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Synthesis of High Oxidation State Molybdenum Imido Heteroatom-Substituted Alkylidene Complexes

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Abstract

Reactions between Mo(NAr)(CHR)(Me₂Pyr)-(OTPP) (Ar = 2,6-*i*-Pr₂C₆H₃, R = H or CHCMe₂Ph, Me₂Pyr = 2,5-dimethylpyrrolide, OTPP = O-2,3,5,6-Ph₄C₆H) and CH₂=CHX where X = B(pin), SiMe₃, *N*-carbazolyl, *N*-pyrrolidinonyl, PPh₂, OPr, or SPh lead to Mo(NAr)(CHX)-(Me₂Pyr)(OTPP) complexes in good yield. All have been characterized through X-ray studies (as an acetonitrile adduct in the case of X = PPh₂). The efficiencies of metathesis reactions initiated by Mo(NAr)(CHX)(Me₂Pyr)(OTPP) complexes can be rationalized on the basis of steric factors; electronic differences imposed as a consequence of X being bound to the alkylidene carbon do not seem to play a major role. Side reactions that promote catalyst decomposition do not appear to be a serious limitation for Mo=CHX species.

INTRODUCTION

The vast majority of high oxidation state imido alkylidene complexes of Mo and W contain CHX alkylidenes in which X is carbon-based, or rarely, X = H.¹ A few M=CHX complexes are known in which X is based on Si¹ or Ge.^{1,2} However, to our knowledge none has been described in which X is based on a heteroatom (e.g., B, N, O, S, P, halide, etc.). The only report of M=CHX derivatives among high oxidation state alkylidene complexes concerns Re derivatives of the type Re(C-*t*-Bu)(CHX)[OCMe(CF₃)₂](THF)₂ where X is OR, SR, or pyrrolidinone.³ In contrast, several Ru=CHX derivatives have been described in which X is based on O, S, or N and for which selected reactions with olefins have been explored.^{4a} Also, several Ru-catalyzed metatheses involving enol ethers have been published.^{4b-c} As olefin metathesis investigations evolve to include CH₂=CHX derivatives where X is not carbon-based (for example, *Z*-selective cross-metathesis reactions where X = OR⁵ or B(pinacolate)⁶), it becomes more important to establish what Mo and W M=CHX complexes can be prepared and how they react with ordinary olefins. Studies of high oxidation state M=CHX compounds also would help clarify to what extent the electronic structure and reactivity of the Mo=C bond are influenced by the presence of a heteroatom substituent.

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Supporting Information. General experimental details, NMR data for **1b** and **2a-2g**, crystal parameters, data acquisition parameters, kinetic analyses, computational details, cif files, and a thermal ellipsoid drawing of **2b**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

RESULTS AND DISCUSSION

We targeted $\text{Mo}(\text{NAr})(\text{CHX})(\text{Me}_2\text{Pyr})(\text{OTPP})$ complexes ($\text{Ar} = 2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3$, $\text{Me}_2\text{Pyr} = 2,5\text{-dimethylpyrrolide}$, $\text{OTPP} = \text{O-}2,3,5,6\text{-Ph}_4\text{C}_6\text{H}$), in part because monoalkoxide pyrrolide (MAP) complexes have produced new and interesting results in the last several years, especially *Z*-selective reactions,^{5,6,7} and because the OTTP ligand lowers the solubility and therefore facilitates isolation of what can otherwise be highly soluble MAP compounds. (An improved synthesis of 2,3,5,6-tetraphenylphenol (HOTPP) is described in the Supporting Information.)

In order to increase the simplicity of a reaction between a Mo alkylidene complex and $\text{CH}_2=\text{CHX}$ (eq 1), we prepared $\text{Mo}(\text{NAr})(\text{CH}_2)(\text{Me}_2\text{Pyr})(\text{OTPP})$ (**1b**) in 79% yield, the Mo analog of the tungsten complex, $\text{W}(\text{NAr})(\text{CH})(\text{Me}_2\text{Pyr})(\text{OTPP})$,^{1c} by treating $\text{Mo}(\text{NAr})(\text{CHCMe}_2\text{Ph})(\text{Me}_2\text{Pyr})(\text{OTPP})$ ⁹ (**1a**) with

(1)

ethylene. The proton NMR spectrum of **1b** in C_6D_6 contains the methyldene proton resonances at 11.77 and 11.58 ppm ($J_{\text{HH}} = 5$ Hz).

