Cationic Molybdenum Imido Alkylidene Complexes

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Addition of 1 equiv of $[HNMe_2Ph]BAr^F_4$ (Ar^F = 3,5-$(CF_3)_2C_6H_3$) to Mo(NAr)($CHCMe_2Ph$)(Pyrrolide)$_2$ (Pyrrolide = parent pyrrolide (Pyr) or 2,5-dimethylpyrrolide (Me_2Pyr)) species in THF produced $[Mo(NAr)(CHCMe_2Ph)(Pyrrolide)(THF)_x]BAr^F_4$ species (x = 2 for Me_2Pyr (**1b**) or 3 (**1a**) for Pyr; Ar = 2,6-diisopropylphenyl). $[Mo(NAr)(CHCMe_2Ph)(Me_2Pyr)(2,4\text{-lutidine})]BAr^F_4$ (**1c**) was formed upon addition of 2,4-lutidine to $[Mo(NAr)(CHCMe_2Ph)(Me_2Pyr)(THF)_2]BAr^F_4$ (**1b**). Addition of 1 equiv of hexafluoro-*tert*-butanol to **1a** produced $\{Mo(NAr)(CHCMe_2Ph)[OC(CF_3)_2Me](THF)_3\}BAr^F_4$ (**3a**), while $\{Mo(NAr)(CHCMe_2Ph)[OCMe(CF_3)_2](THF)_2\}BAr^F_4$ (**3b**) was obtained similarly through addition of hexafluoro-*tert*-butanol to **1b**. Similar reactions produced unstable $[Mo(NAr)(CHCMe_2Ph)(O\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)(THF)]BAr^F_4$ (**3c**) and $[Mo(NAr)(CHCMe_2Ph)(OAdamantyl)(THF)_2]BAr^F_4$ (**3d**). Treatment of **1b** with 2 equiv of 2,6-diisopropylphenol yielded $[Mo(NAr)(CH_2CMe_2Ph)(O\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_2]BAr^F_4$ (**4**). Compound **3a** reacts with ethylene to yield $\{Mo(NAr)(CH_2CH_2)[OC(CF_3)_2Me](THF)_3\}BAr^F_4$ (**6**). The reaction between Mo(NAr)($CHCMe_2Ph$)$(OTf)_2$(dme) and 2 equiv of Li(MesPyr) (MesPyr = 2-mesitylpyrrolide) gave Mo(NAr)($CHCMe_2Ph$)$(MesPyr)_2$ (**2**), but no cationic species could be prepared that contain 2-mesitylpyrrolide. Compounds **1a**, **1c**, **2**, **3a**, **4**, and **6** were characterized crystallographically.

Introduction

The vast majority of high oxidation state Mo and W catalysts that have been developed for the metathesis of alkenes are neutral species of the type M(NR)(CHR′)$(OR'')_2$ or M(NR)(CHR′)(diolate).[1] In contrast, *cationic* tungsten[2] or molybdenum[3] imido alkylidene complexes are rare, especially those in which the metal has an electron count of less than 18. Since bimolecular coupling of alkylidenes is a major mode of decomposition of neutral alkylidene complexes, especially methylene complexes, we felt that bimolecular decomposition might be slower in cationic species. Therefore, we have been exploring the synthesis of some cationic high oxidation state alkylidene species that contain bulky ligands.

In a previous paper we chose to explore cationic molybdenum β-diketiminate complexes prepared from complexes of the type Mo(NR)(CHR′)(Ar-nacnac)(OTf) (Ar-nacnac = $[ArNC(Me)]_2CH$, OTf = trifluoromethanesulfonate, R′ = CMe_3 or CMe_2Ph).[4] Reaction of Mo(NR)(CHR′)(Ar-nacnac)(OTf) with $NaBAr^F_4$ (Ar^F = 3,5-$(CF_3)_2C_6H_3$) afforded the cationic species $\{Mo(NR)(CHR')(Ar\text{-}nacnac)(THF)_n\}BAr^F_4$ (n = 0 or 1, depending on the nature of Ar). These cationic species reacted with olefins, but in general were poor metathesis catalysts with short catalyst lifetimes. Instability of these cationic species in some cases could be ascribed to decomposition reactions that involve the nacnac ligands. However, we also considered the possibility that the chelating nature of the nacnac ligand might restrict rearrangement of metalacyclobutane complexes that are required for productive turnover. Therefore, we decided to prepare cationic molybdenum complexes that do not contain a chelating monoanionic ligand, an example being $[Mo(NAr)(CHR')(OR'')(S)_n]BAr^F_4$, where S is a solvent such as THF or some other two-electron donor. That opportunity presented itself as a consequence of the recent synthesis of various bispyrrolide complexes with the empirical formula Mo(NR)(CHR′)(pyrrolide)$_2$.[5] Many of these species react readily with alcohols and therefore would be expected to react readily with $[BAr^F_4]^-$ acids. The results of these experiments are reported here.

Results and Discussion

Synthesis of Cationic Monopyrrolide Complexes. Addition of 1 equiv of $[HNMe_2Ph]BAr^F_4$ to the bispyrrolide species[5,6] in tetrahydrofuran produced cationic **1a** (eq 1) as a fine crystalline powder in 81% yield. Compound **1a** is an 18*e* species if π donation from the imido ligand is included. In methylene chloride-d_2, the ^{1}H NMR spectrum of **1a** at room temperature revealed the alkylidene H_α resonance at 13.93 ppm with a J_{CH} value of 119 Hz and the C_α resonance at 322.2 ppm; the J_{CH} value is characteristic of a *syn* alkylidene isomer, as shown in eq 1.

Crystals of **1a** suitable for X-ray diffraction were isolated from a mixture of diethyl ether and pentane (Table 1). Compound **1a** is a six-coordinate octahedral species with three THF ligands in a *fac* arrangement *trans* to the imido, alkylidene,

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(6) The reader should refer to ref 5 for details of the structure of the bispyrrolide in eq 1.

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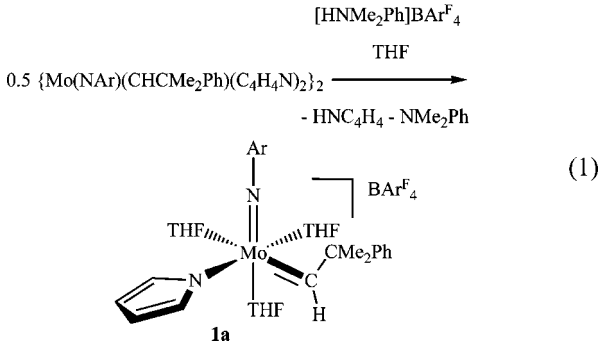
Table 1. Crystallographic Data for 1a, 1c, and 2[a]

	1a (07011)	**1c** (07164)	**2** (07178)
empirical formula	$C_{72}H_{74}BF_{24}MoN_2O_{3.50}$	$C_{67}H_{58}BF_{24}MoN_3$	$C_{48}H_{57}MoN_3$
fw	1586.08	1467.91	771.91
temperature (K)	100(2)	100(2)	203(2)
cryst syst	monoclinic	monoclinic	monoclinic
space group	*P*2(1)/*n*	*P*2(1)/*n*	*P*2(1)/*n*
unit cell dimens (Å, deg)	$a = 18.4389(6)$	$a = 24.9162(9)$	$a = 11.3790(6)$
	$b = 21.1079(7)$	$b = 18.8260(7)$	$b = 19.8001(10)$
	$c = 18.8695(6)$	$c = 28.0325(11)$	$c = 18.8237(10)$
	$\beta = 95.3130(10)$	$\beta = 93.7380(10)$	$\beta = 99.000(2)$
volume (Å^3)	7312.6(4)	13121.3(9)	4188.9(4)
Z	4	8	4
density (calcd; Mg/m^3)	1.441	1.486	1.224
absorp coeff (mm^{-1})	0.288	0.311	0.348
F(000)	3244	5952	1632
cryst size (mm^3)	0.30 × 0.25 × 0.15	0.50 × 0.45 × 0.30	0.30 × 0.25 × 0.20
θ range (deg)	1.76 to 29.57	1.06 to 30.26	1.97 to 29.85
index ranges	$-25 \le h \le 25$, $-29 \le k \le 28$, $-26 \le l \le 26$	$-35 \le <h = 35$, $-26 \le k \le 26$, $-39 \le l \le 39$	$-15 \le h \le 15$, $-27 \le k \le 27$, $-25 \le l \le 26$
no. of reflns collected	145 199	355 073	94 578
no. of indep reflns	20 491 [*R*(int) = 0.0490]	38 819 [*R*(int) = 0.0591]	12 047[*R*(int) = 0.0438]
completeness to θ	99.9%	99.1%	100%
max. and min. transmn	0.9580 and 0.9185	0.9124 and 0.8598	0.9336 and 0.9027
no. of data/restraints/params	20 491/2908/1150	38 819/5039/1995	12 047/1/484
goodness-of-fit on F^2	1.045	1.050	1.042
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0409, wR2 = 0.0927	R1 = 0.0476, wR2 = 0.1068	R1 = 0.0316, wR2 = 0.0769
R indices (all data)	R1 = 0.0602, wR2 = 0.1027	R1 = 0.0716, wR2 = 0.1215	R1 = 0.0435, wR2 = 0.0847
larg diff peak and hole (e Å^{-3})	0.848 and −0.444	1.504 and −1.076	0.610 and −0.604

[a] All structures were determined with 0.71073 Å radiation. The absorption correction was semiempirical from equivalents, and the method of refinement was full-matrix least-squares on F^2.



1a (1)

and pyrrolide ligands, as shown in Figure 1. The Mo−O bond lengths for the THF ligands *trans* to the imido and alkylidene ligands are 2.3101(12) and 2.3612(13) Å, respectively, while the Mo−O bond length *trans* to the pyrrolide is 2.1945(13) Å. The Mo═C and Mo═N bond lengths are unexceptional. The alkylidene is in the *syn* orientation with Mo−C(1)−C(2) = 143.13(14)°, a typical Mo−C(1)−C(2) angle for a *syn* alkylidene in a high oxidation state Mo species.

