

Simple Molybdenum(IV) Olefin Complexes of the Type Mo(NR)(X)(Y)(olefin)

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Exposure of heptane solutions of Mo(NAr)(CHCMe₂Ph)(Me₂Pyr)(OAr) (**1a**; Ar = 2,6-diisopropylphenyl), Mo(NAr)(CHCMe₃)(Me₂Pyr)[OCMe(CF₃)₂] (**1b**), and Mo(NAr)(CHCMe₂Ph)(Me₂Pyr)(OSiPh₃) (**1c**) to one atmosphere of ethylene for 12 h yields the ethylene complexes, Mo(NAr)(CH₂CH₂)(Me₂Pyr)(OAr) (**2a**), Mo(NAr)(CH₂CH₂)(Me₂Pyr)[OCMe(CF₃)₂] (**2b**), and Mo(NAr)(CH₂CH₂)(Me₂Pyr)(OSiPh₃) (**2c**). Addition of 1 equiv of triphenylsilanol to a solution of **2c** gives Mo(NAr)(CH₂CH₂)(OSiPh₃)₂ (**3**) readily. Mo(NAr)(CHCMe₂Ph)(OTf)₂(dme) reacts slowly with ethylene (60 psi) in toluene at 80 °C to give *cis* and *trans* isomers of Mo(NAr)(CH₂CH₂)(OTf)₂(dme) (**4a**) in the ratio of ~2(*cis*):1. Addition of lithium 2,5-dimethylpyrrolide to **4a** under 1 atm of ethylene produces Mo(NAr)(CH₂CH₂)(η¹-Me₂Pyr)(η⁵-Me₂Pyr) (**5a**). Mo(NAr)(CHCMe₂Ph)(η¹-MesPyr)₂ (MesPyr = 2-mesitylpyrrolide) reacts cleanly with ethylene in benzene at 60 °C over a period of four days to give exclusively Mo(NAr)(CH₂CH₂)(MesPyr)₂ (**5b**). Treatment of **5b** with 2 equiv of (CF₃)₂CHOH in ether yields Mo(NAr)(CH₂CH₂)[OCH(CF₃)₂]₂(Et₂O) (**6**). Neat styrene reacts with **2c** and **3** to generate the styrene complexes, Mo(NAr)(CH₂CHPh)(Me₂Pyr)(OSiPh₃) (**7**) and Mo(NAr)(CH₂CHPh)(OSiPh₃)₂ (**8**), respectively. Similarly, the *trans*-3-hexene complex, Mo(NAr)(*trans*-3-hexene)(OSiPh₃)₂ (**9a**), can be prepared from **3** and neat *trans*-3-hexene. When **3** is exposed to 1 atm of ethylene, the molybdacyclopentane species, Mo(NAr)(C₄H₈)(OSiPh₃)₂ (**10**), is generated. X-ray structural studies were carried out on **2c**, **5a**, **6**, **8**, **9a**, and **10**. All evidence suggests that alkene exchange at the Mo(IV) center is facile, followed by *cis,trans* isomerization and isomerization via double bond migration. In addition, trace amounts of alkylidene complexes are formed that result in slow metathesis reactions of free olefins to give (e.g.) a distribution of all possible linear olefins from an initial olefin and its double bond isomers.

Introduction

Ethylene is a product of olefin metathesis reactions that involve one or more terminal olefins. High oxidation state molybdenum and tungsten imido alkylidene complexes¹ react with ethylene to give methylidene complexes, which are the least stable alkylidenes toward bimolecular decomposition, and unsubstituted metallacyclobutane complexes, which are the most stable metallacycles toward loss of an olefin. Ethylene also has been proposed to promote rearrangement of an unsubstituted metallacyclobutane to an olefin and thereby to lead to decomposition of high oxidation state alkylidene catalysts.²

Perhaps the most informative studies concerning reactions between alkylidene complexes and ethylene in solution have employed ¹³C-labeled ethylene. Reactions between ¹³C₂H₄

and tungsten biphenolate and binaphtholate catalysts have been studied most thoroughly.^{2,3} (Fewer studies have been reported for analogous Mo complexes.⁴) Among the species observed in solution are an unsubstituted tungstacyclobutane complex, an ethylene complex, an unsubstituted tungstacyclopentane complex, and a heterochiral dimeric methylidene complex. Ethylene has also been employed in order to study the mechanism of catalyst decomposition and formation of bimetallic species. For example, the tungstacyclobutane complex, W(NAr^{Cl})(Biphen)(C₃H₆) (Ar^{Cl} = 2,6-Cl₂C₆H₃; Biphen = 6,6'-dimethyl-3,3',5,5'-tetra-*t*-butyl-1,1'-biphenyl-2,2'-diolate), was found to decompose to yield (inter alia) the dimeric, heterochiral methylidene complex, [W(NAr^{Cl})(Biphen)(μ-CH₂)₂], which decomposed further to yield homochiral [W(NAr^{Cl})(Biphen)]₂(μ-CH₂CH₂), which in turn lost ethylene to yield [W(NAr^{Cl})(Biphen)]₂.⁵ The ethylene complexes that have been prepared in reactions between

