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Synthesis and Evaluation of Molybdenum and Tungsten Monoaryloxide Halide Alkylidene Complexes for *Z*-Selective Cross-Metathesis of Cyclooctene and *Z*-1,2-Dichloroethylene

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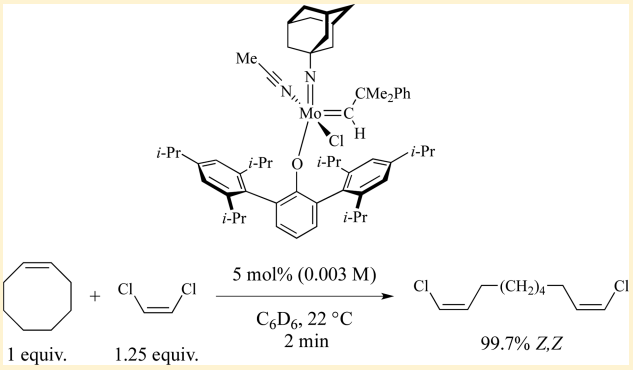
Supporting Information

ABSTRACT: Molybdenum complexes with the general formula Mo(NR)(CHR′)(OR″)(Cl)(MeCN) (R = *t*-Bu or 1-adamantyl; OR″ = a 2,6-terphenoxide) recently have been found to be highly active catalysts for cross-metathesis reactions between *Z*-internal olefins and *Z*-1,2-dichloroethylene or *Z*-$(CF_3)CH{=}CH(CF_3)$. In this paper we report methods of synthesizing new potential catalysts with the general formula M(NR)(CHR′)(OR″)(Cl)(L) in which M = Mo or W, NR = N-2,6-diisopropylphenyl or NC_6F_5, and L is a phosphine, a pyridine, or a nitrile. We also test and compare all catalysts in the cross-metathesis of *Z*-1,2-dichloroethylene and cyclooctene. Our investigations indicate that tungsten complexes are inactive in the test reaction either because the donor is bound too strongly or because acetonitrile inserts into a W=C bond. The acetonitrile or pivalonitrile Mo(NR)(CHR′)(OR″)(Cl)(L) complexes are found to be especially reactive because the 14e Mo(NR)(CHR′)(OR″)Cl core is accessible through dissociation of the nitrile to a significant extent. Pivalonitrile can be removed (>95%) from Mo(NAr)($CHCMe_2Ph$)(OHMT)(Cl)(*t*-BuCN) (Ar = 2,6-diisopropylphenyl; OHMT = 2,6-dimesitylphenoxide) to give 14e Mo(NAr)($CHCMe_2Ph$)(OHMT)Cl in solution as a mixture of *syn* and *anti* (60:40 at 0.015 M) nitrile-free isomers, but these 14e complexes have not yet been isolated in pure form. The *syn* isomer of Mo(NAr)($CHCMe_2Ph$)(OHMT)Cl binds pivalonitrile most strongly. Other Mo(NR)(CHR′)(OR″)(Cl)(L) complexes can be activated through addition of $B(C_6F_5)_3$. High stereoselectivities (>98% *Z*,*Z*) of $ClCH{=}CH(CH_2)_6CH{=}CHCl$ are not restricted to *tert*-butylimido or adamantylimido complexes; 96.2% *Z* selectivity is observed with boron-activated Mo(NC_6F_5)(CHR′)(OHIPT)(Cl)($PPhMe_2$). So far no Mo=CHCl complexes, which are required intermediates in the test reaction, have been observed in NMR studies at room temperature.



INTRODUCTION

High-oxidation-state molybdenum and tungsten complexes of the type M(Z)(CHR)(X)(Y), where Z is an imido (M = Mo or W) or an oxo ligand (M = W), have been explored as initiators of many types of olefin metathesis reactions in the last several years.[1] The most effective combinations primarily are those in which Y is a sterically demanding terphenoxide such as 2,6-dimesitylphenoxide (OHMT) and X is pyrrolide (Pyr) or 2,5-dimethylpyrrolide (Me_2Pyr).[2] These "MAP" (monoalkoxide pyrrolide) complexes have been found to be useful for *Z*-selective metathesis reactions of small molecules[3] and the ring-opening metathesis polymerization of cyclic olefins to give *cis*, *syndiotactic* polymers.[4] The most recent advances in metatheses of small molecules include the *Z*-selective[5] or *E*-selective[6] syntheses of halogenated alkenes from olefins that contain one or more electron withdrawing substituents, e.g., ClCH=CHCl,[5,6] BrCH=CHBr,[5,6] FCH=CHBr,[5,6] or, most recently, $(CF_3)CH{=}CH(CF_3)$.[7]

In the search for Mo=CHX complexes (X = Cl or Br), which are required intermediates in reactions that involve ClCH=CHCl or BrCH=CHBr, the monobromide complex, Mo(NAd)($CHCMe_2Ph$)(OHMT)(Br)(py) (Ad = 1-adamantyl and py = pyridine), was isolated in low yield.[7] An X-ray study showed that the structure of Mo(NAd)($CHCMe_2Ph$)-(OHMT)(Br)(py) is close to a square pyramid (τ = 0.21[8]) with the *syn* alkylidene in the apical position. We proposed that Mo(NAd)($CHCMe_2Ph$)(OHMT)(Br)(py) is formed when HBr, which is generated in an unknown manner in the complex reaction mixture, reacts with Mo(NAd)($CHCMe_2Ph$)-(OHMT)(Pyr). We saw no evidence for Mo=CHX

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intermediates in these reactions and began to suspect that 14e Mo(NR)(CHX)(OAr)(X) (OAr = aryloxide; X = Cl or Br) complexes might be key intermediates in cross-coupling reactions with electron-poor olefins. Therefore, we turned our attention to developing viable synthetic routes to monoaryloxide halide complexes.

A few monoaryloxide chloride ("MAC") alkylidene complexes had been published before Mo(NAd)(CHCMe$_2$Ph)(OHMT)(Br)(py) was discovered. They are Mo(NAr$_{Mes2}$)(CHCMe$_2$Ph)(OHMT)(Cl)(py), where NAr$_{Mes_2}$ is the sterically demanding 2,6-dimesitylphenylimido ligand,[9] tungsten oxo complexes such as W(O)(CH-*t*-Bu)(OHIPT)(Cl)(PMe$_2$Ph) (OHIPT = O-2,6-(2,4,6-*i*-Pr$_3$C$_6$H$_2$)$_2$C$_6$H$_3$),[10] and *tert*-butylimido complexes such as W(N-*t*-Bu)(CH-*t*-Bu)(OHMT)(Cl)(py).[11] In all X-ray studies the five-coordinate structures are close to square pyramids with the alkylidene in the apical position and the halide *trans* to the neutral 2e donor ligand (see Table S2 in the Supporting Information (SI)).

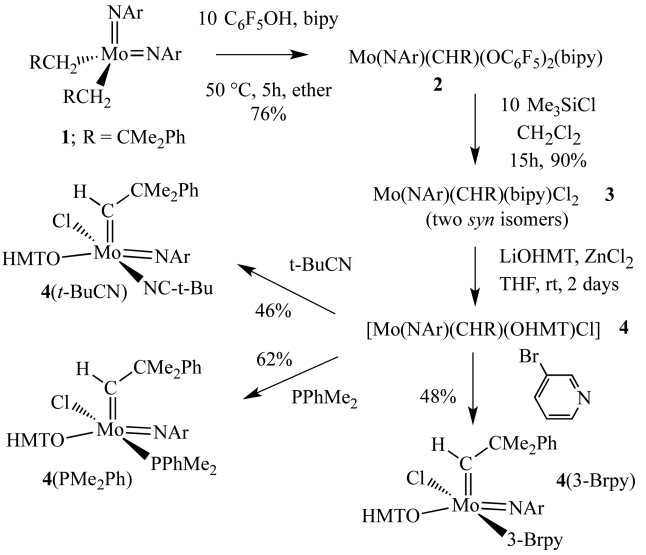
In a recent paper[7] we reported a route to 16e Mo monoaryloxide halide complexes in which acetonitrile is the donor ligand, namely Mo(N-*t*-Bu)(CH-*t*-Bu)(OHIPT)(X)(MeCN) (X = Cl, Br) and Mo(NAd)(CHCMe$_2$Ph)(OAr)(Cl)(MeCN) (OAr = OHMT or OHIPT). The acetonitrile complexes were found to be highly active for the *Z*-selective cross-metathesis reactions between *Z*-ClCH=CHCl and a selection of olefins, including cyclooctene. Pyridine analogues were much slower as a consequence of the stronger binding of pyridine to the 14e Mo(NAd)(CHCMe$_2$Ph)(OAr)Cl core compared to acetonitrile. The pyridine adducts can be activated through addition of 1 equiv of B(C$_6$F$_5$)$_3$, which sequesters all pyridine as (py)B(C$_6$F$_5$)$_3$. Because of what appear to be high reactivities, high selectivities, and unique abilities of nitrile adducts of Mo monoaryloxide halide complexes in cross-metathesis reactions involving electron-poor olefins as cross-partners,[7] we explore further in this paper the syntheses of monoaryloxide halide complexes of Mo and W and, in a test reaction, compare their activities in the ring-opening cross-metathesis (ROCM) between *Z*-ClCH=CHCl and cyclooctene to give ClCH=CH(CH$_2$)$_6$CH=CHCl.

