Syntheses and Structures of Molybdenum Imido Alkylidene Pyrrolide and Indolide Complexes

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An X-ray structural study of Mo(NAd)($CHCMe_2Ph$)(2,5-$Me_2NC_4H_2$)$_2$ (**1**; Ad = 1-adamantyl) reveals it to contain one η^1-2,5-$Me_2NC_4H_2$ ring and one η^5-2,5-$Me_2NC_4H_2$ ring. The structures of Mo(NAr)($CHCMe_2Ph$)(pyrrolide)$_2$ (Ar = 2,6-*i*-$Pr_2C_6H_3$) complexes that contain 2,3,4,5-tetramethylpyrrolides, 2,5-diisopropylpyrrolides, or 2,5-diphenylpyrrolides are analogous to that of **1**. In contrast, Mo(NAr)(CH_2CMe_2Ph)(indolide)$_2$ (**6**) was shown to contain two η^1-bound indolides. Monohexafluoro-*t*-butoxide pyrrolide (MAP) species can be prepared, either through addition of one equiv of Me(CF_3)$_2$COH to a bispyrrolide or through reactions between the lithium pyrrolide and the bishexafluoro-*t*-butoxide. A trimethylphosphine adduct of a bispyrrolide, Mo(NAd)($CHCMe_2Ph$)(η^1-NC_4H_4)$_2$(PMe_3), has been prepared and structurally characterized, while a PMe_3 adduct of MAP hexafluoro-*t*-butoxide species was found to have PMe_3 bound approximately *trans* to the pyrrolide. This adduct serves as a model for the structure of the initial olefin adduct in olefin metathesis.

Introduction

The pyrrolide (or pyrrolyl) anion is isoelectronic with the cyclopentadienide anion and therefore has been of interest as a supporting ligand in inorganic and organometallic chemistry for some time.[1−4] A pyrrolide binds most often to a single metal center in either an η^1 (through N) or η^5 fashion, although several monometallic and bimetallic variations are known. A variety of group 4 species[5] and group 5 species[6] have been structurally characterized. In contrast, group 6 examples of pyrrolide complexes are relatively rare.[7]

We became interested in the possibility of preparing Mo(NR)($CHCMe_2R'$)X_2 (R′ = Me or Ph) species in which X would be protonated upon addition of monoalcohols or diols. We viewed this approach as a means of synthesizing Mo(NR)($CHCMe_2R'$)(OR")$_2$ species, primarily catalysts that contain enantiomerically pure biphenolate or binaphtholate ligands.[8] This approach would be especially valuable if catalysts could be prepared *in situ*, that is, if the reactions were high yielding, and if the product of protonation (HX) were a poor ligand that would not interfere with subsequent metathesis reactions by Mo(NR)($CHCMe_2R'$)(OR″)$_2$ species. Initial studies that involved Mo(NAr)(CH-*t*-Bu)(CH_2-*t*-Bu)$_2$ (Ar = 2,6-diisopropylphenyl) species revealed that often only *one* equivalent of alcohol reacts readily to yield Mo(NAr)(CH-*t*-Bu)(CH_2-*t*-Bu)(OR) or Mo(NAr)(CH_2-*t*-Bu)$_3$(OR) species.[9] A second approach in which X = NPh_2 revealed that protonation of both X groups was possible, but was often slow and incomplete.[10] We then turned to bispyrrolide species. (Pyrrolide complexes of Mo were virtually unknown at the time.) We found that Mo(NR)($CHCMe_2R'$)(NC_4H_4)$_2$ species could be prepared and isolated in high yields and moreover that they would react readily with monoalcohols and diols to give bisalkoxide metathesis catalysts.[11] Bis(2,5-dimethylpyrrolide) complexes, Mo(NR)($CHCMe_2Ph$)(Me_2Pyr)$_2$ (R = 2,6-*i*-$Pr_2C_6H_3$, 2,6-$Me_2C_6H_3$, 1-Adamantyl, 2-$CF_3C_6H_4$), also were prepared in >80% isolated yields and shown to be precursors to biphenolate and

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binaphtholate complexes upon addition of various biphenols or binaphthols.[12] Monoalcohols were shown to add to bisdimethylpyrrolide species also to give monoalkoxide monopyrrolide (MAP) species, which were of interest initially because of their ability to catalyze enyne metathesis.[13] More recent work in which the alkoxide in the MAP species is enantiomerically pure suggests that reactions that involve diastereomers constitute a potentially powerful new approach to asymmetric metathesis and perhaps other metathesis-based reactions.[14]

An X-ray structural study of Mo(NAr)(CHCMe$_2$Ph)(NC$_4$H$_4$)$_2$ (Ar = 2,6-*i*-Pr$_2$C$_6$H$_3$) showed it to be an unsymmetric dimer, {Mo(NAr)(*syn*-CHCMe$_2$Ph)(η^5-NC$_4$H$_4$)(η^1-NC$_4$H$_4$)}-{Mo(NAr)(*syn*-CHCMe$_2$Ph)(η^1-NC$_4$H$_4$)$_2$}, in which the nitrogen in the η^5-pyrrolide behaves as a donor to the other Mo.[11] The electron count in the Mo(NAr)(*syn*-CHCMe$_2$Ph)(η^5-NC$_4$H$_4$)(η^1-NC$_4$H$_4$) half-is 18, and in the Mo(NAr)(*syn*-CHCMe$_2$Ph)(η^1-NC$_4$H$_4$)$_2$(Ndonor) half-is 16. Low temperature NMR spectra are consistent with the structure in the solid state, although at room temperature it is clear that the dimeric species is highly fluxional, a process that is believed to include dissociation of the dimer into its monomeric components in addition to interconversion of η^5 and η^1 pyrrolides. Accessibility to intermediate Mo(NAr-)(*syn*-CHCMe$_2$Ph)(η^1-NC$_4$H$_4$)$_2$ as part of the fluxional process is proposed to be the reason why {Mo(NAr)(*syn*-CHCMe$_2$Ph)(η^5-NC$_4$H$_4$)(η^1-NC$_4$H$_4$)}{Mo(NAr)(*syn*-CHCMe$_2$Ph)(η^1-NC$_4$H$_4$)$_2$} reacts readily with alcohols to give monoalkoxide and bisalkoxide species, i.e., the alcohol probably coordinates to an electron deficient metal center (probably 14e) before a proton transfers to a pyrrolide. We have no proof that this is in fact the case.

In this paper we report structural studies of several bispyrrolide species in which the pyrrolide is substituted (2,5-dimethyl, 2,3,4,5-tetramethyl, 2,5-diisopropyl, and 2,5-diphenyl), a bisindolide complex, monohexafluoro-*t*-butoxide complexes, and trimethylphosphine adducts.

Results

Bispyrrolides. An X-ray structural study of Mo(NAd)(CHCMe$_2$Ph)(2,5-Me$_2$NC$_4$H$_2$)$_2$ (**1**; Ad = 1-adamantyl) reveals that one of the pyrrolide ligands is bound in an η^5 fashion and the other in an η^1 fashion (Figure 1).[15] The alkylidene is in the *syn* orientation with Mo−C(1)−C(2) = 141.7(3)° and Mo−N(3)−C(31) = 160.7(2)°. The η^5-2,5-Me$_2$NC$_4$H$_2$ ring is essentially symmetrically bound to the metal. Proton NMR spectra of bis-2,5-dimethylpyrrolide species at room temperature typically contain a single sharp alkylidene resonance, but broad pyrrolide resonances,[12] and carbon NMR spectra suggestive of a *syn* isomer (J_{CH} = 120 Hz) in all cases. Proton NMR spectra of reported 2,5-dimethylpyrrolide complexes at − 80 °C are consistent with species that contain one η^1-2,5-Me$_2$NC$_4$H$_2$ ring and one η^5-2,5-Me$_2$NC$_4$H$_2$ ring, as found for **1** in the solid state. At room temperature we believe that mirror symmetric Mo(NAd)(CHCMe$_2$Ph)($\eta^1$2,5-Me$_2$NC$_4$H$_2$)$_2$ is formed on the NMR time scale. All η^1,η^5 species contain 18e if the imido electron pair is included.

Bispyrrolide complexes that contain two 2,3,4,5-tetramethylpyrrolides, two 2,5-diisopropylpyrrolides, or two 2,5-diphenylpyrrolides can be prepared readily, although unoptimized isolated yields are variable (eq 1). X-ray structural studies of **2** (Figure 2), **3** (Figure 3), and **4** (Figure 4) reveal them to have structures analogous to that of **1**. In each case, the η^5-pyrrolide is essentially symmetrically bound to the metal. Selected distances and angles can be found in the figure captions and all supporting structural data can be found in the Supporting Information.

A room temperature ^{1}H NMR spectrum of **2** in C$_6$D$_6$ displays sharp singlets at 2.07 and 1.80 ppm, which correspond to two

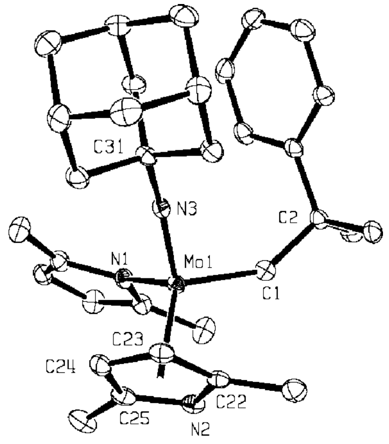


Figure 1. Thermal ellipsoid drawing of Mo(NAd)(CHCMe$_2$Ph)(η^1-2,5-NC$_4$H$_2$Me$_2$)(η^5-2,5-NC$_4$H$_2$Me$_2$) (**1**). Selected distances (Å) and angles (deg): Mo−N(1) = 2.117(3), Mo−C(1) = 1.938(3), Mo−N(2) = 2.391(3), Mo−N(3) = 1.720(3), Mo−C(22) = 2.358(3), Mo−C(23) = 2.406(3), Mo−C(24) = 2.472(3), Mo−C(25) = 2.448(3); Mo−N(3)−C(31) = 160.7(2), Mo−C(1)−C(2) = 141.7(3).

