Some Organometallic Chemistry of Molybdenum Complexes that Contain the $[HIPTN_3N]^{3-}$ Triamidoamine Ligand, $\{[3,5\text{-}(2,4,6\text{-}i\text{-}Pr_3C_6H_2)_2C_6H_3NCH_2CH_2]_3N\}^{3-}$

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Reactions between $[HIPTN_3N]Mo(N_2)$ and ethylene, acetylene, or CO yield **Mo**(η^2-C_2H_4), **Mo**(η^2-C_2H_2), and **Mo**(CO), respectively ($[HIPTN_3N]^{3-}$ = [3,5-(2,4,6-*i*-$Pr_3C_6H_2)_2C_6H_3NCH_2CH_2]_3N^{3-}$; HIPT = hexaisopropylterphenyl; $[HIPTN_3N]Mo$ = **Mo**). All are paramagnetic C_3 symmetric species. Attempts to prepare **Mo**(CO) through reduction of **Mo**Cl with Na/Hg in THF under carbon monoxide yielded [**Mo**(CO)]Na, in which the sodium ion is believed to be bound within the HIPT aryl system. Addition of a variety of acids such as $[Et_3NH]BAr'_4$ to [**Mo**(CO)]Na led to formation of the carbonyl hydride, **Mo**(CO)H, which also could be prepared by treating **Mo**H with CO. Reactions between **Mo**H and ethylene, 1-hexene, or 1-octene in benzene yield paramagnetic, red **Mo**(CH_2R) complexes (CH_2R = ethyl, hexyl, or octyl). **Mo**Me could be prepared by treating **Mo**Cl with $AlMe_3$ at room temperature over a period of 2 days. Treatment of **Mo**H with acetylene affords yellow diamagnetic **Mo**(η^2-$CHCH_2$) plus polyacetylene. The **Mo**CH_2R complexes decompose at ∼150 °C to yield the alkylidyne complexes, **Mo**≡CR, quantitatively. No change was observed upon heating a toluene solution of **Mo**CH_3 to 160 °C for 24 h. However, **Mo**≡CH could be prepared from a mixture of **Mo**Cl, 3 equiv of dichloromethane, and a large excess of magnesium powder in THF under argon at 90 °C. Although we have seen no evidence of thermal rearrangement of **Mo**(η^2-$CHCH_2$) to **Mo**≡CCH_3, that rearrangement is readily catalyzed by [2,6-LutH]BAr'_4. Attempts to prepare **Mo**-C≡CH from [**Mo**(NH_3)]BAr'_4 and NaC≡CH led to formation of a yellow crystalline compound that was shown in an X-ray study to be one in which the acetylide had "inserted" into an *ortho* C−H bond in the phenyl ring attached to the amido nitrogen. Orange paramagnetic **Mo**CN can be isolated in good yield from the reaction between [**Mo**(NH_3)]BPh_4 and $[Bu_4N]CN$ in fluorobenzene. Electrochemical studies in 0.1 M $[Bu_4N]$-BAr'_4 in PhF at room temperature revealed reversible couples for **Mo**$(C_2H_4)^{+/0}$ and **Mo**$(C_2H_2)^{+/0}$ at −0.42 and −0.94 V, respectively, while **Mo**(CN) exhibits two redox processes at −0.27 and −1.61 V that we assign to the **Mo**$(CN)^{+/0}$ and **Mo**$(CN)^{0/-}$ redox couples, respectively. Addition of $[Cp_2Fe]BAr'_4$ to a solution of **Mo**(η^2-C_2H_2) in C_6D_6 produces diamagnetic [**Mo**(η^2-C_2H_2)]BAr'_4, while addition of $[Cp_2Fe]BAr'_4$ to a C_6D_6 solution of **Mo**(η^2-C_2H_4) led to formation of diamagnetic [**Mo**(C_2H_4)]BAr'_4. Structures of **Mo**(C_2H_4), [**Mo**(C_2H_4)]-BAr'_4, **Mo**(CH_2CH_3), and "**Mo**(C≡CH)" were determined through X-ray studies.

Introduction

We have been studying chemistry of Mo and W complexes that contain the triamidoamine ligand $[HIPTN_3N]^{3-}$ (where $[HIPTN_3N]^{3-}$ = [3,5-(2,4,6-*i*-$Pr_3C_6H_2)_2C_6H_3NCH_2CH_2]_3N^{3-}$; HIPT = hexaisopropylterphenyl; $[HIPTN_3N]Mo$ = **Mo**), which is relevant to the reduction of dinitrogen to ammonia.[1−6] We have shown that dinitrogen can be reduced catalytically to ammonia in heptane in the presence of **Mo** complexes (e.g., **Mo**(N_2), **Mo**-N=NH, [**Mo**=N-NH_2]$^+$, **Mo**≡N, [**Mo**(NH_3)]$^+$, and **Mo**H), a proton source ([2,6-lutidinium]BAr'_4 where Ar′ = 3,5-$(CF_3)_2C_6H_3$), and an electron source (e.g., decamethylchromocene).[3,6] Steric protection of partially reduced nitrogen entities within the trigonally symmetric pocket against bimolecular decomposition reactions is believed to be one of the reasons why many potential intermediates can be prepared and why catalytic reduction of dinitrogen to ammonia is possible at a single metal center. However, it should be noted that analogous hexamethylterphenyl and hexa-*tert*-butylterphenyl derivatives yield little or no ammonia (respectively) from dinitrogen under the same conditions as the hexaisopropylterphenyl derivatives,[4] so proper tuning of the steric protection is crucial.

Although this is the first time that dinitrogen has been reduced catalytically in a relatively well-defined

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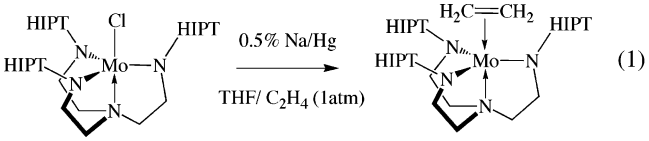
manner,[7] it is not known whether these observations have any bearing on the question as to how dinitrogen is reduced to ammonia by molybdenum-containing nitrogenases.[8−22] Although dinitrogen almost certainly is reduced at a $MoFe_7S_9$ cluster within the enzyme, the detailed structure of which has been elucidated in considerable detail in the past decade,[11,16−18,23−25] it is fair to say that we still do not know exactly how dinitrogen is reduced in the MoFe nitrogenase.

The MoFe nitrogenase is known to reduce many substrates besides dinitrogen, among them acetylene and isonitriles.[9,22,26] Therefore we have the opportunity to determine to what extent certain organometallic **Mo** derivatives will serve as catalyst precusors for formation of ammonia, and whether and how substrates other than dinitrogen might be reduced. This is one reason we have begun to explore some simple organometallic chemistry of **Mo**. Another reason is that we have explored a good deal of relatively simple organometallic chemistry of triamidoamine ($[RN_3N]^{3-} = [(RNCH_2CH_2)_3N]^{3-}$) complexes of Mo and W (where R is trimethylsilyl or pentafluorophenyl)[27−33] as well as $[Me_3SiN_3N]^{3-}$ complexes of tantalum[34−36] in the past decade. Although we have shown that many new and interesting species can be prepared and new reactions carried out within the trigonal coordination pocket, complexes that contain the $[HIPTN_3N]^{3-}$ ligand are likely to be much more stable against various decomposition reactions than complexes that contain $[TMSN_3N]^{3-}$ or $[C_6F_5N_3N]^{3-}$ ligands. For example, in $[TMSN_3N]$W complexes both silyl migration and CH activation in a silyl methyl group have been observed.[32] Therefore it will be of interest to determine what type of organometallic chemistry will be possible in relatively robust **Mo** systems compared with that observed in other $[RN_3N]$Mo systems.

Results and Discussion

Reactions that Involve Replacement of Dinitrogen from [HIPTN$_3$N]Mo(N$_2$). Ethylene (1 atm) reacts with **Mo**(N_2) (**Mo** = $[HIPTN_3N]$Mo) in benzene at room temperature over a period of 2 days to yield rose-red paramagnetic **Mo**(C_2H_4). The reaction proceeds much more readily at 60 °C under 1 atm of ethylene. However, the most convenient and most direct synthesis of **Mo**(C_2H_4) consists of the reduction of **Mo**Cl with an excess of 0.5% Na amalgam in THF under an ethylene atmosphere (eq 1). The corresponding ^{13}C-labeled complex was prepared readily in a similar manner. The proton NMR spectrum of **Mo**(C_2H_4) shows no resonances for the backbone or ethylene methylene groups, only broad resonances at 7.18, 2.88, and 1.34 ppm for aromatic, isopropyl methine, and isopropyl methyl groups, respectively. Upfield-shifted ligand backbone methylene resonances also have not been observed in other ethylene complexes in this general category, e.g., $[TMSN_3N]Mo(C_2H_4)$ and $[C_6F_5N_3N]Mo(C_2H_4)$.[31]



(1)

An X-ray study showed the ethylene complex to have the expected structure (Figure 1, Tables 1 and 2). The ethylene is oriented approximately perpendicular to the Mo−N(3) vector. The Mo−C bond lengths are 2.190(7) and 2.196(7) Å, while the C(1)−C(2) bond length is 1.369(10) Å. The Mo−N_{amido} bond lengths are all near 2.00 Å, and the Mo−N_{amine} bond length is 2.211(5) Å; all are typical for compounds of this general type. The only slight lengthening of the C(1)−C(2) bond from what it is in free ethylene suggests that **Mo**(η^2-C_2H_4) is best viewed as a low-spin Mo(III) ethylene complex with three electrons in the frontier π orbitals (d_{xz} and d_{yz}), instead of a molybdacyclopropane (Mo(V)) complex. This compound should be compared to other ethylene complexes in the general class of triamidoamine complexes of Ta,[34] Mo,[31] and W,[31] although **Mo**(C_2H_4) is the only derivative whose structure has been determined in an X-ray study.

Reaction of **Mo**(N_2) with 2−10 equiv of dry and oxygen-free acetylene affords paramagnetic, emerald green **Mo**(C_2H_2) in good yield (eq 2) along with an

(7) The only other known catalytic reduction of dinitrogen was discovered by Shilov over twenty years ago (Shilov, A. E. *Russ. Chem. Bull. Int. Ed.* **2003**, *52*, 2555). This system requires and is catalytic with respect to Mo, employs a strong reducing agent and methanol as the solvent, and yields a mixture of ammonia and hydrazine in which ammonia constitutes <10% (1 part in 11) of the mixture. The amount of dihydrogen produced is not known, and the mechanism of reduction has not been elucidated.

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Table 1. Crystal Data and Structure Refinement for [HIPTN$_3$N]Mo(C$_2$H$_4$), [HIPTN$_3$N]Mo(CH$_2$CH$_3$), "[HIPTN$_3$N]Mo(CCH)", and {[HIPTN$_3$N]Mo(C$_2$H$_4$)}BAr′$_4$[a]

	Mo(C$_2$H$_4$)	**Mo**(CH$_2$CH$_3$)	"**Mo**(CCH)"	[**Mo**(C$_2$H$_4$)]$^+$
empirical formula	$C_{119.50}H_{167}MoN_4$	$C_{119.50}H_{171.50}MoN_4$	$C_{122.75}H_{173.50}MoN_4$	$C_{153}H_{186.50}BF_{24}MoN_4$
fw	1755.51	1760.05	1801.10	2644.31
temp (K)	193(2)	100(2)	100(2)	100(2)
cryst syst	monoclinic	monoclinic	trigonal	monoclinic
space group	*P*2(1)/*c*	*P*2(1)/*c*	*P*3*c*1	*C*2/*c*
unit cell dimens (Å, deg)	$a = 16.063(4)$	$a = 16.1387(7)$	$a = 43.616(3)$	$a = 51.612(3)$
	$b = 19.355(5)$	$b = 19.6879(10)$	$b = 43.616(3)$	$b = 19.3084(10)$
	$c = 35.056(9)$	$c = 34.1544(17)$	$c = 24.703(3)$	$c = 32.2092(17)$
	$\alpha = 90$	$\alpha = 90°$	$\alpha = 90$	$\alpha = 90$
	$\beta = 91.478(8)$	$\beta = 93.147(2)$	$\beta = 90$	$\beta = 111.507(2)$
	$\gamma = 90$	$\gamma = 90$	$\gamma = 120$	$\gamma = 90$
volume (Å^3)	10895(5)	10835.8(9)	40697(7)	29863(3)
Z	4	4	12	8
density (calcd; Mg/m^3)	1.070	1.079	0.882	1.176
absorp coeff (mm^{-1})	0.167	0.168	0.136	0.166
F(000)	3816	3834	11760	11164
cryst size (mm^3)	0.20 × 0.15 × 0.10	0.25 × 0.20 × 0.10	0.20 × 0.15 × 0.10	0.37 × 0.25 × 0.20
θ range (deg)	1.16 to 20.81	1.58 to 26.02	1.65 to 18.00	1.60 to 24.71
index ranges	$-16 \le h \le 16$	$-19 \le h \le 19$	$-32 \le h \le 0$	$-60 \le h \le 56$
	$-19 \le k \le 19$	$-24 \le k \le 24$	$0 \le k \le 37$	$0 \le k \le 22$
	$-30 \le l \le 35$	$-41 \le l \le 42$	$0 \le l \le 21$	$0 \le l \le 37$
no. of reflns collected	36 731	189 662	246 843	234 477
no. of indep reflns	11 392 [*R*(int) = 0.0995]	21 355 [*R*(int) = 0.0968]	9347 [*R*(int) = 0.1405]	25 477 [*R*(int) = 0.0495]
compl to $\theta = 20.81°$ (%)	100.0	100.0	99.9	100.0
max. and min. transmn	0.9835 and 0.96730	.9834 and 0.9591	0.9866 and 0.9734	0.9676 and 0.9411
no. of data/restraints/params	11 392/1550/1211	21 355/487/1177	9347/1689/1210	25 477/5569/2246
goodness-of-fit on F^2	1.027	1.034	2.411	1.053
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0668	R1 = 0.0473	R1 = 0.1178	R1 = 0.0849
	wR2 = 0.1584	wR2 = 0.1061	wR2 = 0.3227	wR2 = 0.2135
R indices (all data)	R1 = 0.1217	R1 = 0.0778	R1 = 0.1382	R1 = 0.1216
	wR2 = 0.1858	wR2 = 0.1191	wR2 = 0.3300	wR2 = 0.2594
peak and hole (e Å^{-3})	0.775 and −0.511	0.912 and −0.588	1.215 and −0.434	2.110 and −1.700

[a] In all cases the wavelength was 0.71073 Å, the refinement method was full-matrix least-squares on F^2,and the absorption correction was semiempirical from equivalents. $[BAr'_4]^- = \{B[3,5\text{-}(CF_3)_2C_6H_3]_4\}^-$.