Upon treating Mo(NAr)(CHCMe$_2$Ph)(Me$_2$Pyr)$_2$ (Me$_2$Pyr = 2,5-Me$_2$NC$_4$H$_2$)[5b] with [HNMe$_2$Ph]BAr$^F_4$ in THF, [Mo(NAr)(CHCMe$_2$Ph)(Me$_2$Pyr)(THF)$_2$]BAr$^F_4$ (**1b**) was isolated in 71% yield as a burnt orange crystalline powder. The additional steric hindrance presented by the 2,5-dimethylpyrrolide ligand apparently limits coordination of only two THF ligands to the metal center, according to solution proton NMR studies. The exact coordination geometry of the molecule in solution is unclear because the THF proton resonances are broad. At room temperature, the ^{1}H NMR spectrum of the sample in methylene chloride displays four THF resonances at 3.84, 3.70, 2.02, and 1.83 ppm in the ratios 2:6:4:4. The *syn* alkylidene proton resonance is found at 14.26 ppm (J_{CH} = 128 Hz). Upon cooling the solution to −80 °C, two alkylidene proton resonances are observed at 14.17 and 13.77 ppm. Therefore at least two isomers must be present at −80 °C, and some equilibration process is rapid on the NMR time scale at room temperature. Upon treating

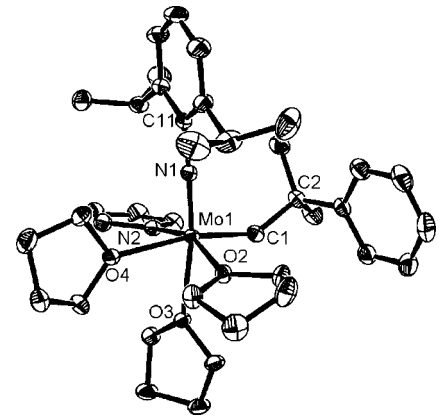


Figure 1. Thermal ellipsoid (50%) rendering of {Mo(NAr)(CHCMe$_2$Ph)(NC$_4$H$_4$)(THF)$_3$}BAr$^F_4$ (**1a**). Hydrogen atoms, a minor disorder, solvent molecules, and the anion are not shown for clarity. Selected bond distances (Å) and angles (deg): Mo1−C1 = 1.9209(19); Mo1−N1 = 1.7329(15); Mo1−N2 = 2.0810(15); Mo1−O2 = 2.1945(13); Mo1−O3 = 2.3101(12); Mo1−O4 = 2.3612(13); Mo1−C1−C2 = 143.13(14); N1−Mo1−O3 = 170.11(6); O4−Mo1−C1 = 168.85(6); N2−Mo1−O2 = 159.11(6); Mo1−N1−C11 = 177.06(13).

1b with 1 equiv of 2,4-lutidine in dichloromethane, [Mo(NAr)(CHCMe$_2$Ph)(Me$_2$Pyr)(2,4-Lut)]BAr$^F_4$ (**1c**) could be isolated as a yellow powder in 99% yield (eq 2). Proton NMR studies suggest that this is a *syn* species and that THF is not present. Asymmetry at the metal center is suggested by the presence of two singlet resonances for the backbone protons of the pyrrolide and a total of six singlets for the methyl groups on the lutidine, pyrrolide, and alkylidene ligands.

An X-ray structure of **1c** (Table 1) reveals it to contain one bound 2,4-lutidine and an η^5-dimethylpyrrolide in a pseudotetrahedral arrangement around the metal (Figure 2). The metal therefore has an 18*e* count. The Mo−pyrrolide centroid distance is 2.10 Å, the Mo−N5 distance is 2.411(2) Å, and two of the

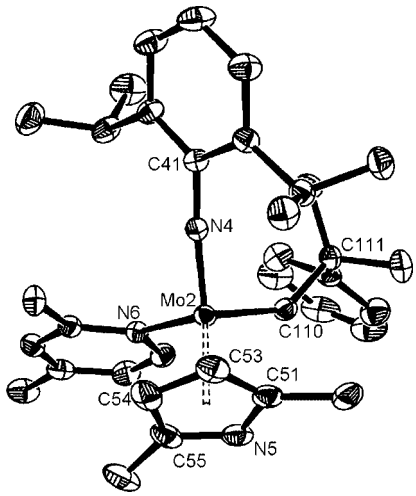
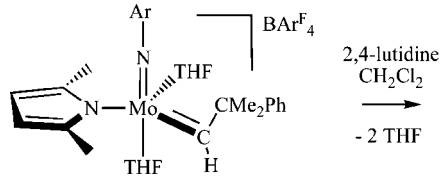
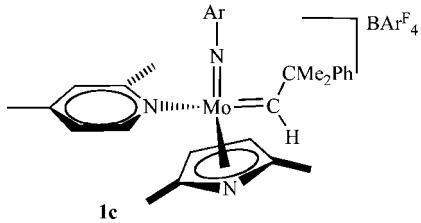


Figure 2. Thermal ellipsoid (50%) rendering of one of the two crystallographically independent molecules in the structure of $[Mo(NAr)(CHCMe_2Ph)(Me_2Pyr)(2,4\text{-}Me_2NC_5H_3)]BAr^F{}_4$ (**1c**). Hydrogen atoms, the anion, and the second molecule of the asymmetric unit are not shown. Selected bond distances (Å) and angles (deg): Mo2−C110 = 1.937(2); Mo2−N4 = 1.7396(18); Mo2−N5 = 2.4114(19); Mo2−N6 = 2.1908(18); Mo2−C51 = 2.343(2); Mo2−C53 = 2.359(2); Mo2−C54 = 2.459(2); Mo2−C55 = 2.479(2); Mo2−Centroid of pyrrolide = 2.096; Mo2−C110−C111 = 139.94(16); Mo2−N4−C41 = 170.24(15).



1b (2)

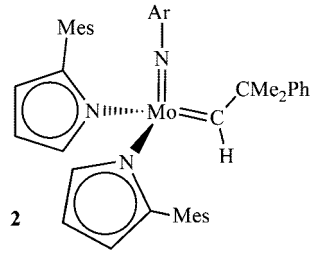


1c

Mo−C single bond lengths (2.460(3) and 2.479(2) Å) are longer than the other two Mo−C bonds (2.344(2) and 2.360(2) Å). This Mo−pyrrolide centroid distance is comparable to the W−centroid distance (2.08 Å) in the 2,5-dimethylpyrrolenine species $\{W(N\text{-}2,6\text{-}Cl_2C_6H_3)(CHCMe_3)(Me_2Pyr)(2,5\text{-}Me_2NC_4H_3)\}BAr^F{}_4$.[7] The Mo−N6 distance (2.1908(18) Å) is typical for a 2*e* donor bound to Mo. The alkylidene is in the *syn* orientation. All other bond distances and angles are unexceptional.

The structures of **1a** and **1c** suggest that more sterically demanding pyrrolides might be desirable in order to avoid 18*e* counts at the metal and, in particular, pyrrolides that are unlikely to be able to bind to the metal in an η^5 fashion. Therefore we explored the synthesis of compounds that contain the 2-mesitylpyrrolide ligand (MesPyr). Treatment of 2-mesitylpyrrole[8] with *n*-butyllithium in diethyl ether produced Li(MesPyr). The reaction between $Mo(NAr)(CHCMe_2Ph)(OTf)_2(dme)$ and 2 equiv of Li(MesPyr) gave $Mo(NAr)(CHCMe_2Ph)(MesPyr)_2$ (**2**) (eq 3), which was isolated as orange blocks in 54% yield. According to proton NMR studies, **2** has a mirror plane on the NMR time scale that relates the two pyrrolides and a *syn* alkylidene with $\delta H_\alpha = 11.56$ ppm and $J_{CH} = 120$ Hz.

$$Mo(NAr)(CHCMe_2Ph)(OTf)_2(dme) \xrightarrow[-\ 2\ LiOTf\ -\ dme]{+\ 2\ Li(MesPyr)} \quad (3)$$



2

An X-ray study reveals that **2** has a pseudotetrahedral structure in which the two MesPyr ligands are both bound in an η^1 fashion (Table 1, Figure 3). The perpendicular orientation of the mesityl ring with respect to the pyrrolide ring and the overall steric demands of the MesPyr ligand evidently prevent η^5 coordination of one of the pyrrolides, as found in Mo(NAd)(CHCMe$_3$)(η^5-Me$_2$Pyr)(η^1-Me$_2$Pyr)[9] and W(NAr)(CHCMe$_2$Ph)(η^5-Me$_2$Pyr)(η^1-Me$_2$Pyr).[7] Therefore **2** is a 14-electron species if no possible π bonding from the pyrrolide nitrogen to the metal is included. Metal−ligand bond lengths in general are slightly shorter in **2** than in **1a** or **1c** as a consequence of its lower electron count and coordination number (e.g., Mo=C = 1.8660(16) Å in **2** and 1.932(2) Å in **1c**).

Unfortunately, addition of $[HNMe_2Ph]BAr^F{}_4$ to **2** in THF yielded only an oily mixture of unidentified materials. An oily mixture of unidentified products also was formed when $[HNMe_2Ph]BAr^F{}_4$ was added to **2** in dichloromethane in the presence of excess 2,4-lutidine.

Synthesis of Cationic Monoalkoxides. Addition of 1 equiv of hexafluoro-*tert*-butanol to **1a** produced $\{Mo(NAr)(CHCMe_2Ph)[OC(CF_3)_2Me](THF)_3\}BAr^F{}_4$ (**3a**), which was isolated in 82% yield as a yellow powder (eq 4). The analogous compound, $\{Mo(NAr)(CHCMe_2Ph)[OCMe(CF_3)_2](THF)_2\}BAr^F{}_4$ (**3b**), was obtained in 91% yield similarly through addition of hexafluoro-*tert*-butanol to $\{Mo(NAr)(CHCMe_2Ph)(Me_2Pyr)(THF)_2\}BAr^F{}_4$. The low values for J_{CH} (~119 Hz) suggest that a *syn* alkylidene is present in **3a** and **3b**.

An X-ray study of **3a** (Table 2) revealed it to have a pseudo-octahedral structure with the hexafluoro-*tert*-butoxide *trans* to the imido ligand (Figure 4). The THF *trans* to the alkylidene is weakly bound (Mo−O(2) = 2.4398(13) Å) compared to the mutually *trans* THF ligands (Mo−O = 2.1495(11) Å and 2.1527(11) Å). Therefore it is not surprising that 16*e* **3b** can be isolated, in which only two THF ligands are present.

Treating the cationic pyrrolide complexes with other monodentate alcohols produced monoalkoxide complexes similar to **3a**. For example, $[Mo(NAr)(CHCMe_2Ph)(O\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)(THF)]BAr^F{}_4$ (**3c**, $\delta H_\alpha = 14.73$ ppm) was isolated in 90% crude yield upon treating $[Mo(NAr)(CHCMe_2Ph)(Me_2Pyr)(THF)_2]BAr^F{}_4$ with 2,6-diisopropylphenol, and $[Mo(NAr)(CHCMe_2Ph)(OAd)(THF)_2]BAr^F{}_4$ (**3d**, $\delta H_\alpha = 15.07$ ppm) was isolated

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Table 2. Crystallographic Data for 3a, 4, and 6[a]