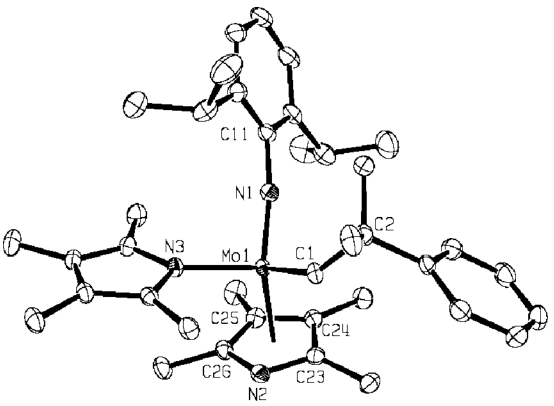
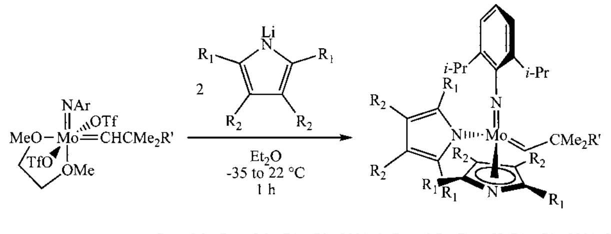


Figure 2. Thermal ellipsoid drawing of Mo(NAr)(CHCMe$_2$Ph)(η^1-2,3,4,5-NC$_4$Me$_4$)(η^5-2,3,4,5-NC$_4$Me$_4$) (**2**). Selected distances (Å) and angles (deg): Mo−N(1) = 1.7479(13), Mo−C(1) = 1.9360(15), Mo−N(2) = 2.4188(13), Mo−N(3) = 2.0915(12), Mo−C(23) = 2.4294(15), Mo−C(24) = 2.4368(15), Mo−C(25) = 2.5113(15), Mo−C(26) = 2.4591(15); Mo−N(1)−C(11) = 172.41(11), Mo−C(1)−C(2) = 140.63(11).



(1)

R$_1$ = Me, R$_2$ = Me, R' = Ph, 23%, **2**; R$_1$ = i-Pr, R$_2$ = H, R' = Ph, 83%, **3**; R$_1$ = Ph, R$_2$ = H, R' = Me, 52%, **4**; R$_1$ = Ph, R$_2$ = H, R' = Ph, 78%, **5**.

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(15) Crystallographic tables and CIF files for all structurally characterized compounds can be found in the Supporting Information.

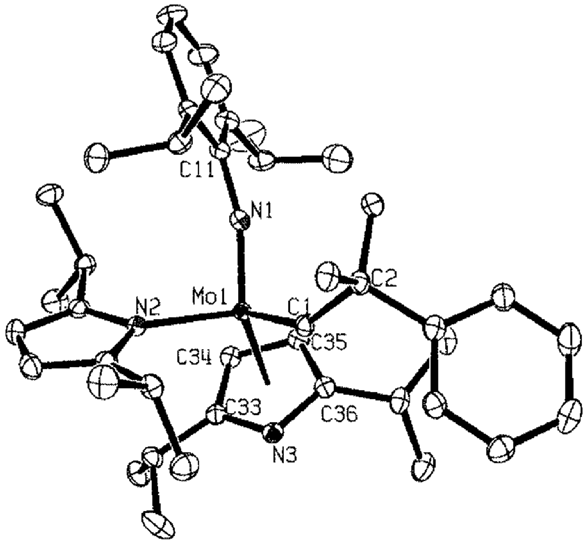


Figure 3. Thermal ellipsoid drawing of Mo(NAr)(CHCMe$_2$Ph)(η^1-2,5-i-Pr$_2$NC$_4$H$_2$)(η^5-2,5-i-Pr$_2$NC$_4$H$_2$) (**3**). Selected distances (Å) and angles (deg): Mo−N(1) = 1.7351(14), Mo−C(1) = 1.9342(17), Mo−N(2) = 2.1106(14), Mo−N(3) = 2.4945(14), Mo−C(33) = 2.5390(16), Mo−C(34) = 2.4761(17), Mo−C(35) = 2.3758(17), Mo−C(36) = 2.4146(17); Mo−N(1)−C(11) = 165.80(12), Mo−C(1)−C(2) = 141.40(13).

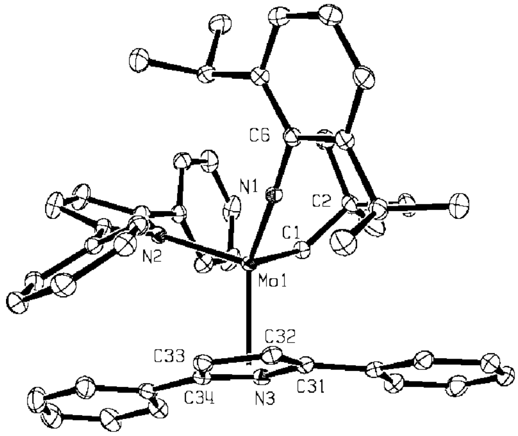


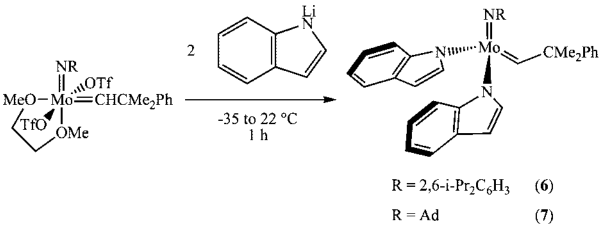
Figure 4. Thermal ellipsoid drawing of Mo(NAr)(CHCMe$_3$)(η^1-2,5-NC$_4$H$_2$Ph$_2$)(η^5-2,5-NC$_4$H$_2$Ph$_2$) (**4**). Selected distances (Å) and angles (deg): Mo−N(1) = 1.7369(11), Mo−C(1) = 1.9286(12), Mo−N(2) = 2.1145(10), Mo−N(3) = 2.5375(10), Mo−C(31) = 2.4095(12), Mo−C(32) = 2.3957(12), Mo−C(33) = 2.5060(12), Mo−C(34) = 2.5824(12); Mo−N(1)−C(6) = 177.57(9), Mo−C(1)−C(2) = 137.23(9).

pyrrolide methyl resonances (12 H each), consistent with mirror symmetric Mo(NAr)(CHCMe$_2$Ph)(η^1-2,3,4,5-NC$_4$Me$_4$)$_2$ being formed on the NMR time scale. At −80 °C (in toluene-d$_8$) several unresolved broad methyl resonances are found between 1 and 3 ppm for the pyrrolide methyl groups, but only one alkylidene proton resonance is observed, consistent with a molecule that possesses no symmetry. We propose that the lowest energy species at this temperature is one in which one of the 2,3,4,5-tetramethylpyrrolide ligands is bound in an η^5 fashion and the other is bound in an η^1 fashion.

The room temperature proton NMR spectrum of **4** in CD$_2$Cl$_2$ reveals one pyrrolide proton resonance at 6.01 ppm and a single broad methine resonance at 3.04 ppm. At −40 °C two methine resonances are found at 3.40 and 2.35 ppm and three pyrrolide proton resonances at 6.45, 6.06, and 5.31 ppm in a ratio of 1:2:1, characteristic of a molecule with no symmetry and a diisopropylphenylimido ring that does not rotate rapidly on the NMR time scale. The spectrum of **4** at −40 °C is characteristic of an η^1, η^5 species.

The most interesting case is the proton NMR spectrum of **3** between room temperature and −70 °C in toluene-d$_8$ (Figure 5). At 20 °C only a single alkylidene resonance (at 13.53 ppm) with J$_{CH}$ characteristic of a *syn* species (124 Hz) and a single pyrrolide proton resonance (at 6.11 ppm) are observed (in a ratio of 1:4). At − 70 °C *two* alkylidene resonances are observed at 14.05 (J$_{CH}$ = 124 Hz) and 12.94 ppm (15%) along with four pyrrolide proton resonances for the major species and a single pyrrolide proton resonance for the minor species. The set of four pyrrolide proton resonances is consistent with a molecule that possesses no symmetry, namely Mo(NAr)(CHCMe$_2$Ph)(η^1-2,5-*i*-Pr$_2$NC$_4$H$_2$)(η^5-2,5-*i*-Pr$_2$NC$_4$H$_2$), and a η^1-2,5-*i*-Pr$_2$NC$_4$H$_2$ ligand that is rotating slowly about the Mo−N bond. The other set of pyrrolide resonances (15%) is consistent with a molecule that possesses a mirror plane, which we propose is Mo(NAr)(CHCMe$_2$Ph)(η^1-2,5-*i*-Pr$_2$NC$_4$H$_2$)$_2$, and pyrrolides that rotate readily on the NMR time scale about the Mo−N bond. In short, at low temperature a mixture of the η^1,η^5 (85%) and η^1,η^1 (15%) species is observed, while at room temperature the two species interconvert readily on the NMR time scale and the ratio of the two cannot be determined. Similar behavior is observed in CD$_2$Cl$_2$; at −70 °C 7% of Mo(NAr)(CHCMe$_2$Ph)(η^1-2,5-*i*-Pr$_2$NC$_4$H$_2$)$_2$ is present according to integration of the alkylidene protons. Elemental analysis is consistent with the proposed species and the variable temperatrue NMR results are the same from one sample to another, so the presence of two isomers in low temperature NMR spectra seems to be the only logical conclusion. It should be pointed out that Mo(NAr)(CHCMe$_2$Ph)(η^1-2,5-*i*-Pr$_2$NC$_4$H$_2$)$_2$ is similar to that of a related structurally characterized pyrrolide complex, Mo(NAr)(CHCMe$_2$Ph)(η^1-2-MesitylNC$_4$H$_3$)$_2$,[16] in which the pyrrolides cannot bind in an η^5 manner, and to the bisindolide reported here (*vide infra*).

