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Molybdenum Complexes that Contain a Calix[6]azacryptand Ligand as Catalysts for Reduction of N_2 to Ammonia

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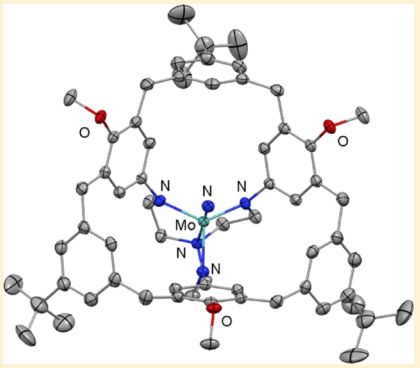
Supporting Information

ABSTRACT: $[CAC(OMe)_6]Mo(N)$ (**3**, where $[CAC]^{3-}$ is a calix[6]azacryptand ligand derived from a [6]calixarene) has been prepared in a reaction between $Li_3[CAC(OMe)_6]$ and $(t\text{-BuO})_3Mo(N)$. An X-ray structural study showed **3** to have a structure similar to that of $[HIPTN_3N]Mo(N)$ (where $[HIPTN_3N]^{3-}$ is $[(3,5\text{-}(2,4,6\text{-triisopropylphenyl})_2C_6H_3NCH_2CH_2)_3N]^{3-}$). The relatively rigid $[CAC(OMe)_6]^{3-}$ ligand in **3** forms a bowl-shaped cavity defined by a 24-atom macrocyclic ring. The $Mo-N_{amido}-C_{ipso}$ angles are ∼8° smaller in **3** than they are in $[HIPTN_3N]Mo(N)$. Methoxides on the three linking units point into the cavity above the nitride in **3**, whereas the three methoxides on phenyl rings attached to the amido nitrogen atoms point away from the cavity. An analogous $[CAC(OMe)_3(H)_3]Mo(N)$ complex (**9**) was prepared in which the three methoxides pointing into the cavity in **3** have been replaced by protons. Its structure differs little from that of **3**. The nitride could be protonated in **3** to give $\{[CAC(OMe)_6]Mo(NH)\}^+$, which could be reduced (reversibly) to $[CAC(OMe)_6]Mo(NH)$. Catalytic reduction of molecular nitrogen under a variety of conditions with either Ph_2NH_2OTf or HBArf ($BArf^-$ = $\{B[3,5(CF_3)_2C_5H_3]_4\}^-$) as the acid and a Co metallocene or KC_8 as the reducing agent between −78 and 22 °C in diethyl ether shows that 1.20−1.34 equivalents of ammonia are formed starting with either $[CAC(OMe)_6]Mo(N)$ (50% ^{15}N) or $[CAC(OMe)_3(H)_3]Mo(N)$ (50% ^{15}N).



INTRODUCTION

Molybdenum complexes that contain a $[(HIPTNCH_2CH_2)_3N]^{3-}$ ligand in which HIPT is 3,5-(2,4,6-triisopropylphenyl)$_2C_6H_3$ (Figure 1 left) catalyze the reduction of molecular nitrogen to ammonia in the presence of [2,6-lutidinium][B(3,5-$(CF_3)_2C_6H_3)_4$] as the acid and decamethylchromocene as the reducing agent in heptane at room temperature and pressure.[1] Approximately four equivalents of nitrogen are reduced to give NH_3 and H_2 in a ratio of ∼2:1 (∼60% efficiency in electrons). Loss of the $[HIPTN_3N]^{3-}$ ligand is one cause of limited turnover in the $[HIPTN_3N]Mo$-catalyzed reduction.[2] Extensive experimental studies are consistent with a distal mechanism of reduction in which the first equivalent of ammonia and a Mo(VI) nitride intermediate are formed after addition of three protons and three electrons to a Mo(III) nitrogen complex.[3]

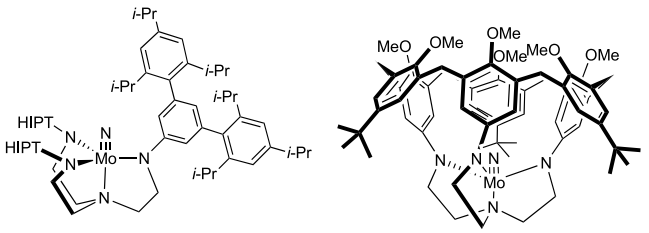


Figure 1. Structures of $[HIPTN_3N]Mo(N)$ (left) and $[CAC(OMe)_6]Mo(N)$ (right).

Some version of proton-coupled electron transfer[4] appears to be necessary to form a $[HIPTN_3N]M-N{=}NH$ intermediate from $[HIPTN_3N]M(N_2)$ to avoid energetically disfavored outright protonation of the nitrogen ligand or addition of an electron to give $\{[HIPTN_3N]M(N_2)\}^-$, which can only be prepared with a strong reducing agent such as sodium. Other molybdenum systems have been reported and developed,[5,6] along with multidentate phosphine-based systems that contain iron,[7] ruthenium,[8] osmium,[8] cobalt,[9] or vanadium.[10] In all cases, a metallocene or KC_8 is the reducing agent. Approximately, 230 equivalents of ammonia reportedly have been obtained with a Mo catalyst system.[5i] An iron-based catalyst has also been reported that produces hydrazine relatively selectively using $CoCp_2^*$ as the reducing agent and Ph_2NH_2OTf as the acid;[11] hydrazine must be formed through a proximal or alternating mechanism.