RESULTS AND DISCUSSION

Synthesis of Mo(NAr) MAC Complexes. We chose to explore the synthesis of Mo=NAr (Ar = 2,6-*i*-Pr$_2$C$_6$H$_3$) complexes as alternatives to adamantyl or *tert*-butylimido complexes because sterically hindered NAr complexes tend to be more stable toward bimolecular decomposition.[1b,12,13]

The reaction between Mo(NAr)$_2$(CH$_2$CMe$_2$Ph)$_2$, 2,2′-bipyridine (bipy), and pentafluorophenol in diethyl ether shown in Scheme 1 is modeled after syntheses of adamantylimido and *tert*-butylimido complexes.[7,14−16] The reaction between **1**, C$_6$F$_5$OH, and bipy is extremely slow at 22 °C and generates a mixture of alkylidene complexes. However, at 50 °C in a sealed vessel Mo(NAr)(CHCMe$_2$Ph)(bipy)(OC$_6$F$_5$)$_2$ (**2**) could be prepared in 76% yield as a sparingly soluble yellow solid; only one major (>95%) alkylidene resonance for **2** was observed in the ^{1}H NMR spectrum. In the presence of pentafluorophenol alone, no alkylidene product is observed. Therefore, coordination of bipy must accelerate the α hydrogen abstraction process through binding to the metal in some intermediate on the way to **2**. (α-Abstraction is known to be accelerated by ligand binding to the dialkyl precursor complex.[12a,b]) Bipy/HCl combinations have

Scheme 1. Synthesis of Mo(NAr) MAC Complexes



been successful for the synthesis of W alkylidenes,[17] but they generally have not been effective for the synthesis of Mo alkylidene complexes.[15] The alkylidene ligand in **2** is in the *syn* orientation on the basis of the value for J_{CH} (125 Hz).[2] The two pentafluorophenoxide ligands are not equivalent according to ^{19}F NMR spectra, and the presence of two Ar methine ^{1}H resonances suggests that rotation of Ar around the N−C bond is slow on the NMR time scale.

The reaction between **2** and TMSCl afforded minimally soluble Mo(NAr)(CHCMe$_2$Ph)(bipy)Cl$_2$ (**3**) in 90% yield as a mixture of two isomers. The reaction between **3**, LiOHMT, and ZnCl$_2$ then gave Mo(NAr)(CHCMe$_2$Ph)(OHMT)Cl (**4**) as a pentane-soluble intermediate that could be converted into Mo(NAr)(CHCMe$_2$Ph)(OHMT)(Cl)(*t*-BuCN) (**4**(*t*-BuCN)) in 46% yield, Mo(NAr)(CHCMe$_2$Ph)(OHMT)(Cl)(PPhMe$_2$) (**4**(PMe$_2$Ph)) in 62% yield, or Mo(NAr)(CHCMe$_2$Ph)(OHMT)(Cl)(3-Brpy) (**4**(3-Brpy)) in 48% yield upon addition of pivalonitrile, dimethylphenylphosphine, or 3-bromopyridine, respectively (Scheme 1). Pivalonitrile was chosen because it might be more labile than acetonitrile. Synthesis of an adduct of **4** in essentially five steps from molybdate is relatively convenient, in part because minimally soluble **2** and **3** are readily isolated, **4** need not be isolated, impurities formed in the synthesis of **4** are not soluble in pentane, and sparingly soluble five-coordinate adducts of **4** can be isolated in moderate to good yield.

An X-ray study of **4**(*t*-BuCN) (Figure 1) showed it to have nearly a square pyramidal structure (τ = 0.11[8]) with the neophylidene ligand in the apical position and in a *syn* orientation. The pivalonitrile ligand is in a basal position *trans* to the chloride. None of the distances or angles is unusual, and the overall structure is similar to those of Mo(NAd)(CHCMe$_2$Ph)(OHMT)(Br)(py) (τ = 0.21[7]) and Mo(N-*t*-Bu)(CH-*t*-Bu)(OHIPT)(Cl)(3-Brpy) (τ = 0.21[7]). In all structures so far (see Table S2 in SI), including those mentioned in the Introduction, the neutral 2e donor is found to be *trans* to the halide. If the nitrile dissociates and an olefin coordinates to the metal in the same position to form a trigonal bipyramidal metallacyclobutane complex, the imido and aryloxide ligands would be in apical positions in the intermediate. Loss of the olefin product with minimal

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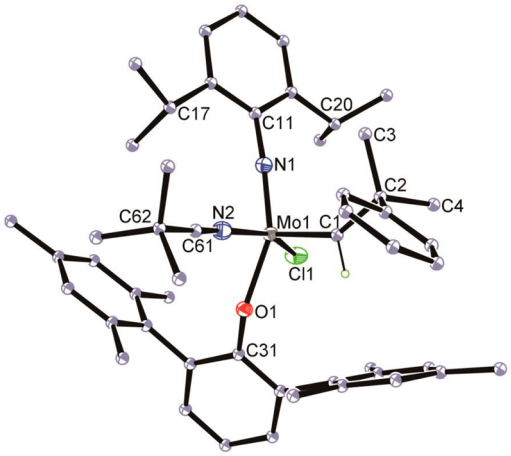

Figure 1. Structure of Mo(NAr)(CHCMe$_2$Ph)(OHMT)(Cl)(*t*-BuCN). Hydrogen atoms, except on C1, have been omitted for clarity. Ellipsoids are shown at 50% probability.

rearrangement of that metallacyclobutane at the metal center would then generate the intermediate 14e nitrile-free *syn* alkylidene complex with the opposite configuration at the metal center. Inversion of configuration appears to be facile for Mo complexes that are stereogenic at the metal, as shown in ROMP studies with MAP initiators.[4]

NMR Studies of Mo(NAr) Derivatives. ^{1}H NMR studies of MAC complexes that contain a pyridine ligand (e.g., **4**(3-Brpy) in Scheme 1) show that the complex is exclusively a *syn* alkylidene ($J_{CH} \approx 125$ Hz; see SI). Similarly, ^{1}H NMR spectra of **4**(PMe$_2$Ph) show a doublet alkylidene ^{1}H resonance at 12.47 ppm ($J_{HP} = 5.3$ Hz), and the ^{31}P NMR spectrum shows a single phosphorus resonance at 5.52 ppm. In neither case is there any evidence for observable "base-off" 14e complexes in solution, according to ^{1}H NMR studies at a total metal concentration of ~0.01 M at room temperature. However, both **4**(3-Brpy) and **4**(PMe$_2$Ph) can be activated toward cross-metathesis through addition of B(C$_6$F$_5$)$_3$ (*vide infra*), so some base must dissociate from the metal at room temperature in order eventually to be sequestered by B(C$_6$F$_5$)$_3$.

The ^{1}H NMR spectrum of **4**(*t*-BuCN) is significantly different from spectra of **4**(3-Brpy) and **4**(PMe$_2$Ph). In toluene-d_8 at 15 mM concentration and 22 °C, the spectrum of **4**(*t*-BuCN) reveals a minor (19%), comparatively sharp alkylidene signal at 13.10 ppm and a major, fairly broad alkylidene signal at 12.42 ppm (Figure 2a). The position and shape of the resonance at 13.10 ppm are relatively independent of concentration, while the broad resonance moves upfield from 12.56 ppm at 52 mM to 12.31 ppm at 7.6 mM and also broadens further (Figure 2a). The 13.10 ppm peak is most intense (22%) in the 7.6 mM sample and weakest (3%) in the 52 mM sample. The J_{CH} values for these alkylidenes can be measured at high signal-to-noise levels (at 52 mM) and are found to be 152 Hz for the resonance at 13.10 ppm and 127 Hz for the upfield resonance. All data are consistent with the 13.10 peak being the alkylidene resonance for a 14e *nitrile-free anti* complex. We ascribe the broad and shifting upfield resonance to a mixture of *syn*-**4**(*t*-BuCN) and nitrile-free complex (*syn*-**4**) that interconvert on the NMR time scale as a consequence of the rapid dissociation of pivalonitrile from **4**(*t*-BuCN). The relative amounts of *syn*-**4**(*t*-BuCN) and *syn*-**4** in a sample of *syn*-**4**(*t*-BuCN) changes with total concentration in the expected manner (Figure 2a). Because an alkylidene can rotate readily

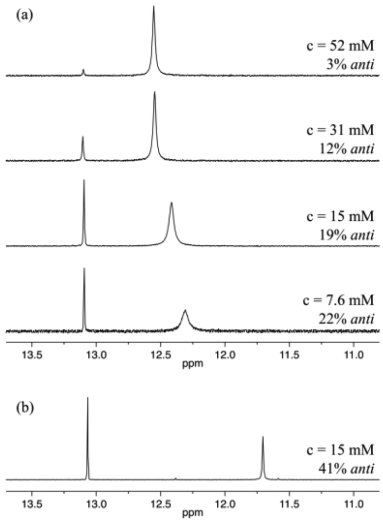

Figure 2. ^{1}H NMR spectra in the alkylidene region of (a) ~0.01 M Mo(NAr)(CHCMe$_2$Ph)(OHMT)(Cl)(*t*-BuCN) in toluene-d_8 and (b) after removal of >95% of the *t*-BuCN.

only in a 14e complex,[18] the intramolecular conversion of a 14e *syn*-alkylidene to an *anti*-alkylidene intermediate will compete with the bimolecular reaction of a 14e *syn*-alkylidene species with substrate.

When 1 equiv of B(C$_6$F$_5$)$_3$ is added to an NMR sample of Mo(NAr)(CHCMe$_2$Ph)(OHMT)(Cl)(*t*-BuCN), *or if t-BuCN is removed from a sample in toluene that is taken to dryness in vacuo at 22 °C in several cycles*, the intensity of the 13.10 peak ($J_{CH} = 152$ Hz) increases to 41% of the total, and the less intense upfield resonance shifts to 11.71 ppm ($J_{CH} = 122$ Hz) and sharpens (Figure 2b); less than 5% of the original *t*-BuCN is present in the sample shown in Figure 2b, according to this ^{1}H NMR spectrum. The resonance at 11.71 ppm (Figure 2b) can be ascribed to *syn*-**4** whose resonance is slightly broadened by a small percentage of exchanging nitrile binding to it to give *syn*-**4**(*t*-BuCN). The spectrum shown in Figure 2b is unchanged between −80 and 25 °C. The same mixture of *syn*-**4** and *anti*-**4** is generated upon addition of 1 equiv of B(C$_6$F$_5$)$_3$ to **4**(PPhMe$_2$). Finally, addition of 1 equiv of pivalonitrile or PPhMe$_2$ to the mixture of *syn*-**4** and *anti*-**4** (Figure 2b) yields ^{1}H NMR spectra identical to the spectra of **4**(*t*-BuCN) and **4**(PMe$_2$Ph), respectively, at the same concentration.