A Bisindolide Species. Addition of two equivalents of Li(indolide) to Mo(NAr)(CH$_2$CMe$_2$Ph)(OTf)$_2$(DME) at −30 °C cleanly produces Mo(NAr)(CH$_2$CMe$_2$Ph)(indolide)$_2$ (**6**) in 76% yield after crystallization from diethyl ether at room temperature (eq 2). The ^{1}H NMR spectrum at room temperature is consistent with a C_S symmetric species on the average, suggesting that the two indolide ligands either are both η^1 bound, or that η^1 and η^5 bound indolides interconvert readily. The alkylidene proton displays a J_{CH} of 116 Hz, indicative of a *syn* orientation of the alkylidene with respect to the imido group. Mo(NAd)(CH$_2$CMe$_2$Ph)(indolide)$_2$ (**7**) also can be prepared, although toluene rather than diethyl ether must be used during the salt metathesis reaction. The ^{1}H NMR spectrum of **7** in C$_6$D$_6$ at 23 °C also reveals a C_S symmetric species with a *syn* orientation of the alkylidene (J_{CH} = 113 Hz). Interestingly, **6**



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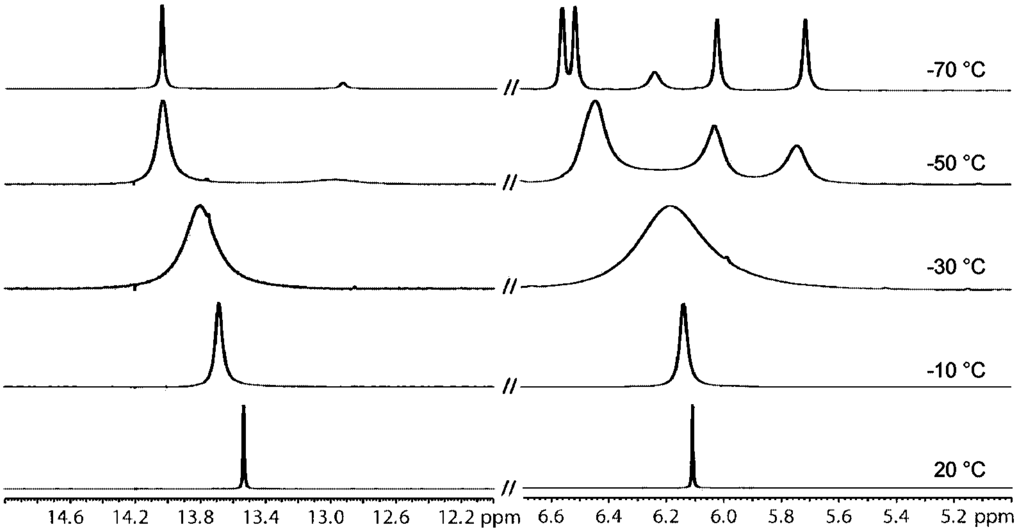


Figure 5. Variable-temperature ^{1}H NMR spectroscopic studies of Mo(NAr)(CHCMe$_2$Ph)(2,5-i-Pr$_2$NC$_4$H$_2$)$_2$ (**3**) in toluene-d_8.

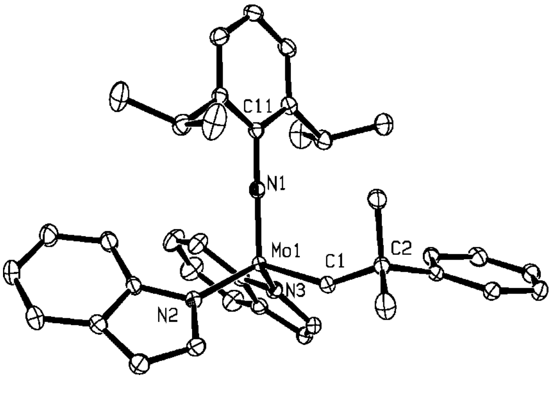
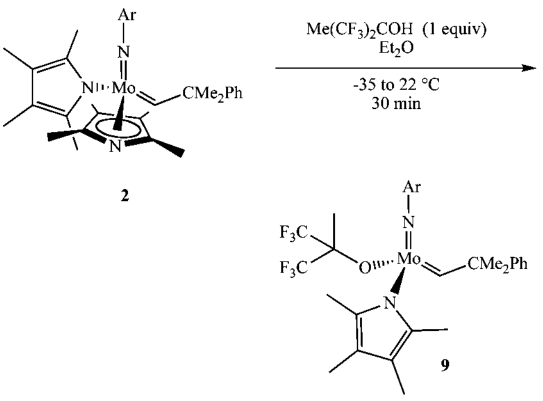


Figure 6. Thermal ellipsoid drawing of Mo(NAr)(CHCMe$_2$Ph)(η1-indolide)$_2$ (**6**). Selected distances (Å) and angles (deg): Mo−N(1) = 1.7317(10), Mo−C(1) = 1.8626(12), Mo−-N(2) = 2.0288(10), Mo−N(3) = 2.0278(10); Mo−N(1)−C(11) = 175.04(9), Mo−C(1)−C(2) = 148.49(9), N(2)−Mo−N(3) = 120.58(4).

binds tetrahydrofuran to form a THF adduct, Mo(NAr)(CHCMe$_2$Ph)(indolide)$_2$(THF) **8**, as one might expect for a 14e species in which the metal is relatively electron poor. For **8** the alkylidene H$_\alpha$ proton resonates at 12.67 ppm and displays a J_{CH} =120 Hz consistent with a *syn* orientation of the alkylidene.

X-ray quality crystals of **6** were obtained from toluene at −30 °C (Figure 6). Mo−N$_{indolide}$ distances were found to be 2.0288(10) Å, which are similar to those found for Mo−N$_{pyrrolide}$. The N(2)−Mo−N(3) angle of 120.58(4)° is larger than what is found in other pseudotetrahedral molybdenum imido alkylidenes and is possibly due to steric repulsion between the two indolide benzene rings. However, almost certainly electronic factors also contribute to the η^1,η^1 isomer being lowest in energy.

Monohexafluoro-*t*-butoxide Complexes. Addition of 1 equiv of Me(CF$_3$)$_2$COH to Mo(NAr)(CHCMe$_2$Ph)(2,3,4,5-Me$_4$NC$_4$)$_2$ (**2**) yields Mo(NAr)(CHCMe$_2$Ph)(2,3,4,5-Me$_4$NC$_4$)[OC(CF$_3$)$_2$Me] (**9**) cleanly (eq 3). Mo(NAr)(CHCMe$_2$Ph)[OC(CF$_3$)$_2$Me]$_2$ was not detected in the crude reaction mixture by ^{1}H NMR spectroscopy. Compound **9** is the tetramethylpyrrolide analog of known Mo(NAr)(CHCMe$_2$Ph)(2,5-Me$_2$NC$_4$H$_2$)[OC(CF$_3$)$_2$Me].[13] A structural study of Mo(NAr)(CHCMe$_2$Ph)(2,5-Me$_2$NC$_4$H$_2$)(OAr) revealed that an η^1 pyrrolide is present, even though only a 14e count is reached; we presume that an η^5 pyrrolide is untenable for steric reasons. We of course do not know with certainty that an η^1-pyrrolide ring is present in **9**, as drawn in eq 3. For the moment we assume that to be the case. An η^5 pyrrolide is likely to be much more feasible in a circumstance where steric interactions between the four ligands are minimized.

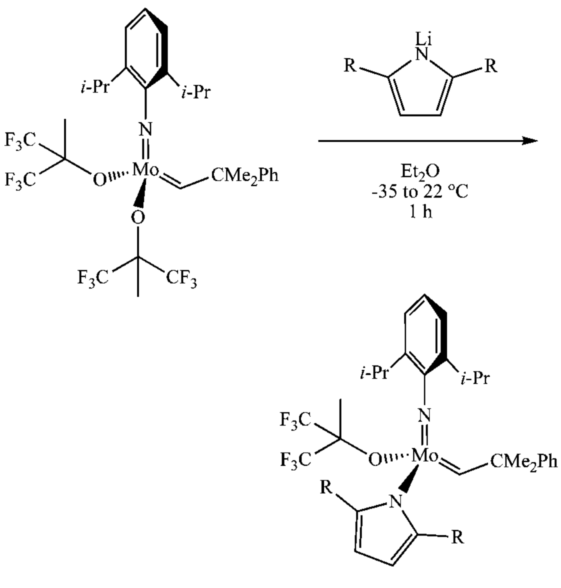


(3)

A similar reaction between **3** and Me(CF$_3$)$_2$COH produced Mo(NAr)(CHCMe$_2$Ph)(2,5-*i*-Pr$_2$NC$_4$H$_2$)[OC(CF$_3$)$_2$Me] (**10**). This reaction produced a mixture of starting material, monoalkoxide, and bisalkoxide species if **3** was not purified thoroughly through recrystallization. A possible cause is contamination of **3** with residual lithium diisopropylpyrrolide. Protonolysis of **4** with 1 equiv of Me(CF$_3$)$_2$COH also led to a mixture of starting material, monoalkoxide, and bisalkoxide species, from which no monoalkoxide species could be isolated.

An alternative strategy that yielded **10** and Mo(NAr)(CHCMe$_2$Ph)(2,5-Ph$_2$NC$_4$H$_2$)[OC(CF$_3$)$_2$Me] (**11**) consisted of salt metathesis of Mo(NAr)(CHCMe$_2$Ph)[OC(CF$_3$)$_2$Me]$_2$ with 1 equiv of the lithium pyrrolide (eq 4). Again we cannot be certain that η^1 pyrrolides are present in the monoalkoxides, as drawn. Slow protonolysis is likely to be the result of a crowded coordination sphere that limits the ability of hexafluoro-*t*-butanol to first bind to the metal through an oxygen lone pair.

