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Molybdenum Imido Alkylidene Complexes that Contain a β-Diketiminate Ligand

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The molybdenum β-diketiminate complexes Mo(NR)(CHCMe$_2$R′)(Ar-nacnac)(OTf) (R = 2,6-diisopropylphenyl, 2,6-dimethylphenyl, 1-adamantyl, 2,6-dichlorophenyl, or 2-*tert*-butylphenyl; Ar = 2,6-dichlorophenyl, 2,6-dimethylphenyl, 3,5-dimethylphenyl, or 2,6-difluorophenyl; R′ = Me or Ph; Ar-nacnac = [ArNC(Me)]$_2$CH; OTf = trifluoromethanesulfonate) have been prepared from Mo(NR)(CHCMe$_2$R′)(OTf)$_2$(DME) by metathesis with the corresponding Li{Ar-nacnac} salt. Reaction of Mo(NR)(CHCMe$_2$R′)(Ar-nacnac)(OTf) with NaBAr$_{f4}$ (Ar$_f$ = 3,5-(CF$_3$)$_2$C$_6$H$_3$) in the presence or absence of THF affords the cationic species {Mo(NR)(CHCMe$_2$R′)(Ar-nacnac)(THF)$_n$}{BAr$_{f4}$} (n = 0 or 1) depending on the nature of Ar. The reactivity of the cationic β-diketiminate (nacnac) complexes toward olefins has been examined, as has the thermal decomposition modes of the neutral and cationic nacnac complexes. Results demonstrate that the cationic species have short catalyst lifetimes and that decomposition modes dominate the chemistry of several of the nacnac complexes.

Introduction

The vast majority of high oxidation state Mo and W catalysts that have been developed for the metathesis of alkenes have been neutral species of the type M(NR)(CHR′)(OR″)$_2$ or M(NR)(CHR′)(diolate) in which the initial alkylidene (e.g., neopentylidene), imido group (e.g., 2,6-diisopropylphenylimido), and alkoxides or diolate (e.g., hexafluoro-*tert*-butoxide or 3,3′-di-*tert*-Bu-5,5′,6,6′-tetramethyl-1,1′-biphenyl-2,2′-diolate, respectively) are all relatively sterically demanding.[1] In contrast, *cationic* metathesis catalysts that contain tungsten[2] or molybdenum[3] are rare, especially those in which the anion is relatively noncoordinating. In the case of ruthenium, several catalytically active cationic alkylidene complexes have been published.[4] One might expect the metal center in high oxidation state cationic imido alkylidene complexes to be more electrophilic, although it is difficult to predict whether metathesis turnover would be more or less competitive in cationic species relative to metallacyclobutane rearrangement or bimolecular alkylidene decomposition reactions.

Recently we reported in a preliminary fashion the preparation of cationic imido alkylidene complexes in which a β-diketonate or a β-diketiminate ligand is present and the anion is the relatively poorly coordinating {B[3,5-(CF$_3$)$_2$C$_6$H$_3$]$_4$}$^-$ ({BAr$_{f4}$}$^-$) anion.[5] We showed that while complexes such as {Mo(*N*-2,6-*i*-Pr$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(TMHD)(THF)}{BAr$_{f4}$} (TMHD = 2,2,6,6-tetramethylheptane-3,5-dionato) could be prepared readily, there was little evidence at that time, and little has been gathered since then,[6] that β-diketonate species are active metathesis catalysts. For example, we noted that {Mo(*N*-2,6-*i*-Pr$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(TMHD)(THF)}{BAr$_{f4}$} reacts with ethylene to give cyclopropane, an unusual third pathway for decomposition of early metal high oxidation state catalysts.[7] In contrast, on the basis of preliminary studies, β-diketiminate complexes seemed more promising than β-diketonate complexes. Also, β-diketiminates are now a well-established class of supporting ligands in organotransition metal chemistry.[8,9] Recent Ti and V complexes in which a metal−carbon double or triple bond is present are especially relevant.[10] In this paper we report the preparation of a variety of cationic molybdenum alkylidene complexes that contain a β-diketiminate ligand. The molybdenum compounds described here, which include those described in our initial report, are some of the first examples of Mo nacnac complexes.[11]

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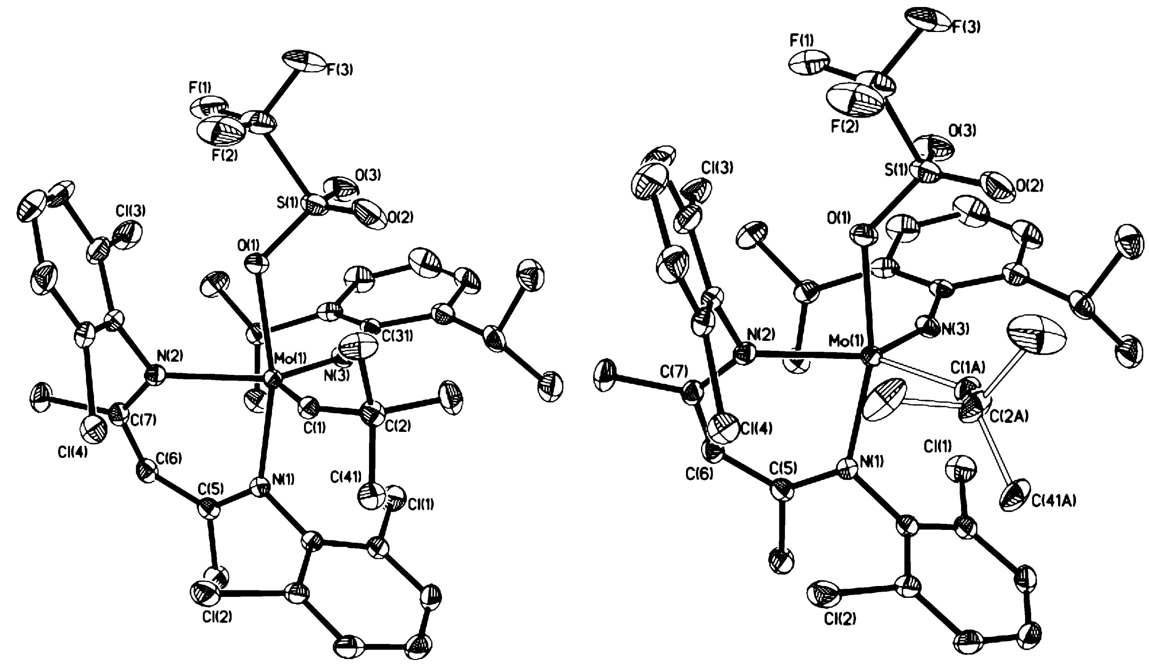

Figure 1. Thermal ellipsoid drawing (35%) of **1a** showing the *syn* (left) and *anti* (right) components of the disordered structure. Hydrogen atoms, cocrystallized diethyl ether, and minor components of disordered atoms are omitted for clarity. The phenyl groups originating on atoms C(41) and C(41A) have also been omitted for clarity. Selected bond distances (Å) and angles (deg): Mo(1)−C(1) = 1.858(3); Mo(1)−N(1) = 2.1266(16); Mo(1)−N(2) = 2.147(16); Mo(1)−N(3) = 1.7356(16); Mo(1)−O(1) = 2.5193 (14); Mo(1)−C(1)−C(2) = 152.6(3); N(3)−Mo(1)−C(1) = 112.02(12); N(2)−Mo(1)−N(1) = 83.91(6); Mo(1)−N(3)−C(31) = 155.6(3); Mo(1)−C(1A) = 2.002(8); Mo(1)−C(1A)−C(2A) = 128.5(7); N(3)−Mo(1)−C(1A) = 93.9(3).

Table 1. Crystal Data and Structure Refinement for 1a, 4a, and 3a″[a]

	1a	4a	3a″
Reciprocal net ident. code	06066	06192	06187
empirical formula	$C_{42}H_{47}Cl_4F_3MoN_3O_{3.5}S$	$C_{80}H_{76}BCl_2F_{24}MoN_3O$	$C_{44}H_{54}F_3MoN_3O_3S$
fw	976.63	1729.09	857.90
cryst syst	monoclinic	triclinic	monoclinic
space group	$P2(1)/n$	$P\bar{1}$	$P2(1)$
unit cell dimens	$a = 11.0969(5)$ Å	$a = 11.4290(4)$ Å	$a = 10.7550(5)$ Å
	$b = 17.9753(8)$ Å	$b = 18.7038(7)$ Å	$b = 17.4054(9)$ Å
	$c = 21.9851(8)$ Å	$c = 19.0217(7)$ Å	$c = 22.5561(12)$ Å
	$\alpha = 90°$	$\alpha = 95.7510(10)°$	$\alpha = 90°$
	$\beta = 92.2900(10)°$	$\beta = 94.0100(10)°$	$\beta = 92.020(2)°$
	$\gamma = 90°$	$\gamma = 101.9670(10)°$	$\gamma = 90°$
volume	4381.9(3) $Å^3$	3940.6(2) $Å^3$	4219.8(4) $Å^3$
Z	4	2	4
density (calcd)	1.480 g/cm^3	1.457 g/cm^3	1.350 g/cm^3
absorp coeff	0.647 mm^{-1}	0.338 mm^{-1}	0.415 mm^{-1}
$F(000)$	2004	1764	1792
cryst size	$0.25 \times 0.20 \times 0.15$ mm^3	$0.35 \times 0.25 \times 0.10$ mm^3	$0.30 \times 0.10 \times 0.08$ mm^3
θ range for data collection	1.85 to 29.57°	1.65 to 29.57°	1.48 to 29.13°
index ranges	$-15 \leq h \leq 15$,	$-15 \leq h \leq 15$,	$-14 \leq h \leq 14$,
	$-24 \leq k \leq 24$,	$-25 \leq k \leq 25$,	$-23 \leq k \leq 23$,
	$-30 \leq l \leq 30$	$-26 \leq l \leq 26$	$0 \leq l \leq 30$
no. of reflns collected	94 631	88 758	26 565
no. of indep reflns	12 298 [R(int) = 0.0629]	22 050 [R(int) = 0.0316]	26 569[b]
completeness to $\theta = 29.57°$	100.0%	99.7%	99.5%
max. and min. transmn	0.9092 and 0.8551	0.9670 and 0.8909	0.9675 and 0.8855
no. of data/restraints/params	12 298/1468/874	22 050/2444/1192	26 569/986/1026
goodness-of-fit on F^2	1.086	1.025	1.009
final R indices [$I > 2\sigma(I)$]	R1 = 0.0374, wR2 = 0.0908	R1 = 0.0407, wR2 = 0.1056	R1 = 0.0389, wR2 = 0.0765
R indices (all data)	R1 = 0.0452, wR2 = 0.0947	R1 = 0.0471, wR2 = 0.1099	R1 = 0.0450, wR2 = 0.0782
largest diff peak and hole	0.847 and 0.489 e·$Å^{-3}$	1.103 and 0.589 e·$Å^{-3}$	0.970 and 0.647 e·$Å^{-3}$

[a] Diffraction data was collected at 100(2) K using Mo Kα radiation with a wavelength of 0.71073 Å. The absorption correction was semiempirical from equivalents, and the refinement method used was full-matrix least-squares on F^2. [b] Compound **3a″** crystallized as a non-meriohedral twin; absolute structure factor = −0.017(15).

Results

Synthesis of Monotriflate and Cationic Nacnac Complexes. The first nacnac ligand we chose to explore was one that contains 2,6-dichlorophenyl substituents (Ar^{Cl}-nacnac).[12] $Mo(NR)(CHCMe_2R')(Ar^{Cl}\text{-nacnac})(OTf)$ (eq 1, **1a**; R = 2,6-i-$Pr_2C_6H_3$, R′ = Ph, OTf = OSO_2CF_3) was prepared by treating $Mo(N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)(CHCMe_2Ph)(OTf)_2(DME)$ with Li{Ar^{Cl}-

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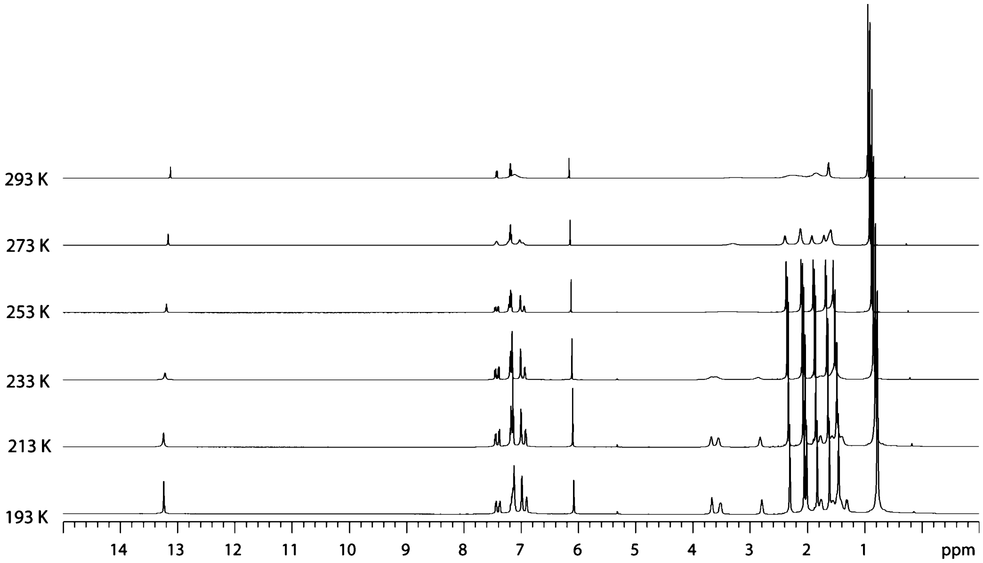
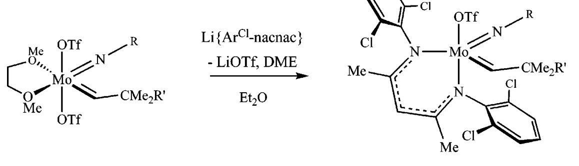


Figure 2. Variable-temperature 500 MHz ^{1}H NMR spectrum of **4c** in methylene chloride-d_2.

nacnac} in diethyl ether and isolated as yellow crystals in 83% yield. ^{1}H NMR spectra in benzene-d_6 at 20 °C indicate that **1a** is a 1:4 mixture of *anti* ($\delta H_\alpha = 15.29$ ppm) to *syn* ($\delta H_\alpha = 12.30$ ppm) isomers. The *syn* resonance was assigned on the basis of the observed J_{CH} value of 116 Hz. A J_{CH} value for the *anti* species could not be determined due to its relatively low concentration. However, chemical shift patterns for *syn* and *anti* isomers follow a similar trend in all of the compounds discussed herein, with *anti* alkylidene resonances being found 1.5−3 ppm downfield of *syn* alkylidene resonances.

