Synthesis of Cationic Molybdenum Imido 2-Adamantylidene Complexes from Bispyrrolides via Cationic Pyrrolenine Complexes

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ABSTRACT: Mo(N-*t*-Bu)(Adene)(Me_2Pyr)$_2$ (**2a**) (Adene = 2-Adamantylidene, Me_2Pyr = 2,5-dimethylpyrrolide) and Mo(NAr)(Adene)(Me_2Pyr)$_2$ (**2b**) (Ar = 2,6-diisopropylphenyl) were prepared through addition of $LiMe_2Pyr$ to Mo(N-*t*-Bu)(Adene)(Triflate)$_2$(dme) and Mo(NAr)(Adene)(Triflate)$_2$(dme) complexes, respectively. Addition of one equivalent of [Me_2PhNH][BAr^F_4] (Ar^F = 3,5-$(CF_3)_2C_6H_3$) and more than two equivalents of pivalonitrile to Mo(NC_6F_5)(Adene)(Me_2Pyr)$_2$, followed by one equivalent of HMTOH (2,6-$Mesityl_2C_6H_3OH$), led to isolation of yellow crystalline Mo(NC_6F_5)(Adene)(OHMT)(Piv)$_2$(BAr^F_4) (**3**; Piv = pivalonitrile). Reactions analogous to that for **3** were found to produce Mo(NC_6F_5)(Adene)[$OC(CF_3)_3$](Piv)$_2$(BAr^F_4) **(4)**, Mo(NC_6F_5)(Adene)(OHMT)($Ph^{F6}CN$)$_2$(BAr^F_4) **(5**; $Ph^{F6}CN$ = 3,5-$(CF_3)_2C_6H_3CN$ **)**, Mo(NAr)(Adene)(OHMT)($Ph^{F6}CN$)$_2$(BAr^F_4) **(6)**, Mo(NAr)(Adene)[$OC(CF_3)_3$](Piv)$_2$(BAr^F_4) **(7)**, and Mo(N-*t*-Bu)(Adene)(OHMT)($Ph^{F6}CN$)$_2$(BAr^F_4) **(8)**. Compounds **3**, **6**, and **7** were found to have basically square pyramidal structures with *trans* nitriles in two basal positions. The bisnitrile complexes are active metathesis catalysts in the presence of one equivalent of $B(C_6F_5)_3$, consistent with the 14e mononitrile cationic complexes being the active species. The 14e complex required for metathesis is accessed most readily in bis $Ph^{F6}CN$ complexes.

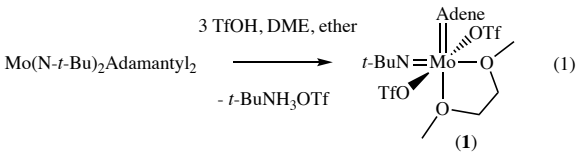
INTRODUCTION

Although relatively few high oxidation state cationic alkylidene complexes have been reported compared with neutral complexes,[1,2] the number has increased through recent studies in which an NHC (N-heterocyclic carbene) is present. The NHC provides steric bulk and has been shown for selected complexes through DFT calculations and Moessbauer spectroscopy to stabilize a cation for electronic reasons.[3] The traditional approach to the synthesis of cations is to generate the cation in the last step through removal of an anionic ligand. In 2007[2a] it was reported that the bispyrrolide complexes W(NAr)($CHCMe_2Ph$)(η^1-Me_2Pyr)(η^5-Me_2Pyr) and W(NAr_{Cl})($CHCMe_3$)(η^1-Me_2Pyr)(η^5-Me_2Pyr) (Ar = 2,6-diisopropylphenyl, Ar_{Cl} = 2,6-dichlorophenyl) react with [$PhMe_2NH$][BAr^F_4] (Ar^F = 3,5-$(CF_3)_2C_6H_3$) in dichloromethane to yield cationic species that contain one η^5-Me_2Pyr ligand and one 2,5-dimethylpyrrolenine ligand formed through addition of a proton to a Me_2Pyr ligand, *e.g.*, [W(NAr_{Cl})($CHCMe_3$)(Me_2Pyr){$NC_4(H_3$-2,3,4)(Me_2-2,5)}]BAr^F_4. Analogous syntheses of Mo complexes[2b] showed that [Mo(NAr)($CHCMe_2Ph$)(Pyrrolide)$(THF)_x$]BAr^F_4 species could be isolated and characterized. Other isolated complexes included [Mo(NAr)($CHCMe_2Ph$)(Me_2Pyr)(2,4-lutidine)]BAr^F_4, {Mo(NAr)($CHCMe_2Ph$)[$OC(CF_3)_2Me$]$(THF)_3$}BAr^F_4, and {Mo(NAr)($CHCMe_2Ph$)[$OCMe(CF_3)_2$]$(THF)_2$}BAr^F_4. The THF adducts were found to be relatively poor metathesis initiators as a consequence of THF coordination. The advantage of this "pyrrolenine route" to cations is that when the sterically demanding pyrrolenine dissociates or is displaced from the cationic center it isomerizes to 2,5-dimethylpyrrole rapidly and essentially irreversibly. Therefore the cation is prepared early in the synthesis and further chemistry can be explored in the cationic realm, in particular chemistry having to do with proton movement within the primary coordination sphere. An example of proton mobility in the primary coordination sphere is treatment of [Mo(NAr)($CHCMe_2Ph$)(Me_2Pyr)$(THF)_2$]BAr^F_4 with two equivalents of 2,6-diisopropylphenol to give [Mo(NAr)(CH_2CMe_2Ph)(O-2,6-*i*-$Pr_2C_6H_3)_2$]BAr^F_4, a rare example of a Mo(VI) cationic alkyl complex.[2b]

