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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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-(CF₃)CH=CH(CF₃). 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 NC₆H₄Bu, 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)L core is accessible through dissociation of the nitrile to a significant extent. Pivalonitrile can be removed (>95%) from Mo(NAd)(CHCMe₂Ph)(OHMT)(Cl)(I-BuCN) (Ar = 2,6-diisopropylphenyl; OHMT = 2,6-dimesitylphenoxide) to give 14e Mo(NAd)(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(NAd)(CHCMe₂Ph)(OHMT)(Cl) binds pivalonitrile most strongly. Other Mo(NR)(CHR')(OR')(Cl)(L) complexes can be activated through addition of B(C₆H₅)₃. High stereoselectivities (>98% ZZ) of CICH=CH(CH₂)₂CH=CHCl are not restricted to t-butylimido or adamantylimido complexes; 96.2% Z selectivity is observed with boron-activated Mo(NC₆H₄Bu)(CHCMe₂Ph)(OHHT)(Cl)(PPPh₂Me₂). 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. 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). These "MAP" (MonoAlkoxide Pyrrolylde) complexes have been found to be useful for Z-selective metathesis reactions of small molecules and the ring-opening metathesis polymerization of cyclic olefins to give cis,syniodiatactic polymers. The most recent advances in metatheses of small molecules include the Z-selective or E-selective syntheses of halogenated alkenes from olefins that contain one or more electron withdrawing substituents, e.g., CHCl=CHCl, BrCH=CHBr, FCH=CHBr, or, most recently, (CF₃)CH=CH(CF₃).

While searching for Mo=CHX complexes (X = Cl or Br), which are required intermediates in reactions that involve CHCl=CHCl or BrCH=CHBr, the monobromide complex, Mo(NAd)(CHCMe₂Ph)(OHMT)(Br)(pyridine) (Ad = 1-adamantyl), was isolated in low yield. 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 HBr, which is generated in an unknown manner in 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)(CHR)(X)(OAr)(Y) (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)(CHCMe₂Ph)(OHMT)(Br)(py) was discovered. They are Mo(NAr₅Me₅)(CHCMe₂Ph)(OHMT)(Cl)(py), where NAr₅Me₅ is the sterically demanding 2,6-dimesitylphenylimido ligand, tungsten oxo complexes such as W(O)(CH-t-Bu)(OHHT)(Cl)(PM₂Me₂Ph) (OHHT = O-2,6-(2,4,6-i-Pr₃C₆H₂)₂C₆H₃), and t-butylimido complexes such as W(N-t-Bu)(CH-t-Bu)(OHHT)(Cl)(py). 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 SI).

In a recent paper we reported a route to 16e Mo monoaryloxide halide complexes in which acetonitrile is the donor ligand, namely Mo(N-tert-Bu)(CH-t-But)(OH-HTP)(X)(MeCN) (X = Cl, Br) and Mo(NAd)(HCMe2Ph)(OAr)(Cl)(MeCN) (OAr = OHMT or OHHTP). The acetonitrile complexes were found to be highly active for the Z-selective cross-metathesis reactions between Z-CICH=CHCl and a selection of olefins, including cyclooctene. Pyridine analogs were much slower as a consequence of the stronger binding of pyridine to the 14e Mo(NAd)(HCMe2Ph)(OAr)Cl core compared to acetonitrile. The pyridine adducts can be activated through addition of one equivalent of B(C6F5)3, which sequesters all pyridine as (py)2B(C6F5)3. Because of what appear to be high reactivities, high selectivities, and unique abilities of nitride adducts of Mo monoaryloxide halide complexes in cross-metathesis reactions involving electron-poor olefins as cross-partners, 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-CICH=CHCl and cyclooctene to give CICH=CH(CH2)CH=CHCl.