Reaction of **6**, **7**, or **8** with one equivalent of Me(CF$_3$)$_2$COH in either toluene or a mixture of pentane and benzene at either 22 or −30 °C gave a complex mixture of products from which no monoalkoxide monoindolide complex could be isolated. This result illustrates the sensitive nature of protonolysis of the first indolide versus protonolysis of the second indolide, a circumstance that is likely to vary dramatically with the nature of the pyrrolide or indolide ligand in question, along with other



(4)

R = i-Pr (**10**); R = Ph (**11**)

cumulative steric interactions within the monoalkoxide intermediate.

Trimethylphosphine Adducts. Evidence for the ready dissociation of bispyrrolide dimers as part of a rapid fluxional process consists of immediate formation of Mo(NAd)(CHCMe$_2$Ph)(η^1-NC$_4$H$_4$)$_2$(PMe$_3$) (**12**) upon addition of one equivalent (per Mo) of trimethylphosphine to {Mo(NAd)(CHCMe$_2$Ph)(NC$_4$H$_4$)$_2$}$_2$ (Ad = 1-adamantyl).[11] A single alkylidene proton resonance at 12.49 ppm (J_{HP} = 5 Hz) suggests that only a single isomer is present. An X-ray structural study reveals that trimethylphosphine binds to one of the $C_{alkylidene}N_{imido}N_{pyrrolide}$ faces of the pseudotetrahedral species, that is, *cis* to the equatorial imido and alkylidene ligands (Figure 7). The structure is distorted from a TBP with N(3)−Mo−P(1) = 164.37(5)°. The alkylidene is in the *syn* orientation with C(2)−C(1)−Mo = 146.52(15)°, which pushes away the adamantyl group and leads to a significantly smaller Mo−N−C angle than expected (C(22)−N(1)−Mo = 158.77(14)°), a circumstance that has been observed in other PMe$_3$ adducts such as Mo(NAr)(CHCMe$_3$)[OCMe(CF$_3$)$_2$]$_2$(PMe$_3$).[17]

Trimethylphosphine adducts were generated upon addition of PMe$_3$ to the monoalkoxide monopyrrolide species (eq 5). An X-ray study of **16** showed that PMe$_3$ coordinates *trans* to the pyrrolide (Figure 8). The coordination environment of **16** can be viewed as a square pyramid with the alkylidene in the apical position. The PMe$_3$ is weakly coordinated, judging from the relatively long Mo−P bond (2.5514(5) Å). When **16** is dissolved in solution at 22 °C (60 mM) an equilibrium is established immediately between the four-coordinate species (**11**) and the PMe$_3$ adduct (**16**), according to ^{1}H NMR spectroscopy. A decrease in temperature leads to an increase in the concentration of the PMe$_3$ adduct (δ 14.75 ppm) in solution, relative to four-coordinate **11** (δ 12.71 ppm). Trimethylphosphine coordinates slightly more strongly to Mo(NAr)(CHCMe$_2$Ph)(*i*-Pr$_2$Pyr)[OC(CF$_3$)$_2$Me] (**10**), since only 10% of the four-coordinated species **10** is detected in solution in an equilibrium with the PMe$_3$ adduct **15** (60 mM). In the case of the dimethyl and tetramethyl MAP species, PMe$_3$ is bound even more strongly, with only the PMe$_3$ adducts (**13** and **14**, respectively) being observed by ^{1}H NMR spectroscopy in solution at 22 °C (50 mM).

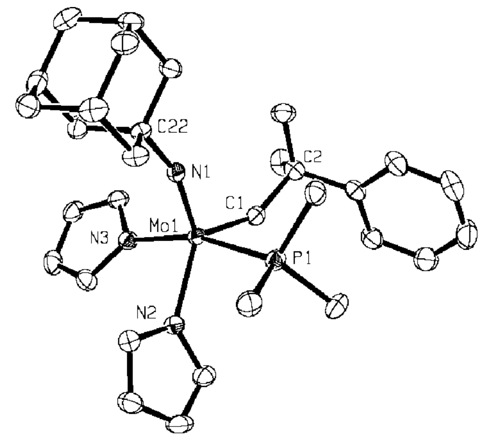


Figure 7. Thermal ellipsoid drawing of Mo(NAd)(CHCMe$_2$Ph)(NC$_4$H$_4$)$_2$(PMe$_3$) (**12**). Selected distances (Å) and angles (deg): Mo−N(1) = 1.7252(16), Mo−C(1) = 1.885(2), Mo−N(2) = 2.1183(17), Mo−N(3) = 2.1377(17), Mo−P(1) = 2.5270(6); C(22)−N(1)−Mo = 158.77(14), C(2)−C(1)−Mo = 146.52(15), N(1)−Mo−C(1) = 106.44(8), N(1)−Mo−N(2) = 129.54(7), N(1)−Mo−N(3) = 98.44(7), N(1)−Mo−P(1) = 91.17(6), C(1)−Mo−N(2) = 122.75(8), C(1)−Mo−N(3) = 100.41(8), C(1)−Mo−P(1) = 88.53(6), N(2)−Mo−N(3) = 84.12(7), N(2)−Mo−P(1) = 80.26(5), N(3)−Mo−P(1) = 164.37(5).

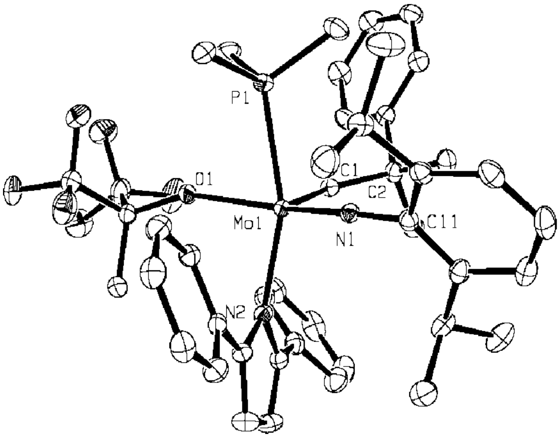


Figure 8. Thermal ellipsoid drawing of Mo(NAr)(CHCMe$_2$Ph)(2,5-Ph$_2$NC$_4$H$_2$)[OC(CF$_3$)$_2$Me](PMe$_3$) (**16**). Selected distances (Å) and angles (deg): Mo−N(1) = 1.7464(16), Mo−C(1) = 1.903(2), Mo−N(2) = 2.1779(16), Mo−O(1) = 2.0846(14), Mo−P(1) = 2.5514(5); Mo−N(1)−C(11) = 177.09(14), Mo−C(1)−C(2) = 145.04(14), P(1)−Mo−N(2) = 160.77(4).

Discussion

The structures of **1**−**4** are all essentially the same and similar to that of a related tungsten complex, W(NAr)(CHCMe$_3$)(η^1-2,5-Me$_2$NC$_4$H$_2$)(η^5-2,5-Me$_2$NC$_4$H$_2$).[18] Therefore we believe that when sterically possible the lowest energy bispyrrolide species usually will be an 18e complex of this type. The η^1,η^1 isomer is readily accessible, even though the total number of electrons is four less than that in the η^1,η^5 isomer, and in some cases could constitute a significant fraction of the mixture at room

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

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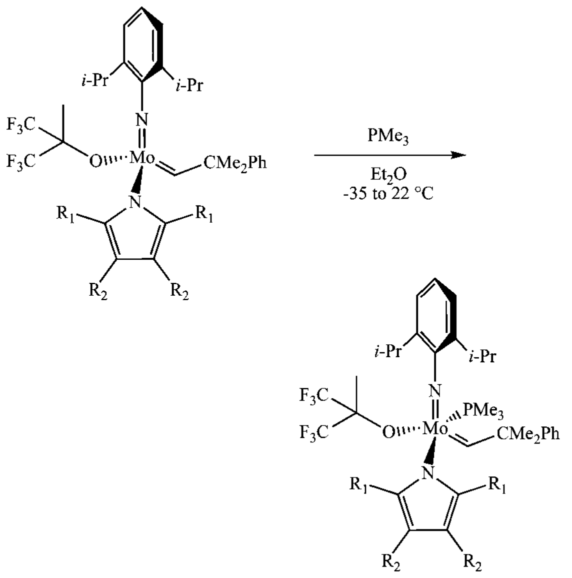

(5)

R_1 = Me,R_2 = H (**13**); R_1 = Me,R_2 = Me (**14**); R_1 = i-Pr,R_2 = H (**15**); R_1 = Ph,R_2 = H (**16**).

temperature. In certain circumstances the η^1,η^1 isomer is the sole observed species, as in the bisindolide reported here and in the bis-2-mesitylpyrrolide species.[16] We propose that formation of the η^1,η^1 isomer is required for an alcohol can attack the metal. Therefore the amount of η^1,η^1 isomer that is present, along with the rate of interconversion of η^1 and η^5 pyrrolides and steric factors overall in both η^1,η^1 and η^1,η^5 isomers, are important factors that determine the rate of reaction of bispyrrolides with alcohols. When reactions with alcohols are most likely to yield monoalkoxide pyrrolide (MAP) species selectively is still not fully known, in part because the precise mechanism of pyrrolide protonation is not known, but also because of the delicate steric balance within the intermediate monoalkoxide and the bisalkoxide. Although the electron pair on the η^5-pyrrolide is susceptible to direct attack by strong acids,[11,18] we favor addition of most alcohols to the metal to form an initial adduct followed by proton transfer to C(2) of an η^1-pyrrolide to give an intermediate pyrrolenine complex.

