Synthesis of High-Oxidation-State Mo=CHX Complexes, Where X = Cl, CF₃, Phosphonium, CN

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S *Supporting Information*

ABSTRACT: Reactions between (Z)-XCH=CHX, where X = Cl, CF₃, CN, and Mo(N-t-Bu)(CH-t-Bu)(OHIPT)Cl(PPh₂Me) (OHIPT = O-2,6-(2,4,6-i-Pr₃C₆H₂)₂C₆H₃) produce Mo(N-t-Bu)(CHX)(OHIPT)Cl(PPh₂Me) complexes. Addition of 2,2′-bipyridyl (Bipy) yields Mo(N-t-Bu)(CHX)(OHIPT)Cl(Bipy) complexes, which could be isolated and structurally characterized. The reaction between Mo(N-t-Bu)(CH-t-Bu)(OHMT)Cl(PPh₂Me) (OHMT = O-2,6-(2,4,6-Me₃C₆H₂)₂C₆H₃) and (Z)-ClCH=CHCl in the presence of Bipy produces a mixture that contains both Mo(N-t-Bu)(CHCl)(OHMT)Cl(PPh₂Me) and Mo(N-t-Bu)(CHCl)(OHMT)Cl(Bipy), but the relatively insoluble product that crystallizes from toluene-d₈ is the phosphoniomethylidene complex [Mo(N-t-Bu)(CHPPh₂Me)(OHMT)Cl(Bipy)]Cl. The Mo(N-t-Bu)(CHX)(OHIPT)Cl(PPh₂Me) complexes (X = Cl, CF₃) were confirmed to initiate the stereoselective cross-metathesis between (Z)-5-decene and (Z)-XCH=CHX.
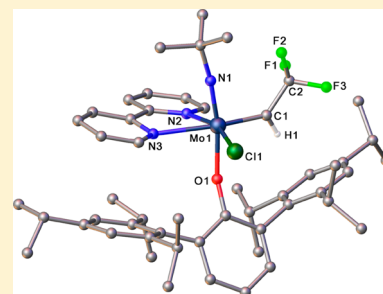
Monoaryloxide monochloride molybdenum based metathesis initiators of the type Mo(NR)(CHR′)(OAr)Cl(L) (where OAr is a sterically demanding 2,6-terphenoxide[1] and L a 2e donor ligand) have been found to promote stereoselective (E or Z) metathesis reactions between "ordinary" olefins and ClCH=CHCl, BrCH=CHF, or (CF₃)CH=CH(CF₃).[2] Vinyl halides are desirable cross-partners in cross-metathesis reactions because alkenyl halide (X = Cl, Br) products subsequently can be used in other catalytic reactions.[2e] Ruthenium-catalyzed cross-metathesis reactions that use vinyl chlorides (CH₂=CHCl, ClCH=CHCl (E or Z), or (E)-MeCH=CHCl) or fluorides have been the subject of several investigations periodically since 2000.[3] Although alkenyl halide products have been observed, the reactions are not stereoselective and turnovers are limited, in part due to the formation of ruthenium carbide complexes.[4] The preparation and isolation of Mo=CHX complexes are keys to understanding the stabilities and reactivities of Mo=CHX complexes versus Mo=CHR complexes in cross-metathesis reactions, where R is a carbon-based group or H. To our knowledge no Mo=CHX intermediate in a cross-metathesis reaction that involves XCH=CHX (e.g., X = Cl, CF₃) has been observed. We have now found a way to prepare Mo=CHCl, Mo=CHCF₃, and Mo=CHCN complexes and have structurally characterized 2,2′-bipyridine adducts thereof.