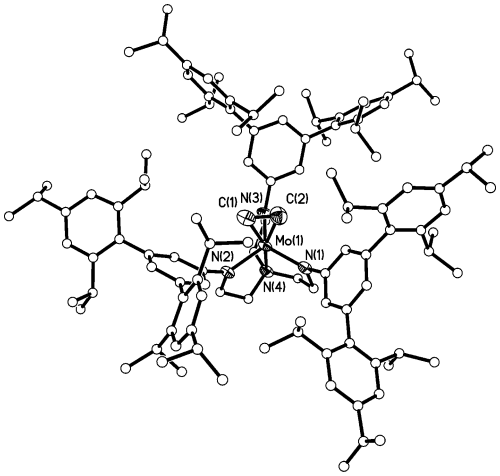
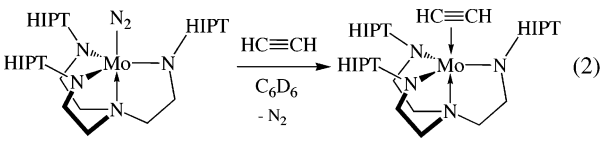


Figure 1. Molecular structure of [HIPTN$_3$N]Mo(C$_2$H$_4$). The Mo atom and all atoms directly bonded to it are drawn in their 50% thermal ellipsoid representations, with the other atoms as circles of arbitrary radius. Hydrogen atoms, disorders of isopropyl groups, and solvent molecules have been omitted for clarity.

insoluble purple-black solid that we assume to be polyacetylene. This reaction, unlike the reaction between **Mo**(N$_2$) and ethylene, is rapid (seconds) at room temperature. The ^{13}C-labeled compound can be prepared in a similar manner. No residual **Mo**(N$_2$) can be detected in IR spectra (as Nujol mulls). In **Mo**(C$_2$H$_2$) a relatively weak absorption at 1637 cm^{-1} is assigned as the ν_{CC} stretch of the coordinated alkyne on the basis of the absence of this absorption in the ^{13}C-labeled compound and a new shoulder at 1582 cm^{-1} that is close to the calculated ν_{CC} frequency of 1578 cm^{-1} expected in the^{13}C-labeled species. As in **Mo**(C$_2$H$_4$), upfield-shifted ligand backbone methylene resonances are not observed. An attempted X-ray structure of **Mo**(C$_2$H$_2$) showed the acetylene to be bonded to the metal in the expected fashion (η^2-C$_2$H$_2$), although the acetylene was disordered over three orientations within the coordination pocket. The disorder was not resolved satisfactorily, and therefore the structure will not be discussed in detail. In [TMSN$_3$N]Ta(η^2-C$_2$H$_2$) the acetylene was found to line up approximately along one of the Ta−N bond vectors.[34]



(2)

A solution of **Mo**(C$_2$H$_4$) in C$_6$D$_6$ was exposed to several equivalents of C$_2$H$_2$ in a J-Young tube. Polyacetylene formed over a period of 5 min, and the ^{1}H NMR spectrum indicated that virtually all of the acetylene had been consumed. However, no **Mo**(C$_2$H$_2$) or free C$_2$H$_4$ could be detected. Apparently ethylene is not replaced by acetylene rapidly under these conditions. The mechanism through which acetylene is polymerized in these systems is not known. Propagation must be fast compared to initiation, since little **Mo**(C$_2$H$_4$) appears to be consumed in the process.

When a solution of **Mo**(N$_2$) in benzene was exposed to CO (1 atm) and heated to ~60 °C overnight, the color changed from brown to red. Upon removal of all volatiles in vacuo, red **Mo**(CO) could be isolated virtually quan-

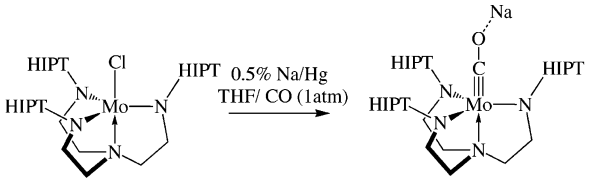
Table 2. Selected Bond Distances (Å) and Angles (deg) for [HIPTN$_3$N]Mo(C$_2$H$_4$), {[HIPTN$_3$N]Mo(C$_2$H$_4$)}BAr′$_4$, "[HIPTN$_3$N]Mo(CCH)", and [HIPTN$_3$N]Mo(CH$_2$CH$_3$)

	Mo(C$_2$H$_4$)	[**Mo**(C$_2$H$_4$)]$^+$	"**Mo**(CCH)"	**Mo**(CH$_2$CH$_3$)
Mo−N(1)	1.989(5)	1.958(4)	1.968(9)	1.9804(19)
Mo−N(2)	2.000(4)	1.991(5)	1.965(9)	1.9826(19)
Mo−N(3)	1.979(5)	1.965(4)	1.996(8)	1.9828(18)
Mo−N(4)	2.211(5)	2.262(4)	2.263(9)	2.276(2)
Mo−C(1)	2.190(7)	2.155(7)	1.924(11)	2.179(3)
Mo−C(2)	2.196(7)	2.250(6)	2.232(12)	
C(1)−C(2)	1.369(10)	1.315(10)	1.429(15)	1.514(3)
N(1)−Mo−N(2)	114.66(19)	111.93(18)	115.8(4)	119.31(8)
N(1)−Mo−N(3)	115.7(2)	121.09(16)	118.1(3)	115.51(8)
N(1)−Mo−N(4)	79.1(2)	76.42(14)	78.8(4)	79.57(8)
N(2)−Mo−N(3)	118.82(19)	111.72(16)	116.5(3)	115.22(8)
N(2)−Mo−N(4)	79.14(18)	78.67(16)	78.5(3)	78.93(8)
N(3)−Mo−N(4)	78.52(19)	75.51(15)	81.5(3)	79.65(8)
C(2)−C(1)−Mo	72.0(4)	76.6(4)	82.1(7)	120.91(17)
C(1)−C(2)−Mo	71.6(4)	68.7(4)	58.6(6)	99.13(9)[a]
C(1)−Mo−C(2)	36.4(3)	34.7(2)	39.3(4)	178.25(9)[b]

[a] N(3)−Mo−C(1). [b] C(1)−Mo−N(4).

titatively. A sharp, strong absorption was found at 1892 cm^{-1} in the IR spectrum (in Nujol), which is close to the ν_{CO} value reported for [C$_6$F$_5$N$_3$N]Mo(CO) (ν_{CO}(Nujol) = 1889 cm^{-1})[31] and slightly greater than that for [TMSN$_3$N]Mo(CO) (ν_{CO}(Nujol) = 1841 and 1832 cm^{-1}).[31] Broad resonances in the ^{1}H NMR spectrum of **Mo**(CO) at +19.79 and −30.12 ppm are assigned to the ligand backbone (NC*H*$_2$) resonances. These should be compared with backbone methylene resonances at 13.17 and −38.04 ppm in [TMSN$_3$N]Mo(CO) and 12.85 and −23.90 ppm in [C$_6$F$_5$N$_3$N]Mo(CO).[31]

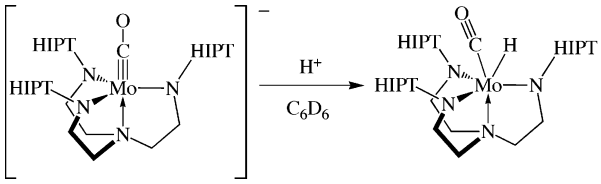
An attempt to prepare **Mo**(CO) through reduction of **Mo**Cl with 0.5% Na/Hg in THF under carbon monoxide yielded [**Mo**(CO)]Na as a yellow-orange crystalline solid after recrystallization from either heptane or pentane (eq 3). Since there are no resonances in the ^{1}H NMR spectrum for THF, the sodium ion is likely to be coordinated to the oxygen and to the aromatic rings of HIPT in a manner similar to that found in {[HIPTN$_3$N]-WN$_2$}K.[5] The ^{13}C-labeled analogue, [**Mo**(^{13}CO)]Na, displayed a singlet at +232.5 ppm in the ^{13}C{^{1}H} NMR spectrum. This chemical shift should be compared to



(3)

that found for the carbonyl carbon in {[C$_6$F$_5$N$_3$N]Mo-(CO)}Na(15-crown-5) (226.7 ppm) and {[C$_6$F$_5$N$_3$N]W-(CO)}Na(15-crown-5) (224.2 ppm).[31] The "oxycarbyne" description shown in eq 3 is of course an extreme, but it is consistent with the relatively low energy ν_{CO} observed in [**Mo**(CO)]Na and [**Mo**(^{13}CO)]Na at 1632 and 1601 cm^{-1}, respectively. These values are lower than those reported for {[C$_6$F$_5$N$_3$N]Mo(CO)}Na(15-crown-5) (1701 cm^{-1}) and {[C$_6$F$_5$N$_3$N]W(CO)}Na(THF)$_3$ (1726 cm^{-1}), but similar to that reported for {[C$_6$F$_5$N$_3$N]W-(CO)}Na(15-crown-5) (1628 cm^{-1}).[31] Attempts to prepare [TMSN$_3$N]Mo(CO) or [C$_6$F$_5$N$_3$N]Mo(CO) directly through reduction of [TMSN$_3$N]MoCl or [C$_6$F$_5$N$_3$N]MoCl under CO with strong reducing agents (e.g., sodium amalgam) also led to formation of {[RN$_3$N]Mo(CO)}$^-$ species.

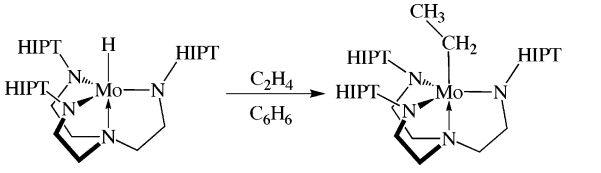
Upon addition of 1 equiv of [H(Et$_2$O)$_2$]BAr′$_4$, [3,5-LutH]BAr′$_4$, or [Et$_3$NH]BAr′$_4$ to a solution of [**Mo**(CO)]-Na or [**Mo**(CO)]Na(18-C-6), the color changed to yellow and a new diamagnetic compound could be isolated along with small amounts of free ligand and **Mo**(CO). A ^{13}C{^{1}H} NMR spectrum of the ^{13}CO derivative revealed a singlet at 200.5 ppm which appeared as a doublet in the proton-coupled ^{13}C NMR spectrum with a C−H coupling of 24.5 Hz. A doublet that we assign to the **Mo**H proton was also found in the ^{1}H NMR spectrum at −0.08 ppm with a C−H coupling value of 24.3 Hz. This diamagnetic product is believed to be the hydrido-carbonyl complex **Mo**(H)(CO), as shown in eq 4, rather than **Mo**≡COH, on the basis of comparison of NMR and IR data with data for [TMSN$_3$N]W(H)(CO), whose structure has been determined in an X-ray study.[37] The IR spectrum of **Mo**(H)(CO) shows a ν_{CO}



(4)

stretch at 1853 cm^{-1} (in C$_6$D$_6$), which shifts to 1810 cm^{-1} (in C$_6$D$_6$) in the ^{13}CO derivative. No Mo−H stretches are obvious in IR spectra. The CO stretch in [TMSN$_3$-N]W(H)(CO) is found at 1766 cm^{-1}. The hydride resonance in [TMSN$_3$N]W(H)(CO) was located at 2.80 ppm in the ^{1}H NMR spectrum with $J_{HC\alpha}$ = 12 Hz (in the ^{13}C-labeled compound) and $J_{WC\alpha}$ = 15.6 Hz. In the tungsten ^{13}C-labeled complex the CO stretch was found at 1727 cm^{-1} and the chemical shift in the ^{13}C{^{1}H} NMR spectrum was 209 ppm with J_{WC} = 133 Hz. **Mo**(H)(CO) also can be prepared by treating **Mo**H (see below) with CO.

Reactions that Involve [HIPTN$_3$N]MoH. The reaction between **Mo**H and ethylene in benzene yields paramagnetic, red **Mo**(CH$_2$CH$_3$) quantitatively (eq 5).



(5)

(37) Dobbs, D. A.; Schrock, R. R.; Davis, W. M. *Inorg. Chim. Acta* **1997**, *263*, 171.

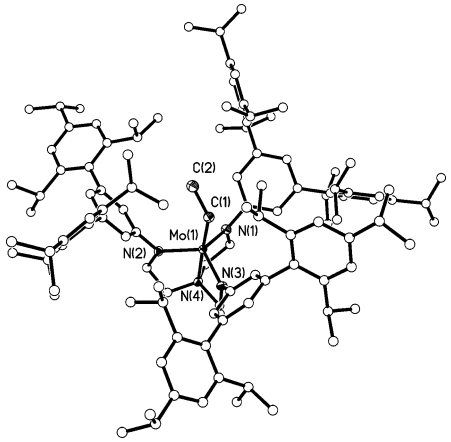


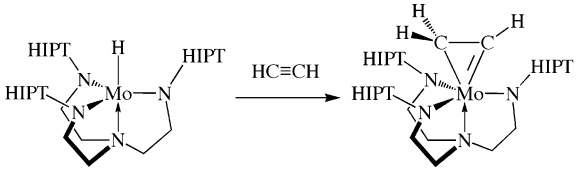
Figure 2. Molecular structure of [HIPTN$_3$N]Mo(CH$_2$CH$_3$). The Mo atom and all atoms directly bonded to it are drawn in their 50% thermal ellipsoid representations, with the other atoms as circles of arbitrary radius. Hydrogen atoms, disorders of isopropyl groups, and solvent molecules have been omitted for clarity.

Upfield resonances characteristic of methylene backbone protons in Mo(IV) complexes of this general type (e.g., [TMSN$_3$N]MoR where R = Me, Et, Bu, CH$_2$Ph, CH$_2$SiMe$_3$, etc.[28]) were found in the proton NMR spectrum at −25.89 and −75.90 ppm. The relative areas of the −75.90 ppm resonance versus the −25.89 ppm resonance suggest that the ethyl's methyl resonance is coincident with a −75.90 ppm resonance. In [TMSN$_3$N]Mo(CH$_2$CH$_3$) the ligand backbone methylene resonances were found at −25.05 and −60.0 ppm, with the ethyl's methyl resonance at −51.5 ppm.[28] No resonances for the ethyl carbons in **Mo**(CH$_2$CH$_3$) could be observed in the ^{13}C NMR spectrum of **Mo**(^{13}CH$_2$^{13}CH$_3$).

An X-ray structure of **Mo**(CH$_2$CH$_3$) (Figure 2 and Tables 1 and 2) showed it to contain a normal ethyl ligand, as shown by the Mo−C(1) bond length (2.179(3) Å), the C(1)−C(2) bond length (1.514(3) Å), and the Mo−C(1)−C(2) angle (120.91(17)°). Therefore we believe any α or β agostic interaction is unlikely. Agostic interactions also seem unlikely since only two orbitals (d_{xz} and d_{yz}) are available for either interaction and one electron is present in each of these orbitals. The structure of **Mo**(CH$_2$CH$_3$) should be compared to the structures of [TMSN$_3$N]Mo(CD$_3$) and [TMSN$_3$N]Mo(cyclohexyl).[28]

Analogous reactions between **Mo**H and 1-hexene or 1-octene yield **Mo**(hexyl) and **Mo**(octyl), respectively. We assume that the alkyls are terminal, although we cannot exclude the possibility that they are internal on the basis of the information in hand. As expected, both compounds are paramagnetic, exhibiting backbone methylene resonances around −10 and −68 ppm in ^{1}H NMR spectra in C$_6$D$_6$. In both compounds a very broad peak at −52 ppm is observable, which we believe to be a resonance either for a methylene group in the alkyl chain or for the methyl group at the end of the chain.

