Published in final edited form as:

Organometallics. 2018 June 11; 37(11): 1641–1644. doi:10.1021/acs.organomet.8b00168.

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

Sudarsan VenkatRamami[‡], Richard R. Schrock^{†,*}, Amir Hoveyda[†], Peter Müller[‡], and Charlene Tsay[‡]

[‡]Department of Chemistry 6-331, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

[†]Department of Chemistry, Merkert Chemistry Center, Boston College, Chestnut Hill, Massachusetts 02467

Abstract

Reactions between $Z\text{-XCH=CHX}$ where X = Cl, CF₃, or 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 $Z\text{-ClCH=CHCl}$ 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-*d*₈ 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 or CF₃) were confirmed to initiate the stereoselective cross-metathesis between Z -5-decene and $Z\text{-XCH=CHX}$.

Monoaryloxide monochloride molybdenum-based metathesis initiators of the type Mo(NR)(CHR')(OAr)Cl(L) (where OAr is a sterically demanding 2,6-terphenoxide¹ 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 or 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 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

*Corresponding Author: rrs@mit.edu.

Supporting Information

The following Supporting Information is available free of charge on the ACS Publications website: (i) Full experimental details including NMR data and spectra for new compounds; (ii) X-ray crystallographic files for four complexes.

The authors declare no competing financial interests.

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 or 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 equation 1 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 to 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 why complexes in which OAr = O-2,3,5,6-tetraphenylphenoxide are relatively inactive. We also found that although PPh₂Me is *fully* dissociated when OAr = hexa-*t*-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** and **1b** with *Z*-ClCH=CHCl could provide the opportunity to observe and isolate Mo=CHCl complexes.

(1)

(2)

Compound **1b** reacts in seconds with several equivalents of *Z*-ClCH=CHCl (*Z*-DCE) in C₆D₆ or toluene-*d*₈ at 22 °C to give *Z*-ClCH=CH-*t*-Bu and what we propose is Mo(N-*t*-Bu)(CHCl)(OHIPT)Cl(PPh₂Me) (**2b**). Its alkylidene proton resonance is a doublet at 9.56 ppm in C₆D₆ with *J*_{HP} = 5.3 Hz and *J*_{CH} = 156 Hz. A ¹H-¹³C HSQC NMR experiment locates the alkylidene C_α resonance at 267.7 ppm. The high solubility of **2b** prevented its crystallization, so Bipy was added to give Mo(N-*t*-Bu)(CHCl)(OHIPT)Cl(Bipy) (**3b**), 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 (Cl points toward the imido ligand) with the Bipy 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-Cl angle (128.92(18)°) and the Mo=C1 distance (1.944 Å) are not unusual for high oxidation state Mo *syn* alkylidene complexes (see SI).⁷ The value for J_{CH} (154 Hz) in **2b** is high compared to a J_{CH} expected for a *syn* Mo=CHR analog 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(PPh₂Me) (**2b**, eq 2) is proposed to be analogous to that of Mo(N-*t*-Bu)(CH-*t*-Bu)(OHMT)Cl(PPh₂Me),⁵ a square pyramid (τ = 0.24)⁹ with the alkylidene in the apical position and the N-*t*-Bu and OHMT ligands *trans* to one another.

The reaction between **1a** and *Z*-ClCH=CHCl in toluene-*d*₈ at 22 °C is sluggish compared to the rate of the reaction between **1b** and *Z*-ClCH=CHCl because PPh₂Me is not dissociated in the OHMT complex to as great an extent in **1a** as it is in **1b**. Upon heating the reaction mixture to 50 °C for 2 h a doublet alkylidene resonance that we ascribe to Mo(N-*t*-Bu)(CHCl)(OHMT)Cl(PPh₂Me) (**2a**) appears 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** declines. The isolated crystals (**4a**) were found to exhibit a doublet alkylidene proton resonance at 12.81 ppm with J_{HP} = 4.1 Hz (in CD₂Cl₂).