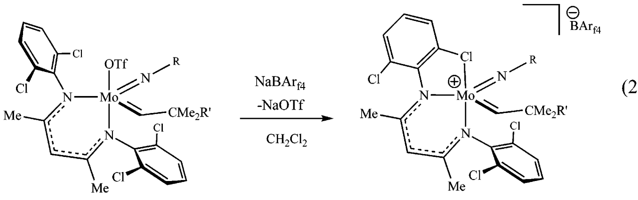


(1)

R = 2,6-*i*-Pr$_2$C$_6$H$_3$, R' = Ph, **1a**
R = 2,6-Me$_2$C$_6$H$_3$, R' = Ph, **1b**
R = 1-adamantyl, R' = Ph, **1c**
R = 2,6-Cl$_2$C$_6$H$_3$, R' = Me, **1d**

The crystal structure of **1a** (Figure 1 and Table 1) shows it to be a distorted trigonal bipyramid in which the alkylidene carbon, imido nitrogen, and one nacnac nitrogen atom lie approximately in the equatorial plane. The structure shows several disordered atoms, all of which were modeled satisfactorily. (See Supporting Information.) The most significant aspect of the disorder is the presence of both *syn* (70%) and *anti* (30%) alkylidene ligands (Figure 1 parts A and B, respectively). The refined occupancies of the *syn* and *anti* components are very similar to the ratios observed spectroscopically in solution. The bond distances and angles are largely in the expected range, with the Mo(1)−N(3)−C(31) angle (155.6(3)°), Mo(1)−C(1)−C(2) angle (152.6(3)°), and Mo(1)−C(1) distance (1.858(3) Å) being characteristic of a *syn* isomer. In contrast, Mo(1)−C(1A) in the *anti* isomer is 2.002(8) Å and Mo(1)−C(1A)−C(2A) is 128.5(7)°. Other bond distances and angles, some of which can be found in the caption to Figure 1, are unexceptional. It should be noted that there is no Mo−Cl interaction in the solid state. Analogous triflate complexes possessing *β*-diketonate ligands demonstrated a tendency to form six-coordinate 18-electron complexes.[6] The nacnac ligand therefore appears better suited to stabilize unsaturated complexes.

The reaction between **1a** and NaBAr$_{f4}$ generated the cationic species, **2a** (eq 2; R = 2,6-*i*-Pr$_2$C$_6$H$_3$, R′ = Ph). ^{1}H NMR spectra in methylene chloride-d_2 indicate that predominantly the *syn* isomer is present ($\delta H_\alpha = 13.10$ ppm, $\delta C_\alpha = 320.0$ ppm, $J_{CH} = 116$ Hz). Variable-temperature spectra from 20 to −90 °C show that the methine protons of the aryl imido become magnetically inequivalent near −40 °C, as do the nacnac methyl protons. (See Supporting Information.) Such inequivalencies are consistent with low-temperature binding of an *ortho* chlorine atom in one of the two 2,6-dichlorophenyl groups to molybdenum, as shown in eq 2.



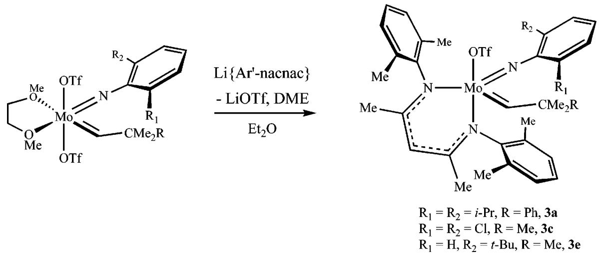
(2)

R = 2,6-*i*-Pr$_2$C$_6$H$_3$, R' = Ph, **2a**
R = 2,6-Me$_2$C$_6$H$_3$, R = Ph, **2b**
R = 1-adamantyl, R' = Ph, **2c**
R = 2,6-Cl$_2$C$_6$H$_3$, R' = Me, **2d**

The structure of **2a**, which has been reported previously, is a distorted trigonal bipyramid in which the alkylidene has the *anti* configuration.[5] The main finding is that an *ortho* chlorine atom is indeed coordinated to the metal in the solid state, consistent with the spectroscopically observed lack of symmetry in the low-temperature limit. We propose that compound **2a** is fluxional on the NMR time scale at higher temperatures as a consequence of rapid dissociation and reassociation of chlorine donors to give an averaged spectrum with apparent C_s symmetry.

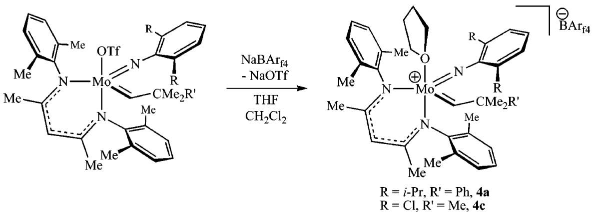
Monotriflate species possessing imido groups other than 2,6-diisopropylphenyl can be prepared in yields that range from 36 to 41% (**1b**−**1d**, eq 1). Subsequent treatment of monotriflates **1b**−**1d** with NaBAr$_{f4}$ as shown in eq 2 yielded salts **2b**−**2d**, for which NMR spectra again suggest that an *ortho* chlorine atom in one Ar^{Cl} group weakly coordinates to the metal at low temperatures. The ^{1}H NMR spectrum of {Mo(*N*-2,6-Me$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(Ar^{Cl}-nacnac)}{BAr$_{f4}$} (**2b**) at −60 °C reveals a major (13.74 ppm 88%) and a minor alkylidene resonance (13.04 ppm, 12%), both consistent with *syn* isomers. The appearance of two isomers at lower temperatures is consistent with formation of diastereomers as a consequence of coordination of the *ortho* chlorine atoms. Similar results were also obtained with {Mo(*N*-1-adamantyl)(CHCMe$_2$Ph)(Ar^{Cl}-nacnac)}{BAr$_{f4}$} (**2d**), which displayed two alkylidene proton resonances at 0 °C at 13.40 and 13.12 ppm in a ratio of 3:5.

We next examined a nacnac ligand possessing 2,6-dimethylphenyl substituents (Ar′-nacnac).[5] Reaction of Li{Ar′-nacnac} with Mo(NR)(CHCMe$_2$R′)(OTf)$_2$(DME) in diethyl ether gives the nacnac complexes shown in eq 3 in 71−79% yield. Complexes **3a**, **3c**, and **3e** are all pentane-insoluble microcrystalline powders that may be crystallized conveniently from diethyl ether. Proton NMR spectra of all three compounds are consistent with the structure depicted in eq 3. In samples of **3a** rotation about the *N*−aryl bond in the diketiminate is slow on the NMR time scale, as judged by sharp singlet resonances for each of the aryl methyl groups. Rotation of the imido aryl ring in **3a** is also hindered, as evidenced by inequivalent methine resonances.



(3)

Cations **4a** and **4c** were prepared in methylene chloride in the presence of several equivalents of THF, as shown in eq 4; isolated yields exceed 85%. Reactions in methylene chloride in the absence of THF led only to unidentifiable decomposition products, although peaks characteristic of CH activation of one of the benzylic methyl groups were observable in several instances (see later). In solution at 20 °C, coordinated THF is observed to exchange rapidly with free THF according to proton NMR spectra of both **4a** and **4c** in methylene chloride-d_2. The alkylidene in each case is the *syn* isomer, as judged by J_{CH} values near 115 Hz for each. Variable-temperature spectra down to −80 °C are consistent with a slowing of various rotational processes, including rotation of the THF ligand, on the NMR time scale (Figure 2).



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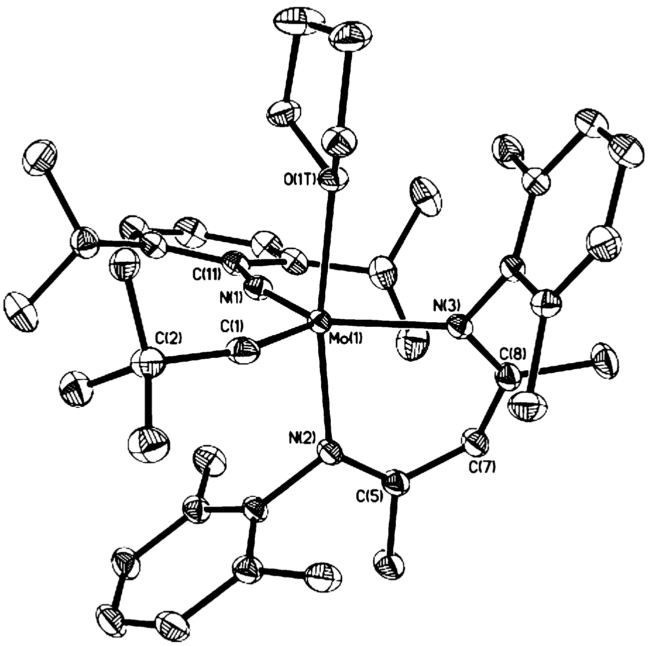
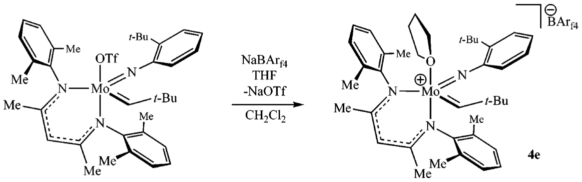


Figure 3. Thermal ellipsoid drawing (50%) of the cation of **4a**. Hydrogen atoms, the phenyl group of the neophylidene, and the cocrystallized molecule of CH$_2$Cl$_2$ are omitted for clarity. Selected bond distances (Å) and angles (deg): Mo(1)−C(1) = 1.909(2); Mo(1)−N(1) = 1.7460(16); Mo(1)−N(2) = 2.1435(16); Mo(1)−N(3) = 2.1220(16); Mo(1)−O(1T) = 2.2417(13); Mo(1)−C(1)−C(2) = 155.26(17); Mo(1)−N(1)−C(11) = 162.68(15); N(1)−Mo(1)−C(1) = 110.49(9); N(2)−Mo(1)−N(3) = 84.99(6).

Crystals of **4a** suitable for X-ray diffraction were grown by slow cooling of a saturated methylene chloride/pentane solution at −25 °C. The solid-state structure is shown in Figure 3, and refinement details are listed in Table 1. The structure of **4a** is consistent with the low-temperature spectral limit observed in solution for both **4a** and **4c**. As in **2a**, the alkylidene, imide, and one nacnac nitrogen atom occupy the equatorial plane of a trigonal bipyramid. The second nacnac nitrogen and the THF molecule bind in axial positions, completing the coordination sphere. All bond lengths and angles (Figure 3 caption) are consistent with other five-coordinate solvent adducts[13] of this type. The Mo(1)−O(1T) bond length of 2.2417(13) Å is consistent with a dative interaction and significantly shorter than the Mo−Cl dative interaction of 2.581(5) Å observed in the solid-state structure of **2a**.[5] The relatively large Mo(1)−C(1)−C(2) and Mo(1)−N(1)−C(11) angles (155.26(17)° and 162.68(15)°, respectively) are characteristic of *syn* alkylidene complexes of this general type.

Triflate abstraction from compound **3e** was found to give an orange crystalline solid after crystallization from methylene chloride/pentane that is believed to be largely the cationic species **4e** (eq 5). However, **4e** decomposes readily in a manner described in a later section below and, therefore, cannot be isolated in pure form.



(5)

The 3,5-dimethylphenyl-substituted nacnac ligand (Ar″-nacnac)[14] was examined next in order to compare it with the Ar′-nacnac ligand. Reaction of Li{Ar″-nacnac} with Mo(*N*-2,6-*i*-Pr$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(OTf)$_2$(DME) in diethyl ether afforded complex **5a** in 75% yield as an orange-red crystalline solid (eq 6). The 2,6-diisopropylphenyl ring in **5a** rotates rapidly at room temperature, while rotation of the 3,5-dimethylphenyl rings is hindered, as judged by broadened resonances for the *o*-H resonances of the 3,5-dimethylphenyl rings. Recrystallized samples of **5a** show predominantly the *syn* isomer (92%; δH_α = 12.12 ppm, J_{CH} = 116 Hz in benzene-d_6).

Addition of NaB(C$_6$F$_5$)$_4$·THF to a methylene chloride-d_2 solution of **5a** produced what is tentatively assigned as the

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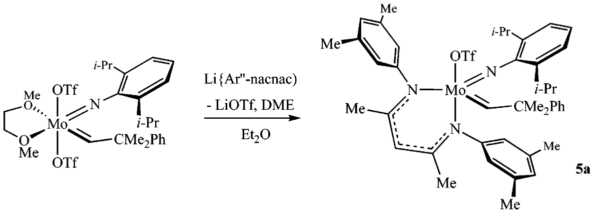
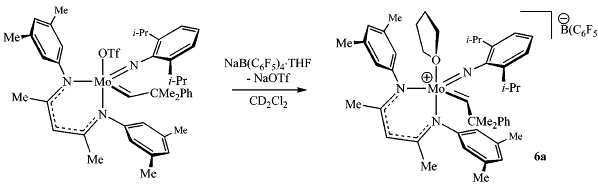
[13] Schrock, R. R.; Crowe, W. E.; Bazan, G. C.; DiMare, M.; O'Regan, M. B.; Schofield, M. H. *Organometallics* **1991**, *10*, 1832.

[14] Laitar, D. S.; Mathison, C. J. N.; Davis, W. M.; Sadighi, J. P. *Inorg. Chem.* **2003**, *42*, 7354.