Preliminary results suggest that bispyrrolide complexes are relatively unreactive toward olefins, especially when the η^1,η^5 isomer is the lowest energy species. Even ethylene reacts only slowly at 60 °C with $W(NAr)(CHCMe_3)(\eta^1\text{-}2,5\text{-}Me_2Pyr)(\eta^5\text{-}2,5\text{-}Me_2Pyr)$, and when it does it yields isolable and structurally characterized $W(NAr)(CH_2)(\eta^1\text{-}2,5\text{-}Me_2Pyr)(\eta^5\text{-}2,5\text{-}Me_2Pyr)$.[18] It is believed that $W(NAr)(CH_2)(\eta^1\text{-}2,5\text{-}Me_2Pyr)(\eta^5\text{-}2,5\text{-}Me_2Pyr)$ is relatively stable toward bimolecular decomposition in solution at 60 °C in part because of its 18e count and the presence of relatively bulky ligands. In contrast, MAP species are highly reactive, perhaps in many cases much more reactive than bisalkoxides. Calculations by Eisenstein on Mo(NR)(CHR′)(D)(A) species (D = donor, an alkyl, and A = acceptor, an alkoxide) suggest that the lowest energy transition state for metathesis is the result of olefin approach to the metal *trans* to the donor group.[19] The structure of $Mo(NAr)(CHCMe_2Ph)(2,5\text{-}Ph_2\text{-}Pyr)[OC(CF_3)_2Me](PMe_3)$ is potentially interesting in this light, since where PMe_3 binds in bisalkoxide complexes correlates with the nature of the initial olefin adduct according to theoretical studies of bisalkoxide complexes. The recent report of an especially rapid as well as efficient asymmetric synthesis of a natural product[14] is evidence that controlling the chirality and reactivity at the metal in diastereomers in which four different ligands are bound to the metal center is likely to be a powerful new approach in metathesis chemistry. MAP species also have been shown to be active for enyne metathesis.[13] Although it is not yet known to what extent the nature of the pyrrolide (or a related ligand) influences the outcome of each type of reaction, the pyrrolide is likely to be a significant variable, along with the nature of the imido group, the alkoxide, the metal (Mo or W), and the alkylidene. Therefore hundreds or even thousands of MAP catalysts can be envisioned, and many of them may be accessible *in situ* through addition of an alcohol to a bispyrrolide species. We expect that the number of possible MAP variations and the flexibility in designing MAP species will lead to applications outside of asymmetric metathesis, e.g., in ROMP polymerizations. In future reports we will explore some of the many variations of MAP species and applications of them toward a wide variety of metathesis reactions.

Experimental Section

General. All manipulations of air and moisture sensitive materials were conducted under a nitrogen atmosphere in a Vacuum Atmospheres drybox or on a dual-manifold Schlenk line. The glassware, including NMR tubes were oven-dried prior to use. Ether, pentane, toluene, dichloromethane, toluene and benzene were degassed with dinitrogen and passed through activated alumina columns and stored over 4 Å Linde-type molecular sieves. Dimethoxyethane was vacuum distilled from a dark purple solution of sodium benzophenone ketyl, and degassed three times by freeze−pump−thaw technique. The deuterated solvents were dried over 4 Å Linde-type molecular sieves prior to use. ^1H, ^{13}C spectra were acquired at room temperature unless otherwise noted using Varian spectrometers and referenced to the residual $^1H/^{13}C$ resonances of the deuterated solvent (^1H: $CDCl_3$, δ 7.26; C_6D_6, δ 7.16; CD_2Cl_2, δ 5.32. ^{13}C: $CDCl_3$, δ 77.23; C_6D_6, δ 128.39; CD_2Cl_2, δ 54.00) and are reported as parts per million relative to tetramethylsilane. ^{19}F NMR spectra were referenced externally to fluorobenzene (δ - 113.15 ppm upfield of $CFCl_3$). ^{31}P NMR spectra were referenced externally to phosphoric acid 85% (δ 0 ppm). High resolution mass spectrometry measurements were performed at the MIT Department of Chemistry Instrument Facility, and elemental analyses were performed by H. Kolbe Mikroanalytisches Laboratorium, Mülheim an der Ruhr, Germany and Midwest Microlab, Indianapolis, Indiana.

$Mo(NAd)(CHCMe_2Ph)(2,5\text{-}Me_2NC_4H_2)_2$ (**1**),[12] $Mo(NAr)(CHCMe_2Ph)(2,5\text{-}Me_2NC_4H_2)_2$,[11] $2,5\text{-}Ph_2NC_4H_3$,[20] and $2,5\text{-}i\text{-}Pr_2NC_4H_3$[21] were prepared as described in the literature.

$Mo(NAr)(CHCMe_2Ph)(2,3,4,5\text{-}Me_4NC_4)_2$ (2). A cold solution of $2,3,4,5\text{-}Me_4NC_4Li$ (288 mg, 2.23 mmol, 2 equiv) in 5 mL diethylether was added dropwise to a cold suspension of $Mo(NAr)(CHCMe_2Ph)(dme)(OTf)_2$ (881 mg, 1.11 mmol, 1 equiv) in 5 mL diethylether. The reaction mixture was stirred at room temperature for 1 h. The volatile materials were removed under vacuum. The reaction mixture was extracted with CH_2Cl_2 and filtered through celite. After recrystallization from diethylether 166 mg of red crystals were obtained (yield = 23%). ^1H NMR (500 MHz, C_6D_6) δ 12.51 (s, 1H, *syn* Mo=C*H*, J_{CH} = 125.1 Hz), 7.35 (d, 2H, *Ar*, J = 7.5 Hz), 7.13 (t, 2H, *Ar*, J = 7.5 Hz), 7.06−6.93 (m, 4H, *Ar*), 3.62 (sept, 2H, MeC*H*Me, J = 6.7 Hz), 2.07 (s, 12H, NC_4Me_2), 1.80 (s, 12H, NC_4Me_2), 1.70 (s, 6H, C*Me*$_2$Ph), 1.16 (d, 12H, *Me*CH*Me*, J = 6.7 Hz); ^{13}C NMR (125 MHz, C_6D_6) δ 305.0,

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152.9, 150.5, 147.9, 132.4, 128.9, 127.9, 126.7, 126.5, 124.4, 120.3, 58.0, 32.1, 27.2, 25.3, 16.0, 11.2. Anal. salcd for $C_{38}H_{53}MoN_3$: C, 70.46; H, 8.25; N, 6.49; Found: C, 70.26; H, 8.21; N, 6.37.

X-Ray quality crystals were grown from diethyl ether at −30 °C.

Mo(NAr)(CHCMe$_2$Ph)(2,5-*i*-Pr$_2$NC$_4$H$_2$)$_2$ (3). A cold solution of 2,5-*i*-Pr$_2$NC$_4$H$_2$Li (307 mg, 1.95 mmol, 2 equiv) in 5 mL diethylether was added dropwise to a cold suspension of Mo(NAr)(CHCMe$_2$Ph)(OTf)$_2$(dme) (713 mg, 0.977 mmol, 1 equiv) in 5 mL diethylether. The reaction mixture was stirred at room temperature for 1 h. The reaction mixture changed from yellow to red. The volatile materials were removed under vacuum. The reaction mixture was extracted with CH_2Cl_2. The crude product was recrystallized from Et$_2$O/pentane to yield 586 mg of red crystals (yield = 83%): ^{1}H NMR (500 MHz, C_6D_6) δ 13.58 (s, 1H, *syn* Mo=C*H*, J_{CH} = 124.6 Hz), 7.37 (d, 2H, *Ar*, *J* = 7.7 Hz), 7.22−6.91 (m, 6H, *Ar*), 6.18 (s, 4H, NC$_4$*H*$_2$), 3.65 (sept, 2H, MeC*H*Me, *J* = 6.5 Hz), 2.79 (sept, 4H, MeC*H*Me, *J* = 6.5 Hz), 1.78 (s, 6H, C*H*$_3$), 1.24 (d, 12H, *Me*CH*Me*, *J* = 6.5 Hz), 1.16 (d, 12H, *Me*CH*Me*, *J* = 6.5 Hz), 1.08 (br, 12H, *Me*CH*Me*); ^{13}C NMR (125 MHz, C_6D_6) δ 305.8, 153.9, 150.0, 149.2 (br), 146.9, 129.0, 128.7, 126.8, 126.6, 124.4, 105.0, 58.1, 31.9, 31.2, 28.8, 25.9, 25.0 (br), 24.8. Anal. calcd for $C_{42}H_{61}MoN_3$: C, 71.67; H, 8.73; N, 5.97; Found: 71.87; H, 8.69; N, 6.01.

X-Ray quality crystals were grown from a mixture of diethyl ether and pentane at −30 °C.

Mo(NAr)(CHCMe$_3$)(2,5-Ph$_2$NC$_4$H$_2$)$_2$ (4). A cold suspension of 2,5-Ph$_2$NC$_4$H$_2$Li (309 mg, 1.37 mmol, 2 equiv) in 5 mL diethylether was added dropwise to a cold suspension of Mo(NAr)(CHCMe$_3$)(OTf)$_2$(dme) (500 mg, 0.685 mmol, 1 equiv) in 5 mL diethylether. The reaction mixture was stirred at room temperature for 1 h. The volatile materials were removed under vacuum. The compound was extracted with CH_2Cl_2 and filtered through celite. After recrystallization from a mixture of CH_2Cl_2 and pentane 279 mg of yellow crystals were obtained (yield = 52%): ^{1}H NMR (500 MHz, CD_2Cl_2) δ 13.64 (s, 1H, *syn* Mo=C*H*, J_{CH} = 132.0 Hz), 7.59 (br, 8H, *Ar*), 7.37−7.10 (m, 5H, *Ar*), 6.04 (br s, 4H, NC$_4$*H*$_2$), 3.07 (br, 2H, MeC*H*Me), 1.13 (br, 12H, *Me*CH*Me*), 0.22 (s, 9H, C*Me*$_3$); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 333.9, 152.2, 129.5, 128.2, 127.8, 124.3, 51.5, 31.5, 27.9, 26.4, 23.2. Anal. calcd for $C_{49}H_{51}MoN_3$: C, 75.66; H, 6.61; N, 5.40; Found: C, 75.48; H, 6.54; N, 5.32.

X-Ray quality crystals were grown from a mixture of dichloromethane and pentane at −30 °C.