An X-ray structural study (Figure 2) of **4a** showed it to be the “phosphoniomethylidene” derivative, [Mo(N-*t*-Bu)(CHPPh₂Me)(OHMT)Cl(Bipy)]Cl. Phosphoniomethylidene complexes were first prepared employing anions of phosphorus ylides.¹⁰ Sundermeyer has also published several examples (e.g., for Nb, Ta, W, and Re),¹¹ but phosphoniomethylidene complexes perhaps are best known for Ru complexes of 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*-(CF₃)CH=CH(CF₃) (*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).^{2f} The reaction between **1b** and five equivalents of *Z*-HFB in C₆D₆ at 22 °C generates *Z*-(*t*-Bu)CH=CH(CF₃) and what we propose is Mo(N-*t*-Bu)(CHCF₃)(OHIPT)Cl(PPh₂Me) (**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 C₆D₆ is found at 9.66 ppm as a broad and relatively featureless multiplet that spans 200 Hz (0.4 ppm) as a consequence of coupling of the alkylidene proton to both P and F. A broadband decoupled ¹H{³¹P} NMR spectrum reveals the expected quartet multiplicity for the alkylidene proton with a ³ J_{HF} coupling constant of approximately 12.6 Hz. The ¹⁹F NMR spectrum in C₆D₆ shows a doublet centered at –54.3 ppm (³ J_{HF} = 10.1

Hz) for $Z-(t\text{-Bu})\text{CH}=\text{CH}(\text{CF}_3)$ and a broad multiplet at -55.2 ppm for the CF_3 group in **4b**. Addition of Bipy to the C_6D_6 solution of $\text{Mo}(\text{N}-t\text{-Bu})(\text{CHCF}_3)(\text{OHIPT})\text{Cl}(\text{PPh}_2\text{Me})$ gave $\text{Mo}(\text{N}-t\text{-Bu})(\text{CHCF}_3)(\text{OHIPT})\text{Cl}(\text{Bipy})$ (**5b**) readily, as evidenced by the appearance of a quartet resonance at 11.29 ppm ($^3J_{\text{HF}} = 16.1$ Hz) in C_6D_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_6D_6 ($^3J_{\text{HF}} = 16.2$ Hz). An analogous reaction between $\text{Mo}(\text{N}-t\text{-Bu})(\text{CH}-t\text{-Bu})(\text{OHMT})\text{Cl}(\text{PPh}_2\text{Me})$ and $Z\text{-HFB}$ is too slow to yield an analogous $\text{Mo}(\text{N}-t\text{-Bu})(\text{CHCF}_3)(\text{OHMT})\text{Cl}(\text{PPh}_2\text{Me})$ complex and first metathesis product, $Z-(t\text{-Bu})\text{CH}=\text{CH}(\text{CF}_3)$, in any significant yield.

An X-ray structural study of **5b** (Figure 3) showed it to be analogous to the other structures described here. The alkylidene proton was located in the difference Fourier map and refined semi-freely ($\text{Mo1-C1-H1} = 118.1(15)^\circ$). The Mo1-C1-C2 angle ($133.77(17)^\circ$) is relatively normal for high oxidation state Mo *syn* alkylidene complexes, as is the $\text{Mo}=\text{C1}$ distance ($1.948(2)$ Å; see SI).