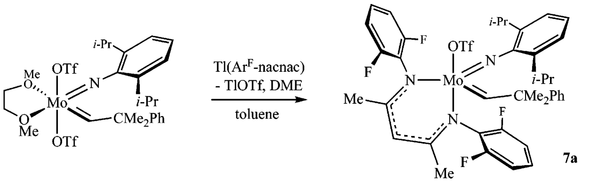
(6)

cationic complex **6a** (eq 7). Complex **6a** exists as a single isomer with an alkylidene resonance at 14.23 ppm. The chemical shift of **6a** is suggestive of an *anti* alkylidene isomer, although definitive evidence (J_{CH} value) could not be gathered. The remainder of the spectrum is broad, and coordinated THF appears to exchange readily with free THF. The 2,6-diisopropylphenyl ring appears to rotate readily on the NMR time scale at 20 °C. Attempts to isolate the BAr_{f4} salt of the cation have resulted in oily, intractable materials, and decomposition of **6a** cannot be ruled out.



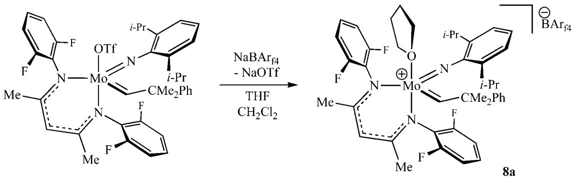
(7)

In analogy with the Ar^{Cl}-nacnac ligand, Ar^{F}-nacnac[15] (Ar^{F} = 2,6-difluorophenyl) was prepared and examined as a potential ligand. In contrast to the nacnac ligands discussed above, salt metathesis reactions similar to those in eq 2 with Li{Ar^{F}-nacnac} did not afford the desired *β*-diketiminate complex; only starting materials were recovered. However, the synthesis of **7a** was accomplished in toluene through use of the thallium complex, Tl(Ar^{F}-nacnac)[15] (eq 8). Compound **7a** is similar to compounds discussed above, and NMR spectra indicate the presence of both *syn* and *anti* isomers in a 1:1.5 ratio, respectively. The alkylidene proton resonance for the *syn* isomer appears at 12.42 ppm with a J_{CH} value of 116 Hz in benzene-d_6. The alkylidene resonance for the *anti* isomer appears at 14.90 ppm (J_{CH} = 145 Hz) and shows a small coupling (J = 1.2 Hz), presumably to fluorine. This small coupling may be indicative of fluorine coordination in the *anti* isomer. No coupling could be resolved for the *syn* isomer.



(8)

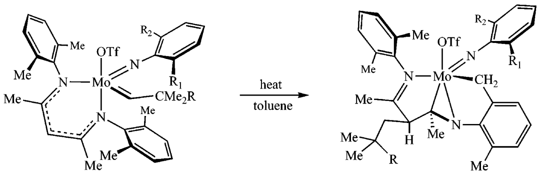
Reaction of **7a** with $NaBAr_{f4}$ in the absence of THF led only to decomposition. We had expected that intramolecular fluorine coordination would be sufficient to stabilize the cation. Either that is not the case, or coordination of an *ortho* fluorine leads to some further decomposition. However, in the presence of THF, a cationic species may be isolated in moderate yield (**8a**, eq 9). The spectroscopic features of **8a** are consistent with the structure shown in eq 9. The 2,6-diisopropylphenyl ring appears to be rotating slowly at 20 °C, as evidenced by distinct broadened methine resonances. The THF ligand displays two multiplet resonances near 2.5 ppm, consistent with free rotation about the Mo–O bond. Unlike compounds **4a** and **4c**, the coordinated THF molecule in **8a** does not appear to exchange readily with free THF on the NMR time scale at 20 °C. The alkylidene proton in the *anti* isomer (~5%) shows a coupling to fluorine of 3.5 Hz; no such coupling is apparent in the *syn* isomer. Compound **8a** has resisted attempts at recrystallization and requires several days to precipitate from concentrated solutions. These results cast some doubt on the proposed structure of **8a** since decomposition may have occurred in the time required for crystallization. As a result of the difficulties in preparing and handling **8a**, no further reactivity was examined.



(9)

Decomposition Reactions. The propensity for nacnac ligands to undergo intramolecular transformations has been demonstrated in a number of different systems across the transition series. Several of the compounds that have been described above decompose in relatively well-defined ways to yield new organometallic species. Some of those decomposition pathways are reported here.

At or above 60 °C, solutions of **3a**, **3c**, and **3e** decompose to yield molybdaziridine species (**3a′′**, **3c′′**, and **3e′′**) shown in eq 10. The nature of these compounds was determined by subjecting **3a′′** to an X-ray diffraction study. Compound **3a′′** crystallizes from diethyl ether with two chemically identical but crystallographically independent molecules in the asymmetric unit. One of the molecules is shown in Figure 4. Metric parameters appear in the caption to Figure 4 and refinement details are listed in Table 1. The most striking feature of **3a′′** is the presence of the neophyl group attached to C(2), which is derived from the original neophylidene ligand in **3a**. One of the CH bonds of the *ortho*-methyl groups has also been activated, resulting in a new metal–carbon bond. The former nacnac ligand is now best described as a chelating η^1/η^2-diimine ligand with an additional bond from the benzylic methyl group. The diimine description is borne out well in the bond lengths and angles (Figure 4 caption and Supporting Information).



$R_1 = R_2 = i$-Pr, R = Ph, **3a''**
$R_1 = R_2 = $ Cl, R = Me, **3c''**
$R_1 = $ H, $R_2 = t$-Bu, R = Me, **3e''**

(10)

The spectroscopic features of **3a′′** are in accord with the solid-state structure. The proton attached to C(2) appears at 4.12 ppm as a triplet with J_{HH} = 4.5 Hz in benzene-d_6. The ^{13}C NMR was assigned with the help of HSQC and HMBC experiments, which located carbon atoms C(1) and C(3) at 197.8 and 82.8 ppm, respectively in benzene-d_6. Mindiola and others have reported benzylic CH activation reactions of aryl-nacnac ligands,[16] but the decomposition mode shown in eq 3 to our

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[15] Dai, X, Ph.D. Thesis, Georgetown University, 2003.

[16] Basuli, F.; Bailey, B. C.; Watson, L. A.; Tomaszewski, J.; Huffman, J. C.; Mindiola, D. J. *Organometallics* **2005**, *24*, 1886.

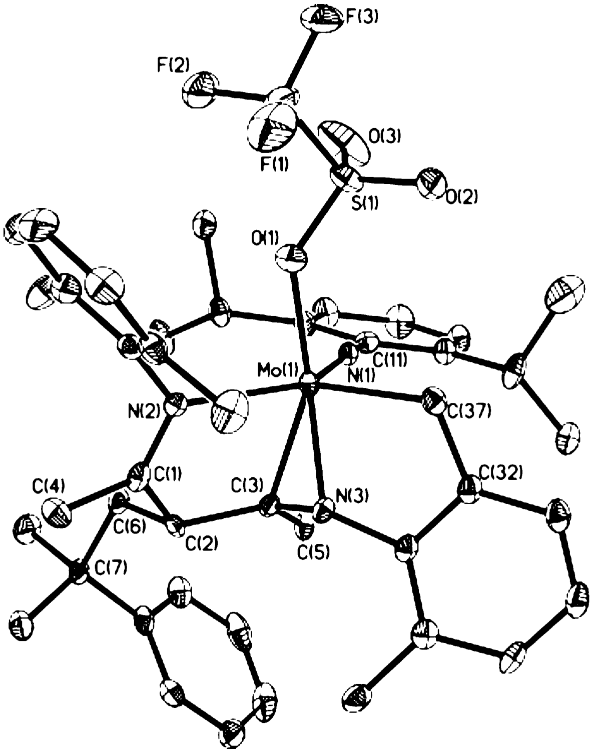
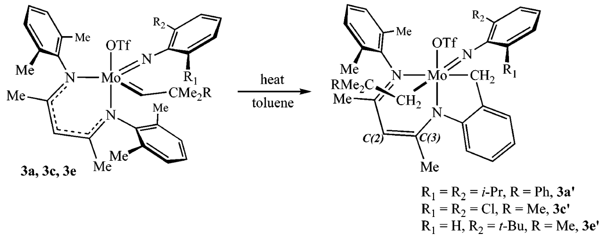


Figure 4. Thermal ellipsoid drawing (50%) of one of the two independent molecules of **3a″** in the asymmetric unit. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Mo(1)−N(1) = 1.723(3); Mo(1)−N(2) = 2.239(3); Mo(1)−N(3) = 1.992(3); Mo(1)−C(37) = 2.165(3); Mo(1)−C(3) = 2.207(3); Mo(1)−O(1) = 2.127(2); C(3)−N(3) = 1.380(4); C(1)−N(2) = 1.285(4); C(1)−C(2) = 1.505(5); N(1)−Mo(1)−C(37) = 97.24(13); N(1)−Mo(1)−N(2) = 136.09(10).

knowledge has not been reported before. The qualitative rate of decomposition in compounds **3a**, **3c**, and **3e** was observed to roughly follow the order **3a** ≈ **3e** > **3c**.

To further examine the thermal decomposition pathway of **3a**, reaction kinetics were followed by ^{1}H NMR. In toluene-d_8, **3a** decomposes in a smooth, first-order manner between 60 and 90 °C through several half-lives with no intermediates being observed (see Supporting Information for kinetic plots). An Eyring plot for the reaction is shown in Figure 5. We propose a mechanism for the reaction that consists of rate-limiting addition of a CH bond from an *ortho* methyl group across the Mo═C bond of the alkylidene ligand. This proton transfer generates a putative dialkyl intermediate of the type shown in eq 11. The neophyl ligand then adds across a C═C bond of the nacnac ligand generating **3a″**. The possibility that addition of the neophyl ligand across the C═C bond of the nacnac ligand occurs in a biomolecular fashion was ruled out by conducting cross-over experiments with **3a** and **3e**. When a benzene-d_6 solution of both compounds was heated to 70 °C, no scrambling of the neophyl/neopentyl ligands between different imides was observed. The only products were **3a″** and **3e″**. Also note that C(6) and the Mo atom are on the same side of the C(2)−C(3) bond, consistent with *cis* addition across the C(2)═C(3) bond shown in eq 11. It is likely that CH addition across the alkylidene ligand is influenced by steric congestion about the coordination sphere of the Mo atom. Not surprisingly, the qualitative trend in decomposition rates observed for **3a**, **3c**, and **3e** roughly parallel the steric properties of the respective imides.

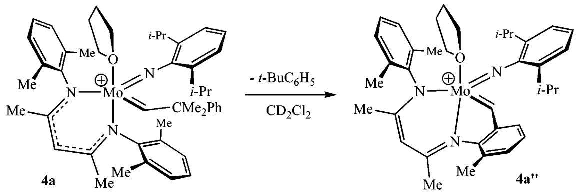


(11)

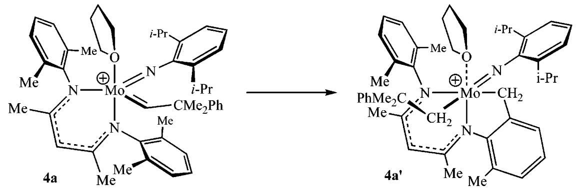
We were somewhat surprised to find that thermolysis of **5a** (lacking *ortho* methyl groups) in benzene-d_6 at 60 °C for 24 h led to decomposition, as judged by ^{1}H NMR spectroscopy. Unfortunately, the nature of the decomposition product is not known at this time, although spectra are consistent with destruction of the alkylidene ligand. Therefore, moving the methyl groups from the 2 and 6 positions of the aryl ring to the 3 and 5 positions does not prevent facile thermal decompositions.

Unlike the monotriflate species possessing 2,6-dimethylphenyl and 3,5-dimethylphenyl nacnac substituents, the complexes bearing 2,6-dichlorophenyl or 2,6-difluorophenyl nacnac substituents appear to be quite stable at elevated temperatures. For example, thermolysis at 70 °C of a benzene-d_6 solution of **7a** for 12 h resulted in no noticeable change by NMR. Similar results were found for **1a**−**1d**.

Cationic species that contain the Ar′-nacnac ligand are also prone to decomposition. For example, solutions of **4a** stored at or even below 20 °C decompose slowly to generate what we propose is **4a″** (eq 12). The intermediate is proposed to be a dialkyl species, **4a′** (eq 13), analogous to **3a′** discussed above. *tert*-Butylbenzene is observed in NMR spectra, consistent with protonation of the original neophylidene ligand. Decomposition of **4a** in methylene chloride-d_2 at 40 °C was found to take place in a first-order manner with $k = 3.23 \times 10^{-4}$ M^{-1} s^{-1}, as determined through ^{1}H NMR studies (see Supporting Information). Unfortunately, **4a″** has resisted attempts at isolation; only oils have been obtained. Although the proposed intermediate, **4a′**, is not observed, its intermediacy is consistent with observation of a related dialkyl species during decomposition of the 2-*tert*-butylphenylimido species described below.