	3a (07005)	**4** (07170)	**6** (07029)
empirical formula	$C_{70}H_{68}BF_{30}MoNO_4$	$C_{78}H_{76}BF_{24}MoNO_2$	$C_{60}H_{60}BCl_2F_{30}MoNO_4$
fw	1664	1622.15	1606.74
temperature (K)	100(2)	100(2)	100(2)
cryst syst	monoclinic	monoclinic	triclinic
space group	*P*2(1)/*n*	*P*2(1)/*m*	$P\bar{1}$
unit cell dimens (Å, deg)	$a = 16.200(2)$	$a = 13.3339(5)$	$a = 12.9370(4)$
	$b = 22.500(3)$	$b = 56.707(2)$	$b = 12.9705(4)$
	$c = 20.048(3)$	$c = 15.0088(5)$	$c = 22.1851(7)$
	$\alpha = 90$	$\alpha = 90$	$\alpha = 89.3430(10)$
	$\beta = 96.045(2)$	$\beta = 90.2990(10)$	$\beta = 75.4770(10)$
	$\gamma = 90$	$\gamma = 90$	$\gamma = 85.3940(10)$
volume (Å^3)	7266.6(18)	11348.4(7)	3591.91(19)
Z	4	6	2
density (calcd; Mg/m^3)	1.521	1.424	1.486
absorp coeff (mm^{-1})	0.305	0.279	0.378
F(000)	3376	4980	1620
cryst size (mm^3)	0.30 × 0.25 × 0.20	0.20 × 0.20 × 0.07	0.30 × 0.25 × 0.20
θ range (deg)	1.71 to 29.57	0.72 to 28.28	0.95 to 29.57
index ranges	$-22 \le h \le 22, -31 \le k \le 31,$ $-26 \le l \le 27$	$-17 \le h \le 17, -75 \le k \le 75,$ $-19 \le l \le 20$	$-17 \le h \le 17, -18 \le k \le 18,$ $-30 \le l \le 30$
no. of reflns collected	158 588	279 787	80 936
no. of indep reflns	20 382 [*R*(int) = 0.0672]	28 423 [*R*(int) = 0.0830]	20 089 [*R*(int) = 0.0313]
completeness to θ	100.0%	100.0%	99.7%
max. and min. transmn	0.9414 and 0.9139	0.9808 and 0.9464	0.9283 and 0.8951
no. of data/restraints/params	20 382/2009 /1177	28 423/6579/2360	20 089/2831/1194
goodness-of-fit on F^2	1.032	1.054	1.060
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0354, wR2 = 0.0874	R1 = 0.0913, wR2 = 0.2251	R1 = 0.0525, wR2 = 0.1489
R indices (all data)	R1 = 0.0482, wR2 = 0.0970	R1 = 0.1187, wR2 = 0.2463	R1 = 0.0625, wR2 = 0.1575
larg diff peak and hole (e Å^{-3})	0.948 and −0.598	2.157 and −1.719	3.141 and −1.343

[a] All structures were determined with 0.71073 Å radiation. The absorption correction was semiempirical from equivalents, and the method of refinement was full-matrix least-squares on F^2.

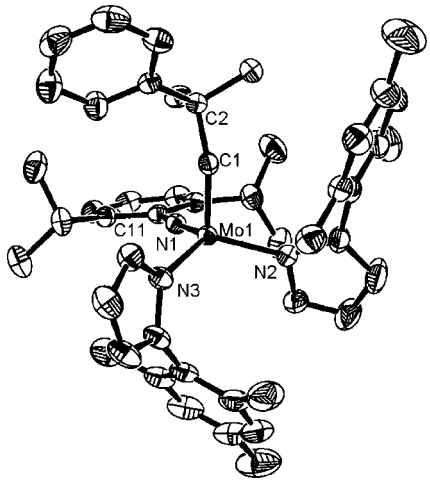


Figure 3. Thermal ellipsoid (50%) rendering of Mo(NAr)(CHCMe$_2$Ph)(MesPyr)$_2$ (**2**). Hydrogen atoms are removed for clarity. Selected bond distances (Å) and angles (deg): Mo1−C1 = 1.8660(16); Mo1−N1 = 1.7361(13); Mo1−N2 = 2.0200(13); Mo1−N3 = 2.0430(13); Mo1−C1−C2 = 146.75(12); Mo1−N1−C11 = 172.45(11).

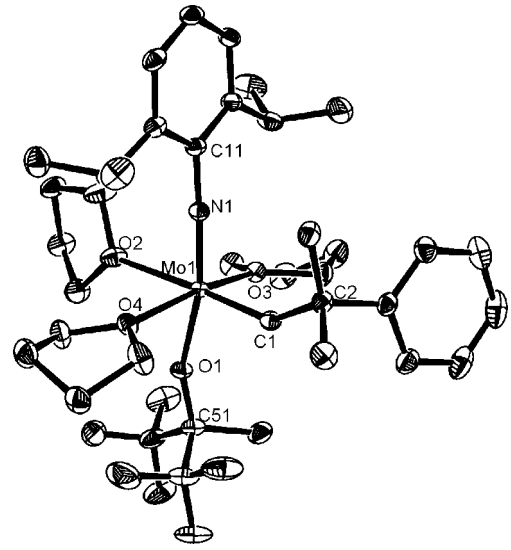
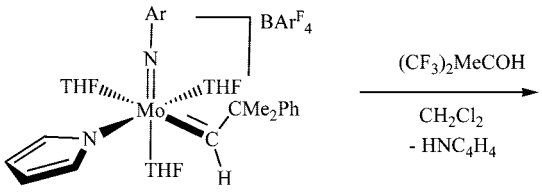


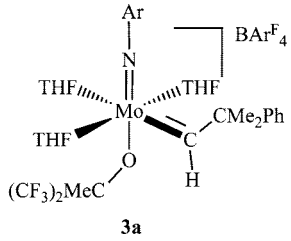
Figure 4. Thermal ellipsoid (50%) rendering of {Mo(NAr)(CHCMe$_2$Ph)[OCMe(CF$_3$)$_2$](THF)$_3$}BAr$^F_4$ (**3a**). Hydrogen atoms, a minor disorder, and the anion are removed for clarity. Selected bond distances (Å) and angles (deg): Mo1−C1 = 1.9227(16); Mo1−N1 = 1.7514(14); Mo1−O1 = 2.0218(11); Mo1−O2 = 2.4398(13); Mo1−O3 = 2.1495(11); Mo1−O4 = 2.1527(11); Mo1−C1−C2 = 143.66(12); N1−Mo1−O1 = 166.31(6); O3−Mo1−O4 = 165.75(4); C1−Mo1−O2 = 176.84(6); Mo1−N1−C11 = 176.30(12).

in 88% crude yield upon treating [Mo(NAr)(CHCMe$_2$Ph)(Pyr)(THF)$_3$]BAr$^F_4$ with 1-adamantanol. However, during recrystallization attempts to purify both **3c** and **3d** in a mixture of diethyl ether and pentane, they decomposed over a period of several days; therefore elemental analyses on recrystallized material could not be obtained. However, elemental analysis of crude **3d** was successful. Attempts to recrystallize about 50 mg of **3c** via vapor diffusion of pentane into a diethyl ether solution of the compound produced a trace amount of [Mo(NAr)(CH$_2$CMe$_2$Ph)(O-2,6-*i*-Pr$_2$C$_6$H$_3$)$_2$]BAr$^F_4$ (**4**).

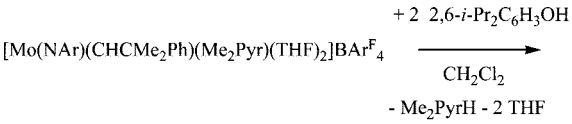
Compound **4** could be prepared and isolated in 29% yield by treating [Mo(NAr)(CHCMe$_2$Ph)(Me$_2$Pyr)(THF)$_2$]BAr$^F_4$ with 2 equiv of 2,6-diisopropylphenol (eq 5, DIPP = 2,6-diisopropylphenoxide). The ^{1}H NMR spectrum of **4** indicates that it has a mirror plane which renders the H$_\alpha$ protons equivalent (at δ 4.06 ppm in methylene chloride-d_2) and β methyl groups in the alkyl equivalent. Treatment of **1a** with 3,3′-di-*tert*-butyl-5,5′,6,6′-tetramethylbiphenyl-2,2′-diol (*rac*-BIPHENH$_2$) also produced an alkyl complex (**5**) in 80% yield, whose proton NMR



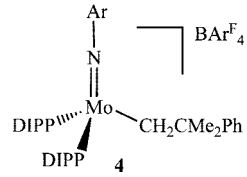
1a (4)



3a



(5)



4

spectrum is characteristic of a chiral species; for example, the H_α protons in the neophyl ligand have chemical shifts of 4.95 and 2.39 ppm with a J_{HH} of 12 Hz.

An X-ray structure of **4** (Table 2, Figure 5) revealed it to be the expected pseudotetrahedral cationic alkyl complex with a Mo−C_α bond length of 2.113(4) Å and a Mo═N bond length of 1.699(3) Å. Other bond lengths and various bond angles are unexceptional. Compounds **4** and **5** are unusual in that they are pseudotetrahedral, electron-deficient, cationic alkyls of Mo(VI). So far we have found no other examples in the literature.

Reactions of Cationic Complexes with Olefins. Complexes **1a**−**c** did not react with ethylene in THF. Compound **1a** decomposed when it was exposed to 1 atm of ethylene in CD_2Cl_2, while **1c** in CD_2Cl_2 did not react with ethylene (1 atm) in 7 days.

The reaction between **3a** and ethylene in CD_2Cl_2 over a period of 2 h yielded **6**, which was isolated in 91% yield (eq 6). In solution the ^{1}H NMR spectrum (CD_2Cl_2, 20 °C) of **6** showed broad resonances for the three THF ligands. At −70 °C each broad resonance separated into two THF resonances in the ratio of 2:1. At room temperature sharp multiplets were found for the ethylene protons at 3.08 and 2.62 ppm and the ethylene carbon resonance was found at 63.47 ppm in bromobenzene-d_5 (J_{CH} = 152 Hz).

An X-ray structure study of **6** (Table 2, Figure 6) revealed that its structure is overall similar to that of **3a**, with the ethylene ligand in place of the alkylidene ligand. The Mo−C(1) bond length is 2.213(2) Å, Mo−C(2) = 2.220(2) Å, and C(1)−C(2) = 1.408(4) Å, similar to other known ethylene complexes of this general type.[10,11] The ethylene is oriented along the O(3)−Mo−O(4) axis, as expected, in order to employ the d orbital in the O(2)−O(3)−Mo−O(4) plane for back-bonding (the same orbital that is employed to form the Mo═C bond in **3a**).

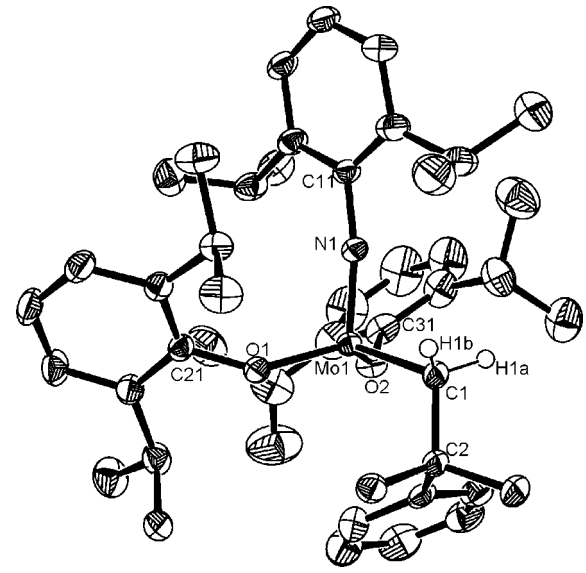


Figure 5. Thermal ellipsoid (50%) rendering of the well-behaved molecule of the structure of [Mo(NAr)(CH$_2$CMe$_2$Ph)(O-2,6-*i*-Pr$_2$C$_6$H$_3$)$_2$]BAr$^F_4$ (**4**). Hydrogen atoms (except for the alkyl's α protons) and the anion are removed for clarity. Selected bond distances (Å) and angles (deg): Mo1−C1 = 2.113(4); Mo1−N1 = 1.699(3); Mo1−O1 = 1.840(3); Mo1−O2 = 1.843(3); Mo1−C1−C2 = 110.1(3), Mo1−N1−C11 = 170.6(3); Mo1−O1−C21 = 145.1(3); Mo1−O2−C31 = 139.4(3).