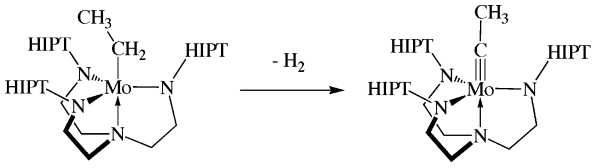
The reaction of **Mo**H with 2−5 equiv of acetylene affords yellow diamagnetic **Mo**(η^2-CHCH$_2$) (eq 6). A purple-black solid is also formed, which we again believe to be polyacetylene. The ^{1}H NMR spectrum of **Mo**(η^2-CHCH$_2$) is characteristic of a diamagnetic compound with C_3 symmetry analogous to [TMSN$_3$N]W(η^2-PhCCH$_2$) and [TMSN$_3$N]W(η^2-PhCCHPh).[37] A triplet resonance at 13.03 ppm corresponds to one proton and is



(6)

assigned to the alkylidene-like η^2-*H*CCH$_2$ proton of the "η^2-vinyl" group. The resonance due to the HCC*H*$_2$ protons is obscured by one of the broad triplets ascribed to the methylene backbone protons at 2.90 ppm. In the proton NMR spectrum of the ^{13}C-labeled analogue two broad doublets are observed at 13.02 ppm (J_{CH} = 192 Hz) and 2.93 ppm (J_{CH} = 160 Hz) for the *H*CCH$_2$ and HCC*H*$_2$ protons, respectively, while doublets are observed at 272.18 and 44.78 ppm (J_{CC} = 41 Hz) in the ^{13}C{^{1}H} NMR spectrum for the H*C*CH$_2$ and HC*C*H$_2$ carbon atoms of the η^2-vinyl group, respectively. These values should be compared with those known for [TMSN$_3$N]W(PhCCH$_2$) (3.65 ppm for WCPhC*H*$_2$, 242.5 ppm for W*C*PhCH$_2$, and 56.58 ppm for WCPh*C*H$_2$). The connectivity in **Mo**(η^2-CHCH$_2$) has been confirmed in an X-ray crystallographic study, although the presence of **Mo**(C$_2$H$_2$) as a cocrystallized impurity prevented a high-quality solution. The observed C_3 symmetry in **Mo**(η^2-CHCH$_2$) and [TMSN$_3$N]W(η^2-PhCCH$_2$) and similar species on the NMR time scale can be ascribed to the degeneracy of the d_{xz} and d_{yz} orbitals involved in bonding of the η^2-vinyl ligand to the metal and therefore facile "rotation" of the η^2-vinyl group about the z axis. (It is not necessary to postulate an η^2-vinyl to η^1-vinyl interconversion, although that possibility cannot be excluded.) It is normal to observe C_3 symmetry in d^0 compounds in this general category, e.g., even in [TMSN$_3$N]W(cyclopentylidene)H.[32]

Alkylidynes. Upon heating a toluene solution of **Mo**(CH$_2$CH$_3$) (generated in situ by reacting **Mo**-H with excess ethylene) to 160 °C in a closed flask, it decomposes smoothly to give **Mo**≡CCH$_3$ in 63% isolated yield. An NMR scale reaction carried out in toluene-d_8 showed that conversion of **Mo**≡CCH$_3$ to **Mo**(CH$_2$CH$_3$) was quantitative (eq 7). NMR spectra of **Mo**≡CCH$_3$ are



(7)

straightforward and typical of Mo(VI) or W(VI) alkylidyne complexes.[38] The alkylidyne carbon resonance was found at 299.3 ppm in C$_6$D$_6$. The rate of formation of **Mo**≡CCH$_3$ was determined by observing the growth of resonances in the proton NMR spectrum at 3.68 and 2.32 ppm in C$_6$D$_6$, which correspond to one set of methylene backbone protons and the methyl protons of the ethylidyne ligand, respectively. A plot of ln(1−F) vs time (where F is the fraction of alkylidyne formed versus time) showed the reaction to be first order in Mo with rate constants 2.76(26) × 10^{-5} s^{-1} (using the 3.68 ppm resonance) and 2.36(7) × 10^{-5} s^{-1} (using the 2.32 ppm resonance), or $k \approx 2.5 \times 10^{-5}$ s^{-1} (half-life ∼460 min)

(38) Murdzek, J. S.; Schrock, R. R. In *Carbyne Complexes*; VCH: New York, 1988.

at 145 °C. Evolution of dihydrogen from Mo and (primarily) W alkyl complexes in an α,α dehydrogenation reaction is well-documented for $[TMSN_3N]MCH_2R$ species[27,28,32] and to a lesser extent for $[C_6F_5N_3N]$-MCH_2R species (M = Mo or W).[29] However, the only $[TMSN_3N]Mo(n\text{-alkyl})$ species that evolves dihydrogen cleanly is $[TMSN_3N]$Mo(neopentyl), since neopentyl most easily undergoes processes that involve one or more α hydrogen atoms(α abstraction, α elimination, or α,α dehydrogenation).[39] In other $[TMSN_3N]Mo(n\text{-alkyl})$ complexes decomposition takes place before, or in competition with, loss of dihydrogen. The stability of the $[HIPTN_3N]^{3-}$ system toward intermolecular decomposition reactions and intramolecular decomposition reactions (e.g., CH cleavage[32]) therefore allows the relatively high temperature to be reached that is required for the α,α dehydrogenation reaction in $[RN_3N]Mo(n\text{-alkyl})$ complexes to take place without complications. α,α Dehydrogenation reactions for $[TMSN_3N]W(CH_2R)$ complexes are believed to be orders of magnitude faster than for $[TMSN_3N]Mo(CH_2R)$ complexes, so much so that $[TMSN_3N]W(CH_3)$ is the only observable $[TMSN_3N]W$-(CH_2R) species. (α,α Dehydrogenation in methyl species is believed to be the slowest by orders of magnitude.) Unfortunately no direct comparison of the rates for Mo and W have been possible to date. Addition of ethylene to $[TMSN_3N]WH$ is known to lead to $[TMSN_3N]W{\equiv}CCH_3$ at room temperature, presumably via formation of $[TMSN_3N]WCH_2CH_3$ followed by loss of dihydrogen.[37]

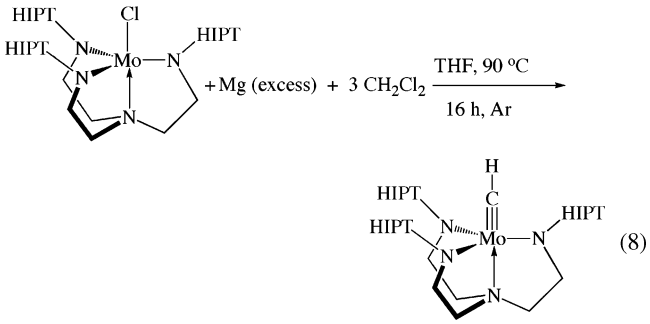
First-order decompositions of **Mo**(CH_2CH_3) and **Mo**-(hexyl) were followed side by side in $C_6D_5CD_3$ at 152 ± 1 °C in sealed J-Young tubes with triphenylmethane as the internal standard. The rates of formation of **Mo**≡CCH_3 and **Mo**≡CC_5H_{11} were determined by observing the growth of a resonance for the methylene backbone protons in the proton NMR spectra of the alkylidyne complexes near 3.7 ppm. The rate constants were found to be $1.00(3) \times 10^{-4}$ and $1.20(5) \times 10^{-4}$ s^{-1}, respectively.

Decomposition of $[HIPTN_3N]$Mo(hexyl) in the presence of 5 equiv of 1-octene led to formation of a statistical mixture of $[HIPTN_3N]Mo{\equiv}CC_5H_{11}$ and $[HIPTN_3N]$-$Mo{\equiv}CC_7H_{15}$ (∼1:6), according to carbon NMR spectra of the resulting mixture. Therefore it appears that β hydride elimination to form the olefin and **Mo**H is fast relative to α,α dehydrogenation to give the alkylidyne species, although that equilibrium lies far to the side of the alkyl complexes.

As in the case of $[TMSN_3N]Mo(CH_3)$,[28] all attempts to promote loss of hydrogen from **Mo**(CH_3) (see below for the synthesis) did not produce **Mo**≡CH. No change was observed upon heating a toluene solution of **Mo**CH_3 to 160 °C for 24 h. However, since $[TMSN_3N]Mo{\equiv}CH$ could be prepared by heating $[TMSN_3N]Mo(cyclopropyl)$,[28] we might expect **Mo**≡CH also to be a stable species. But in view of the difficulties associated with preparing alkyls in reactions between $[HIPTN_3N]$MoCl and alkylating agents (see later), it seems doubtful that we would be able to prepare **Mo**(cyclopropyl) and ultimately **Mo**≡CH in this manner.

In the last several years, a new approach to alkylidyne triamido complexes has been discovered. Cummins devised a synthesis of alkylidyne complexes of the type $[N(t\text{-Bu})Ar]_3Mo{\equiv}CCH_2SiMe_3$ (Ar = 3,5-$Me_2C_6H_3$) and their conversion to $(AdO)_3Mo{\equiv}CR$ species upon treatment with 1-adamantanol.[40] In 1999, Fürstner reported that $Mo[N(t\text{-Bu})Ar]_3$ reacted readily at room temperature with CH_2Cl_2 to produce a mixture of $[N(t\text{-Bu})$-$Ar]_3MoCl$ and $[N(t\text{-Bu})Ar]_3Mo{\equiv}CH$.[41] In 2003 Moore[42] reported that compounds of the type $[N(t\text{-Bu})Ar]_3Mo{\equiv}$CR (R = H, Me, Et) could be prepared readily in good yield from $[N(t\text{-Bu})Ar]_3Mo$ or $[N(t\text{-Bu})Ar]_3MoCl$ in the presence of magnesium and RCH_2Cl_2 in THF and that these species could be used as precursors to triphenoxide alkylidyne complexes of the type that are known to metathesize alkynes.[38,43,44] Therefore, to synthesize $[HIPTN_3N]Mo{\equiv}CH$, we adopted a strategy analogous to that employed by Moore.

A mixture of **Mo**Cl, 3 equiv of dichloromethane, and a large excess of magnesium powder in THF was heated at 90 °C in vacuo in a sealed tube for 16 h. A proton NMR spectrum showed that **Mo**Cl had been consumed completely and **Mo**≡CH had formed in good yield (eq 8). (Dinitrogen must be avoided in order to prevent formation of magnesium derivatives of {**Mo**-N=N}$^-$.[2,6]) The yield of yellow **Mo**≡CH is ∼65%, although the high solubility of this compound in pentane is at least partially responsible for the modest isolated yield. The details of how such reactions proceed are not known.



(8)

The NMR spectrum of **Mo**≡CH is unremarkable. The methylidyne proton resonance is found at 4.46 ppm, while the alkylidyne carbon resonance is found at 288.4 ppm. For comparison the proton and carbon methylidyne resonances in $[TMSN_3N]Mo{\equiv}CH$ are found at 5.54 and 284.3 ppm,[28] respectively, and in $[(3,5\text{-}Me_2C_6H_3)(t\text{-}$Bu)$N]_3Mo{\equiv}CH$ at 5.66 and 287.5 ppm,[45,46] respectively. An attempt to prepare **Mo**≡CMe under analogous conditions from $MeCHCl_2$ and **Mo**Cl gave <5% of **Mo**≡CMe. The sterically crowded nature of the $[HIPTN_3N]^{3-}$ ligand is likely to be a significant factor preventing ready formation of **Mo**≡CMe.

Addition of [2,6-LutH]BAr′$_4$ to samples of **Mo**≡CH and **Mo**≡CMe in C_6D_6 led to no reaction, even after heating the samples at 120 °C for 2 days. When **Mo**≡CR was mixed with both [2,6-LutH]BAr′$_4$ and Cp*$_2$Cr

(39) Schrock, R. R. In *Reactions of Coordinated Ligands*; Braterman, P. R., Ed.; Plenum: New York, 1986.

(40) Tsai, Y. C.; Diaconescu, P. L.; Cummins, C. C. *Organometallics* **2000**, *19*, 5260.

(41) Fuerstner, A.; Mathes, C.; Lehmann, C. W. *J. Am. Chem. Soc.* **1999**, *121*, 9453.

(42) Zhang, W.; Kraft, S.; Moore, J. S. *Chem. Commun.* **2003**, 832.

(43) McCullough, L. G.; Schrock, R. R.; Dewan, J. C.; Murdzek, J. S. *J. Am. Chem. Soc.* **1985**, *107*, 5987.

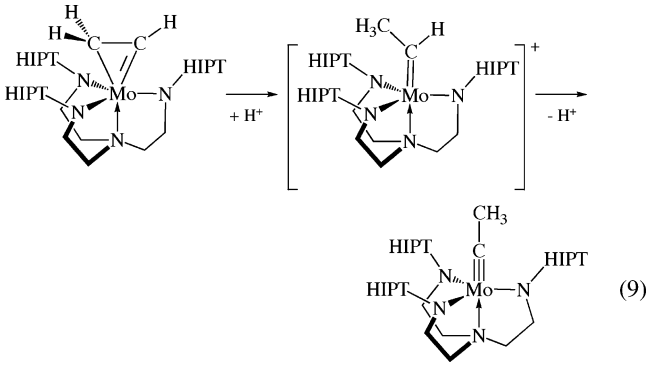
(44) Schrock, R. R. *Acc. Chem. Res.* **1986**, *19*, 342.

(45) Peters, J. C.; Odom, A. L.; Cummins, C. C. *Chem. Commun.* **1997**, 1995.

(46) Greco, J. B.; Peters, J. C.; Baker, T. A.; Davis, W. M.; Cummins, C. C.; Wu, G. *J. Am. Chem. Soc.* **2001**, *123*, 5003.

in C_6D_6, no reaction involving **Mo**≡CR again was observed; only H_2 was generated.

In view of the stability of **Mo**≡CCH_3, and the many rearrangements reported for W triamidoamine alkyl complexes,[32] we were curious as to whether **Mo**(η^2-$CHCH_2$) would rearrange to **Mo**≡CCH_3 upon heating. However, we saw no evidence for such a rearrangement in C_6D_6 at 80 °C after 2 h; only decomposition was observed. On the other hand, in the process of exploring the potential protonation of **Mo**(η^2-$CHCH_2$) by [2,6-LutH]BAr'_4 to yield [**Mo**(η^2-CH_2CH_2)]$^+$, a known compound (see below), we noticed that **Mo**(η^2-$CHCH_2$) rearranged to **Mo**≡CCH_3. Kinetic studies were carried out in C_6D_6 with Ph_3CH as the internal standard; disappearance of the triplet resonance at 13.03 ppm corresponding to the η^2-C*H*CH_2 proton of the vinyl group was monitored. The isomerization is first order in Mo in the presence of [2,6-LutH]BAr'_4 (2.57 mM) with $k_{obs} = 1.10(5) \times 10^{-5}$ s^{-1}. Upon doubling the concentration of [2,6-LutH]BAr'_4, $k_{obs} = 2.00(4) \times 10^{-5}$ s^{-1}, which suggests that the reaction is first order in [2,6-LutH]-BAr'_4. If we assume that d[**Mo**(η^2-$CHCH_2$)]/d$t = -k$[Mo-(η^2-$CHCH_2$)][LutHBAr′$_4$], then the calculated second-order rate constants are $4.27(20) \times 10^{-3}$ and $3.89(8) \times 10^{-3}$ M^{-1} s^{-1} for these two runs. We propose that a proton is delivered to the CH_2 carbon atom in **Mo**(η^2-$CHCH_2$) by [2,6-LutH]BAr'_4 to form intermediate [**Mo**=$CHCH_3$]$^+$, from which 2,6-lutidine then removes the α proton to yield **Mo**≡CCH_3 (eq 9).