Mo(NAr)(CHCMe$_2$Ph)(2,5-Ph$_2$NC$_4$H$_2$)$_2$ (5). A cold solution of 2,5-Ph$_2$NC$_4$H$_2$Li (227 mg, 1.01 mmol, 2 equiv) in 5 mL diethylether was added dropwise to a cold suspension of Mo(NAr)(CHCMe$_2$Ph)(OTf)$_2$(dme) (399 mg, 0.504 mmol, 1 equiv) in 5 mL diethylether. The reaction mixture was stirred at room temperature for 1 h. The volatile materials were removed under vacuum. The compound was extracted with CH_2Cl_2 and filtered through celite. After recrystallization from a mixture of toluene and pentane 330 mg of yellow-orange crystals were obtained (yield = 78%). ^{1}H NMR (500 MHz, CD_2Cl_2) δ 13.82 (s, 1H, *syn* Mo=C*H*, J_{CH} = 134.2 Hz), 7.50 (br, 7H, *Ar*), 7.29−7.06 (m, 12H, *Ar*), 7.01−6.88 (m, 3H, *Ar*), 6.20 (d, 2H, *Ar*, *J* = 7.1 Hz), 6.05 (br s, 4H, NC$_4$*H*$_2$), 3.08 (br, 2H, MeC*H*Me), 1.16 (br app d, 6H, *Me*CH*Me*), 1.10 (br, 6H, *Me*CH*Me*), 0.92 (s, 6H, C*Me*$_2$Ph); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 329.7, 152.1, 150.6, 148.6, 136.3, 129.4 (br), 128.7, 128.2, 128.0, 127.6, 126.2 (br), 124.3 (br), 108.0 (br), 57.5, 28.1, 26.7, 26.4. Anal. calcd for $C_{54}H_{53}MoN_3$: C, 77.22; H, 6.36; N, 5.00; Found: C, 76.91; H, 6.38; N, 5.04.

Mo(NAr)(CHCMe$_2$Ph)(indolide)$_2$ (6). Mo(NAr)(CHCMe$_2$Ph)(OTf)$_2$(dme) (1.00 g, 1.28 mmol, 1 equiv) was dissolved in 10 mL of −30 °C Et$_2$O. Li(indolide) (0.319 g, 2.65 mmol, 2.05 eq) was added portionwise to the rapidly stirring solution over the course of 5 min. The solution was then allowed to warm to room temperature and was stirred for 90 min during which time the color of the solution became deep red-orange. All volatile components were removed *in vacuo* and resulting yellow powder was extracted with 20 mL of toluene which was filtered through medium porosity sintered glass frit. The toluene was removed *in vacuo* then the resulting solid was left to crystallize from saturated Et$_2$O solution at −30 °C. Mo(NAr)(CHCMe$_2$Ph)(indolide)$_2$ (0.620 g, 0.98 mmol, yield = 76%) was isolated as an orange microcrystalline solid: ^{1}H NMR (C_6D_6) δ 11.87 (s, 1H, J_{CH} = 116 Hz, Mo=C*H*), 7.76 (d, 2H, J_{CH} = 8.2 H, ind), 7.65 (d, 2H, J_{CH} = 7.7 Hz, ind), 7.65 (d, 2H, J_{CH} = 7.7 Hz, ind), 7.41 (m, 2H, J_{CH} = 3.2 Hz, ind), 7.33 (d, 2H, $^1J_{CH}$ = 8.2 Hz, $^2J_{CH}$ = 0.9 Hz, ind), 7.19 (d, 2H, N*Ar*), 7.10 (t, 1H, N*Ar*), 6.59 (dd, 2H, $^1J_{CH}$ = 3.2 Hz, $^2J_{CH}$ = 0.9 Hz, ind), 3.42 (septet, 2H, C*H*Me$_2$), 1.65 (s, 6H, C*Me*$_2$Ph), 0.86 (d, 12H, CH*Me*$_2$). ^{13}C{^{1}H} NMR (C_6D_6): δ 286.8 (Mo=C), 154.1, 147.9, 147.3, 145.0, 139.6, 131.1, 129.5, 129.2, 127.4, 126.6, 123.9, 123.2, 122.2, 121.0, 115.6, 107.8, 56.6, 30.9, 29.0, 24.0. Anal. calcd. for $C_{38}H_{41}N_3Mo$: C, 71.80; H, 6.50; N, 6.61; Found: C, 71.63; H, 6.43; N, 6.54.

X-Ray quality crystals were grown from toluene at −30 °C.

Mo(NAd)(CHCMe$_2$Ph)(indolide)$_2$ (7). Mo(NAd)(CHCMe$_2$Ph)(OTf)$_2$(dme) (0.500 g, 0.66 mmol, 1 equiv) was dissolved in 5 mL of −30 °C toluene. Li(indolide) (0.165 g, 1.34 mmol, 2.05 eq) was added portionwise to the rapidly stirring solution over the course of 5 min. The solution was then allowed to warm to room temperature and was stirred for 90 min during which time the color of the solution became dark yellow. The resulting toluene solution which was filtered through medium porosity sintered glass frit and then all volatile components were removed *in vacuo.* The resulting oil was then triturated in 20 mL of pentane to give 260 mg (0.43 mmol, yield = 64%) of Mo(NAd)(CHCMe$_2$Ph)(indolide)$_2$ as a yellow powder which was isolated by filtration. ^{1}H NMR (C_6D_6): δ 11.47 (s, 1H, J_{CH} = 113 Hz, Mo=C*H*), 7.92 (d, 2H, ind), 7.69 (d, 2H, ind), 7.52 (d, 2H, ind), 7.36 (d, 2H, ind), 7.28 (t, 2H, CHMe*Ph*), 7.21 (t, 2H, ind), 7.12 (t, 2H, CHMe*Ph*), 7.23(t, 1H, CHMe*Ph*), 6.64 (d, 2H, ind), 1.92 (br, 6H, N*Ad*), 1.71 (br, 3H, N*Ad*), 1.65 (s, 6H, C*Me*$_2$Ph), 1.27 (m, 6H, N*Ad*). ^{13}C{^{1}H} NMR (C_6D_6): δ 280.2 (Mo=C), 148.7, 145.7, 140.4, 131.2, 129.8, 129.3, 127.3, 123.1, 122.2, 121.1, 115.6, 107.6, 79.1, 53.9, 46.0, 36.1, 32.0, 20.4. Anal. calcd for $C_{36}H_{39}N_3Mo$: C, 70.92; H, 6.45; N, 6.89; Found: C, 71.08; H, 6.95; N, 6.95.

Mo(NAr)(CHCMe$_2$Ph)(indolide)$_2$(THF)(8). Mo(NAr)(CHCMe$_2$Ph)(OTf)$_2$(dme) (1.00 g, 1.28 mmol, 1 equiv) was dissolved in 10 mL of −30 °C Et$_2$O. Li(indolide) (0.319 g, 2.65 mmol, 2.05 equiv) was added as a solid to the rapidly stirring solution over the course of 5 min. The solution was then allowed to warm to room temperature and was stirred for 90 min during which time the color of the solution became deep red-orange. All volatile components were removed *in vacuo* and resulting yellow powder was extracted with 20 mL of toluene which was filtered through medium porosity sintered glass frit. The toluene was removed *in vacuo* then the resulting solid was dissolved in 5 mL of THF and left −30 °C for 18 h. All volatiles were removed *in vacuo* and the resulting dark yellow solid was triturated in 10 mL of pentane and isolated by filtration (0.623 g, 0.88 mmol, yield = 69%). ^{1}H NMR (C_6D_6): δ 12.67 (s, 1H, J_{CH} = 120 Hz, Mo=C*H*), 7.72 (m, 4H, ind), 7.41 (d, 2H, J_{CH} = 7.7 Hz, ind), 7.38 (d, 2H, J_{CH} = 7.7 Hz, ind), 7.14 (m, 6H), 6.82 (m, 2H), 6.70 (d, 2H, ind), 3.42 (septet, 2H, C*H*Me$_2$), 3.08 (t, 4H, δ-THF), 1.76 (s, 6H, C*Me*$_2$Ph), 0.90 (q, 4H, δ-THF), 0.81 (d, 12H, CH*Me*$_2$). ^{13}C{^{1}H} NMR (C_6D_6): δ 293.6 (Mo=C), 152.7, 150.7, 148.4, 144.7, 139.7, 131.1, 129.5, 129.4, 127.4, 126.6, 124.8, 121.8, 121.0, 120.2, 114.4, 104.9, 71.2, 56.9, 31.2, 28.1, 25.2, 24.6. Anal. calcd for $C_{42}H_{49}N_3OMo$: C, 71.37; H, 6.85; N, 5.95; Found: C, 71.32; H, 6.78; N, 5.97.

Mo(NAr)(CHCMe$_2$Ph)(2,3,4,5-Me$_4$NC$_4$)[OC(CF$_3$)$_2$Me] (9). A cold solution of Me(CF$_3$)$_2$COH (75 mg, 0.41 mmol, 1 equiv) in 5 mL diethylether was added dropwise to a cold solution of Mo(NAr)(CHCMe$_2$Ph)(2,3,4,5-Me$_4$NC$_4$)$_2$ (265 mg, 0.41 mmol, 1 equiv) in 5 mL diethylether. The reaction mixture was stirred at room temperature for 30 min. The volatile materials were removed under vacuum. Pentane was added and the reaction mixture was placed at −30 °C overnight. White crystals (2,3,4,5-Me_4NHC_4) are formed and the solution was decanted (3×). The volatile materials were removed under vacuum to generate 217 mg of red oil (yield = 75%). ^{1}H NMR (500 MHz, C_6D_6) δ 12.41 (s, 1H, *syn* Mo═C*H*, J_{CH} = 119.2 Hz), 7.31 (d, 2H, *Ar*, J = 7.7 Hz), 7.13 (t, 2H, *Ar*, J = 7.7 Hz), 7.03−6.95 (m, 4H, *Ar*), 3.69 (br, 2H, MeC*H*Me), 2.18 (br s, 6H, C*H*$_3$), 1.89 (s, 6H, C*H*$_3$), 1.71 (s, 3H, C*H*$_3$), 1.60 (s, 3H, C*H*$_3$), 1.30−1.00 (m, 15H, *Me*CH*Me* and C*H*$_3$); ^{13}C NMR (125 MHz, C_6D_6) δ 289.9, 153.6, 148.3, 148.1 (br), 129.2, 129.0, 128.7, 128.5, 128.3, 127.0, 126.5, 123.8, 81.6 (sept), 55.5, 31.5 (app q), 30.3 (app q), 29.1 (br), 24.1 (br), 19.3, 14.3 (br), 10.5 (br); ^{19}F NMR (282 MHz, C_6D_6) δ −78.05 (q, J = 9.3 Hz), −78.25 (q, J = 9.3 Hz). Anal. calcd for $C_{34}H_{44}F_6MoN_2O$: C, 57.79; H, 6.28; N, 3.96; Found: C, 57.99; H, 6.41; 4.02.

