Synthesis and Evaluation of Molybdenum and Tungsten Monoaryloxide Halide Alkylidene Complexes for Z-Selective Cross-Metathesis of Cyclooctene and 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 1,2-dichloroethylene or Z-(CF3)CH=CH(CH2)2Cl. 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-disopropylphenyl or NC6F5, 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=CH 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)(CHCMe2Ph)(OHMT)(Cl)(t-BuCN) (Ar = 2,6-disopropylphenyl; OHMT = 2,6-dimesitylphenoxide) to give 14e Mo(NAr)(CHCMe2Ph)(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)(CHCMe2Ph)(OHMT)Cl binds pivalonitrile most strongly. Other Mo(NR)(CHR)(OR')(Cl)(L) complexes can be activated through addition of B(C6F5)3. High stereoselectivities (>98% Z,Z) of ClCH=CH(CH2)2CH=CHCl are not restricted to tert-butylimido or adamantylimido complexes; 96.2% Z selectivity is observed with boron-activated Mo(NC6F5)(CHR)(OHPT)(Cl)(PPhMe2). 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 (Me2Pyr).2 These “MAP” (monoalkoxide pyrrolide) complexes have been found to be useful for Z-selective metathesis reactions of small molecules3 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-selective5 or E-selective6 syntheses of halogenated alkene 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, (CF3)CH==CH(CF3).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)(CHCMe2Ph)(OHMT)(Br)(py) (Ad = 1-adamantyl and py = pyridine), was isolated in low yield.1 An X-ray study showed that the structure of Mo(NAd)(CHCMe2Ph)(OHMT)(Br)(py) is close to a square pyramid (τ = 0.21°) with the syn alkylidene in the apical position. We proposed that Mo(NAd)(CHCMe2Ph)(OHMT)(Br)(py) is formed when the complex reaction mixture, reacts with Mo(NAd)(CHCMe2Ph)(OHMT)(Pyr). We saw no evidence for Mo==CHX...
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(N(Nd)(CHCMe2Ph)-(OHMT)(Br)(py) was discovered. They are Mo(N(ARMe2)(CHCMe2Ph)(OHMT)(Cl)(py), where NRMes2 is the sterically demanding 2,6-dimethylphenylimido ligand,9 tungsten oxo complexes such as W(0)(CH-t-Bu)(OHPT)(Cl)-(PMe2Ph)(OHIPT) = O-2,6-(2,4,6-i-Pr3C6H2)2C6H3,10 and tert-butylmido 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 paper7 we reported a route to 16e Mo monoaryloxide halide complexes in which acetonitrile is the donor ligand, namely Mo(N(AR)(CHCMe2Ph)(OAr)-Cl(MeCN) (X = Cl, Br) and Mo(N(AD)(CHCMe2Ph)(OAr)-Cl)(MeCN) (OAr = OHMT or OHIPT). The acetonitrile donor ligands are much slower as a consequence of the stronger binding of the fluoride ligand to the 14e Mo(NAd)(CHCMe2Ph)(OAr)Cl core compared to acetonitrile. The pyridine adducts can be activated through addition of 1 equiv of B(C6F5)3 which sequesters all pyridine as (py)B(C6F5)3. Because of what appear to be high reactivities, high selectivities, and unique abilities of nitrite 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-CICCl=CHCl and cyclooctene to give CICH=CH(CH2)4CICH=CHCl.

Results and Discussion

Synthesis of Mo(NAr) MAC Complexes.