Addition of 6 equiv of pivalonitrile to the sample at 15 mM sample (Figure 2a) leads to sharpening and shifting of the *syn* resonance from 12.42 downfield to 12.79 ppm and broadening and shifting of the *anti* resonance from 13.10 to 13.41 ppm (now 13% of the total instead of 19%), consistent with pivalonitrile binding also to *anti*-**4**, although the equilibrium favors *syn*-**4**(*t*-BuCN). Therefore, in the presence of an additional 12 equiv of pivalonitrile, only one resonance at 12.81 ppm can be observed for a mixture of *syn*-**4** and *syn*-**4**(*t*-BuCN) that contains a high percentage of *syn*-**4**(*t*-BuCN); the average resonance for *anti*-**4** and *anti*-**4**(*t*-BuCN) is no longer observable (see SI). In summary, *syn*-**4** and *anti*-**4** have about the same energy in solution (Figure 2b). Pivalonitrile binds to both *syn*-**4** and *anti*-**4**, but it binds to the *syn* isomer much more strongly than to the *anti* isomer. The rate of pivalonitrile exchange at a metal concentration of ~0.01 M is on the order of the NMR time scale at room temperature (Figure 2). From the position of the average *syn*-alkylidene resonance in the 7.6

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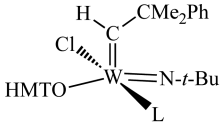
mM sample we can estimate that the amount of *syn*-**4** is ~45% of the mixture of interconverting *syn*-**4** and *syn*-**4**(*t*-BuCN) at 7.6 mM in toluene-d_8, or about 25% of the total concentration of 14e and 16e *syn* and *anti* complexes in solution. The mixture whose partial NMR spectrum is shown in Figure 2b begins to show signs of decomposition only after ~4 h in C_6D_6 at 22 °C, but attempts to isolate either *syn*-**4** or *anti*-**4**, or a mixture, in crystalline form so far have not been successful. Nevertheless, the ^{1}H NMR spectrum of the red-orange foam that is obtained upon removing solvent *in vacuo* from a mixture of *syn*-**4** and *anti*-**4** at 22 °C is unchanged.

We considered the possibility that 14e *anti*-Mo(NAr)(CHCMe$_2$Ph)(OHMT)Cl might form a dimer in solution with two bridging chlorides. In order to evaluate our proposal, we carried out DOSY experiments on the mixture of *anti*-**4**, *syn*-**4**, and *syn*-**4**(*t*-BuCN) at 22 °C in toluene-d_8. We found that the hydrodynamic volumes of the *anti* and *syn* complexes are the same within experimental error, which would not be the case if Mo(NAr)(CHCMe$_2$Ph)(OHMT)Cl were a dimer (see SI). Therefore, we propose that *anti*-Mo(NAr)(CHCMe$_2$Ph)(OHMT)Cl is a monomer in solution.

Experiments analogous to those just described for Mo═NAr chloride complexes have been carried out for pyridine and acetonitrile adducts of Mo═NAd and Mo═N-*t*-Bu complexes reported previously,[7] but the 14e MAC complexes generated in these cases are qualitatively much less stable toward decomposition in solution and therefore less amenable to study. Because Mo(NAr)(CHR′)(OHMT)(Cl)(*t*-BuCN) is an effective (but much slower) catalyst than a Mo *tert*-butylimido or adamantylimido complex (*vide infra*), we propose that the behavior of other Mo nitrile complexes is similar to the behavior of Mo(NAr)(CHR′)(OHMT)(Cl)(*t*-BuCN) in solution.

Synthesis of W(N-*t*-Bu) MAC Complexes. Pyridinium chloride was used in the synthesis of W(NR)(CH-*t*-Bu)(py)$_2$Cl$_2$ from W(NR)$_2$(CH$_2$-*t*-Bu)$_2$ (R = Ad or *t*-Bu).[17] Therefore, we prepared W═NR complexes in order to compare their catalytic activities with Mo compounds. Neophylidene MAC complexes were prepared from W(N-*t*-Bu)$_2$(CH$_2$CMe$_2$Ph)$_2$ in a manner closely analogous to the preparation of Mo neopentylidene complexes. W(N-*t*-Bu)(CHCMe$_2$Ph)(OHMT)(Cl)(py) (**5**(py)) was synthesized from W(N-*t*-Bu)(CHCMe$_2$Ph)(py)$_2$Cl$_2$ in 69% yield and W(N-*t*-Bu)(CHCMe$_2$Ph)(OHMT)(Cl)(3-Brpy) (**5**(3-Brpy)) from W(N-*t*-Bu)(CHCMe$_2$Ph)(3-Brpy)$_2$Cl$_2$ in 51% yield (Figure 3).

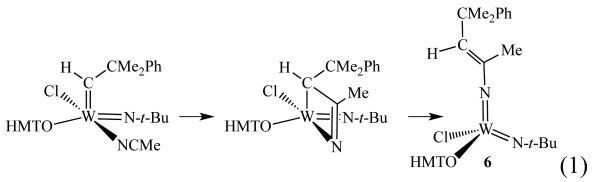


L = py, 3-Brpy, or *t*-BuCN

Figure 3. General structure of W MAC complexes, **5**(py), **5**(3-Brpy), and **5**(*t*-BuCN).

Addition of B(C$_6$F$_5$)$_3$ to W(N-*t*-Bu)(CHCMe$_2$Ph)(OHMT)Cl (**5**), followed by addition of pivalonitrile to the solution of **5**, generated W(N-*t*-Bu)(CHCMe$_2$Ph)(OHMT)(Cl)(*t*-BuCN) (**5**(*t*-BuCN)). Highly soluble **5** could not be isolated in crystalline form on the scale on which the reaction was performed, but is stable enough to prepare in solution. A ^{1}H NMR analysis of **5** showed a single alkylidene resonance at 8.24 ppm that we assign to the *syn* isomer (J_{CH} = 117 Hz; J_{WH} = 15 Hz).[17]

An attempt to prepare **5**(MeCN) through addition of acetonitrile to a solution of **5** led to formation of a mixture of **5**(MeCN) and what we propose to be W(N-*t*-Bu)[NC(Me)═CHCMe$_2$Ph](OHMT)Cl (**6**; eq 1). Attempts to isolate **6** from



(1)

the mixture in pentane yielded colorless crystals of **5**(MeCN), the structure of which was confirmed through an X-ray study (*vide infra*). **5**(MeCN) could be converted into **6** in the presence of added acetonitrile, but upon removal of solvent *in vacuo* no **5**(MeCN) reformed, according to ^{1}H NMR analysis, and **6** decomposed in C_6D_6 to yield HMTOH and unidentified metal-containing products. The proposed structure of **6** that was prepared through the use of isotopically labeled Me^{13}CN is supported by NMR studies ($^2J_{^{13}CH}$ measurement and heteronuclear bond correlation NMR experiments; see SI). Only one configuration of the vinylimido ligand is observed in **6**.

We propose that **6** is formed through insertion of the nitrile into the W═C bond to give an azametallacyclobutene intermediate (eq 1). However, because **5**(MeCN) can be isolated, it is likely that **6** (or a MeCN adduct thereof) is formed from a bisacetonitrile complex (i.e., **5**(MeCN)$_2$). We suggest that **5**(*t*-BuCN) can be prepared because the azametallacyclobutene intermediate or **5**(*t*-BuCN)$_2$ do not form readily for steric reasons. Reactions between high oxidation state alkylidenes and nitriles were first observed for various tantalum neopentylidene complexes;[19a,b] these tantalum products were mixtures of *E* and *Z* isomers. We cannot entirely exclude the possibility that **6** is a 1-azametallacyclobut-4-ene instead of a vinylimido complex. 1-Aza-titanacyclobut-4-enes have been prepared in reactions in which intermediate Cp$_2$Ti═C═CH$_2$ (formed from decomposition of Cp$_2$Ti(CH═CH$_2$)(CH$_3$)) is trapped by nitriles,[20] and one such complex has been structurally characterized.

An X-ray study of **5**(MeCN) (Figure 4) showed it to have a structure analogous to that of **4**(*t*-BuCN) (Figure 1), i.e., an approximate square pyramid (τ = 0.27[8]) with the alkylidene (C1) in the apical position and the acetonitrile (N2) bound *trans* to the chloride ligand. The M−N(2) distance is slightly shorter in the W complex (2.161(3) Å) than in the Mo complex (2.1732(11) Å), which is consistent with what is expected to be a stronger M−N bond for a third row metal (vs a second row metal), although that small bond length difference could also be attributed to greater steric crowding in the Mo complex. The acetonitrile is bent away from the OHMT ligand (W1−N2−C21 = 167.9(3)°), and the imido ligand is tipped away from the *syn* alkylidene (W1−N1−C11 = 161.0(2)°), as one might expect on the basis of steric interactions between the terphenoxide and nitrile ligand and between the imido ligand and the *syn* alkylidene substituent, respectively.[1b,12]

Synthesis of Mo(NC$_6$F$_5$) Complexes. Mo-based pentafluorophenylimido MAP complexes have proven to be especially efficient for *Z*-selective and *E*-selective cross-meta-