Both **1a** and **1b** react cleanly with $\text{CH}_2=\text{CHB}(\text{pin})$ to give $\text{Mo}(\text{NAr})[\text{CHB}(\text{pin})](\text{Me}_2\text{Pyr})(\text{OTPP})$ (**2a**), which is obtained as an orange solid in 83% yield. An X-ray study of **2a** (Figure 1) reveals that it contains an *anti* alkylidene ligand (i.e., the B(pin) substituent points away from the imido ligand) with a $\text{Mo}=\text{C}$ bond length of 1.8825(1) Å and a $\text{Mo}=\text{C}-\text{B}$ bond angle of 106.19(7)° (Table 1). These values should be compared with those for $\text{Mo}(\text{NAr})(\text{CHCMe}_2\text{Ph})(\text{Me}_2\text{Pyr})(\text{OTPP})$ (**1a**, Table 1).⁶ NBO calculations reveal that the empty p orbital on B is conjugated with the $\text{Mo}=\text{C}$ orbital (Figure 2), but the contribution from the B orbital (99% p) is only 3.7% of the $\text{Mo}=\text{C}$ Natural Localized Molecular Orbital (NLMO). There is no evidence from either the NBO calculations or the $\text{Mo1}\cdots\text{O2}$ distance (2.837 Å) that there is any significant electronic interaction between Mo1 and O2. A few structurally characterized 16e *anti* alkylidene complexes (i.e., five-coordinate intramolecular or intermolecular adducts) of this general type are known in which the $\text{M}-\text{C}-\text{C}$ angle is 135–150°.^{1,10}

The proton NMR spectrum of **2a** (Figure 3) at 20 °C reveals broad alkylidene proton resonances characteristic of interconverting *syn* and *anti* isomers. Variable-temperature NMR studies (Figure 3) show one alkylidene resonance at high temperature and deconvolution and sharpening of two resonances at low temperature. Modeling the temperature dependence yields values of $H^\ddagger = 8.7(3)$ kcal/mol and $S^\ddagger = 0.02$ kcal/mol K; at 298 K the rate of interconversion is 28 s⁻¹. Therefore, both *syn* and *anti* isomers are accessible on a sub-second time scale in **2a** (at 298 K) and have approximately the same energies. The relatively high rate of alkylidene rotation is consistent with a $\text{Mo}(+)\text{-C}=\text{B}(-)$

resonance form, although the π component of the Mo=C bond is only *slightly* decreased according to NBO calculations (*vide supra*).

The reaction between **1b** and $\text{CH}_2=\text{CHSiMe}_3$ yields $\text{Mo}(\text{NAr})(\text{CHSiMe}_3)(\text{Me}_2\text{Pyr})(\text{OTPP})$ (**2b**) as an orange solid in 47% yield. Compound **2b** is a single (*syn*) isomer in the solid state (see Table 1 and SI) and in solution (^1H NMR in C_6D_6). *Syn* and *anti* isomers of $\text{Mo}(\text{NAr})(\text{CHSiMe}_3)(\text{OAr})_2$ and $\text{W}(\text{NAr})(\text{CHSiMe}_3)(\text{OAr})_2$ have been observed in solution¹¹ and have been shown to interconvert readily at room temperature with a relatively low barrier (not quantified).¹² Since the amount of *anti* **2b** in solution is small, we cannot know whether *syn* and *anti* isomers of **2b** also interconvert readily.

The reaction between **1b** and $\text{CH}_2=\text{CH}(\text{Carbaz})$ (Carbaz = *N*-carbazolyl) yields $\text{Mo}(\text{NAr})[\text{CH}(\text{Carbaz})](\text{Me}_2\text{Pyr})(\text{OTPP})$ (**2c**) as an orange solid in 81% yield. Compound **2c** is a single *syn* isomer in the solid state (see Table 1) and in solution ($J_{\text{CH}} = 134$ Hz; ^1H NMR in C_6D_6). The structure of **2c** (Figure 4) is consistent with previously characterized MAP complexes.