Loss of the triamidoamine ligand and consequently the catalytic activity in the $[HIPTN_3N]Mo$ system has been ascribed to protonation of amido nitrogen atoms.[2] We envisioned that loss of the triamidoamine ligand could be prevented if the three amido arms were connected, but the only synthesis of such a ligand was too inefficient to allow

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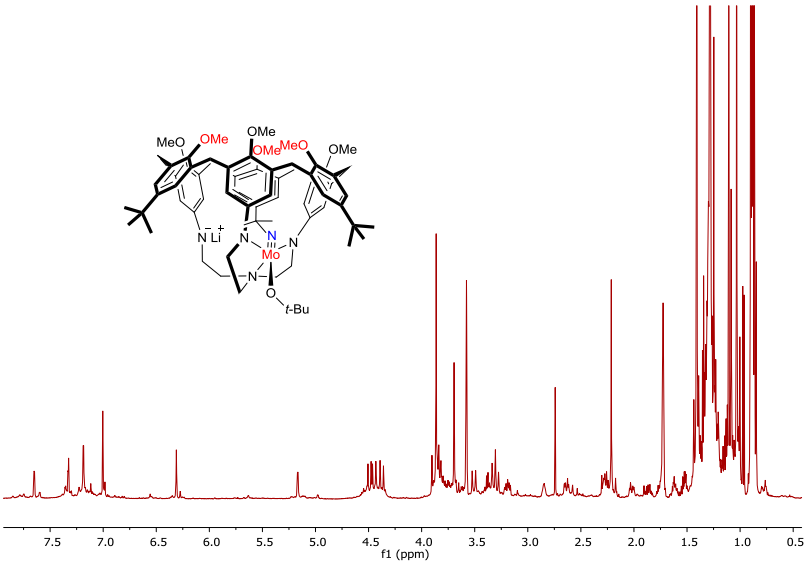


Figure 2. Proton NMR spectrum of **2**.

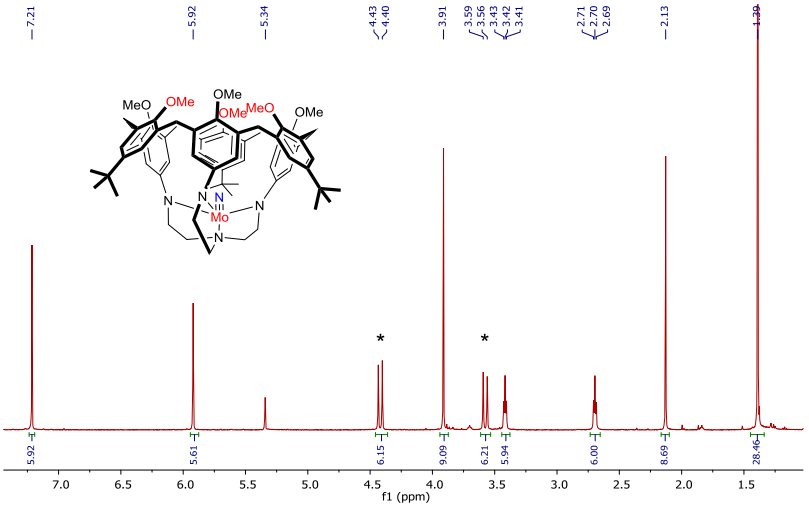


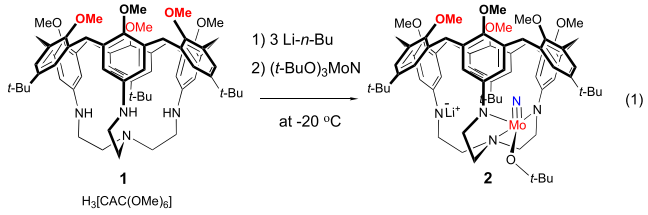
Figure 3. Proton NMR spectrum of **3**.

insertion of Mo and evaluation of the resulting complex for reducing nitrogen.[12] An alternative is a complex that contains the calix[6]azacryptand $[CAC(OMe)_6]^{3-}$ ligand (Figure 1 right), in which the tren unit is attached to the large rim of the calix core.[13] The *N*-aryl bonds in the $[CAC(OMe)_6]^{3-}$ ligand are linked in the 3 and 5 positions to a similar aryl spacer unit, thus creating a relatively rigid and sterically protected binding pocket or cavity whose essential structural feature is a 24 atom macrocyclic ring.

In this paper, we prepare $[CAC(OMe)_6]Mo(N)$ (Figure 1 right) and an analog, $[CAC(OMe)_3(H)_3]Mo(N)$, in which three methoxides are replaced by protons and evaluate them both for N_2 reduction. To our knowledge, this is the first experimental exploration of a transition-metal complex that contains this type of calix[6]azacryptand ligand.

RESULTS

Synthesis of Nitride Complexes. Addition of three equivalents of LiBu to $H_3[CAC(OMe)_6]$ (**1**, eq 1) in tetrahydrofuran (THF) at −20 °C followed by addition of $(t\text{-BuO})_3Mo(N)$ and warming the reaction mixture to 22 °C yields a complex that we propose is a LiO-*t*-Bu adduct (**2**, eq 1) of the desired $[CAC(OMe)_6]Mo(N)$ complex. The relatively complex proton NMR spectrum of **2** (Figure 2)



suggests that it has mirror symmetry. It can be converted into $[CAC(OMe)_6]Mo(N)$ (**3**) and Li-O-*t*-Bu by heating the reaction mixture at 130 °C for 1.5 days. The proton NMR spectrum of **3** (Figure 3) is consistent with its C_{3v} symmetry. The complex patterns for the methylene protons in the CH_2 groups between all aryl rings in the NMR spectrum of **2** simplify to yield two doublets at 4.41 and 3.57 ppm in the NMR spectrum of **3** (* in Figure 3); other simplifications are equally dramatic. The yield of isolated **3** from 50 mg of **1** is 68%. $[CAC(OMe)_6]Mo(^{11S}N_{0.5}{}^{14}N_{0.5})$ (**3**-$^{15}N_{0.5}{}^{14}N_{0.5}$) was

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also prepared starting with $(t\text{-BuO})_3Mo(^{15}N_{0.5}{}^{14}N_{0.5})$. The 50% labeling in the ammonium ion formed upon treatment of **3**-$^{15}N_{0.5}{}^{14}N_{0.5}$ with HCl was confirmed by ^1H NMR integration to be 1.00(1):1.00(1).

An X-ray study of **3** (Figure 4) showed that its structure is similar to that of $[HIPTN_3N]Mo(N)$.[14] The Mo−N_{amido}, Mo−N_{amine}, and Mo≡N distances and Mo−N−C_{ipso} angles in **3** and $[HIPTN_3N]Mo(N)$ are listed in Table 1. The only significant difference between the parameters shown in Table 1 for $[HIPTN_3N]Mo(N)$ and those for **3** is that the Mo−N−C_{ipso} angles in **3** are ∼8° smaller than they are in $[HIPTN_3N]Mo(N)$. We ascribe this difference to the fact that the aryl substituents in $[HIPTN_3N]Mo(N)$ are not linked together while the aryl substituents in **3** are locked into a relatively rigid configuration dictated by the constraints of the 24 atom macrocyclic ring. The aryl rings bound to the three amido nitrogens in **3** are all perpendicular to the Mo−N_{amido}−C plane, which leads to the methoxides (with O1 atoms in Figure 4) on those aryl rings pointing away from the cavity in which the metal sits. In contrast, the methoxides (O2 atoms in Figure 4) in the three linking units point into the cavity above the nitride ligand. It is unclear to what degree the aryl rings on which those methoxides are found can rotate away from the metal. Ultimately that rotation might be limited by steric interaction between the *p*-*t*-butyl groups and the methylene groups in the ligand backbone and access to N3 or other ligands in the pocket restricted for steric reasons. The Mo in **3** is 0.27 Å above the plane formed by the three amido nitrogen atoms, as was found also in $[HIPTN_3N]Mo(N)$.