(9)

Attempts to Prepare [HIPTN$_3$N]MoX Complexes (X = alkyl, cyanide, acetylide). Alkylation of **Mo**Cl with LiMe under a variety of conditions gave a mixture of unreacted **Mo**Cl, **Mo**(N_2) (the major product), and other unidentified products, either at room temperature or at −35 °C. Treatment of a mixture of H_3[HIPTN$_3$N] and $MoCl_4(THF)_2$ with LiMe at −35 °C in THF, a type of reaction that led to [ArN$_3$N]MoMe (where Ar is a simple aryl group),[47] affords the same mixture of products as reactions between **Mo**Cl and LiMe. Apparently the major reaction is reduction of **Mo**Cl by LiMe to "[**Mo**Cl]$^-$", which then loses chloride and binds dinitrogen to yield **Mo**(N_2). A reaction between [**Mo**(NH_3)]-BAr'_4 and LiMe in THF again led to primarily **Mo**(N_2), again by reduction of Mo(IV) to Mo(III). An important difference between **Mo**Cl and [TMSN$_3$N]MoCl, for example, where [TMSN3N]MoR complexes are prepared readily (R = Me, Et, Bu, CH_2Ph, CH_2SiMe_3, etc.[28]), is a greater degree of steric crowding in [HIPTN$_3$N]M species, a circumstance that is likely to inhibit nucleophilic attack at the metal center and favor electron transfer.

The reaction between 1.2 equiv of $AlMe_3$ and **Mo**Cl (∼0.1 M) in C_6D_6 led to the disappearance of **Mo**Cl and formation of **Mo**Me after 40 h at 22 °C. **Mo**Me was prepared and isolated in 28% yield by stirring a mixture of **Mo**Cl with 2−3 equiv of $AlMe_3$ in benzene for 2 days. (Like all compounds in this general category, **Mo**Me is highly soluble in saturated hydrocarbons and therefore cannot be isolated in high yield on relatively small scales.) The ^{1}H NMR spectrum of **Mo**Me exhibits two ligand backbone C*H*$_2$ resonances at −14.8 and −66.3 ppm in C_6D_6. For comparison, the proton NMR spectrum of [TMSN$_3$N]MoMe in C_6D_6 contains resonances for the backbone methylene protons at −25.00 and −83.24 ppm.[28] These should be compared with backbone resonances at −25.89 and −75.90 ppm in **Mo**(ethyl) and −10 and −68 ppm in **Mo**(hexyl) and **Mo**(octyl).

Attempts to prepare **Mo**Et in a reaction between $AlEt_3$ and **Mo**Cl under conditions similar to those used to prepare **Mo**Me led to formation of **Mo**Et in a yield of ∼25% mixed with **Mo**(C_2H_4) and other unidentified species. Heating a mixture of **Mo**Et and $AlEt_3$ under the same conditions led to consumption of **Mo**Et, so it is possible that **Mo**Et is in fact the primary product, but it reacts further with $AlEt_3$ to give **Mo**(C_2H_4). In any case, the reaction between **Mo**H and ethylene is clearly a superior method of preparing **Mo**Et.

We felt that we might be able to prepare **Mo**-C≡CR derivatives since [TMSN$_3$N]Mo-C≡CR species can be prepared readily if R is not a proton.[48] Attempts to make [TMSN$_3$N]Mo-C≡CH led to the formation of the "tail-to-tail" acetylide coupling product, [TMSN$_3$N]Mo≡C-CH=CH-C≡Mo[TMSN$_3$N].[48] Therefore steric hindrance might prevent a similar coupling between **Mo**-C≡CH species. Examples of acetylide coupling in related triamido species have been reported.[49]

Heating a mixture of [**Mo**(NH_3)]BAr'_4 and NaC≡CH in fluorobenzene to 90 °C for 3 h led to formation of a yellow crystalline compound in 57% isolated yield. The proton NMR spectrum of this compound suggests that it is diamagnetic and that it has no symmetry. Therefore is unlikely to be **Mo**-C≡CH, which should be paramagnetic, or **Mo**≡C-CH=CH-C≡Mo[HIPTN$_3$N], which is expected to be diamagnetic and to have C_3 symmetry on the NMR time scale. Reactions between **Mo**Cl and NaC≡CH in C_6D_5Cl at 80 °C for several hours did not lead to the yellow product, only to apparent decomposition.

A difficult X-ray structural determination of the yellow product showed that the acetylide has "inserted" into an *ortho* C−H bond in the phenyl ring attached to the amido nitrogen (eq 10; Figure 3 and Tables 1 and 2). The C−C bond distance is 1.429(15) Å, while the Mo−C distances are 1.924(11) and 2.232(12) Å. Therefore this compound can be placed in the category of an η^2-vinyl complex, similar to **Mo**(η^2-$CHCH_2$) described above. The "alkylidene" proton resonance was found at 13.50 ppm, while the other proton resonance in the η^2-vinyl moiety could be observed at 4.69 ppm; these two

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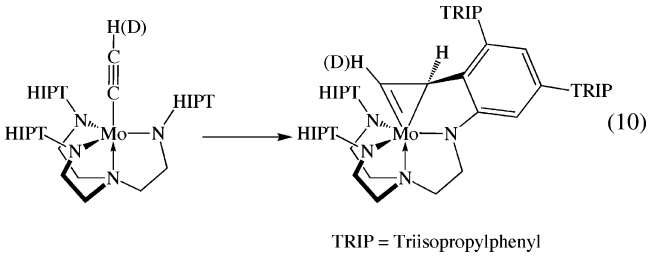

protons are coupled with $J_{HH} = 2.4$ Hz. In the ^{13}C NMR spectrum, the two η^2-vinyl carbon resonances were found at 287.6 and 65.4 ppm with C−H coupling constants of 189.3 and 162.9 Hz, respectively. The product of the reaction between [**Mo**(NH_3)]BAr'_4 and NaC≡CD in fluorobenzene does not have the "alkylidene" H_α resonance at 13.50 ppm. Therefore it appears, at least in the absence of a double labeling experiment, that the "alkylidene proton" comes from the acetylide and the benzylic proton from the phenyl ring as a consequence of "insertion" of the acetylide into the *ortho* C−H bond of the phenyl ring bound to the amido nitrogen. At this stage we assume that **Mo**-C≡CH forms, but is unstable. The mechanism of conversion of **Mo**-C≡CH into observed products is not known. At face value one could be tempted to ascribe some carbenoid character to the α carbon atom in the intermediate acetylide complex.

Orange paramagnetic **Mo**CN can be isolated in good yield from the reaction between [**Mo**(NH_3)]BPh_4[2] and [Bu_4N]CN in fluorobenzene. During the course of the reaction, colorless crystals of [Bu_4N]BPh_4 were deposited. No absorption in the IR spectrum of **Mo**CN that could be attributed to the ν_{CN} stretch is observed, a situation that is analogous to that reported for crystallographically characterized [$TMSN_3N$]MoCN.[31] Attempts to prepare **Mo**CN via the reaction between **Mo**Cl with Me_3SiCN failed; the reaction was slow even at temperatures above 100 °C, and when neat Me_3SiCN was employed at these temperatures, an unidentified yellow solid precipitated from solution. The reaction between **Mo**Cl with Me_3SiCN was not studied further.

Addition of $B(C_6F_5)_3$ to **Mo**CN in C_6D_6 resulted in the formation of a green solution that we propose contains a $B(C_6F_5)_3$ adduct of **Mo**CN, namely, **Mo**CN→$B(C_6F_5)_3$. This assignment is based upon a strong absorption in the IR spectrum at 2184 cm^{-1} that we assign to the ν_{CN} stretch, as well as ^{19}F and ^1H NMR spectroscopic data that are consistent with this proposal. Apparently the substantial change in dipole moment makes the CN stretch in **Mo**CN→$B(C_6F_5)_3$ readily observable. Unfortunately, all attempts to obtain crystals of **Mo**CN→$B(C_6F_5)_3$ from heptane led only to re-formation of **Mo**CN and $B(C_6F_5)_3$.

Electrochemical Studies and Syntheses of Cationic Species. Electrochemical studies[50] on several of the compounds reported here were carried out in 0.1 M [Bu_4N]BAr'_4 (where Bu is *n*-butyl) in PhF at room temperature (Table 3). The advantages of relatively inert electrolytes and solvents were demonstrated more than a decade ago[51] and have been featured in several studies by Geiger in the last few years.[52−56] Therefore we have employed these conditions in relatively routine electrochemical (CV) studies.

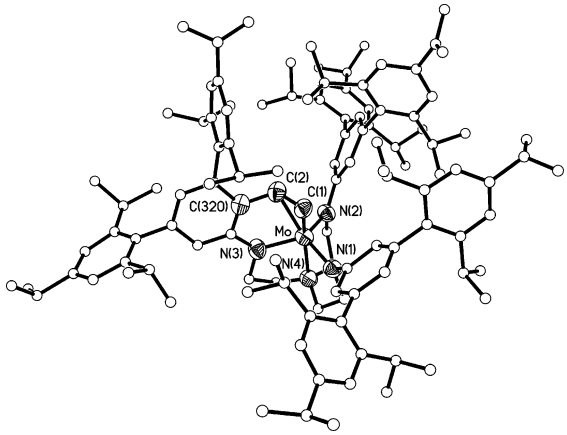

Figure 3. Molecular structure of "[$HIPTN_3N$]Mo(CCH)". The Mo atom, all atoms directly bonded to it, and C(320) are drawn in their 50% thermal ellipsoid representations, with the other atoms as circles of arbitrary radius. Hydrogen atoms and solvent molecules have been omitted for clarity.

Table 3. Cyclic Voltammetric and Differential Pulse Voltammetric Data Obtained for Various Compounds Based on [$HIPTN_3N$]Mo and Referenced to the $Cp_2Fe^{+/0}$ Couple[a]

redox couple	$E_{1/2}$ (V vs Cp_2Fe)	ref
[$HIPTN_3N$]Mo$(N_2)^{0/-}$	−2.01	6
[$HIPTN_3N$]Mo$(NH_3)^{+/0}$	−1.63	6
[$HIPTN_3N$]Mo$(N_2)^{+/0}$	−0.66	6
[$HIPTN_3N$]Mo$(CN)^{+/0}$	−0.27	this work
[$HIPTN_3N$]Mo$(CN)^{0/-}$	−1.61	this work
[$HIPTN_3N$]Mo$(C_2H_4)^{+/0}$	−0.42	this work
[$HIPTN_3N$]Mo$(C_2H_2)^{+/0}$	−0.94	this work
[$HIPTN_3N$]Mo$(\eta^2$-$CHCH_2)^{+/0}$	+0.54 (E_{pa})	this work
$Cp_2Co^{+/0}$	−1.33	6
$Cp^*_2Cr^{+/0}$	−1.63	6
$Cp^*_2Co^{+/0}$	−2.01	6

[a] Cyclic voltammetry at 1.6 mm Pt working electrode or 3.0 mm glassy carbon working electrode at 22 °C in 0.1 M [Bu_4N]BAr'_4 in PhF at scan rates of 10−200 mV/s.

No reductions were observed for **Mo**(C_2H_4), **Mo**(C_2H_2), or **Mo**$(\eta^2$-$CHCH_2)$ in the region −1.5 to −2.7 V (vs $Cp_2Fe^{+/0}$). However, **Mo**$(C_2H_4)^{+/0}$ and **Mo**$(C_2H_2))^{+/0}$ redox couples can be observed at −0.42 and −0.94 V, respectively, which are reversible on the CV time scale (50 mV s^{-1}), while **Mo**(CN) exhibits two redox processes at −0.27 and −1.61 V that we assign to the **Mo**$(CN)^{+/0}$ and **Mo**$(CN)^{0/-}$ redox couples, respectively. The **Mo**(CN) couples should be compared with those at −0.66 V for **Mo**$(N_2)^{+/0}$ and at −2.01 V for **Mo**$(N_2)^{0/-}$;[6] that is, **Mo**(CN) is harder to oxidize but easier to reduce than **Mo**(N_2), which can be rationalized on the basis of the metal's oxidation state in each circumstance (formally Mo(IV) in **Mo**(CN) vs Mo(III) in **Mo**(N_2)). The **Mo**$(CN)^{0/-}$ couple (−1.61 V) is found at almost the same potential as that for **Mo**$(NH_3)^{+/0}$ (−1.63 V).[6]

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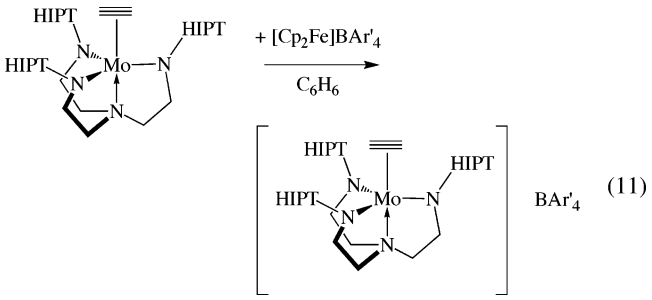
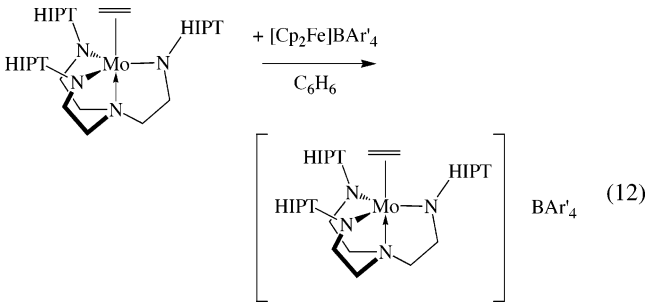
Upon addition of a slight excess of $[Cp_2Fe]BAr'_4$ to a solution of **Mo**(η^2-C_2H_2) in C_6D_6, ferrocene was formed along with the diamagnetic [**Mo**(η^2-C_2H_2)]BAr'_4 (eq 11).



(11)

The relatively sharp ^{1}H NMR resonances associated with the acetylene in [**Mo**(η^2-C_2H_2)]BAr'_4 are found at 11.34 ppm. The proton resonances in [**Mo**(η^2-$^{13}C_2H_2$)]-BAr'_4 appear as a complex second-order splitting pattern centered around 11.3 ppm, whereas in the $^{13}C\{^1H\}$ NMR spectrum the resonance assigned to the acetylene carbon atoms appears as a singlet at 214.6 ppm. In the proton-coupled ^{13}C NMR spectrum a second-order pattern again was found that was similar to the pattern found in the ^{1}H NMR spectrum.