We chose to explore the synthesis of Mo==NAr (Ar = 2,6-i-Pr3C6H2) complexes as alternatives to adamantyl or tert-butylmido complexes because sterically hindered NAr complexes tend to be more stable toward bimolecular decomposition.12,13,15

The reaction between Mo(NAr2)(CH2CMe2Ph)2, 2',2'-bipyridine (bipy), and pentfluoroethenyl in diethyl ether shown in Scheme 1 is modeled after syntheses of adamantylimido and tert-butylmido complexes.14-16

The reaction between Mo(NAr)(CHCMe2Ph)bipy(OC6F5)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 1H NMR spectrum. In the presence of pentfluoroethenyl 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 been successful for the synthesis of W alkylidenes,15 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 JCH (125 Hz).2 The two pentfluoroethenoxide ligands are not equivalent according to 19F NMR spectra, and the presence of two Ar methine 1H 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)(CHCMe2Ph)bipyCl3 (3) in 90% yield as a mixture of two isomers. The reaction between 3, LiOHMT, and ZnCl2 then gave Mo(NAr)(CHCMe2Ph)(OHMT)(Cl)(4) as a pentane-soluble intermediate that could be converted into Mo(NAr)(CHCMe2Ph)(OHMT)(Cl)(i-tBuCN) (4-tBuCN) in 46% yield, Mo(NAr)(CHCMe2Ph)(OHMT)(Cl)(PPhMe2) (4(PMe2Ph)) in 62% yield, or Mo(NAr)(CHCMe2Ph)(OHMT)(Cl)(3-Bryp) (4(3-Bryp)) in 48% yield upon addition of pivalonitrile, dimethylphenylphosphine, or 3-bromopyridine, respectively (Scheme 1). Pivalonitrile was chosen as 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(tBuCN) (Figure 1) showed it to have nearly a square pyramidal structure (r = 0.1119) 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)(CHCMe2Ph)(OHMT)(Br)(py) (r = 0.21) and Mo(N(AR)(CHCMe2Ph)(OHMT)(Cl)(3-Bryp) (r = 0.21). 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
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. 1H 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 complex with a pyridine ligand (e.g., t-BuCN). Hydrogen atoms, except on C1, have been omitted for clarity. Ellipsoids are shown at 50% probability.

Figure 1. Structure of Mo(NAr)(CHCMe2Ph)(OHMT)(Cl)(t-BuCN). Hydrogen atoms, except on C1, have been omitted for clarity. Ellipsoids are shown at 50% probability.

Figure 2. 1H NMR spectra in the alkylidene region of (a) ~0.01 M Mo(NAr)(CHCMe2Ph)(OHMT)(Cl)(t-BuCN) in toluene-\textit{d}_6 and (b) after removal of >95% of the t-BuCN.

3NMR spectra in the alkylidene region of (a) ~0.01 M Mo(NAr)(CHCMe2Ph)(OHMT)(Cl)(t-BuCN) and (b) after removal of >95% of the t-BuCN.

only in a 14e complex, 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(C₆F₅)₃ is added to an NMR sample of Mo(NAr)(CHCMe₂Ph)(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 1H 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(C₆F₅)₃ to 4(PPhMe₂). Finally, addition of 1 equiv of pivalonitrile or PPhMe₂ to the mixture of syn-4 and anti-4 (Figure 2b) yields 1H NMR spectra identical to the spectra of 4(t-BuCN) and 4(PPhMe₂), 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
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-d8, 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 C6D6 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 1H 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)−(CHCMe2Ph)(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-d8. 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)(CHCMe2Ph)(OHMT)Cl were a dimer (see SI). Therefore, we propose that anti-Mo(NAr)(CHCMe2Ph)-(OHMT)Cl is a monomer in solution. Experiments analogous to those just described for Mo=NR chloride complexes have been carried out for pyridine and acetonitrile adducts of Mo=NR and Mo=NR-t-Bu complexes reported previously,14 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)2Cl2 from W(NR)(CH2-t-Bu)2 (R = Ad or t-Bu). Therefore, we prepared W=NR complexes in order to compare their catalytic activities with Mo compounds. Neophyldiene MAC complexes were prepared from W(N-t-Bu)2(CHCMe2Ph)3 in a manner closely analogous to the preparation of Mo neopentyldiene complexes, W(N-t-Bu)-(CHCMe2Ph)(OHMT)(Cl)(py)2 (5(py)) was synthesized from W(N-t-Bu)(CHCMe2Ph)(OHMT)(Cl)(3-Bppy)2 (5(3-Bppy)) from W(N-t-Bu)(CHCMe2Ph)(3-Bppy)2Cl2 in 51% yield (Figure 3).