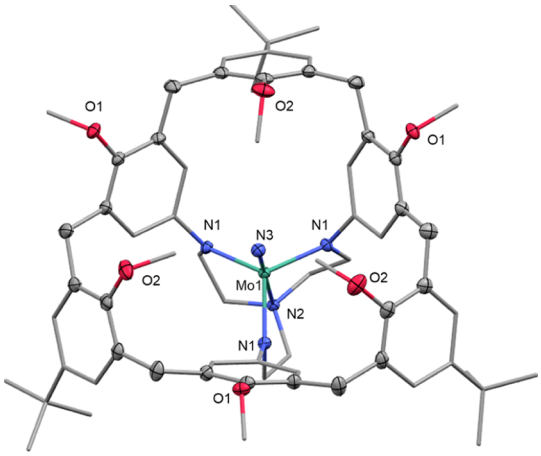


Figure 4. Structure of $[CAC(OMe)_6]Mo(N)$ (**3**).

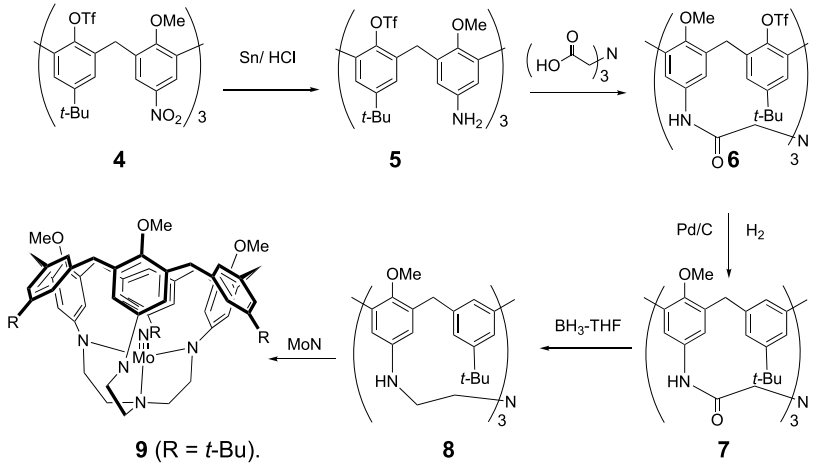
Table 1. M−N Distances (Å) and Mo−N−C_{ipso} Angles (deg) in $[HIPTN_3N]Mo(N)$, $[CAC(OMe)_6]Mo(N)$ (3), and $[CAC(OMe)_3(H)_3]Mo(N)$ (9)

	Mo−N_{amido}	Mo−N_{amine}	Mo≡N
$[HIPTN_3N]Mo(N)$	1.999(8)−2.011(8)	2.399(8)	1.656(8)
3	1.9715(15)	2.404(3)	1.670(3)
9	1.959(3)	2.404(2)	1.675(3)
	Mo−N−C_{ipso} angles		
$[HIPTN_3N]Mo(N)$	128.2−128.8(4)		
3	120.44(11)		
9	119.4(2)		

The only mirror symmetry (analogous to **2**). Compound **6b** is usually ∼40% of the crude mixture (see Figures S3 and S4 in the Supporting Information). NMR studies are consistent with isomer **6b** being one in which one of the linking units is rotated by ∼180° (a two down, one up arrangement of the links) and interconversion of **6a** and **6b** is not rapid on the chemical time scale at 22 °C. This proposal is consistent with the fact that **6a** and **6b** are converted into the same compound (**7**) upon removal of the triflate groups through hydrogenation of the mixture. Compound **7** can then be reduced to $H_3[CAC(OMe)_3(H)_3]$ (**8**) in high yield. An X-ray structure of **8** confirms that the methoxides in the linking units are absent (see the Supporting Information).

The reaction between $Li_3[CAC(OMe)_3(H)_3]$ and $(t\text{-BuO})_3Mo(N)$ to give $[CAC(OMe)_3(H)_3]Mo(N)$ (**9**) requires less time (125−130 °C for ∼30 min) than the analogous reaction that gives **3**. We propose that the $[CAC(OMe)_3(H)_3]^{3-}$ ligand can be put on the metal more readily

Scheme 1. Synthesis of $H_3[CAC(OMe)_3(H)_3]$ (8) and $[CAC(OMe)_3(H)_3]Mo(N)$ (9)



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because the steric demands encountered in that process are less severe. An X-ray structural study shows that the structure of **9** (Figure 5 and Table 1) is essentially identical to that of **3**,

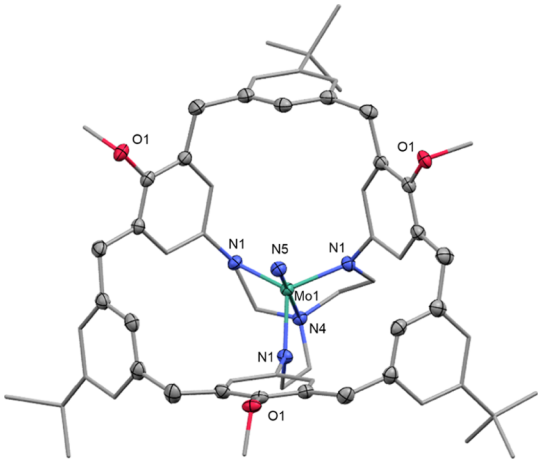

Figure 5. Structure of $[CAC(OMe)_3(H)_3]Mo(N)$ (**9**).

which suggests that the OMe_{link} groups do not play any significant role in determining the configuration of the macrocyclic bowl that surrounds the cavity. As expected, the Mo−N−C_{ipso} angles in **9** are essentially the same as they are in **3**, that is, smaller by ∼8° than they are in $[HIPTN_3N]Mo(N)$ (Table 1). $[CAC(OMe)_3H_3]Mo(^{15}N_{0.5}{}^{14}N_{0.5})$ (**3**-$^{15}N_{0.5}{}^{14}N_{0.5}$) was also prepared starting with $(t\text{-BuO})_3Mo(^{15}N_{0.5}{}^{14}N_{0.5})$.