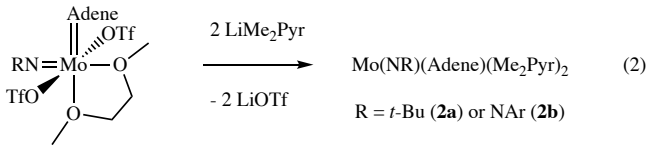
In this paper we report the synthesis of cationic Mo imido 2-adamantylidene complexes via the pyrrolenine route. Adamantylidene complexes[4,5] were chosen over Mo=CHR complexes[1] (R = *t*-Bu or CMe_2Ph) in order to eliminate any possible formation of alkylidyne complexes through loss of an alkylidene α proton.

Results and Discussion

Mo(N-*t*-Bu)(Adene)$(OTf)_2$(DME) (**1**) was prepared through a standard method of inducing α hydrogen abstraction to give an alkylidene, namely addition of three equivalents of triflic acid to Mo(N-*t*-$Bu)_2$(2-Adamantyl)$_2$ in the presence of dimethoxyethane (equation 1). Mo(NAr)(Adene)$(OTf)_2$(DME)[4a] and Mo(NC_6F_5)(Adene)$(OTf)_2$(DME)[4b] have already been prepared in this manner. As is usually the case for bistriflate complexes of this type, two isomers are observed, one that contains *trans* triflates and one that contains *cis* triflates. The chemical shift for the Adene α carbon atoms are 357.7 ppm (minor isomer) and 348.7 ppm (major isomer) in the (sharp) ^{13}C NMR spectrum of **1**. The resonances in the proton NMR spectrum

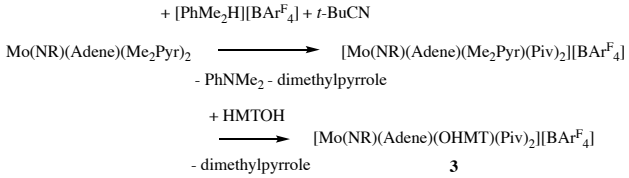


of **1** in CD_2Cl_2 are relatively broad, but at -40 °C sharp resonances are observed in the proton NMR spectrum in CD_2Cl_2 for two isomers in a ratio of approximately 3:1, consistent with interconversion of the two isomers on the proton NMR time scale as a consequence of dissociation of dme at room temperature.



Mo(N-*t*-Bu)(Adene)$(Me_2Pyr)_2$ (**2a**) and Mo(NAr)(Adene)$(Me_2Pyr)_2$ (**2b**) were prepared through addition of $LiMe_2Pyr$ to the bistriflates (equation 2), as reported for Mo(NC_6F_5)(Adene)$(Me_2Pyr)_2$.[4b] An X-ray structure of Mo(NC_6F_5)(Adene)$(Me_2Pyr)_2$ showed that it contains one η^1 and one η^5-dimethyl pyrrolide. Compound **2a** also appears to be a single isomer, according to NMR spectra, presumably with a structure analogous to that of Mo(NC_6F_5)(Adene)$(Me_2Pyr)_2$. In contrast, NMR spectra of **2b** suggest that it is a mixture of two isomers in a ratio of ~3:1. The alkylidene α carbon resonances in **2b** are found at 336.1 and 334.3 ppm. We propose that the **2b** isomers are the η^1,η^5-bisdimethyl pyrrolide complex and the η^1,η^1-bisdimethyl pyrrolide complex. Examples of both types have been published.[2,5,6]

The addition of one equivalent of $[Me_2PhNH][BAr^F_4]$ and more than two (usually ~5) equivalents of pivalonitrile (Piv) to Mo(NC_6F_5)(Adene)$(Me_2Pyr)_2$, followed after some time (~3h) by one equivalent of HMTOH, led to formation and isolation of yellow crystalline Mo(NC_6F_5)(Adene)(OHMT)$(Piv)_2(BAr^F_4)$ (**3**) in 82% yield. NMR studies suggest that Mo(NC_6F_5)(Adene)$(Me_2Pyr)(Piv)_2(BAr^F_4)$ is formed in the first stage, while the second pyrrolide is protonated and substituted by OHMT in the second stage (Scheme 1). The second protonation with HMTOH seems likely to consist of coordination of HMTOH through O, then movement of the proton from O to a pyrrolide ligand to give a pyrrolenine, followed by dissociation and isomerization of it to dimethylpyrrole.



Scheme 1. Synthesis of [Mo(NC_6F_5)(Adene)(OHMT)$(Piv)_2$][BAr^F_4].

A structural study of **3** revealed the cation to be a square pyramid with the adamantylidene ligand at the apex (Figure 1) and with Mo=C = 1.913(3) and M-C_α-C_β angles that differ by 11.4 ° (Table 1). The Mo-N(nitrile) distances are 2.163(3) and 2.152(3). Other distances and angles (see SI) are similar to what has been found for other cationic nitrile complexes of this general type.[3,7]