The reaction between **1b** and $\text{CH}_2=\text{CH}(\text{Pyrrol})$ (Pyrrol = *N*-pyrrolidinonyl) yields $\text{Mo}(\text{NAr})[\text{CH}(\text{Pyrrol})](\text{Me}_2\text{Pyr})(\text{OTPP})$ (**2d**) as a pink solid in 81% yield. Compound **2d** is approximately a trigonal bipyramid ($\tau = 0.70$)¹³ in which the carbonyl group is coordinated to the metal in an apical position (Figure 5). The alkylidene is *anti* with $J_{\text{CH}} = 166$ Hz; this configuration is expected on the basis of similar structures being observed for Re ($J_{\text{CH}} = 173$ Hz)³ and Ru⁴ complexes. The Mo=C bond distance in **2d** is longer than Mo=C bond distances in Table 1, probably as a consequence of the *anti* orientation of the alkylidene along with the fact that **2d** is five-coordinate. However, C=N multiple bond character (and a consequent increase in the Mo=C bond length) is also suggested through NBO calculations.

The reaction between **1b** and $\text{CH}_2=\text{CHPh}_2$ yields $\text{Mo}(\text{NAr})(\text{CHPh}_2)(\text{Me}_2\text{Pyr})(\text{OTPP})$ (**2e**) as a red solid in 63% yield. Crystals were isolated as an orange acetonitrile adduct of **2e** (**2e'**) in 79% yield. The X-ray crystal structure of **2e'** is shown in Figure 6. Compound **2e'** is approximately a square pyramid ($\tau = 0.20$) with a *syn* orientation of the alkylidene in the apical position and an acetonitrile coordinated in a basal position *trans* to the pyrrolide. The Mo=C distance and Mo=C—P angle are normal and the phosphorus is essentially pyramidal. NBO calculations reveal little to no contribution of the phosphorus lone pair to the Mo=C bond, which is reasonable considering that the phosphine lone pair is predominantly of s character and the reduced capacity of heavier main group elements to form multiple bonds to carbon.¹⁴ In solution, **2e** is a mixture of *syn* and *anti* isomers, as judged from its temperature-dependent proton NMR spectrum (Figure 7). The constant for coupling of the alkylidene proton to phosphorus in **2e** (the upfield resonance with $J_{\text{CH}} = 130$ Hz) is essentially zero, but approximately 5 Hz in the *anti* analog of **2e** (the downfield doublet). Small (including zero) $^2J_{\text{HP}}$ values in general are not unusual.¹⁵

The ^1H NMR spectrum of **2e'** (in toluene- d_8 or C_6D_6 ; Figure 8) at 20 °C is virtually the same as the corresponding ^1H NMR spectrum of **2e** (Figure 7), consistent with acetonitrile not being bound strongly to the metal in solution at room temperature under these conditions. The temperature-dependent NMR spectrum of **2e'** in the presence of ~1.5 additional equivalents of MeCN (2.5 total MeCN per Mo) reveals similar coalescence behavior upon heating as the spectrum of **2e**. Upon cooling the sample, however, it appears that acetonitrile binds weakly to the *syn* isomer, as judged by a strong downfield shift of the *syn* alkylidene resonance at low temperatures (Figure 8). In contrast, the alkylidene proton of *anti* isomer is relatively unaffected at low temperatures (Figure 8 *versus* Figure 7). We attribute lack of binding of acetonitrile to the *anti* isomer to donation of the phosphorus

electron pair to the π^* component of the Mo=N bond in *anti*-**2e**, which is the orbital that receives electron density in an agostic CH $\cdots$ interaction in a typical *syn* alkylidene isomer.¹⁶