RESULTS AND DISCUSSION

Synthesis of Mo(NAr) MAC complexes

We chose to explore the synthesis of Mo=NaAr (Ar = 2,6-di-Pr2C6H3) complexes as alternatives to adamantyl or t-butylidin complexes because sterically hindered NaAr complexes tend to be more stable toward bimolecular decomposition. The reaction between Mo(NAr)2(CH2CMe2Ph)2, 2,2'-bipyridine (bipy), and pentafluorophenol in diethyl ether shown in Scheme 1 is modeled after syntheses of adamantylidino and t-butylidin complexes. The reaction between 1, C6F5OH, 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)(HCMe2Ph)(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 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. Bipy/HCl combinations have been successful for the synthesis of W alkylidenes, but they generally have not been effective for the synthesis of Mo alkylidene complexes. The alkylidene ligand in 2 is in the syn orientation on the basis of the value for fC3 (125 Hz). The two pentafluorophenoxide 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)(HCMe2Ph)(bipy)Cl2 (3) in 90% yield as a mixture of two isomers. The reaction between 3, LiOHMT, and ZnCl2 then gave Mo(NAr)(HCMe2Ph)(OHMT)Cl (4) as a pentane-soluble intermediate that could be converted into Mo(NAr)(HCMe2Ph)(OHMT)(Cl)(t-BuCN) (4(t-BuCN)) in 46% yield, Mo(NAr)(HCMe2Ph)(OHMT)(Cl)(PPhMe2) (4(PPhMe2)) in 62% yield, or Mo(NAr)(HCMe2Ph)(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) with the neopentyldiene 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 that of Mo(NAr)(CHCM2Ph)(OHMT)(Br(py)) (τ = 0.21) and Mo(N-t-Bu)(CH-t-Bu)(OHIPT)(Cl)(3-Brpy) (τ = 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 nitride dissociates and an olefin coordinates to the metal in the same position to form a trigonal bipyramidal metallacylobutane complex, the imido and arylexilide ligands would be in apical positions in the intermediate.

Loss of the olefin product with minimal rearrangement of that metallacylobutane 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.  

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 (JCH ~125 Hz; see SI). Similarly, 1H NMR spectra of 4(PM2Ph) show a doublet alkylidene 1H resonance at 12.47 ppm (JHH = 5.3 Hz) and the 31P 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 1H NMR studies at a total metal concentration of ~0.01 M at room temperature. However, both 4(3-Brpy) and 4(PM2Ph) can be activated toward cross-metathesis through addition of B(C6F5)3 (vide infra), so some base must dissociate from the metal at room temperature in order eventually to be sequestered by B(C6F5)3.

The 1H NMR spectrum of 4(t-BuCN) is significantly different from spectra of 4(3-Brpy) and 4(PM2Ph). In toluene-d8 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 is 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 JCH 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 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 one equivalent of B(C6F5)3 is added to an NMR sample of Mo(NAr)(CHCM2Ph)(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 (JCH = 152 Hz) increases to 41% of the total and the less intense upfield resonance shifts to 11.71 ppm (JCH = 122 Hz) and sharpens (Figure 4b); 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 °C and 25 °C. The same mixture of syn-4 and anti-4 is generated upon addition of one equivalent of B(C6F5)3 to 4(PPhMe2). Finally, addition of one equivalent 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(PM2Ph), respectively, at the same concentration.

Addition of 6 equivalents 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 12 additional equivalents 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 ~0.01M 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 hours in Cd6 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-$d_6$. 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, 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=t-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).

Therefore, we prepared W=NR complexes in order to compare their catalytic activities with Mo compounds. Neophenyldiene MAC complexes were prepared from W(N-t-Bu)$_2$(CH$_3$;CMe$_2$Ph)$_2$ in a manner closely analogous to the preparation of Mo neophenyldiene 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).

**Addition of B(C$_5$F$_3$)$_3$ to 5(py)**

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; $J_{HH} = 15$ Hz).

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 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 Cl$_2$ 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 ($J_{JCH}$ measurement and heteronuclear bond correlation NMR experiments; see SI). Only one configuration of the vinylimidoo complex (vide infra) 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 (equation 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; 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 vinylimidoo complex. 1-Aza-titanacyclobut-4-enes have been prepared in reactions in which intermediate Cp$_2$Ti=C=CH$_2$ is trapped by nitriles, and one such complex has been structurally characterized.

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

Figure 4. The structure of W(N-t-Bu)(CHCMe$_2$Ph)(OHMT)(Cl)(MeCN). (Hydrogen atoms, except on C1, have been omitted for clarity. Ellipsoids are drawn at 30% probability.)