Recently we found that the most successful Mo(N-t-Bu)(CH-t-Bu)(OAr)Cl(PPh₂Me) initiators in the test reaction shown in eq 1 (**DCDD** = 1,10-dichloro-1,9-decadiene) are those in which OAr is OHMT (in **1a**) or OHIPT (in **1b**).[5] The reason is that the large OAr ligand encourages dissociation of PPh₂Me, which is required to access the catalytically active 14e Mo(N-t-Bu)(CH-t-Bu)(OAr)Cl core. A low degree of dissociation of phosphine is
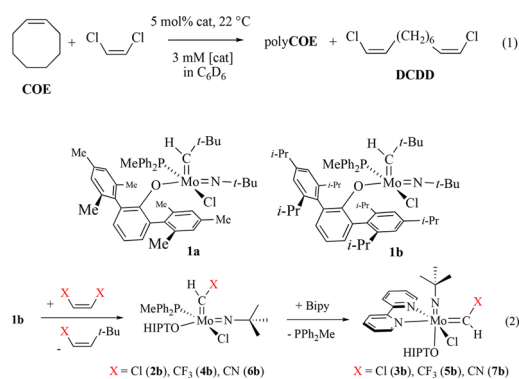
therefore likely to be the reason complexes in which OAr = O-2,3,5,6-tetraphenylphenoxide (OTPP) are relatively inactive. We also found that although PPh₂Me is *fully* dissociated when OAr = hexa-*tert*-butylterphenoxide (OHTBT),[6] the 14e Mo(N-t-Bu)(CH-t-Bu)(OHTBT)Cl core is simply too crowded to react readily with either cyclooctene or (Z)-ClCH=CHCl. Therefore, we felt that reactions of **1a,b** with (Z)-ClCH=CHCl could provide the opportunity to observe and isolate Mo=CHCl complexes.

Compound **1b** reacts in seconds with several equivalents of (Z)-ClCH=CHCl ((Z)-DCE) in C₆D₆ or toluene-d₈ at 22 °C to give (Z)-ClCH=CH-t-Bu and what we propose is Mo(N-t-Bu)(CHCl)(OHIPT)Cl(PPh₂Me) (**2b**; eq 2). Its alkylidene proton resonance is a doublet at 9.56 ppm in C₆D₆ with J_{HP} = 5.3

$$\text{COE} + \text{Cl}\diagup\diagdown\text{Cl} \xrightarrow[\text{3 mM [cat] in C}_6\text{D}_6]{\text{5 mol\% cat, 22 °C}} \text{polyCOE} + \text{Cl}\diagup(\text{CH}_2)_6\diagdown\text{Cl} \quad (1)$$

X = Cl (**2b**), CF₃ (**4b**), CN (**6b**)   X = Cl (**3b**), CF₃ (**5b**), CN (**7b**)   (2)

Hz and J_{CH} = 156 Hz. A ^{1}H−^{13}C HSQC NMR experiment located the alkylidene C_α resonance at 267.7 ppm. The high solubility of **2b** prevented its crystallization; therefore, Bipy was added to give Mo(N-*t*-Bu)(CHCl)(OHIPT)Cl(Bipy) (**3b**; eq 2), whose alkylidene resonance is observed at 10.19 ppm in toluene-d_8 (J_{CH} = 155 Hz). Removal of solvent *in vacuo* and trituration of the residue allowed pure **3b** to be isolated and recrystallized.

An X-ray structural study (Figure 1) showed **3b** to contain a *syn* alkylidene (Cl2 points toward the imido ligand) with the Bipy
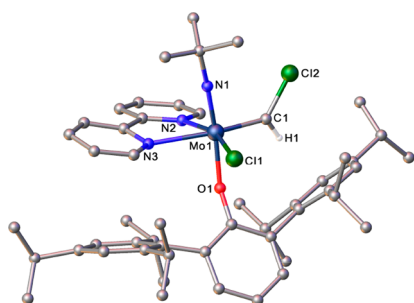

Figure 1. Molecular structure of Mo(N-*t*-Bu)(CHCl)(OHIPT)Cl-(Bipy) (**3b**). All hydrogen atoms (except on C1), lattice solvent, and disordered atoms have been omitted for clarity.