Metathesis of cyano-substituted olefins (acrylonitrile) with molybdenum catalysts was first explored by Crowe,¹³ who used $\text{Mo}(\text{N}-2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)(\text{CHCMe}_2\text{Ph})[\text{OC}(\text{CF}_3)_2\text{Me}]_2$ as the initiator. Others have periodically explored similar metathesis reactions, mostly with ruthenium complexes.¹⁴ These reports, and the successful reactions between **1b** and $Z\text{-ClCH}=\text{CHCl}$ or $Z\text{-(CF}_3\text{)CH}=\text{CH}(\text{CF}_3)$ just described, encouraged us to try the reaction between **1b** and $Z\text{-(CN)CH}=\text{CH}(\text{CN})$. Compound **1b** reacts with two equivalents of $Z\text{-(CN)CH}=\text{CH}(\text{CN})$ in C_6D_6 at a concentration of 0.041 M (for **1b**) at 22°C to give $\text{Mo}(\text{N}-t\text{-Bu})(\text{CHCN})(\text{OHIPT})\text{Cl}(\text{PPh}_2\text{Me})$ (**6b**). The doublet alkylidene proton resonance for **6b** in C_6D_6 is centered at 8.73 ppm ($^3J_{\text{HP}} = 7.4$ Hz; $J_{\text{CH}} = 154$ Hz). In a one bond $^1\text{H}-^{13}\text{C}$ correlation (HSQC) NMR experiment the C_α resonance was found to be at 231.1 ppm. Addition of Bipy to the solution of **6b** gave $\text{Mo}(\text{N}-t\text{-Bu})(\text{CHCN})(\text{OHIPT})\text{Cl}(\text{Bipy})$ (**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 alkylidene of **7b** with the resonance at 10.33 ppm in C_6D_6 is obtained selectively upon recrystallization of the mixture.

Crystals of **7b** suitable for an X-ray study were grown upon addition of one equivalent of Bipy in 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 coordinated *trans* to the alkylidene and the chloride ligands. The *t*-butyl imido and the HIPTO ligands occupy the apical positions. The alkylidene proton was located in the difference Fourier map and refined semi-freely ($\text{Mo1-C1-H1} = 115.7(16)^\circ$). The Mo1-C1-C2 angle ($129.21(18)^\circ$) is relatively normal for high oxidation state Mo *syn* alkylidene complexes, as is the $\text{Mo}=\text{C1}$ distance ($1.961(2)$ Å); all are similar to analogous distances and angles found in **3b** and **5b** (see SI).

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

between *Z*-5-decene and a slight excess of $XCH=CHX$ ($X = Cl$ or CF_3 ; eq 3) and that the selectivity for formation of the *Z* metathesis products approaches 100%. The results are shown in Table 1.

(3)

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_2Me in **4b** is rapidly exchanging (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 equation 1 through addition of one equiv of $B(C_6F_5)_3$ to **2b** followed by the addition of the olefinic partners have failed. Addition of one equiv of $B(C_6F_5)_3$ 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 $Mo=CHCl$, $Mo=CHCF_3$, $Mo=CHCN$, and $Mo=CHPPh_2Me$ complexes reported here are the only structurally-characterized examples for molybdenum. 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, $\{W(NAr)(CHCN)[OC(CF_3)_2Me]_2\}_4$ and a tetrameric complex in which acetonitrile has inserted twice into the $W=C$ bond to give a diazatungstanacyclohexadiene complex.¹⁵ Addition of $CH_2=CHX$ (e.g., $X = B(pin)$, PPh_2 , $O-n-Pr$, and SPh , *inter alia*) to $Mo(NAr)(CHR)(Me_2Pyr)(OTPP)$ ($Ar = 2,6-i-Pr_2C_6H_3$, $R = H$ or $CHCMe_2Ph$, $Me_2Pyr = 2,5$ -dimethylpyrrolide, $OTPP = O-2,3,5,6-Ph_4C_6H$) complexes led to $Mo(NAr)(CHX)(Me_2Pyr)(OTPP)$ complexes,¹⁶ but attempts to prepare $Mo=CHCl$ complexes in this manner failed. We could find no examples in the literature of structurally characterized $M=CHCF_3$ or $M=CHCl$ complexes.

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.

ACKNOWLEDGMENT

We are grateful for financial support from the National Institutes of Health (GM-59426) and from the National Science Foundation (CHE-1463707).