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 ($	au = 0.27^\circ$) 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.5,6

Synthesis of Mo(NC6F5) complexes

Mo-based pentafluorophenylimido MAP complexes have proven to be especially efficient for Z-selective and E-selective cross-metathesis 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(NC6F5) 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(NC6F5)(CHMe2Ph)(OHMT)(Cl)(PMe2Ph) (8a(PMe2Ph)) and Mo(NC6F5)(CHMe2Ph)(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 (r = 0.10) with the alkylidene (C1) in the apical position and the phosphate bond 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 monoaaryloxide 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 phosphine in solution. However, the phosphine can be removed from 8a(PMe2Ph) and 8b(PMe2Ph) with Ph3CB(C6F5) or B(C6F5)3 (in C6D6) 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 and 0.1M concentration and 1H NMR spectra of either 8a or 8b in C6D6 at a concentration of ~0.1 M show little change after 6 hours. We propose that removal of the phosphine is
successful because both Ph₃CB(C₆F₅)₂ or 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. Cyclooctene alternatively can be polymerized in the test reaction, but poly(COE) so formed can also be "de-polymerized". The normalized ratios of COE (A), poly(COE) (B), and CICH=CHCH₂CH=CHCl (C) were followed by ¹H NMR over a period of up to 24 h (C₆D₆, 22 °C, 3 mM initiator concentration). Relevant data are presented in Tables I-IV; the complete set of results can be found in the SI.

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\text{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 minutes or less; four more (runs 4, 7, 10, and 11) reached >98% in 6 hours. When a 1% loading was used (run 3) a lower yield of product was observed after 2 minutes 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-((t-Bu)₂C₆H₄)C₆H₅; 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 hours 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 six hours (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 hour. 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-Bryp and t-BuCN ligands in tungsten t-butyldimino complexes are not sufficiently labile to produce viable quantities of 14e MAC complexes. The combination of NC₆F₅ and ODFT (O-2,6-((t-Bu)₂C₆H₄)C₆H₅) ligands limits the lability of 3-Bryp in run 18 (Table 2).

Table 1. ROCM of A with DCE to give B and/or C

| Run/initiator | 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')(OHMT)(Cl)(MeCN) (1%) | 1/24/75 | 1/24/75 |
| 4 Mo(NR)(CHR')(OHMT)(Cl)(3-Bpy) | 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) | 0/0/99 | 0/5/95 |
| 7 Mo(NR)(CHR')(OTTBT)(Cl)(3-Bpy) | 66/33/1 | 2/57/41 |
| 8 Mo(NAd)(CHR')(OHIPT)(Cl)(MeCN) | 0/15/85 | 0/6/94 |
| 9 Mo(NR)(CHR)(OHMT)(Cl)(MeCN) | 0/6/94 | 0/5/95 |

Table 2. Attempted ROCM of A with DCE to give B and/or C

| Run/initiator | 1 h |
|--------------|-----|
| 12 Mo(NAr)(CHR')(OHMT)(Cl)(PMe₂Ph) | 100/0/0 |
| 13 Mo(NR)(CHR')(OHMT)(Cl)(1-Me-imad) | 100/0/0 |
| 14 Mo(NC₆F₅)(CHR')(OHMT)(Cl)(PPhMe2) | 100/0/0 |
| 15 Mo(NC₆F₅)(CHR')(OHMT)(Cl)(PPhMe2) | 100/0/0 |
| 16 Mo(NAr)(CHR')(OHMT)(Cl)(3-Bpy) | 99/1/0 |
| 17 Mo(NAd)(CHR')(OHMT)(Br)(py) | 17/83/0 |
| 18 Mo(NC₆F₅)(CHR')(ODFT)(Cl)(3-Bpy) | 89/11/0 |
| 19 W(NR)(CHR')(OHMT)(Cl)(3-Bpy) | 100/0/0 |
| 20 W(NR)(CHR)(OHMT)(Cl)(RCN) | 80/20/0 |

Table 3. ROCM of A with DCE to give B and/or C after addition of B(C₆F₅)₃ (+LA)

| Run/initiator | 30 min | 60 min |
|--------------|--------|--------|
| 21 Mo(NAr)(CHR')(OHMT)(Cl)(3-Bpy)+LA | 0/12/87 | 0/5/95 |
| 22 Mo(NR)(CHR')(OHMT)(Cl)(PMe₂Ph)+LA | 0/7/93 | 0/4/96 |
| 23 Mo(NC₆F₅)(CHR')(ODFT)(Cl)(3-Bpy)+LA | 0/64/36 | --- |
| 24 Mo(NC₆F₅)(CHR')(OHMT)(Cl)(PPhMe₂) | 0/0/100 | --- |
| 25 Mo(NC₆F₅)(CHR')(OHMT)(Cl)(PPhMe₂) +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-Bpy)+LA | 72/260 | 68/32/0 |
| 28 Mo(NR)(CHR')(OHMT)(Cl)(3-Bpy)+LA | 0/0/100 in 2 min | --- |
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 stereoselectivity of C. High field ¹H NMR spectra (500 MHz or more in CD₃Cl or CDCl₃) 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 ¹H 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 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(NC₅F₅)₂(CHR')(OHPT)(Cl)(PPhMe₂) in the presence of B(C₆F₅)₃ (run 19). The importance of the aryloxide to the level of stereoselectivity is manifested in the results for the analogous reaction involving Mo(NC₅F₅)₂(CHR')(OHPT)(Cl)(PPhMe₂) (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 OHPT 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.