One potentially important and encouraging characteristic of the amido nitrogens in both CAC ligand systems (Figures 4 and 5) is that they are effectively locked in a planar configuration by the ligand framework. Therefore, it seems likely that the amido nitrogens would not be protonated readily because the resulting nitrogen center would have to become tetrahedral. A rigid CAC ligand framework also would appear to make dissociation of the central nitrogen donor (N4 in Figure 5) even less likely than in the $[HIPTN_3N]Mo$ system.

Synthesis of Mo═NH$^+$ and Mo═NH Complexes. Compound **3** was protonated by $[Et_2O]_2H[BArf]$, [2,6-lutidinium][BArf], HOTf, or Ph_2NH_2OTf in dichloromethane to give $\{[CAC(OMe)_6]Mo(NH)\}^+X^-$ (**3H**$^+$X$^-$; X$^-$ = BArf$^-$ or OTf$^-$) whose proton NMR spectra (one is shown in Figure 6) are characteristic of a molecule with C_{3v} symmetry. The weak and broad Mo═NH resonance in **3H**$^+$ is found at 5.99 ppm. This assignment was confirmed through protonation of $[CAC(OMe)_6]Mo(^{15}N_{0.5}{}^{14}N_{0.5})$ to give a 1:1 mixture of $\{[CAC(OMe)_6]Mo(^{15}NH)\}^+$ and $\{[CAC(OMe)_6]Mo(^{14}NH)\}^+$ in which the resonance for the former is a doublet with J_{15NH} = 100 Hz (see inset in Figure 6). This J_{15NH} value should be compared with that for J_{15NH} in $\{(HMTN_3N)Mo(^{15}NH)\}^+$ (75 Hz).[15] Addition of LiO-*t*-Bu to a sample of $\{[CAC(OMe)_6]Mo(NH)\}^+$ yielded $[CAC(OMe)_6]Mo(N)$ immediately. We conclude that (reversible) protonation of the nitride at 22 °C in dichloromethane is not sterically blocked by the three methoxides pointing into the cavity and protonation of the nitride is preferred over protonation of an amido nitrogen. [2,6-Lutidinium]$^+$ would seem to be the most problematic potentially in terms of sterics, yet it readily protonates **3**.

$\{[CAC(OMe)_6]Mo(NH)\}^+$ (**3H**$^+$) was reduced with KC_8 or $CrCp^*_2$ to generate what we propose is paramagnetic $[CAC(OMe)_6]Mo(NH)$. $[CAC(OMe)_6]Mo(NH)$ was stable for 3−4 days at room temperature, with only a minor amount of decomposition to give $[CAC(OMe)_6]Mo(N)$, and was reoxidized to $\{[CAC(OMe)_6]Mo(NH)\}^+$ with $[FeCp_2]PF_6$. $[CAC(OMe)_6]Mo(NH)$ is analogous to $[HIPTN_3N]Mo(NH)$, which is formed through reduction of $\{[HIPTN_3N]Mo(NH)\}^+$.[15] In the absence of any additional reducing agent, $[HIPTN_3N]Mo(NH)$ decomposes slowly to $[HIPTN_3N]Mo(N)$. The apparent greater stability of $[CAC(OMe)_6]Mo(NH)$ suggests that the instability of $[HIPTN_3N]Mo(NH)$ might result from its more open and less rigid coordination sphere.

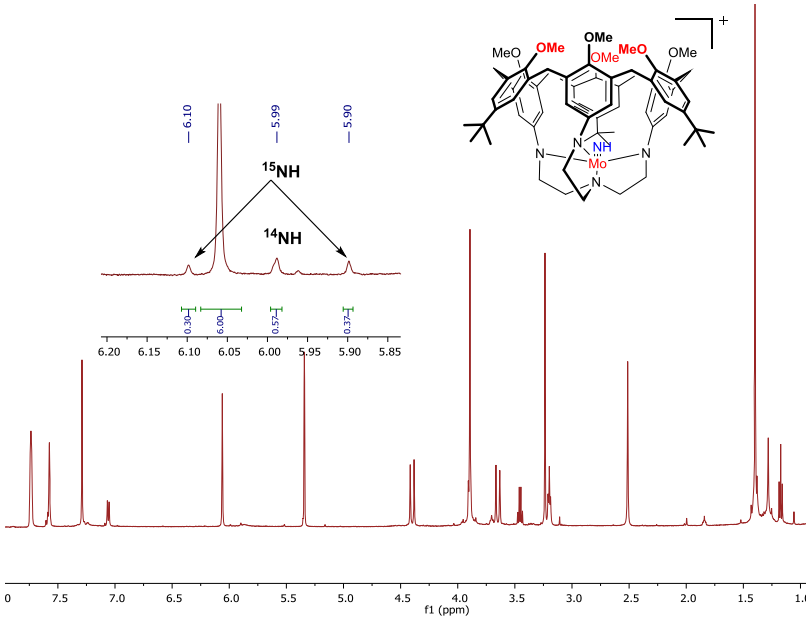

Figure 6. ^{1}H NMR spectrum (500 MHz, CD_2Cl_2) of $\{[CAC(OMe)_6]Mo(NH)\}^+$[BArf]$^-$ prepared from $[CAC(OMe)_6]Mo(^{14}N)$ (bottom) or $[CAC(OMe)_6]Mo(^{14}N_{0.5}{}^{15}N_{0.5})$ (inset) and [2,6-lutidinium]BArf$^-$.

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Although compound **3** is hydrolyzed readily by aqueous NaOH, it was unchanged after 3 days in acetone-d_6 at 22 °C in the presence of ∼30 equivalents of water.