REFERENCES

- (1). (a) "A One-Pot Synthesis of *m*-Terphenyls via a Two-Aryne Sequence" Du CJF; Hart H; Ng KKD *J. Org. Chem* 1986, 51, 3162–3165. (b) "Isolation and X-ray crystal structure of a monomeric, σ -bonded aryllithium etherate complex $[\text{Li}(\text{Et}_2\text{O})_2\text{-2,4,6-Ph}_3\text{C}_6\text{H}_2]$ " Power PP; Olmstead MM *J. Organometal. Chem* 1991, 408, 1–6. (c) "New terphenylphenoxides of group 13 and 14 elements" Stanciu C; Richards AF; Stender M; Olmstead MM; Power PP *Polyhedron* 2006, 25, 477–483.
- (2). (a) "Direct Synthesis of *Z*-Alkenyl Halides by Catalytic Cross-Metathesis" Koh M-J; Nguyen TT; Zhang H; Schrock RR; Hoveyda AH *Nature* 2016, 531, 459–465. [PubMed: 27008965] (b) "Kinetically *E*-selective Catalytic Olefin Metathesis" Nguyen TT; Koh M-J; Shen X; Romiti F; Schrock RR; Hoveyda AH *Science* 2016, 352, 569–575. [PubMed: 27126041] (c) "Synthesis and Evaluation of Molybdenum and Tungsten Monoaryloxide Halide Alkylidene Complexes for *Z*-Selective Cross Metathesis of Cyclooctene and *Z*-1,2-Dichloroethylene" Lam JK; Zhu C; Bukhryakov KV; Schrock RR; Müller PM; Hoveyda AH *J. Am. Chem. Soc* 2016, 138, 15774–15783. [PubMed: 27934034] (d) "Molybdenum Chloride Complexes as Catalysts for Stereoselective Olefin Metathesis" Koh MJ; Nguyen TT; Lam J; Torker S; Hyvl J; Schrock RR; Hoveyda AH *Nature* 2017, 542, 80–85. [PubMed: 28114300] (e) "Synthesis of *E*- and *Z*-trisubstituted alkenes by catalytic cross-metathesis" Nguyen TT; Koh MJ; Mann TY; Schrock RR; Hoveyda AH *Nature* 2017, 552, 347–354. [PubMed: 29293209]
- (3). (a) "Cross-Metathesis of Vinyl Halides. Scope and Limitations of Ruthenium-Based Catalysts" Macnaughtan ML; Gary JB; Gerlach DL; Johnson MJA; Kampf JW *Organometallics* 2009, 28, 2880–2887. (b) "Olefin Metathesis Reactions with Vinyl Halides: Formation, Observation, Interception, and Fate of the Ruthenium-Monohalomethylidene Moiety" Macnaughtan ML; Johnson MJA; Kampf JW *J. Am. Chem. Soc* 2007, 129, 7708–7709. [PubMed: 17542588] (c) "Olefin cross-metathesis with vinyl halides" Sashuk V; Samojlowicz C; Szadkowska A; Grela K *Chem. Commun* 2008, 2468–2470. (d) "Synthesis of Functionalized Olefins by Cross and Ring-Closing Metatheses" Chatterjee AK; Morgan JP; Scholl M; Grubbs RH *J. Am. Chem. Soc* 2000, 122, 3783–3784. (e) "Synthesis, Structure, and Olefin Metathesis Activity of Two Ruthenium Monofluoromethylidene Complexes" Macnaughtan ML; Johnson MJA; Kampf JW *Organometallics* 2007, 26, 780–782. (f) "Olefin Metathesis with 1,1-Difluoroethylene" Trnka TM; Day MW; Grubbs RH *Angew. Chem., Int. Ed* 2001, 40, 3441–3443. (g) "Improved reactivity in the conversion of nitrile-functionalized olefins by metathesis" Vancompernelle T; Vignona P; Trivelli X; Mortreux A; Gauvin RM *Cat. Comm* 2016, 77, 75–78.
- (4). (a) "The Metathesis-Facilitated Synthesis of Terminal Ruthenium Carbide Complexes: A Unique Carbon Atom Transfer Reaction" Carlson RG; Gile MA; Heppert JA; Mason MH; Powell DR; Van der Velde D; Vilain JM *J. Am. Chem. Soc* 2002, 124, 1580–1581. [PubMed: 11853424] (b) "Two Generalizable Routes to Terminal Carbido Complexes" Caskey SR; Stewart MH; Kivela JE; Sootsman JR; Johnson MJA; Kampf JW *J. Am. Chem. Soc* 2005, 127, 16750–16751. [PubMed: 16316197]
- (5). "Syntheses of Molybdenum Adamantylimido and *t*-Butylimido Alkylidene Chloride Complexes Using HCl and Diphenylmethylphosphine" Bukhryakov KV; VenkatRamani S; Tsay C; Hoveyda AH; Schrock RR *Organometallics* 2017, 36, 4208–4214.
- (6). "Synthesis of 2,6-Hexatertiarybutylterphenyl Derivatives, 2,6-(2,4,6-*t*-Bu₃C₆H₂)₂C₆H₃X, where X = I, Li, OH, SH, N₃, or NH₂" Bukhryakov KV; Schrock RR; Hoveyda AH; Müller P; Becker J *Org. Lett* 2017, 19, 2607–2609. [PubMed: 28459588]
- (7). (a) "High Oxidation State Multiple Metal-Carbon Bonds" Schrock RR *Chem. Rev* 2002, 102, 145–180. [PubMed: 11782131] (b) "High Oxidation State Molybdenum and Tungsten Complexes Relevant to Olefin Metathesis" Schrock RR *Handbook of Metathesis*, Vol 1, 2nd Ed., Wiley-VCH, Weinheim, Grubbs RH and Wenzel AG, Ed., 2015, pp. 1–32.
- (8). ¹H NMR (C₆D₆; 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).
- (9). "Synthesis, Structure, and Spectroscopic Properties of Copper(II) Compounds containing Nitrogen-Sulphur Donor Ligands; the Crystal and Molecular Structure of Aqua[1,7-bis(N-methylbenzimidazol-2'-yl)-2,6-dithiaheptane]copper(ii) Perchlorate" Addison AW; Rao TN; Van Rijn J; Veschoor GC; Reedijk J J. *Chem. Soc., Dalton Trans* 1984, 1349–1356.