ligand coordinated *trans* to the alkylidene and chloride ligands. The alkylidene proton was located in the difference Fourier map (Mo1−C1−H1 = 120(2)°). The Mo1−C1−Cl2 angle (128.92(18)°) and the Mo=C1 distance (1.944 Å) are not unusual for high-oxidation-state Mo *syn* alkylidene complexes (see the Supporting Information).[7] The value for J_{CH} (154 Hz) in **2b** is high in comparison to a J_{CH} value expected for a *syn* Mo=CHR analogue when R is a carbon-based group (115−130 Hz), but J_{CH} values in vinyl halides are inherently high.[8] The structure of Mo(N-*t*-Bu)(CHCl)(OHIPT)Cl(PPh$_2$Me) (**2b**; eq 2) is proposed to be analogous to that of Mo(N-*t*-Bu)(CH-*t*-Bu)(OHMT)Cl(PPh$_2$Me) (**1a**),[5] a square pyramid (τ_5 = 0.24)[9] with the alkylidene in the apical position and the N-*t*-Bu and OHMT ligands *trans* to one another.

The rate of the reaction between **1a** and (*Z*)-ClCH=CHCl in toluene-d_8 at 22 °C is slow in comparison to the rate of the reaction between **1b** and (*Z*)-ClCH=CHCl because PPh$_2$Me is not dissociated in the OHMT complex (**1a**) to as great an extent as it is in **1b**. When the reaction mixture was heated to 50 °C for 2 h, a doublet alkylidene resonance that we ascribe to Mo(N-*t*-Bu)(CHCl)(OHMT)Cl(PPh$_2$Me) (**2a**) appeared at 11.08 ppm along with (*Z*)-ClCH=CH-*t*-Bu olefinic proton resonances. Addition of Bipy to **2a** and heating the sample to 50 °C led to formation of what we propose is Mo(N-*t*-Bu)(CHCl)(OHMT)-Cl(Bipy) (**3a**), which has an alkylidene resonance at 10.5 ppm. Continued heating leads to deposition of crystals on the walls of the NMR tube as the intensity of the alkylidene resonance for **3a** decreases. The isolated crystals (**4a**) were found to exhibit a doublet alkylidene proton resonance at 12.81 ppm with J_{HP} = 4.1 Hz (in CD$_2$Cl$_2$).

An X-ray structural study of **4a** (Figure 2) showed it to be the "phosphoniomethylidene" derivative [Mo(N-*t*-Bu)-(CHPPh$_2$Me)(OHMT)Cl(Bipy)]Cl. Phosphoniomethylidene complexes were first prepared by employing anions of phosphorus ylides.[10] Sundermeyer has also reported several examples (e.g., for Nb, Ta, W, and Re),[11] but phosphoniomethylidene complexes perhaps are best known for Ru complexes of
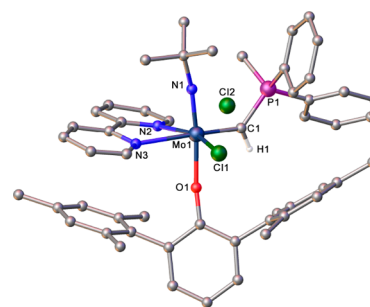

Figure 2. Molecular structure of [Mo(N-*t*-Bu)(CHPPh$_2$Me)(OHMT)-Cl(Bipy)]Cl (**4a**). All hydrogen atoms (except on C1) and lattice solvent have been omitted for clarity.

the type that are active for olefin metathesis.[12] They usually are formed in a reaction between an intermediate, and sometimes observable, Ru=CHCl complex and a phosphine originally present on the metal.