Addition of $[Cp_2Fe]BAr'_4$ to a C_6D_6 solution of **Mo**(η^2-C_2H_4) led to formation of ferrocene and [**Mo**(C_2H_4)]BAr'_4 (eq 12). Both ^{1}H and $^{13}C\{^1H\}$ NMR spectra for [**Mo**(C_2-



(12)

H_4)]BAr'_4 and [**Mo**($^{13}C_2H_4$)]BAr'_4 (prepared in situ) suggest that the cation is diamagnetic. However, the ethylene proton resonance, which appears at 5.14 ppm (a doublet in the ^{13}C-labeled complex), and the ethylene carbon atom resonance, which appears at 84.3 ppm, are both quite broad. When the ^{1}H NMR sample is cooled, the 5.14 ppm resonance shifts upfield, and when the sample is heated, the ethylene resonance shifts downfield. There is no exchange of the coordinated ethylene with free ethylene in [**Mo**(C_2H_4)]$^+$ on the NMR time scale.

For comparison, it should be noted that oxidation of compounds of the type [RN_3N]M(C_2H_4) (where R = $SiMe_3$, M = Mo; R = C_6F_5, M = W) have been reported in the literature. Oxidation of [$TMSN_3N$]Mo(C_2H_4) with $[Cp_2Fe]OTf$ in CH_2Cl_2 yields [$TMSN_3N$]Mo(OTf) (in 6 h at 22 °C),[28] whereas oxidation of [$C_6F_5N_3N$]W(C_2H_4) yields {[$C_6F_5N_3N$]W(C_2H_4)}OTf.[31] Presumably, ethylene in {[$TMSN_3N$]Mo(C_2H_4)}OTf is readily replaced by triflate, whereas ethylene in {[$C_6F_5N_3N$]W(C_2H_4)}OTf is not, even in the presence of the more electron-withdrawing [$C_6F_5N_3N$]$^{3-}$ ligand. In {[$C_6F_5N_3N$]W-(C_2H_4)}[OTf] (in $CDCl_3$)[31] the ethylene protons appear as a singlet at 3.10 ppm. In [$TMSN_3N$]Ta(C_2H_4) the ethylene proton resonance appears at 2.15 ppm (in C_6D_6) and the ethylene carbon resonance appears at 62.6 ppm.[34]

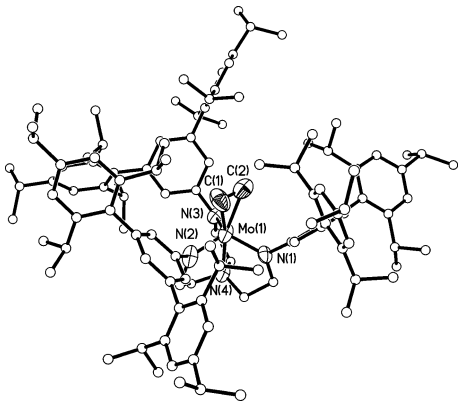


Figure 4. Molecular structure of {[$HIPTN_3N$]Mo(C_2H_4)}-BAr'_4. The Mo atom and all atoms directly bonded to it are drawn in their 50% thermal ellipsoid representations, with the other atoms as circles of arbitrary radius. Hydrogen atoms, solvent molecules, and the anion have been omitted for clarity.

We do not know why the ethylene proton resonance in **Mo**(C_2H_4)$^+$ is broad. One possibility is electron transfer between **Mo**(C_2H_4)$^+$ and a trace of residual **Mo**(C_2H_4) (either a self-exchange or one that includes $Cp_2Fe^{0/+}$). Another possibility is that the ground state of {[$HIPTN_3N$]Mo(C_2H_4)}$^+$ is a singlet, but a triplet is thermally accessible. Studies aimed at resolving this issue are ongoing.

An X-ray structure of [**Mo**(C_2H_4)]BAr'_4 was completed (Figure 4, Tables 1 and 2), although it was complicated by a (resolved) disorder involving the $BAr'_4{}^-$ anion. (See Experimental Section.) The Mo−C(1) and Mo−C(2) bond distances in [**Mo**(C_2H_4)]BAr'_4 are essentially the same as they are in **Mo**(C_2H_4). The C(1)−C(2) distance is shorter than what it is in **Mo**(C_2H_4), consistent with a lesser degree of back-bonding to ethylene, although even that difference is only marginal.

Conclusions

Organometallic complexes that contain the [$HIPTN_3N$]$^{3-}$ ligand appear to be much more robust than those that contain trimethylsilyl- or pentafluorophenyl-based ligands. However, the crowded nature of [$HIPTN_3N$]$^{3-}$ ligands slows reactions at the metal center in many cases. The [$HIPTN_3N$]$^{3-}$ systems are not completely robust, as evidenced by the complication observed in the attempt to prepare an acetylide derivative. Nevertheless, [$HIPTN_3N$]$^{3-}$ ligands would appear to be more robust in general than other triamidoamine ligands employed to date. Studies concerning the use of several of the species reported here as catalyst precursors for the reduction of dinitrogen to ammonia will be reported in due course elsewhere.

Experimental Section

General Procedures. All experiments were conducted under nitrogen in a Vacuum Atmospheres drybox or using standard Schlenk techniques. Glassware was dried at ~190 °C overnight. Pentane was washed with HNO_3/H_2SO_4 (5/95 v/v), sodium bicarbonate, and water, dried with $CaCl_2$, and then sparged with nitrogen and passed through alumina

columns. Dry and deoxygenated benzene was purchased from Aldrich and passed through Q5 and alumina columns. Dry and deoxygenated THF was purchased from Aldrich and passed through an alumina column. Toluene was sparged with nitrogen, passed through alumina columns, and vacuum-transferred from sodium benzophenone ketyl. Fluorobenzene was dried by vigorous stirring over P_2O_5 and then vacuum distilled followed by degassing by three freeze−pump−thaw cycles. Benzene-d_6 was degassed (freeze−pump−thaw) and vacuum-transferred from sodium benzophenone ketyl. Tetramethylsilane was purchased from Lancaster and vacuum-transferred from Na_3K benzophenone.

MoCl, **Mo**N_2, [**Mo**(NH_3)]BPh_4, and **Mo**H were prepared according to published procedures,[2,6] as were $NaBAr'_4$[57] and [Cp_2Fe]BAr'_4.[58] Calcium carbide, 2,6-lutidine, anhydrous 1 M HCl in diethyl ether, $NaBPh_4$, Cp_2Fe, ethylene, CO, $^{13}C_2H_2$ and $^{13}C_2H_4$, 1-hexene, and 1-octene were purchased from commercial sources and used as received. Acetylene (BOC, Grade 2.6) was purified by slowly bubbling it through a fine frit in a trap containing concentrated H_2SO_4 (after previously passing nitrogen through the H_2SO_4 for several hours) and then a dry ice/acetone trap to remove water and dissolved acetone. A large Schlenk flask containing 3 Å molecular sieves was carefully backfilled with acetylene (1 atm). This flask was then immersed in a liquid-N_2/Et_2O slush bath and a vacuum applied in an attempt to remove any oxygen impurities. Acetone was dried over 4 Å molecular sieves and vacuum transferred onto 4 Å molecular sieves. This was repeated three times.

Dry and oxygen-free acetylene was prepared by adding water to CaC_2. Typically powdered CaC_2 (∼1.3 g) was added via an addition tube to a three-necked 1 L flask containing benzene (10 mL) in ∼0.6 mL of water that had been degassed via several freeze−pump−thaw cycles and still under vacuum. After all visible signs of gas evolution had ceased (several hours), the flask was then placed in a dry ice/acetone cooling bath for ∼10 min and the contents of the headspace transferred to a 500 mL Schlenk flask fitted with a Kontes Teflon plug (containing some anhydrous $CaCl_2$) immersed in liquid N_2. The receiving flask was then sealed and allowed to warm to room temperature, during which time the solid acetylene vaporized. The pressure of acetylene was kept slightly below 1 atm.

Routine ^{1}H NMR spectra were recorded on either a Varian Unity or a Mercury 300 MHz spectrometer at room temperature. Data are listed in parts per million downfield from tetramethylsilane and referenced either to internal tetramethylsilane or to the resonance for C_6D_5H at 7.16 ppm. ^{13}C NMR spectra were recorded at 75.5 MHz and referenced to the residual solvent peak. Infrared spectra were recorded on a Nicolet Avatar 360 FT-IR spectrometer either as a Nujol mull (KBr plates) or in a demountable solution cell (0.2 mm Teflon spacer, KBr plates). Electrochemical measurements were carried out with a BAS CV-50W potentiostat. Platinum disk (1.6 mm dia) or a glass carbon disk (3 mm dia), a platinum wire, and a silver wire submerged in a solution of 0.1 M [Bu_4N]BAr'_4 in PhF were used as working, auxiliary, and reference electrodes, respectively. All measurements were done in 0.1 M [Bu_4N]BAr'_4 in PhF and referenced externally and/or internally to Cp_2Fe or Cp_2Co.

[HIPTN$_3$N]Mo(C_2H_4). Method A. A 250 mg sample of [HIPTN$_3$N]Mo(N_2) was dissolved in benzene (10 mL) in a Schlenk flask. The flask was then evacuated and filled with ethylene (1 atm), and the solution was heated to 60 °C for 21 h. All solvents were removed from the reddish solution to afford a red solid. Pentane (5 mL) was added to the residue, and the solution was cooled to −40 °C. A fine crystalline sample of [HIPTN$_3$N]Mo(C_2H_4) was isolated (∼100 mg).

Method B. A 2.00 g sample of [HIPTN$_3$N]MoCl was placed in a 250 mL flask along with a glass stir bar, and 100 mL of THF was added. Sodium amalgam (0.5%, ∼8 mL) was added, and the solution was degassed with three freeze−pump−thaw cycles. Ethylene (1 atm) was then introduced, and the reaction mixture was stirred overnight. The color of the solution changed slowly from orange to red. All solvents were then removed in vacuo to afford a red residue that was dissolved in pentane. The red solution was filtered through Celite and concentrated in vacuo to yield a finely crystalline, rose-red solid; yield 1.43 g (72%): ^{1}H NMR δ 7.18 (s, aromatic C*H*), 2.88 (m, C*H*(CH_3)$_2$), 1.34 (br s, CH(C*H*$_3$)$_2$). Anal. Calcd for $C_{116}H_{163}MoN_4$: C, 81.50; H, 9.61; N, 3.28. Found: 81.39; H, 9.50; N, 3.18.

Preparation of [HIPTN$_3$N]Mo(C_2H_2). A sample of [HIPTN$_3$N]Mo(N_2) (300 mg) was placed in a 50 mL Schlenk flask along with 5 mL of benzene. The flask was then degassed three times (freeze−pump−thaw cycles) before adding dry and oxygen-free acetylene (5−10 equiv). Over a period of 1 h at room temperature the color of the solution changed to olive green and a purple-black precipitate formed. All volatiles were removed in vacuo, and the residue was dissolved in heptane. The solution was filtered through Celite in order to remove the purple solid. The emerald green solution was then concentrated to ∼1 mL and placed in the −40 °C freezer overnight. An emerald green crystalline solid was isolated, washed with heptane, and dried in vacuo; yield 234 mg (78%): ^{1}H NMR (C_6D_6, 20 °C) δ 7.22 (s), 5.75 (v br s), 2.91 (br m), 1.33 (br s), 1.25 (br s). No other resonances were observed. Anal. Calcd for $C_{116}H_{161}MoN_4$: C, 81.60; H, 9.50; N, 3.28. Found: C, 81.43; H, 9.36; N, 3.11.

[HIPTN$_3$N]Mo($^{13}C_2H_2$). In a J-Young NMR tube ∼50 mg of [HIPTN$_3$N]MoN_2 was dissolved in C_6D_6 (0.5 mL). This solution was then degassed by three freeze−pump−thaw cycles and several equivalents of $^{13}C_2H_2$ were then added. The solution was then allowed to thaw with the solution turning emerald green. Some purple solid precipitated from the solution after 10 min. The ^{1}H NMR spectrum was then recorded and indicated that most of the dinitrogen complex had been consumed. The solution was then filtered through Celite to remove the solid and then stripped to dryness. The green residue was then redissolved in the minimum amount of heptane from which crystals grew via slow evaporation of the solvent. Anal. Calcd for $C_{114}{}^{13}C_2H_{161}MoN_4$: C, 81.62; H, 9.50; N, 3.28. Found: C, 81.47; H, 9.28; N, 3.18.

[HIPTN$_3$N]Mo(CO). [HIPTN$_3$N]Mo(N_2) (200 mg) was dissolved in benzene (5 mL), and the solution was degassed twice (freeze−pump−thaw) before CO (1 atm) was introduced. The solution was then heated to 60 °C overnight, during which time the color changed to red. All solvents were removed in vacuo to leave a red residue. Pentane (1−2 mL) was added, and the reddish-brown product was isolated and dried in vacuo for several hours: ^{1}H NMR δ 20.15 (br s, 6H, NC*H*$_2$), 6.95 (s, 12H, 3,5,3″,5″-*H*), 2.86 (sept, J_{HH} = 6.3 Hz, 6H, 4′,4″-C*H*(CH_3)$_2$), 1.84 (br s, 36 H, 2,6,2″,6″-CH(C*H*$_3$)$_2$), 1.44 (br s, 12H, 4′,4″-C*H*(CH_3)$_2$), 1.26 (d, J_{HH} = 6.6 Hz, 36H, 4′,4″-CH(C*H*$_3$)$_2$), 1.02 (br s, 36H, 2,6,2″,6″-CH(C*H*$_3$)$_2$), −1.85 (s, 3H, 4-*H*), −8.21 (br s, 6H, 4′,6′-*H*), −30.50 (br s, 6H, NC*H*$_2$); IR (Nujol) cm^{-1} 1892 (ν_{CO}), (C_6D_6) 1888 (ν_{CO}). Anal. Calcd for $C_{115}H_{159}MoN_4O$: C, 80.80; H, 9.37; N, 3.28. Found: C, 80.71; H, 9.34; N, 3.14.

[HIPTN$_3$N]Mo(^{13}CO) was prepared similarly. IR (C_6D_6) cm^{-1} 1845 ($\nu 13_{CO}$), 1802($\nu 13_C 18_O$). Anal. Calcd for $C_{114}{}^{13}CH_{159}MoN_4O$: C, 80.76; H, 9.42; N, 3.27. Found: C, 80.64; H, 9.26; N, 3.12.