(12)



(13)

It was noted above that compound **4e** (eq 5) could not be isolated cleanly, unlike its 2,6-diisopropylphenylimido analogue, **4a**. Examination of the reaction in ^{1}H NMR experiments demonstrated that **4e** is formed initially, but it decomposes readily over a period of 2−3 h at room temperature to a new complex, **4e′**. The spectroscopic features of **4e′** are consistent with a dialkyl complex on the basis of the appearance of doublet resonances in the ^{1}H NMR spectrum at 4.45 and 2.75 ppm

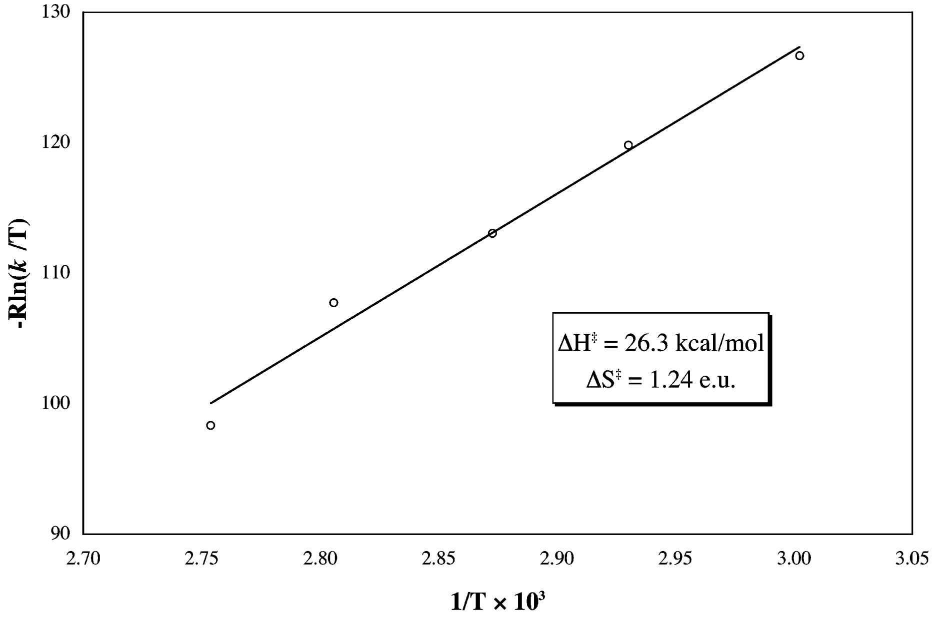
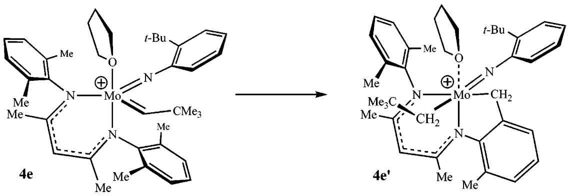


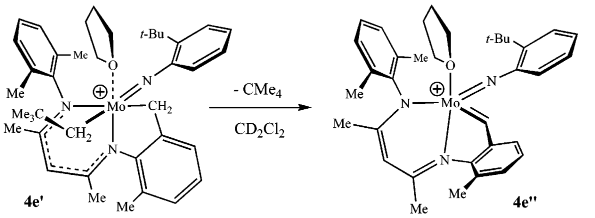
Figure 5. Eyring plot for the thermal reaction of **3a** in toluene-d_8.

(methylene chloride-d_2). One possible structure is shown in eq 14.



(14)

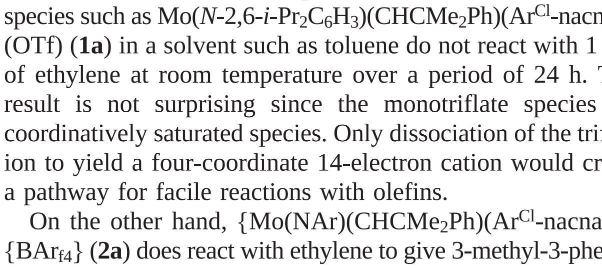
Four methylene proton doublets would be expected for a compound with this structure, although the complexity of the NMR spectrum and the presence of significant quantities of **4e** prevented assignment of all the resonances. Furthermore, **4e′** decomposes at 20 °C to a new alkylidene complex that we propose is **4e″** (eq 15), an analogue of compound **4a″**.



(15)

Compound **4e′** can be observed, unlike **4a′**, since the 2-*tert*-butylphenylimido group is less sterically demanding than the 2,6-diisopropylphenylimido group and the subsequent α-abstraction in **4e′** to yield **4e″** is relatively slow. It is not known whether THF is coordinated strongly to the metal in **4e′** or not, but it should be noted that coordination of THF (and other donor ligands) is known to accelerate α-abstraction reactions in tantalum neopentyl species.[17]

Compound **3a″** was allowed to react with $NaB(C_6F_5)_4 \cdot THF$ in methylene chloride-d_2. Observation of the reaction by ^1H NMR revealed slow conversion ($t_{1/2} \approx 1$ h) to a new species with very similar spectral features to **3a″**. (See Experimental Section.) This species is tentatively assigned as the cationic THF adduct (**3a‴**) shown in eq 16. The THF molecule is bound strongly to Mo in **3a‴**, as evidenced by the absence of rapid exchange with free THF. Compound **3a‴** is quite stable, which rules out the possibility of it being the "dialkyl" intermediate that decomposes to **4a″** (eq 12).



(16)

Reactions of nacnac Complexes with Olefins. Monotriflate species such as $Mo(N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)(CHCMe_2Ph)(Ar^{Cl}\text{-nacnac})(OTf)$ (**1a**) in a solvent such as toluene do not react with 1 atm of ethylene at room temperature over a period of 24 h. This result is not surprising since the monotriflate species are coordinatively saturated species. Only dissociation of the triflate ion to yield a four-coordinate 14-electron cation would create a pathway for facile reactions with olefins.

On the other hand, $\{Mo(NAr)(CHCMe_2Ph)(Ar^{Cl}\text{-nacnac})\}\{BAr_{f4}\}$ (**2a**) does react with ethylene to give 3-methyl-3-phenyl-1-butene, the initial metathesis product. However, it was not possible to identify any product in what appeared to be complex mixtures. Similar results were obtained in reactions between ethylene and **2b**−**d**. All four cationic catalysts (**2a**−**2d**) polymerized 44 equiv of norbornene over a period of ~20 min, affording polynorbornene with various *cis*/*trans* ratios, but no resonances for alkylidene intermediates were observed.

When solutions of **2a**, **2b**, and **2c** in methylene chloride-d_2 were exposed to 19, 25, and 16 equiv of *N*,*N*-diallyltosylamine, respectively, at room temperature for 20 min, 4 equiv of the ring-closed metathesized product was observed. When compound **2d** was mixed with 19 equiv of *N*,*N*-diallyltosylamine at room temperature for 20 min, all 19 equiv was converted to product.

Compound **2a** in methylene chloride-d_2 was exposed to 3 equiv of allyltrimethylsilane for 20 min in the presence of anthracene as the internal standard. A new alkylidene resonance

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[17] (a) Schrock, R. R. In *Reactions of Coordinated Ligands*; Braterman, P. R., Ed.; Plenum: New York, 1986; Vol. 1, pp 221−283. (b) Rupprecht, G. A.; Messerle, L. W.; Fellmann, J. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 6236.

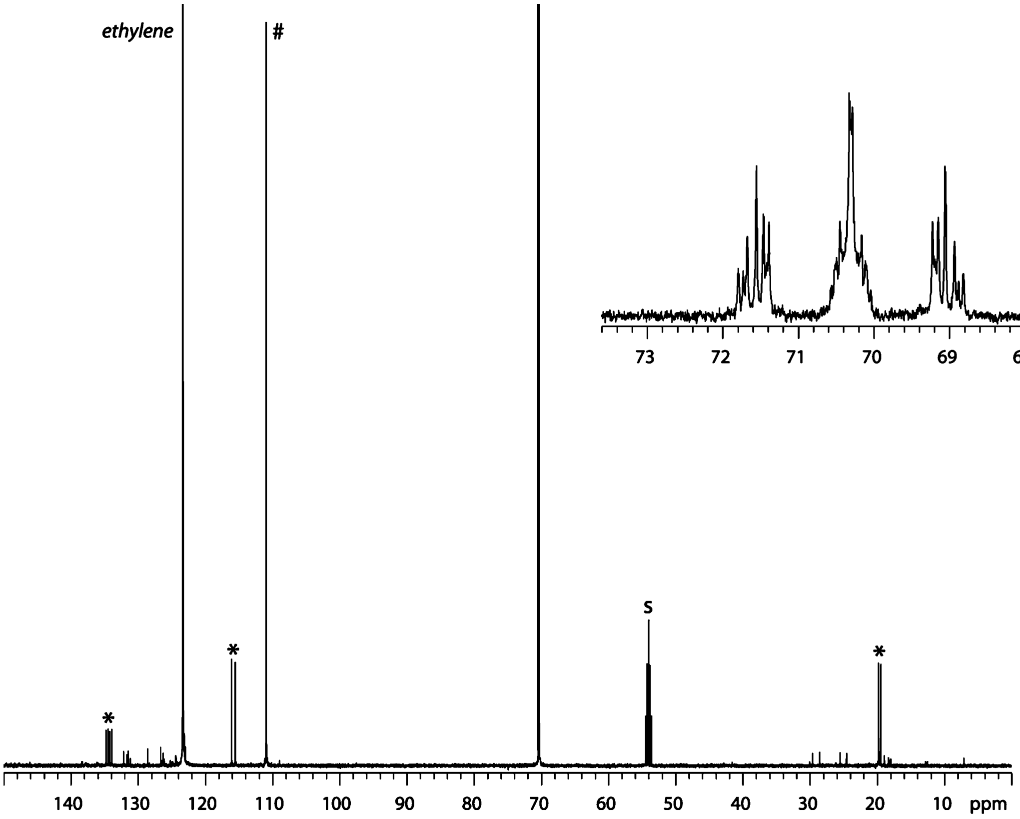
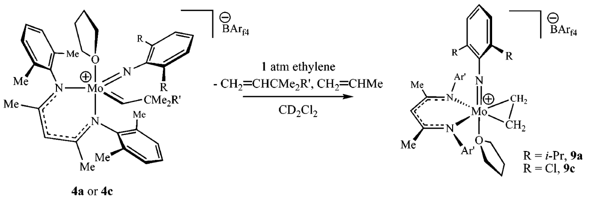


Figure 6. 125 MHz $^{13}C\{^1H\}$ NMR spectrum of the reaction of **4a** with 1 atm of ethylene-^{13}C. The inset shows the region of the spectrum near 70 ppm without ^1H decoupling. s = CD_2Cl_2; # = $^{13}CH_2{=}CHCMe_2Ph$; * = $^{13}CH_2{=}^{13}CH^{13}CH_3$.

was observed at 13.59 ppm, compared to the resonance for **2a** at 13.10 ppm; the ratio was ~1:1. The broad alkylidene resonance for the new species sharpens into a triplet at 13.86 ppm upon addition of THF to the sample. The new compound decomposes over a period of 1−2 h; it could not be isolated nor identified. Related experiments with vinyltrimethylsilane were not successful.

Reactions between compounds **4a** and **4c** and vinyltrimethylsilane, *N*,*N*-diallyltosylamine, and norbornene were explored. Both **4a** and **4c** would polymerize 100 equiv of norbornene in methylene chloride-d_2 in seconds. Reaction of **4a** with vinyltrimethylsilane was slow and no product could be identified. In contrast, vinyltrimethylsilane reacted with **4c** to yield a new species with resonances that we ascribe to *syn* and *anti* isomers of a $Mo{=}CHSiMe_3$ species at 15.35 and 16.47 ppm, respectively. The $Mo{=}CHSiMe_3$ species appeared relatively stable in solution at 20 °C, but no attempt was made to isolate it. Both **4a** and **4c** would ring-close *N*,*N*-diallyltosylamine in 10 min (12% and 33%, respectively), but no additional conversion was observed.

Solutions of **4a** and **4c** in methylene chloride-d_2 were exposed to 1 atm of ethylene gas. Both cations react rapidly to yield what we propose to be ethylene complexes (**9a** and **9c**, eq 17). Resonances for 3-methyl-3-phenylbutene (the initial metathesis product) and propylene are clearly evident in ^1H NMR and ^{13}C NMR spectra. Protons of the ethylene ligand appear as a set of multiplets at 2.57 and 0.86 ppm (in methylene chloride-d_2). Reactions in methylene chloride-d_2 that employ $^{13}CH_2{=}^{13}CH_2$ lead to spectra such as that involving **4a** shown in Figure 6, in which both partially labeled 3-methyl-3-phenylbutene and completely labeled propylene can be observed, along with a carbon resonance for the labeled coordinated ethylene at 70.3 ppm (J_{CH} = 157 Hz). The molecule has mirror symmetry on the NMR time scale. Formation of propylene is consistent with β-hydrogen rearrangement of an intermediate unsubstituted metallacyclobutane complex. Rearrangement of metallacycles and formation of ethylene complexes have been observed before in imido bisalkoxide systems, and two ethylene complexes that result from reactions that involve ethylene have been isolated.[7,18] Unfortunately, attempts to crystallize either **9a** or **9b** resulted only in decomposition.



(17)

Conclusions

Experiments described in the preceding sections lead us to conclude that cationic nacnac complexes can be relatively stable if they contain a neopentylidene or a neophylidene ligand. However, even these species can undergo reactions that involve the nacnac backbone or CH activation in a nacnac nitrogen substituent. Although the initial neopentylidene or neophylidene species can react with olefins in a metathesis-like fashion, it seems clear that several significant problems prevent metathesis activity that we have come to expect from a relatively stable catalyst. Unfortunately, we can only guess at the precise nature of these problems and the reason for them. Certainly, the nacnac ligand itself seems compromised. But whether any problems can be traced to the relatively rigid nature of the nacnac ligand or to its relatively restricted bite angle we cannot say. It is also

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(18) Arndt, S.; Schrock, R. R.; Müller, P. *Organometallics* **2007**, *26*, 1279.

much too early to conclude that the cationic nature of these species itself leads to unstable products and side reactions. In order to explore this issue, we hope to prepare and explore other types of cations, including those that do not contain chelating supporting ligands.

Experimental Section

General Comments. All manipulations were performed in oven-dried (200 °C) glassware under an atmosphere of nitrogen on a dual-manifold Schlenk line or in a Vacuum Atmospheres glovebox. HPLC grade organic solvents were sparged with nitrogen, passed through activated alumina, and stored over 4 Å Linde-type molecular sieves prior to use. Benzene-d_6 and toluene-d_8 were dried over sodium/benzophenone ketyl and vacuum distilled prior to use. Methylene chloride-d_2 and bromobenzene-d_5 were dried over CaH_2 and vacuum distilled prior to use. NMR spectra were recorded on Varian Mercury and Varian INOVA spectrometers operating at 300 and 500 MHz (^{1}H), respectively. Chemical shifts for ^{1}H and ^{13}C spectra were referenced to the residual ^{1}H/^{13}C resonances of the deuterated solvent (^{1}H: C_6D_6, δ 7.16; $C_6D_5CD_3$, δ 2.09; CD_2Cl_2, δ 5.32; C_6D_5Br, δ 7.29; ^{13}C: C_6D_6, δ 128.39; CD_2Cl_2, δ 54.00) and are reported as parts per million relative to tetramethylsilane. ^{19}F NMR spectra were referenced externally to fluorobenzene (δ -113.15 ppm upfield of $CFCl_3$). Elemental analyses were performed by H. Kolbe Microanalytics Laboratory, Mülheim an der Ruhr, Germany.