Reactions analogous to that just described for **3** were found to yield Mo(NC_6F_5)(Adene)[$OC(CF_3)_3$]$(Piv)_2(BAr^F_4)$ **(4)**, Mo(NC_6F_5)(Adene)(OHMT)$(Ph^{F6}CN)_2(BAr^F_4)$ **(5**; $Ph^{F6}CN$ = 3,5-$(CF_3)_2C_6H_3CN$ **)**, Mo(NAr)(Adene)(OHMT)$(Ph^{F6}CN)_2(BAr^F_4)$ **(6)**, Mo(NAr)(Adene)[$OC(CF_3)_3$]$(Piv)_2(BAr^F_4)$ **(7)**, Mo(N-*t*-Bu)(Adene)(OHMT)$(Ph^{F6}CN)_2(BAr^F_4)$ **(8)**. Compounds **6** and **7** were found to have structures analogous to that of **3** (Figures 2 and 3), *i.e.*, square pyramids with *trans* nitriles in two basal positions. Comparison of Mo(Adene) bond distances can be found in Table 1. The differences in the Mo-C_α-C_β angles in **3**, **6**, and **7** are similar to what has been found in other 16e Adene complexes.[4,5]

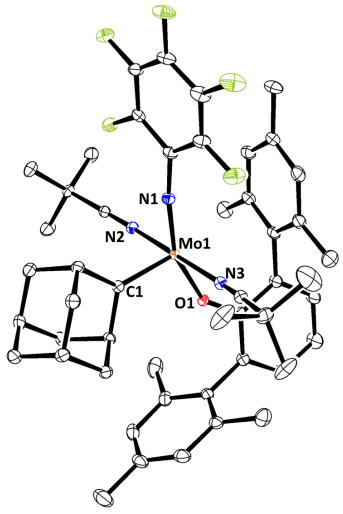


Figure 1. A thermal ellipsoid plot (30%) of the cation in **3** (τ = 0.35).

Table 1. Comparisons of Mo(Adene) Bond Lengths and Angles

	M=C_α (Å)	M-C_α-$C_{\beta1}$(°)	M-C_α-$C_{\beta2}$(°)	Δ(°)	δ C_α
3	1.913(3)	129.3(2)	117.9(2)	11.4	374.1
6	1.9216(15)	130.25(11)	117.85(10)	12.4	377.9
7	1.905(3)	132.1(4)	115.0(4)	17.1	365.6

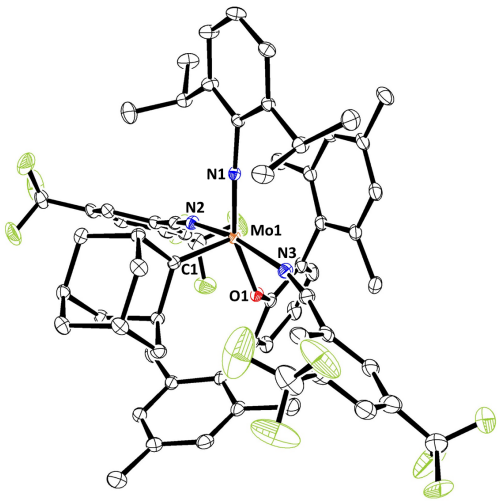


Figure 2. A thermal ellipsoid plot (30%) of the cation in **6** (τ = 0.14).

Addition of $[HNMe_2Ph][BAr^F{}_4]$ to $Mo(NC_6F_5)(Adene)(Me_2Pyr)_2$ in CH_2Cl_2 in the presence of N,N-dimethylaniline led to what appears to be rapid decomposition. No products analogous to those described here were observed in similar scouting experiments with pyridine, 2, 4-dimethylpyridine, quinuclidine, dimethylphenylphosphine, or DME as donor ligands. All efforts to isolate a 14e mononitrile adduct, either through limiting the amount of nitrile present or scavenging one of the nitriles from an isolated bisnitrile complex with $B(C_6F_5)_3$, have failed so far.

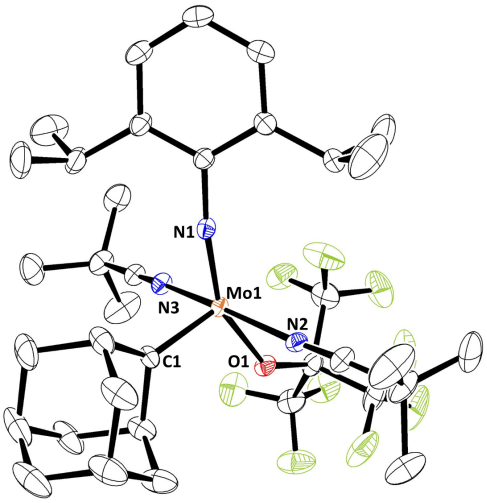


Figure 3. A thermal ellipsoid plot (30%) of the cation in **7** (τ = 0.25).

Acetonitrile has been found to be useful for isolating and purifying four-coordinate 14e Mo or W alkylidene complexes that are exceedingly soluble in pentane (with which MeCN is not miscible) or diethyl ether, usually through formation of a more readily-crystallized and purified five-coordinate 16e adduct.[8] An advantage of acetonitrile is that it often can be removed *in vacuo* from even a solid sample, and thereby can serve as a means of isolating and purifying a highly soluble four-coordinate compound. A potential complication is insertion of acetonitrile into the M=C bond to yield a vinylimido ligand,[7,9] although an insertion of that type has not been published for Mo compounds of the type described here. Insertion is much less likely in the case of pivalonitrile (for steric reasons).[9b] Pivalonitrile has seen increased use in the last several years in Mo and W alkylidene chemistry.[3,4b,7] Nitriles are more weakly bound and sterically not as demanding near the metal as phosphine or pyridine ligands. The advantage of $Ph^{F6}CN$ is its greater lability. For example, in the ^{19}F NMR spectrum of **7** in the presence of $B(C_6F_5)_3$, resonances were observed at 62.84 ppm and 70.40 ppm for the 4-coordinate complex and 134.93-164.93 ppm for $Ph^{F6}CN(B(C_6F_5)_3)$; unfortunately, the pure 4-coordinate complex could not be crystallized from the mixture and isolated in pure form.