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)(OHPT)(Cl)(MeCN) | 99.7 | 0.3 | –0 |
| 2 Mo(NR)(CHR)(OHPT)(Cl)(MeCN) | 99.5 | 0.5 | –0 |
| 19 Mo(NC₅F₅)(CHR)(OHPT)(Cl)(PPhMe₂) | 96.2 | 3.8 | –0 |
| 28 Mo(NR)(CHR)(OHPT)(Cl)(3-Bpy)+LA | 99.5 | 0.5 | –0 |
| 10 Mo(NAr)(CHR)(OHMT)(Cl)(RCN) | 61.3 | 34.6 | 4.1 |
| 20 Mo(NC₅F₅)(CHR)(OHMT)(Cl)(PPhMe₂) | 66.4 | 30.4 | 3.2 |
| 21 Mo(NAr)(CHR)(OHMT)(Cl)(3-Bpy)+LA | 63.3 | 33.3 | 3.4 |

An interesting question is how much faster are the test reactions with monochloro complexes versus those initiated by a pyrroliide complex. Mo(NAd)(CHCMe₂Ph)(OHMT)(Pyr) was found to be a relatively slow initiator, with no C being formed within the first 2 minutes (63:32/0) (%A:B:C), but 81% C was generated (0/19/81) after 1 hour with a Z,Z,Z,E,E,E ratio of 98.5:1.5 (GC analysis). In contrast, the composition of the product mixture in the case of Mo(NAd)(CHCMe₂Ph)(OHMT)(Cl)(MeCN) was 0:12:82 in 2 minutes and the selectivity is >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)(CHCMe₂Ph)(OHMT)(Cl)(MeCN) is the initiator compared to Mo(NAd)(CHCMe₂Ph)(OHMT)(Pyr) as the initiator. However, in spite of the >98% stereoselectivities for both reactions, we cannot conclude that Mo(NAd)(CHCMe₂Ph)(OHMT)(Cl) (formed in situ) is solely responsible for the activity of Mo(NAd)(CHCMe₂Ph)(OHMT)(Pyr).

We ascribe the high activities in the test reaction to circumstances in which a significant amount of base-free 14e alkylidene is present, i.e., either a Mo=CHCl or a Mo=CH(CH₂)₂CH=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)(CHCMe₂Ph)(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'(OAr)(X)(L) can be prepared in a process involving intermediates that contain pentafluorophenoxide and 2,2'-bipyridine. Addition of Me₂PHCHCl to Mo(NC₅F₅)(CH₂CMCH₂Ph) leads to Mo(NC₅F₅)(CHR')(PMe₂Ph)(Cl), from which Mo(NC₅F₅)(CHR')(OAr)(Cl)(PMe₂Ph) is prepared readily. When L is acetone or pivalonitrile rapid and reversible loss of nitride in solution affords a mixture enriched in the nitride-free 14e M(NC₅F₅)(CHR')(OAr)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-CICH=CH(CH₂)₂CH=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 alkylidene 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 vinylidime complex. Because Mo(NR)(CHX)OArX, 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, CH₂Cl₂, EtO, 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 H₂SO₄, followed by water and a saturated solution of aqueous NaHCO₃, and dried over CaCl₂ 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. ¹H NMR spectra were obtained on 400 or 500...
Mo(N-t-Bu)(CH-t-Bu)(bipy)Cl₂ (233 mg, 0.500 mmol, 1.00 equiv) was suspended in Et₂O (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 ZnCl₂ (68 mg, 0.500 mmol, 1.00 equiv) in THF (10 mL). After stirring at 22 °C for 4 h, the reaction mixture was filtered through Celite and concentrated to give 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 stirring 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 C₆₈H₆₀BrClMoN₁₂O₆: 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 MoC₆H₅Cl₂(2.52 mmol) was added to a −30 °C solution of W(N-t-Bu)(py)₂Cl₂ (1.0 g, 1.8 mmol) in 40 mL of Et₂O. After stirring 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). The yellow precipitate was collected and used directly in the following step.

W(N-t-Bu)₂(CH₂CMe₂Ph)₂ (500 mg, 0.84 mmol) was dissolved in Et₂O (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 was collected by filtration and used directly in the following step.