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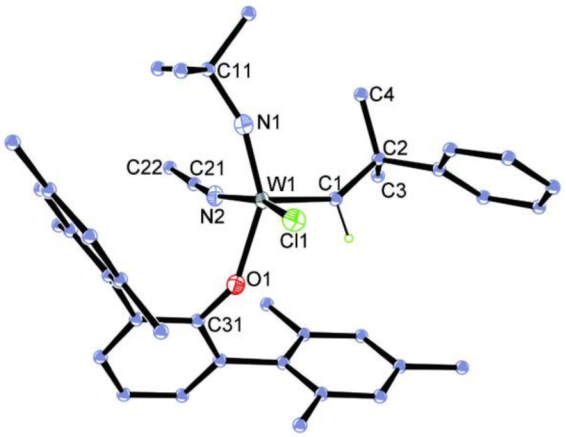
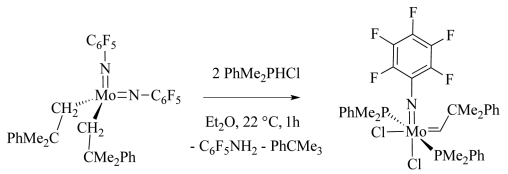


Figure 4. Structure of W(N-*t*-Bu)($CHCMe_2Ph$)(OHMT)(Cl)(MeCN). Hydrogen atoms, except on C1, have been omitted for clarity. Ellipsoids are shown at 50% probability.

thesis reactions in which an electron-poor halogenated olefin is one of the olefin partners.[5,6] If monoaryloxide monochloride or monobromide complexes are the most active catalysts in these reactions, it would be highly desirable to find a more efficient route to them. Initial syntheses of $Mo(NC_6F_5)$ MAC complexes involved the protonation of MAP complexes with pyridinium halide acids, as described for the early syntheses of Mo(NR) MAC complexes (R = *t*-Bu and Ad).[7] This sequence requires the synthesis of a bispyrrolide complex and subsequent reactions that involve protonations with pyridinium halides and give products in low yields. Therefore, such a route to $Mo(NC_6F_5)(CHMe_2Ph)(OHMT)(X)(L)$ complexes where X is either Cl or Br is restricted to those where L is either pyridine or 3-bromopyridine. Finally, our attempts to adapt the strategy of using a mixture of pentafluorophenol and bipy to generate $Mo(NC_6F_5)$ alkylidene complexes have been unsuccessful.

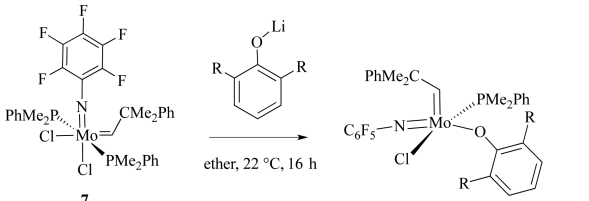
Our search for alternative routes to monochloride complexes led the discovery that 2 equiv of $Me_2PhPHCl$ reacts smoothly with $Mo(NC_6F_5)_2(CH_2CMe_2Ph)_2$ to yield $C_6F_5NH_2$, $PhCMe_3$, and the dichlorobisphosphine alkylidene derivative, $Mo(NC_6F_5)(CHCMe_2Ph)L_2Cl_2$ (**7**, L = PMe_2Ph), as a single isomer that contains a plane of symmetry and a single type of phosphine, consistent with the structure shown in eq 2. So far,



7; 66% yield (2)

we have found that addition of either $Ph_2MePHCl$ or Me_3PHCl to $W(NC_6F_5)_2(CH_2CMe_2Ph)_2$ or $Mo(NR)_2(CH_2CMe_2Ph)_2$ (R = 2,6-$Me_2C_6H_3$ or 2,6-*i*-$Pr_2C_6H_3$) led to complex mixtures that do not contain any significant quantities of alkylidenes, according to ^1H NMR analysis. Also, treatment of Mo(N-*t*-Bu)$_2$(CH_2-*t*-Bu)$_2$ with phosphonium halides generated a complex mixture of alkylidene-containing compounds along with other unidentified products. As has been reported previously,[21] pyridinium chlorides do not deliver a bispyridine analogue of **7**. In spite of these unfavorable preliminary results, we are hopeful that other successful syntheses of analogues of **7** from $Mo(NC_6F_5)_2(CH_2CMe_2Ph)_2$ or $Mo(NC_6F_5)_2(CH_2CMe_3)_2$ can be developed, or that **7** will emerge as a versatile synthetic intermediate for other classes of $Mo(NC_6F_5)$ alkylidene complexes.

Addition of either LiOHMT or LiOHIPT to **7** leads to the MAC complexes as the phosphine adducts, $Mo(NC_6F_5)(CHCMe_2Ph)(OHMT)(Cl)(PMe_2Ph)$ (**8a**(PMe_2Ph)) and $Mo(NC_6F_5)(CHCMe_2Ph)(OHIPT)(Cl)(PMe_2Ph)$ (**8b**(PMe_2Ph)) (eq 3). Syntheses leading to **8a**(PMe_2Ph) and **8b**(PMe_2Ph) in four steps from molybdate are currently the most efficient way to prepare $Mo(NC_6F_5)$ alkylidene complexes.



7

8a; R = Mesityl; 71%
8b; R = 2,4,6-*i*-$Pr_3C_6H_2$; 65% (3)

An X-ray study of **8b**(PMe_2Ph) (Figure 5) revealed a structure analogous to those of **4**(*t*-BuCN) (Figure 1) and

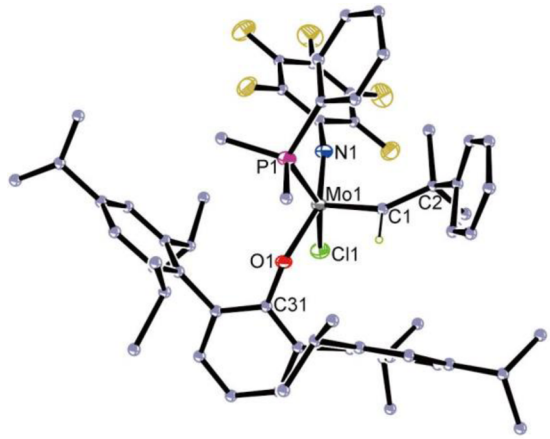


Figure 5. Structure of $Mo(NC_6F_5)(CHCMe_2Ph)(OHIPT)(Cl)(PMe_2Ph)$. Hydrogen atoms, except on C1, have been omitted for clarity. Ellipsoids are shown at 50% probability.

5(MeCN) (Figure 4), i.e., a square pyramid (τ = 0.10) with the alkylidene (C1) in the apical position and the phosphine bound *trans* to the chloride. The imido ligand is bent away from the *syn* alkylidene substituent, as expected (Mo1−N1−C11 = 160.67(10)°). The Mo−P distance (2.511 Å) is analogous to the W−P distance in WO(CH-*t*-Bu)(OHIPT)(Cl)($PPhMe_2$) (2.528 Å). The seven crystallographically characterized monoaryloxide halide complexes (see Table S2 in SI) are all OHMT or OHIPT complexes in which the M−O distance varies from 1.969 to 1.992 Å.

Compounds **8a**(PMe_2Ph) and **8b**(PMe_2Ph) have sharp, concentration-independent alkylidene doublet resonances in their ^1H spectra, consistent with no significant degree of dissociation of phosphine in solution. However, the phosphine can be removed from **8a**(PMe_2Ph) and **8b**(PMe_2Ph) with $Ph_3CB(C_6F_5)_4$ or $B(C_6F_5)_3$ (in C_6D_6) to yield the respective phosphine-free 14e complexes, **8a** and **8b** in solution, according to NMR studies. The reactions are complete in ~1 h at 22 °C

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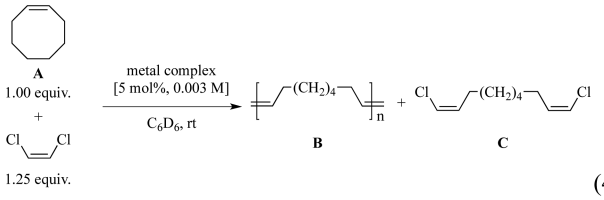
J. Am. Chem. Soc. 2016, 138, 15774−15783

and 0.1 M concentration, and ^{1}H NMR spectra of either **8a** or **8b** in C_6D_6 at a concentration of ~0.1 M show little change after 6 h. We propose that removal of the phosphine is successful because both $Ph_3CB(C_6F_5)_4$ and $B(C_6F_5)_3$ are soluble in benzene, each binds phosphine rapidly and essentially irreversibly to give Lewis acid adducts, and the adducts do not interfere with the metathesis reaction.

Reactivities of Monohalide Complexes in the ROCM of Cyclooctene and *Z*-1,2-Dichloroethylene. As a test reaction we investigated the ROCM of *cis*-cyclooctene (COE) and *Z*-1,2-dichloroethylene (DCE; 1.25 equiv) in C_6D_6 (eq 4).



(4)

Cyclooctene alternatively can be polymerized in the test reaction, but poly(COE) so formed can also be "depolymerized". The normalized ratios of COE (**A**), poly(COE) (**B**), and ClCH=CH$(CH_2)_6$CH=CHCl (**C**) were followed by ^{1}H NMR over a period of up to 24 h (C_6D_6, 22 °C, 3 mM initiator concentration). Relevant data are presented in Tables 1–4; the complete set of results can be found in the SI.