A preliminary examination of metathesis activity for the homocoupling of 1-decene (2.5% catalyst) in dichloromethane by **3** – **6** showed that only **5** and **6** were modestly active (91% and 61% complete in 24 h) to give a mixture of *cis* and *trans* 9-octadecene (see SI). At 1% catalyst loading the yield of octadecene was 71% and 36% after three days, respectively. In the presence of 1% catalyst and one equivalent of $B(C_6F_5)_3$, however, all were relatively active, yielding 70-98% *cis* and *trans* octadecene in one hour. All were active for the polymerization of cyclooctene, but **3** – **7** were by far the most active (complete in <15 min) for polymerization of cyclooctene in the presence of one equivalent of $B(C_6F_5)_3$ (see SI). Polymerizations by **3** and **5** were complete in minutes at catalyst loadings of 0.1 % or lower. For 0.1 mol% **3**, polymerization was complete in 5 minutes; at 0.01 mol% loading it was 52% complete within 24 h. For 0.01 mol% **5**, polymerization was complete in 5 minutes. 2,3-Dicarbomethoxynorbornadiene could also be polymerized, but readily by 1% catalyst only in the presence of $B(C_6F_5)_3$. For **3** and **5** the reaction was complete in 5 minutes to give essentially all *cis* polymer with 84% to 97% syndiotacticity, respectively. All of the above experiments suggest that one nitrile must be lost from the bisnitrile initiator in order to generate the reactive 14e initiator, a process that is facilitated through capture of a dissociated nitrile with $B(C_6F_5)_3$ (*vide supra*), and that $3,5\text{-}(CF_3)_2C_6H_3CN$ dissociates more readily than pivalonitrile to give 14e initiators under comparable conditions (*vide supra*). It is not yet known whether cationic Mo=CHR intermediates in metathesis reactions might be subject to loss of an α proton, a process that may depend upon whether a relatively good base is present (*e.g.*, in the substrate) or not. The high *cis,syndio* content of the poly(2,3-dicarbomethoxynorbornadiene) formed with **3** and **5** suggests that a mononitrile complex has the property of switching chirality of the metal center with each insertion step, although that specificity does not seem to be as high as with related neutral MAP (monoalkoxide pyrrolide) initiators.[10]

Conclusion

The pyrrolenine route seems to be a potentially more general way to synthesize molybdenum imido alkylidene monocations in greater variety than routes that reaquire generation of the cation in the last step. More generally, what has been presented here is likely to make possible a more thorough and systematic examination of "proton management" among C, N, and O atoms in the primary coordination sphere of ligands in cations that contain a variety of donor ligands, monoanionic ligands, and imido ligands. These results also draw attention

to the potential of sterically demanding nitriles as donor ligands in high oxidation state molybdenum alkylidene chemistry.

Experimental

Unless otherwise noted, all manipulations were carried out using standard Schlenk or glovebox techniques under an N_2 atmosphere. Tetrahydrofuran (THF), diethyl ether (Et_2O), 1,2-dimethoxyethane (DME), dichloromethane (DCM) and pentane were dried and deoxygenated by purging with argon followed by passage through activated alumina in a solvent purification system followed by storage over 4 Å molecular sieves. Non-halogenated and non-nitrile containing solvents were tested with a standard purple solution of sodium benzophenone ketyl in THF to confirm effective removal of moisture. Pivalonitrile, 3,5-bis(trifluoromethyl)benzonitrile ($Ph^{F6}CN$), perfluoro-tert-butanol, and sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ($NaBAr^F_4$, Ar^F= 3,5-bis-(trifluoromethyl)phenyl) were purchased from commercial suppliers. Lithium-2,5-dimethylpyrrolide, anilinium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ($[Me_2NHPh][BAr^F_4]$) and hexamethylterphenol (HMTOH = HO-2,6-(2,4,6-$Me_3C_6H_2$)$_2C_6H_3$)) were prepared according to literature procedures.[1] Syntheses of Mo(NAr)(Adene)$(OTf)_2$(DME) (Ar = 2,6-diisopropylphenyl) and Mo(NC_6F_5)(Adene)$(Me_2Pyr)_2$ were prepared as reported in the literature.[4] Elemental analyses were performed at Atlantic Microlab, Inc., Norcross, GA. Deuterated solvents were purchased from Cambridge Isotope Laboratories Inc., degassed, and dried over activated 4 Å molecular sieves for at least 24 h prior to use. NMR spectra were recorded on Bruker Avance 600 MHz, Bruker Avance 500 MHz and Bruker Avance 300 MHz spectrometers. ^{1}H and ^{13}C chemical shifts are reported in ppm relative to tetramethylsilane using residual solvent as an internal standard. ^{19}F chemical shifts are reported in ppm relative to fluorobenzene as an external standard.