W(N-t-Bu)₂(CH₂CMe₂Ph)(py)Cl₂ (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 C₆₈H₆₀Cl₂OW: 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
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)(CHCMe₂Ph)(3-Brpy)Cl₂ (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 and subjected to vacuum twice to remove excess benzene to afford W(N-t-Bu)(CHCMe₂Ph)(OHMT)(Cl)(3-Brpy) (60 mg, 51% yield) as a yellow solid.

W(N-t-Bu)(CHCMe₂Ph)(OHMT)(Cl)(3-Brpy) has also been prepared from W(N-t-Bu)(CHCMe₂Ph)(OHMT)(Cl)(py). B(C₆F₅)(271 mg, 0.53 mmol) was added to a solution of W(N-t-Bu)(CHCMe₂Ph)(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 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. Calcld for C₆₄H₄₃BrClO₂: C, 65.78; H, 5.54; N, 3.08. Found: C, 56.44; H, 5.28; N, 2.85.

Attempted isolation of W(N-t-Bu)(CHCMe₂Ph)(OHMT)(Cl)(3-Brpy) from the mixture in pentane yielded colorless crystals of W(N-t-Bu)(CHCMe₂Ph)(OHMT)(Cl)(MeCN), an X-ray study of which was carried out as described above (see SI for details).

The resulting mixture was filtered through a pad of Celite on a glass frit. 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 EtO and pentane. The solid was collected by filtration to give the title compound (305 mg, 90%) as a yellow solid which was recrystallized from a mixture of EtO and pentane. Anal. Calcld for C₆₄H₄₃BrClO₂: C, 71.96; H, 7.32. The compound was then insoluble in DMSO, and repeated attempts to isolate pure material for satisfactory elemental analysis were unsuccessful.

Mo(NAr₂)(CHCMe₂Ph)(bipy)(OC₆F₅₂)

Mo(NAr₂)(CHCMe₂Ph)₂ (900 mg, 1.26 mmol) was dissolved in Et₂O (20 mL). The solution cooled to −25 °C in a freezer and treated with a pre-chilled solution of pentafluorophenol (1.16 g, 6.30 mmol) in Et₂O (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 EtO and pentane. The solid was collected by filtration to give Mo(NAr₂)(CHCMe₂Ph)(bipy)(OC₆F₅₂) (890 mg, 76%) as a yellow solid which was recrystallized from a mixture of EtO and pentane. Anal. Calcld for C₆₅H₄₃MoN₇O₂: C, 57.09; H, 4.03; N, 4.54. Found: C, 57.09; H, 4.00; N, 4.40.

Mo(NAr₂)(CHCMe₂Ph)(bipy)Cl₂

Mo(NAr₂)(CHCMe₂Ph)₂ (500 mg, 0.54 mmol) was dissolved in CH₂Cl₂ (5 mL) and treated with TMSCI (0.25 mL, 0.68 mmol). After 15 h the volatiles were removed in vacuo. Et₂O 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 ¹H NMR and repeat attempts to isolate pure material for satisfactory elemental analysis were unsuccessful.

Mo(NAr₂)(CHCMe₂Ph)(OHMT)(Cl)(t-BuCN)

Mo(NAr₂)(CHCMe₂Ph)(OC₆F₅₂)(bipy)Cl₂ (100 mg, 0.159 mmol) was suspended in Et₂O (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 ZnCl₂ (35.6 mg, 0.159 mmol) in THF (10 mL). After stirring at 22 °C for 40 h, the reaction mixture was filtered through Celite and the
The residue was dissolved in cold pentane (2 mL) and filtered through Celite. The resulting brown residue was dissolved in EtO (5 mL) and filtered through Celite. The resulting brown precipitate was washed with pentane (3 x 5 mL) and the remaining solid was extracted with pentane (5 mL) and filtered through Celite. The green solid was rinsed with cold pentane (1 mL); yield 89 mg (62% yield). Anal. Calcd for C56H38F25Mo: C, 66.69; H, 6.72; N, 1.05. Found: C, 65.68; H, 6.82; N, 1.05.

The title compound was prepared in 71% yield as an orange solid. The compound was described in Table 1 above as an orange solid. The compound was also described in Table 1 as an orange solid.

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REFERENCES

Supporting Information

ASSOCIATED CONTENT

AUTHOR INFORMATION

Notes

Corresponding Author

We refer the reader to the Supporting Information for complete details of the structure and composition of the title compound. The title compound was prepared in 71% yield as an orange solid. The compound was described in Table 1 above as an orange solid. The compound was also described in Table 1 as an orange solid.