Table 1. ROCM of A with DCE To Give B and/or C

run, initiator[a]	*x*/*y*/*z*[b]	
	2 min	**10 min**
1, Mo(NAd)(CHR′)(OHIPT)(Cl)(MeCN)	**0/0/100**	**0/0/100**
2, Mo(NR)(CHR)(OHIPT)(Cl)(MeCN)	**0/0/100**	**0/0/100**
3, Mo(NR)(CHR)(OHIPT)(Cl)(MeCN) (1%)	1/24/75	1/24/75
4, Mo(NR)(CHR)(OHIPT)(Cl)(3-Brpy)	32/32/36	0/24/75
5, Mo(NR)(CHR)(OHMT)(Br)(MeCN)	**0/4/96**	**0/4/96**
6, Mo(NR)(CHR)(OTTBT)(Cl)(MeCN)	0/9/91	**0/5/95**
7, Mo(NR)(CHR)(OTTBT)(Cl)(3-Brpy)	66/33/1	2/57/41
8, Mo(NAd)(CHR′)(OHMT)(Cl)(MeCN)	0/15/85	**0/6/94**
9, Mo(NR)(CHR)(OHMT)(Cl)(MeCN)	**0/6/94**	**0/5/95**
	1 h	**6 h**
4, Mo(NR)(CHR)(OHIPT)(Cl)(3-Brpy)	**0/0/100**	**0/0/100**
7, Mo(NR)(CHR)(OTTBT)(Cl)(3-Brpy)	0/8/92	**0/0/100**
10, Mo(NAr)(CHR′)(OHMT)(Cl)(RCN)	0/7/93	**0/0/100**
11, Mo(NAr)(CHR′)(OHMT)(Cl)(RCN) (1%)	0/15/85	**0/2/98**

[a]R = *t*-Bu; R′ = CMe_2Ph; Ar = 2,6-diisopropylphenyl. [b]*x*/*y*/*z* = %**A**/%**B**/%**C** by ^{1}H NMR.

In Table 1 we list some of the most successful reactions in which no $B(C_6F_5)_3$ was added. Six transformations produced greater than 94% **C** in 10 min or less; four more (runs 4, 7, 10, and 11) reached >98% in 6 h. When a 1% loading was used (run 3) a lower yield of **C** was observed after 2 min with the yield remaining unchanged, consistent with earlier catalyst death at 1% loading compared to 5% loading. In contrast to the parent pyridine ligand, 3-bromopyridine is labile enough to give satisfactory yields (run 4 after 1 h). The reaction rate is approximately the same when the catalyst contains OTTBT (O-2,6-(3,5-(*t*-Bu)$_2C_6H_3)_2C_6H_3$;[6] run 6) instead of OHMT or OHIPT. (It should be noted that the unsuccesful elemental analyses of the two OTTBT neopentylidene complexes suggest that they decompose more readily than analogous OHMT or OHIPT complexes; see SI for a complete report.) Mo(NAr)(CHR′)(OHMT)(Cl)(RCN) is a slower catalyst that requires 6 h to reach full conversion to **C** (run 10); we attribute this difference to the steric demand of the Ar group. At 1% loading of Mo(NAr)(CHR′)(OHMT)(Cl)(RCN) **C** was obtained in 98% yield in 6 h (run 11); this transformation is slower than that in run 3, but the intermediates seem to survive longer under the reaction conditions. The conversion in the case of $Mo(NC_6F_5)$(CHR′)(OHMT)(Cl)(py) (run 29 in the SI) is limited by pyridine being more strongly bound to a more electron-deficient metal.

In Table 2 we summarize the results of the attempted ROCM reactions in the absence of $B(C_6F_5)_3$ in which no **C** was formed after 1 h. These experiments involve Mo catalysts that contain relatively strongly bound 2e donor ligands (PMe_2Ph, 1-methylimidazole, or pyridine in the bromide complex) or 3-bromopyridine in Mo(NAr) or $Mo(NC_6F_5)$ complexes. We propose that the 3-Brpy and *t*-BuCN ligands in tungsten *tert*-butylimido complexes are not sufficiently labile to produce viable quantities of 14e MAC complexes. The combination of NC_6F_5 and ODFT (O-2,6-$(C_6F_5)_2C_6H_3$) ligands limits the lability of 3-Brpy in run 18 (Table 2).

Table 2. Attempted ROCM of A with DCE To Give B and/or C[a]

run/initiator	1 h
12, Mo(NAr)(CHR′)(OHMT)(Cl)(PMe_2Ph)	100/0/0
13, Mo(NR)(CHR)(OHIPT)(Cl)(1-Me-imid)	100/0/0
14, $Mo(NC_6F5)$(CHR′)(OHMT)(Cl)($PPhMe_2$)	100/0/0
15, $Mo(NC_6F5)$(CHR′)(OHIPT)(Cl)($PPhMe_2$)	100/0/0
16, Mo(NAr)(CHR′)(OHMT)(Cl)(3-Brpy)	99/1/0
17, Mo(NAd)(CHR′)(OHMT)(Br)(py)	17/83/0
18, $Mo(NC_6F5)$(CHR′)(ODFT)(Cl)(3-Brpy)	89/11/0
19, W(NR)(CHR′)(OHMT)(Cl)(3-Brpy)	100/0/0
20, W(NR)(CHR′)(OHMT)(Cl)(RCN)	80/20/0

[a]See Table 1 footnotes.

In Table 3 we show the results of experiments involving reactions that were initiated or accelerated through addition of $B(C_6F_5)_3$ as a Lewis acid (LA) to scavenge the 2e neutral ligand. In most cases no conversion was observed in the absence of $B(C_6F_5)_3$ (runs 12 and 14–18 in Table 2). Mo(NR)(CHR)(OHIPT)(Cl)(3-Brpy) requires 1 h to reach

Table 3. ROCM of A with DCE To Give B and/or C after Addition of $B(C_6F_5)_3$ (+LA)[a]

run, initiator	30 min	60 min
21, Mo(NAr)(CHR′)(OHMT)(Cl)(3-Brpy) + LA	0/12/87	**0/5/95**
22, Mo(NAr)(CHR′)(OHMT)(Cl)(PMe_2Ph) + LA	0/7/93	**0/4/96**
23, $Mo(NC_6F_5)$(CHR′)(ODFT)(Cl)(3-Brpy) + LA	0/64/36	–
24, $Mo(NC_6F_5)$(CHR′)(OHMT)(Cl)($PPhMe_2$) + LA	**0/0/100**	–
25, $Mo(NC_6F_5)$(CHR′)(OHIPT)(Cl)($PPhMe_2$) + LA	0/1/99	**0/0/100**
26, Mo(NAd)(CHR′)(OHMT)(Br)(py) + LA	0/5/95	–
27, W(NR)(CHR′)(OHMT)(Cl)(3-Brpy) + LA	72/28/0	68/32/0
28, Mo(NR)(CHR)(OHIPT)(Cl)(3-Brpy) + LA	**0/0/100 in 2 min**	

[a]See Table 1 footnotes.

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J. Am. Chem. Soc. 2016, 138, 15774–15783

full conversion (Table 1, run 4), but full conversion is reached in 2 min in the presence of $B(C_6F_5)_3$ (run 28 in Table 3). It should be noted that even PMe_2Ph could be scavenged from Mo (runs 24 and 25). Either 3-bromopyridine cannot be scavenged from W or another fundamental complication involving the three reactions with a W-based complex is the cause of the observed limited activity. At this point we favor the first explanation.

An important aspect of the test reaction is the stereochemistry of **C**. High-field ^{1}H NMR spectra (500 MHz or more in C_6D_6 or $CDCl_3$) are sufficient for measuring the ratio of *Z,Z*-**C** and *E,Z*-**C** in the absence of *E,E*-**C**, but GC studies are required when *E,E*-**C** is present. Experiments with a Mo(N-*t*-Bu) or Mo(NAd) catalysts showed a strong preference for formation of *Z,Z*-**C** (>98%), according to ^{1}H NMR spectra. The stereochemical purity of **C** according to GC analysis was found to be >96% *Z,Z*-**C** in four experiments (runs 1, 2, 19, and 28 in Table 4). A value of 99.7% *Z,Z*-**C** with 0.3% *Z,E*-**C** implies

Table 4. Stereoselectivity of ROCM: Product Distributions Determined by GC (Selected Runs)

run, initiator	*Z,Z*-**C**	*Z,E*-**C**	*E,E*-**C**
1, Mo(NAd)(CHR′)(OHIPT)(Cl)(MeCN)	99.7	0.3	∼0
2, Mo(NR)(CHR)(OHIPT)(Cl)(MeCN)	99.5	0.5	∼0
19, Mo(NC_6F_5)(CHR′)(OHIPT)(Cl)($PPhMe_2$) + LA	96.2	3.8	∼0
28, Mo(NR)(CHR)(OHIPT)(Cl)(3-Brpy) + LA	99.5	0.5	∼0
10 Mo(NAr)(CHR′)(OHMT)(Cl)(RCN)	61.3	34.6	4.1
20 Mo(NC_6F_5)(CHR′)(OHMT)(Cl)($PPhMe_2$) + LA	66.4	30.4	3.2
21 Mo(NAr)(CHR′)(OHMT)(Cl)(3-Brpy) + LA	63.3	33.3	3.4

an overall selectivity of 99.8% *Z*- selectivity per C=C bond. High selectivities are not limited to Mo(NAd) or Mo(N-*t*-Bu) catalysts, as shown by the 96.2% *Z,Z* selectivity with which **C** is generated with Mo(NC_6F_5)(CHR′)(OHIPT)(Cl)($PPhMe_2$) in the presence of $B(C_6F_5)_3$ (run 19). The importance of the aryloxide to the level of stereoselectivity is manifested in the results for the analogous reaction involving Mo(NC_6F_5)(CHR′)(OHMT)(Cl)($PPhMe_2$) (66.4:30.4:3.2 *Z,Z*:*Z,E*:*E,E*). It is therefore clear that selectivity for forming *Z,Z*-**C** product is high primarily (but not exclusively) when Mo(N-*t*-Bu) or Mo(NAd) complexes are the initiators, or when OHIPT is the aryloxide ligand, or both. In the case of Mo(NAr)(CHR′)(OHMT)(Cl)(*t*-BuCN) (run 10), the NAr ligand is too large relative to the OHMT ligand to allow exclusive formation of metallacyclobutane intermediates where all substituents are oriented toward the imido ligand.