Mo(N-*t*-Bu)(Adene)$(OTf)_2$(DME) (1). A solution of Mo(N-*t*-Bu)$_2$(2-Adamantyl)$_2$ (1.0 g, 1.966 mmol) in DME (8.0 mL) was cooled to –30 °C and a cold solution (–30 °C) of TfOH (0.521 mL, 5.897 mmol) in DME (4.0 mL) was added dropwise. The reaction mixture was allowed to warm to room temperature (22 °C) and stirred for 12 h. All the volatiles were removed under reduced pressure and the residue was dissolved in cold DCM (12.0 mL, –30 °C) and the mixture was filtered through a small plug of Celite. The solvent was removed from the filtrate in vacuum and the dark-yellow residue was redissolved in a minimum amount of ether and left at -30 °C overnight during which time a canary-yellow solid formed. The solid was washed with cold ether (3 x 1.0 mL, –30 °C) and finally with cold pentane (3 x 1.0 mL, –30 °C). Additional crops could be obtained from the concentrated mother liquor at -30 °C; yield 1.098 g (81%): ^{1}H NMR (600 MHz, CD_2Cl_2) δ 4.90 (s, 1H), 4.81 (s, 1H), 4.05 (s, 4H; major isomer), 3.98 (s, 4H; minor isomer), 3.68 (s, 6H; major isomer), 3.53 (s, 6H; minor isomer), 2.63 (s, 1H), 2.36 (s, 2H), 2.02 (s, 1H), 1.86-1.72 (m, 8H), 1.51 (s, 9H); ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2) δ 357.73 (minor isomer), 348.73 (major isomer), 128.97, 128.18, 119.64 (q, *J* = 320.1), 77.90, 75.33, 74.22, 71.50, 70.10, 64.73, 60.62, 46.73, 38.68, 38.19, 36.89, 36.71, 33.54, 29.59, 27.27, 26.82; ^{19}F{^{1}H} NMR (564 MHz, CD_2Cl_2) δ -77.64 (s, 6F; minor isomer), -78.61 (s, 6F; major isomer). Anal. Calcd for $C_{20}H_{33}F_6MoNO_8S_2$ (689.55 g/mol; +1/3 C_5H_{12}): C, 36.47%; H, 5.23%; N, 1.96%. Found: C, 36.58%; H, 5.55%; N, 2.30%.

Mo(N-*t*-Bu)(Adene)$(Me_2Pyr)_2$ (2a). Lithium-2,5-dimethylpyrrolide (225 mg, 2.23 mmol) in Et_2O (1.0 mL) was added to a –30 °C solution of Mo(N-*t*-Bu)$(C_{10}H_{14})(OTf)_2$(DME) (750 mg, 1.087 mmol) in Et_2O (5.0 mL). The reaction mixture was warmed to 22 °C and stirred for 2 h. The solvent was removed under reduced pressure and the residue was extracted with cold DCM and passed through a small plug of Celite. The solvent was removed *in vacuo* to yield an orange-yellow product which was dissolve in minimum amount of pentane. The solution was stored at -30 °C overnight. The yellow product was filtered off, washed with minimum amount of cold pentane (3 x 0.2 mL) and finally dried *in vacuo*; yield 356.8 mg (67%). ^{1}H NMR (600 MHz, CD_2Cl_2) δ 6.02 (s, 4H), 5.00 (s, 1H), 4.20 (s, 1H), 2.34 (d, *J* = 12 Hz, 2H), 2.21 (s, 12H), 2.14 (d, *J* = 12 Hz, 2H), 2.02 (s, 2H), 1.97 (d, *J* = 12 Hz, 4H), 1.86 (s, 2H), 1.61 (s, 9H). ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2) δ 322.61, 137.35, 108.37, 106.12, 75.82, 62.51, 48.81, 40.29, 39.99, 37.74, 32.00, 28.02, 18.09. Anal. Calcd for $C_{26}H_{39}MoN_3$ (489.58 g/mol; + 0.4 CH_2Cl_2): C, 60.57%; H, 7.66%; N, 8.03%. Found: C, 60.57%; H, 7.84%; N, 7.88%.

Mo(NAr)(Adene)$(Me_2Pyr)_2$ (2b). Lithium-2,5-dimethylpyrrolide (130.6 mg, 1.29 mmol) in Et_2O (1.0 mL) was added to a –30 °C solution of Mo(NAr)(Adene)$(OTf)_2$(DME) (Ar = 2,6-diisopropylphenyl; 500 mg, 0.629 mmol) in Et_2O (4.0 mL). The reaction mixture was warmed to 22 °C and stirred for 2 h. The solvent was removed under reduced pressure and the residue was extracted with cold pentane. The extract was passed through a small plug of Celite. The solvent was removed from the filtrate *in vacuo* to yield an orange-red product which was dissolved in a minimum amount of pentane and solution was stored at -30 °C overnight. The orange crystalline product was filtered off, washed with minimum amount of cold pentane (3 x 0.2 mL) and dried *in vacuo*; yield 306.7 mg (82%). ^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.27-7.17 (m, 3H), 6.09 (s, 4H), 6.00 (s, 4H), 5.02 (s, 1H), 4.87 (s, 1H), 4.43 (s, 1H), 4.23 (s, 1H), 3.99-3.95 (m, 2H), 3.64-3.60 (m, 2H), 2.36 (d, *J* = 12 Hz, 2H), 2.19 (s, 12H), 2.01-1.98 (m, 4H), 1.94-1.91 (m, 2H), 1.88-1.84 (m, 2H), 1.80-1.78 (m, 4H), 1.65-1.62 (m, 1H), 1.32 (d, *J* = 6 Hz, 12H), 1.16 (d, J = 6 Hz, 12H). Selected resonances for major isomer: 6.09 (s, 4H), 5.02 (s, 1H), 4.43 (s, 1H), 3.64-3.60 (m, 2H), 2.36 (d, *J* = 12 Hz, 2H), 1.16 (d, J = 6 Hz, 12H) and selected resonances for minor isomer: 6.00 (s, 4H), 4.87 (s, 1H), 4.23 (s, 1H), 3.99-3.95 (m, 2H), 1.94-1.91 (m, 2H), 1.65-1.62 (m, 1H), 1.32 (d, *J* = 6 Hz, 12H). ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2) δ 336.06 (major isomer), 334.25 (minor isomer), 151.87, 150.82, 147.85, 146.56, 138.53, 127.79, 127.72, 126.36, 124.04, 123.62, 123.22, 109.04, 106.22, 61.90, 60.68, 50.69, 40.65, 40.56, 38.84, 38.11, 37.99, 37.74, 37.42, 33.75, 28.35, 28.08, 27.96, 27.80, 27.76, 25.01, 24.74, 24.12, 17.96. Anal. Calcd for $C_{34}H_{47}MoN_3$ (593.73 g/mol; +0.2 CH_2Cl_2): C, 67.26%; H, 7.82%; N, 6.88%. Found: C, 67.22%; H, 7.93%; N, 6.85%.

