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High Oxidation State Molybdenum Imido Heteroatom-Substituted Alkylidene Complexes

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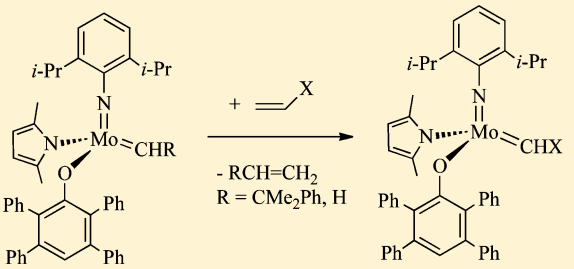
Supporting Information

ABSTRACT: Reactions between 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) and CH_2=CHX where X = B(pin), $SiMe_3$, *N*-carbazolyl, *N*-pyrrolidinonyl, PPh_2, OPr, or SPh lead to Mo(NAr)(CHX)(Me_2Pyr)(OTPP) complexes in good yield. All have been characterized through X-ray studies (as an acetonitrile adduct in the case of X = PPh_2). The efficiencies of metathesis reactions initiated by Mo(NAr)(CHX)(Me_2Pyr)(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.



X = B(pin), $SiMe_3$, *N*-carbazolyl, *N*-pyrrolidinonyl, PPh_2, OPr, SPh

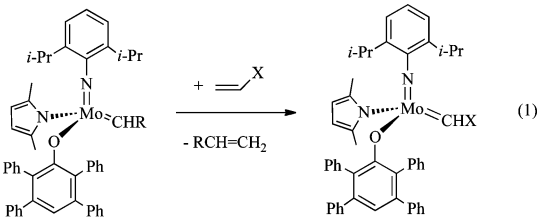
INTRODUCTION

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 Si[1] or Ge.[1,2] However, to our knowledge no complexes have been described in which X is based on a heteroatom (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)[$OCMe(CF_3)_2$]$(THF)_2$ where X is OR, SR, or pyrrolidinonyl.[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−e] As olefin metathesis investigations evolve to include CH_2=CHX derivatives where X is not carbon-based (for example, *Z*-selective cross-metathesis reactions where X = OR[5] 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.

RESULTS AND DISCUSSION

We targeted Mo(NAr)(CHX)(Me_2Pyr)(OTPP) complexes (Ar = 2,6-*i*-$Pr_2C_6H_3$, Me_2Pyr = 2,5-dimethylpyrrolide, OTPP = O-2,3,5,6-Ph_4C_6H), in part because monoalkoxide pyrrolide (MAP) complexes have produced new and interesting results in the last several years, especially *Z*-selective reactions,[5−7] and because the OTPP 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 CH_2=CHX (eq 1), we prepared



1a; R = CMe_2Ph
1b; R = H

2a-g (see Table 1)

(1)

Mo(NAr)(CH_2)(Me_2Pyr)(OTPP) (**1b**) in 79% yield, the Mo analogue of the tungsten complex, W(NAr)(CH_2)(Me_2Pyr)(OTPP),[1c] by treating Mo(NAr)($CHCMe_2Ph$)(Me_2Pyr)(OTPP)[9] (**1a**) with ethylene. The proton NMR spectrum of **1b** in C_6D_6 contains the methylidene proton resonances at 11.77 and 11.58 ppm (J_{HH} = 5 Hz).

Both **1a** and **1b** react cleanly with CH_2=CHB(pin) to give Mo(NAr)[CHB(pin)](Me_2Pyr)(OTPP) (**2a**), which is ob-