An interesting question is how much faster are the test reactions with monochloride complexes versus those initiated by a pyrrolide complex. Mo(NAd)($CHCMe_2Ph$)(OHMT)(Pyr) was found to be a relatively slow initiator, with no **C** being formed within the first 2 min (63/32/0) (%**A**/%**B**/%**C**), but 81% **C** was generated (0/19/81) after 1 h with a *Z,Z*:*Z,E* ratio of 98.5:1.5 (GC analysis). In contrast, the composition of the product mixture in the case of Mo(NAd)($CHCMe_2Ph$)(OHMT)(Cl)(MeCN) was 0:12:82 in 2 min, and the selectivity was >98:2 *Z,Z*:*Z,E* (NMR analysis). Therefore, we can deduce that the test reaction is at least ∼100 times faster when Mo(NAd)($CHCMe_2Ph$)(OHMT)(Cl)(MeCN) is the initiator compared to Mo(NAd)($CHCMe_2Ph$)(OHMT)(Pyr) as the initiator. However, in spite of the >98% stereoselectivities for both reactions, we cannot conclude that Mo(NAd)($CHCMe_2Ph$)(OHMT)Cl (formed *in situ*) is *solely* responsible for the activity of Mo(NAd)($CHCMe_2Ph$)(OHMT)(Pyr).

We ascribe the high activities in the test reaction to circumstances in which a significant amount of base-free 14e alkylidenes is present, i.e., either a Mo=CHCl or a Mo=$CH(CH_2)_8CH$=CHCl intermediate. Of course, we cannot determine how much of what type of base-free complex is present in each circumstance *under catalytic conditions* at any specific time, but we are confident that the observations described in an earlier section for Mo(NAr)($CHCMe_2Ph$)(OHMT)(Cl)(*t*-BuCN) can be generalized in a qualitative sense.

CONCLUSIONS

We conclude that monoaryloxide halide complexes of Mo or W with the general formula M(NR)(CHR′)(OAryl)(X)(L) can be prepared in a process involving intermediates that contain pentafluorophenoxide and 2,2′-bipyridine. Addition of $Me_2PhPHCl$ to Mo(NC_6F_5)$_2$(CH_2CMe_2Ph)$_2$ leads to Mo(NC_6F_5)(CHR′)(PMe_2Ph)$_2$(Cl)$_2$ from which Mo(NC_6F_5)(CHR′)(OAryl)(Cl)(PMe_2Ph) is prepared readily. When L is acetonitrile or pivalonitrile, rapid and reversible loss of nitrile in solution affords a mixture enriched in the nitrile-free 14e M(NC_6F_5)(CHR′)(OAryl)X complex. Molybdenum complexes are highly active catalysts for the cross-metathesis of cyclooctene and *Z*-1,2-dichloroethylene to give almost exclusively *Z,Z*-ClCH=$CH(CH_2)_6CH$=CHCl in several cases. Complexes where a neutral 2e ligand is strongly bound to the metal are poor initiators, but these complexes can be activated through addition of a suitable Lewis acid. In general, increased steric crowding at the metal in arylimido complexes relative to alkylimido complexes results in the arylimido complexes being more stable and longer-lived under catalytic conditions, but also less reactive and *Z*-selective. Mo(NAr)(CHR′)(OHMT)Cl complexes can be characterized in solution as a mixture of *anti* and *syn* isomers, but attempts to crystallize the 14e variants were unsuccessful. Tungsten catalysts are inferior catalysts either because the donor is bound too tightly and/or the W=C bond reacts with a nitrile to yield a vinylimido complex. Because Mo(NR)(CHX)(OAryl)X, a necessary cross-metathesis intermediate, has not been observed through NMR studies, we propose that Mo=CHCl complexes are relatively unstable and react rapidly with cyclooctene in the chosen test reaction.

EXPERIMENTAL SECTION

General Considerations. All air- and moisture-sensitive materials were manipulated under a nitrogen atmosphere in a Vacuum Atmospheres glovebox or on a dual-manifold Schlenk line. Glassware was either oven-dried or flame-dried prior to use. Acetonitrile, benzene, CH_2Cl_2, Et_2O, 1,2-dimethoxyethane, and toluene were degassed, passed through activated alumina columns, and stored over 4 Å Linde-type molecular sieves prior to use. Pentane was washed with H_2SO_4, followed by water and a saturated solution of aqueous $NaHCO_3$, and dried over $CaCl_2$ pellets for at least 2 weeks prior to use in the solvent purification system. Deuterated solvents were dried over 4 Å Linde-type molecular sieves prior to use. ^{1}H NMR spectra were obtained on 400 or 500 MHz spectrometers and ^{13}C NMR spectra on 101, 125, or 151 MHz machines. Chemical shifts for ^{1}H and ^{13}C spectra are reported as parts per million relative to tetramethylsilane and referenced to the residual ^{1}H or ^{13}C resonances of the deuterated solvent (^{1}H δ: benzene 7.16, chloroform 7.26, methylene chloride 5.32; ^{13}C δ: benzene 128.06, chloroform 77.16, methylene chloride

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53.84). Gas chromatography was performed on an Agilent system equipped with an HP-5 column (ID 320 μm, film 0.25 μm, length 30 m). Pyridinium chloride was purchased from Sigma-Aldrich or Alfa Aesar and sublimed prior use. TMSCl was purchased from Alfa Aesar and degassed by a freeze−pump−thaw method prior to use. $B(C_6F_5)_3$ was purchased from Strem and sublimed prior to use. Pivalonitrile and 1-methylimidazole were purchased from Alfa Aesar, distilled over CaH, and stored over 4 Å Linde-type molecular sieves prior to use. LiOAr was prepared by addition of 1 equiv of *n*-butyllithium to a cold pentane or Et_2O solution of ArOH, and the solid was collected on a glass frit, washed with pentane, and dried *in vacuo*. Mo(NR)-$(CHCMe_2R')(bipy)Cl_2$ (R = Ad or *t*-Bu, R′ = Me or Ph), Mo(NR)$(CHCMe_2R')$(OHMT)(MeCN)Cl (R = Ad or *t*-Bu, R′ = Me or Ph), Mo(NR)$(CHCMe_2R')$(OHMT)(MeCN)Cl (R = Ad or *t*-Bu, R′ = Me or Ph), and Mo(N-*t*-Bu)(CH-*t*-Bu)(OHIPT)(3-Brpy)Cl were prepared as reported elsewhere.[7] $W(N\text{-}t\text{-}Bu)_2(py)_2Cl_2$,[17] Mo-(NAd)$(CHCMe_2Ph)(Pyr)_2$,[22] Mo(NAd)$(CHCMe_2Ph)$(Pyr)-(OHMT),[23] and $Mo(NC_6F_5)(CHCMe_2Ph)$(ODFT)(Me_2Pyr)-(MeCN)[21] were prepared as described in the literature.

Mo(NAd)(CHCMe₂Ph)(OHMT)(Cl)(py). Mo(NAd)$(CHCMe_2Ph)$-(Pyr)(OHMT) (345 mg, 0.446 mmol) and pyridinium chloride (59 mg, 0.510 mmol, 1.14 equiv) were suspended in toluene (5 mL). The reaction mixture was stirred at 22 °C for 2 h and filtered through Celite. The Celite was washed with toluene (5 mL), and the combined filtrate was concentrated to dryness. The residue was recrystallized by layering a CH_2Cl_2 solution (1.5 mL) with *n*-pentane (6 mL) at −30 °C. The resulting off-white crystals were collected by filtration and dried under reduced pressure to afford the title compound (189 mg, 0.230 mmol, 52%). Anal. Calcd for $C_{49}H_{57}ClMoN_2O$: C, 71.65; H, 6.99; N, 3.41. Found: C, 71.95; H, 7.27; N, 3.16.

Mo(N-t-Bu)(CH-t-Bu)(OTTBT)(Cl)(MeCN). Mo(N-*t*-Bu)(CH-*t*-Bu)-$(Cl)_2$(bipy) (416 mg, 0.896 mmol, 1.00 equiv) was suspended in Et_2O (50 mL), and the mixture was chilled to −25 °C. A solution of LiOTTBT (452 mg, 0.896 mmol, 1.00 equiv) and $ZnCl_2$ (122 mg, 0.896 mmol, 1.00 equiv) in THF (10 mL) was added. The mixture was stirred at 22 °C for 4 h and filtered through Celite. The filtrate was taken to dryness *in vacuo* to give a brown foam. The brown foam was extracted with pentane (30 mL), and the extract was filtered through Celite. Acetonitrile (0.1 mL) was added to this brown pentane solution. After the mixture was stirred for 1 h, the resulting brown slurry was taken to dryness. The residue thus obtained was triturated with pentane (∼2 mL), and the mixture was chilled to −25 °C for 12 h. The resulting solid was collected by filtration and washed with cold pentane (∼1 mL) to give Mo(N-*t*-Bu)(CH-*t*-Bu)(OTTBT)(Cl)-(MeCN) (510 mg, 71% yield) as a tan solid. Anal. Calcd for $C_{46}H_{67}ClMoN_2O$: C, 68.92; H, 8.62; N, 3.58. Found: C, 68.04; H, 8.52; N, 3.44. (See SI for a complete set of unsuccessful elemental analyses.)

Mo(N-t-Bu)(CH-t-Bu)(OTTBT)(Cl)(3-Brpy). Mo(N-*t*-Bu)(CH-*t*-Bu)-$(bipy)Cl_2$ (233 mg, 0.500 mmol, 1.00 equiv) was suspended in Et_2O (50 mL), and the mixture was chilled to −25 °C in the glovebox freezer. The suspension was treated slowly with a solution of LiOTTBT (238 mg, 0.500 mmol, 1.00 equiv) and $ZnCl_2$ (68 mg, 0.500 mmol, 1.00 equiv) in THF (10 mL). After being stirred at 22 °C for 4 h, the reaction mixture was filtered through Celite and concentrated to give a brown foam. The brown foam was extracted with pentane (30 mL), and the extract was filtered through Celite to give a brown solution to which 3-bromopyridine (48 μL, 0.500 mmol, 1.00 equiv) was added. After being stirred for 1 h, the resulting slurry was concentrated to dryness. The residue thus obtained was triturated with pentane (∼2 mL) and chilled to −25 °C overnight. The resulting solid was collected by filtration and washed with cold pentane (∼1 mL) to afford Mo(N-*t*-Bu)(CH-*t*-Bu)(OTTBT)(Cl)(3-Brpy) (292 mg, 64% yield) as a pale pink solid. Anal. Calcd for $C_{48}H_{68}BrClMoN_2O$: C, 64.03; H, 7.61; N, 3.11. Found: C, 62.75; H, 7.41; N, 3.09. (See SI for a complete set of unsuccessful elemental analyses.)