Catalytic Reduction of Nitrogen. Reductions of nitrogen were explored with **3**-$^{15}N_{0.5}{}^{14}N_{0.5}$ and **9**-$^{15}N_{0.5}{}^{14}N_{0.5}$ under $^{14}N_2$ (Table 2). Most batchwise reductions were carried out at −78 °C followed by warming the mixtures to 22 °C after all reagents were added; variations are explained briefly in the footnotes of Table 2 and at length in the Supporting Information. The amount of ammonia was determined through NMR analysis of ammonium chloride in DMSO-d_6 with NaBArf as the internal standard in the case of **3** treated with KC_8/HBArf; the yield is 1.40 equivalents. Because the determination of NH_4Cl using 2.0−3.0 mg of NaBArf as an internal standard has an estimated error of ±10%, the equivalents of ammonia in Table 2 were calculated according to the ratio of $^{14}NH_4^+$ to $^{15}NH_4^+$, assuming that $^{15}NH_4^+$ = 0.5 equiv in all cases. The results were all within the range of 1.19−1.34 equiv of ammonia with an average of 1.26(±0.06). Any ammonia beyond 0.5 equiv of $^{14}NH_4^+$ and 0.5 equiv of $^{15}NH_4^+$ must come from atmospheric $^{14}N_2$. Therefore, we propose that all nitrides are converted into [CAC]Mo(NH_3), ammonia is replaced by nitrogen, and ∼0.25 equiv of additional $^{14}NH_3$ is formed thereafter. We do not know at what temperature ammonia in [CAC]Mo(NH_3) is displaced by nitrogen or how fast or when. (In all cases, the experiments terminated at 22 °C.) We propose that some variation of the distal mechanism is operating and that loss of the ligand is *not* the most significant limitation to catalytic reduction in these systems. Turnover could be limited by a relatively slow rate of conversion of [CAC]Mo(NH_3) to [CAC]Mo(N_2) *relative to* the rate of formation of hydrogen, even when the entire run is done at 22 °C (Table 2). Given that exchange of ammonia for nitrogen in the [HIPTN$_3$N]Mo system involves the formation of intermediate six-coordinate [HIPTN$_3$N]Mo(NH_3)(N_2), the pocket in each [CAC]Mo system may simply be too small and/or too rigid to allow an octahedrally coordinated intermediate to be formed as readily as [HIPTN$_3$N]Mo(NH_3)(N_2). It is also plausible that steps beyond formation of [CAC]Mo(N_2) are relatively slow compared with formation of hydrogen.

Table 2. Batchwise Reductions of N_2

compound	H^+ (equiv)	e (equiv)	NH_3
3-$^{15}N_{0.5}{}^{14}N_{0.5}$	Ph_2NH_2OTf (108)	$CoCp_2^*$ (54)	1.20[a]
	Ph_2NH_2OTf (108)	$CoCp_2$ (54)	1.20
	Ph_2NH_2OTf (108)	$CoCp_2$ (54)	1.20[b]
	HBArf (96)	KC_8 (84)	1.28[b]
	HBArf (96)	KC_8 (84)	1.34[b]
	HBArf (96)	KC_8 (84)	1.30[c]
	HOTf (96)	KC_8 (84)	1.32[d]
9-$^{15}N_{0.5}$	$^{14}N_{0.5}$HBArf-(96)	KC_8 (84)	1.30[a]
	Ph_2NH_2OTf (96)	KC_8 (84)	1.28[a]
	Ph_2NH_2OTf (108)	$CoCp_2^*$ (54)	1.19[a]
	Ph_2NH_2OTf (108)	$CoCp_2$ (54)	1.20[a]
		Avg 1.26 (±0.06)	

[a] −78 °C. [b] −78 °C, N_2 flow. [c] 22 °C. [d] 40 psi/−40 °C.

We were surprised to find that one attempted reduction of nitrogen using [HIPTN$_3$N]Mo(N) in the batchwise mode described for [CAC]Mo(N) complexes at room temperature yielded only 0.85 equivalents of ammonia, *less* than that found for [CAC]Mo(N) complexes and not catalytic. We therefore examined [CAC(OMe)$_6$]Mo(N) as a catalyst under the conditions that led to formation of ∼8 equivalents of ammonia with [HIPTN$_3$N]Mo(N) as an initial catalyst.[1] [CAC(OMe)$_6$]Mo(N) produced only 0.35 equiv of ammonia (one experiment only). These results illustrate that the efficiency of nitrogen reduction by protons and electrons strongly depends on matching the conditions with the catalyst and cannot be reliably predicted, as shown by the recent report of batchwise reduction with a Mo pincer system to give ∼10 equiv of ammonia.[6]

DISCUSSION

The goal of the work described here was to protect the Mo center against bimolecular decomposition reactions with an unusual type of triamidoamine ligand that is relatively rigid and relatively difficult to be protonated and removed from the metal and therefore to increase the long-term stability and activity of the catalyst. However, differences between the [CAC]Mo systems and the [HIPTN$_3$N]Mo systems in sum have prevented our reaching that goal. Among the differences that might prove important are that $[CAC]^{3-}$ ligands contain methoxides in the para positions of the phenyl rings attached to the amido nitrogens, and therefore are likely be more electron-donating that the $[HIPTN_3N]^{3-}$ ligands. $[CAC]^{3-}$ ligands are also clearly less flexible than a $[HIPTN_3N]^{3-}$ ligand. The coordination pocket of a $[CAC]^{3-}$ ligand is also significantly smaller. A smaller coordination pocket in the $[CAC]^{3-}$ ligands does not itself limit protonation and reduction of at least a *nitride* to ammonia, so N_β atoms in molecular nitrogen and other N_xH_y intermediates *should* also be accessible to protonation or hydrogen bonding of acids to various intermediates. Our expectation that [CAC(OMe)$_6$]Mo(N) would be inferior to [CAC(OMe)$_3$H$_3$]Mo(N) in terms of the efficiency of nitrogen reduction, also was not met; reagents appear to be able to access the coordination pocket in both $[CAC(OMe)_6]^{3-}$ and $[CAC(OMe)_6]^{3-}$ systems.

Reiher[16] has studied the [CAC(OMe)$_6$]Mo system in detail theoretically and concluded that it will suffer some significant drawbacks as a catalyst compared with the [HIPTN$_3$N]Mo system. In his summary Reiher states that "all reactions which are challenging for the original Yandulov−Schrock catalyst become more endothermic." Two of the most important reactions are protonation of a dinitrogen ligand and the exchange of ammonia for nitrogen. A lower basicity of a terminally bound N_2 ligand in [CAC(OMe)$_6$]Mo(N_2) compared with [HIPTN$_3$N]Mo(N_2) seems likely to translate into weaker hydrogen bonding of an acid to the nitrogen and therefore slower conversion of [CAC(OMe)$_6$]Mo(N_2) into [CAC(OMe)$_6$]Mo=N−NH. Reiher also states that the exchange of NH_3 for N_2 required to close the cycle might be difficult to achieve. Any or all of these problems could contribute to the observed poor catalytic performance for [CAC]Mo(N_2) complexes relative to [HIPTN$_3$N]Mo complexes.