![Figure 3. General structure of W MAC complexes, 5(py), 5(3-Bppy), and 5(t-BuCN).](image)

Addition of B(C6F5)3 to W(N-t-Bu)(CHCMe2Ph)(OHMT)Cl (5), followed by addition of pivalonitrile to the solution of 5, generated W(N-t-Bu)-(CHCMe2Ph)(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 1H NMR analysis of 5 showed a single alkylidene resonance at 8.24 ppm that we assign to the syn isomer (JCH = 117 Hz; JWH = 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)≡CHCMe2Ph](OHMT)(Cl)(6; eq 1). Attempts to isolate 6 from 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 1H NMR analysis, and 6 decomposed in C6D6 to yield HMTOH and unidentified metal-containing products. The proposed structure of 6 that was prepared through the use of isotopically labeled Me13CN is supported by NMR studies (δ1H measurement and heteronuclear bond correlation NMR experiments; see SI). Only one configuration of the vinylidino ligand is observed in 6.

We propose that 6 is formed through insertion of the nitride 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 alkylidynes 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 vinylidino complex. 1-Aza-titanacyclobut-4-enes have been prepared in reactions in which intermediate Cp2Ti==CMeCH≡CMe is trapped by nitrides,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°) 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 sterice 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 sterice interactions between the terphenoxide and nitrile ligand and between the imido ligand and the syn alkylidene substituent, respectively.16,12

**Synthesis of Mo(NC6F5) Complexes.** Mo-based pentafluorophenylimido MAP complexes have proven to be especially efficient for Z-selective and E-selective cross-meta-
thesis reactions in which an electron-poor halogenated olefin is one of the olefin partners. 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(NC₆F₅)MAC complexes involved the protonation of MAP complexes with pyridinium halide acids, as described for the early syntheses of Mo(NR)₂MAC complexes (R = t-Bu and Ad). 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(NC₆F₅)(CHMe₂Ph)(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(NC₆F₅)alkylidene complexes have been unsuccessful.

Our search for alternative routes to monochloride complexes led the discovery that 2 equiv of Me₂PhPHCl reacts smoothly with Mo(NC₆F₅)₂(CH₂CMe₂Ph)₂ to yield C₆F₅NH₂, PhCMe₃, and the dichlorobisphosphine alkylidene derivative, Mo(NC₆F₅)(CHCMe₂Ph)L₂Cl₂ (7, L = PMe₂Ph), 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, we have found that addition of either Ph₂MePHCl or Me₂PHCl to W(NC₆F₅)₂(CH₂CMe₂Ph)₂ or Mo(NR)₂(CH₂CMe₂Ph)₂ (R = 2,6-Me₂C₆H₄ or 2,6-i-Pr₂C₆H₄) 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(CH₂-t-Bu)₂ with phosphonium halides generated a complex mixture of alkylidene-containing compounds along with other unidentified products. As has been reported previously, pyridinium chlorides do not deliver a bipyridine analogue of 7. In spite of these unfavorable preliminary results, we are hopeful that other successful syntheses of analogues of 7 from Mo(NC₆F₅)₂(CH₂CMe₂Ph)₂ or Mo(NC₆F₅)₂(CH₂CMe₂Ph)₂ can be developed, or that 7 will emerge as a versatile synthetic intermediate for other classes of Mo(NC₆F₅) alkylidene complexes.