The reaction between **1a** or **1b** and CH₂=CHOPr yields Mo(NAr)(CHOPr)(Me₂Pyr)(OTPP) (**2f**) as an orange solid in 51% isolated yield. Its proton NMR spectrum at 22 °C shows a single alkylidene resonance with $J_{\text{CH}} = 140$ Hz, which should be compared with $J_{\text{CH}} = 135$ Hz for the *syn* isomer of Re(C-t-Bu)(CHOEt)[OCMe(CF₃)₂](THF)₂ and 163 Hz for the *anti* isomer of Re(C-t-Bu)(CHOEt)[OCMe(CF₃)₂](THF)₂ in solution.³ An X-ray study confirms that **2f** is a *syn* isomer in the solid state (Figure 9) with a Mo=C1 bond that is slightly elongated and a C1-O bond that is shortened (1.343(4) Å) compared to the C2-O bond length of 1.435(5) Å. NBO calculations reveal that the O lone pair donates electron density into the Mo=C π^* orbital (Figure 10). The NLMO of the lone pair contains a 7.0% contribution from the alkylidene carbon and a 3.4% contribution from Mo (98% d character).

The reaction between **1a** or **1b** and CH₂=CHSPh yields Mo(NAr)(CHSPh)(Me₂Pyr)(OTPP) (**2g**), which can be isolated as a red solid in 68% yield. Its proton NMR spectrum at 22 °C shows a single alkylidene resonance with $J_{\text{CH}} = 146$ Hz. An X-ray study shows that **2g** is the *syn* isomer in the solid state (Figure 11) with a Mo=C1 bond that is slightly elongated (1.9112(15) Å), a C1-S bond (1.7179(16) Å) that is shorter than the C2-S bond (1.7803(16) Å), and a C2-S-C2 bond angle of 105.99(8)°. The NLMO of the S lone pair contains a 5.1% contribution from the alkylidene carbon and a 4.7% contribution from Mo (98% d character).

In order to probe the competency of complexes **2a-2g** as initiators for olefin metathesis reactions compared to **1a**, the conversion of 1-octene to *E/Z* 7-tetradecene by 5 mol% catalyst in C₆D₆ in a closed system (J-Young NMR tube) was monitored over time. The results are shown in Table 2. All reactions reach equilibrium (~50% *E/Z* 7-tetradecene) in 0.5 h except the one involving **2d**. The slow initiation by **2d** is no surprise, given the relatively strong binding of the pyrrolidinone carbonyl group to the metal. Conversion is limited by equilibria that involve ethylene under the conditions employed.

In Table 3 are shown the relative amounts of the initial M=CHX complex and the heptylidene complex formed from it in the reactions between **1a** and **2a-2g** and 20 equivalents of 1-octene. All except **2b**, **2d**, and **2g** form some observable and relatively constant amount of heptylidene (Mo=CHR) over a period of 10 h. Because **2b** and **2g** still carry out metathesis homocoupling rapidly (Table 2), we ascribe the lack of observable heptylidene to a thermodynamic preference for the Mo=CHX species in each case. In the case of **2d**, the slow rate of homocoupling (*vide supra*) also suggests that the rate of initiation is slow.

Table 4 lists the total amount of alkylidene remaining in reactions between Mo=CHX complexes and 1-octene in C₆D₆ at 22 °C versus an internal standard as a function of time. All except **2d**, which is essentially inert, have decomposed to a significant degree after 24 h. In most cases decomposition is likely to involve bimolecular coupling of alkylidenes (especially methylidenes) or rearrangement of metallacyclobutane complexes, including unsubstituted metallacycles.¹⁷

In order to investigate the relative reactivity of the heteroatom-substituted alkylidene complexes toward internal olefins, compounds **1a** and **2a-2g** were treated with 15 equivalents of *cis*-4-octene in C₆D₆ and the disappearance of Mo=CHX was monitored over time by ¹H NMR *versus* an internal standard. Complexes **1a**, **2b**, **2c**, **2d**, **2e**, and **2g** showed

little to no conversion, even after 2 days. In contrast, **2a** and **2f** were rapidly converted to butylidene in a pseudo-first-order fashion.

(2)

A kinetic study of the rate of conversion to butylidene (equation 2) yielded first-order rate constants of $9.9 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$ for **2a** and $1.2 \times 10^{-3} \text{ M}$ for **2f** (See SI for details). Compound **2f** reacts with *cis*-4-octene about ten times faster than **2a** reacts with *cis*-4-octene, perhaps largely because the CHOPr ligand in **2f** is much smaller than the CHB(pin) ligand in **2a** near the metal. The relative rates of reaction of the *syn* or the *anti* isomers of **2a** are not known. Of the remaining unreactive species, **1a**, **2c**, and **2e** contain alkylidenes that are relatively sterically demanding. Finally, **2b**, **2d**, and **2g** show a strong preference to remain as Mo=CHX forms in the presence of terminal olefins (see Table 3), so the same should be true in the presence of an internal olefin.