Unfortunately, the relatively long syntheses of [CAC(OMe)$_6$]Mo(N) and [CAC(OMe)$_3$(H)$_3$]Mo(N) and low

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yields in more than one step have limited the amounts that can be made to less than 1 g, usually ∼100 mg. We therefore have not been able to expand our studies to include other crucial intermediates that are analogous to those prepared and characterized in the [HIPTN$_3$N]Mo system, for example, [CAC]MoN$_2$, [CAC]Mo═N−NH, [CAC]Mo(NH$_3$)$^+$, and [CAC]Mo(NH$_3$), and to track down the problem(s) in an actual catalytic reaction through mechanistic studies that involve intermediates in the proposed distal nitrogen reduction. We also have not been able to identify the Mo compounds that remain in a typical nitrogen reduction reaction that has run its course.

In general, greater success in reducing nitrogen involves complexes that are based on sterically demanding multidentate phosphine ligands,[5] which are not readily protonated and removed from the metal. However, it should be pointed out that there are a few reports of M−P bonds that have H atoms bridging between M and P[17] and one example of H bonded to P only (a metallohydrophosphorane).[18] In one case,[17a] the bridging H atom arises through addition of a proton to an *anionic Mo(IV) nitride complex*, that is, a proton adds to an M−P bond instead of the nitrogen atom in an anionic nitride! Therefore, even multidentate phosphine ligands are not immune to protonation of an M−P bond and ultimately removal from the metal.

CONCLUSIONS

We conclude that the delicate balancing of at least a dozen or so reactions that are required to reduce molecular nitrogen with protons and electrons can be disrupted by what we had hoped to be a solution to ligand loss from the metal in triamidoamine systems and that leads to low efficiencies of forming ammonia relative to hydrogen under the chosen conditions. On the positive side, it should be noted that the [CAC(OMe)$_6$]$^{3-}$ or [CAC(OMe)$_3$(H)$_3$]$^{3-}$ compounds may be the only examples that contain a trigonally symmetric, sterically protected, and rigid substrate-binding pocket that is relatively accessible to reagents at the open end of the complex. We hope that the ligand syntheses can be improved in future studies and other ligand variations of Mo or other metal derivatives can be prepared to expand our knowledge concerning the potential of these unusual [CAC]$^{3-}$ ligands in the chemistry of M(3+) or higher oxidation state complexes.

EXPERIMENTAL SECTION

General. H$_3$[CAC(OMe)$_6$] (1), Calix(OMe)$_3$(OTf)$_3$(NO$_2$)$_3$ (4; Scheme 1),[13] Mo(N)(O-*t*-Bu)$_3$,[19] CoCp*$_2$,[20] Ph$_2$NH$_2$OTf,[7b] KC$_8$, and [Et$_2$O]$_2$HBArf (BArf$^-$ = [B(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$]$^-$) were prepared according to literature procedures. All air- and moisture-sensitive materials were manipulated under a nitrogen atmosphere in a Vacuum Atmospheres glovebox or on a dual-manifold Schlenk line. All glassware were either oven-dried or flame-dried prior to use. Benzene, THF, diethyl ether, *n*-hexane, and toluene were degassed, passed through activated alumina columns, and stored over 4 Å Linde-type molecular sieves prior to use. Pentane was washed with H$_2$SO$_4$, followed by water and saturated aqueous NaHCO$_3$, and dried over CaCl$_2$ pellets for at least 2 weeks prior to use in the solvent purification system. Deuterated solvents were dried over 4 Å Linde-type molecular sieves prior to use. ^{1}H NMR spectra were obtained on 300 or 500 MHz spectrometers and ^{13}C NMR spectra on 101 or 151 MHz spectrometers at ambient 22 °C. Chemical shifts for ^{1}H and ^{13}C spectra are reported as parts per million relative to tetramethylsilane and referenced to the residual ^{1}H or ^{13}C resonances of the deuterated solvent (^{1}H δ benzene 7.16, dimethylsulfoxide 2.50, methylene chloride 5.32, chloroform 7.26; ^{13}C δ benzene 128.06, methylene chloride 53.84). ^{19}F NMR (282 MHz) spectra were recorded in proton-decoupled mode and referenced to external standard CFCl$_3$.

[CAC(OMe)$_6$]Mo(N) (3). H$_3$[CAC(OMe)$_6$] (50 mg, 0.049 mmol) was dissolved in 3.0 mL of THF (under N$_2$) in a 20 mL vial and the solution was cooled to −20 °C before adding 2.5 M *n*-butyllithium (58 μL, 0.146 mmol). The reaction was stirred for 5−10 min at −20 °C, and then a −20 °C solution (∼2 mL) of (*t*-BuO)$_3$Mo≡N (16.0 mg, 0.049 mmol) was added to the solution and the mixture was stirred for 20 min. The reaction mixture became blue-green. A proton NMR spectrum, of a similar reaction performed in THF-d_8 (∼1 mL) indicates that intermediate **2** (eq 1) has formed. The solution containing **2** was heated at 130 °C for ∼1−1.5 days. The solution was concentrated under reduced pressure to give a solid residue. A mixture of MeCN/Et$_2$O (2:0.5 mL) was added at −20 °C and compound **3** was filtered off; yield 38 mg (68%). Compound **3** also can be isolated by passing a solution of the final mixture through a neutral alumina column (in a pipette) using THF. [CAC(OMe)$_6$]-Mo(^{15}N) (50%-labeled) was prepared similarly from 50% ^{15}N-labeled (*t*-BuO)$_3$Mo(^{15}N). Pale yellow crystals of **3** for X-ray analysis were grown by slow evaporation of an acetonitrile solution inside the glovebox: ^{1}H NMR (500 MHz, CD$_2$Cl$_2$, Figures 3 and S7): δ 7.21 (s, ArH, 6H), 5.92 (s, ArH, 6H), 4.42 (d, J = 15 Hz, ArCH$_{2ax}$, 6H), 3.91 (s, OMe, 9H) 3.57 (d, J = 15 Hz, ArCH$_{2eq}$, 6H), 3.41 (t, J = 5 Hz, NCH$_2$, 6H), 2.69 (t, J = 5 Hz, NCH$_2$, 6H), 2.14 (s, OMe, 9H), 1.32 (s, *t*-Bu, 27H); ^{13}C NMR (500 MHz, C$_6$D$_6$, Figure S8): δ 159.04, 155.69, 152.81, 145.39, 135.42, 133.88, 128.10, 124.25, 61.69, 59.14, 56.64, 51.59, 33.95, 31.45, 31.37. Anal. Calcd for C$_{66}$H$_{81}$MoN$_5$O$_6$: C, 69.76; H, 7.19; N, 6.16. Found: C, 69.65; H, 7.11; N, 5.81.