Addition of either LiOHMT or LiOHIPT to 7 leads to the MAC complexes as the phosphate adducts, Mo(NC₆F₅)(CHCMe₂Ph)(OHMT)(Cl)(PMe₂Ph) (8a(PMe₂Ph)) and Mo(NC₆F₅)(CHCMe₂Ph)(OHIPT)(Cl)(PMe₂Ph) (8b(PMe₂Ph)) (eq 3). Syntheses leading to 8a(PMe₂Ph) and 8b(PMe₂Ph) in four steps from molybdate are currently the most efficient way to prepare Mo(NC₆F₅) alkylidene complexes.

An X-ray study of 8b(PMe₂Ph) (Figure 5) revealed a structure analogous to those of 4(t-BuCN) (Figure 1) and 5(MeCN) (Figure 4), i.e., a square pyramid (τ = 0.10) with the alkylidene (C1) in the apical position and the phosphate 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)(PPhMe₂) (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(PMe₂Ph) and 8b(PMe₂Ph) have sharp, concentration-independent alkylidene doublet resonances in their ¹H spectra, consistent with no significant degree of dissociation of phosphate in solution. However, the phosphate can be removed from 8a(PMe₂Ph) and 8b(PMe₂Ph) with Ph₃CB(C₆F₅)₄ or B(C₆F₅)₃ (in C₆D₆) to yield the respective phosphate-free 14e complexes, 8a and 8b in solution, according to NMR studies. The reactions are complete in ~1 h at 22 °C.
and 0.1 M concentration, and ¹H NMR spectra of either 8a or 8b in C₆D₆ at a concentration of ~0.1 M show little change after 6 h. We propose that removal of the phosphine is successful because both Ph₃CB(C₆F₅)₃ and B(C₆F₅)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 C₆D₆ (eq 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(CH₂)₆CH=CHCl (C) were followed by ¹H NMR over a period of up to 24 h (C₆D₆, 2 2). 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

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

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</tr>
<tr>
<td>18, Mo(NC₆F₅)(CHR')(ODFT)(Cl)(3-Brpy)</td>
<td>89/11/0</td>
</tr>
<tr>
<td>19, W(NR)(CHR')(OHMT)(Cl)(3-Brpy)</td>
<td>100/0/0</td>
</tr>
<tr>
<td>20, W(NR)(CHR')(OHMT)(Cl)(RCN)</td>
<td>80/20/0</td>
</tr>
</tbody>
</table>

In Table 1 we list some of the most successful reactions in which no B(C₆F₅)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-((C₆F₅)₂C₆H₃)₂C₆H₃, run 6) instead of OHMT or OHIPT. (It should be noted that the unsuccessful 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(NC₆F₅)(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(C₆F₅)₃ in which no C was formed after 1 h. These experiments involve Mo catalysts that contain relatively strongly bound 2e donor ligands (PMe₂Ph, 1-methylimidazole, or pyridine in the bromide complex) or 3-bromopyridine in Mo(NAr) or Mo(NC₆F₅) complexes. We propose that the 3-Brpy and tert-buylimido complexes are not sufficiently labile to produce viable quantities of 14e MAC complexes. The combination of NC₆F₅ and ODFT (O-2,6-((C₆F₅)₂C₆H₃)₂C₆H₃) ligands limits the lability of 3-Brpy in run 18 (Table 2).

Table 3. ROCM of A with DCE To Give B and/or C after Addition of B(C₆F₅)₃ (+LA)