Preparation of [HIPTN$_3$N]Mo(CO)Na. A solution of 210 mg of [HIPTN$_3$N]Mo(CO) in THF (5 mL) containing ∼5 g of 0.5% Na/Hg was stirred in a vial containing a glass-coated stirrer bar. After 1 h the solution was filtered through Celite and all volatiles were removed in vacuo. The orange solid was

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then dissolved in heptane (4−5 mL), and the solution was filtered through Celite. Removal of all solvents yielded 185 mg of the orange product (87% yield): ^{1}H NMR (C_6D_6) δ 7.70 (br s, 6H, 2′,6′-*H*), 7.19 (s, 12H, 3′,5′,3′,5′′-*H*), 6.50 (t, 3H, J_{HH} = 1.5 Hz, 4-*H*), 3.78 (br t, 6H, NCH_2), 3.39 (sept, J_{HH} = 7.0 Hz, 12H, CH(CH_3)$_2$), 2.86 (sept, J_{HH} = 7.0 Hz, 6H, CH(CH_3)$_2$), 2.04 (br s, 6H, NCH_2), 1.31 (d, J_{HH} = 7.0 Hz, 36H, CH(CH_3)$_2$), 1.23 (d, J_{HH} = 7.0 Hz, 36H, CH(CH_3)$_2$), 1.13 (d, J_{HH} = 7.0 Hz, 36H, CH(CH_3)$_2$); IR (C_6D_6) cm^{-1} 1632 (ν_{CO}).

[HIPTN$_3$N]Mo(^{13}CO)Na. A solution of 103 mg of [(HIPTN$_3$N)Mo(^{13}CO)] in THF (20 mL) and 7 g of 0.5% Na/Hg was stirred in a vial containing a glass-coated stirrer bar for several hours. The solution was filtered through Celite, and then all solvents were removed in vacuo. The yellow-orange residue was then redissolved in heptane and refiltered through Celite to afford a clear-yellowish solution. This solution was reduced in volume in vacuo and left to stand to yield 60 mg of an orange solid (58% yield): ^{1}H NMR (C_6D_6) δ 7.68 (br s, 6H, 2′,6′-*H*), 7.14 (s, 12H, 3′,5′,3′′,5′′-*H*), 6.47 (t, 3H, J_{HH} = 1.5 Hz, 4-*H*), 3.76 (br t, 6H, NCH_2), 3.36 (sept, J_{HH} = 7.0 Hz, 12H, CH(CH_3)$_2$), 2.84 (sept, J_{HH} = 7.0 Hz, 6H, CH(CH_3)$_2$), 2.01 (br s, 6H, NCH_2), 1.28 (d, J_{HH} = 7.0 Hz, 36H, CH(CH_3)$_2$), 1.21 (d, J_{HH} = 7.0 Hz, 36H, CH(CH_3)$_2$), 1.11 (d, J_{HH} = 7.0 Hz, 36H, CH(CH_3)$_2$); ^{13}C{^{1}H} NMR (partial spectrum) δ 232.5 (s); IR (C_6D_6) cm^{-1} 1601 ($\nu_{^{13}CO}$). Anal. Calcd for $C_{114}{}^{13}CH_{159}MoN_4ONa$: C, 79.74; H, 9.25; N, 3.28. Found: C, 79.62; H, 9.30; N, 3.06.

Preparation of [HIPTN$_3$N]Mo(CO)H. Method A. [HIPTN$_3$N]Mo(CO)Na (150 mg) was dissolved in C_6H_6 (2 mL), and [Et$_3$NH][BAr′$_4$] (100 mg) was added. The color changed immediately from orange to yellow. The reaction mixture was allowed to stir for 1 h and then filtered through Celite. All solvents were removed in vacuo, and the solid was redissolved in heptane; 90 mg of yellow crystals was isolated: ^{1}H NMR δ 7.20 (s, 12H, 3′,5′,3′′,5′′-*H*), 7.18 (s, 6H, 2′,6′-*H*), 6.64 (s, 3H, 4-*H*), 3.64 (br t, 6H, NCH_2), 3.11 (sept, J_{HH} = 6.6 Hz, 12H, CH(CH_3)$_2$), 2.94 (sept, J_{HH} = 6.9 Hz, 6H, CH(CH_3)$_2$), 2.10 (br s, 6H, NCH_2), 1.38 (d, J_{CH} = 6.9 Hz, 36H, CH(CH_3)$_2$), 1.26 (d, J_{CH} = 6.9 Hz, 36H, CH(CH_3)$_2$), 1.14 (d, J_{CH} = 6.9 Hz, 36H, CH(CH_3)$_2$), −0.08 (d, J_{CH} = 24.3 Hz, 1H). Anal. Calcd for C, 80.75; H, 9.43; N, 3.28. Found: C, 80.66; H, 9.38; N, 3.18.

Method B. [HIPTN$_3$N]Mo(^{13}CO)H. In a J-Young NMR tube 15 mg of [HIPTN$_3$N]MoH was dissolved in C_6D_6 (0.5 mL). The NMR tube was then degassed via three freeze−pump−thaw cycles, and ∼1 atm of ^{13}CO was added to the frozen solution. Upon thawing the sample, the color of the solution changed immediately from brick-red to bright yellow. The reaction appears to be quantitative by ^{1}H NMR spectroscopy: ^{1}H NMR δ 7.20 (s, 12H, 3′,5′,3′′,5′′-*H*), 7.18 (s, 6H, 2′,6′-*H*), 6.64 (s, 3H; 4-*H*), 3.64 (br t, 6H, NCH_2), 3.11 (sept, J_{HH} = 6.6 Hz, 12H, CH(CH_3)$_2$), 2.94 (sept, J_{HH} = 6.9 Hz, 6H, CH(CH_3)$_2$), 2.10 (br s, 6H, NCH_2), 1.38 (d, J_{CH} = 6.9 Hz, 36H, CH(CH_3)$_2$), 1.26 (d, J_{CH} = 6.9 Hz, 36H, CH(CH_3)$_2$), 1.14 (d, J_{CH} = 6.9 Hz, 36H, CH(CH_3)$_2$), −0.08 (d, J_{CH} = 24.3 Hz, 1H); ^{13}C{^{1}H} NMR (partial spectrum) δ 200.5 (J_{CH} = 24.4 Hz); IR (C_6D_6) cm^{-1} 1810 ($\nu_{^{13}CO}$).

In a J-Young NMR tube 23 mg of [HIPTN$_3$N]Mo(^{13}CO)Na was dissolved in C_6D_6 (∼0.5 mL) and a slight excess of [Et$_3$NH]BAr′$_4$ was added. A slightly lighter yellow solution was formed along with some colorless crystals. The ^{1}H NMR spectrum was essentially identical to that reported above.

[HIPTN$_3$N]MoMe. A mixture of [HIPTN$_3$N]MoCl (325 mg, 189 μmol), AlMe$_3$ (210 μmL, 2 M in heptane, 420 mmol), and benzene (5 mL) was sealed in an Schlenk bulb, and the solution was stirred for 2 days. All volatile components were removed in vacuo, and the residue was extracted with 10 mL of pentane. The extracts were filtered through Celite, and the pentane was removed in vacuo. Approximately 3 mL of SiMe$_4$ was added in order to dissolve the residue, and the solution was cooled to −35 °C overnight. The brown-red crystals that formed were collected by filtration and recrystallized twice from heptane to afford 89 mg (28%) of the microcrystalline product: ^{1}H NMR (C_6D_6, 20 °C) δ 12.0 (br s, 6H, 4′,6′-*H*), 7.24 (br s, 12H, 3,5,3′′,5′′-*H*), 3.13 (br s, 12H, 2,6,2′′,6′′-CHMe$_2$), 2.99 (br m, 6H, 4,4′′-CHMe$_2$), 1.37 (d, J_{HH} = 6.3 Hz, 72H, CH(CH_3)$_2$), 1.33 (br s, 36H, CH(CH_3)$_2$), −14.8 (br s, 6H, NCH_2), −66.3 (br s, 6H, NCH_2). Anal. Calcd for $C_{115}H_{162}MoN_4$: C, 81.42; H, 9.62; N, 3.30. Found: C, 81.26; H, 9.68; N, 3.18.

[HIPTN$_3$N]Mo^{13}CH$_2{}^{13}$CH$_3$. (HIPTN$_3$N)MoH (155 mg) was dissolved in C_6H_6 (10 mL) in a Schlenk flask. The headspace was evacuated via three freeze−pump−thaw cycles, and $^{13}C_2H_4$ (ca, 360 Torr in 40 mL) was added. The solution color changed immediately from brick-red to red upon thawing the sample. All volatiles were removed after 1 h, and the red residue was redissolved in heptane (1−2 mL). A red crystalline solid was isolated (93 mg, 59% yield): ^{1}H NMR (C_6D_6, 20 °C) δ 7.24 (br s, 12H, 3′,5′,3′′,5′′-*H*), 3.12 (br s, 12H, 2,6,2′′,6′′-CH(CH$_3$)$_2$), 2.98 (br m, 6H, 4,4′′-CH(CH$_3$)$_2$), 1.39 (d, J_{HH} = 6.3 Hz, 36H, CH(CH_3)$_2$), 1.33 (br s, 80H, CH(CH_3)$_2$ and 2,2′′-H), −2.09 (br, 6H, 2′,6′-*H*?), −25.89 (br, 6H, NCH_2), −75.90 (br, >6H, NCH_2 and $^{13}CH_2{}^{13}CH_3$). Anal. Calcd for $C_{114}{}^{13}C_2H_{164}MoN_4$: C, 81.47; H, 9.65; N, 3.27. Found: C, 81.65; H, 9.46; N, 3.17.

Unlabeled samples were prepared similarly.

[HIPTN$_3$N]Mo(*n*-hexyl). A benzene solution of [HIPTN$_3$N]MoH (180 mg, 107 μmol) containing 1-hexene (51 mg, 607 μmol) was stirred at room temperature for 24 h. All volatile components were removed in vacuo, and the residue was extracted with 5 mL of heptane. The extracts were combined and filtered through Celite. The filtrates were concentrated and cooled to −35 °C for several days. The resulting brown-red crystals were collected by filtration, washed with cold pentane, and dried in vacuo to afford 136 mg (72% yield) of microcrystalline product: ^{1}H NMR (C_6D_6, 20 °C) δ 10.0 (br s, 6H, 4′,6′-*H*), 7.32 (s, 12H, 3,5,3′′,5′′-*H*), 5.00 (br s, 6H, Mo−CH$_2$(CH_2)$_3$CH$_2$CH$_3$), 3.21 (br s, 12H, 2,6,2′′,6′′-CHMe$_2$), 2.99 (br m, 6H, 4,4′′-CHMe$_2$), 2.40 ((br s, 2H, Mo-CH$_2$(CH$_2$)$_3$CH_2-CH$_3$), 1.42 (d, J_{HH} = 5.7 Hz, 36H, CH(CH_3)$_2$), 1.33 (br s, 36H, CH(CH_3)$_2$), 1.25 (br s, 36H, CH(CH_3)$_2$), −9.9 (br s, 6H, NCH_2), −52 (br s, 2H, Mo-CH_2(CH$_2$)$_4$CH$_3$), −68.4 (br s, 6H, NCH_2). Anal. Calcd for $C_{120}H_{172}MoN_4$: C, 81.58; H, 9.81; N, 3.17. Found: C, 81.34; H, 9.75; N, 3.12.

[HIPTN$_3$N]Mo(*n*-octyl). A procedure analogous to that used to synthesize [HIPTN$_3$N]Mo(hexyl) was followed, starting from [HIPTN$_3$N]MoH (195 mg, 116 μmol) and 1-octene (42 mg, 375 μmol); yield 129 mg (62%) of microcrystalline brown-red crystals: ^{1}H NMR (C_6D_6, 20 °C) δ 9.90 (br s, 6H, 4′,6′-*H*), 7.32 (s, 12H, 3,5,3′′,5′′-*H*), 5.20 (br, s, 6H, Mo−CH$_2$(CH_2)$_6$CH$_3$), 3.21 (br s, 12H, 2,6,2′′,6′′-CHMe$_2$), 3.03 (br m, 6H, 4,4′′-CHMe$_2$), 2.40 (br s, 2H, Mo−CH$_2$(CH_2)$_6$CH$_3$), 1.42 (d, J_{HH} = 4.5 Hz, 36H, CH(CH_3)$_2$), 1.34 (br s, 36H, CH(CH_3)$_2$), 1.25 (br s, 36H, CH(CH_3)$_2$), 0.78 (br s, 3H, Mo-CH$_2$(CH$_2$)$_6$CH_3), −10.2 (br s, 6H, NCH_2), −52.3 (br s, 2H, Mo-CH_2(CH$_2$)$_6$CH$_3$), −68.5 (br s, 6H, NCH_2). Anal. Calcd for $C_{122}H_{176}MoN_4$: C, 81.65; H, 9.88; N, 3.12. Found: C, 81.48; H, 9.79; N, 3.04.

Preparation of [HIPTN$_3$N]Mo(η^2-CHCH$_2$). [HIPTN$_3$N]MoH (85 mg) was dissolved in 2 mL of C_6H_6 in a 25 mL Schlenk flask. The flask was then degassed several times (freeze−pump−thaw). Dry and oxygen-free C_2H_2 (5−10 equiv) was then added to the flask and the solution left to stir for 1 h at room temperature. During this time, the color of the solution changed to yellow and a purple precipitate formed. All volatiles were then removed in vacuo. The residue was redissolved in heptane, and the mixture was filtered through Celite to remove the purple solid. The solvents were removed in vacuo to yield a total of 70 mg of product: ^{1}H NMR (C_6D_6, 20 °C) δ 13.03 (t, J_{HH} = 3.4 Hz, 1H, CH-CH$_2$), 7.19 (s, 12H, 3′,5′,3′′,5′′-*H*), 6.76 (d, J_{HH} = 1.4 Hz, 6H, 2′,6′-*H*), 6.56 (br t, J_{HH} = 1.2 Hz, 3H, 4-*H*), 3.75 (br t, 6H, NCH_2), 3.07 (sept, J_{HH} = 6.9 Hz, 12H, CH(CH$_3$)$_2$), 2.90 (sept, J_{HH} = 6.9 Hz, 6H, CH(CH$_3$)$_2$, CH−CH_2 obscured), 2.25 (br s, 6H, NCH_2), 1.34 (d, J_{HH} = 6.9 Hz, 36H, CH(CH_3)$_2$), 1.26 (d, J_{HH} = 6.9 Hz, 36H, CH(CH_3)$_2$), 1.15 (d, J_{HH} = 6.6 Hz, 36H, CH(CH_3)$_2$). Anal. Calcd

for $C_{116}H_{162}MoN_4$: C, 81.55; H, 9.56; N, 3.28. Found: C, 81.38; H, 9.44; N, 3.14.

Formation of [HIPTN$_3$N]Mo(η^2-CHCH$_2$) from {[HIPTN$_3$N]-Mo(C$_2$H$_2$)}BAr′$_4$ was also observed. {[HIPTN$_3$N]Mo(C$_2$H$_2$)}-BAr′$_4$ (16 mg) was dissolved in ~0.4 mL of C_6D_6 in a J-Young NMR tube, and 6 μL of LiBEt$_3$H (1M in THF) was added via a microsyringe. The tube was sealed and shaken to ensure complete mixing. The color changed rapidly from green to yellow, and a white precipitate formed. The ^{1}H NMR spectrum of this solution indicated that [HIPTN$_3$N]Mo(η^2-CHCH$_2$) had formed quantitatively.