Metathesis reactions have been reported that use (*Z*)-(CF$_3$)CH=CH(CF$_3$) ((*Z*)-HFB) as a cross-metathesis partner and Mo(N-*t*-Bu)(CH-*t*-Bu)(OHIPT)Cl(MeCN) as the initiator (from which MeCN readily dissociates).[2d] The reaction between **1b** and 5 equiv of (*Z*)-HFB in C$_6$D$_6$ at 22 °C generates (*Z*)-(*t*-Bu)CH=CH(CF$_3$) and what we propose is Mo(N-*t*-Bu)-(CHCF$_3$)(OHIPT)Cl(PPh$_2$Me) (**4b**). The reaction at 22 °C requires approximately 36 h to proceed to completion (at a concentration of 0.057 M for **1b**). The alkylidene proton resonance in **4b** in C$_6$D$_6$ is found at 9.66 ppm as a broad and relatively featureless multiplet that spans 200 Hz as a consequence of coupling of the alkylidene proton to both ^{31}P and ^{19}F. A broad-band decoupled ^{1}H{^{31}P} NMR spectrum reveals the expected quartet multiplicity for the alkylidene proton with a $^3J_{HF}$ coupling constant of 12.6 Hz. The ^{19}F NMR spectrum in C$_6$D$_6$ shows a doublet centered at −54.3 ppm ($^3J_{HF}$ = 10.1 Hz) for (*Z*)-(*t*-Bu)CH=CH(CF$_3$) and a broad multiplet at −55.2 ppm for the CF$_3$ group in **4b**. Addition of Bipy to a C$_6$D$_6$ solution of **4b** gave Mo(N-*t*-Bu)(CHCF$_3$)(OHIPT)Cl(Bipy) (**5b**) readily, as evidenced by the appearance of a quartet resonance at 11.29 ppm ($^3J_{HF}$ = 16.1 Hz) in C$_6$D$_6$ for the alkylidene proton. The corresponding ^{19}F resonance for the CF$_3$ group in **5b** is found as a doublet at −53.6 ppm in C$_6$D$_6$ ($^3J_{HF}$ = 16.2 Hz). An analogous reaction between Mo(N-*t*-Bu)(CH-*t*-Bu)(OHMT)-Cl(PPh$_2$Me) (**1a**) and (*Z*)-HFB is too slow to yield Mo(N-*t*-Bu)(CHCF$_3$)(OHMT)Cl(PPh$_2$Me) and the first metathesis product, (*Z*)-(*t*-Bu)CH=CH(CF$_3$), in any significant yield.

An X-ray study of **5b** (Figure 3) showed the structure to be similar to the others described here. The alkylidene proton was located in the difference Fourier map and refined semifreely (Mo1−C1−Hl = 118.1(15)°). The Mo1−C1−C2 angle (133.77(17)°) is relatively normal for high-oxidation-state Mo *syn* alkylidene complexes, as is the Mo=C1 distance (1.948(2) Å; see the Supporting Information).

Metathesis of cyano-substituted olefins (acrylonitrile) with molybdenum catalysts was first explored by Crowe,[13] who used Mo(N-2,6-*i*-Pr$_2$C$_6$H$_3$)(CHCMe$_2$Ph)[OC(CF$_3$)$_2$Me]$_2$ as the initiator. Others periodically have explored similar metathesis reactions, mostly with ruthenium complexes.[14] These reports, and the successful reactions between **1b** and (*Z*)-ClCH=CHCl or (*Z*)-(CF$_3$)CH=CH(CF$_3$) just described, encouraged us to try to the reaction between **1b** and (*Z*)-(CN)CH=CH(CN). Compound **1b** reacts with 2 equiv of (*Z*)-(CN)CH=CH(CN) in C$_6$D$_6$ at a concentration of 0.041 M (for **1b**) at 22 °C to give

Figure 3. Molecular structure of Mo(N-*t*-Bu)(CHCF$_3$)(OHIPT)Cl-(Bipy) (**5b**). All hydrogen atoms (except on C1), lattice solvent, and disordered atoms have been omitted for clarity.