<table>
<thead>
<tr>
<th>run/initiator</th>
<th>3 min</th>
<th>60 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>21, Mo(NAr)(CHR')(OHMT)(Cl)(3-Brpy) + LA</td>
<td>0/12/87</td>
<td>0/5/95</td>
</tr>
<tr>
<td>22, Mo(NAr)(CHR')(OHMT)(Cl)(PMe₂Ph) + LA</td>
<td>0/7/93</td>
<td>0/4/96</td>
</tr>
<tr>
<td>23, Mo(NC₆F₅)(CHR')(ODFT)(Cl)(3-Brpy) + LA</td>
<td>0/6/36</td>
<td>–</td>
</tr>
<tr>
<td>24, Mo(NC₆F₅)(CHR')(OHMT)(Cl)(PPhMe₂) + LA</td>
<td>0/0/100</td>
<td>–</td>
</tr>
<tr>
<td>25, Mo(NC₆F₅)(CHR')(OHMT)(Cl)(PPhMe₂) + LA</td>
<td>0/1/99</td>
<td>0/0/100</td>
</tr>
<tr>
<td>26, Mo(NAd)(CHR')(OHMT)(Br)(py) + LA</td>
<td>0/5/95</td>
<td>–</td>
</tr>
<tr>
<td>27, W(NR)(CHR')(OHMT)(Cl)(3-Brpy) + LA</td>
<td>72/28/0</td>
<td>68/32/0</td>
</tr>
<tr>
<td>28, Mo(NR)(CHR')(OHMT)(Cl)(RCN) + LA</td>
<td>0/0/100</td>
<td>0/0/100</td>
</tr>
</tbody>
</table>

See Table 1 footnotes.
full conversion (Table 1, run 4), but full conversion is reached in 2 min in the presence of B(C\(_6\)F\(_5\))\(_3\) (run 28 in Table 3). It should be noted that even PMe\(_3\)-Ph 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 stereoch- emistry of C. High-field \(^1\)H NMR spectra (500 MHz or more in C\(_6\)D\(_6\) or CDCl\(_3\)) are sufficient for measuring the ratio of \(Z,Z\)- and \(E,Z\)- in the absence of \(E,E\)-, but GC studies are required when \(E,E\)- is present. With reactions of Mo(N-t-Bu) or Mo(NAd) catalysts showed a strong preference for formation of \(Z,Z\)- (\textgreater 98%), according to \(^1\)H NMR spectra. The stereoselective purity of C according to GC analysis was found to be \(\geq 96\% \ Z,Z\)- in four experiments (runs 1, 2, 19, and 28 in Table 4). A value of 99.7% \(Z,Z\)- C with 0.3% \(E,E\)- C implies 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\(_6\)F\(_5\))\(_2\)(CH\(_2\)CMe\(_2\)Ph)\(_2\) (run 19). The importance of the aryloxide to the level of stereoselectivity is manifested in the results for the analogous reaction involving Mo(NC\(_6\)F\(_5\))\(_2\) (CHR\(_{\text{R1}}\))(OHIMPT)\(_3\) (PPhMe\(_2\)) + LA. 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 OHIMPT is the aryloxide ligand, and/or the W= split bond reacts with a nitrile to yield a vinylidene complex. Because Mo(NR)(CHR\(_{\text{R1}}\))(OHIMPT)\(_3\) + LA and Mo(NAd)(CHR\(_{\text{R1}}\))(OHIMPT)\(_3\) + LA are not stable under catalytic conditions, but also less reactive and \(Z\)-selective. Mo(NAr)(CHR\(_{\text{R1}}\))(OHIMPT)\(_3\) can be characterized in solution as a mixture enriched in the nitrile-free 14e M(NC\(_6\)F\(_5\))(CHR\(_{\text{R1}}\))(OHIMPT)\(_3\) complex. Molybdenum complexes are highly active catalysts for the cross-metathesis of cyclooctene and Z-1,2-dichloroethylene to give almost exclusively \(Z\)-CH=CH=(CH\(_2\))\(_n\)CH=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.