Materials. $Mo(NR)(CHCMe_2R')(OTf)_2(DME)$ precursors, $NaBAr_{f4}$, Ar′-nacnac, Ar^F-nacnac, Ar″-nacnac, and Ar^{Cl}-nacnac were prepared according to published procedures cited in the text. Lithium salts of the various nacnac ligands were prepared through addition of *n*-BuLi to a pentane solution of the corresponding diketimine. $NaB(C_6F_5)_4 \cdot THF$ was prepared through addition of NaH to a THF solution of $\{HNMe_2Ph\}\{B(C_6F_5)_4\}$ (Strem) followed by crystallization from THF/pentane. TlOAc was purchased from commercial vendors and used as received. All methathesis substrates were prepared and purified according to published procedures. Experimental procedures for compounds **1a**, **2a**, and **3a** were communicated previously in a preliminary fashion[5] and are repeated below for convenience.

Crystallography. 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 ($\lambda = 0.71073$ Å), performing φ- and ω-scans. All structures were solved by direct methods using SHELXS[19] and refined against F^2 on all data by full-matrix least-squares with SHELXL-97.[20] All non-hydrogen atoms were refined anisotropically. Unless described otherwise, all hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms they are linked to (1.5 times for methyl groups). See Supporting Information for a full discussion of each structure.

Mo(*N*-2,6-*i*-Pr$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(Ar^{Cl}-nacnac)(OTf) (1a). A flask containing 2.714 g (3.43 mmol) of $Mo(N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)(CHCMe_2Ph)(OTf)_2(DME)$ and 20 mL of diethyl ether was chilled at −25 °C for 1 h. To the solution was added 1.351 g (3.43 mmol) of Li{Ar^{Cl}-nacnac} as a solid in one portion. The color of the reaction mixture changed from orange to dark red immediately and the mixture was allowed to stir overnight at room temperature. All volatiles were removed *in vacuo*. The remaining red residue was extracted into toluene, and the extract was filtered through a bed of Celite. The volatiles were again removed from the filtrate *in vacuo*. The residue was dissolved in 5 mL of diethyl ether and layered with 10 mL of pentane. The mixture was set aside at −25 °C for 18 h to afford 2.683 g (83%) of fine yellow crystals. The compound was a 7:3 mixture of *syn* to *anti* isomers in solution: ^{1}H NMR (300 MHz, C_6D_6) δ 15.29 (s, 1, *anti* MoCH_α), 12.30 (s, 1, *syn* MoCH_α), *syn isomer only* 7.13 (m, 14, Ar), 5.78 (s, 1, nacnac-C*H*), 5.64 (sep, 1, C*H*Me$_2$), 3.56 (sep, 1, C*H*Me$_2$), 2.67 (s, 3, nacnac-*Me*), 2.40 (s, 3, nacnac-*Me*), 2.31 (s, 3, C*Me*$_2$Ph), 2.19 (d, 3, CH*Me*$_2$), 2.03 (s, 3, C*Me*$_2$Ph), 1.93 (d, 3, CH*Me*$_2$), 1.87 (m, 6, CH*Me*$_2$); ^{13}C NMR (125 MHz, CD_2Cl_2) *both isomers* δ 325.2 (*anti* MoC_α), 304.4 (*syn* MoC_α), 167.5 (*syn* *C*=N), 169.3 (*syn* *C*=N), 169.0 (*anti* *C*=N), 167.0 (*anti* *C*=N), 155.0, 154.0, 151.9, 150.9, 150.8, 150.0, 149.7, 149.1, 148.6, 146.2, 145.1, 144.1, 133.9, 133.1, 132.9, 132.3, 131.9, 131.4, 130.3, 130.0, 129.7, 129.6, 129.4, 129.2, 129.1, 128.8, 128.7, 128.6, 128.5, 128.1, 128.0, 127.9, 127.0, 126.8, 126.5, 126.4, 126.3, 125.8, 123.5, 123.2, 122.9, 122.8, 119.5 (q, $J_{CF} = 319$ Hz, *C*F$_3$), 104.8 (*anti* nacnac-*C*H), 104.7 (*syn* nacnac-*C*H), 57.5 (*anti* *C*Me$_2$Ph), 56.9 (*syn* *C*Me$_2$Ph), 34.4, 33.3, 32.2, 30.8, 28.7, 28.2, 26.7, 25.6, 25.5, 24.9, 24.6, 24.2, 24.0, 23.9, 22.6; ^{19}F NMR (282 MHz) δ −76.6. Anal. Calcd for $C_{40}H_{42}Cl_4F_3MoN_3O_3S$: C, 51.13; H, 4.51; Cl, 15.07; N, 4.47. Found: C, 51.21; H, 4.46; Cl, 15.14; N, 4.37.

Mo(*N*-2,6-Me$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(Ar^{Cl}-nacnac)(OTf) (1b). To a solution of 1.002 g (0.831 mmol) of $Mo(N\text{-}2,6\text{-}Me_2C_6H_3)(CHCMe_2Ph)(OTf)_2(DME)$ in 20 mL of diethyl ether was added 0.390 g (0.831 mmol) of $Li(Et_2O)$\{Ar^{Cl}-nacnac\} as a solid in one portion. The reaction mixture became red and homogeneous after being stirred at room temperature for 2 h. The solution was allowed to stir at room temperature for a further 18 h. All volatiles were removed *in vacuo*, and the remaining red residue was extracted into toluene. The extract was filtered through a bed of Celite, and the volatiles were again removed from the filtrate *in vacuo*. The residue was dissolved in methylene chloride and layered with pentane. The mixture was set aside at −25 °C for 3 days to afford 0.299 g (41%) of the product as orange blocks: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 12.40 (s, 1, *syn* MoCH_α, $J_{CH} = 117$ Hz), 7.45 (d, 1, Ar), 7.40 (d, 1, Ar), 7.28 (m, 4, Ar), 7.17 (m, 2, Ar), 6.93 (t, 2, Ar), 6.84 (br d, 2, Ar), 6.79 (br d, 1, Ar), 6.66 (t, 1, Ar), 5.96 (s, 1, nacnac-C*H*), 2.60 (s, 3, Me), 2.24 (s, 3, Me), 2.22 (s, 3, Me), 2.09 (s, 3, Me) 1.86 (s, 3, Me), 1.49 (s, 3, Me); ^{19}F NMR (282 MHz) δ −77.4. Anal. Calcd for $C_{36}H_{34}Cl_4F_3MoN_3O_3S$: C, 48.94; H, 3.88; Cl, 16.05; N, 4.76. Found: C, 48.78; H, 3.80; Cl, 16.00; N, 4.67.

Mo(*N*-2,6-Cl$_2$C$_6$H$_3$)(CH-*t*-Bu)(Ar^{Cl}-nacnac)(OTf) (1c). To a solution of 0.753 g (0.637 mmol) of $Mo(N\text{-}2,6\text{-}Cl_2C_6H_3)(CH\text{-}t\text{-}Bu)(OTf)_2(DME)$ in 20 mL of diethyl ether was added 0.298 g (0.637 mmol) of $Li(Et_2O)$\{Ar^{Cl}-nacnac\} as a solid in one portion. The reaction mixture immediately became homogeneous and turned deep red. After stirring the mixture for 7 h at room temperature, all volatiles were removed *in vacuo*. The red residue was extracted into toluene, and the extract was filtered through a bed of Celite. The volatiles were again removed from the filtrate *in vacuo*, and the residue was triturated with diethyl ether to give 0.218 g (40%) of the product as a burnt orange powder: ^{1}H NMR (300 MHz, CD_2Cl_2) δ 12.66 (s, 1, MoCH_α, $J_{CH} = 116$ Hz), 7.41 (d, 2, *m*-Ar^{Cl}), 7.19 (m, 5, *m*-Ar^{Cl} + *p*-Ar^{Cl}), 7.28 (m, 4, *m*-Ar^{Cl}), 6.95 (t, 1, *p*-Ar^{Cl}), 6.85 (t, 1, *p*-Ar^{Cl}), 5.94 (s, 1, nacnac-C*H*), 2.06 (s, 3, nacnac-*Me*), 1.93 (s, 3, nacnac-*Me*), 1.23 (s, 9, *t*-Bu); ^{19}F NMR (282 MHz) δ −77.9. Anal. Calcd for $C_{29}H_{26}Cl_6F_3MoN_3O_3S$: C, 40.40; H, 3.04; Cl, 24.67; N, 4.87. Found: C, 40.26; H, 3.72; Cl, 24.36; N, 4.79.

Mo(*N*-1-adamantyl)(CHCMe$_2$Ph)(Ar^{Cl}-nacnac)(OTf) (1d). A flask containing 0.702 g (0.917 mmol) of $Mo(N\text{-}1\text{-}adamantyl)(CHCMe_2Ph)(OTf)_2(DME)$ and 8 mL of diethyl ether was chilled at −25 °C for 1 h. To the solution was added 0.429 g (0.917 mmol) of $Li(Et_2O)$\{Ar^{Cl}-nacnac\} as a solid in one portion. After stirring the mixture at room temperature for 2 h, the cloudy and colorless reaction mixture changed to red and became homogeneous. The reaction was allowed to stir for a further 18 h at room temperature. All volatiles were removed *in vacuo*, and the remaining red residue

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(19) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467.

(20) Sheldrick, G. M. *SHELXL 97*; University of Göttingen: Germany, 1997.

was extracted into toluene. The extract was filtered through a bed of Celite, and the volatiles were again removed from the filtrate *in vacuo*. The residue was dissolved in 2 mL of diethyl ether and layered with 8 mL of pentane. The mixture was set aside at −25 °C for 2 days to afford 0.299 g (36%) of the product as yellow blocks: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 12.95 (s, 1, *syn* MoCH_α, J_{CH} = 115 Hz), 7.27 (m, 11, Ar), 5.94 (s, 1, nacnac-C*H*), 1.91, 1.72, 1.48 (three overlapping broad singlets, 27, adamantyl, CMe_2-Ph + nacnac-*Me*); ^{19}F NMR (282 MHz) δ −79.1. Anal. Calcd for $C_{38}H_{40}Cl_4F_3MoN_3O_3S$: C, 49.96; H, 4.41; Cl, 15.52; N, 4.60. Found: C, 50.08; H, 4.39; Cl, 15.39; N, 4.47.

{Mo(*N*-2,6-*i*-$Pr_2C_6H_3$)(CHCMe_2Ph)(Ar^{Cl}-nacnac)}{BAr_{f4}} (2a). A flask containing 2.033 g (2.16 mmol) of Mo(*N*-2,6-*i*-$Pr_2C_6H_3$)(CHCMe_2Ph)(Ar^{Cl}-nacnac)(OTf) in 25 mL of methylene chloride was chilled in the glovebox freezer to −25 °C for 1 h. To the cold solution was added 1.915 g (2.16 mmol) of NaBAr_{f4} as a solid. The reaction mixture changed from light red to dark red rapidly. After stirring the mixture for 3 h at room temperature it was filtered through a bed of Celite, and the filtrate was concentrated *in vacuo* to give a red oil. Crystallization of the oil from a mixture of methylene chloride and pentane afforded 2.689 g (61%) of the product as red blocks. Crystals suitable for X-ray diffraction were grown by vapor diffusion of pentane into a saturated methylene chloride solution: ^{1}H NMR (300 MHz, CD_2Cl_2) δ 13.11 (s, 1, MoCH_α, J_{CH} = 116 Hz), 7.74 (s, 8, *o*-Ar_f), 7.57 (s, 4, *p*-Ar_f), 7.51 (d, 2, Ar), 7.37 (d, 2, Ar), 7.22 (m, 8, Ar), 6.95 (d, 2, Ar), 6.17 (s, 1, nacnac-C*H*), 3.37 (br sep, 2, C*H*Me_2), 2.19 (s, 6, nacnac-*Me*), 1.29 (s, 6, CMe_2Ph), 1.20 (d, 12, CHMe_2); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 320.0 (MoC_α), 169.4 (2, *C*=N), 162.4 (q, J_{CB} = 50 Hz, *ipso*-Ar_f), 154.3, 147.4, 145.9, 145.5, 144.9, 135.5 (*o*-Ar_f), 132.8, 131.8, 131.5, 131.2, 130.5, 129.3 (q, J_{CF} = 32 Hz, *m*-Ar_f), 128.5, 128.0, 127.7, 126.5, 126.0, 125.5, 125.3 (q, J_{CF} = 272 Hz, *C*F_3), 124.3, 118.1 (m, *p*-Ar_f), 109.9 (nacnac-*C*H), 57.3 (*C*Me_2Ph), 31.2, 28.7, 24.4, 23.6; ^{19}F NMR (282 MHz) δ −62.8. Anal. Calcd for $C_{71}H_{54}BCl_4F_{24}MoN_3$: C, 51.37; H, 3.29; Cl, 8.58; N, 2.54. Found: C, 51.62; H, 3.19; Cl, 8.61; N, 2.47.

{Mo(*N*-2,6-$Me_2C_6H_3$)(CHCMe_2Ph)(Ar^{Cl}-nacnac)}{BAr_{f4}} (2b). A solution of 1.205 g (1.26 mmol) of Mo(*N*-2,6-$Me_2C_6H_3$)(CHCMe_2Ph)(Ar^{Cl}-nacnac)(OTf) in 20 mL of methylene chloride was chilled at −25 °C for an hour, at which point 1.330 g (1.50 mmol) of NaBAr_{f4} was added as a solid in one portion. The reaction mixture changed from yellow to deep orange and LiOTf precipitated immediately. The mixture was stirred at room temperature for 18 h and filtered through a plug of Celite. All volatiles were removed from the filtrate *in vacuo*, and the resulting oil was triturated until solid began to precipitate. The crude solid was purified by precipitation from a mixture of methylene chloride and pentane to afford 0.950 g (43%) of red-brown powder. The compound was a 3:1 mixture of *syn* to *anti* isomers: ^{1}H NMR (300 MHz, CD_2Cl_2) δ 14.85 (br s, 1, *anti* MoCH_α), 13.03 (br s, 1, *syn* MoCH_α), *syn isomer only* 7.73 (s, 8, *o*-Ar_f), 7.56 (s, 4, *p*-Ar_f), 7.31 (m, 14, Ar), 6.07 (s, 1, nacnac-C*H*), 2.42 (br s, 6, Ar′-*Me*), 2.14 (s, 6, nacnac-*Me*), 1.50 (br s, 6, CMe_2Ph); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 322.8 (MoC_α), 168.7 (2, *C*=N), 162.3 (q, J_{CB} = 49 Hz, *ipso*-Ar_f), 145.4, 144.8, 137.7, 135.4 (*o*-Ar_f), 130.7, 129.4 (qq, J_{CF} = 32 Hz, *m*-Ar_f), 128.9, 128.8, 128.4, 127.7, 126.6, 126.3, 124.1, 121.9, 118.1 (m, *p*-Ar_f), 109.5 (nacnac-*C*H), 57.3, 29.2, 23.1, 20.8; ^{19}F NMR (282 MHz) δ −62.8. Anal. Calcd for $C_{67}H_{46}BCl_4F_{24}MoN_3$: C, 50.37; H, 2.90; Cl, 8.88; N, 2.63. Found: C, 50.09; H, 2.96 Cl, 8.78; N, 2.48.