- (10). (a) "The Coordination Chemistry of Ylides" Kaska WC *Coord. Chem. Rev* 1983, 48, 1–58. (b) "Organoactinoid chemistry with phosphoylids" Gilge JW; Cramer RE; Bruck MA; Higa KT; Panchantheswaran K *Inorg. Chim. Acta* 1985, 110, 139–143.
- (11). (a) "Heavily π -Bond-Loaded Tungsten Phosphonio-Alkylidyne Complexes via a Domino Transylidation Cascade at (Organoimido)tungsten Tetrachlorides" Li X; Schopf M; Stephan J; Harms K; Sundermeyer J *Organometallics* 2002, 21, 2356–2358. (b) "Synthesis of the First Stable 2-Chromaaxetane and its Homologues via α -Phosphonio(methylidene) Complexes of Hexavalent Chromium, Molybdenum, and Tungsten" Sundermeyer J; Weber K; Pritzkow H *Angew. Chem. Int. Ed. Engl* 1993, 32, 731. (c) " $(\alpha$ -Triphenylphosphonio)methylidene Imido Complexes of Molybdenum, Tungsten and Rhenium: the First Complexes Exhibiting Metal-Ligand Multiple-bonding with Two Carbon as well as Two Nitrogen Centres" Sundermeyer J; Weber K; Nürnberg O J. Chem. Soc., Chem. Commun 1992, 1631–1633. (d) "Phosphorus Ylide as a Precursor for the Formation of New High-Valent Tantalum Phosphonio Methylidyne Complexes" Li X; Wang A; Wang L; Sun H; Harms K; Sundermeyer J *Organometallics* 2007, 26, 1411–1413. (e) "Higher-valent derivatives of the d-metal acids: XII. α -Phosphonio(methylidene) complexes of niobium and tantalum containing the metallocene-like $[(\eta^5\text{-C}_5\text{R}_5)\text{M}(\text{N}^t\text{Bu})]$ core" Schmidt S; Sundermeyer J; Möller F J. *Organometal. Chem* 1994, 475, 157–166.
- (12). (a) "Rapidly Initiating Ruthenium Olefin-Metathesis Catalysts" Romero PE; Piers WE; McDonald R *Angew. Chem., Int. Ed* 2004, 43, 6161–6165. (b) "Generation and Spectroscopic Characterization of Ruthenacyclobutane and Ruthenium Olefin Carbene Intermediates Relevant to Ring Closing Metathesis Catalysis" van der Eide EF; Romero PE; Piers WE; McDonald R J. Am. Chem. Soc 2008, 130, 4485–4491. [PubMed: 18321104] (c) "Thermal Decomposition Modes for Four-Coordinate Ruthenium Phosphonium Alkylidene Olefin Metathesis Catalysts" Leitao EM; Dubberley SR; Piers WE; Wu Q; McDonald R *Chemistry* 2008, 14, 11565–11572. [PubMed: 19035588] (d) "Mechanistic Studies on 14-Electron Ruthenacyclobutanes: Degenerate Exchange with Free Ethylene" Romero PE; Piers WE J. Am. Chem. Soc 2007, 129, 1698–1704. [PubMed: 17243686] (e) "Synthesis, characterization and olefin metathesis studies of a family of ruthenium phosphonium alkylidene complexes" Dubberley SR; Romero PE; Piers WE; McDonald R; Parvez M *Inorg. Chim. Acta* 2006, 359, 2658–2664. (f) "Direct Observation of a 14-Electron Ruthenacyclobutane Relevant to Olefin Metathesis" Romero PE; Piers WE J. Am. Chem. Soc 2005, 127, 5032–5033. [PubMed: 15810833] (g) "Kinetic and Thermodynamic Analysis of Processes Relevant to Initiation of Olefin Metathesis by Ruthenium Phosphonium Alkylidene Catalysts" Leitao EM; van der Eide EF; Romero PE; Piers WE; McDonald R J. Am. Chem. Soc 2010, 132, 2784–2794. [PubMed: 20136131] (h) "A thermally robust ruthenium phosphonium alkylidene catalyst — the effect of more bulky N-heterocyclic carbene ligands on catalyst performance in olefin metathesis reactions" Leitao EM; Piers WE; Parvez M *Can. J. Chem* 2013, 91, 935–942. (i) "Photogeneration of a Phosphonium Alkylidene Olefin Metathesis Catalyst" Khalimon AY; Leitao EM; Piers WE *Organometallics* 2012, 31, 5634–5637. (j) "Ruthenium Metallacycles Derived from 14-Electron Complexes. New Insights into Olefin Metathesis Intermediates" Wenzel AG; Grubbs RH J. Am. Chem. Soc 2006, 128, 16048–16049. [PubMed: 17165753] (k) "Synthesis, structure and catalytic study of chloro-bridged two-core ruthenium carbene complexes" Qiao W; Shao M; Wang J J. *Organometal. Chem* 2012, 713, 197–202.
- (13). "Acrylonitrile Cross-Metathesis: Coaxing Olefin Metathesis Reactivity from a Reluctant Substrate" Crowe WE; Goldberg DR J. Am. Chem. Soc 1995, 117, 5162–5163.
- (14). (a) "A Practical and Highly Active Ruthenium-Based Catalyst that Effects the Cross-Metathesis of Acrylonitrile" Love JA; Morgan JP; Trnka TM; Grubbs RH *Angew. Chem. Int. Ed* 2002, 41, 4035–4037. (b) "Cross metathesis of bio-sourced fatty nitriles with acrylonitrile" Bidange J; Fischmeister C; Bruneau C; Dubois J-L; Couturier J-L *Monats. Chemie* 2015, 146, 1107–1113. (c) "A green route to nitrogen-containing groups: the acrylonitrile cross-metathesis and applications to plant oil derivatives" Miao X; Dixneuf PH; Fischmeister C; Bruneau C *Green Chem* 2011, 13, 2258–2271. (d) "Highly active phosphine-free carbene ruthenium catalyst for cross-metathesis of acrylonitrile with functionalized olefins" Bai C-X; Zhang W-Z; He R; Lu X-B; Zhang Z-Q *Tetrahedron Letters* 2005, 46, 7225–7228. (e) "Highly selective cross metathesis with acrylonitrile using a phosphine free Ru-complex" Randl S; Bessler S; Wakamatsu H; Blechert S *Synlett* 2001, 3, 430–432. (f) "Nitro-Substituted Hoveyda-Grubbs Ruthenium Carbenes: Enhancement of Catalyst Activity through Electronic Activation" Michrowska AB;