Mo(NC_6F_5)(Adene)(OHMT)$(Piv)_2(BAr^F_4)$ (3). A solution of $[Me_2PhNH][BAr^F_4]$ (123.3 mg, 0.125 mmol) in 1.0 mL

DCM was added dropwise to a -30 °C dichloromethane solution (6.0 mL) of $Mo(NC_6F_5)(Adene)(Me_2Pyr)_2$ (75 mg, 0.125 mmol) and pivalonitrile (52 mg, 0.625 mmol). The reaction mixture was stirred at room temperature for 3 hours and HMTOH (43.4 mg, 0.131 mmol) was added to the reaction mixture to replace the other 2, 5-dimethyl pyrrolide ligand. The reaction mixture was allowed to stir at room temperature for another 18 h. All volatiles were removed under reduced pressure. Pentane (2.0 mL) was added to the residue and the mixture was stirred for 15-minutes. Pentane was decanted and this process was repeated twice. The crude residue was placed in a vacuum, during which time the oily residue becomes semi-solid. The solid was dissolved in 1.0 mL of DCM, followed by the addition of 1.0 mL ether and 5.0 mL pentane. Finally, the cloudy solution was placed at -30 °C for 2 days during which time a yellow crystalline solid precipitated which was filtered off, washed with pentane and dried under vacuum; yield 181.6 mg (82%). ^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.72 (s, 8H), 7.56 (s, 4H), 7.12 (d, J = 6 Hz, 2H), 7.02-7.01 (m, 1H), 6.99 (s, 2H), 6.81 (s, 2H), 4.69 (s, 1H), 3.43 (s, 1H), 2.36 (s, 3H), 2.10 (s, 6H), 2.07 (s, 6H), 1.87 (d, J = 12 Hz, 2H), 1.78 (s, 3H), 1.76 (d, J = 12 Hz, 2H), 1.66-1.61 (m, 3H), 1.51 (d, J = 12Hz, 3H), 1.45 (s, 18H), 1.37 (s, 2H). ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2) δ 374.07, 162.68 (q, J = 49.8 Hz), 158.76, 145.09, 143.43, 141.77, 141.08, 139.30, 139.07, 138.34, 137.62, 137.41, 137.06, 136.73, 136.55, 135.67, 135.38, 132.30, 131.98, 131.43, 130.61, 130.42, 130.15, 129.94, 129.73, 129.62, 129.07, 125.47 (q, J = 271.8 Hz), 122.76, 118.32, 64.43, 52.75, 38.47, 36.25, 30.93, 27.77, 27.09, 22.20, 21.52, 21.17, 20.80. ^{19}F{^{1}H} NMR (564 MHz, CD_2Cl_2) δ -62.75 (s, 24F), -148.74 (d, J = 22.56 Hz, 2F), -157.70 (t, J = 19.74 Hz, 1F), -162.88 (t, J = 19.74 Hz, 2F). Anal. Calcd for $C_{82}H_{69}BF_{29}MoN_3O$ (1770.2 g/mol; + 1 CH_2Cl_2): C, 53.74%; H, 3.86%; N, 2.27%. Found: C, 53.78%; H, 3.83%; N, 2.36%. A single crystal suitable for X-ray diffraction was obtained from a 1:1:5 volumetric mixture of DCM/ether/pentane at –30 °C.

$Mo(NC_6F_5)(Adene)(OC_4F_9)(Piv)_2(BAr^F_4)$ (4). This compound was prepared as described for **3** from $[Me_2NHPh][BAr^F_4]$ (98.6 mg, 0.1 mmol) in 1.0 mL DCM, a dichloromethane solution (5.0 mL) of $Mo(NC_6F_5)(Adene)(Me_2Pyr)_2$ (60 mg, 0.1 mmol), pivalonitrile (41.6 mg, 0.5 mmol), and perfluoro-*t*-butanol (35.4 mg, 0.15 mmol). The yellow crystalline precipitate was filtered off, washed with pentane, and dried *in vacuo*; yield 154.3 mg (92%): ^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.72 (s, 8H), 7.56 (s, 4H), 5.05 (s, 1H), 4.90 (s, 1H), 2.15 (d, J = 12 Hz, 2H), 2.08 (d, J = 12 Hz, 2H), 2.02 (s, 1H), 1.99 (s, 3H), 1.93 (d, J = 12 Hz, 2H), 1.80 (s, 2H), 1.48 (s, 9H), 1.34 (s, 9H); ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2) δ 380.54, 162.53 (q, J = 49.8 Hz), 146.61, 144.93, 142.85, 142.40, 141.11, 140.32, 139.14, 137.45, 135.52, 131.74, 131.22, 129.67 (q, J = 31.7 Hz), 125.32 (q, J = 273.3 Hz), 122.92, 120.98, 119.84, 118.19, 66.27, 52.28, 47.57, 39.36, 38.59, 36.09, 30.71, 28.10, 27.62, 27.26; ^{19}F{^{1}H} NMR (564 MHz, CD_2Cl_2) δ -62.88 (s, 24F), -73.43 (s, 9F), -147.77 (d, J = 16.92 Hz, 2F),-152.70 (t, J = 19.74 Hz, 1F), -161.55 (t, J = 16.92 Hz, 2F). Anal. Calcd for $C_{62}H_{44}BF_{38}MoN_3O$ (1675.76 g/mol; +1 C_5H_{12}): C, 46.04%; H, 3.23%; N, 2.40%. Found: C, 46.34%; H, 2.91%; N, 2.62%.