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tained 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 Mo=C bond length of 1.8825(1) Å and a Mo=C−B bond angle of 106.19(7)° (Table 1). These values should be compared with those for Mo(NAr)(CHCMe$_2$Ph)(Me$_2$Pyr)(OTPP) (**1a**, Table 1).[6] NBO calculations reveal that the empty p orbital on B is conjugated with the Mo=C π orbital (Figure 2), but the contribution from the B orbital (99% p) is only 3.7% of the Mo=C π natural localized molecular orbital (NLMO). There is no evidence from either the NBO calculations or the Mo1···O2 distance (2.837 Å) that there is any significant electronic interaction between Mo1 and O2. A few structurally characterized 16*e* *anti* alkylidene complexes (i.e., five-coordinate intramolecular or intermolecular adducts) of this general type are known in which the M−C−C angle is 135−150°.[1,10]

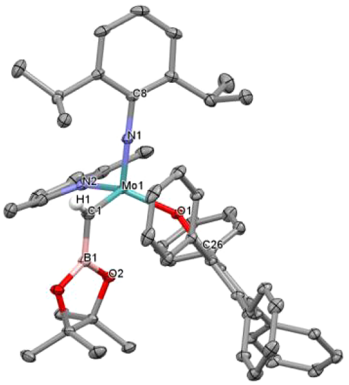

Figure 1. Thermal ellipsoid drawing of **2a** from XRD study.

Table 1. Selected Mo=C Bond Lengths (Å) and Mo=C−X Bond Angles (deg) for Mo(NAr)(CHX)(Me$_2$Pyr)(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.

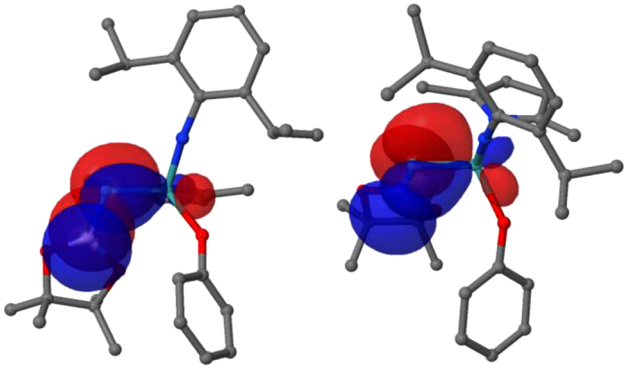

Figure 2. Overlap of the filled Mo=C π bond and the empty B p orbital in **2a** (preorthogonalized NBOs at the 0.02 isovalue). H atoms and OTPP phenyl rings have been omitted for clarity.

The proton NMR spectrum of **2a** (Figure 3) at 20 °C reveals broad alkylidene α 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 $\Delta H^{\ddagger}$ = 8.7(3) kcal/mol and $\Delta S^{\ddagger}$ = 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 subsecond time scale in **2a** (at 298 K) and have approximately the same energies. The relatively high rate of alkylidene rotation is consistent with a Mo(+)−C=B(−) resonance form, although the π component of the Mo=C bond is only *slightly* decreased according to NBO calculations (*vide supra*).

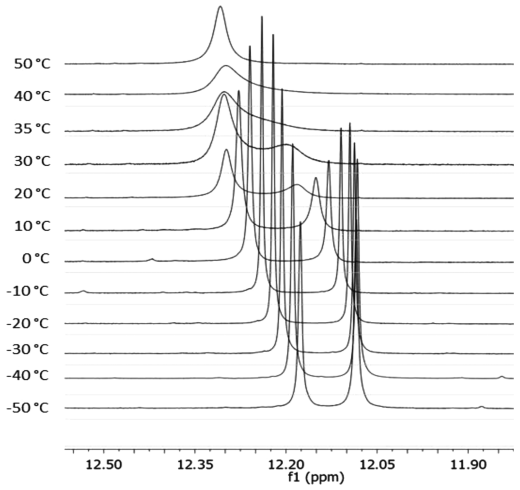

Figure 3. Temperature-dependent ^{1}H NMR spectra of **2a** in toluene-d_8 in the alkylidene proton region.