Preparation of [HIPTN$_3$N]Mo(η^2-^{13}CH^{13}CH$_2$). In a J-Young NMR tube 15 mg of [HIPTN$_3$N]MoH was dissolved in C_6D_6 (0.5 mL). The NMR tube was then degassed via three freeze−pump−thaw cycles, and then 3 equiv of $^{13}C_2H_2$ was added to the frozen solution. Upon thawing the sample, the color of the solution changed immediately from brick-red to yellow and insoluble polyacetylene formed. The reaction appears to be quantitative by ^{1}H NMR spectroscopy: ^{1}H NMR (C_6D_6, 20 °C) δ 13.02 (br d, J_{CH} = 191.9 Hz, 1H, ^{13}C*H*-^{13}CH$_2$), 7.19 (s, 12H, 3′,5′,3″,5″-*H*), 6.76 (s, 6H, 2′,6′-*H*), 6.56 (s, 3H, 4-*H*), 3.75 (br t, 6H, NC*H*$_2$), 3.07 (sept, J_{HH} = 6.6 Hz, 12H, C*H*(CH$_3$)$_2$), 2.93 (d, J_{CH} = 160.1 Hz, 2H, ^{13}CH-^{13}C*H*$_2$), 2.90 (sept, J_{HH} = 6.9 Hz, 6H, C*H*(CH$_3$)$_2$), 2.25 (br s, 6H, NC*H*$_2$), 1.34 (d, J_{HH} = 6.9 Hz, 36H, CH(C*H*$_3$)$_2$), 1.26 (d, J_{HH} = 6.9 Hz, 36H, CH(C*H*$_3$)$_2$), 1.15 (d, J_{HH} = 6.9 Hz, 36H, CH(C*H*$_3$)$_2$); ^{13}C-{^{1}H} NMR (C_6D_6, 20 °C) (partial) 272.18 (d, J_{CC} = 41 Hz, Mo^{13}*C*H^{13}CH$_2$) and 44.78 (d, J_{CC} = 41 Hz, Mo^{13}CH^{13}*C*H$_2$).

[HIPTN$_3$N]Mo≡CH. A THF (25 mL) solution of [HIPTN$_3$N]-MoCl (1.176 g, 0.264 685 μmol) was treated with CH_2Cl_2 (150 mg, 1.76 mmol) and Mg (148 mg, 6.17 mmol) in a Schlenk flask. The resulting mixture was freeze−pump−thaw degassed five times, and the flask was heated to 90 °C for 16 h. Volatiles were removed in vacuo, and the residue was extracted with 25 mL of pentane. The extracts were filtered through Celite, and the filtrate was concentrated and cooled to −35 °C overnight. The yellow microcrystals that formed were recrystallized from pentane and were collected by filtration in three crops, washed with cold pentane, and dried in vacuo to afford 760 mg of product (yield 65%): ^{1}H NMR (C_6D_6, 20 °C) δ 7.73 (s, 6H, 4′,6′-*H*), 7.20 (s, 12H, 3,5,3″,5″-*H*), 6.55 (s, 3H, 2′-*H*), 4.47 (s, 1H, C*H*), 3.65 (br t, 6H, NC*H*$_2$), 3.12 (sept, J_{HH} = 6.9 Hz, 12H, 2,6,2″,6″-C*H*Me$_2$), 2.92 (sept, J_{HH} = 6.9 Hz, 6H, 4,4″-C*H*Me$_2$), 1.92 (br t, 6H, NC*H*$_2$), 1.36 (d, J_{HH} = 6.9 Hz, 36H, 4,4″-CH(C*H*$_3$)$_2$), 1.23 (d, J_{HH} = 6.9 Hz, 36H, 2,6,2″,6″-CH-(C*H*$_3$)$_2$), 1.11 (br d, J_{HH} = 6.9 Hz, 36H, 2,6,2″,6″-CH(C*H*$_3$)$_2$); ^{13}C NMR (C_6D_6 20 °C) δ 288.4 (Mo≡C), 162.1, 148.3, 147.3, 140.9, 138.7, 126.0, 120.9, 119.9 (phenyl-*C*), 57.1 (N*C*H$_2$), 51.1 (N*C*H$_2$), 35.3 (*C*HMe$_2$), 31.2 (*C*HMe$_2$), 25.1 (CH(*C*H$_3$)$_2$), 25.0 (CH(*C*H$_3$)$_2$). Anal. Calcd for $C_{115}H_{160}N_4Mo$: C, 81.51; H, 9.52; N, 3.31. Found: C, 81.59; H, 9.40; N, 3.26.

Preparation of [HIPTN$_3$N]Mo≡CCH$_3$. A solution of [HIPTN$_3$N]MoH (510 mg, 303 μmol) in 15 mL of toluene in a 25 mL Schlenk flask was degassed several times (freeze−pump−thaw). Dry and oxygen-free C_2H_4 (~5 equiv) was then added to the flask and the solution left to stir overnight at room temperature. The excess ethylene was removed under partial vacuum, and the resulting red solution was heated at 160−165 °C for 4 h. The solution color changed to yellow-brown. All volatiles were then removed in vacuo, the residue was extracted with 10 mL of pentane, and the mixture was filtered through Celite. The resulting solution was concentrated in vacuo and cooled at −35 °C overnight to afford 320 mg (62% yield) of yellow microcrystalline product: ^{1}H NMR (C_6D_6, 20 °C) δ 7.45 (d, J_{CH} = 1.2 Hz, 6H, 2′,6′-*H*), 7.24 (br s, 12H, 3′,5′,3″,5″-*H*), 6.67 (br t, 3H, 4-*H*), 3.68 (br t, 6H, NC*H*$_2$), 2.06 (br s, 6H, NC*H*$_2$), 1.36 (d, J_{HH} = 7.2 Hz, 36H, CH(C*H*$_3$)$_2$), 1.23 (d, J_{HH} = 6.9 Hz, 36H, CH(C*H*$_3$)$_2$), 1.13 (d, J_{HH} = 6.9 Hz, 36H, CH(C*H*$_3$)$_2$); ^{13}C NMR (C_6D_6 20 °C, partial) δ 299.3 (Mo≡C), 57.7 (N*C*H$_2$), 51.2 (N*C*H$_2$). Anal. Calcd for $C_{116}H_{162}N_4Mo$: C, 81.55; H, 9.56; N, 3.28. Found: C, 81.32; H, 9.61; N, 3.22.

[HIPTN$_3$N]Mo≡^{13}C^{13}CH$_3$. ^{1}H NMR δ 7.45 (d, J_{CH} = 1.2 Hz, 6H, 2.06 (br s, 6H, NC*H*$_2$), 1.36 (d, J_{HH} = 7.2 Hz, 36H, CH-(C*H*$_3$)$_2$), 1.23 (d, J_{HH} = 6.9 Hz, 36H, CH(C*H*$_3$)$_2$), 1.13 (d, J_{HH} = 6.9 Hz, 36H, CH(C*H*$_3$)$_2$).

[HIPTN$_3$N]Mo≡CC$_5$H$_{11}$. A $C_6D_5CD_3$ (0.5 mL) solution of [HIPTN$_3$N]Mo(hexyl) (~40 mg) was sealed in a J-Young NMR tube and heated to 165 °C for 4 h: ^{1}H NMR ($C_6D_5CD_3$, 20 °C) δ 7.26 (s, 6H, 4′,6′-*H*), 7.18 (s, 12H, 3,5,3″,5″-*H*), 6.58 (s, 3H, 2′-*H*), 3.63 (br t, 6H, NC*H*$_2$), 3.04 (sept, J_{HH} = 6.6 Hz, 12H, 2,6,2″,6″-C*H*Me$_2$), 2.91 (sept, J_{HH} = 6.6 Hz, 6H, 4,4″-C*H*Me$_2$), 2.64 (br s, 2H, Mo≡C(C*H*$_2$)$_4$CH$_3$), 2.20 (br t, 6H, NC*H*$_2$), 1.99 (br s, 2H, Mo≡C(C*H*$_2$)$_4$CH$_3$), 1.36 (d, J_{HH} = 6.9 Hz, 36H, 4,4″-CH(C*H*$_3$)$_2$), 1.25 (br s, 36H, 2,6,2″,6″-CH(C*H*$_3$)$_2$), 1.19 (br s, 36H, 2,6,2″,6″-CH(C*H*$_3$)$_2$); several hexyl proton peaks overlap with isopropyl resonances; ^{13}C NMR ($C_6D_5CD_3$ 20 °C, partial) δ 305.5 (Mo≡*C*), 59.1 (N*C*H$_2$), 51.8 (N*C*H$_2$), 46.8 (Mo≡C*C*H$_2$).

[HIPTN$_3$N]Mo≡CC$_7$H$_{15}$. A $C_6D_5CD_3$ (0.5 mL) solution of [HIPTN$_3$N]Mo(octyl) (~70 mg) was sealed in a J-Young NMR tube and heated to 155 °C for 4 h: ^{1}H NMR ($C_6D_5CD_3$, 20 °C) δ 7.24 (s, 6H, 4′,6′-*H*), 7.15 (s, 12H, 3,5,3″,5″-*H*), 6.58 (s, 3H, 2′-*H*), 3.63 (br t, 6H, NC*H*$_2$), 3.04 (septet, J_{HH} = 6.5 Hz, 12H, 2,6,2″,6″-C*H*Me$_2$), 2.92 (septet, J_{HH} = 6.5 Hz, 6H, 4,4″-C*H*Me$_2$), 2.54 (br t, 2H, Mo≡C(C*H*$_2$)$_4$CH$_3$), 2.21 (br t, 6H, NC*H*$_2$), 1.96 (br m, 4H, Mo≡C(C*H*$_2$)$_4$CH$_3$), 1.35 (d, J_{HH} = 6.9 Hz, 36H, 4,4″-CH(C*H*$_3$)$_2$), 1.25 (br s, 36H, 2,6,2″,6″-CH(C*H*$_3$)$_2$), 1.19 (br s, 36H, 2,6,2″,6″-CH(C*H*$_3$)$_2$); several octyl proton peaks overlap with isopropyl resonances; ^{13}C NMR ($C_6D_5CD_3$ 20 °C, partial) δ 305.3 (Mo≡*C*), 59.3 (N*C*H$_2$), 51.9 (N*C*H$_2$), 47.1 (Mo≡C*C*H$_2$).

Decomposition of [HIPTN$_3$N]Mo(hexyl) in the Presence of 1-Octene. A mixture of [HIPTN$_3$N]Mo(hexyl) (75.0 mg, 42.5 μmol) and 1-octene (27.0 mg, 220.9 μmol) was sealed in a J-Young NMR tube and heated to 155 °C for 4 h; ^{13}C NMR ($C_6D_5CD_3$ 20 °C, partial) δ 305.4 (Mo≡*C*, weak and broad peak), 59.3 (N*C*H$_2$ of [HIPTN$_3$N]Mo≡CC$_7$H$_{15}$), 59.1 (N*C*H$_2$ of [HIPTN$_3$N]Mo≡CC$_5$H$_{11}$), 52.0 (N*C*H$_2$ of [HIPTN$_3$N]Mo≡CC$_7$H$_{15}$), 51.9 (N*C*H$_2$ of [HIPTN$_3$N]Mo≡CC$_5$H$_{11}$), 47.1 (Mo≡C*C*H$_2$ of [HIPTN$_3$N]Mo≡CC$_7$H$_{15}$), 46.8 (Mo≡C*C*H$_2$ of [HIPTN$_3$N]Mo≡CC$_5$H$_{11}$).

Preparation of {[HIPTN$_3$N]Mo(C$_2$H$_4$)}BAr′$_4$. A sample of [HIPTN$_3$N]Mo(C$_2$H$_4$) (200 mg, 0.117 mmol) was dissolved in 10 mL of C_6H_6, and 126 mg of [Cp$_2$Fe]BAr′$_4$ (0.120 mmol) was added. This solution was stirred for 30 min, during which time most of the solids had dissolved and the solution had turned orange-brown. All of the volatiles were removed in vacuo to afford a brown solid. The solid was then heated to ~40 °C under high vacuum in order to remove Cp$_2$Fe. Crystals were grown from a heptane solution stored at −35 °C: ^{1}H NMR (C_6D_6, 20 °C) δ 8.37 (br s, 8H, C$_6$*H*$_3$-3,5-(CF$_3$)$_2$), 7.68 (br s, 4H, C$_6$*H*$_3$-3,5-(CF$_3$)$_2$), 7.12 (s, 12H, 3′,5′,3″,5″-*H*), 6.70 (s, 3H; 4′-*H*), 6.45 (s, 6H, 4′,6′-H), 5.05 (br s, 4H, C$_2$*H*$_4$), 3.24 (br t, 6H, NC*H*$_2$), 2.86 (sept, J_{HH} = 6.6 Hz, 6H; 4,4″-C*H*(CH$_3$)$_2$), 2.64 (sept, J_{HH} = 7.2 Hz, 12H, 2,6,2″,6″-C*H*(CH$_3$)$_2$ plus the other NC*H*$_2$ resonance), 1.30 (d, J_{HH} = 6.6 Hz, 36H, CH(C*H*$_3$)$_2$), 1.11 (d, J_{HH} = 6.6 Hz, 36H, CH(C*H*$_3$)$_2$), 1.04 (d, J_{HH} = 6.9 Hz, 36H, CH(C*H*$_3$)$_2$); ^{19}F{^{1}H} NMR (C_6D_6, 20 °C) δ −61.9 (s). Anal. Calcd for $C_{148}H_{175}BF_{24}MoN_4$: C, 69.09; H, 6.86; N, 2.18. Found: C, 68.79; H, 6.80; N, 2.06.

In Situ Preparation of [(HIPTN$_3$N)Mo(^{13}C$_2$H$_4$)]BAr′$_4$. [HIPTN$_3$N]Mo(η^2-^{13}C$_2$H$_4$)] (50 mg, 0.029 mmol) was dissolved in ~0.6 mL of C_6D_6 in a J-Young NMR tube. [Cp$_2$Fe]BAr′$_4$ (32 mg, 0.120 mmol) was added and the tube shaken after sealing. The NMR tube was then centrifuged to remove all of the solid to the top of the tube: ^{1}H NMR (C_6D_6, 20 °C) δ 8.37 (br s, 8H, C$_6$*H*$_3$-3,5-(CF$_3$)$_2$), 7.70 (br s, 4H, C$_6$*H*$_3$-3,5-(CF$_3$)$_2$), 7.14 (s, 12H, 3′,5′,3″,5″-*H*), 6.69 (s, 3H, 4′-*H*), 6.44 (s, 6H, 4′,6′-H), 5.40 (br s, 2H, ^{13}C$_2$*H*$_4$), 4.91 (br s, 2H, ^{13}C$_2$*H*$_4$), 3.21 (br t, 6H, NC*H*$_2$), 2.88 (sept, J_{HH} = 6.6 Hz, 6H, 4,4″-C*H*(CH$_3$)$_2$), 2.65 (sept, J_{HH} = 7.2 Hz, 12H, 2,6,2″,6″-C*H*(CH$_3$)$_2$ plus the other NC*H*$_2$ resonance), 1.31 (d, J_{HH} = 6.6 Hz, 36H, CH(C*H*$_3$)$_2$), 1.12 (br s, 36H, CH(C*H*$_3$)$_2$), 1.05 (br s, 36H, CH(C*H*$_3$)$_2$); ^{13}C{^{1}H} NMR spectrum (C_6D_6, 20 °C, partial) δ 84.3 (br s).