1,3,5-Trimethoxy-2,4,6-tristriflate-calix[6]arenetrianiline (Calix(OMe)$_3$(OTf)$_3$(NH$_2$)$_3$) (5). A 500 mL bomb flask was filled with a 150 mL solution of **4** (10.0 g, 7.26 mmol) in THF. Tin metal was added in the form of micro pellets (8.61 g, 72.5 mmol). Concentrated HCl (20 mL) was added and the flask was closed with a Teflon stopper, and the reaction mixture was stirred for 2 days. The final mixture was concentrated in vacuo, and the resulting dark oily mixture was dissolved in dichloromethane (300 mL). The organic layer was washed with NaHCO$_3$ solution (3 × 200 mL) and separated from the aqueous layer. The aqueous layer was extracted with dichloromethane (300 mL). The combined organic layers were washed with deionized water (200 mL), dried over MgSO$_4$, and concentrated under reduced pressure. The oily product was dissolved in 30 mL of ethyl acetate, and the solution was filtered through silica. The concentrated organic layer was loaded onto a silica column, and the product was eluted with a 45:45:10 mixture of hexane/dichloromethane/ethylacetate. The reddish colored solid was stirred in methanol/DCM (1:1 mixture), and colorless crystals of final compound was obtained after standing the mixture at −20 °C; yield 7.61 g (81% yield). ^{1}H NMR (500 MHz, CDCl$_3$): δ 6.74 (s, ArH, 6H), 6.37 (s, ArH, 6H), 4.22 (s, ArCH$_2$, 6H), 3.77 (s, OMe and ArCH$_2$, 15H), 3.12 (s, NH$_2$, 6H), 0.80 (s, *t*-Bu, 27H); ^{19}F NMR (300 MHz, CDCl$_3$) δ 74.7 ppm.

1,3,5-Trimethoxy-2,4,6-tristriflate-calix[6]arene-nitrilotriacetamide, (Calix(OMe)$_3$(OTf)$_3$(N)(CH$_2$CONH)$_3$) (6). Triethylamine (380 mg, 3.7 mmol) was added to a solution of nitrilotriacetic acid (148.3 mg, 0.78 mmol) dissolved in *N*,*N*-dimethylformamide (∼5 mL); all of the nitrilotriacetic acid dissolved after stirring the mixture for ∼30 min. PyBOP (400 mg, 0.78 mmol) was added as solid under an N$_2$ atmosphere at rt, and the reaction was stirred for 30 min. The solution was added to a solution of Calix(OMe)$_3$(OTf)$_3$(NH$_2$)$_3$ (**5**) (approximately 1.0 g, 0.78 mmol) in a mixture of *N*,*N*-dimethylformamide (190 mL) and chloroform (450 mL). The reaction mixture was sealed tightly and stirred for 3 h at 50 °C. Another 400 mg of PyBOP was added, and the mixture was stirred for another 3 h at 50 °C. After a total of 6 h, a final 1.2 g of PyBOP was added and the reaction mixture was stirred overnight (12 h) at 50 °C. (Every addition of PyBOP was done under a flow of N$_2$.) The dark yellow solution was then cooled to room temperature and concentrated under reduced pressure. The resulting residue was dissolved in dichloromethane (300 mL). Analysis of a crude sample by ^{1}H NMR showed that two compounds, C_{3v} symmetric **6a** and

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mirror symmetric **6b**, were present. The organic layer was washed with 50 mL of a 3% wt NH_4OH aqueous solution followed by deionized water (3 × 200 mL). It was dried over $MgSO_4$ and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography (dichloromethane/EtOAc: 50/50) to yield a mixture of **6a** and **6b** as a white solid (~220 mg, 20% yield). This mixture was hydrogenated (see below) to yield a single compound. A small sample of pure **6a** was isolated through column chromatography, and its proton NMR data are as follows: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.92 (s, NH, 3H), 7.34 (s, ArH, 6H), 6.24 (s, ArH, 6H), 4.71 (d, J = 16.2 Hz, $ArCH_2$, 6H), 3.83 (s, OMe, 9H) 3.64 (d, J = 16.2 Hz, $ArCH_2$eq, 6H), 3.46 (s, NCH_2, 6H), 1.41 (s, t-Bu, 27H).

1,3,5-Trimethoxy-calix[6]arene-nitrilotriacetamide, (Calix-(OMe)$_3$(H)$_3$(N)(CH$_2$CONH)$_3$) (7). Triethylamine (0.5 mL, 3.58 mmol) was added to a THF solution of **6** (110 mg, 0.13 mmol) followed by addition of 150 mg of Pd/C (10% Pd on C). The mixture was pressurized with H_2 (1200 psi) and heated at 70−80 at °C for 3−4 days. The dark yellow solution was then cooled to room temperature and concentrated under reduced pressure. The resulting residue was dissolved in dichloromethane (300 mL), which was washed with 50 mL of a 10% NH_4OH aqueous solution and deionized water (3 × 200 mL). The solution was dried over $MgSO_4$, and the filtrate was concentrated under reduced pressure. The resulting residue was purified by flash column chromatography (dichloromethane/EtOAc: 50/50) to yield **7** as a white solid (110 mg, 88% yield): ^{1}H NMR (500 MHz, C_6D_6): δ 8.54 (s, NH, 3H), 7.27 (s, ArH, 6H), 7.09 (s, ArH, 6H), 6.60 (s, ArH, 3H), 4.14 (d, J = 16.2 Hz, $ArCH_2$, 6H), 3.73 (d, J = 16.2 Hz, $ArCH_2$, 6H) 3.30 (s, OMe, 9H), 2.76 (s, NCH_2, 6H), 1.33 (s, t-Bu, 27H).