{Mo(*N*-2,6-$Cl_2C_6H_3$)(CH-*t*-Bu)(Ar^{Cl}-nacnac)}{BAr_{f4}} (2c). A solution of 0.767 g (0.889 mmol) of Mo(*N*-2,6-$Cl_2C_6H_3$)(CH-*t*-Bu)(Ar^{Cl}-nacnac)(OTf) (0.767 g, 0.889 mmol) in 20 mL of methylene chloride was chilled at −25 °C for 1 h, at which point 0.788 g (0.889 mmol) of NaBAr_{f4} was added as a solid in one portion. The reaction mixture changed from yellow to deep orange, and LiOTf precipitated immediately. After stirring at room temperature for 24 h, the mixture was filtered through a bed of Celite and all volatiles were removed from the filtrate *in vacuo*. The resulting oil was triturated with pentane until solid appeared. Reprecipitation of the resulting solid from a mixture of methylene chloride and pentane gave 1.218 g (87%) of a red-brown powder: ^{1}H NMR (300 MHz, CD_2Cl_2) δ 15.75 (br s, *anti* MoCH_α), 13.64 (br s, *syn* MoCH_α), *syn isomer only* 7.72 (s, 8, *o*-Ar_f), 7.55 (s, 4, *p*-Ar_f), 7.35 (d, 2, *m*-Ar^{Cl}), 7.43 (br m, 3, Ar), 7.25 (br m, 4, Ar), 6.29 (s, 1, nacnac-C*H*), 2.16 (s, 6, nacnac-*Me*), 1.05 (s, 9, *t*-Bu); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 335.2 (MoC_α), 168.7 (2, *C*=N), 162.4 (q, J_{CB} = 50 Hz, *ipso*-Ar_f), 151.6 (br), 144.4, 135.4 (*o*-Ar_f), 130.7 (br), 130.1, 129.5 (qq, J_{CF} = 32 Hz, *m*-Ar_f), 129.1, 128.7, 125.2 (q, J_{CF} = 272 Hz, *C*F_3), 118.1 (m, *p*-Ar_f), 110.7 (nacnac-*C*H), 51.6 (*C*Me_2Ph), 29.9, 23.1 (*C*Me_3); ^{19}F NMR (282 MHz) δ −62.7. Anal. Calcd for $C_{60}H_{38}BCl_6F_{24}MoN_3$: C, 45.72; H, 2.43; Cl, 13.49; N, 2.67. Found: C, 45.63; H, 2.40; Cl, 13.54; N, 2.56.

{Mo(*N*-1-adamantyl)(CHCMe_2Ph)(Ar^{Cl}-nacnac)}{BAr_{f4}} (2d). A flask containing 0.299 g (0.327 mmol) of Mo(*N*-1-adamantyl)(CHCMe_2Ph)(Ar^{Cl}-nacnac)(OTf) and 6 mL of methylene chloride was chilled at −25 °C for 1 h. To the cold solution was added 0.316 g (0.356 mmol) of NaBAr_{f4} as a solid in one portion. The reaction mixture changed from yellow to red after stirring at room temperature for 2 h. The mixture was allowed to stir for an additional 18 h at room temperature and filtered through a bed of Celite. The filtrate was concentrated *in vacuo* to give a foam. Crystals were obtained from a mixture of methylene chloride and pentane at −25 °C to afford 0.523 g (98%) of the product as a fine yellow powder: ^{1}H NMR (300 MHz, CD_2Cl_2) δ 13.32 (br s, 1, MoCH_α), 7.75 (s, 8, *o*-Ar_f), 7.58 (s, 4, *p*-Ar_f), 7.44 (m, 4, Ar), 7.21 (br m, 11, Ar), 6.07 (br s, 1, nacnac-C*H*), 2.14, 2.06, 1.61 (sharp s overlapping with two br s, 27, adamantly + CMe_2Ph + nacnac-*Me*); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 324.8 (MoC_α), 162.4 (q, J_{CB} = 50.0 Hz, *ipso*-Ar_f), 145.6 (br), 135.5 (*o*-Ar_f), 131.2 (v br), 129.5 (qq, J_{CF} = 32 Hz, *m*-Ar_f), 129.3, 128.9, 127.5, 126.5, 125.2 (q, J_{CF} = 272 Hz, *C*F_3), 109.2 (br, nacnac-*C*H), 118.1 (m, *p*-Ar_f), 78.9 (br, adamantly-N*C*), 55.1 (*C*Me_2Ph), 44.5 (br, adamantly-*C*), 35.8, 30.0, 29.5 (br, adamantly-*C*) 22.9; ^{19}F NMR (282 MHz) δ −65.1. Anal. Calcd for $C_{69}H_{52}BCl_4F_{24}MoN_3$: C, 50.92; H, 3.22; Cl, 8.71; N, 2.58. Found: C, 50.79; H, 3.29; Cl, 8.68; N, 2.48.

Mo(*N*-2,6-*i*-$Pr_2C_6H_3$)(CHCMe_2Ph)(Ar′-nacnac)(OTf) (3a). A flask was charged with 1.650 g (2.08 mmol) of Mo(*N*-2,6-*i*-$Pr_2C_6H_3$)(CHCMe_2Ph)$(OTf)_2$(DME) and 40 mL of diethyl ether. The mixture was chilled briefly at −25 °C before 0.656 g (2.10 mmol) of Li{Ar′-nacnac} was added as a solid in one portion. The mixture was allowed to stir at room temperature for 20 h, during which time it became homogeneous and turned orange-yellow. All volatiles were removed *in vacuo*, and the residue was extracted with 30 mL of toluene. The extract was filtered through a plug of Celite and evaporated to dryness. The residue was dissolved in a minimal amount of diethyl ether and set aside at −25 °C overnight to yield 1.413 g (79%) of orange needles: ^{1}H NMR (500 MHz, C_6D_6) δ 11.56 (s, 1, MoCH_α, J_{CH} = 118 Hz), 7.25 (d, 2, *o*-CMe_2*Ph*), 7.14 (t, 2, *m*-CMe_2*Ph*), 7.12 (br t, 1, *p*-Ar′), 7.06 (t, 1, *p*-CMe_2*Ph*), 7.04 (br d, 2, *m*-*N*-2,6-*i*-$Pr_2C_6H_3$), 6.93 (br d, 1, *m*-Ar′), 6.82 (t, 1, *p*-*N*-2,6-*i*-$Pr_2C_6H_3$), 6.74 (br d, 1, *m*-Ar′), 6.61 (br d, 1 *m*-Ar′), 6.54 (br m, 2, *m*/*p*-Ar′), 5.39 (s, 1, nacnac-C*H*), 4.94 (sep, 1, C*H*Me_2), 2.75 (sep, 1, C*H*Me_2), 2.35 (s, 3, Me), 2.21 (s, 3, Me), 2.15 (s, 3, Me), 1.81 (s, 3, Me), 1.77 (s, 3, Me), 1.65 (s, 3, Me), 1.60 (d, 3, CHMe_2), 1.59 (s, 3, Me), 1.34 (m, 6, Me + CHMe_2), 1.20 (d, 3, CHMe_2), 1.14 (d, 3, CHMe_2); ^{13}C NMR (125 MHz, CD_2Cl_2) *many peaks broad* δ 299.1 (MoC_α), 167.7 (2, *C*=N), 153.5, 153.3, 149.9, 148.4, 147.8, 145.5, 133.6, 132.5, 131.9, 131.3, 129.6, 129.3, 128.9, 128.8 128.7, 126.7, 126.4, 126.3, 125.8, 123.5, 122.9, 119.5 (q, J_{CF} = 319 Hz, *C*F_3), 104.8 (nacnac-*C*H), 56.7 (*C*Me_2Ph), 33.6, 32.1, 28.1, 26.4, 25.5, 25.3 (nacnac-*Me*), 24.3 (nacnac-*Me*), 23.9, 20.2, 19.2; ^{19}F NMR (282 MHz) δ −76.1. Anal. Calcd for $C_{44}H_{54}F_3MoN_3O_3S$: C, 61.60; H, 6.34; N, 4.90. Found: C, 61.72; H, 6.46; N, 4.81.

Mo(*N*-2,6-$Cl_2C_6H_3$)(CH-*t*-Bu)(Ar′-nacnac)(OTf) (3c). A flask was charged with 0.714 g (1.00 mmol) of Mo(*N*-2,6-$Cl_2C_6H_3$)(CH-*t*-Bu)$(OTf)_2$(DME) and 20 mL of diethyl ether. Li{Ar′-nacnac} (0.319 g, 1.02 mmol) was added to the solution as a solid in one portion. The reaction was stirred at room temperature for 18 h. All volatiles were removed *in vacuo*, and the residue extracted into a 4:1 mixture of toluene and methylene chloride. The mixture was filtered through a bed of Celite and the solution volume concentrated to ∼3 mL *in vacuo*. Several volumes of pentane were added until a wine-red precipitate formed. The mixture was set aside at −25 °C for 30 min. The solid was collected by filtration and washed with pentane to yield 0.595 g (71%) of a deep red microcrystalline powder: ^{1}H NMR (500 MHz, C_6D_6) δ 11.93 (s, 1, MoC*H*$_\alpha$, $J_{CH} = 115$ Hz), 7.12 (d, 1, *m*-Ar′), 7.04 (t, 1, *p*-Ar′), 7.01 (d, 1, *m*-Ar′), 6.79 (d, 1, *m*-Ar′), 6.64 (t, 1, *p*-Ar′), 6.56 (m, 3, *m*-Ar′ + *m*-2,6-$Cl_2C_6H_3$), 6.10 (t, 1, *p*-2,6-$Cl_2C_6H_3$), 5.47 (s, 1, nacnac-C*H*), 2.44 (s, 3, Me), 2.31 (s, 3, Me), 2.13 (s, 3, Me), 1.91 (s, 3, Me), 1.58 (s, 3, nacnac-*Me*), 1.51 (s, 9, *t*-Bu), 1.45 (s, 3, nacnac-*Me*); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 311.9 (MoC$_\alpha$), 167.4 (*C*═N), 166.8 (*C*═N), 153.8, 149.6, 147.7, 140.0, 134.3, 131.8, 131.6, 130.1, 129.6, 128.9, 128.5, 128.4, 128.2, 126.9, 126.5, 125.7, 119.4 (q, $J_{CF} = 319$ Hz, CF_3), 104.6 (nacnac-*C*H), 50.4 (*C*Me$_3$), 30.7 (C*Me*$_3$), 25.8, 23.7, 21.5, 20.9, 19.6, 18.8; ^{19}F NMR (282 MHz) δ −77.2. Anal. Calcd for $C_{33}H_{38}Cl_2F_3MoN_3O_3S$: C, 50.78; H, 4.91; N, 5.38. Found: C, 52.06, 53.98; H, 5.10, 4.71; N, 5.15, 5.06. The variable and incorrect analytical results are due to residual toluene (∼5% by NMR), which could not be removed *in vacuo* at room temperature, and higher temperatures would risk decomposition.

Mo(*N*-2-*t*-BuC_6H_4)(CH-*t*-Bu)(Ar′-nacnac)(OTf) (3e). A flask was charged with 0.792 g (1.13 mmol) of Mo(*N*-2-*t*-BuC_6H_4)(CH-*t*-Bu)$(OTf)_2$(DME) and 35 mL of diethyl ether. To this stirring solution was added 0.390 g (1.25 mmol) of Li{Ar′-nacnac} as a solid in one portion. The mixture was stirred at room temperature for 2 h, during which time it became homogeneous and turned yellow-brown. All volatiles were removed *in vacuo*, and the residue was extracted into 30 mL of toluene. The solution was filtered through Celite, and the solvents were removed *in vacuo*. The residue was dissolved in a minimal amount of diethyl ether and set aside at −25 °C for 24 h, during which time the compound precipitated as an orange, microcrystalline solid (0.693 g; 74%): ^{1}H NMR (500 MHz, C_6D_6) δ 11.43 (s, 1, MoC*H*$_\alpha$, $J_{CH} = 116$ Hz), 8.18 (v br, 1, *o*-2-*t*-BuC$_6$*H*$_4$), 7.09 (t, 1, Ar), 7.03 (m, 3, Ar), 6.90 (t, 1, Ar), 6.76 (t, 1, Ar), 6.65 (m, 3, Ar), 5.36 (s, 1, nacnac-C*H*), 2.39 (s, 3, Me), 2.18 (s, 6, Me), 1.58 (s, 3, Me), 1.42 (s, 3, Me), 1.37 (s, 9, *t*-Bu), 1.35 (s, 9, *t*-Bu); ^{13}C NMR (125 MHz, CD_2Cl_2) *many peaks broad* δ 310.3 (MoC$_\alpha$), 167.7 (*C*═N), 167.4 (*C*═N), 154.6, 154.2, 147.9, 132.9, 132.8, 132.5, 131.5, 129.5, 129.4, 129.3, 129.2, 129.1, 128.4, 128.3, 126.0, 125.7, 119.5 (q, $J_{CF} = 319$ Hz, CF_3), 104.5 (nacnac-*C*H), 51.3 (*C*Me$_3$), 36.70, 32.70, 30.73, 25.49, 24.43, 20.79, 20.69, 20.05, 19.46; ^{19}F NMR (282 MHz) δ −77.2. Anal. Calcd for $C_{37}H_{48}F_3MoN_3O_3S$: C, 57.88; H, 6.30; N, 5.47. Found: C, 57.89; H, 6.39; N, 5.41.