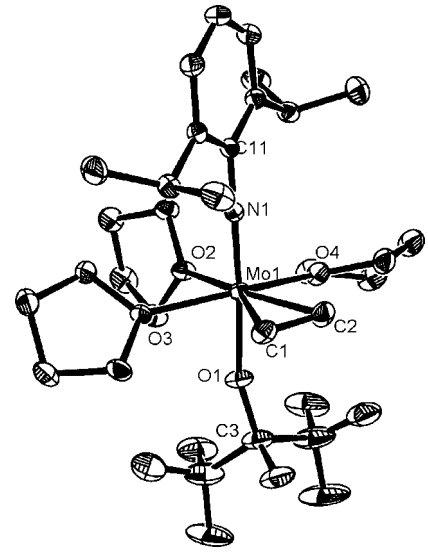
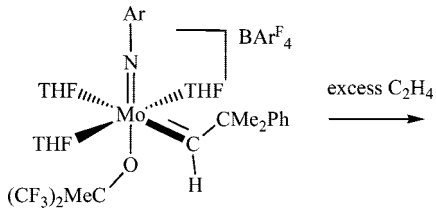


Figure 6. Thermal ellipsoid (50%) rendering of {Mo(NAr)(C$_2$H$_4$)[OCMe(CF$_3$)$_2$](THF)$_3$}BAr$^F_4$ (**6**). Hydrogen atoms, a minor disorder, a disordered pentane, and the anion are removed for clarity. Selected bond distances (Å) and angles (deg): Mo1−C1 = 2.213(2); Mo1−C2 = 2.220(2); Mo1−N1 = 1.7558(19); Mo1−O1 = 2.0196(17); Mo1−O2 = 2.2499(16); Mo1−O3 = 2.2013(17); Mo1−O4 = 2.2051(17); C1−C2 = 1.408(4); Mo1−C1−C2 = 71.76(14); Mo1−C2−C1 = 71.20(14); Mo1−N1−C11 = 178.17(16); Mo1−O1−C3 = 157.7(2); N1−Mo1−O1 = 175.71(8).

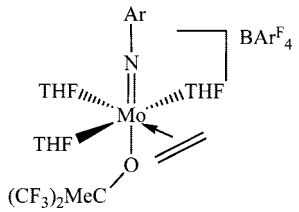
When a degassed, frozen solution of **3a** (∼40 mg) in CD_2Cl_2 (∼0.6 mL) in an NMR tube was exposed to ∼300 mmHg of ^{13}C ethylene, the ^{1}H NMR spectrum of the solution ∼15 min after being thawed showed that a methylidene complex had been

(10) Tsang, W. C. P.; Jamieson, J. Y.; Aeilts, S. L.; Hultzsch, K. S.; Schrock, R. R.; Hoveyda, A. H. *Organometallics* **2004**, *23*, 1997.

(11) Arndt, S.; Schrock, R. R.; Mueller, P. *Organometallics* **2007**, *26*, 1279.



3a (6)



6

formed (Figure 7) whose proton resonances are found at 14.77 and 13.68 ppm (J_{HH} = 5 Hz, J_{CH} = 140 and 166 Hz, respectively); the J_{HH} = 5 Hz and J_{CH} = 140 and 166 Hz values are comparable to those found for other (rare) high oxidation state methylene complexes.[7,12] The ^{13}C NMR spectrum of this mixture shows a C_α resonance at 302.30 ppm. A small amount of a metallacyclopentane complex (doublet resonances at 121.52 and 18.31 ppm, J_{CC} = 43 Hz) is present along with 3-methyl-3-phenyl-1-butene (singlet resonance at 110.95 ppm) and the ethylene complex (resonance at 63.40 ppm). No resonance for free ethylene was observed. In an analogous sample that contained 30 mg of **3a**, the metallacyclopentane complex and propylene (dd, 134.34 ppm, J_{CC} = 70 and 42 Hz; d, 115.81 ppm, J_{CC} = 70 Hz; d, 19.63, J_{CC} = 42 Hz) could be observed clearly (Figure 8). After 15 min the ^{13}C NMR spectrum showed a decrease in free ethylene and formation of 1-butene (Figure 9; dd at 141.21 ppm with J_{CC} = 70 and 42 Hz; d at 113.38 ppm with J_{CC} = 70 Hz; dd at 27.25 ppm with J_{CC} = 42 and 35 Hz; d at 13.46 ppm with J_{CC} = 35 Hz). We conclude that the metallacyclopentane complex rearranges to 1-butene via β-hydride elimination. When isolated **6** was exposed to 1 atm of ethylene, ethylene was dimerized catalytically to 1-butene.

The mechanism (Scheme 1) that explains how the products mentioned above are formed has precedent in the literature.[10,13] Upon exposure to ethylene, a solution of **3a** first forms an unobservable substituted metallacyclobutane complex. The metallacycle releases 3-methyl-3-phenyl-1-butene to form a molybdenum methylidene complex, which reacts with another ethylene to yield an unsubstituted metallacyclobutane (also not observed in this case, but see below). The unsubstituted metallacyclobutane complex rearranges to form propylene, a rearrangement that may be promoted by ethylene.[10] Propylene is displaced by ethylene to form the ethylene complex (**6**), and **6** then reacts with ethylene to yield the metallacyclopentane, which is an intermediate in the catalytic formation of 1-butene. It should be noted that the particular species that are observed in any given experiment may depend greatly upon the conditions of that experiment.

A degassed sample of complex **3c** (~30 mg in ~0.6 mL of CD_2Cl_2) was treated with 1 atm of ethylene at room temperature to give ~5% of a methylidene complex with H_α resonances at δ 14.93 and 13.72 ppm (J_{HH} = 4.5 Hz) after 15 min. Similarly,

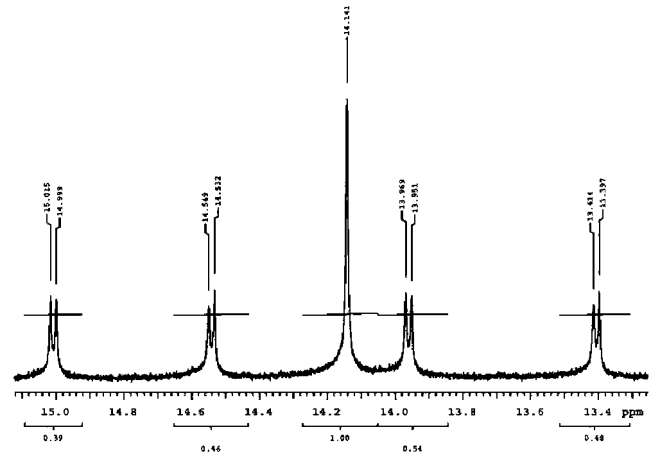


Figure 7. ^{1}H NMR spectrum of the reaction of **3a** in CD_2Cl_2 and ^{13}C ethylene after approximately 15 min of reaction time at room temperature. Only the alkylidene region is depicted.

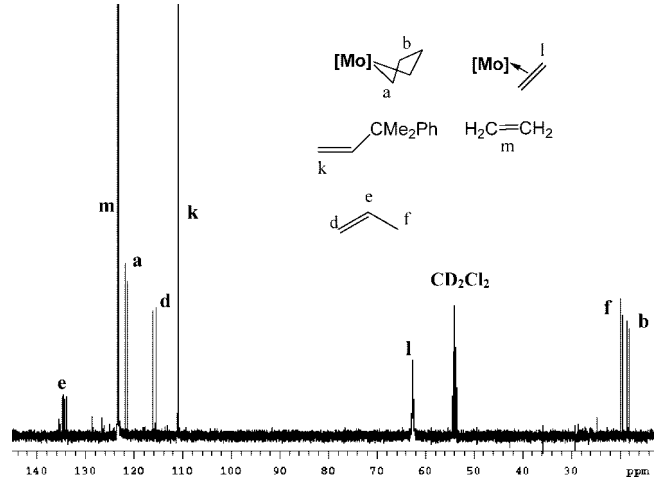


Figure 8. ^{13}C NMR after exposing **3a** (CD_2Cl_2) to ~300 mmHg of ^{13}C-ethylene at room temperature for approximately 5 min.

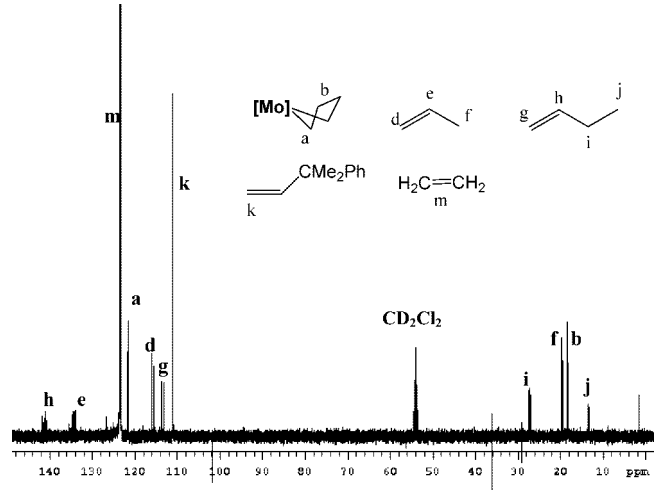
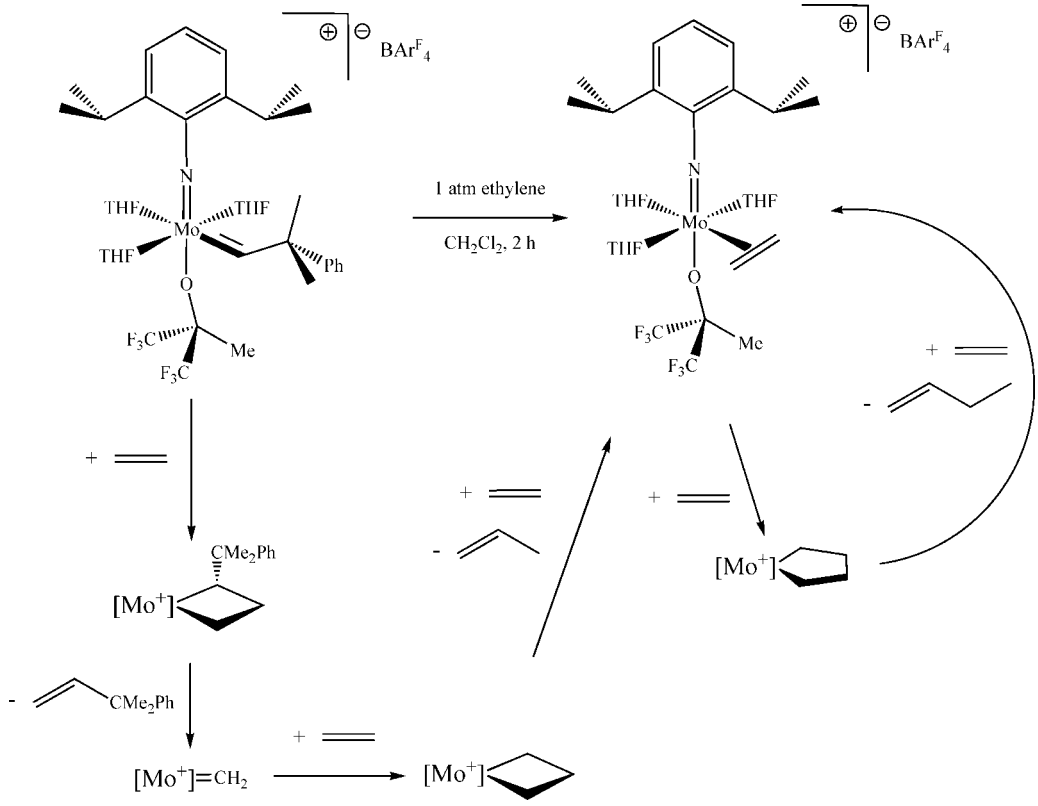