1,3,5-Trimethoxy-calix[6]arene-tren, H$_3$[CAC(OMe)$_3$(H)$_3$] (8). Borane−THF complex 4 mL (1.0 M 4.0 mmol) in 10 mL of dry THF was added under an N_2 flow to a solution of **7** (110 mg, 0.11 mmol) in dry THF (10 mL). The mixture was refluxed for 18 h and then 100% ethanol 2 mL was added slowly and the mixture continued to be heated at 80 °C for 4 h. The solution was cooled to room temperature and concentrated under reduced pressure. The resulting residue was dissolved in dichloromethane (10 mL) and loaded onto a silica column. The product was purified by flash column chromatography (dichloromethane/EtOAc: 50/50) to yield $H_3[CAC(OMe)_3(H)_3]$ as a white solid (88 mg, 83% yield): ^{1}H NMR (500 MHz, C_6D_6): δ 7.31 (s, ArH, 6H), 6.66 (s, ArH, 3H), 6.16 (s, ArH, 6H), 4.27 (d, J = 15 Hz, $ArCH_{2ax}$, 6H), 3.93 (d, J = 15 Hz, $ArCH_2$eq, 6H) 3.42 (s, OMe, 9H), 3.35 (s, NH, 3H) 2.42 (s, NCH_2, 6H), 2.21 (s, NCH_2, 6H), 1.30 (s, t-Bu, 27H); ^{1}H NMR (500 MHz, CD_3Cl): δ 7.11 (s, ArH, 6H), 6.28 (s, ArH, 3H), 6.17 (s, ArH, 6H), 4.05 (d, J = 15 Hz, $ArCH_{2ax}$, 6H), 3.80 (d, J = 15 Hz, $ArCH_{2eq}$, 6H), 3.51 (s, OMe, 9H), 2.98 (s, NCH_2, 6H), 2.91 (s, NCH_2, 6H), 1.32 (s, t-Bu, 27H); ^{13}C NMR (500 MHz, C_6D_6): δ 151.17, 149.32, 145.56, 141.28, 134.70, 128.63, 124.35, 113.82, 60.79, 59.62, 45.24, 35.81, 34.63, 31.66.

Trimethoxy-calix[6]arenetren-MoN (9). $H_3[CAC(OMe)_3(H)_3]$ (**8**) (20 mg, 0.021 mmol) was dissolved in 3.0 mL of THF (under an N_2 atmosphere) in a 20 mL vial and the solution was kept at −20 °C for 20 min before adding 2.5 M n-butyllithium (25 μL, 0.064 mmol). The mixture was stirred for 5−10 min, and a cold solution (~2 mL) of $(t\text{-BuO})_3$MoN (7.1 mg, 0.021 mmol) was added to the above solution of **8** and stirred for 20 min. The reaction mixture turned a blue-green color. The resulting mixture was heated at 125−130 °C for ~30 min. Heating the reaction mixture at 130 °C yielded the desired C_{3V} symmetric compound. It is very important to keep the temperature above 125 °C to complete the Mo insertion successfully. A reaction at 115−120 °C leads to the formation of ligand. The final compound (**9**) was isolated as a precipitate after adding MeCN/Et_2O (~1 mL MeCN and minimum amount of ether to dissolve solid residues) solution at −20 °C. The isolated yield was 12 mg (54% yield). Yellow crystals for the X-ray analysis were grown by slow evaporation of MeCN under ambient temperature inside the glovebox: ^{1}H NMR (500 MHz, C_6D_6): δ 7.37 (s, ArH, 6H), 7.09 (s, ArH, 3H), 6.95 (s, ArH, 6H), 4.44 (d, J = 15 Hz, $ArCH_{2ax}$, 6H), 4.00 (d, J = 15 Hz, $ArCH_2$eq, 6H) 3.50 (s, J = 15 Hz, OMe, 9H), 3.04 (t, J = 5 Hz, NCH_2, 6H), 1.68 (t, J = 5 Hz, NCH_2, 6H), 1.28 (s, t-Bu, 27H); ^{1}H NMR (500 MHz, CD_3Cl): δ 7.21 (s, ArH, 6H), 7.09 (s, ArH, 3H), 6.38 (s, ArH, 6H), 4.24 (d, J = 15 Hz, $ArCH_{2ax}$, 6H), 3.80 (s, J = 15 Hz, OMe, 9H), 3.74 (d, J = 15 Hz, $ArCH_2$eq, 6H), 3.59 (t, J = 5 Hz, NCH_2, 6H), 2.80 (t, J = 5 Hz, NCH_2, 6H), 1.35 (s, t-Bu, 27H); ^{13}C NMR (500 MHz, C_6D_6): δ 160.51, 153.54, 151.25, 141.24, 133.42, 129.53, 125.51, 123.91, 60.39, 55.21, 52.23, 36.03, 34.60, 31.61. So far, elemental analyses of **9** unexpectedly have not been satisfactory, but NMR and X-ray analyses leave no room for doubt about its nature.

Synthesis of 6 Using 2,2,2-Nitrilotriacetyl Chloride. A solution of **5** (200 mg, 0.115 mmol) prepared in dichloromethane ~15 mL (in a glovebox) was treated with 3.0 equiv of 1.0 M HCl in ether for ~30 min and then 2,2,2-nitrilotriacetyl chloride (38.0 mg, 0.155 mmol). The solution was stirred for about 15 min and then triethylamine ~8 equiv dissolved in dichloromethane (~8 mL) was added slowly over an hour and the final mixture was stirred for another 30 min. A crude sample analyzed by ^{1}H NMR indicated the formation of $Calix(OMe)_3(OTf)_3[(CH_2CONH)_3N]$. The organic layer was washed with 50 mL of a 3% wt NH_4OH aqueous solution and deionized water (3 × 100 mL) and then dried over $MgSO_4$ and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography (dichloromethane/EtOAc: 50/50) to give pure **6** as a white solid (40 mg, 18% yield). The yield of product in this procedure is essentially the same as described earlier, but isolation is much easier. At this stage, no optimization of the yield of **6** prepared through this approach has been addressed.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.8b02903.

Miscellaneous details of the syntheses and NMR spectra for all compounds, details of the metathesis experiments, and X-ray crystallographic files for the three structures (PDF)

Accession Codes

CCDC 1872314−1872315 and 1872317 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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