W(N-t-Bu)(CHCMe₂Ph)(OHMT)(Cl)(py). A solution of Me_2PhCCH_2MgCl (0.5 M, 7.2 mL, 3.6 mmol) in Et_2O was added to a −30 °C solution of $W(N\text{-}t\text{-}Bu)_2(py)_2Cl_2$ (1.0 g, 1.8 mmol) in 40 mL of Et_2O. After being stirred at 22 °C for 15 h, the mixture was filtered through a pad of Celite, and the Celite was further washed with several portions of Et_2O. The solvent was removed from the filtrate *in vacuo* to afford a yellow oil (750 mg, 70% yield) whose ^1H and ^{13}C NMR spectra are consistent with it being $W(N\text{-}t\text{-}Bu)_2(CH_2CMe_2Ph)_2$ (and by analogy with $W(N\text{-}t\text{-}Bu)_2(CH_2t\text{-}Bu_3)_2$.[13]

$W(N\text{-}t\text{-}Bu)_2(CH_2CMe_2Ph)_2$ (500 mg, 0.84 mmol) was dissolved in Et_2O (20 mL), and the solution was cooled to −30 °C in the glovebox freezer. Pyridinium chloride (291 mg, 2.52 mmol) was added, and the mixture was stirred at 22 °C for 18 h. The color of the solution changed from yellow to brown, and a precipitate formed. The mixture was filtered through a pad of Celite, and the Celite was further washed with toluene several times. The solvent was removed from the filtrate *in vacuo* to yield a yellow residue, which was dissolved in a minimum of toluene and poured into pentane (50 mL). The yellow precipitate consisting of W(N-*t*-Bu)$(CHCMe_2Ph)(py)_2Cl_2$ (223 mg, 43% yield) was collected by filtration and used directly in the next step.

W(N-*t*-Bu)$(CHCMe_2Ph)(py)_2Cl_2$ (300 mg, 0.487 mmol) and LiOHMT (180 mg, 0.536 mmol) were dissolved in benzene (15 mL) in a 50 mL Schlenk bomb. The bomb was heated at 80 °C for 15 h and then cooled to 22 °C. The resulting mixture was filtered through a pad of Celite on a glass frit. Volatiles were removed from the filtrate *in vacuo*. Pentane was added to the mixture and removed *in vacuo* twice to give the product as a yellow powder, affording 280 mg of the desired product (69% yield). Anal. Calcd for $C_{43}H_{51}ClN_2OW$: C, 62.14; H, 6.18; N, 3.37. Found: C, 62.65; H, 6.21; N, 3.12. *This compound is analogous to W(N-t-Bu)(CH-t-Bu)(OHMT)(Cl)(py), which was synthesized by the same method and was analyzed successfully.*[11]

W(N-t-Bu)(CHCMe₂Ph)(OHMT)(Cl)(3-Brpy). $W(N\text{-}t\text{-}Bu)_2(CH_2CMe_2Ph)_2$ (500 mg, 0.84 mmol) was dissolved in Et_2O (20 mL), and the solution was allowed to cool to −30 °C. 3-Bromopyridinium chloride (490 mg, 2.52 mmol) was added, and the mixture was stirred at 22 °C for 12 h. The mixture was filtered through a pad of Celite, and the Celite was further washed three times with toluene. The solvent was removed from the filtrate *in vacuo* to give a yellow residue, which was dissolved in a minimum of toluene and poured into pentane (50 mL). The resulting yellow precipitate consisting of W(N-*t*-Bu)$(CHCMe_2Ph)(3\text{-}Brpy)_2Cl_2$ (356 mg, 55% yield) was collected by filtration and used directly in the next step.

W(N-*t*-Bu)$(CHCMe_2Ph)(3\text{-}Brpy)_2Cl_2$ (100 mg, 0.129 mmol) and LiOHMT (47.8 mg, 0.142 mmol) were dissolved in benzene (10 mL) in a 50 mL Schlenk bomb. The bomb was heated at 80 °C for 15 h and then allowed to cool to 22 °C. The resulting mixture was filtered through a pad of Celite on a glass frit. All solvents were removed from the filtrate *in vacuo*. Pentane was added to the mixture and removed *in vacuo* twice to remove excess benzene to afford W(N-*t*-Bu)-$(CHCMe_2Ph)$(OHMT)(Cl)(3-Brpy) (60 mg, 51% yield) as a yellow solid.

W(N-*t*-Bu)$(CHCMe_2Ph)$(OHMT)(Cl)(3-Brpy) has also been prepared from W(N-*t*-Bu)$(CHCMe_2Ph)$(OHMT)(Cl)(py). $B(C_6F_5)_3$ (67.6 mg, 0.132 mmol) was added to a solution of W(N-*t*-Bu)$(CHCMe_2Ph)$(OHMT)(Cl)(py) (100 mg, 0.12 mmol) in benzene (5 mL). The reaction mixture was stirred at 22 °C for 1 h, and the solvents were removed from the mixture *in vacuo*. Pentane was added and removed *in vacuo* twice to remove benzene. Pentane was added, and the mixture was filtered through a pad of Celite on a glass frit. The solvents were removed *in vacuo* to form a sticky yellow solid, which was dissolved in pentane (2 mL) and treated with 3-bromopyridine (13 μL, 0.13 mmol). The mixture was stirred at 22 °C for 1 h, and the resulting yellow precipitate (52.4 mg, 48%) was collected by filtration. Anal. Calcd for $C_{43}H_{50}WBrClON_2$: C, 56.75; H, 5.54; N, 3.08. Found: C, 56.44; H, 5.28; N, 2.85.

W(N-t-Bu)(CHCMe₂Ph)(OHMT)(Cl)(t-BuCN). $B(C_6F_5)_3$ (271 mg, 0.53 mmol) was added to a solution of W(N-*t*-Bu)$(CHCMe_2Ph)$-(OHMT)(Cl)(py) (400 mg, 0.48 mmol) in benzene (10 mL). The mixture was stirred at 22 °C for 1 h, and the solvents were removed from the mixture *in vacuo*. Pentane was added and removed *in vacuo* twice to remove benzene. Pentane was added, and the mixture was filtered through a pad of Celite on a glass frit. The volatiles were

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J. Am. Chem. Soc. 2016, 138, 15774−15783

removed *in vacuo* to form a sticky yellow solid. The solid was dissolved in pentane (2 mL), and pivalonitrile (66 μL, 0.50 mmol) was added. The mixture was stirred at 22 °C for 1 h. The yellow precipitate (256 mg, 64% yield) was collected by filtration. Anal. Calcd for $C_{43}H_{55}WClON_2$: C, 61.84; H, 6.64; N, 3.35. Found: C, 61.39; H, 6.27; N, 3.19.

Attempted synthesis of W(N-t-Bu)(CHCMe$_2$Ph)(OHMT)(Cl)(MeCN). $B(C_6F_5)_3$ (54.3 mg, 0.106 mmol) was added to a solution of W(N-*t*-Bu)(CHCMe$_2$Ph)(OHMT)(Cl)(py) (80 mg, 0.096 mmol) in benzene (3 mL). The mixture was stirred at 22 °C for 1 h, and the solvents were removed from the mixture *in vacuo*. Pentane was added, and the mixture was subjected to vacuum twice to remove benzene. Pentane was added, and the mixture was filtered through a pad of Celite on a glass frit. The solvents were removed *in vacuo* to form a sticky yellow solid. The solid was dissolved in pentane (1 mL), and acetonitrile (7.5 μL, 0.144 mmol) was added. The mixture was stirred at 22 °C for 10 min. The pale-yellow precipitate (35 mg, 46%) was collected by filtration. A ^{1}H NMR spectrum showed this product to be a mixture of W(N-*t*-Bu)(CHCMe$_2$Ph)(OHMT)(MeCN)Cl and what we propose to be W(N-*t*-Bu)[NC(Me)=CHCMe$_2$Ph](OHMT)Cl. Anal. Calcd for $C_{40}H_{49}WClON_2$: C, 60.57; H, 6.23; N, 3.53. Found: C, 60.66; H, 6.07; N, 3.33.

Attempted isolation of W(N-*t*-Bu)[NC(Me)=CHCMe$_2$Ph](OHMT)Cl from the mixture in pentane yielded colorless crystals of W(N-*t*-Bu)(CHCMe$_2$Ph)(OHMT)(Cl)(MeCN), an X-ray study of which was carried out as described above (see SI for details).

W(N-*t*-Bu)(CHCMe$_2$Ph)(OHMT)(Cl)(MeCN) can be converted into W(N-*t*-Bu)[NC(Me)=CHCMe$_2$Ph](OHMT)Cl in the presence of acetonitrile, but upon solvent removal *in vacuo* no W(N-*t*-Bu)(CHCMe$_2$Ph)(OHMT)(Cl)(MeCN) reformed, according to a ^{1}H NMR spectrum; however, W(N-*t*-Bu)[NC(Me)=CHCMe$_2$Ph](OHMT)Cl decomposed in C_6D_6 with time to yield unidentified products, including HMTOH.