{[HIPTN$_3$N]Mo(C$_2$H$_2$)}BAr′$_4$. [HIPTN$_3$N]Mo(C$_2$H$_2$) (175 mg, 0.102 mmol) was dissolved in 10 mL of C$_6$H$_6$. To this emerald green solution was added 108 mg of [Cp$_2$Fe]BAr′$_4$ (0.103 mmol), and the solution was stirred for 30 min, during which the color changed to dark green. All volatiles were removed in vacuo, and the green residue was redissolved in the minimum amount of heptane. After several days, a green crystalline solid was isolated and was then placed on a high-vacuum line to remove Cp Fe; the yield was essentially quantitative: ^{1}H NMR (C$_6$D$_6$, 20 °C) δ 11.34 (s, 2H, C$_2H_2$), 8.39 (br s, 8H, C$_6H_3$-3,5-(CF$_3$)$_2$), 7.65 (br s, 4H, C$_6H_3$-3,5-(CF$_3$)$_2$), 7.13 (s, 12H, 3′,5′,3″,5″-*H*), 6.54 (t, J_{HH} = 1.4 Hz, 3H; 4′-*H*), 6.45 (d, J_{HH} = 1.1 Hz, 6H; 4′,6′-H), 3.82 (br t, 6H, NCH_2), 2.87 (sept, J_{HH} = 6.9 Hz, 6H; 4,4″-C*H*(CH$_3$)$_2$), 2.60 (sept, J_{HH} = 6.9 Hz, 12H, 2,6,2″,6″-C*H*(CH$_3$)$_2$ + the other NCH_2 resonance), 1.31 (d, J_{HH} = 6.6 Hz, 36H, CH(CH_3)$_2$), 1.12 (d, J_{HH} = 6.9 Hz, 36H, CH(CH_3)$_2$), 1.03 (d, J_{HH} = 6.9 Hz, 36H, CH(CH_3)$_2$); ^{19}F{^{1}H} NMR (C$_6$D$_6$, 20 °C) δ −61.95 (s). Anal. Calcd for C$_{148}$H$_{173}$BF$_{24}$MoN$_4$: C, 69.15; H, 6.78; N, 2.18. Found: C, 68.87; H, 6.69; N, 2.10.

{[HIPTN$_3$N]Mo(^{13}C$_2$H$_2$)}BAr′$_4$ was prepared similarly. The proton resonance at 11.30 ppm was part of a complex second-order pattern. The ^{13}C{^{1}H} resonance at 214.6 ppm was a singlet that in the proton-coupled spectrum became a second-order pattern.

[HIPTN$_3$N]MoCN. A sample of {[HIPTN$_3$N]Mo(NH$_3$)}BPh$_4$ (600 mg) was dissolved in PhF (20 mL), and [Bu$_4$N]CN (77 mg) was added. After 5 min stirring the solution had changed color from red to orange and colorless crystals of [Bu$_4$N]BPh$_4$ had formed. The solution was stirred for a further 1 h, and then all of the volatiles were removed in vacuo. The orange residue was triturated with pentane (10 mL), and the orange solid was filtered off. The orange solid was separated from the colorless crystals by adding the minimum amount of C$_6$H$_6$ and filtering the solution through Celite. The benzene was removed in vacuo, and 1−2 mL of pentane was added to the residue. Crystals of orange [HIPTN$_3$N]MoCN were collected in three crops; yield 352 mg (72%): ^{1}H NMR (C$_6$D$_6$, 20 °C) δ 7.23 (br s, 12H, 3′,5′,3″,5″-*H*), 3.59 (br s, 12H, 2,6,2″,6″-C*H*(CH$_3$)$_2$), 2.98 (sept, J_{HH} = 6.3 Hz, 6H, 4,4″-C*H*(CH$_3$)$_2$), 1.45 (br s, 72H, 2,6,2″,6″-CH(CH_3)$_2$), 1.38 (d, J_{HH} = 6.3 Hz, 36H, 4,4″-CH(CH_3)$_2$), 1.25 (s, 6H, 4′,6′-H), −1.93 (s, 3H, 2′-H), −26.89 (br s, 6H, NCH_2), −33.13 (br s, 6H, NCH_2). Anal. Calcd for C$_{115}$H$_{159}$MoN$_5$: C, 80.89; H, 9.39; N, 4.10. Found: C, 81.06; H, 9.46; N, 3.97.

In Situ Observation of [HIPTN$_3$N]MoCN←B(C$_6$F$_5$)$_3$). [(HIPTN$_3$N)MoCN] (20 mg) in a J-Young NMR tube was dissolved in ∼0.6 mL of C$_6$D$_6$, and B(C$_6$F$_5$)$_3$ (∼6 mg) was added. After 12 h the color of the solution had changed from orange to green: ^{1}H NMR (C$_6$D$_6$, 20 °C) δ 7.23 (br s, 12H, 3′,5′,3″,5″-*H*), 6.65, 3.54 (br s, 12H, 2,6,2″,6″-C*H*(CH$_3$)$_2$), 2.98 (sept, J_{HH} = 6.0 Hz, 6H, 4,4″-C*H*(CH$_3$)$_2$), 1.70, 1.45 (br s, 72H, 2,6,2″,6″-CH(CH_3)$_2$), 1.38 (d, J_{HH} = 6.3 Hz, 36H, 4,4″-CH(CH_3)$_2$), 1.25 (s, 3H, 2′-H), −1.93, −26.89, −33.13; ^{19}F{^{1}H} NMR (C$_6$D$_6$, 20 °C) δ −12527 (br s, o-C$_6$F$_5$), −156.42 (s), −158.90 (s); IR (C$_6$D$_6$) cm^{-1} (s) 2184 (ν_{CN}).

Reaction of {[HIPTN$_3$N]Mo(NH$_3$)}BAr′$_4$ with NaC≡CH. A mixture of {[HIPTN$_3$N]Mo(NH$_3$)}BAr′$_4$ (336 mg, 131.9 μmol), NaC≡CH (19 mg, 396 mmol), and fluorobenzene (5 mL) was sealed in an Schlenk bulb and heated at 90 °C for 3 h while stirring. Volatiles were removed in vacuo, and the residue was extracted into 10 mL of pentane. The extract solution was filtered through Celite, concentrated in vacuo, and cooled to −35 °C overnight. The yellow powder was collected by filtration and recrystallized from heptane to afford 128 mg of microcrystalline product; yield 58%: ^{1}H NMR (C$_6$D$_6$, 20 °C, partial) δ 13.59 (d, J_{HH} = 2.4 Hz, 1H, Mo=C-*H*), 7.19, (m, 14H, Ar-*H*), 6.96 (s, 2H, Ar-*H*), 6.82 (s, 1H, Ar-*H*), 6.55 (br s, 1H, Ar-*H*), 6.37 (s, 1H, Ar-*H*), 6.29 (d, 2H, Ar-*H*), 4.69 (d, J_{HH} = 2.4 Hz, 1H, Mo-C-*H*)), 4.15 (br m, 1H, NCH_2), 3.97 (br m, 1H, NCH_2), 3.68 (br d, 1H, NCH_2), 3.49 (br m, 3H, NCH_2), 3.24 (br m, 3H, NCH_2), 3.12 (br m, 18H, Ar-C*H*Me$_2$), 2.36 (br m, 2H, NCH_2), 2.12 (br m, 3H, NCH_2), 1.96 (br m, 1H, NCH_2), 1.46 (d, J_{HH} = 6.9 Hz, 36H, 4,4″-CH(CH_3)$_2$), 1.32 (d, J_{HH} = 6.9 Hz, 36H, 2,6,2″,6″-CH(CH_3)$_2$), 1.24 (br d, J_{HH} = 5.7 Hz, 36H, 2,6,2″,6″-CH(CH_3)$_2$); ^{13}C NMR (C$_6$D$_6$, 20°C, partial) δ 288.4 (J_{CH} = 287.6 Hz, Mo=*C*H), 159.0, 157.6, 152.6, 147.7, 147.6, 147.4, 147.3, 147.2, 146.9, 141.5, 140.4, 139.3, 138.4, 138.1, 137.8, 137.7, 127.1, 125.7, 120.5, 120.3, 108.5, 65.4 (J_{CH} = 162.9 Hz, N*C*H$_2$), 54.0 (N*C*H$_2$), 53.5 (N*C*H$_2$), 52.3 (N*C*H$_2$), 51.9 (N*C*H$_2$), 35.0 (*C*HMe$_2$), 32.2 (*C*HMe$_2$), 30.9 (*C*HMe$_2$), 29.4 (*C*HMe$_2$), 25.7, 24.8, 24,7, 24.6, 24.5, 23.1. Anal. Calcd for C$_{116}$H$_{160}$MoN$_4$: C, 81.64; H, 9.45; N, 3.28. Found: C, 81.83; H, 9.52; N, 3.17.

Preparation of NaC≡CD. Solid CaC$_2$ (1.3 g, 20.3 mmol) was added via an addition tube to a three-neck 1 L flask containing a solution of benzene (10 mL) and D$_2$O (0.6 mL, 33.3 mol) that had been previously degassed in several freeze−pump−thaw cycles and still under vacuum. The mixture was stirred for several hours, and the flask was then placed in a dry ice/acetone cooling bath for about 20 min. The contents of the headspace was transferred to a 500 mL Schlenk flask containing some anhydrous CaCl$_2$ immersed in liquid N$_2$. The receiving flask was then sealed and allowed to warm to room temperature.

After the acetylene was dried overnight over anhydrous CaCl$_2$, it was transferred into another 500 mL flask containing sodium sand (0.35 g) and THF (20 mL). The flask was then sealed and the reaction mixture was stirred overnight and heated to 45−50 °C for 2 h. The white slurry was carefully decanted out and filtered through a frit to afford 0.225 g of white powder. No further purification was required. Na^{13}C≡^{13}CH was prepared by the same procedure from H^{13}C≡^{13}CH and sodium sand in THF.

Reaction of {[HIPTN$_3$N]Mo(NH$_3$)}BAr′$_4$ with NaC≡CD. A procedure analogous to reaction of {[HIPTN$_3$N]Mo(NH$_3$)}BAr′$_4$ with NaC≡CH was followed, starting from {[HIPTN$_3$N]Mo(NH$_3$)}BAr′$_4$ (210 mg, 82 μmol) and NaC≡CD (40 mg, 816 μmol); yield 89 mg (64%) yellow crystals.

Reaction of {[HIPTN$_3$N]Mo(NH$_3$)}BAr′$_4$ with Na^{13}C≡^{13}CH. A procedure analogous to the reaction of {[HIPTN$_3$N]Mo(NH$_3$)}BAr′$_4$ with Na^{13}C≡^{13}CH was followed, starting from {[HIPTN$_3$N]Mo(NH$_3$)}BAr′$_4$ (212 mg, 82.8 μmol) and Na^{13}C≡^{13}CH (48 mg, 960 μmol). The resulting pentane extract was dried in vacuo and dissolved in C$_6$D$_6$. ^{1}H NMR (C$_6$D$_6$, 20 °C) δ 13.82 (d, Mo=C-*H*), 13.19 (d, Mo=C-*H*), 4.97 (s, Mo-C-*H*), 4.423 (s, Mo-C-*H*); ^{13}C NMR (C$_6$D$_6$, 20 °C, partial) δ 287.6 (d, J_{CC} = 38.1 Hz, Mo=*C*H), 65.4 (d, J_{CC} = 38.1 Hz, Mo-*C*H).

X-ray Structural Studies. Low-temperature diffraction data were collected on a Siemens Platform three-circle diffractometer coupled to a Bruker-AXS Smart Apex CCD detector with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å), performing φ- and ω-scans. All structures were solved by direct methods using SHELXS[59] and refined against F^2 on all data by full-matrix least squares with SHELXL-97.[60] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms bonded to carbon atoms (except on carbon atoms that bind directly to metal atoms) were included into the model at geometrically calculated positions and refined using a riding model. Coordinates for the other hydrogen atoms were taken from the difference Fourier synthesis and refined freely with the help of distance restraints. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the *U* value of the atoms they are linked to (1.5 times for methyl groups). Crystal and structural refinement data are listed in Table 1 for all four structures.

Most of the isopropyl groups in all of the structures were disordered, and whenever such a disorder could be modeled successfully, it was refined with the help of similarity re-

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straints on 1−2 and 1−3 distances and displacement parameters as well as rigid bond restraints for anisotropic displacement parameters. The relative occupancies for the disordered components were refined freely, while constraining the total occupancy of both components to unity.

The crystals giving rise to the datasets for structures [HIPTN$_3$N]Mo(C$_2$H$_4$) and "[HIPTN$_3$N]Mo(CCH)" only diffracted to relatively low resolution, which led to a low data-to-parameter ratio in the refinement of those structures. This is a problem encountered relatively frequently with compounds that contain the large and flexible [HIPTN$_3$N]$^{3-}$ ligands, and similarity restraints and rigid-bond restraints for anisotropic displacement parameters were applied to all atoms in those two structures to counteract the correlation effects arising from the low number of data. All structures contain disordered solvent molecules (toluene in [HIPTN$_3$N]Mo(C$_2$H$_4$) and hexane or heptane in the other three). In all structures, crystallographic symmetry elements are involved in these disorders. This leads to noninteger values for the number of the carbon and/or hydrogen atoms in the empirical formulas of three of those structures.

The structure of "[HIPTN$_3$N]Mo(CCH)" may be twinned by merohedry with the true space group being $P\bar{3}$ instead of $P\bar{3}c1$ (twin law 0 1 0 1 0 0 0 0 0−1). Unfortunately, the twin refinement was not stable. The main reason for this is probably the insufficient quality and low resolution of the data. Therefore this structure is reported as untwinned in the higher symmetric space group. The crystal structure of this molecule is suboptimal. Unfortunately all attempts to obtain better crystals failed, and we believe that at least some meaningful conclusions can be drawn from this structure, which justifies including it in this publication.

In the structure of {[HIPTN$_3$N]Mo(C$_2$H$_4$)}{BAr′$_4$}, the anion is disordered over two positions. To counteract the correlation between coordinates and anisotropic displacement parameters of the disordered atoms, similarity restraints on 1−2 and 1−3 distances and displacement parameters as well as rigid bond restraints for anisotropic displacement parameters were applied. The occupancies of the two components were not refined freely but constrained to 0.5, as the crystallographic inversion center is involved in the disorder. One relatively high residual electron density maximum (2.1 electrons per Å^3) is located 0.91 Å away from the Mo atom. No meaningful assignment could be made for this peak, and we believe that absorption effects and Fourier truncation errors are the cause for this spurious electron density.

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Supporting Information Available: Fully labeled thermal ellipsoid drawing, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates for [HIPTN$_3$N]Mo(C$_2$H$_4$) (04044), [HIPTN$_3$N]Mo(CH$_2$CH$_3$) (04200), "[HIPTN$_3$N]Mo(CCH)" (05021), and {[HIPTN$_3$N]Mo(C$_2$H$_4$)}BAr′$_4$ (05034). This material is available free of charge via the Internet at http://pubs.acs.org. Data for the four structures are also available to the public at http://www.reciprocalnet.org/. The number in parentheses above identifies each structure at this site.

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