Figure 9. ^{13}C NMR after exposing **3a** (CD_2Cl_2) to ~300 mmHg of ^{13}C-ethylene at room temperature for 15 min.

a frozen and degassed sample of complex **3c** (~30 mg in ~0.6 mL of CD_2Cl_2) was treated with ~300 mmHg of ^{13}C-ethylene. After 30 min, ^{13}C NMR spectra showed evidence of an ethylene complex (carbon resonance at 57.62 ppm), in addition to 3-methyl-3-phenyl-1-butene and ethylene. After 3 h, the ethylene

(12) Fox, H. H.; Lee, K.-K.; Park, L. Y.; Schrock, R. R. *Organometallics* **1993**, *12*, 759.
(13) Tsang, W. C. P.; Hultzsch, K. S.; Alexander, J. B.; Peter, J.; Bonitatebus, J.; Schrock, R. R.; Hoveyda, A. H *J. Am. Chem. Soc.* **2003**, *125*, 2653.

Scheme 1

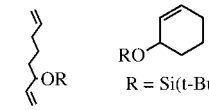
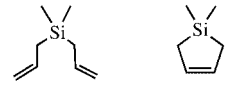
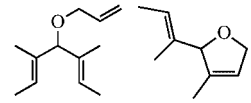
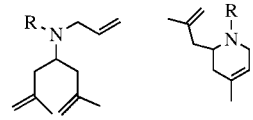


resonance had disappeared and *trans*-2-butene (dd, 126.32 ppm, J_{CC} = 28 and 16 Hz; dd, 18.18 ppm, J_{CC} = 28 and 16 Hz) and *cis*-2-butene (dd, 125.06 ppm, J_{CC} = 27 and 16 Hz; dd, 12.66 ppm, J_{CC} = 27 and 16 Hz) were observed. 2-Butene is believed to be formed through catalytic metathesis of 1-propene.

When a degassed sample of complex **3d** (~30 mg in ~0.6 mL of CD_2Cl_2) was treated with 1 atm of ethylene at room temperature, no methylidene complex was observed after 15 min. A frozen and degassed sample of complex **3d** (~30 mg in ~0.6 mL of CD_2Cl_2) was treated with ~300 mmHg of ^{13}C-ethylene. After 30 min, ^{13}C NMR spectra showed the sample to contain 3-methyl-3-phenyl-1-butene, ethylene, and a metallacyclobutane complex (doublet at 104.00 ppm with J_{CC} = 13 Hz and a triplet at −0.19 ppm with J_{CC} = 13 Hz). After 5 h, the metallacyclobutane complex had disappeared. After 24 h, *cis* and *trans* 2-butene were present in addition to ethylene, 3-methyl-3-phenyl-1-butene, and 1-butene. No ethylene complex was observed in this case.

The monoalkoxide species **3a**, **3c**, and **3d** (5 mol %) catalyze the conversion of 1-hexene to 5-decene in 1 h at 22 °C (90%, 90%, and 45%, respectively) and the ring-closure diallytosylamine to give the expected cyclopentene product after 24 h at 60 °C in 90%, 60%, and 20% yields, respectively. Attmpted ring-closing reactions on selected substrates in CD_2Cl_2 (shown in Table 3) generally were inefficient and low yielding, with the maximum product yield being 88%. Finally, **3b** was found to initiate ROMP polymerization of 2,3-dicarbomethoxynorbornadiene (100 equiv) in 30 min at 22 °C in mixtures of dichloromethane and toluene. The polymer was isolated in 87% yield. Carbon NMR studies indicated that the polymer is ~95% *cis* but not highly tactic.[14]

Table 3. Ring-Closing Reactions with 3b in CD_2Cl_2

entry	substrate	product	mol% cat	time/°C	% conv
1		R = Si(t-Bu)Me$_2$	5	2 d/22	88
2			5	2 d/22	44
3			5	2 d/70	56
4		R = p-methoxyphenyl	5	2 d/70	57

Conclusions

The work described here confirms that cationic imido alkylidene species can be prepared and that they are viable metathesis catalysts. However, at least with the catalysts and substrates that we have examined so far, cationic species do not appear to have any significant advantages over neutral species. In fact it appears that cationic alkylidenes are less stable than neutral species. However it is not yet known whether a lower stability can be ascribed to a bimolecular coupling of alkylidenes, especially methylenes, rearrangement of metalacyclobutanes to olefins, or other decomposition pathways.

(14) (a) McConville, D. H.; Wolf, J. R.; Schrock, R. R. *J. Am. Chem. Soc.* **1993**, *115*, 4413. (b) Bazan, G. C.; Khosravi, E.; Schrock, R. R.; Feast, W. J.; Gibson, V. C.; O'Regan, M. B.; Thomas, J. K.; Davis, W. M. *J. Am. Chem. Soc.* **1990**, *112*, 8378.

Experimental Section

General Comments. Glassware was oven-dried at 175 °C and purged with nitrogen on a dual-manifold Schlenk line or cooled in the evacuated antechamber of a nitrogen-filled glovebox. Experiments were conducted either in a nitrogen drybox or a dual-manifold Schlenk line under dinitrogen. HPLC grade diethyl ether, toluene, pentane, tetrahydrofuran, and methylene chloride were sparged with nitrogen and passed through activated alumina; in addition, benzene was passed through a copper catalyst; organic solvents were then stored over activated 4 Å Linde-type molecular sieves. Methylene chloride-d_2 and benzene-d_6 were sparged with nitrogen and stored over activated 4 Å Linde-type molecular sieves prior to use. NMR spectra were obtained on Varian 300 or 500 MHz spectrometers, reported in δ (parts per million) relative to tetramethylsilane, and referenced to the residual ^{1}H/^{13}C signals of the deuterated solvent (^{1}H (δ): benzene 7.16, methylene chloride 5.32; ^{13}C (δ): benzene 128.39, methylene chloride 54.00). ^{19}F NMR spectra were referenced to an external sample of neat fluorobenzene at δ −113.15 ppm relative to $CFCl_3$. H. Kolbe Microanalytics Laboratory (Mülheim an der Ruhr, Germany) provided the elemental analyses results. $[HNMe_2Ph]BAr^F_4$ was obtained by treating $NaBAr^F_4$ with $[HNMe_2Ph]Cl$ in diethyl ether or dichloromethane. All other reagents were used without further purification unless noted otherwise. $Mo(NR)(CHCMe_2Ph)(NC_4H_4)_2$ and $Mo(NR)(CHCMe_2Ph)(2,5\text{-}Me_2NC_4H_2)_2$ were prepared as described in the literature.[5]

$[Mo(NAr)(CHCMe_2Ph)(NC_4H_4)(THF)_3]BAr^F_4$ (1a). $Mo(NAr)(CHCMe_2Ph)(Pyr)_2$ (0.506 g, 0.945 mmol) was dissolved in 10 mL of THF to give a dark yellow solution, and to this solution was added $[HNMe_2Ph]BAr^F_4$ (0.931 g, 0.945 mmol) as a solid in one portion. The reaction mixture became light yellow immediately and was stirred at room temperature for 45 min. All volatiles were then removed, leaving behind an oil. Pentane was added to the oil, and all volatiles were removed *in vacuo*. This was repeated three more times to yield a yellow solid. The solid was redissolved in a minimum amount of diethyl ether, and pentane (∼5 mL) was layered on top of this solution. A fine yellow crystalline powder was isolated after 24 h at −27 °C; yield = 1.188 g (81%): ^{1}H NMR (500 MHz, CD_2Cl_2) δ 13.93 (s, 1, *syn* $MoCH_\alpha$, $^1J_{CH}$ = 119 Hz), 7.72 (s, 8, *o-H* of BAr^F_4), 7.56 (s, 4, *p-H* of BAr^F_4), 7.30 (m, 8, *Ar-H*), 6.42 (br s, 2, NC_4H_4), 6.12 (t, 2, NC_4H_4), 3.76 (br s, 12, *THF-H*), 3.44 (q, 2, Et_2O), 3.10 (m, 2, $CHMe_2$), 1.98 (br s, 12, *THF-H*), 1.85 (s, 3, $CHCMe_2Ph$), 1.67 (s, 3, $CHCMe_2Ph$), 1.16 (t, 3, Et_2O), 1.13 (d, 6, $CHMe_2$), 1.10 (d, 6, $CHMe_2$); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 322.15 (MoC_α), 162.41 (q, $^1J_{C^{11}B}$ = 50 Hz, *ipso-C* of BAr^F_4), 152.29, 151.61, 147.59, 135.46, 130.92, 129.58, 129.54 (qq, $^2J_{CF}$ = 31 Hz, $^3J_{C^{11}B}$ = 3 Hz, *m*-Ar of BAr^F_4), 127.74, 126.16, 125.3 (q, J_{CF} = 272 Hz, BAr^F_4),125.12, 124.17, 122.01, 118.14 (m, *p*-Ar of BAr^F_4), 110.72, 58.93, 32.06, 30.00, 27.94, 26.20, 25.94, 24.60; ^{19}F NMR (282 MHz, CD_2Cl_2) δ −62.77.