Bujok R; Harutyunyan S; Sashuk V; Dolgonos G; Grela K J. Am. Chem. Soc 2004, 126, 9318–9325. [PubMed: 15281822] (g)“Tandem Catalytic Acrylonitrile Cross–Metathesis and Hydrogenation of Nitriles with Ruthenium Catalysts: Direct Access to Linear α,ω -Aminoesters from Renewables” Miao X; Fischmeister C; Bruneau C; Dixneuf PH; Dubois J-L; Couturier J-L Chem Sus Chem 2012, 5, 1410–1414.(h)“Renewable materials as precursors of linear nitrile-acid derivatives *via* cross-metathesis of fatty esters and acids with acrylonitrile and fumaronitrile” Malacea R; Fischmeister C; Bruneau C; Dubois J-L; Couturier J-L; Dixneuf PH Green Chem 2009, 11, 152–155.(i)“Improved reactivity in the conversion of nitrile-functionalized olefins by metathesis” Vancompernelle T; Vignon P; Trivelli X; Mortreux A; Gauvin RM Catal Comm 2016, 77, 75–78.(j)“Effective and Inexpensive Acrylonitrile Cross-Metathesis: Utilisation of Grubbs II Precatalyst in the Presence of Copper(I) Chloride” Rivard M; Blechert S Eur. J. Org. Chem 2003, 2225–2228.(k)“Alkene metathesis: the search for better catalysts” Deshmukh PH; Blechert S Dalton Trans 2007, 2479–2491. [PubMed: 17563782] (l)“Ruthenium–alkylidene catalysed cross-metathesis of fatty acid derivatives with acrylonitrile and methyl acrylate: a key step toward long-chain bifunctional and amino acid compounds” Miao X; Malacea R; Fischmeister C; Bruneau C Dixneuf PH Green Chem 2011, 13, 2911–2919.(m)“A Highly Efficient Ruthenium Catalyst for Metathesis Reactions” Grela K; Harutyunyan S; Michrowska AB Angew. Chem 2002, 114, 4210–4212.