{Mo(*N*-2,6-*i*-$Pr_2C_6H_3$)($CHCMe_2Ph$)(Ar′-nacnac)(THF)}{BAr$_{f4}$} (4a). A flask was charged with 0.502 g (0.585 mmol) of Mo(*N*-2,6-*i*-$Pr_2C_6H_3$)($CHCMe_2Ph$)(Ar′-nacnac)(OTf), 1 mL of THF, and 25 mL of methylene chloride. The solution was cooled to −25 °C, and 0.513 g (0.592 mmol) of solid NaBAr$_{f4}$ was added in one portion. The mixture was stirred at room temperature for 5 min. All volatiles were removed *in vacuo*. The residue was extracted with methylene chloride, and the mixture was filtered through Celite. The extract's volume was reduced to ∼5 mL *in vacuo*, and the solution was layered with several volumes of pentane. The product crystallized at −25 °C as an orange microcrystalline solid; yield 0.887 g (92%). Crystals suitable for X-ray diffraction were grown by slowly cooling a saturated solution of methylene chloride and pentane at −25 °C: ^{1}H NMR (238 K, 500 MHz, CD_2Cl_2) δ 12.18 (s, 1 MoC*H*$_\alpha$, $J_{CH} = 116$ Hz), 7.75 (s, 8, *o*-Ar$_f$), 7.58 (s, 4, *p*-Ar$_f$), 7.28 (d, 2 Ar), 7.19 (br m, 4 Ar), 7.03 (br d, 1 Ar), 5.91 (br s, 1 nacnac-C*H*), 4.75 (br m, 1 C*H*Me$_2$), 3.5 (v br, 4 OC*H*$_2$), 2.71 (br m, 1 C*H*Me$_2$), 2.33 (s, 3 Me), 2.13 (s, 3 Me), 1.95 (s, 3 Me), 1.89 (s, 3 Me), 1.82 (s, 3 Me), 1.73 (s, 3 Me), 1.52 (s, 3 Me), 1.44 (br s, 3 Me), 1.29 (br m, 12 CH*Me*$_2$), 0.95 (s, 3 Me); ^{13}C NMR (238 K, 125 MHz, CD_2Cl_2) δ 317.6 (MoC$_\alpha$), 168.9 (*C*N), 167.4 (*C*N), 161.9 (q, $J_{CB} = 49.6$ Hz, *ipso*-Ar$_f$), 154.3, 153.9, 148.0, 147.1, 143.9, 143.1, 135.1, 134.9 (*o*-Ar$_f$), 132.7, 131.1, 131.0, 130.4, 129.7, 129.5, 129.4, 129.1, 128.9 (qq, $J_{CF} = 31.3$ Hz, *m*-Ar$_f$), 127.8, 127.4, 126.7, 125.9, 124.7 (q, $J_{CF} = 272$ Hz, *C*F$_3$), 124.6, 124.5, 117.7 (m, *p*-Ar$_f$), 105.7 (nacnac-*C*H), 80.2 (O*C*H$_2$), 79.3 (O*C*H$_2$), 56.6 (*C*Me$_2$Ph), 31.3, 29.7, 28.2, 27.3, 26.5, 25.5, 25.3, 25.2, 25.1, 25.0, 23.8, 19.6, 19.4, 19.3, 18.8; ^{19}F NMR (293 K, 472 MHz) δ −62.4. Anal. Calcd for $C_{79}H_{74}BF_{24}MoN_3O$: C, 57.71; H, 4.54; N, 2.53. Found: C, 57.48; H, 4.68; N, 2.45.

{Mo(*N*-2,6-$Cl_2C_6H_3$)($CHCMe_3$)(Ar′-nacnac)(THF)}{BAr$_{f4}$} (4c). A flask was charged with 0.183 g (0.235 mmol) of Mo(*N*-2,6-$Cl_2C_6H_3$)(CH-*t*-Bu)(Ar′-nacnac)(OTf), 1 mL of THF, and 20 mL of methylene chloride. The solution was cooled to −25 °C, and NaBAr$_{f4}$ (0.255 g, 0.257 mmol) was added as a solid in one portion. The mixture was allowed to stir at room temperature for 10 min. All volatiles were removed *in vacuo*. The residue was extracted into methylene chloride, and the extract was filtered through Celite. The solvent volume was reduced to ∼2 mL *in vacuo* and layered with several volumes of pentane. The mixture was set aside at −25 °C for 2 days to afford 0.322 g (87%) of red crystals: ^{1}H NMR (300 MHz, CD_2Cl_2) δ 13.11 (s, 1, MoC*H*$_\alpha$, $J_{CH} = 116$ Hz), 7.72 (s, 8, *o*-Ar$_f$), 7.56 (s, 4, *p*-Ar$_f$), 7.41 (d, 2, *m*-Ar^{Cl}), 7.16 (t, 1, *p*-Ar^{Cl}), 7.11 (br, 6, Ar′), 6.15 (s, 1, nacnac-C*H*), 3.1 (v br, 4, OC*H*$_2$), 2.26 (br, 6, Me), 1.84 (br m, 12, Me), 1.62 (m, 4, OCH$_2$C*H*$_2$), 0.94 (s, 9, *t*-Bu); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 332.8 (MoC$_\alpha$), 168 (v br, *C*═N), 162.4 (q, $J_{CB} = 49.9$ Hz, *ipso*-Ar$_f$), 151.4 (*ipso*-Ar^{Cl}), 135.4 (*m*-Ar$_f$), 130.3 (*m*-Ar^{Cl}), 130.2 (*o*-Ar^{Cl}), 130.1 (*p*-Ar^{Cl}), 129.5 (q, $J_{CF} = 32.5$ Hz, *m*-Ar$_f$), 129.1 (br, Ar′), 128.0 (br, Ar′), 125.2 (q, $J_{CF} = 271$ Hz, *C*F$_3$), 118.0 (sep, $J_{CF} = 3.8$ Hz, *p*-Ar$_f$), 106.9 (nacnac-*C*H), 80.6 (br, O*C*H$_2$CH$_2$), 51.8 (*C*Me$_3$), 31.4 (C*Me*$_3$), 26.1, 25.2, 19.5; ^{19}F NMR (282 MHz) δ −63.3. Anal. Calcd for $C_{68}H_{58}BCl_2F_{24}MoN_3O$: C, 52.13; H, 3.73; N, 2.68. Found: C, 52.19; H, 3.80; N, 2.64.

{Mo(*N*-2-*t*-BuC_6H_4)(CH-*t*-Bu)(Ar′-nacnac)(THF)}{BAr$_{f4}$} (4e). Compound **4e** was prepared in analogous fashion to that used to prepare **4a** and **4c**, starting from 0.155 g (0.20 mmol) of Mo(*N*-2-*t*-BuC_6H_4)(CH-*t*-Bu)(Ar′-nacnac)(OTf) and 0.192 g (0.22 mmol) of NaBAr$_{f4}$. Upon recrystallization from a mixture of methylene chloride and pentane, 0.279 g of a bright orange powder was obtained. NMR spectra showed the compound to be a mixture of two compounds, **4e** and **4e′**, as well as a mixture of *syn* and *anti* isomers of **4e**: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 14.52 (s, *anti* MoC*H*$_\alpha$), 11.85 (v br s, *syn* MoC*H*$_\alpha$), 11.08 (v br s, *syn* MoC*H*$_\alpha$), 7.75 (s, *o*-Ar$_f$), 7.60 (s, *p*-Ar$_f$), 7.2 (v br m, Ar), 6.15 (s, *anti* nacnac-C*H*), 6.0 (v br s, *syn* nacnac-C*H*), 3.6 (v br m, THF), 2.60 (s, Me), 2.30 (br s, Me), 2.10 (br m, Me), 1.90 (s, *t*-Bu), 1.83 (br s, Me), 1.75 (br m, THF), 1.65 (s, *t*-Bu), 1.56 (s, *t*-Bu), 1.1 (br, Me).

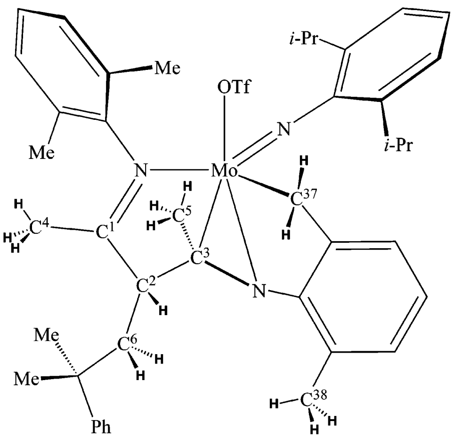
Mo(*N*-2,6-*i*-$Pr_2C_6H_3$)($CHCMe_2Ph$)(Ar″-nacnac)(OTf) (5a). A flask was charged with 1.190 g (1.50 mmol) of Mo(*N*-2,6-*i*-$Pr_2C_6H_3$)($CHCMe_2Ph$)$(OTf)_2$(DME) and 25 mL of diethyl ether. The solution was chilled to −25 °C, and Li{Ar″-nacnac} (0.473 g; 1.51 mmol) was added as a solid in one portion. The mixture was allowed to stir at room temperature for 2 h, during which time the color darkened from yellow to yellow-brown. All volatiles were removed *in vacuo* and the residue extracted into 20 mL of toluene. The extract was filtered through Celite and evaporated to dryness *in vacuo*. The resulting solid was recrystallized from a minimal amount of diethyl ether to yield an orange-red crystalline solid (0.970 g, 75%). The compound was found to exist as a 15:1 mixture of *syn* and *anti* isomers: ^{1}H NMR (300 MHz, C_6D_6) δ 14.30 (s, 1, *anti* MoC*H*$_\alpha$), 12.12 (s, 1, *syn* MoC*H*$_\alpha$, $J_{CH} = 117$ Hz), *syn isomer* *only* 7.35 (d, 2, *o*-CMe$_2$*Ph*), 7.17 (t, 2, *m*-CMe$_2$*Ph*), 7.05 (t, 1, *p*-CMe$_2$*Ph*), 6.94 (br s, 2, *o*-Ar″), 6.81 (m, 3, *m*/*p*-*N*-2,6-*i*-Pr$_2$C$_6$*H*$_3$), 6.74 (s, 1, *p*-Ar″), 6.26 (s, 1, *p*-Ar″), 5.91 (br s, 2, *o*-Ar″), 5.28 (s, 1, nacnac-C*H*), 3.56 (sep, 2, C*H*Me$_2$), 2.30 (s, 3, Me), 2.27 (s, 6, Ar″-*Me*), 1.87 (br s, 6, Ar″-*Me*), 1.77 (s, 3, Me), 1.70 (s, 3, Me), 1.47 (s, 3, Me), 1.34 (d, 6, CH*Me*$_2$), 1.04 (d, 6, CH*Me*$_2$); ^{13}C NMR (125 MHz, C$_6$D$_6$) δ 297.8 (MoC$_\alpha$), 167.1 (*C*=N), 165.4 (*C*=N), 154.5, 152.2, 149.4, 149.0, 147.6 (br), 138.6 (br), 129.1, 128.9, 127.3, 126.9, 126.6, 126.1 (br), 123.0, 122.2 (br), 120.7 (q, *C*F$_3$, J_{CF} = 319 Hz), 104.8 (nacnac-*C*H), 55.3 (*C*Me$_2$Ph), 32.6 (br), 31.0, 27.9, 24.7 (br m), 24.1, 21.6 (br); ^{19}F NMR (282 MHz) δ −76.7. Anal. Calcd for $C_{44}H_{54}F_3MoN_3O_3S$: C, 61.60; H, 6.34; N, 4.90. Found: C, 61.54; H, 6.31; N, 4.86.

Tl(Ar^F-nacnac). A flask was charged with 0.519 g (1.58 mmol) of Li{Ar^F-nacnac} and 25 mL of tetrahydrofuran. To the solution was added 0.415 g (1.58 mmol) of Tl(OAc) as a solid in one portion. The mixture was allowed to stir in the dark for 24 h at room temperature. All volatiles were removed *in vacuo*, and the residue was extracted into diethyl ether. The solution was filtered through Celite, and the solvent volume was reduced to ∼7 mL *in vacuo*. The solution was set aside at −25 °C for several days to afford the product as a yellow solid, which was isolated by filtration and dried *in vacuo*; yield 0.515 g (62%): ^{1}H NMR (300 MHz, C$_6$D$_6$) δ 6.67 (m, 4, *m*-Ar^F), 6.49 (m, 2, *o*-Ar^F), 4.92 (br s, 1, nacnac-C*H*), 1.90 (s, 6, Me); ^{19}F NMR (282 MHz) δ 121.3 (d, J_{TlF} = 753 Hz, Ar^F). Spectroscopic features were consistent with previously reported values.[15]