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

<table>
<thead>
<tr>
<th>run, initiator</th>
<th>(Z,Z)-C</th>
<th>(E,E)-C</th>
<th>(Z,E)-C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1, Mo(NAd)(CHR(_{\text{R1}}))(OHIMPT)(_3)(MeCN)</td>
<td>99.7</td>
<td>0.3</td>
<td>~0</td>
</tr>
<tr>
<td>2, Mo(NR)(CHR(_{\text{R1}}))(OHIMPT)(_3)(MeCN)</td>
<td>99.5</td>
<td>0.5</td>
<td>~0</td>
</tr>
<tr>
<td>19, Mo(NC(_6)F(_5))(<em>2)(CHR(</em>{\text{R1}}))(OHIMPT)(_3)(PPhMe(_2)) + LA</td>
<td>96.2</td>
<td>3.8</td>
<td>~0</td>
</tr>
<tr>
<td>28, Mo(NR)(CHR(_{\text{R1}}))(OHIMPT)(_3)(1-BuCN) + LA</td>
<td>99.5</td>
<td>0.5</td>
<td>~0</td>
</tr>
<tr>
<td>10, Mo(NAr)(CHR(_{\text{R1}}))(OHIMPT)(_3)(RCN)</td>
<td>61.3</td>
<td>34.6</td>
<td>4.1</td>
</tr>
<tr>
<td>20, Mo(NC(_6)F(_5))(<em>2)(CHR(</em>{\text{R1}}))(OHIMPT)(_3)(PPhMe(_2)) + LA</td>
<td>66.4</td>
<td>30.4</td>
<td>3.2</td>
</tr>
<tr>
<td>21, Mo(NAr)(CHR(_{\text{R1}}))(OHIMPT)(_3)(1-BuCN)</td>
<td>63.3</td>
<td>33.3</td>
<td>3.4</td>
</tr>
</tbody>
</table>

### CONCLUSIONS

We conclude that monoaryloxide halide complexes of Mo or W with the general formula M(NR)(CHR)\(_{\text{R1}}\)(OAryl)(X)(L) can be prepared in a process involving intermediates that contain pentavalent arylidenes and 2,2'-bipyridine. Addition of Mo(NH\(_2\))HCl to Mo(NC\(_6\)F\(_5\))\(_2\)(CH\(_2\)CMe\(_2\)Ph)\(_2\) leads to Mo(NC\(_6\)F\(_5\))(CHR\(_{\text{R1}}\))(OHIMPT)\(_3\)(Cl)\(_2\) from which Mo(NC\(_6\)F\(_5\))(CHR\(_{\text{R1}}\))(OHIMPT)\(_3\)(Cl)(PMe\(_2\)Ph) 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\(_6\)F\(_5\))(CHR\(_{\text{R1}}\))(OHIMPT)\(_3\) complex. Molybdenum complexes are highly active catalysts for the cross-metathesis of cyclooctene and Z-1,2-dichloroethylene to give almost exclusively \(Z\)-CH=CH=(CH\(_2\))\(_n\)CH=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.

### 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. Actonitrile, benzene, CH\(_3\)Cl\(_2\), EtO\(_2\)\(_2\), 1,2-dimethoxyethane, and toluene were degassed, passed through activated alumina columns, and stored over 4 Å Linde-type molecular sieves prior to use. Sodium carbonate, and dried over CaCl\(_2\) pellets for at least 2 weeks prior to use. Pentane was washed with H\(_2\)SO\(_4\), 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.

The pentane was dried over 4 Å Linde-type molecular sieves prior to use. Deuterated solvents were dried over 4 Å Linde-type molecular sieves prior to use. 1H 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 tetrakis (hydrido)borate 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 7.17, methylene chloride 4.06).
Gas chromatography was performed on an Agilent system equipped with an HP-5 column (ID 320 mm, film thickness 0.25 μm, length 30 m). Pyridinium chloride was purchased from Sigma-Aldrich or Alfa Aesar and sublimed prior use. TMSI was purchased from Alfa Aesar and degassed by a freeze–pump–thaw method prior to use. B(C6F5)3 was purchased from Strem and sublimed prior to use. Pyridonitrile and I-methyldinicotinoyl were purchased from Alfa Aesar, distilled over CaH2, and stored over 4 Å Linde-type molecular sieves prior to use.