(15). “Structure and reactivity studies of the first tungsten cyanoalkylidene complex” Cameron TM; Gamble AS; Abboud KA; Boncella JM Chem. Commun 2002, 1148–1149.

(16). “Synthesis of High Oxidation State Molybdenum Imido Heteroatom-Substituted Alkylidene Complexes” Townsend EM; Kilyanek SM; Schrock RR; Müller P; Smith SJ; Hoveyda AH Organometallics 2013, 32, 4612–4617. [PubMed: 24082360]

Figure 1. Molecular structure of $\text{Mo}(\text{N-}t\text{-Bu})(\text{CHCl})(\text{OH IPT})\text{Cl}(\text{Bipy})$. All hydrogen atoms (except on C1), lattice solvent, and disordered atoms have been omitted for clarity.

Figure 2. Molecular structure of [Mo(N-*t*-Bu)(CHPh₂Me)(OHMT)Cl(Bipy)]Cl. All hydrogen atoms (except on C1) and lattice solvent have been omitted for clarity.

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

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

Table 1.

Results of reactions between **2b** and **4b** with *Z*-5-Decene and *Z*-XCH=CHX in C₆D₆ (X = Cl or CF₃).

Equiv of A	X	T (°C)	% Conv to B (120 min)	% Z of B
3	Cl	22	66 ^a	>99 ^b
10 ^c	CF ₃	50	82	>99 ^c

^a Addition of two equiv of *Z*-DCE generates >99% of the expected **B**.

^b Determined by GC.

^c Determined by ¹⁹F NMR spectroscopy.