CONCLUSIONS

Molybdenum and tungsten imido M=CHX complexes in which X is based on B, Si, N, P, O, or S can be prepared readily. Rates of metathesis reactions can be rationalized on the basis of steric factors; electronic differences due to the presence of X bound to the alkylidene carbon do not seem to play a major role. However, the thermodynamic preference for catalyst resting state during a reaction depends on the nature of X. Side reactions do not appear to lead to a dramatic increase in rates of catalyst decomposition. Therefore, Mo=CHX compounds could be intermediates in the known metathesis reactions that involve Mo=CHX complexes in which X is based on O⁵ or B,⁶ and metathesis reactions that involve S- or P-based Mo=CHX complexes should be possible. The data so far suggest that the presence of X on the alkylidene carbon does not alter the nature of the alkylidene and olefin metathesis reactions that involve them dramatically.

EXPERIMENTAL

Mo(NAr)(CH₂)(Me₂Pyr)(OTPP) (**1b**)

A stir bar, 576 mg of **1a** (0.644 mmol, 1.0 equiv), and 30 mL pentane were added to a 100 mL Schlenk bomb in a glovebox. (Compound **1a** did not completely dissolve.) The bomb was sealed, brought out of the box, and subjected to three freeze-pump-thaw cycles on a vacuum line. The solution was exposed to 1 atm ethylene and stirred for 3 h. The product precipitated as a light red powder. The bomb was brought into the glovebox and the solid was filtered off and washed with cold pentane; yield 395 mg (79% yield). Anal. Calcd for C₄₉H₄₈MoN₂O: C, 75.76; H, 6.23; N, 3.61. Found: C, 75.59; H, 6.35; N, 3.55.

Mo(NAr)(CHBpin)(Me₂Pyr)(OTPP) (**2a**)

In the glovebox, a 50 mL round-bottom flask was charged with a stir bar, 10 mL toluene, 175 mg **1b** (0.225 mmol, 1.0 equiv), and 57.3 μL vinylboronic acid pinacol ester (0.338

mmol, 1.5 equiv). The flask was capped and the contents were stirred for 3 h at room temperature. The solvent was removed *in vacuo*. Pentane (10 mL) was added and the solvent was removed *in vacuo* again. Pentane (10 mL) was again added and the red slurry was stirred and filtered to obtain 135 mg of pale orange product (66% yield). Compound **2a** can also be synthesized using the same procedure from Mo(NAr)(CHCMe₂Ph)(Me₂Pyr)(OTPP) and two equivalents of vinylboronic acid pinacol ester in 83% yield. Anal. Calcd for C₅₅H₅₉MoBN₂O₃: C, 73.17; H, 6.59; N, 3.10. Found: C, 72.82; H, 6.81; N, 2.93.

Mo(NAr)(CHSiMe₃)(Me₂Pyr)(OTPP) (**2b**)

In the glovebox, a 50 mL round-bottom flask was charged with a stir bar, 10 mL toluene, 166 mg **1b** (0.214 mmol, 1.0 equiv.), and 157 μ L trime-thylvinylsilane (1.07 mmol, 5.0 equiv.). The flask was capped and the contents stirred for 2 h at RT, after which time the solvent was removed *in vacuo*. Pentane was added (10 mL) and the solvent was removed *in vacuo* again. Pentane was again added (5 mL) and the red slurry was stirred and filtered to obtain 86 mg pure orange solid product (47% yield). Anal. Calcd for C₅₂H₅₆MoN₂OSi: C, 73.56; H, 6.65; N, 3.30. Found: C, 73.24; H, 6.66; N, 3.21.