Mo(NAr)(CHCMe$_2$Ph)(bipy)(OC$_6$F$_5$)$_2$. Mo(NAr)$_2$(CHCMe$_2$Ph)$_2$ (900 mg, 1.26 mmol) was dissolved in Et$_2$O (20 mL). The solution was cooled to −25 °C in a freezer and treated with a prechilled solution of pentafluorophenol (1.16 g, 6.30 mmol) in Et$_2$O (10 mL). The resulting orange solution was stirred at 22 °C for 2 h and then treated with solid bipy (217 mg, 1.39 mmol) in one portion. The mixture was refluxed for 5 h. The volatiles were removed *in vacuo*, and the resulting solid was washed with a mixture of Et$_2$O and pentane. The solid was collected by filtration to give Mo(NAr)(CHCMe$_2$Ph)(bipy)(OC$_6$F$_5$)$_2$ (890 mg, 76%) as a yellow solid which was recrystallized from a mixture of Et$_2$O and pentane. Anal. Calcd for $C_{44}H_{37}F_{10}MoN_3O_2$: C, 57.09; H, 4.03; N, 4.54. Found: C, 57.09; H, 4.00; N, 4.40.

Mo(NAr)(CHCMe$_2$Ph)(bipy)Cl$_2$. Mo(NAr)(CHCMe$_2$Ph)(OC$_6$F$_5$)$_2$(bipy) (500 mg, 0.54 mmol) was dissolved in CH_2Cl_2 (20 mL) and treated with TMSCl (0.68 mL, 5.4 mmol). After 15 h the volatiles were removed *in vacuo*. Et$_2$O was added to the yellow solid, which was collected by filtration to give the title compound (305 mg, 90%). This compound was too insoluble to obtain a ^{13}C NMR, and repeated attempts to isolate pure material for satisfactory elemental analysis were unsuccessful.

Mo(NAr)(CHCMe$_2$Ph)(OHMT)(Cl)(t-BuCN). Mo(NAr)(CHCMe$_2$Ph)(bipy)Cl$_2$ (100 mg, 0.159 mmol) was suspended in Et$_2$O (40 mL), and the mixture was cooled to −25 °C. The suspension was treated slowly with a suspension of LiOHMT (53.5 mg, 0.159 mmol) and $ZnCl_2$ (35.6 mg, 0.159 mmol) in THF (10 mL). After being stirred at 22 °C for 40 h, the mixture was filtered through Celite, and the solvent was removed *in vacuo* to give a brown solid, which was rinsed with pentane (5 mL) and filtered through Celite to give a brown solution. Pivalonitrile (20 μL) was added, and the resulting yellow precipitate was collected by filtration and washed with cold pentane (∼1 mL) to give the product; 61 mg (46% yield) as a yellow solid. Anal. Calcd for $C_{51}H_{63}ClMoN_2O$: C, 71.94; H, 7.46; N, 3.29. Found: C, 71.96; H, 7.32; N, 3.29.

Mo(NAr)(CHCMe$_2$Ph)(OHMT)(Cl)(3-Brpy). Mo(NAr)(CHCMe$_2$Ph)(bipy)Cl$_2$ (100 mg, 0.159 mmol) was suspended in Et$_2$O (40 mL), and the mixture was cooled to −25 °C in a freezer. The suspension was treated slowly with a suspension of LiOHMT (53.5 mg, 0.159 mmol) and $ZnCl_2$ (35.6 mg, 0.159 mmol) in THF (10 mL). After being stirred at 22 °C for 40 h, the reaction mixture was filtered through Celite, and the solvent was removed *in vacuo* to give a brown solid, which was rinsed with pentane (5 mL) and filtered through Celite to give a brown solution. 3-Bromopyridine (25 μL) was added to the brown solution, and the resulting blue precipitate was collected by filtration and washed with cold pentane (∼1 mL) to give the product (70 mg, 48% yield) as a blue-green solid. Anal. Calcd for $C_{51}H_{58}BrClMoN_2O$: C, 66.13; H, 6.31; N, 3.02. Found: C, 65.78; H, 6.36; N, 2.96.

Mo(NAr)(CHCMe$_2$Ph)(OHMT)(Cl)(PMe$_2$Ph). Mo(NAr)(CHCMe$_2$Ph)(bipy)Cl$_2$ (100 mg, 0.159 mmol) was suspended in Et$_2$O (40 mL), and the mixture was cooled to −25 °C in a freezer. The suspension was treated with a suspension of LiOHMT (53.5 mg, 0.159 mmol) and $ZnCl_2$ (35.6 mg, 0.159 mmol) in THF (10 mL). After being stirred at 22 °C for 40 h, the reaction mixture was filtered through Celite, and the solvent was removed *in vacuo* to give a brown solid. The brown solid was extracted with pentane (5 mL) and filtered through Celite. Dimethylphenylphosphine (25 μL) was added to the brown pentane solution, and after 10 min the resulting yellow solid was collected by filtration and washed with cold pentane (∼1 mL); yield 89 mg (62% yield). Anal. Calcd for $C_{54}H_{65}ClMoNOP$: C, 71.55; H, 7.23; N, 1.55. Found: C, 71.57; H, 7.29; N, 1.31.

Mo(NC$_6$F$_5$)(CHCMe$_2$Ph)(ODFT)(Cl)(3-Brpy). Mo(NC$_6$F$_5$)(CHCMe$_2$Ph) (Me$_2$pyr)(ODFT)(NCMe) (280 mg, 0.289 mmol, 1.00 equiv) was dissolved in toluene, cooled to −25 °C in a freezer, and treated with 3-bromopyridinium chloride (56 mg, 0.289 mmol, 1.00 equiv). The mixture was stirred at 22 °C for 12 h, filtered through Celite, and concentrated *in vacuo* to give dark brown tar-like material. This material was washed with pentane (3 × 5 mL), and the remaining brown residue was dissolved in Et$_2$O (2 mL), diluted with pentane (2 mL), and filtered to give a yellow solution. Removal of solvent *in vacuo* gave Mo(NC$_6$F$_5$)(CHCMe$_2$Ph)(ODFT)(Cl)(3-Br-py) (180 mg, 60% yield) as a yellow solid. Anal. Calcd for $C_{39}H_{19}BrClF_{15}MoN_2O$: C, 45.57; H, 1.86; N, 2.73. Found: C, 45.63; H, 1.93; N, 2.73.

Mo(NC$_6$F$_5$)(CHCMe$_2$Ph)(PPhMe$_2$)$_2$Cl$_2$. Mo(NC$_6$F$_5$)$_2$(CH$_2$CMe$_2$Ph)$_2$ (1.00 g, 1.38 mmol, 1.00 equiv) was dissolved in Et$_2$O (6 mL), and Me$_2$PhPHCl (0.48 g, 2.76 mmol, 2.00 equiv) was added as a solid in one portion. The resulting suspension was stirred for 1 h at 22 °C, during which time the phosphonium salt dissolved and a yellow precipitate formed, which was collected by filtration, washed with 4 mL of cold Et$_2$O, and dried under vacuum to give Mo(NC$_6$F$_5$)(CHCMe$_2$Ph)(PPhMe$_2$)$_2$Cl$_2$·Et$_2$O (760 mg, 66% yield) as a yellow solid. Anal. Calcd for $C_{32}H_{34}Cl_2F_5MoNP_2$: C, 50.81; H, 4.53; N, 1.85. Found: C, 50.77; H, 4.59; N, 1.82.

Mo(NC$_6$F$_5$)(CHCMe$_2$Ph)(OHIPT)(Cl)(PPhMe$_2$). Mo(NC$_6$F$_5$)(CHCMe$_2$Ph)(PPhMe$_2$)$_2$Cl$_2$·Et$_2$O (640 mg, 0.771 mmol, 1.00 equiv) was suspended in Et$_2$O (15 mL) and cooled to −25 °C in a freezer. A cold solution (−25 °C) of HIPT-OLi (339 mg, 0.771 mmol, 1.00 equiv) in 5 mL of Et$_2$O was added slowly, and the resulting suspension was stirred for 16 h at 22 C. The reaction mixture was filtered through Celite, and volatiles were evaporated *in vacuo*. The residue was dissolved in pentane (20 mL) and filtered through Celite. The resulting brown solution was stirred at 22 °C for 1 h. During this time a yellow precipitate formed, which was collected by filtration, washed with 4 mL of cold pentane, and dried under vacuum to give Mo(NC$_6$F$_5$)(CHCMe$_2$Ph)(PPhMe$_2$)(OHIPT)(Cl) (540 mg, 65% yield) as a yellow solid.

Despite repeated attempts to purify the material, samples submitted for elemental analysis consistently gave lower C content than expected. This circumstance may be the result of incomplete combustion of the fluorinated organic fragments. Anal. Calcd for $C_{60}H_{72}ClF_5MoNOP$: C, 66.69; H, 6.72; N, 1.30. Found: C, 65.68; H, 6.82; N, 1.05.

Mo(NC$_6$F$_5$)(CHCMe$_2$Ph)(OHMT)(Cl)(PPhMe$_2$). The title compound was prepared in 71% yield as an orange powder as described above for Mo(NC$_6$F$_5$)(CHCMe$_2$Ph)(OHIPT)(Cl)(PPhMe$_2$). Elemental analyses again were low in carbon. An example is Anal. Calcd for $C_{48}H_{48}ClF_5MoNOP$: C, 63.20; H, 5.30; N, 1.54. Found: C, 61.58; H, 5.20; N, 1.56.

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■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b10499.

Full experimental details, including NMR data and spectra for new compounds, complete table of reactivities, and GC traces; X-ray crystallographic data for complexes **4**(*t*-BuCN), **5**(MeCN), and **8b**(PMe_2Ph) and comparisons with other structures; and a full description of all catalytic studies (PDF)

X-ray crystallographic file for **4**(*t*-BuCN) (CIF)

X-ray crystallographic file for **5**(MeCN) (CIF)

X-ray crystallographic file for **8b**(PMe_2Ph) (CIF)

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Notes

The authors declare no competing financial interest.

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