The reaction between **1b** and CH$_2$=CHSiMe$_3$ yields Mo(NAr)(CHSiMe$_3$)(Me$_2$Pyr)(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 (^{1}H NMR in C$_6$D$_6$). *Syn* and *anti* isomers of Mo(NAr)(CHSiMe$_3$)(OAr)$_2$ and W(NAr)(CHSiMe$_3$)(OAr)$_2$ have been observed in solution[11] 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 CH$_2$=CH(Carbaz) (Carbaz = *N*-carbazolyl) yields Mo(NAr)[CH(Carbaz)](Me$_2$Pyr)(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_{CH} = 134 Hz; ^{1}H NMR in C$_6$D$_6$). The structure of **2c** (Figure 4) is consistent with previously characterized MAP complexes.

The reaction between **1b** and CH$_2$=CH(Pyrrol) (Pyrrol = *N*-pyrrolidinonyl) yields Mo(NAr)[CH(Pyrrol)](Me$_2$Pyr)(OTPP) (**2d**) as a pink solid in 81% yield. Compound **2d** is approximately a trigonal bipyramid (τ = 0.70)[13] in which the

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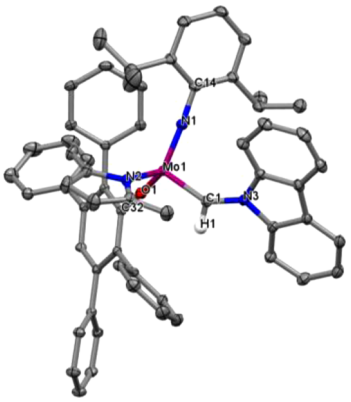

Figure 4. Thermal ellipsoid drawing of **2c** from XRD study.

carbonyl group is coordinated to the metal in an apical position (Figure 5). The alkylidene is *anti* with J_{CH} = 166 Hz; this

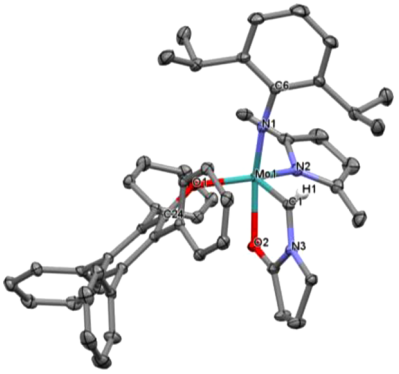

Figure 5. Thermal ellipsoid drawing of **2d** from XRD study.

configuration is expected on the basis of similar structures being observed for Re (J_{CH} = 173 Hz)[3] and Ru[4] 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 CH_2=$CHPPh_2$ yields Mo(NAr)($CHPPh_2$)(Me_2Pyr)(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 (τ = 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 π bond, which is reasonable considering that the phosphorus 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_{CH} = 130 Hz) is essentially zero, but approximately 5 Hz in the *anti* analog of

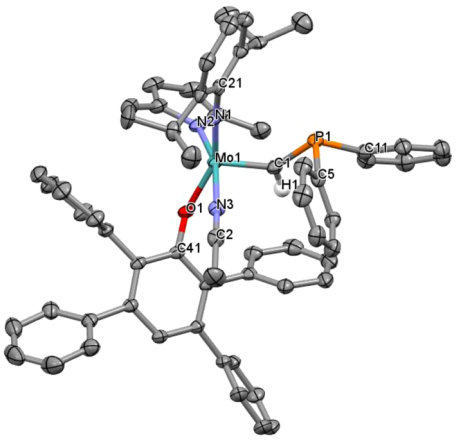

Figure 6. Thermal ellipsoid drawing of **2e**′ from XRD study.

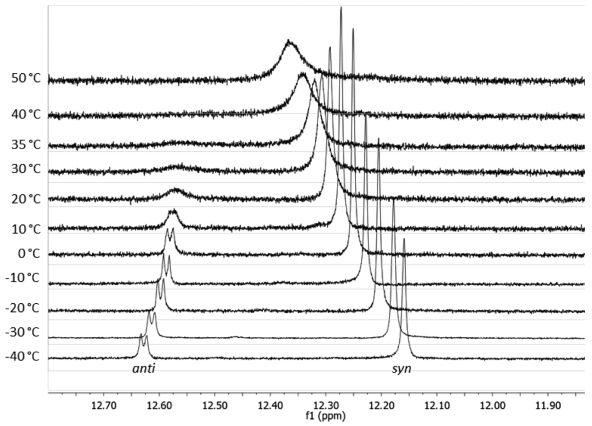

Figure 7. Temperature-dependent ^{1}H NMR spectra of **2e** in the alkylidene proton region in toluene-d_8.