$[Mo(NAr)(CHCMe_2Ph)(Me_2NC_4H_2)(THF)_2]BAr^F_4$ (1b). $Mo(NAr(CHCMe_2Ph)(Me_2Pyr)_2$ (1.667 g, 2.817 mmol) was dissolved in ∼20 mL of THF, and to the red solution was added $[HNMe_2Ph][BAr^F_4]$ (3.053 g, 3.098 mmol) in one portion as a solid. The resulting mixture darkened immediately and was stirred for 30 min at room temperature. All volatiles were then removed *in vacuo* to yield an oil. Pentane was added to the oil, the mixture was stirred for ∼5 min, and the volatiles were removed *in vacuo*. This was repeated once more to yield a red solid, which was then redissolved in a minimum amount of a 1:1 mixture of ether and pentane (∼10 mL). The solution was allowed to stand at −27 °C overnight. A burnt orange crystalline solid was isolated; yield 2.682 g (71%): ^{1}H NMR (500 MHz, CD_2Cl_2) δ 14.23 (s, 1, $MoCH_\alpha$, $^1J_{CH}$ = 128 Hz), 7.72 (s, 8, *o-H* of BAr^F_4), 7.56 (s, 4, *p-H* of BAr^F_4), 7.32 (m, 8, *Ar-H*), 6.31 (br s, 1, $NC_4H_2Me_2$), 5.91 (br s, 1, $NC_4H_2Me_2$), 3.84 (m, 2, *THF-H*), 3.70 (m, 6, *THF-H*), 3.20 (sept, 2, $CHMe_2$), 2.42 (s, 3, *Me*), 2.36 (s, 3, *Me*), 2.02 (m, 6, *THF-H*), 1.83 (m, 2, *THF-H*), 1.81 (s, 3, *Me*), 1.68 (s, 3, *Me*), 1.31 (d, 12, $CHMe_2$); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 325.36 (MoC_α), 162.35 (q, $^1J_{C^{11}B}$ = 50 Hz, *ipso-C* of BAr^F_4), 152.32, 147.45, 145.46, 135.39, 130.70, 129.52, 129.51 (qq, $^2J_{CF}$ = 31 Hz, $^3J_{C^{11}B}$ = 3 Hz, *m*-Ar of BAr^F_4), 127.90, 126.60, 125.55 (q, J_{CF} = 272 Hz, CF_3 of BAr^F_4), 124.81, 118.07 (m, *p*-Ar of BAr^F_4), 107.94, 103.8, 86.08, 68.92, 30.13, 29.93, 28.99, 27.98, 26.10, 25.02, 24.57, 24.19, 18.46, 16.91; ^{19}F NMR (282 MHz, CD_2Cl_2) δ −62.78. Anal. Calcd for $C_{68}H_{65}BF_{24}MoN_2O_2$: C, 54.27; H, 4.35; N, 1.86. Found: C, 54.36; H, 4.39; N, 1.84.

$[Mo(NAr)(CHCMe_2Ph)(Me_2Pyr)(2,4\text{-}Me_2NC_5H_3)]BAr^F_4$ (1c). $[Mo(NAr)(CHCMe_2Ph)(Me_2Pyr)(THF)_2]BAr^F_4$ (0.406 g, 0.270 mmol) was dissolved in CH_2Cl_2 (∼2 mL) to give an orange solution. 2,4-Dimethylpyridine (37 μL, 0.319 mmol, 1.18 equiv) was added via syringe to the orange solution. The mixture was stirred at room temperature for ∼10 min. Volatiles were removed *in vacuo* to yield a yellow foam. Pentane (∼3 mL) was added to the foam, and the mixture was stirred for 10 min. Vacuum was applied to remove the volatiles, leaving behind a yellow powder. The solid was dried *in vacuo* for 2 h; yield 0.371 g (99%): ^{1}H NMR (500 MHz, CD_2Cl_2) δ 13.91 (s, 1, $MoCH_\alpha$), 7.73 (br s, 8, *o-H* of BAr^F_4), 7.57 (s, 4, *p-H* of BAr^F_4), 7.30 (m, 11, *Ar-H*), 6.30 (d, 1, $NC_4H_2Me_2$), 5.92 (d, 1, $NC_4H_2Me_2$), 3.10 (sept, 2, $CHMe_2$), 2.50 (s, 3, *Me*), 2.43 (s, 3, *Me*), 2.33 (s, 3, *Me*), 1.76 (s, 3, *Me*), 1.71 (s, 3, *Me*), 1.57 (s, 3, *Me*), 1.22 (d, 12, $CHMe_2$); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 333.68 (MoC_α), 162.01 (q, $^1J_{C^{11}B}$ = 50 Hz, *ipso-C* of BAr^F_4), 160.99, 158.47, 157.45, 156.97, 155.37, 152.29, 151.99, 149.52, 147.19, 145.17, 142.82, 135.37, 130.37, 129.95, 129.56 (qq, $^2J_{CF}$ = 31 Hz, $^3J_{C^{11}B}$ = 3 Hz, *m*-Ar of BAr^F_4), 129.42, 127.74, 126.84, 126.74, 125.41, 125.16 (q, J_{CF} = 272 Hz, CF_3 of BAr^F_4), 124.96, 118.06 (m, *p*-Ar of BAr^F_4), 106.30, 105.97, 61.66, 30.04, 29.77, 28.91, 28.81, 26.49, 24.99, 24.23, 21.66, 18.85, 15.18; ^{19}F NMR (282 MHz, CD_2Cl_2) δ −62.81. Anal. Calcd for $C_{67}H_{58}BF_{24}MoN_3$: C, 54.82; H, 3.98; N, 2.86. Found: C, 54.76; H, 3.88; N, 2.82.

$Mo(NAr)(CHCMe_2Ph)(MesPyr)_2$ (2). $Mo(NAr)(CHCMe_2Ph)(OTf)_2(DME)$ (0.314 g, 0.397 mmol) and Li(MesPyr)(THF) (0.209 g, 0.794 mmol) were mixed as solids. Diethyl ether (∼4 mL) was added to the mixture of solids, and the resulting red-orange mixture was stirred at room temperature for 2 h. The volatiles were then removed *in vacuo*. Toluene was added to the residue, and the mixture was filtered through Celite in order to remove LiOTf. The filtrate was dried *in vacuo* to give a red oil. The oil was dissolved in a minimum amount of a 1:1 mixture of diethyl either and pentane. The solution was stored at −27 °C overnight, and red-orange blocks were filtered off; yield 0.164 g (54%): ^{1}H NMR (500 MHz, C_6D_6) δ 11.56 (s, 1, $MoCH_\alpha$, J_{CH} = 119.6 Hz), 7.11 (m, 4, *Ar-H*), 6.98 (m, 4, *Ar-H*), 6.81 (s, 2, mesityl-*H*), 6.72 (s, 2, mesityl-*H*), 6.64 (br s, 2, NC_4H_3Mes), 6.30 (t, 2, NC_4H_3Mes, J_{HH} = 2.8 Hz), 6.22 (dd, 2, NC_4H_3Mes, J_{HH} = 2.8 Hz), 3.54 (sept, 2, $CHMe_2$), 2.26 (s, 6, *Me*), 2.22 (s, 6, *Me*), 2.05 (s, 6, *Me*), 1.22 (s, 6, *Me*), 1.22 (d, 12, $CHMe_2$); ^{13}C NMR (125 MHz, C_6D_6) δ 287.54 (MoC_α), 154.18, 148.23, 147.73, 140.74, 140.23, 139.43, 138.04, 134.25, 129.61, 129.26, 128.75, 128.69, 126.80, 126.44, 123.91, 112.10, 110.99, 66.48, 55.64, 31.28 ($CHCMe_2Ph$), 28.26 ($CHMe_2$), 24.90 ($CHMe_2$), 22.11 (*para*-mesityl *Me*), 21.58 (*ortho*-mesityl *Me*), 21.21 (*ortho*-mesityl *Me*), 15.95 ($CHCMe_2Ph$). Anal. Calcd for $C_{48}H_{57}MoN_3$: C, 74.69; H, 7.44; 5.44. Found: C, 74.78; H, 7.41; N, 5.38.

$\{Mo(NAr)(CHCMe_2Ph)[OC(CF_3)_2Me](THF)_3\}BAr^F_4$ (3a). Hexafluoro-*tert*-butanol (134 μL, 1.088 mmol) was added to $\{Mo(NAr)(CHCMe_2Ph)(Pyr)(THF)_3\}BAr^F_4$ (1.285 g, 0.830 mmol) in ∼10 mL of CH_2Cl_2. The reaction mixture was stirred at room temperature for 20 min. All volatiles were removed *in vacuo* to give an oil. To the oil was added ∼7 mL of pentane. The resulting mixture was stirred for 5 min, and vacuum was applied to remove all volatiles. This procedure was repeated once more to give a yellow solid, which was washed with pentane and then dried *in vacuo* for 30 min. The yellow solid was dissolved in a minimum amount of a 1:1 mixture of diethyl ether and pentane (∼8 mL) and

stored at −27 °C overnight. A light yellow powder was isolated and dried *in vacuo* for 1 h; yield 1.139 g (82%): ^{1}H NMR (500 MHz, CD_2Cl_2) δ 14.20 (s, 1, *syn* MoCH_α, $^1J_{CH}$ = 119 Hz), 7.79 (s, 8, *o-H* of BAr^F_4), 7.62 (s, 4, *p-H* of BAr^F_4), 7.37 (m, 8, *Ar-H*), 3.92 (m, 4, *THF-H* and C*H*Me$_2$), 3.71 (m, 10, *THF-H* and C*H*Me$_2$), 1.96 (s, 6, CHC*Me*$_2$Ph), 1.85 (br s, 12, *THF-H*), 1.76 (s, 3, OC(CF$_3$)$_2$*Me*), 1.32 (d, 12, CH*Me*$_2$); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 314.68 (MoC_α), 162.48 (q, $^1J_{C^{11}B}$ = 50 Hz, *ipso-C* of BAr^F_4), 152.05, 147.17, 146.48, 135.51, 131.72, 129.93, 129.61 (qq, $^2J_{CF}$ = 31 Hz, $^3J_{C^{11}B}$ = 3 Hz, *m*-Ar of BAr^F_4), 128.33, 126.26, 125.30 (q, J_{CF} = 272 Hz,), 125.15, 124.34, 118.15 (m, *p*-Ar of BAr^F_4), 80.84, 69.25, 66.32, 56.58, 31.09, 25.97, 24.76, 19.64, 15.70; ^{19}F NMR (282 MHz, CD_2Cl_2) δ −61.84, −77.10. Anal. Calcd for $C_{70}H_{68}BF_{30}MoN_2O_4$: C, 50.53; H, 4.12; N, 0.84. Found: C, 50.42; H, 4.17; N, 0.81.

{Mo(NAr)(CHCMe$_2$Ph)[OC(CF$_3$)$_2$Me](THF)$_2$}BAr$^F_4$ (3b). Hexafluoro-*tert*-butanol (38 μL, 0.310 mmol, 1.2 equiv) was added to {Mo(NAr)(CHCMe$_2$Ph)(Me$_2$Pyr)(THF)$_2$}{BAr^F_4} (0.389 g, 0.259 mmol) in ∼10 mL of CH_2Cl_2. The reaction mixture was stirred at room temperature for 20 min. All volatiles were removed *in vacuo*, leaving behind a foam. To the foam was added ∼7 mL of pentane. The resulting mixture was stirred for 5 min, and all volatiles were then removed *in vacuo*. This procedure was repeated once more to give a yellow solid. The yellow solid was washed with pentane and dried *in vacuo* for 1 h, affording 0.374 g (91%): ^{1}H NMR (500 MHz, CD_2Cl_2) δ 14.05 (s, 1, MoCH_α), 7.72 (s, 8, *o-H* of BAr^F_4), 7.56 (s, 4, *p-H* of BAr^F_4), 7.31 (m, 8, *Ar-H*), 3.90 (m, 4, *THF-H*), 3.65 (m, 6, *THF-H* and C*H*Me$_2$), 1.94 (s, 6, CHC*Me*$_2$Ph), 1.82 (m, 8, *THF-H*), 1.72 (s, 3, OC(CF$_3$)$_2$*Me*), 1.30 (d, 12, CH*Me*$_2$). ^{13}C NMR (125 MHz, CD_2Cl_2) δ 313.24 (MoC_α), 162.36 (q, $^1J_{C^{11}B}$ = 50 Hz, *ipso-C* of BAr^F_4), 151.94, 146.84, 146.37, 135.40, 131.75, 129.89, 129.55 (qq, $^2J_{CF}$ = 31 Hz, $^3J_{C^{11}B}$ = 3 Hz, *m*-Ar of BAr^F_4), 128.28, 126.28, 125.20 (q, J_{CF} = 272 Hz, *C*F$_3$ of BAr^F_4), 125.05, 118.09 (m, *p*-Ar of BAr^F_4), 80.77, 56.25, 31.07, 30.87, 25.89, 24.70, 19.54; ^{19}F NMR (282 MHz, CD_2Cl_2) δ −62.82, −78.19. Anal. Calcd for $C_{66}H_{60}F_{30}MoNO_3$: C, 49.80; H, 3.80; N, 0.88. Found: C, 50.02; H, 4.37; N, 1.44.