Despite repeated attempts to purify the material, samples failed to give a complete analysis. The title compound was prepared in 71% yield as an orange solid. The compound was described in Table 1 above as an orange solid. The compound was also described in Table 1 as an orange solid.
(6) Nguyen, T. T.; Koh, M.-J.; Shen, X.; Romiti, F.; Schrock, R. R.; Hoveyda, A. H. *Science* 2016, 352, 569-575.
(7) Koh, M. J.; Nguyen, T. T.; Lam, J.; Torker, S.; Hyvl, J.; Schrock, R. R.; Hoveyda, A. H., submitted for publication.
(8) Addison, A. W.; Rao, T. N.; Van Rijn, J. J.; Veschoor, G. C. J. *Chem. Soc. Dalton Trans.* 1984, 1349-1356.
(9) Gerber, L. C. H.; Schrock, R. R.; Müller, P.; Takase, M. K. *J. Am. Chem. Soc.* 2011, 133, 18142-18144.
(10) Peryshkov, D. V.; Schrock, R. R.; Takase, M. K.; Müller, P.; Hoveyda, A. H. *J. Am. Chem. Soc.* 2011, 133, 20754-20757.
(11) Jeong, H.; Schrock, R. R.; Müller, P. *Organometallics* 2015, 34, 4408-4418.
(12) (a) Schrock, R. R. in Braterman, P. R., Ed. *Reactions of Coordinated Ligands*, Plenum: New York, 1986, p. 221. (b) Schrock, R. R. *Chem. Rev.* 2002, 102, 145-180. (c) Schrock, R. R.; Hoveyda, A. H. *Angew. Chem. Int. Ed.* 2003, 42, 4592-4633.
(13) (a) Schrock, R. R. *Angew. Chem. Int. Ed.* 2006, 45, 3748-3759. (b) Schrock, R. R.; Czekelius, C. C. *Adv. Syn. Catal.* 2007, 349, 55-77. (c) Schrock, R. R. *Adv. Syn. Catal.* 2007, 349, 41-53.
(14) (a) Bell, A. F.; Clegg, W.; Dyer, P. W.; Elsegood, M. R. J.; Gibson, V. C.; Marshall, E. L. *J. Chem. Soc., Chem. Commun.* 1994, 2547-2548. (b) Jeong, H.; Kozer, D. J.; Schrock, R. R.; Smith, S. J.; Zhang, J.; Ren, N.; Hillmyer, M. A. *Organometallics* 2013, 32, 4843-4850.
(15) H. Jeong, Ph.D Thesis, Massachusetts Institute of Technology, Cambridge, Massachusetts, 2015.
(16) Lichtscheidl, A. G.; Ng, V. W. L.; Müller, P.; Takase, M. K.; Schrock, R. R.; Malcolmson, S. J.; Meek, S. J.; Li, B.; Kiesewetter, E. T.; Hoveyda, A. H. *Organometallics* 2012, 31, 4558-4570.
(17) Jeong, H.; Axtell, J.; Török, B.; Schrock, R. R.; Müller, P. *Organometallics* 2012, 31, 6522-6525.
(18) Oskam, J. H.; Schrock, R. R. *J. Am. Chem. Soc.* 1993, 115, 11831-11845.
(19) (a) Schrock, R. R.; Fellmann, J. D. *J. Am. Chem. Soc.* 1978, 100, 3359-3370. (b) Wood, C. D.; McLain, S. J.; Schrock, R. R. *J. Am. Chem. Soc.* 1979, 101, 3210-3222.
(20) Beckhaus, R.; Strauss, I.; Wagner, T.; *Angew. Chem. Int. Ed. Engl.* 1995, 34, 688.
(21) (a) Yuan, J.; Schrock, R. R.; Müller, P.; Axtell, J. C.; Dobereiner, G. E. *Organometallics* 2012, 31, 4650-4653. (b) Yuan, J.; Schrock, R. R.; Gerber, L. C.; Müller, P.; Smith, S. *Organometallics* 2013, 32, 2983-2992.
(22) Hock, A. S.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* 2006, 128, 16373-16375.
(23) Flook, M. M.; Ng, V. W. L.; Schrock, R. R. *J. Am. Chem. Soc.* 2011, 133, 1784-1786.
ClCl (CH2)4 ClCl
5 mol% (0.003 M)
C6D6, 22 °C
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