2e (the downfield doublet). Small (including zero)[2] J_{HP} values in general are not unusual.[15]

The ^{1}H NMR spectrum of **2e**′ (in toluene-d_8 or C_6D_6; Figure 8) at 20 °C is virtually the same as the corresponding ^{1}H 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-depend-

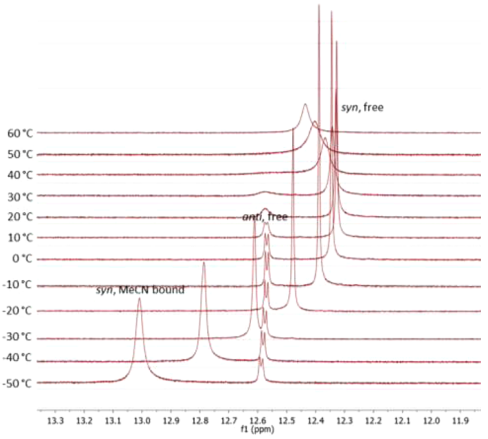

Figure 8. Temperature-dependent ^{1}H NMR spectra of **2e**′ (13 mM in toluene-d_8) in the alkylidene proton region in the presence of ~1.5 equivalents of MeCN.

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ent 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 to 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 the *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 σ^* component of the Mo═N bond in *anti*-**2e**, which is the orbital that receives electron density in an agostic CH_α interaction in a typical *syn* alkylidene isomer.[16]

The reaction between **1a** or **1b** and CH_2═CHOPr yields Mo(NAr)(CHOPr)(Me_2Pyr)(OTPP) (**2f**) as an orange solid in 51% isolated yield. Its proton NMR spectrum at 22 °C shows a single alkylidene resonance with J_{CH} = 140 Hz, which should be compared with J_{CH} = 135 Hz for the *syn* isomer of Re(C-*t*-Bu)(CHOEt)[$OCMe(CF_3)_2$]$(THF)_2$ and 163 Hz for the *anti* isomer of Re(C-*t*-Bu)(CHOEt)[$OCMe(CF_3)_2$]$(THF)_2$ 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

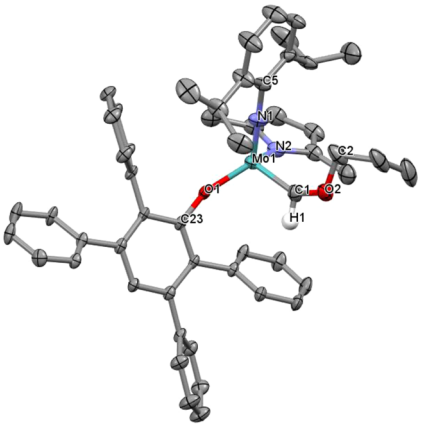

Figure 9. Thermal ellipsoid drawing of **2f** from XRD study.

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 CH_2═CHSPh yields Mo(NAr)(CHSPh)(Me_2Pyr)(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_{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**−**g** as initiators for olefin metathesis reactions compared to **1a**, the conversion of 1-octene to *E*/*Z* 7-tetradecene by 5 mol % catalyst in C_6D_6 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