Mo(NAr)(CHCMe$_2$Ph)(2,5-*i*-Pr$_2$NC$_4$H$_2$)[OC(CF$_3$)$_2$Me] (10). Method 1. A cold solution of $Me(CF_3)_2COH$ (96 mg, 0.53 mmol, 1 equiv) in 5 mL diethylether was added dropwise to a cold solution of Mo(NAr)($CHCMe_2Ph$)(2,5-*i*-$Pr_2NC_4H_2$)$_2$ (372 mg, 0.53 mmol, 1 equiv) in 5 mL diethylether. The reaction mixture was stirred at room temperature for 1 h. The volatile materials were removed under vacuum. After recrystallization from pentane 245 mg of red crystals were obtained (yield = 63%).

Method 2. A cold suspension of 2,5-*i*-$Pr_2NC_4H_2Li$ (85.4 mg, 0.544 mmol, 1 equiv) in 5 mL diethylether was added dropwise to a cold solution of Mo(NAr)($CHCMe_2Ph$)[OC(CF_3)$_2$Me]$_2$ (416 mg, 0.544 mmol, 1 equiv) in 5 mL diethylether. The reaction mixture was stirred at room temperature for 1 h. The reaction mixture changed from yellow to orange to red. The volatile materials were removed under vacuum. Toluene was added and the reaction mixture was placed at −35 °C overnight. White solid is formed and the solution was decanted (3×). The volatile materials were removed under vacuum. After recrystallization from pentane 154 mg of red crystals were obtained (yield = 40%): ^{1}H NMR (500 MHz, C_6D_6) δ 12.71 (s, 1H, *syn* Mo═C*H*, J_{CH} = 119.3 Hz), 7.29 (d, 2H, *Ar*, J = 7.7 Hz), 7.11 (t, 2H, *Ar*, J = 7.7 Hz), 7.02−6.93 (m, 4H, *Ar*), 6.07 (s, 2H, NC$_4$*H*$_2$), 4.10−3.10 (br, 2H, MeC*H*Me), 2.88 (br, 2H, MeC*H*Me), 1.67 (s, 3H, C*H*$_3$), 1.64 (s, 3H, C*H*$_3$), 1.27 (br app d, 6H, MeC*H*Me, J = 6.5 Hz), 1.23 (br app d, 6H, MeC*H*Me, J = 6.5 Hz), 1.15 (app d, 6H, MeC*H*Me, J = 6.5 Hz), 1.11 (s, 3H, C*H*$_3$); ^{13}C NMR (125 MHz, C_6D_6) δ 292.4, 154.0, 148.3, 148.1, 146.9, 129.7, 129.1, 127.1, 126.4, 106.0, 105.9, 81.9, 56.0, 31.6, 31.5, 31.0, 30.7, 30.2, 30.1, 29.2, 25.7, 25.3−22.8 (br), 19.5, 19.4; ^{19}F NMR (282 MHz, C_6D_6) δ −77.52 (q, J = 8.9 Hz), −78.00 (q, J = 8.9 Hz). Anal. calcd for $C_{36}H_{48}F_6MoN_2O$: C, 58.85; H, 6.59; N, 3.81; Found: C, 58.53; H, 6.40; N, 3.96.

Mo(NAr)(CHCMe$_2$Ph)(2, 5-Ph$_2$NC$_4$H$_2$)[OC(CF$_3$)$_2$Me] (11). A cold solution of 2,5-$Ph_2NC_4H_2Li$ (192 mg, 0.853 mmol, 1.1 equiv) in 5 mL diethylether was added dropwise to a cold solution of Mo(NAr)($CHCMe_2Ph$)[OC(CF_3)$_2$Me]$_2$ (594 mg, 0.775 mmol, 1 equiv) in 5 mL diethylether. The reaction mixture was stirred at room temperature for 1 h. The reaction mixture changed from yellow to orange to red. The volatile materials were removed under vacuum. Toluene was added and the reaction mixture was placed at −30 °C overnight. White solid is formed and the solution was decanted (3×). The volatile materials were removed under vacuum. After recrystallization from pentane 405 mg of red crystals were obtained (yield = 65%): ^{1}H NMR (500 MHz, C_6D_6) δ 12.71 (s, 1H, *syn* Mo═C*H*, J_{CH} = 121.6 Hz), 7.69 (d, 4H, *Ar*, J = 7.0 Hz), 7.42−6.70 (m, 14H, *Ar*), 6.52 (br s, 2H, NC$_4$*H*$_2$), 3.02 (br, 2H, MeC*H*Me), 1.51 (s, 3H, C*H*$_3$), 1.28−1.02 (br, 9H, C*H*$_3$), 0.85 (br, 6H, C*H*$_3$), 0.69 (s, 3H, C*H*$_3$); ^{13}C NMR (125 MHz, C_6D_6) δ 296.4, 154.2, 148.5, 148.1, 147.6, 137.5 (br), 129.7 (br), 129.4, 129.3, 128.8, 128.7, 127.5 (br), 126.9, 126.7, 126.2, 124.5, 123.7, 123.0, 112.1 (br), 108.9, 56.1, 29.9, 29.0, 28.4, 25.3, 24.9, 24.1, 23.5, 19.0; ^{19}F NMR (282 MHz, C_6D_6) δ −77.28 (q, J = 9.6 Hz), −78.06 (q, J = 9.6 Hz). Anal. calcd for $C_{42}H_{44}F_6MoN_2O$: C, 62.84; H, 5.52; N, 3.49; Found: C, 62.92; H, 5.58; N, 3.56.

Mo(NAd)(CHCMe$_2$Ph)(NC$_4$H$_4$)$_2$(PMe$_3$) (12). Excess trimethylphosphine (50 μL) was added to 150 mg (0.25 mmol) of Mo(NAd)($CHCMe_2Ph$)(NC_4H_4)$_2$ • tol in diethyl ether. The mixture was stirred at room temperature for 30 min and the solvent was removed *in vacuo*. Mo(NAd)($CHCMe_2Ph$)(NC_4H_4)$_2$(PMe_3) may be crystallized from pentane as orange blocks, yield 100 mg (69%): ^{1}H NMR (300 MHz, C_6D_6) δ 12.49 (d, 1H, J_{H-P} = 4.8 Hz, C*H*CMe$_2$Ph), 7.16−6.98 (m, 5H, CHCMe$_2$*Ph*), 6.97 (s, 4H, NC$_4$*H*$_4$), 6.40 (s, 4H, NC$_4$H$_4$), 1.99 (s, 3H, N*Ad*), 1.9−1.79 (m, 6H, N*Ad*), 1.68 (s, 6H, MoCHC*Me*$_2$Ph), 1.35 (s, 6H, N*Ad*), 0.45 (d, 9H, P*Me*$_3$); ^{13}C NMR (C_6D_6) δ 301.73 (d, 2J_{C-P} = 19.5 Hz, Mo*C*HCMe$_2$Ph,), 148, 132.19, 129.13, 126.37, 125.96, 109.16, 108.62, 42.22, 36.21, 30.03, 16.50 (d, P*Me*$_3$, J_{C-P} = 25 Hz). Anal. calcd for $C_{31}H_{44}MoN_3P$: C, 63.58; H, 7.57; N, 7.17; Found: C, 63.37; H, 7.45; N, 6.04.

Mo(NAr)(CHCMe$_2$Ph)[OCMe(CF$_3$)$_2$](2,5-Me$_2$NC$_4$H$_2$)(PMe$_3$) (13). PMe_3 (31 μL, 23 mg, 0.295 mmol) was syringed into a solution of Mo(NAr)($CHCMe_2Ph$)(2,5-$Me_2NC_4H_2$)[OCMe(CF_3)$_2$] (200 mg, 0.295 mmol) in 10 mL of pentane. The reaction mixture was stirred at room temperature for 30 min during which time a yellow precipitation was observed. The product was isolated by filtration (180 mg, yield = 82%): ^{1}H NMR (C_6D_6, 500 MHz) δ 14.07 (s, 1, *syn* Mo═C*H*, J_{CH} = 122 Hz), 7.27 (d, 2, *Ar*), 7.09 (t, 3, *Ar*), 7.00 (m, 3, *Ar*), 6.22 (s, 1, *Pyr*), 6.00 (s, 1, *Pyr*), 4.23 (br, 1, C*H*Me$_2$), 3.46 (br, 1, C*H*Me$_2$), 2.44 (s, 3, Pyr$_{Me}$), 2.78 (s, 3, Pyr$_{Me}$), 1.81 (s, 3, CHC*Me*$_2$), 1.52 (s, 3, CHC*Me*$_2$), 1.35 (br, 3, CH*Me*$_2$), 1.13 (br, 3, CH*Me*$_2$), 1.08 (s, 3, OC*Me*) 1.05 (br, 3, CH*Me*$_2$), 0.83 (d, 9, Mo(P*Me*$_3$)) 0.79 (br, 3, CH*Me*$_2$); ^{13}C NMR (CD_2Cl_2, 125 MHz) δ 309.55 (Mo═CH), 150.18, 149.24, 147.87, 144.47, 133.04, 132.93, 129.25, 128.89, 127.56, 127.39, 126.57, 126.21, 124.91, 124.28, 123.77, 121.98, 106.24, 81.88, 56.01, 32.43, 28.48, 28.34, 24.96, 24.12, 18.28, 16.46, 15.15, 13.92; ^{19}F NMR (C_6D_6, 282 MHz) δ − 75.58, − 77.12; ^{31}P NMR (C_6D_6, 121 MHz) δ − 5.72; Anal. calcd for $C_{35}H_{49}F_6MoN_2OP$: C, 55.70; H, 6.54; N, 3.71. Found: C, 55.61; H, 6.39; N, 3.63.

