 Hz), 121.5, 119.95, 69.90, 59.38, 55.13, 49.95, 43.45, 37.17, 34.98, 29.20; ^{19}F NMR (C$_6$D$_6$) δ −61.7 ppm.

Measurement of Hydrogen Evolution. Inside the glovebox, a solution of Me$_3$CCH$_2$MgCl (0.21 mL, 1.75 M in Et$_2$O) was diluted with THF (4 mL). The THF solution was transferred to a reaction flask and attached to one end of a swivel frit. At the other end of the swivel frit was placed a second reaction flask containing a stir bar and [Et$_3$NH]{[F$_3$NMe]-MoCl$_3$} (0.075 g, 0.1103 mmol). The reaction assembly was taken out of the glovebox and attached to a high-vacuum line.

The THF solution was freeze−pump−thaw degassed several times. Once properly degassed (∼10^{-6} Torr), the THF solution was added to solid [Et$_3$NH]{[F$_3$NMe]MoCl$_3$} and then frozen to −196 °C. The reaction mixture was allowed to thaw to room temperature and stirred for 4 h. The reaction mixture was again frozen in a liquid nitrogen bath and opened to the Toepler pump. Gas collection occurred over the course of 3 h. The gas was passed through three U-tubes, all of which were immersed in liquid nitrogen, before reaching the pump. This step ensured the removal of any condensable gases, reducing error in the experiment. The reaction setup was then closed to the pump and allowed to thaw for a second round of degassing before collecting again. This process was repeated a third time to ensure complete gas collection. In the end, 91 mmHg of gas was collected into a calibrated volume of 11.9 mL at 23.7 °C. The amount of gas collected was found to be 0.0585 mmol, as determined through the ideal gas law ($PV = nRT$). The gas was then completely burned over a CuO catalyst at 320 °C to verify its composition. A control experiment demonstrated the efficiency of the pump by collecting a predetermined amount of hydrogen in 94% yield.

To confirm the production of [F$_3$NMe]Mo(CH$_2$CMe$_3$)(CCMe$_3$), the product solution was then brought back into the glovebox, and the total volume was measured to be 4.09 mL. A 0.59 mL aliquot was transferred to an NMR tube, and 4 μL of 4-fluorobromobenzene was added as an internal standard. The ^{19}F NMR spectrum of this mixture was acquired, and the number of moles of [F$_3$NMe]Mo(CH$_2$CMe$_3$)(CCMe$_3$) produced was calculated from the relative intensities of the resonances corresponding to the meta fluorine resonance of the [F$_3$NMe]$^{2-}$ ligand aryl rings to that of 4-fluorobromobenzene. A value of 0.0656 mmol was calculated for the total amount of [F$_3$NMe]-Mo(CH$_2$CMe$_3$)(CCMe$_3$) produced in the reaction. A yield of 90% was found for the collected H$_2$ (mmol of H$_2$/mmol of [F$_3$NMe]-Mo(CH$_2$CMe$_3$)(CCMe$_3$)).

Supporting Information Available: Text giving experimental details, labeled thermal ellipsoid drawings, and tables giving crystal data and structure refinement details, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters for [Et$_3$NH]{[F$_5$NMe]WCl$_3$, [F$_5$NMe]Mo-(CH$_2$CMe$_3$)Cl, and [Bu$_4$N]{[CF$_3$NMe]MoCl$_3$}. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data for [Et$_3$NH]{[F$_5$NMe]MoCl$_3$}, [F$_5$NMe]-MoMe$_2$, and [F$_3$NMe]Mo(CH$_2$CMe$_3$)(CCMe$_3$) were deposited as Supporting Information in earlier publications.[22,23]

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