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imido alkylidene complexes and ethylene and that have been isolated and structurally characterized are the five-coordinate species $W(NAr^Cl)(CH_2CH_2)(Biphen)(THF)$,⁵ $Mo(NAr^Cl)(CH_2CH_2)(Biphen)(Et_2O)$,⁴ and $\{Mo(NAr)(CH_2CH_2)[OCMe(CF_3)_2](THF)_3\}B(3,5-(CF_3)_2C_6H_3)_4$.⁶

There is some evidence that alkylidene complexes can be formed in reactions between $Mo(IV)$ or $W(IV)$ imido bisalkoxide or biphenolate complexes and ethylene. For example, vinyltributylstannane is homologated to allyltributylstannane by $Mo(IV)$ complexes in the presence of ethylene.⁷ Although $Mo(NAr^Cl)(CH_2CH_2)(rac\text{-}Biphen)(ether)$ is inactive for ring-closing diallyl ether in 10 days at 22 °C, when 10 equiv of norbornene were added to a benzene solution of 5 mol % $Mo(NAr^Cl)(CH_2CH_2)(rac\text{-}Biphen)(ether)$ and diallyl ether, a 56% yield of 2,4-dihydrofuran was obtained in 10 days.⁸

In the last several years, new types of Mo and W imido alkylidene complexes that have the formula $M(NR)(CHR')(OR'')(Pyr)$, where Pyr is a pyrrolide or substituted pyrrolide ligand and OR'' usually is an aryloxo, have been prepared and explored.⁹ These monoalkoxidepyrrolide (MAP) species can be viewed as third generation high oxidation state imido alkylidene catalysts (after “first generation” bisalkoxides and “second generation” biphenolates and binaphtholates¹). MAP species have many new features of fundamental interest, perhaps the most important of which is the presence of a stereogenic metal center. MAP species have proven to be extraordinarily reactive,^{9,10} as are isoelectronic rhenium alkylidene species that contain a stereogenic metal center.¹¹ Under the right circumstances, many have been found to be long-lived compared to first or second generation catalysts. Initial studies of reactions between MAP species and ethylene showed that when a sterically relatively small set of ligands is present, ethylene complexes are often formed in the presence of ethylene.¹²

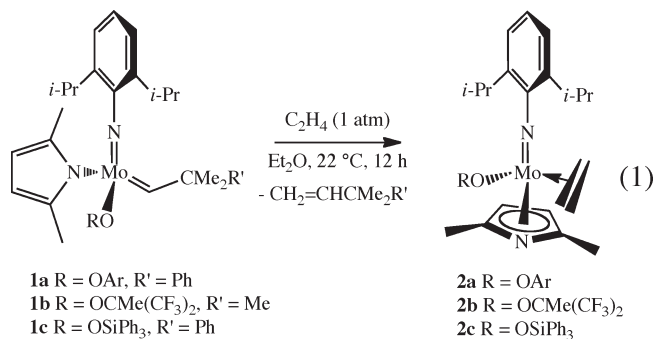
It is interesting to note that olefin complexes of the type $M(NAr)(X)(Y)(olefin)$ ($M = Mo$ or W ; X or $Y =$ alkoxide

or η^1 -pyrrolide) are related to $TaCp^*Cl_2(olefin)$ complexes, which catalyze the dimerization of terminal olefins to tail-to-tail or head-to-tail dimers via a metallacyclopentane “ring-contraction” mechanism.¹³ Complexes that contain $Mo(NAr)(X)(Y)$ or $W(NAr)(X)(Y)$ cores also will dimerize ethylene slowly to 1-butene.^{3,4}

In view of the isomeric relationship between olefin and alkylidene complexes,^{14–16} as well as the roles olefins may play in metathesis chemistry beyond the obvious role as substrates, as has been outlined above, we decided to explore routes to simple $Mo(IV)$ ethylene complexes of the type $Mo(NAr)(X)(Y)(CH_2CH_2)$ and reactions between ethylene complexes and olefins. The results of this investigation are reported here.