Mo(N-*t*-Bu)(CHCN)(OHIPT)Cl(PPh$_2$Me) (6b). The doublet alkylidene proton resonance for **6b** in C$_6$D$_6$ is centered at 8.73 ppm ($^3J_{HP}$ = 7.4 Hz; J_{CH} = 154 Hz). In a one-bond ^{1}H–^{13}C correlation (HSQC) NMR experiment the C$_\alpha$ resonance was found to be at 231.1 ppm. Addition of Bipy to a solution of **6b** gave Mo(N-*t*-Bu)(CHCN)(OHIPT)Cl(Bipy) (**7b**) in a slow reaction that required several hours. In situ NMR monitoring shows the formation of two singlets at 10.73 ppm (25%) and 10.33 ppm (75%) for **7b**, which we ascribe to two isomers. The major isomer of **7b** with the resonance at 10.33 ppm in C$_6$D$_6$ is obtained selectively upon recrystallization of the mixture. The low solubility of **7b** and depletion of the minor isomer upon recrystallization of **7b** has prevented identification of the minor isomer.

Crystals of **7b** suitable for an X-ray study were grown upon addition of 1 equiv of Bipy to a benzene solution of **6b** which was left to stand without stirring. The X-ray structural study (Figure 4) showed that **7b** is analogous to **3b** and **5b**, with the Bipy ligand
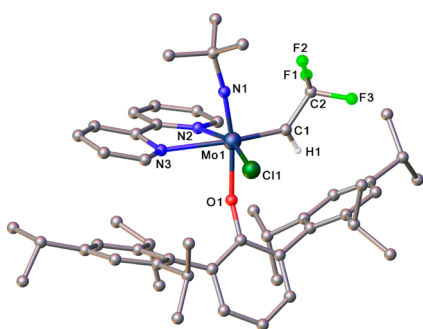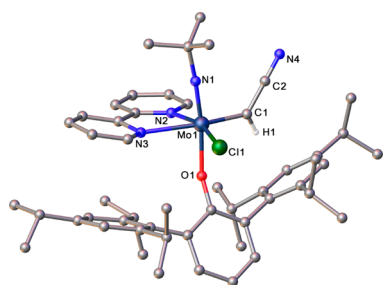

Figure 4. Molecular structure of Mo(N-*t*-Bu)(CH(CN))(OHIPT)Cl-(Bipy) (**7b**). All hydrogen atoms (except on C1), lattice solvent, and disordered atoms have been omitted for clarity.

coordinated *trans* to the alkylidene and the chloride ligands. The *tert*-butyl imido and OHIPT ligands occupy the apical positions. The alkylidene proton was located in the difference Fourier map and refined semifreely (Mo1−C1−Hl = 115.7(16)°). The Mo1−C1−C2 angle (129.21(18)°) is relatively normal for high-oxidation-state Mo *syn* alkylidene complexes, as is the Mo=C1 distance (1.961(2) Å), which parallel the distances and angles found in **3b** and **5b** (see the Supporting Information).

Cross-metathesis reactions between (*Z*)-5-decene and either (*Z*)-DCE or (*Z*)-HFB catalyzed by complexes comparable to either **1a** or **1b** have been reported;[2] these reactions require formation of Mo=CHX (where X = Cl, CF$_3$) intermediates and their reaction with the cross partner. We have confirmed that **2b** and **4b** are viable intermediates in reactions between (*Z*)-5-

decene (**A**) and a slight excess of XCH=CHX (X = Cl, CF$_3$; eq 3) and that the selectivity for formation of the *Z* metathesis products ((*Z*)-**B**) approaches 100%. The results are shown in Table 1.
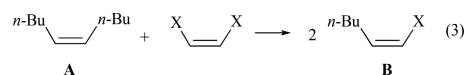
$$n\text{-Bu}\diagup\diagdown n\text{-Bu} \; + \; X\diagup\diagdown X \longrightarrow 2 \; n\text{-Bu}\diagup\diagdown X \quad (3)$$

A   **B**

Table 1. Results of Reactions between 2b and 4b with (Z)-5-Decene and (Z)-XCH=CHX in C$_6$D$_6$ (X = Cl, CF$_3$)

amt of **A** (equiv)	X	*T* (°C)	% conversn to **B**	% *Z* of **B** (120 min)
3	Cl	22	66[a]	>99[b]
10	CF$_3$	50	82	>99[c]

[a]Addition of 2 equiv of (*Z*)-DCE generates >99% of the expected **B**. [b]Determined by GC. [c]Determined by ^{19}F NMR spectroscopy.