[Mo(NAr)(CHCMe$_2$Ph)(O-2,6-*i*-Pr$_2$C$_6$H$_3$)(THF)]BAr$^F_4$ (3c). The same procedure employed for the synthesis of {Mo(NAr)(CHCMe$_2$Ph)[OC(CF$_3$)$_2$Me](THF)$_3$}BAr^F_4 was employed for **3c** starting with [Mo(NAr)(CHCMe$_2$Ph)(Me$_2$Pyr)(THF)$_2$]BAr^F_4. After letting the reaction mixture stir for 20 min at room temperature, all volatiles were removed *in vacuo* to yield a red oil. To the red oil was added ∼5 mL of pentane. The mixture was stirred for 5 min, and all volatiles were removed *in vacuo*. The procedure was repeated once more to give a red solid. The red solid was added to ∼5 mL of pentane. The product was filtered off and dried *in vacuo* for 30 min; crude yield 90% (on a scale with a theoretical yield of 0.188 g): ^{1}H NMR (500 MHz, CD_2Cl_2) δ 14.73 (s, 1, MoCH_α), 7.72 (br s, 8, *o-H* of BAr^F_4), 7.56 (s, 4, *p-H* of BAr^F_4), 7.31 (m, 11, *Ar-H*), 3.77 (m, 8, C*H*Me$_2$ and THF), 1.96 (s, 3, *Me*), 1.82 (m, 7, *Me* and THF), 1.31 (br d, 24, CH*Me*$_2$); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 312.74 (MoC_α), 162.45 (q, $^1J_{C^{11}B}$ = 50 Hz, *ipso-C* of BAr^F_4), 158.78, 151.58, 147.27, 146.92, 141.40, 138.05, 137.28, 135.45 (br s, *o*-Ar of BAr^F_4), 132.10, 130.65, 129.78, 129.52 (qq, $^2J_{CF}$ = 31 Hz, $^3J_{C^{11}B}$ = 3 Hz, *m*-Ar of BAr^F_4), 128.19, 126.09, 125.23 (q, J_{CF} = 272 Hz, BAr^F_4-*C*F$_3$), 125.22, 124.87, 124.73, 123.15, 119.88, 118.15 (m, *p*-Ar of BAr^F_4), 79.66, 66.62, 56.46, 48.29, 34.76, 31.18, 30.06, 28.24, 25.93, 25.05, 24.45, 24.27, 24.10, 23.54, 22.97, 15.49, 14.42; ^{19}F NMR (282 MHz, CD_2Cl_2) δ −62.78. When ∼50 mg of the red powder was dissolved in minimum amount of diethyl ether and pentane was vapor diffused into the ether solution at −27 °C for one week, a few flakes of crystalline material (less than 10% of the mixture) in the oily mixture was characterized by single-crystal X-ray crystallography to be {Mo(NAr)(CH$_2$CMe$_2$Ph)(O-2,6-*i*-Pr$_2$C$_6$H$_3$)$_2$}BAr^F_4. Elemental analyses of crude **3c** were not satisfactory since it could not be purified by recrystallization without decomposing.

[Mo(NAr)(CHCMe$_2$Ph)(OAd)(THF)$_2$]BAr$^F_4$ (3d). The same procedure employed for the synthesis of {Mo(NAr)(CHCMe$_2$Ph)-[OC(CF$_3$)$_2$Me](THF)$_3$}BAr^F_4 was employed starting with [Mo(NAr)(CHCMe$_2$Ph)(Pyr)(THF)$_3$]BAr^F_4. The crude yield was 88% (theory = 0.275 g): ^{1}H NMR (500 MHz, CD_2Cl_2) δ 15.07 (s, 0.3, MoCH_α), 14.52 (s, 0.7, MoCH_α), 7.72 (br s, 8, *o-H* of BAr^F_4), 7.56 (s, 4, *p-H* of BAr^F_4), 7.35 (m, 8, *Ar-H*), 3.75 (m, 10, C*H*Me$_2$ and THF), 2.26 (s, 3, *Me*), 1.82 (m, 25, adamantyl and THF), 1.34 (d, 6, CH*Me*$_2$, J_{HH} = 6.9 Hz), 1.29 (d, 6, J_{HH} = 6.9 Hz); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 328.02 (MoC_α), minor MoC_α could not be detected, 162.43 (q, $^1J_{C^{11}B}$ = 50 Hz, *ipso-C* of BAr^F_4), 148.34, 146.88, 135.38, 133.36, 130.12, 129.55 (qq, $^2J_{CF}$ = 31 Hz, $^3J_{C^{11}B}$ = 3 Hz, *m*-Ar of BAr^F_4), 128.56, 128.35, 126.63, 125.18 (q, J_{CF} = 272 Hz, *C*F$_3$ of BAr^F_4), 124.74, 118.07 (m, *p*-Ar of BAr^F_4), 98.99, 87.16, 79.51, 46.23, 35.51, 32.40, 32.11, 29.83, 25.97, 24.59, 23.76; ^{19}F NMR (282 MHz, CD_2Cl_2) δ −62.80. Compound **3d** decomposed to a significant degree upon attempted recrystallization. However, a sample of the crude material (before recrystallization) did survive in the solid state and analyzed satisfactorily. Anal. Calcd for $C_{72}H_{72}BF_{24}MoNO_3$: C, 55.36; H, 4.65; N, 0.90. Found: C, 55.08; H, 5.13; N, 1.12.

[Mo(NAr)(CH$_2$CMe$_2$Ph)(O-2,6-*i*-Pr$_2$C$_6$H$_3$)$_2$]BAr$^F_4$ (4). [Mo-(NAr)(CHCMe$_2$Ph)(Me$_2$Pyr)(THF)$_2$]BAr^F_4 (0.477 g, 0.317 mmol) was dissolved in 2 mL of CH_2Cl_2 to give a red solution. 2,6-Diisopropylphenol (123 μL, 0.666 mmol) was added via syringe to the solution in one portion at room temperature, and the mixture was stirred at room temperature overnight. Removal of all volatiles from the mixture *in vacuo* gave a red oil. A proton NMR spectrum of the oil showed it to be largely **4**. Methylene chloride (∼1 mL) and a few drops of benzene were added to the oil. The mixture was allowed to sit at −27 °C. Over the course of 2 weeks, three crops of red crystals were collected, affording a total yield of 0.152 g (29%): ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.80 (d, 2, *Ar-H*), 7.75 (br s, 8, *o-H* of BAr^F_4), 7.57 (br s, 4, *p-H* of BAr^F_4), 7.54 (t, 2, *Ar-H*), 7.42 (t, 1, *Ar-H*), 7.16 (m, 9, *Ar-H*), 4.06 (s, 2, C*H*$_2$CMe$_2$Ph), 2.98 (sept, 4, C*H*Me$_2$), 2.86 (sept, 2, C*H*Me$_2$), 1.77 (s, 6, CH$_2$C*Me*$_2$Ph), 1.26 (d, 12, CH*Me*$_2$, J_{HH} = 6.5 Hz), 1.07 (d, 12, CH*Me*$_2$, J_{HH} = 6.5 Hz), 0.95 (d, 12, CH*Me*$_2$, J_{HH} = 6.5 Hz); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 162.48 (q, $^1J_{C^{11}B}$ = 50 Hz, *ipso-C* of BAr^F_4), 161.93, 155.33, 148.55, 144.73, 138.06, 135.38 (br s, *o*-Ar of BAr^F_4), 134.07, 131.42, 130.45, 129.45 (qq, $^2J_{CF}$ = 31 Hz, $^3J_{C^{11}B}$ = 3 Hz, *m*-Ar of BAr^F_4), 129.23, 126.83, 125.18 (q, J_{CF} = 272 Hz, BAr^F_4-*C*F$_3$), 125.17, 124.62, 118.06 (m, *p*-Ar of BAr^F_4), 95.76 (s, MoC_α), 41.47 (CH$_2$*C*Me$_2$Ph), 31.35 (*C*HMe$_2$), 31.20 (CH$_2$C*Me*$_2$Ph), 28.17 (*C*HMe$_2$), 24.42 (CH*Me*$_2$), 24.08 (CH*Me*$_2$), 23.48 (CH*Me*$_2$); ^{19}F NMR (282 MHz, CD_2Cl_2) δ −62.80. Anal. Calcd for $C_{78}H_{76}BF_{24}MoNO_2$: C, 57.75; H, 4.72; N, 0.86. Found: C, 57.84; H, 4.67; N, 0.87.

[Mo(NAr)(CH$_2$CMe$_2$Ph)(*rac*-BIPHEN)]BAr$^F_4$ (5). {Mo(NAr)-(CHCMe$_2$Ph)(Pyr)(THF)$_3$}BAr^F_4 (0.191 g, 0.124 mmol) and *rac*-BIPHEN-H$_2$ (3,3′-di-*tert*-butyl-5,5′,6,6′-tetramethylbiphenyl-2,2′-diol) (0.044 g, 0.124 mmol) were mixed together as solids. Dichloromethane (5 mL) was added at room temperature, and the red mixture was stirred overnight. The mixture was concentrated *in vacuo*, and pentane was added to the residue. The mixture was stored at −27 °C for one week. Red needle-like crystals were isolated; yield 0.160 g (80%): ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.76 (s, 8, *o-H* of BAr^F_4), 7.57 (s, 4, *p-H* of BAr^F_4), 7.24 (m, 10, *Ar-H*), 4.95 (d, 1, C*H*$_2$CMe$_2$Ph, $^2J_{HH}$ = 12 Hz), 2.92 (sept, 2, C*H*Me$_2$), 2.53 (s, 3, *Me*), 2.39 (d, 1, C*H*$_2$CMe$_2$Ph, $^2J_{HH}$ = 12 Hz), 2.22 (s, 3, *Me*), 1.69 (s, 3, *Me*), 1.49 (s, 3, *Me*), 1.46 (s, 9, C*Me*$_3$), 1.41 (s, 3, *Me*), 1.22 (s, 3, *Me*), 1.17 (d, 6, CH*Me*$_2$), 1.13 (s, 9, C*Me*$_3$), 1.06 (d, 6, CH*Me*$_2$); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 162.32 (q, $^1J_{C^{11}B}$ = 49 Hz, *ipso-C* of BAr^F_4), 155.82, 152.58, 149.29, 145.86, 144.70, 142.60, 140.07, 139.29, 138.91, 138.22, 135.72, 135.37, 133.99,

133.26, 130.44, 129.52 (qq, $^2J_{CF} = 31$ Hz, $^3J_{C^{11}B} = 3$ Hz, *m*-Ar of $BAr^F{}_4$), 128.51, 125.82, 125.24 (q, $J_{CF} = 272$ Hz, CF_3 of $BAr^F{}_4$), 125.04, 124.48, 118.05 (m, *p*-Ar of $BAr^F{}_4$), 101.25, 66.41, 43.99, 36.32, 35.40, 32.24, 30.63, 30.57, 30.56, 24.58, 24.54, 22.93, 21.14, 20.86, 17.27, 16.09, 15.52, 14.40; ^{19}F NMR (282 MHz, CD_2Cl_2) δ −62.79. Anal. Calcd for $C_{78}H_{74}BF_{24}MoNO_2$: C, 57.82; H, 4.60; N, 0.86. Found: C, 57.91; H, 4.68; N, 0.90.