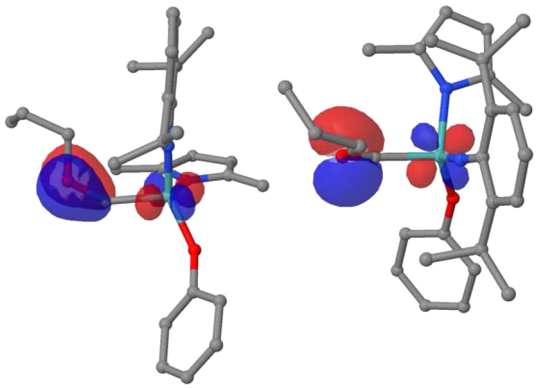

Figure 10. NLMO of the O lone pair (0.02 isovalue) showing an O lone pair overlapping with the Mo═C π antibonding orbital in **2f**. H atoms and the OTPP phenyl rings have been omitted for clarity.

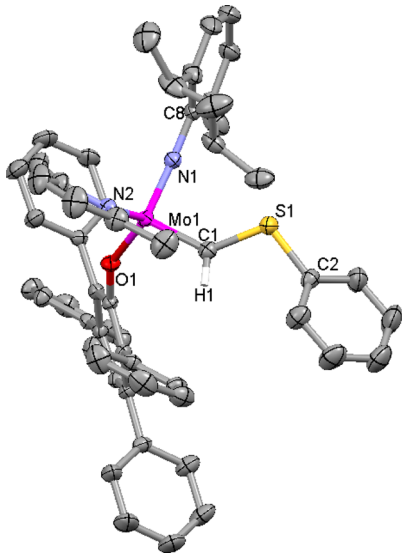

Figure 11. Thermal ellipsoid drawing of **2g** from XRD study.

Table 2. Percent Conversion for Metathesis Homocoupling of 1-Octene by 1a and 2a−g (5 mol %) in C_6D_6 at 22 °C (closed system)

	X	0.5 h	1 h	2 h	10 h
1a	CMe_2Ph	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

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. In general, conversions are 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**−**g** 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

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Table 3. Ratios of M=CHX to M=CHR Complexes Observed in Reactions of 1a and 2a–g with 1-Octene in C_6D_6 at 22 °C

	X	0.5 h	2 h	10 h
1a	CMe_2Ph	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

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 percentage alkylidene remaining in reactions between Mo=CHX complexes and 1-octene in C_6D_6 at 22 °C

Table 4. Percent Total Alkylidene Remaining in Reactions between Mo=CHX Complexes and 1-Octene (15 equiv) in C_6D_6 at 22 °C as a Function of Time

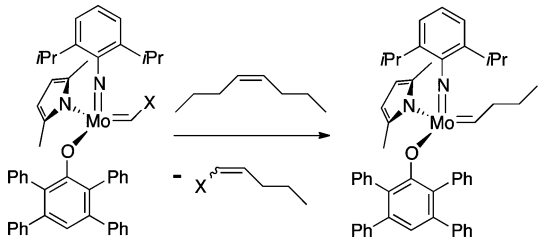
	X	0.5 h[a]	2 h	10 h	24 h
1a	CMe_2Ph	100	82	55	12
2a	B(pin)	100	100	66	18
2b	TMS	100	86	72	63
2c	Carbaz	100	91	68	37
2d	Pyrrol	100	100	100	100
2e	PPh_2	100	92	34	0
2f	OPr	100	95	53	18
2g	SPh	100	92	60	36

[a]Initial alkylidene present after 0.5 h is defined as 100%.

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–g** were treated with 15 equivalents of *cis*-4-octene in C_6D_6 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.

A kinetic study of the rate of conversion to butylidene (eq 2) yielded first-order rate constants of 9.9×10^{-5} M^{-1} s^{-1} for **2a** and 1.2×10^{-3} M for **2f** (see SI for details). Compound **2f** reacts with *cis*-4-octene about 10 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



(2)

preference to remain in the Mo=CHX form 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 O[5] 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 dramatically alter the nature of the alkylidene and olefin metathesis reactions that involve them.