Mo(NAr)(CHCarbaz)(Me₂Pyr)(OTPP) (**2c**)

In the glovebox, a 50 mL round-bottom flask was charged with a stir bar, 10 mL toluene, 165 mg **1b** (0.213 mmol, 1.0 equiv), and 41 mg *N*-vinylcarbazole (0.213 mmol, 1.0 equiv). The flask was capped and the contents were stirred for 4 h at RT. The solvent was removed *in vacuo*, pentane was added (10 mL), and the solvent was removed *in vacuo* again. Pentane was again added (10 mL) and the red slurry was filtered to obtain 163 mg pure orange solid product (81% yield). Anal. Calcd for C₆₁H₅₅MoN₃O: C, 77.77; H, 5.88; N, 4.46. Found: C, 77.47; H, 6.15; N, 4.20.

Mo(NAr)(CHPyrrol)(Me₂Pyr)(OTPP) (**2d**)

In the glovebox, a 50 mL round-bottom flask was charged with a stir bar, 10 mL toluene, 200 mg **1b** (0.257 mmol, 1.0 equiv), and 41 μ L *N*-vinylpyrrolidinone (0.386 mmol, 1.5 equiv). The flask was capped and the contents were stirred for 4 h at RT. The solvents were removed *in vacuo*, pentane was added, and the solvent was removed *in vacuo* again. Pentane was again added and the red slurry was filtered to obtain 171 mg of dark pink product (77% yield). Anal. Calcd for C₅₃H₅₃MoN₃O₂: C, 74.02; H, 6.21; N, 4.89. Found: C, 74.05; H, 6.28; N, 4.76.

Mo(NAr)(CHPh₂)(Me₂Pyr)(OTPP) (**2e**) and MeCN adduct (**2e'**)

In the glovebox, a 50 mL round-bottom flask was charged with a stir bar, 8 mL toluene, 119 mg **1b** (0.153 mmol, 1.0 equiv), and 31 μ L diphenylvinylphosphine (0.153 mmol, 1.0 equiv). The flask was capped and the contents stirred for 3 h at RT, after which time the solvent was removed *in vacuo*. Pentane was added (10 mL) and the solvent was removed *in vacuo* again. Pentane was again added (10 mL) and the red slurry was stirred and filtered to obtain 92 mg of red product (63% yield). The acetonitrile adduct of **2e** can be obtained as an orange powder in 79% yield by adding acetonitrile in place of pentane in the workup. Compound **2e** appears to decompose slowly in the solid state and **2e'** tended to lose acetonitrile. Therefore, consistent elemental analyses of either could not be obtained.

Mo(NAr)(CHOPr)(Me₂Pyr)(OTPP) (**2f**)

In the glovebox, a 50 mL round-bottom flask was charged with a stir bar, 10 mL toluene, 170 mg of **1a** (0.190 mmol, 1.0 equiv), and 43 μ L of propyl vinyl ether (0.380 mmol, 2.0 equiv). The flask was closed and the contents were stirred for 1 h at RT, after which time the solvent was removed *in vacuo*. Pentane was added (10 mL) and the solvent was removed *in*

vacuo again. Pentane was again added (10 mL) and the red slurry was filtered to obtain 81 mg orange product (51% yield). Anal. Calcd for C₅₂H₅₄MoN₂O₂: C, 74.80; H, 6.52; N, 3.36. Found: C, 74.88; H, 6.56; N, 3.36.

Mo(NAr)(CHSPh)(Me₂Pyr)(OTPP) (2g)

In the glovebox, a 50 mL round-bottom flask was charged with a stir bar, 10 mL of toluene, 200 mg of **1a** (0.223 mmol, 1.0 equiv), and 58.3 μ L of phenyl vinyl sulfide (0.446 mmol, 2.0 equiv). The flask was closed and the contents stirred for 19 h at RT, after which time the solvent was removed *in vacuo*. Pentane was added (10 mL) and the solvent was removed *in vacuo* again. Pentane was again added (10 mL) and the red slurry was filtered to obtain 133 mg pink solid product (68% yield). Anal. Calcd for C₅₅H₅₂MoN₂OS: C, 74.64; H, 5.92; N, 3.17. Found: C, 74.46; H, 5.89; N, 2.99.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.
Thermal ellipsoid drawing of **2a** from XRD study.

Figure 2. Overlap of the filled Mo=C bond and the empty B *p* orbital in **2a**. (Pre-orthogonalized NBOs at the 0.02 isovalue) H atoms and OTPP phenyl rings have been omitted for clarity.