The cross-metathesis reaction between (*Z*)-5-decene and (*Z*)-DCE catalyzed by **2b** proceeds efficiently at 22 °C to generate (*Z*)-1-chlorohexene, but >1 equiv of (*Z*)-DCE (relative to (*Z*)-5-decene) is required for a high conversion to **B**. The concentration of **2b** (monitored by integrating the alkylidene resonance at 9.56 ppm) remains approximately constant throughout the course of the reaction. The rate of reaction begins to slow as (*Z*)-DCE is consumed and accelerates upon addition of more (*Z*)-DCE. The cross-metathesis experiment between (*Z*)-5-decene and (*Z*)-HFB initiated by **4b** proceeds relatively efficiently only at 50 °C. Although PPh$_2$Me in **4b** is exchanging rapidly (as evidenced by the broad alkylidene resonance at 9.66 ppm), the reaction between **4b** and (*Z*)-5-decene is relatively slow.

Thus far, attempts to promote the cross-metathesis reaction shown in eq 3 through addition of 1 equiv of B(C$_6$F$_5$)$_3$ to **2b** followed by the addition of the olefinic partners have failed. Addition of 1 equiv of B(C$_6$F$_5$)$_3$ to **2b** in the absence of olefin leads to apparent catalyst decomposition (according to proton NMR spectra).

To our knowledge the Bipy derivatives of the Mo=CHCl, Mo=CHCF$_3$, and Mo=CHCN complexes (**3b**, **5b**, and **7b**, respectively) are the only structurally characterized monomeric examples of each type of Mo=CHX complex in the literature. Phosphoniomethylidene complexes are relatively well known, especially for ruthenium, as noted earlier. Two Ru=CHF complexes have been isolated and structurally characterized,[3a,e] but they are relatively unreactive toward unstrained olefins. An attempt to prepare a high-oxidation-state W=CHCN complex led to a catalytically inactive tetramer, {W(NAr)(CHCN)[OC-(CF$_3$)$_2$Me]$_2$}$_4$, and a tetrameric complex in which acetonitrile has inserted twice into the W=C bond to give a diazatung-stanacyclohexadiene complex.[15] Addition of CH$_2$=CHX (e.g., X = B(pin), PPh$_2$, O-*n*-Pr, SPh, inter alia) to Mo(NAr)(CHR)-(Me$_2$Pyr)(OTPP) (Ar = 2,6-*i*-Pr$_2$C$_6$H$_3$, R = H, CHCMe$_2$Ph, Me$_2$Pyr = 2,5-dimethylpyrrolide, OTPP = O-2,3,5,6-Ph$_4$C$_6$H) complexes led to Mo(NAr)(CHX)(Me$_2$Pyr)(OTPP) complexes,[16] but attempts to prepare Mo=CHCl complexes in this manner failed.

We look forward to exploring the synthesis and reactions of the complexes reported here in more detail as well as preparing and exploring those that contain other electron-withdrawing groups in the alkylidene.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00168.

> Full experimental details, including NMR data and spectra for new compounds, and X-ray crystal structure data (PDF)
>
> Cartesian coordinates for the calculated structures (XYZ)

Accession Codes

CCDC 1831517−1831520 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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(8) ^{1}H NMR (C_6D_6; 500 MHz; 22 °C): (Z)-DCE, 5.52 ppm ($^1J_{CH}$ = 198.2 Hz); (Z)-HFB, 4.95 ppm ($^1J_{CH}$ = 172.0 Hz); (Z)-maleonitrile, 4.12 Hz ($^1J_{CH}$ = 182.8 Hz).

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