To a 0.5 mL of CH2Cl2 solution (1.5 mL) was added 3-bromopyridine (48 mg, 0.500 mmol, 1.00 equiv) in THF (10 mL). After being stirred at 22 °C for 1 h, the mixture was stirred at 22 °C for 12 h. The resulting slurry was collected by filtration and washed with cold pentane (30 mL), and the extract was filtered through Celite. Acetonitrile (0.1 mL) was added to this brown pentane solution. 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)(py) (49 mg, 0.132 mmol) as a tan solid. Anal. Calcld for Mo(N-t-Bu)(CH-t-Bu)(OTTBT)(Cl)(py): C, 67.6; H, 6.82; N, 5.38. Found: C, 68.04; H, 5.82; N, 3.44. (See SI for a complete set of unsuccessful elemental analyses.)

Gas chromatography was performed on an Agilent system equipped with an HP-5 column (ID 320 mm, film thickness 0.25 μm, length 30 m). Pyridinium chloride was purchased from Sigma-Aldrich or Alfa Aesar and sublimed prior use. TMSI was purchased from Alfa Aesar and degassed by a freeze–pump–thaw method prior to use. B(C6F5)3 was purchased from Strem and sublimed prior to use. Pyridonitrile and I-methyldinicotinoyl were purchased from Alfa Aesar, distilled over CaH2, and stored over 4 Å Linde-type molecular sieves prior to use.

A solution of Me2PhCH2CH2MgCl (0.5 M, 7.2 mL, 3.6 mmol) in Et2O was added to a−30 °C solution of W((N-t-Bu)3(py)2Cl2 (1.0 g, 1.8 mmol) in 40 mL of Et2O. 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 Et2O. The solvent was removed from the filtrate in vacuo to afford a yellow oil (750 mg, 70% yield) whose 1H and 13C NMR spectra are consistent with it being W((N-t-Bu)3(CH2)2(C6F5)CH2)2Cl (and by analogy with W((N-t-Bu)3(CH2)2(C6F5)CH2)2Cl).

Gas chromatography was performed on an Agilent system equipped with an HP-5 column (ID 320 mm, film thickness 0.25 μm, length 30 m). Pyridinium chloride was purchased from Sigma-Aldrich or Alfa Aesar and sublimed prior use. TMSI was purchased from Alfa Aesar and degassed by a freeze–pump–thaw method prior to use. B(C6F5)3 was purchased from Strem and sublimed prior to use. Pyridonitrile and I-methyldinicotinoyl were purchased from Alfa Aesar, distilled over CaH2, and stored over 4 Å Linde-type molecular sieves prior to use.

A solution of Me2PhCH2CH2MgCl (0.5 M, 7.2 mL, 3.6 mmol) in Et2O was added to a−30 °C solution of W((N-t-Bu)3(py)2Cl2 (1.0 g, 1.8 mmol) in 40 mL of Et2O. 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 Et2O. The solvent was removed from the filtrate in vacuo to afford a yellow oil (750 mg, 70% yield) whose 1H and 13C NMR spectra are consistent with it being W((N-t-Bu)3(CH2)2(C6F5)CH2)2Cl (and by analogy with W((N-t-Bu)3(CH2)2(C6F5)CH2)2Cl).
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_{32}H_{34}Cl_{2}F_{5}MoNP_{2}: C, 50.81; H, 4.53; N, 1.85. Found: C, 50.77; H, 4.59; N, 1.82.

**Attempted synthesis of W(N-t-Bu)(CHCMe_{2}Ph)(OHMT)(Cl)(MeCN)**

B(C_{6}F_{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 1H 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)2]CHCMe_{2}Ph)(OHMT)Cl. Anal. Calcd for C_{60}H_{62}Cl_{2}F_{5}MoNP_{2}: C, 50.77; H, 4.59; N, 1.82. Found: C, 50.77; H, 4.59; N, 1.82.