Results

Exposure of heptane solutions of $Mo(NAr)(CHCMe_2Ph)(Me_2Pyr)(OAr)$ (**1a**; $Ar = 2,6$ -diisopropylphenyl, $Me_2Pyr = 2,5$ -dimethylpyrrolide) and $Mo(NAr)(CHCMe_3)(Me_2Pyr)[OCMe(CF_3)_2]$ (**1b**) to one atmosphere of ethylene for 12 h led to formation of the ethylene complexes, $Mo(NAr)(CH_2CH_2)(Me_2Pyr)(OAr)$ (**2a**) and $Mo(NAr)(CH_2CH_2)(Me_2Pyr)[OCMe(CF_3)_2]$ (**2b**) in isolated yields of 59% and 63%, respectively (eq 1). Proton NMR spectra in C_6D_6 revealed resonances for bound ethylene at 2.95 (2H), 2.60 (1H), and 1.95 (1H) ppm in **2a** and 2.74 (2H), 2.45 (1H), 2.16 (1H) ppm in **2b**. The presence of four ethylene resonances (two overlapping) suggests that the ethylene does not rotate rapidly on the NMR time scale. A similar reaction between $Mo(NAr)(CHCMe_2Ph)(Me_2Pyr)(OSiPh_3)$ (**1c**) and ethylene led to formation of $Mo(NAr)(CH_2CH_2)(Me_2Pyr)(OSiPh_3)$ (**2c**) in 70% yield (ethylene resonances at 2.87 (1H), 2.70 (1H), and 2.20 (2H) ppm). Experiments employing $^{13}C_2H_4$ revealed ethylene carbon resonances at 56.3 and 60.2 ppm with $J_{CH} = 155$ Hz and $J_{CC} = 39$ Hz for **2a** and at 56.9 and 58.0 ppm with $J_{CH} = 153$ Hz and $J_{CC} = 37$ Hz for **2c**. These chemical shifts and J_{CH} values are similar to those reported in ethylene complexes noted earlier^{5,6} and others reported here.



The results of a single crystal X-ray structural study of **2c** are shown in Figure 1. The $C(1)–C(2)$ bond length is 1.420(3) Å, which should be compared to the ethylene $C–C$ bond lengths in $Mo(NAr^Cl)(CH_2CH_2)(Biphen)(Et_2O)$ (1.400(13) Å),⁴ $W(NAr^Cl)(CH_2CH_2)(Biphen)(THF)$ (1.452(3) Å),⁵ and $\{Mo(NAr)(CH_2CH_2)[OC(CF_3)_2Me](THF)_3\}^+$ (1.408(4) Å).⁶ The

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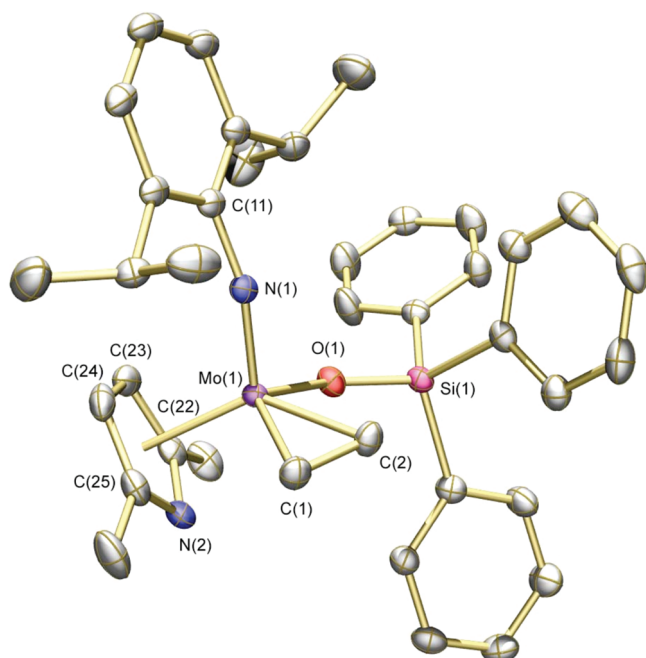


Figure 1. POV-ray drawing of **2c**. Thermal ellipsoids are displayed at 50% probability level. Hydrogen atoms are omitted. Selected distances (Å) and angles (deg): Mo(1)–C(1) = 2.190(2) Å, Mo(1)–C(2) = 2.182(2) Å, Mo(1)–N(1) = 1.7353(18) Å, Mo(1)–O(1) = 2.0080(15) Å, C(1)–C(2) = 1.420(3) Å, Mo(1)–N(2) = 2.3588(18) Å, Mo(1)–C(22) = 2.458(2) Å, Mo(1)–C(23) = 2.506(2) Å, Mo(1)–C(24) = 2.441(2) Å, Mo(1)–C(25) = 2.355(2) Å, Mo(1)–N(1)–C(11) = 163.09(15)°, Mo(1)–O(1)–Si(1) = 149.06(9)°, N(1)–Mo(1)–C(1) = 98.75(9)°, N(1)–Mo(1)–C(2) = 97.89(8)°.