EXPERIMENTAL SECTION

Mo(NAr)(CH_2)(Me_2Pyr)(OTPP) (1b). A stir bar, 576 mg of **1a** (0.644 mmol, 1.0 equiv), and 30 mL of 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%). Anal. Calcd for $C_{49}H_{48}MoN_2O$: C, 75.76; H, 6.23; N, 3.61. Found: C, 75.59; H, 6.35; N, 3.55.

Mo(NAr)(CHBpin)(Me_2Pyr)(OTPP) (2a). In the glovebox, a 50 mL round-bottom flask was charged with a stir bar, 10 mL of toluene, 175 mg of **1b** (0.225 mmol, 1.0 equiv), and 57.3 μL of 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)($CHCMe_2Ph$)(Me_2Pyr)(OTPP) and 2 equivalents of vinylboronic acid pinacol ester in 83% yield. Anal. Calcd for $C_{55}H_{59}MoBN_2O_3$: C, 73.17; H, 6.59; N, 3.10. Found: C, 72.82; H, 6.81; N, 2.93.

Mo(NAr)(CHSiMe_3)(Me_2Pyr)(OTPP) (2b). In the glovebox, a 50 mL round-bottom flask was charged with a stir bar, 10 mL of toluene, 166 mg of **1b** (0.214 mmol, 1.0 equiv), and 157 μL of trimethylvinylsilane (1.07 mmol, 5.0 equiv). The flask was capped, and the contents were 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 of pure orange solid product (47% yield). Anal. Calcd for $C_{52}H_{56}MoN_2OSi$: C, 73.56; H, 6.65; N, 3.30. Found: C, 73.24; H, 6.66; N, 3.21.

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Mo(NAr)(CHCarbaz)(Me$_2$Pyr)(OTPP) (2c). In the glovebox, a 50 mL round-bottom flask was charged with a stir bar, 10 mL of toluene, 165 mg of **1b** (0.213 mmol, 1.0 equiv), and 41 mg of *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 of pure orange solid product (81% yield). Anal. Calcd for $C_{61}H_{55}MoN_3O$: C, 77.77; H, 5.88; N, 4.46. Found: C, 77.47; H, 6.15; N, 4.20.

Mo(NAr)(CHPyrrol)(Me$_2$Pyr)(OTPP) (2d). In the glovebox, a 50 mL round-bottom flask was charged with a stir bar, 10 mL of toluene, 200 mg of **1b** (0.257 mmol, 1.0 equiv), and 41 μL of *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 $C_{53}H_{53}MoN_3O_2$: C, 74.02; H, 6.21; N, 4.89. Found: C, 74.05; H, 6.28; N, 4.76.

Mo(NAr)(CHPPh$_2$)(Me$_2$Pyr)(OTPP) (2e) and MeCN Adduct (2e′). In the glovebox, a 50 mL round-bottom flask was charged with a stir bar, 8 mL of toluene, 119 mg of **1b** (0.153 mmol, 1.0 equiv), and 31 μL of diphenylvinylphosphine (0.153 mmol, 1.0 equiv). The flask was capped, and the contents were 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)(Me$_2$Pyr)(OTPP) (2f). In the glovebox, a 50 mL round-bottom flask was charged with a stir bar, 10 mL of toluene, 170 mg of **1a** (0.190 mmol, 1.0 equiv), and 43 μL 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 of orange product (51% yield). Anal. Calcd for $C_{52}H_{54}MoN_2O_2$: C, 74.80; H, 6.52; N, 3.36. Found: C, 74.88; H, 6.56; N, 3.36.

Mo(NAr)(CHSPh)(Me$_2$Pyr)(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 μL of phenyl vinyl sulfide (0.446 mmol, 2.0 equiv). The flask was closed, and the contents were 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 of pink solid product (68% yield). Anal. Calcd for $C_{55}H_{52}MoN_2OS$: C, 74.64; H, 5.92; N, 3.17. Found: C, 74.46; H, 5.89; N, 2.99.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

General experimental details, NMR data for **1b** and **2a–g**, 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.

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Notes

The authors declare no competing financial interest.

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