$Mo(NC_6F_5)(Adene)(OHMT)(Ph^{F6}CN)_2(BAr^F_4)$ (5). This compound was prepared as described for **3** from a solution of $[Me_2NHPh][BAr^F_4]$ (98.6 mg, 0.1 mmol) in 1.0 mL DCM, a -30 °C dichloromethane solution (5.0 mL) of $Mo(NC_6F_5)(C_{10}H_{14})(Me_2Pyr)_2$ (60 mg, 0.1 mmol), 3,5-bis(trifluoromethyl)benzonitrile ($Ph^{F6}CN$; 49.1 mg, 0.205 mmol), and HMTOH (34.7 mg, 0.105 mmol). The yield of the orange-yellow solid was 189.6 mg (91%): ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.43 (s, 2H), 8.13 (s, 4H), 7.72 (s, 8H), 7.55 (s, 4H), 7.22-7.19 (m, 1H), 7.15 (d, J = 6 Hz, 2H), 6.90 (s, 4H), 4.86 (s, 1H), 3.73 (s, 1H), 2.13 (s, 6H), 2.09 (s, 12H), 1.95 (d, J = 18 Hz, 2H), 1.81 (s, 1H), 1.78 (s, 3H), 1.64 (s, 2H), 1.57 (s, 4H); ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2) δ 381.39, 162.69 (q, J = 49.8 Hz), 158.93, 145.05, 143.39, 141.60, 141.32, 139.90, 139.47, 138.74, 138.20, 137.79, 136.94, 135.69, 135.34, 133.50, 132.71, 132.47, 132.27, 131.12, 130.72, 130.09, 129.88, 129.67, 129.58, 129.47, 128.95, 125.48 (q, J = 273.3 Hz), 123.87, 123.40, 121.58, 120.25, 119.96, 118.30, 110.57, 74.34, 71.15, 67.07, 65.76, 60.05, 49.03, 39.36, 39.12, 35.95, 27.05, 21.66, 21.15; ^{19}F{^{1}H} NMR (564 MHz, CD_2Cl_2) δ -62.81 (s, 24F), -64.12 (s, 12F), -148.82 (d, J = 22.56 Hz, 2F), -155.91 (t, J = 19.74 Hz, 1F), -161.96 (t, J = 19.74 Hz, 2F). Anal. Calcd for $C_{90}H_{57}BF_{41}MoN_3O$ (2082.17 g/mol; +1 CH_2Cl_2): C, 50.44%; H, 2.74%; N, 1.94%. Found: C, 50.82%; H, 2.38%; N, 2.13%.

$Mo(NAr)(Adene)(OHMT)(Ph^{F6}CN)_2(BAr^F_4)$ (6). This compound was prepared as described for **3** from a solution of $[Me_2NHPh][BAr^F_4]$ (99.6 mg, 0.101 mmol) in 1.0 mL DCM, a -30 °C dichloromethane solution (5.0 mL) of $Mo(NAr)(C_{10}H_{14})(Me_2Pyr)_2$ (Ar = 2,6-diisopropylphenyl; 60 mg, 0.101 mmol), 3,5-Bis(trifluoromethyl)benzonitrile ($Ph^{F6}CN$; 49.5 mg, 0.207 mmol), and HMTOH (35.1 mg, 0.106 mmol). The yellow crystalline precipitate was dried *in vacuo*; yield 182.6 mg (87%): ^{1}H NMR (600 MHz, CD_2Cl_2) δ 8.44 (s, 2H), 8.04 (s, 4H), 7.73 (s, 8H), 7.56 (s, 4H), 7.28-7.25 (m, 1H), 7.22 (d, J = 6 Hz, 2H), 7.18-7.15 (m, 3H), 6.91 (s, 4H), 4.93 (s, 1H), 3.85 (s, 1H), 3.54 (q, J = 6 Hz, 2H), 2.08 (s, 12H), 1.91 (s, 8H), 1.82 (s, 4H), 1.68 (s, 2H), 1.60-1.54 (m, 4H), 1.28 (d, J = 6 Hz, 12H); ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2) δ 377.94, 162.44 (q, J = 49.8 Hz), 159.12, 150.27, 146.09, 141.29, 138.74, 136.29, 135.48, 133.27, 132.23, 131.18, 130.61, 129.65, 129.48, 128.72, 127.98, 126.18, 124.37, 124.11, 123.16, 122.56, 121.87, 121.34, 119.90, 118.13, 110.51, 63.40, 52.85, 48.63, 38.94, 38.36, 35.90, 34.79, 29.21, 26.92, 24.24, 21.88, 20.79; ^{19}F{^{1}H} NMR (564 MHz, CD_2Cl_2) δ -62.84 (s, 24F), -63.77 (s, 12F). Anal. Calcd for $C_{96}H_{74}BF_{36}MoN_3O$ (2076.38 g/mol): C, 55.53%; H, 3.59%; N, 2.02%. Found: C, 55.30%; H, 3.54%; N, 1.91%. A single crystal suitable for X-ray diffraction was obtained from a 1:1:5 volumetric mixture of DCM/ether/pentane at –30 °C.