Mo(*N*-2,6-*i*-Pr$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(Ar^F-nacnac)(OTf) (7a). A flask was charged with 0.724 g (0.913 mmol) of Mo(*N*-2,6-*i*-Pr$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(OTf)$_2$(DME) and 25 mL of toluene. To the solution was added 0.482 g (0.916 mmol) of solid Tl(Ar^F-nacnac) in one portion. The mixture was allowed to stir at room temperature for 40 h in the dark. All volatiles were removed *in vacuo*, and the residue was extracted into 25 mL of toluene. The extract was filtered through a pad of Celite and evaporated to dryness. The residue was then dissolved in a minimal amount of diethyl ether and set aside at −25 °C. The product precipitated in two crops of yellow microcrystals that exist as a 1:1.5 mixture of *syn* to *anti* isomers in solution; yield 0.630 g (79%): ^{1}H NMR (300 MHz, C$_6$D$_6$) δ 14.90 (s, 1, *anti* MoC*H*$_\alpha$, J_{CH} = 145 Hz), 12.42 (s, 1, *syn* MoC*H*$_\alpha$, J_{CH} = 117 Hz), 7.42 (d, 2, *anti o*-CMe$_2$*Ph*), 7.35 (d, 2, *syn o*-CMe$_2$*Ph*), 7.18 (t, 2, *anti m*-CMe$_2$*Ph*), 7.16 (t, 2, *syn m*-CMe$_2$Ph), 7.07 (t, 1, *syn p*-CMe$_2$*Ph*), 7.05 (t, 1, *p*-CMe$_2$*Ph*), 6.91 − 6.58 (m, 13, *syn*/*anti* Ar^F + *m*/*p*-2,6-*i*-Pr$_2$C$_6$*H*$_3$), 6.26 (m, 2, *syn* Ar^F), 6.00 (m, 3, *anti* Ar^F), 5.15 (s, 1, *syn* nacnac-C*H*), 5.14 (s, 1, *anti* nacnac-C*H*), 4.08 (br m, 1, *anti* C*H*Me$_2$), 3.81 (sep, 2, *syn* C*H*Me$_2$), 3.37 (br m, 1, *anti* C*H*Me$_2$), 2.12 (s, 3, *anti* Me), 2.01 (s, 3, *syn* Me), 1.90 (s, 3, *syn* Me), 1.88 (s, 3, *anti* Me), 1.70 (br, 3, *anti* CH*Me*$_2$), 1.64 (s, 3, *anti* Me), 1.42 (d, 6, *syn* CH*Me*$_2$), 1.41 (s, 3, *syn* Me), 1.40 (br, 3, *anti* CH*Me*$_2$), 1.39 (s, 3, *anti* Me), 1.34 (d, 6, *syn* CH*Me*$_2$), 1.21 (br, 6, *anti* CH*Me*$_2$); ^{13}C NMR (125 MHz, C$_6$D$_6$) *selected peaks only* δ 322.8 (*anti* MoC$_\alpha$), 303.1 (*syn* MoC$_\alpha$), 169.8 (*syn C*=N), 169.5 (*anti C*=N), 169.0 (*syn C*=N), 167.2 (*anti C*=N), 104.7 (*syn* nacnac-*C*H), 103.7 (*anti* nacnac-*C*H), 56.8 (*syn C*Me$_2$Ph), 54.9 (*anti C*Me$_2$Ph); ^{19}F NMR (282 MHz) δ −76.7 (C*F*$_3$), −114.3 (*anti* Ar*F*), −114.5 (*syn* Ar*F*), −116.2 (*anti* Ar*F*), −117.5 (2, *syn* Ar*F*), −118.4 (*syn* Ar*F*), −119.7 (*anti* Ar*F*), −120.1 (*anti* Ar*F*). Anal. Calcd for $C_{40}H_{42}F_7MoN_3O_3S$: C, 54.98; H, 4.84; N, 4.81. Found: C, 55.05; H, 4.88; N, 4.70.

{Mo(*N*-2,6-*i*-Pr$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(Ar^F-nacnac)(THF)}{BAr$_{f4}$} (8a). This compound was prepared in fashion analogous to that employed to prepare **4a** starting from 0.327 g (0.374 mmol) of **7a** and 0.330 g (0.381 mmol) of NaBAr$_{f4}$. The complex was observed to form an oil upon attempts at crystallization and was finally precipitated as 0.421 g (68%) of a yellow-brown powder: ^{1}H NMR (300 MHz, CD$_2$Cl$_2$) δ 14.86 (d, J_{HF} = 3.5 Hz, *anti* MoC*H*$_\alpha$), 12.75 (s, 1, *syn* MoC*H*$_\alpha$), 7.75 (s, 8, *o*-Ar$_f$), 6.58 (s, 4, *p*-Ar$_f$), 7.4 − 6.9 (m, 9, Ar), 5.94 (s, 1, nacnac-C*H*), 3.7 (v br m, 1, C*H*Me$_2$), 2.84 (m, 2, OC*H*$_2$), 2.45 (m, 2, OC*H*$_2$), 2.17 (s, 3, C*Me*$_2$Ph), 1.94 (s, 3, C*Me*$_2$Ph), 1.57 (s, 3, nacnac-*Me*), 1.36 (m, 4, OCH$_2$C*H*$_2$), 1.28 (br, 6, CH*Me*$_2$), 1.22 (d, 6, CH*Me*$_2$), 1.10 (s, 3, nacnac-*Me*); ^{19}F NMR (470 MHz) δ −62.5 (Ar$_f$), −115.4 (Ar^F), −115.7 (Ar^F), −117.2 (Ar^F), −119.5 (Ar^F). Anal. Calcd for $C_{75}H_{62}BF_{28}MoN_3O$: C, 54.27; H, 3.76; N, 2.53. Found: C, 54.33; H, 3.68; N, 2.46.

Decomposition of 3a to Give 3a″. A flask was charged with 0.103 g (0.119 mmol) of Mo(*N*-2,6-*i*-Pr$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(Ar′-nacnac)(OTf) and 10 mL of toluene. The orange solution was heated to 90 °C for 45 min. All volatiles were removed *in vacuo*, and the residue was crystallized from a minimal amount of diethyl ether at −25 °C to give 0.090 g (89%) of an orange-yellow crystalline solid. Crystals suitable for X-ray diffraction were grown by slow cooling of a saturated diethyl ether solution at 23 °C. NMR assignments are based on ^{1}H, ^{13}C, HSQC, and HMBC experiments: ^{1}H NMR (300 MHz, C$_6$D$_6$) δ 7.11 (m, 2, Ar), 6.97 (m, 6, Ar), 6.79 (m, 4, Ar), 5.38 (d, J_{HH} = 14 Hz, 1, C^{37}*H*$_2$), 4.14 (m, 1, C*H*Me$_2$), 4.12 (t, J_{HH} = 4.5 Hz, 1, C^2*H*), 3.70 (d, J_{HH} = 14 Hz, 1, C^{37}*H*$_2$), 2.63 (dd, J_{HH} = 15 Hz, 4.5 Hz, 1, C^6*H*$_2$), 2.59 (m, 1, C*H*Me$_2$), 2.19 (s, 3, Me), 2.02 (s, 3, Me), 1.77 (dd, J_{HH} = 15 Hz, 4.5 Hz, 1 C^6*H*$_2$), 1.61 (d, 3, CH*Me*$_2$), 1.57 (s, 3, Me), 1.41 (d, 3, CH*Me*$_2$), 1.34 (d, 3, CH*Me*$_2$), 1.23 (s, 3, Me), 1.21 (s, 3, Me), 1.09 (s, 3, Me), 0.65 (d, 3, CH*Me*$_2$), 0.57 (s, 3, Me); ^{13}C NMR (125 MHz, C$_6$D$_6$) δ 197.80 (C^1), 158.03, 153.78, 150.22, 147.89, 146.67, 145.36, 143.92, 129.90, 129.54, 129.50, 129.33, 128.53, 128.52, 128.03, 127.51, 127.31, 126.86, 125.84, 123.68, 123.63, 123.31, 123.05, 120.52 (q, J_{CF} = 319 Hz, *C*F$_3$), 82.83 (C^3), 66.76 (C^{37}), 59.61 (C^2), 46.60 (C^6), 38.61 (C^7), 31.12, 30.70, 28.63, 27.75, 25.88, 25.73, 24.15, 22.20 (C^5), 21.84, 19.84 (C^4), 18.77 (C^{38}), 18.21, 18.18. ^{19}F NMR (282 MHz) δ −77.3 (C*F*$_3$). Anal. Calcd for $C_{44}H_{54}F_3MoN_3O_3S$: C, 61.60; H, 6.34; N, 4.90. Found: C, 61.78; H, 6.42; N, 4.81.



Compound 3a‴. This species was observed spectroscopically by mixing equimolar amounts of **3a″** and NaB(C$_6$F$_5$)$_4$·THF in methylene chloride-*d*$_2$ at 23 °C: ^{1}H NMR (300 MHz) δ 7.49 (d, 2, Ar), 7.35 (t, 2, Ar), 7.22 (t, 1, Ar), 7.16 (m, 4, Ar), 7.08 (d, 1, Ar), 7.07 (t, 1, Ar), 6.95 (d, 1, Ar), 6.89 (m, 2, Ar), 4.54 (d, J_{HH} = 12.9 Hz, C*H*$_2$), 4.50 (t, J_{HH} = 3.0 Hz, C*H*), 3.93 (m, 3, C*H*Me$_2$ + THF), 3.52 (m, 2, THF), 3.01 (d, J_{HH} = 12.9 Hz, 1, C*H*$_2$), 2.79 (dd, J_{HH} = 15.6 Hz, J_{HH} = 3.0 Hz, 1, C*H*$_2$), 2.31 (s, 1, Me), 2.15 (sep, 1, C*H*Me$_2$), 2.14 (s, 3, Me), 1.97 (dd, J_{HH} = 15.6 Hz, J_{HH} = 3.0 Hz, 1, C*H*$_2$), 1.86 (s, 3, Me), 1.82 (m, 4, THF), 1.63 (s, 3, Me), 1.60 (s, 3, Me), 1.51 (d, 3, CH*Me*$_2$), 1.33 (d, 3, CH*Me*$_2$), 1.17 (s, 3, Me), 1.04 (s, 3, Me), 1.03 (d, 3, CH*Me*$_2$), 0.44 (d, 3, CH*Me*$_2$).

Compound 4a″. This species was observed spectroscopically upon thermolysis of a 15 mM solution of **4a** in methylene chloride-*d*$_2$ at 40 °C for 3 h: ^{1}H NMR (500 MHz) δ *including tert-butylbenzene* δ 14.28 (br s, 1, MoC*H*), 8.26 (s, 8, *o*-Ar$_f$), 7.64 (s, 4, *p*-Ar$_f$), 7.34 (d, 2, Ar), 7.27 (t, 1, Ar), 7.22 (d, 1, Ar), 7.14 (m, 3, Ar), 6.99 (d, 1, Ar), 6.83 (t, 1, Ar), 6.69 (d, 2, Ar), 6.53 (d, 1, Ar), 4.85 (br s, 1, nacnac-C*H*), 3.32 (sep, 2, C*H*Me$_2$), 3.28 (m, 2, THF), 2.98 (m, 2, THF), 2.29 (s, 3, Me), 2.10 (br s, 3, Me), 1.87 (s, 3, Me), 1.65 (s, 3, Me), 1.4 − 1.1 (br m, 19, THF + CH*Me*$_2$ + Me), 0.74 (br s, 6, CH*Me*$_2$); ^{13}C NMR (258 K, 125 MHz) δ 299.5 (MoC_α), 166.2 (*C*N), 162.1 (q, J_{CB} = 49.7 Hz, *ipso*-Ar$_f$), 152.5, 151.4, 150.7, 147.0, 146.7 (v br), 143.2, 135.1 (*o*-Ar$_f$), 133.0, 131.5, 129.9, 129.2, 129.1, 129.1 (qq, J_{CF} = 31.3 Hz, *m*-Ar$_f$), 129.0, 127.9, 126.1, 124.9 (q, J_{CF} = 272 Hz, *C*F$_3$), 124.6, 123.8, 119.4, 81.5, 75.8, 28.7, 26.7, 25.4 (br), 24.1, 23.5, 22.1, 19.3, 17.7, 17.5.

Compound 4e″. This species was observed spectroscopically upon thermolysis of a mixture of **4e** and **4e′** at 40 °C for 3 h in methylene chloride-*d*$_2$: ^{1}H NMR (300 MHz) δ 14.13 (s, 1, MoC*H*), 7.73 (s, 8, *o*-Ar$_f$), 7.56 (s, 4, *p*-Ar$_f$), 7.40 (d, 1, Ar), 7.15 (m, 3, Ar), 6.98 (t, 1, Ar), 6.90 (t, 1, Ar), 6.81 (t, 1, Ar), 6.74 (d, 1 Ar), 6.65 (d, 1, Ar) 5.89 (d, 1, Ar), 5.35 (s, 1, nacnac-C*H*), 3.78 (m, 2, THF), 3.41 (m, 4, THF), 2.57 (s, 3, Me), 2.48 (s, 3, Me), 2.06 (s, 3, Me), 1.97 (s, 3, Me), 1.85 (m, 4, THF), 1.58 (s, 9, *t*-Bu), 1.17 (s, 3, Me).

{Mo(*N*-2,6-*i*-Pr$_2$C$_6$H$_3$)(CH$_2$CH$_2$)(Ar′-nacnac)(THF)}{BAr$_{f4}$} (9a). This species was observed spectroscopically by exposing a solution of **4a** to 1 atm of ethylene or ethylene-^{13}*C* at 23 °C in methylene chloride-*d*$_2$: ^{1}H NMR (300 MHz) δ 7.73 (s, 8, *o*-Ar$_f$), 7.56 (s, 4, *p*-Ar$_f$), 7.40 (t, 2, Ar), 7.36−7.26 (m, 5, Ar), 7.15 (d, 2 Ar), 6.46 (s, 1, nacnac-C*H*), 3.65 (br s, 4, THF), 2.85 (sep, 2, C*H*Me$_2$), 2.57 (m, 2, C*H*$_2$CH$_2$), 2.33 (s, 6, Me), 1.93 (s, 6, Me), 1.80 (br s, 4, THF), 1.77 (s, 6, Me), 1.16 (d, 12, CH*Me*$_2$), 0.86 (m, 2, CH$_2$C*H*$_2$); ^{13}C NMR (125 MHz) δ 70.3 (*C*H$_2$, J_{CH} = 157 Hz).

Kinetic Experiments. Kinetic data were obtained by ^{1}H NMR at 500 MHz using temperature values that were calibrated with ethylene glycol. Experiments were performed in either toluene-*d*$_8$ (for **3a**) or methylene chloride-*d*$_2$ (for **4a**) at concentrations of 18.0 and 19.5 mM, respectively.

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Supporting Information Available: Variable-temperature ^{1}H NMR spectra of **2a**, **4a**, and **4a″**. Kinetic plots for thermal degradation of compounds **3a** and **4a**. Labeled thermal ellipsoid drawings, crystal data and structure refinement, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, and anisotropic displacement parameters for all crystallographically characterized compounds. Crystallographic information files in cif format. This material is available free of charge via the Internet at http://pubs.acs.org. X-ray crystallographic data for **1a** (06066), **4a**, (06192), and **3a″** (06187) are also available to the public at http://reciprocal.mit.edu.

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