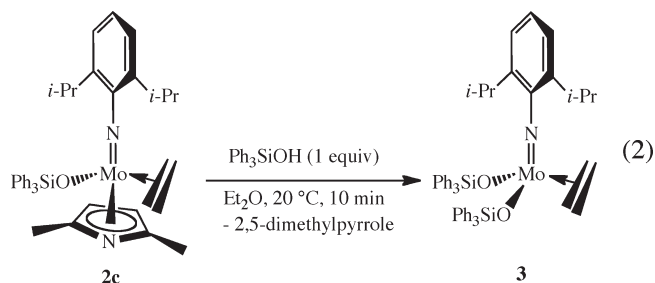
imido ligand bends (Mo(1)–N(1)–C(11) = 163.09(15)°) in response to some significant steric interaction between the triphenylsilyloxy and the 2,6-diisopropylphenylimido ligand. The ethylene is oriented so that its C–C axis is essentially perpendicular to the Mo(1)–N(1) axis (N(1)–Mo(1)–C(1) = 98.75(9)°, N(1)–Mo(1)–C(2) = 97.89(8)°).

A reaction between **1c** and propylene in C₆D₆ led to formation of the ethylidene complex Mo(NAr)(CHMe)(Me₂Pyr)(OSiPh₃) initially, as judged from appearance of a new alkylidene quartet at 12.32 ppm, along with **2c** and other species, but after 1 day at room temperature, only **2c** is observed along with propylene and expected metathesis products (2-butenes, H₂C=CHCMe₂Ph, etc.). Because ethylene is generated in the metathesis reaction and because ethylene is the smallest and most reactive olefin, the ultimate product or products are derived from ethylene.

Addition of CD₂CD₂ (1 atm) to a C₆H₆ solution of **2c** led to immediate formation of Mo(NAr)(CD₂CD₂)(Me₂Pyr)(OSiPh₃), according to ²H NMR spectroscopy. This observation confirms that ethylene exchanges readily in **2c**, either through direct displacement of ethylene by CD₂CD₂ in a five-coordinate intermediate or through rapid formation and breakup of an intermediate five-coordinate molybdacyclopentane (vide infra). Rapid exchange can also be observed employing ¹³C NMR and ¹³C₂H₄.

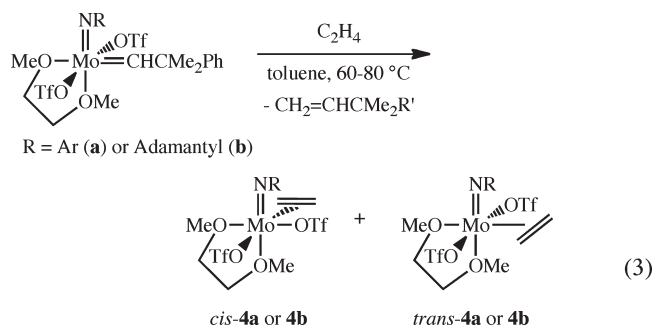
Addition of 1 equiv of triphenylsilanol to a solution of **2c** led to an immediate color change from red to purple. A proton NMR spectrum revealed two pseudo quartets at 2.74 and 1.99 ppm which integrate as two protons each for bound

ethylene in mirror symmetric Mo(NAr)(CH₂CH₂)(OSiPh₃)₂ (**3**) (eq 2). Protonolysis of pyrrolide ligands in these



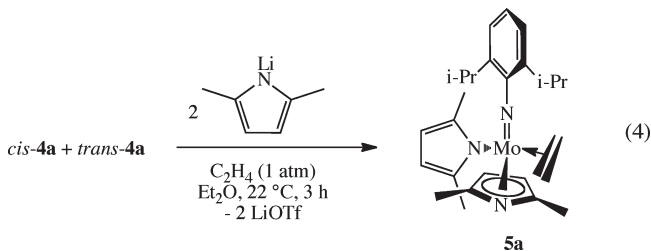
circumstances has been proposed to require coordination of the alcohol oxygen to the metal before proton migration,^{9c} which in turn suggests that the **18e** count in **2c** is first reduced to **14e** through ready formation of intermediate Mo(NAr)(CH₂CH₂)(η¹-Me₂Pyr)(OSiPh₃).