$Mo(NAr)(Adene)(OC_4F_9)(Piv)_2(BAr^F_4)$ (7). This compound was prepared as described for **3** from a solution of $[Me_2NHPh][BAr^F_4]$ (99.6 mg, 0.101 mmol) in 1.0 mL DCM, a -30 °C dichloromethane solution (5.0 mL) of $Mo(NAr)(C_{10}H_{14})(Me_2Pyr)_2$ (Ar = 2,6-diisopropylphenyl; 60.0 mg, 0.101 mmol), pivalonitrile (42.0 mg, 0.505 mmol), and perfluoro-*t*-butanol (35.78 mg, 0.151 mmol). The yellow crystalline precipitate was filtered off, washed with pentane and dried under vacuum; yield 136.7 mg (81%): ^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.85 (s, 8H), 7.66 (s, 4H), 7.33-7.30 (m, 1H),

7.28-7.27 (m, 2H), 5.23 (s, 1H), 4.96 (s, 1H), 3.73-3.69 (m, 2H), 2.22-2.16 (m, 4H), 2.11-2.07 (m, 4H), 2.03 (d, J = 12 Hz, 2H), 1.87 (s, 2H), 1.47 (s, 18H), 1.38-1.35 (m, 12H); $^{13}C\{^{1}H\}$ NMR (151 MHz, CD_2Cl_2) δ 365.64, 162.67 (q, J = 49.8 Hz), 152.87, 147.95, 140.09, 135.66, 131.80, 131.42, 131.17, 129.85 (q, J = 31.71 Hz), 125.46 (q, J = 271.8 Hz), 124.40, 123.16, 121.21, 119.97, 118.34, 60.31, 47.60, 38.46, 38.14, 36.11, 30.87, 30.21, 28.31, 27.81, 27.19, 24.66, 24.22, 23.12; $^{19}F\{^{1}H\}$ NMR (564 MHz, CD_2Cl_2) δ -62.79 (s, 24F), -74.45 (s, 9F). Anal. Calcd for $C_{68}H_{61}BF_{33}MoN_3O$ (1669.97 g/mol): C, 48.91%; H, 3.68%; N, 2.52%. Found: C, 49.25%; H, 3.79%; N, 2.04%. A single crystal suitable for X-ray diffraction was obtained from a 1:1:5 volumetric mixture of DCM/ether/pentane at –30 °C.

Mo(N-*t*-Bu)(Adene))(OHMT)($Ph^{F6}CN$)$_2$(BAr^{F}_4) (8). This compound was prepared as described for **3** from a solution of [Me_2NHPh][BAr^{F}_4] (100.6 mg, 0.102 mmol) in 1.0 mL DCM, a -30 °C dichloromethane solution (5.0 mL) of Mo(N-*t*-Bu)($C_{10}H_{14}$)(Me_2Pyr)$_2$ (50 mg, 0.102 mmol), 3,5-Bis(trifluoromethyl)benzonitrile ($Ph^{F6}CN$; 50.1 mg, 0.209 mmol), and HMTOH (35.4 mg, 0.107 mmol). The oily residue was dried *in vacuo* to give a yellow foam-like solid; yield 169.2 mg (84%): ^{1}H NMR (600 MHz, CD_2Cl_2) δ 8.48 (s, 2H), 8.19 (s, 4H), 7.94 (s, 8H), 7.72 (s, 4H), 7.23-7.20 (m, 3H), 7.11 (s, 4H), 5.20 (s, 1H), 3.69 (s, 1H), 2.45 (s, 6H), 2.26 (s, 12H), 2.12 (d, J = 12 Hz, 2H), 1.93 (d, J = 12 Hz, 2H), 1.84 (s, 2H), 1.76-1.72 (m, 3H), 1.66 (s, 3H), 1.38 (s, 9H); $^{13}C\{^{1}H\}$ NMR (151 MHz, CD_2Cl_2) δ 373.80, 162.83 (q, J = 49.8 Hz), 159.81, 138.15, 137.09, 136.88, 135.82, 135.48, 135.25, 133.74, 133.35, 132.81, 132.51, 132.38, 131.55, 131.41, 130.92, 130.25, 130.05, 129.90, 129.84, 129.63, 128.73, 125.62 (q, J = 273.3 Hz), 123.54, 121.73, 120.28, 118.43, 111.02, 75.51, 74.39, 67.10, 64.40, 50.45, 39.32, 38.73, 36.45, 30.70, 27.32, 21.75, 21.45.\; $^{19}F\{^{1}H\}$ NMR (564 MHz, CD_2Cl_2) δ -62.70 (s, 24F), -64.07 (s, 12F). Anal. Calcd for $C_{88}H_{66}BF_{36}MoN_3O$ (1972.23 g/mol; + 1 CH_2Cl_2): C, 51.96%; H, 3.33%; N, 2.04%. Found: C, 51.40%; H, 3.56%; N, 2.17%. Two attempts to obtain a suitable analysis failed, possibly due to variable amounts of CH_2Cl_2 in the sample.

ASSOCIATED CONTENT

NMR spectra for all compounds and details of X-ray studies and catalytic studies.

Accession Codes

CCDC 2095425-2095427 contain the supplementary crystallographic data for this paper. The data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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BP performed all synthetic work while CT performed all X-ray structural studies.

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Notes

The authors declare no competing financial interest.

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Table of Contents Artwork