Figure 3. Temperature-dependent ^1H NMR spectra of **2a** in $\text{toluene-}d_8$ in the alkylidene proton region.

Figure 4.
Thermal ellipsoid drawing of **2c** from XRD study.

Figure 5.
Thermal ellipsoid drawing of **2d** from XRD study.

Figure 6.
Thermal ellipsoid drawing of **2e'** from XRD study.

Figure 7. Temperature-dependent ^1H NMR spectra of **2e** in the alkylidene proton region in $\text{toluene-}d_8$.

Figure 8. Temperature-dependent ^1H NMR spectra of **2e'** (13 mM in toluene- d_8) in the alkylidene proton region in the presence of ~ 1.5 equivalents of MeCN.

Figure 9.
Thermal ellipsoid drawing of **2f** from XRD study.

Figure 10. The NLMO of the O lone pair (0.02 isovalue) showing an O lone pair overlapping with the Mo=C antibonding orbital in **2f**. H atoms and the OTPP phenyl rings have been omitted for clarity.

Figure 11.
Thermal ellipsoid drawing of **2g** from XRD study.

Table 1

Selected Mo=C bond lengths (Å) and Mo=C-X bond angles (°) for Mo(NAr)(CHX)(Me₂Pyr)(OTPP) complexes.

Cmpd	X	Mo=C	C-X	Mo=C-X
1a	CMe ₂ Ph ^a	1.881(5)	1.518(7)	145.2(4)
2a	B(pin) ^{b,c}	1.8825(1)	1.5525(16)	106.19(7)
2b	SiMe ₃	1.875(2)	1.862(1)	139.96(8)
2c	Carbaz ^d	1.9140(13)	1.3797(16)	143.60(10)
2d	Pyrrol ^{c,e}	1.9578(11)	1.3968(12)	117.47(7)
2e'	PPh ₂ ^f	1.904(2)	1.812(2)	126.1(1)
2f	OPr	1.921(3)	1.343(4)	142.7(3)
2g	SPh	1.9112(15)	1.7179(16)	130.20(9)

^a See ref 6.

^b B(pin) = B(pinacolate)

^c *Anti* configuration.

^d Carbaz = *N*-carbazolyl.

^e Pyrrol = *N*-pyrrolidinonyl.

^f Acetonitrile adduct.

Table 2

% conversion for metathesis homocoupling of 1-octene by **1a** and **2a-2g** (5 mol%) in C₆D₆ at 22 °C (closed system).

	X	0.5 h	1 h	2 h	10 h
1a	CMe ₂ Ph	47	48	48	51
2a	B(pin)	47	47	47	49
2b	TMS	55	54	54	54
2c	Carbaz	50	50	50	53
2d	Pyrrol	0	0	3	12
2e	PPh ₂	48	48	49	53
2f	OPr	47	47	47	49
2g	SPh	53	54	54	58

Table 3

Ratios of M=CHX to M=CHR complexes observed in reactions of **1a** and **2a-2g** with 1-octene in C₆D₆ at 22 °C.

	X	0.5 h	2 h	10 h
1a	CMe ₂ Ph	0:100	0:100	0:100
2a	B(pin)	60:40	57:43	63:37
2b	TMS	100:0	100:0	100:0
2c	Carbaz	77:23	79:21	79:21
2d	Pyrrol	100:0	100:0	100:0
2e	PPh ₂	77:23	70:30	70:30
2f	OPr	13:87	14:86	15:85
2g	SPh	100:0	100:0	100:0

Table 4

Total alkylidene remaining in reactions between Mo=CHX complexes and 1-octene (15 equiv) in C₆D₆ at 22 °C as a function of time.

	X	0.5 h ^a	2 h	10 h	24 h
1a	CMe ₂ Ph	100	82	55	12
2a	B(pin)	100	100	66	18
2b	TMS	100	86	72	63
2c	Carbaz	100	91	68	37
2d	Pyrrol	100	100	100	100
2e	PPh ₂	100	92	34	0
2f	OPr	100	95	53	18
2g	SPh	100	92	60	36

^aInitial alkylidene present after 0.5 h is defined as 100%.