{Mo(NAr)(C_2H_4)[OC(CF_3)$_2$Me](THF)$_3$}$BAr^F{}_4$ (6). {Mo(NAr)(CHCMe$_2$Ph)[OC(CF_3)$_2$Me](THF)$_3$}$BAr^F{}_4$ (0.232 g, 0.139 mmol) was dissolved in ∼10 mL of CH_2Cl_2 in a 25 mL Schlenk flask. After three freeze/pump/thaw cycles the reaction mixture was exposed to 1 atm of ethylene at room temperature. The mixture darkened slightly. The mixture was then stirred for 3 h at room temperature. The volume was reduced to ∼5 mL *in vacuo*. Pentane (∼7 mL) was layered on top of the mixture, and the reaction was stored for 2 days at −27 °C. The yellow crystals were isolated by removing the supernatant and drying the crystals *in vacuo* for 2 h; yield 0.198 g (91%): ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.75 (s, 8, *o-H* of $BAr^F{}_4$), 7.59 (s, 4, *p-H* of $BAr^F{}_4$), 7.23 (m, 3, *Ar-H*), 4.05 (br s, 12, *THF-H*), 3.24 (sept, 2, C*H*Me$_2$), 3.08 (m, 2, C_2H_4), 2.62 (m, 2, C_2H_4), 2.00 (br s, 12, *THF-H*), 1.64 (s, 3, OC(CF_3)$_2$*Me*), 1.27 (d, 12, CH*Me*$_2$); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 162.36 (q, $^1J_{C^{11}B} = 50$ Hz, *ipso-C* of $BAr^F{}_4$), 152.93, 148.28, 135.40, 130.83, 131.72, 129.47 (qq, $^2J_{CF} = 29$ Hz, *m*-Ar of $BAr^F{}_4$), 125.20 (q, $J_{CF} = 272$ Hz, CF_3 of $BAr^F{}_4$), 125.00, 124.04 (q, $J_{CF} = 289$ Hz, CF_3 of OCMe(CF_3)$_2$), 118.08 (m, *p*-Ar of $BAr^F{}_4$), 77.20 (O*C*H$_4$CH$_4$, THF), 63.24 (Mo*C*$_2$H$_2$), 30.17 (OCH$_4$*C*H$_4$, THF), 25.87 (*C*HMe$_2$), 24.71 (CH*Me*$_2$), 19.34 (OC*Me*(CF_3)$_2$); ^{13}C NMR (125 MHz, BrC_6D_5) showed the Mo*C*$_2$H$_4$ at 63.47 with $J_{CH} = 152$ Hz; ^{19}F NMR (282 MHz, CD_2Cl_2) δ −62.81, −78.18. Anal. Calcd for $C_{62}H_{60}BF_{30}MoNO_4$: C, 47.74; H, 3.88; N, 0.90. Found: C, 47.64; H, 3.85; N, 0.88.

Polymerization of 2,3-Dicarbomethoxynorbornadiene. {Mo(NAr)(CHCMe$_2$Ph)[OC(CF_3)$_2$Me](THF)$_2$}$BAr^F{}_4$ (**3b**) (0.033 g, 0.020 mmol) was dissolved in ∼0.5 mL of CH_2Cl_2. The substrate (0.429 g, 2.060 mmol) in 5 mL of toluene was added dropwise to a stirred solution of metal complex at room temperature. The vial was rinsed with toluene (5 mL), and the contents were added to the mixture. The mixture was stirred for 30 min. Benzaldehyde (25 μL) was added to the mixture, which was then stirred for 30 min. The mixture was added dropwise to 75 mL of hexane while stirring the solvent vigorously. A white, gooey material was isolated, and the yellow solvent was discarded. The white material was dissolved in hot THF, and the mixture was added dropwise to another 75 mL of stirred hexane. White, fluffy material precipitated out and was filtered off and dried *in vacuo* for 3 h; yield 0.374 g (87%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.41 (br, =CH), 3.95 (br, methine), 3.75 (s, CO_2*Me*), 2.52 (br, CH*H*), 1.44 (br, (br, C*H*H)); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.41 (*C*O$_2$Me), 142.43 (=*C*CO$_2$Me), 131.61 (CH), 52.25 (CO$_2$*Me*), 44.37 (=*C*H), 38.89 (*C*H$_2$).

General Procedure for Reactions Involving Olefins. About 20 to 30 μmol of alkylidene complex was added to a J-Young NMR tube along with ∼0.6 mL of CD_2Cl_2. In the case of 1-hexene, the substrate was then added to the solution via microsyringe. In the case of ethylene, the solution of the alkylidene complex was degassed by three successive freeze−pump−thaw cycles and then exposed to 1 atm of the gas. In the case of ^{13}C-ethylene, the solution of the alkylidene complex was degassed by three successive freeze−pump−thaw cycles and then the frozen solution was exposed to ∼300 mmHg of the gas. In the case of 1-hexene, diallyltosylamine, and the substrates in Table 3, the substrates were weighed out in a 2 mL vial and CD_2Cl_2 (∼0.4 mL) was added. Then the catalyst was added to the vial in one portion as a solid. The contents were then mixed by slurping the mixture with a pipet and then transferred to a Teflon capped J-Young tube. The vial was then rinsed with ∼0.3 mL of CD_2Cl_2, and the rinse was transferred to the J-Young tube. Spectra were immediately recorded (10−15 min after addition of olefin) at ∼20 °C, but additional spectra were collected over time as needed.

Crystallographic Details. 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 and refined against F^2 on all data by full-matrix least-squares with SHELXL-97. All non-hydrogen atoms were refined anisotropically. Coordinates for the hydrogen atoms on C_α of the alkylidene or alkyl groups were taken from the difference Fourier synthesis and subsequently refined semifreely with the help of distance restraints. All other hydrogen atoms were included in 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).

Compound **1a** crystallizes in the monoclinic space group $P2_1/n$ with one molecule of **1a**, one $[B(Ar^F)_4]^-$ counterion, and half a molecule of diethyl ether per asymmetric unit. Most of the CF_3 groups in the anion were disordered; five of these disorders could be resolved. The solvent molecule is disordered over four positions, two of which are generated from the other two by the crystallographic inversion center. This disorder results in a noninteger value for oxygen in the empirical formula.

Compound **1d** crystallizes in the monoclinic space group $P2_1/n$ with two molecules of **1d** and two $[B(Ar^F)_4]^-$ counterions per asymmetric unit. Most of the CF_3 groups in the $[B(Ar^F)_4]^-$ ions are disordered; nine of these disorders could be resolved.

Compound **3a** crystallizes in the monoclinic space group $P2_1/n$ with one molecule of **3a** and one $[B(Ar^F)_4]^-$ counterion per asymmetric unit. The OCMe(CF_3)$_2$ ligand shows 2-fold disorder corresponding to a rotation about the O−C bond. In addition, two of the THF molecules show well-behaved disorder of two of their carbon positions, and most of the CF_3 groups in the $[B(Ar^F)_4]^-$ ion are disordered; three of these CF_3 disorders could be resolved.

Compound **4** crystallizes in the monoclinic space group $P2_1/m$ with 1.5 molecules of **4** and 1.5 $[B(Ar^F)_4]^-$ counterions per asymmetric unit. The refinement of this structure was particularly challenging, and the quality of the model is not as good as that of the other structures (for refinement and data quality statistics see Tables 1 and 2). One of the two crystallographically independent molecules of each species found in the structure is comparatively well behaved, while the other one is strongly affected by uncommonly complicated disorders. The complete second molecule of **4** is spread over four positions (all atoms), two of which are generated from the other two by the crystallographic mirror, while all atoms of the disordered $[B(Ar^F)_4]^-$ ion are disordered over two positions, also involving the crystallographic mirror. The close proximity of the two heavily disordered molecules to crystallographic symmetry elements results in an effective occupancy of 50% in the asymmetric unit for those atoms, and the second halves of the molecules are generated by the respective symmetry operator. Another consequence of this arrangement is the rather unusual value of $Z = 6$ for this space group. Parametrization of additionally disordered CF_3 groups in the otherwise well-behaved $[B(Ar^F)_4]^-$ ion were trivial when compared to the refinement of the two half-occupied molecules. The quality of the data set on which the structure of compound **4** is based is altogether only mediocre, and it was not possible to locate the two hydrogen atoms on the C_α of either the Mo-alkyl groups in the difference Fourier synthesis. The Mo−C_α as well as the C_α−C_β bond lengths, however, allow us to infer that the C_α must carry two hydrogen atoms. Thus the hydrogen atoms were included at their calculated positions for all three crystallographically independent C_α and refined using a riding model. Bond

lengths and angles between atoms of the heavily disordered molecules are significantly less well determined than those between the corresponding atoms of the well-behaved ones. Therefore, whenever in this paper bond distances and angles are quoted for the structure of compound **4**, those of the well-behaved molecules are used.

Compound **6** crystallizes in the triclinic space group *P* with one molecule of **7**, one $[B(Ar^F)_4]^-$ counterion, and one 3-fold disordered molecule of pentane per asymmetric unit. Disorders of both CF_3 groups in the molecule of **6** and six of the eight CF_3 groups in the $[B(Ar^F)_4]^-$ ion could be resolved.

All disorders were refined with the help of similarity restraints on 1−2 and 1−3 distances and displacement parameters as well as rigid bond restraints for anisotropic displacement parameters. Occupancy ratios were refined freely, while constraining the sum of occupancies of all components of any given disorder to unity. In the case of the disorders in the structure of compound **4**, some of the disordered phenyl rings were constrained to assume the shape of perfect hexagons and planarity restraints were applied to all aromatic systems in the disordered molecules. In addition, the anisotropic displacement ellipsoids of all fluorine atoms in the heavily disordered molecule of compound **4** were restrained to assume approximately spherical shape within a standard uncertainty of 0.2 $Å^2$ (applied to the U^{ij} terms of the anisotropic displacement tensor).

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Supporting Information Available: 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** (07011), **1c** (07164), **2** (07178), **3a** (07005), **4** (07170), and **6** (07029) are also available to the public at http://reciprocal.mit.edu.

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