Mo(NAr)(CHCMe$_2$Ph)(2,3,4,5-Me$_4$NC$_4$)[OC(CF$_3$)$_2$Me](PMe$_3$) (14). PMe_3 (10.7 μL, 0.104 mmol, 1.1 equiv) was syringed into a solution of Mo(NAr)($CHCMe_2Ph$)(2,3,4,5-Me_4NC_4)[OCMe(CF_3)$_2$] (66.5 mg, 0.0941 mmol, 1 equiv) in 5 mL of pentane. The reaction mixture was stirred at room temperature for 30 min during which time a red precipitation was observed. The product was isolated by filtration (58 mg, yield = 78%): ^{1}H NMR (300 MHz, C_6D_6) δ 14.02 (d, 1H, *syn* Mo═C*H*, J_{CH} = 124.8 Hz, J_{PH} = 4.8 Hz), 7.29 (d, 2H, *Ar*, J = 7.5 Hz), 7.10 (t, 2H, *Ar*, J = 7.5 Hz), 7.05−6.85 (m, 4H, *Ar*), 4.17 (br, 1H, MeC*H*Me), 3.58 (br, 1H, MeC*H*Me), 2.33 (s, 3H, C*H*$_3$), 2.24 (s, 3H, C*H*$_3$), 2.22 (s, 3H, C*H*$_3$), 2.02 (s, 3H, C*H*$_3$), 1.80 (s, 3H, C*H*$_3$), 1.56 (s, 3H, C*H*$_3$), 1.48−0.60 (br m, 12H, *Me*CH*Me*), 1.01 (s, 3H, C*H*$_3$), 0.86 (d, 9H, P*Me*$_3$, J = 8.7 Hz); ^{13}C NMR (125 MHz, C_6D_6) δ 308.5 (d, J_{PC} = 17.8 Hz), 150.5, 148.2, 129.2, 128.7, 128.5, 128.3, 127.9, 127.7 (br), 127.3, 127.2, 127.0, 126.3 (br), 125.0, 114.1, 114.0, 55.8, 28.4, 25.0 (br), 14.5 (br); ^{19}F NMR (282 MHz, C_6D_6) δ −75.61 (q, J = 8.9 Hz), −77.20 (q, J = 8.9 Hz); ^{31}P NMR (121 MHz, C_6D_6) δ 6.15. Anal. calcd for $C_{37}H_{53}F_6MoN_2OP$: C, 56.77; H, 6.82; N, 3.58; Found: C, 56.77; H, 6.75; N, 3.52.

Mo(NAr)(CHCMe$_2$Ph)(2,5-*i*-Pr$_2$NC$_4$H$_2$)[OC(CF$_3$)$_2$Me](PMe$_3$) (15). PMe_3 (46 μL, 0.443 mmol, 1 equiv) was syringed into a solution of Mo(NAr)($CHCMe_2Ph$)(2,5-i$Pr_2NC_4H_2$)[OCMe(CF_3)$_2$] (325.3 mg, 0.443 mmol, 1 equiv) in 5 mL of pentane. The reaction mixture was stirred at room temperature for 30 min during which time a yellow precipitation was observed. The product was isolated by filtration (269 mg, yield = 75%): ^{1}H NMR (500 MHz, C_6D_6) δ 14.27 (d, 1H, *syn* Mo═C*H*, J_{CH} = 124.1 Hz, J_{PH} = 4.5 Hz), 7.31 (d, 2H, *Ar*, J = 7.8 Hz), 7.10 (t, 2H, *Ar*, J = 7.8 Hz), 7.05−6.85

(m, 4H, *Ar*), 6.33 (d, 1H, NC$_4$*H*, *J* = 2.9 Hz), 6.20 (d, 1H, NC$_4$*H*, *J* = 2.9 Hz), 4.22 (sept, 1H, MeC*H*Me, *J* = 6.7 Hz), 3.50 (sept, 1H, MeC*H*Me, *J* = 6.7 Hz), 3.03 (sept, 1H, MeC*H*Me, *J* = 6.7 Hz), 2.98 (sept, 1H, MeC*H*Me, *J* = 6.7 Hz), 1.78 (s, 3H, C*H*$_3$), 1.66 (d, 3H, C*H*$_3$, *J* = 6.7 Hz), 1.59 (s, 3H, C*H*$_3$), 1.42 (d, 3H, C*H*$_3$, *J* = 6.7 Hz), 1.33 (t, 6H, C*H*$_3$, *J* = 6.7 Hz), 1.22 (s, 3H, C*H*$_3$), 1.17 (d, 3H, C*H*$_3$, *J* = 6.7 Hz), 1.08 (d, 3H, C*H*$_3$, *J* = 6.7 Hz), 0.97 (d, 3H, C*H*$_3$, *J* = 6.7 Hz), 1.04−0.70 (br, 9H), 0.76 (d, 3H, C*H*$_3$, *J* = 6.7 Hz); ^{13}C NMR (125 MHz, C$_6$D$_6$) δ 310.1 (d, J_{PC} = 18.3 Hz), 150.7, 150.0, 148.0, 146.9, 144.4, 143.9, 143.5, 129.3, 127.4, 126.4, 126.3, 125.6, 125.1, 123.7, 104.9, 104.8, 128.5 (overlap with *C*$_6$D$_6$), 128.3 (overlap with *C*$_6$D$_6$), 103.8, 103.6, 56.3, 32.5 (br), 31.3 (br), 31.1 (br), 28.8, 28.6, 28.4, 25.5; ^{19}F NMR (282 MHz, C$_6$D$_6$) δ −74.39 (q, *J* = 9.1 Hz), −76.48 (q, *J* = 9.1 Hz); ^{31}P NMR (121 MHz, C$_6$D$_6$) δ −4.76. Anal. calcd for $C_{39}H_{57}F_6MoN_2OP$: C, 57.77; H, 7.09; N, 3.46; Found: C, 57.50; H, 6.91; N, 3.43.

Mo(NAr)(CHCMe$_2$Ph)(2,5-Ph$_2$NC$_4$H$_2$)[OC(CF$_3$)$_2$Me](PMe$_3$) (16). PMe$_3$ (26 μL, 0.249 mmol, 1.1 equiv) was added dropwise to a cold solution of Mo(NAr)(CHCMe$_2$Ph)(2,5-Ph$_2$NC$_4$H$_2$)-[OC(CF$_3$)$_2$Me] (182 mg, 0.227 mmol, 1 equiv) in 5 mL pentane. The reaction mixture was stirred at room temperature for 30 min. The reaction mixture changed from red to orange. After recrystallization from pentane 159 mg of orange crystals were obtained (yield = 80%): ^{1}H NMR (500 MHz, C$_6$D$_6$) δ 14.75 (d, 1H, *syn* Mo=C*H*, J_{CH} = 125.7 Hz, J_{PH} = 5.5 Hz), 8.12 (d, 2H, *Ar*, *J* = 7.0 Hz), 7.63 (d, 2H, *Ar*, *J* = 7.0 Hz), 7.43 (t, 2H, *Ar*, *J* = 7.5 Hz), 7.27 (d, 2H, *Ar*, *J* = 8.0 Hz), 7.12 (t, 2H, *Ar*, *J* = 8.0 Hz), 7.03 (t, 2H, *Ar*, *J* = 7.5 Hz), 7.01−6.85 (m, 2H, *Ar*), 6.79 (t, 1H, *Ar*, *J* = 7.5 Hz), 6.72−6.60 (m, 3H, *Ar*), 3.72 (br, 1H, MeC*H*Me), 3.03 (br, 1H, MeC*H*Me), 1.53 (s, 3H, C*H*$_3$), 1.40 (s, 3H, C*H*$_3$), 1.23 (br, 3H, C*H*$_3$), 0.96 (d, 9H, P*Me*$_3$, *J* = 9.0 Hz), 0.95 (overlap br, 6H, C*H*$_3$), 0.58 (s, 3H, C*H*$_3$), 0.56 (br, 3H, C*H*$_3$); ^{13}C NMR (125 MHz, C$_6$D$_6$) δ 316.0 (d, J_{PC} = 18.1 Hz), 151.6 (br), 150.25, 148.7, 145.5, 144.1, 143.0 (d, *J* = 3.1 Hz), 141.5, 140.4, 131.0 (d, *J* = 7.1 Hz), 129.8, 129.2, 128.0, 127.3, 126.5, 126.3, 125.8, 125.7, 125.5, 124.6 (br), 122.7 (br), 115.0 (d, *J* = 10.6 Hz), 113.1 (d, *J* = 4.7 Hz), 83.6 (sept, O*C*(CF$_3$)$_2$, J_{CF} = 27.5 Hz), 58.0, 56.1, 31.0−14.0 (br); ^{19}F NMR (282 MHz, C$_6$D$_6$) δ −70.82 (q, *J* = 10.3 Hz), −72.68 (q, *J* = 10.3 Hz); ^{31}P NMR (121 MHz, C$_6$D$_6$) δ −3.09. Anal. calcd for $C_{45}H_{53}F_6MoN_2OP$: C, 61.50; H, 6.08; N, 3.19; Found: C, 61.22; H, 5.95; N, 3.33.

X-Ray quality crystals were grown from pentane at −30 °C.

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Supporting Information Available: Crystallographic data and CIF files for all structurally characterized compounds. This material is available free of charge via the Internet at http://pubs.acs.org. Data for the structures are also available to the public at http://www.reciprocalnet.org/.

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