**Mo(Nar)(CHCMe_{2}Ph)(bipy)(OC_{6}F_{5})_{2}**

Mo(Nar)(CHCMe_{2}Ph)(bipy) (900 mg, 1.26 mmol) was dissolved in Et_{2}O (20 mL). The solution was cooled to 22 °C for 10 min. The pale yellow precipitate (35 mg, 46%) was collected by filtration. A 1H NMR spectrum showed the product to be W(N-t-Bu)(CHCMe_{2}Ph)(OHMT)(Cl)(MeCN) reformed, according to a 1H NMR spectrum; however, W(N-t-Bu)[NC(Me)2]CHCMe_{2}Ph)(OHMT)Cl was the major product.

**Mo(Nar)(CHCMe_{2}Ph)(bipy)(OC_{6}F_{5})_{2}**

Mo(Nar)(CHCMe_{2}Ph)(bipy) (500 mg, 0.54 mmol) was dissolved in CH_{2}Cl_{2} (20 mL) and treated with TMS Cl (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 13C NMR, and repeated attempts to isolate pure material for satisfactory elemental analysis were unsuccessful.

**Mo(Nar)(CHCMe_{2}Ph)(bipy)(OC_{6}F_{5})_{2}**

Mo(Nar)(CHCMe_{2}Ph)(bipy)Cl (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 (33.5 mg, 0.159 mmol) and ZnCl_{2} (33.6 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_{32}H_{34}BrCl_{2}MoNO_{3}: 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_2Ph)**

Mo(Nar)(CHCMe_{2}Ph)(bipy)Cl (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 (33.5 mg, 0.159 mmol) and ZnCl_{2} (33.6 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_{51}H_{63}BrCl_{2}MoNO_{3}: C, 71.57; H, 7.23; N, 1.55. Found: C, 71.57; H, 7.23; N, 1.31.

**Mo(NCF_3)(CHCMe_{2}Ph)(ODFT)(Cl)(3-Br-py)**

Mo(NCF_3)(CHCMe_{2}Ph)(Me-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-bromopyridinidine (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 (5 × 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(NCF_3)(CHCMe_{2}Ph)(ODFT)(Cl)(3-Br-py) (180 mg, 60% yield) as a yellow solid. Anal. Calcd for C_{32}H_{34}BrCl_{2}MoNO_{3}: C, 45.57; H, 1.86; N, 2.73. Found: C, 45.63; H, 1.93; N, 2.73.

**Mo(NCF_3)(CHCMe_{2}Ph)(bipy)(PPhMe_2)Cl**

Mo(NCF_3)(CHCMe_{2}Ph)(bipy)Cl_{2} (1.00 g, 1.38 mmol, 1.00 equiv) was dissolved in Et_{2}O (6 mL), and Me_{2}PPhCHCl (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 the white precipitate 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(NCF_3)(CHCMe_{2}Ph)(PPhMe_2)Cl_{2} (760 mg, 66% yield) as a yellow solid. Anal. Calcd for C_{32}H_{34}BrCl_{2}MoNO_{3}: C, 50.81; H, 4.53; N, 1.85. Found: C, 50.77; H, 4.59; N, 1.82.

**Mo(NCF_3)(CHCMe_{2}Ph)(OHPT)(Cl)(PPhMe_2)**

Mo(NCF_3)(CHCMe_{2}Ph)(PPhMe_2)Cl (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 suspension 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(NCF_3)(CHCMe_{2}Ph)(PPhMe_2)(OHPT)(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_{51}H_{63}Cl_{2}MoNO_{3}: C, 66.69; H, 6.72; N, 1.30. Found: C, 65.68; H, 6.82; N, 1.05.

The title compound was prepared in 71% yield as an orange powder as described above for Mo(NCF_3)(CHCMe_{2}Ph)(OHPT)(Cl)(PPhMe_2). Elemental analyses again were low in carbon. An example is Anal. Calcd for C_{51}H_{63}Cl_{2}MoNO_{3}: 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(PMe2Ph) 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(PMe2Ph) (CIF)

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**Notes**

The authors declare no competing financial interest.

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**REFERENCES**