To prepare potentially a large variety of ethylene complexes, we attempted to prepare an ethylene complex through a reaction between Mo(NAr)(CHCMe₂Ph)(OTf)₂(dme) and ethylene. Mo(NAr)(CHCMe₂Ph)(OTf)₂(dme) was found to react slowly with ethylene (60 psi) in toluene at 80 °C. After two days, a red ethylene complex can be isolated in 86% yield. The ¹H NMR spectrum revealed several multiplet resonances between 4 and 2.5 ppm that could be ascribed to an ethylene ligand, while the ¹⁹F NMR spectrum showed three singlet resonances at δ –78.26, –78.30, and –78.59 for triflate ligands in approximately a 1:1:1 ratio. All data are consistent with the reaction between Mo(NAr)(CHCMe₂Ph)(OTf)₂(dme) and ethylene giving *cis* and *trans* isomers of Mo(NAr)(CH₂CH₂)(OTf)₂(dme) (**4a**) in the ratio of 2:1, respectively (eq 3). The reaction between Mo(NAr)(OTf)₂(CHCMe₂Ph)(dme) and ethylene most likely proceeds through metathesis to yield Mo(NAr)(OTf)₂(CH₂)(dme), which then decomposes in the presence of ethylene to give the observed product. To our knowledge, the reaction shown in eq 3 is the only metathetical reaction of Mo(NAr)(OTf)₂(CHCMe₂Ph)(dme) to have been reported. Using a similar procedure (1 atm ethylene; 60 °C, 6 h), Mo(NAd)(CH₂CH₂)(OTf)₂(dme) (**4b**) can be obtained as approximately a 2:1 mixture of *cis* and *trans* isomers, respectively.

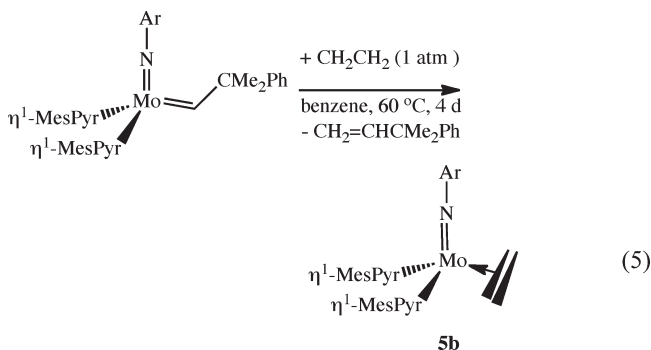


Addition of lithium 2,5-dimethylpyrrolide to **4a** under 1 atm of ethylene led to formation of Mo(NAr)(CH₂CH₂)(η¹-Me₂Pyr)(η⁵-Me₂Pyr) (**5a**) (eq 4). If the reaction is attempted in the absence of ethylene, a significant amount of decomposition is observed. Compound **5a** could not be prepared through a reaction between Mo(NAr)(CHCMe₂Ph)(η¹-Me₂Pyr)(η⁵-Me₂Pyr) and ethylene (1 atm) at 80 °C. Two ethylene resonances were found at 51.3 and 48.1 ppm. A single crystal X-ray structural study of **5a** (Figure 2) confirms that the pyrrolide

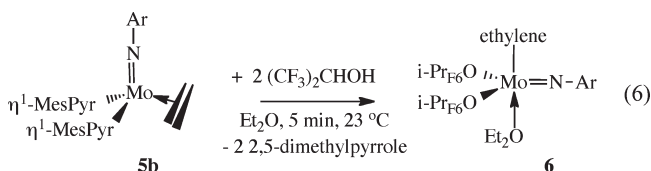
ligands are bound in an η^1 and η^5 manner. The C(1)–C(2) bond length is 1.404(4) Å. The N(1)–Mo(1)–C(1) and N(1)–Mo(1)–C(2) angles (87.32(8)° and 101.17(8)°, respectively) suggest that ethylene is twisted a few degrees from being perpendicular to the Mo–N(1) bond.



In contrast to the failure to prepare **5a** through a reaction between Mo(NAr)(CHCMe₂Ph)(Me₂Pyr)₂ and ethylene, Mo(NAr)(CHCMe₂Ph)(η^1 -MesPyr)₂⁶ (MesPyr = 2-mesitylpyrrolide) reacts cleanly with ethylene in benzene at 60 °C over a period of four days to give Mo(NAr)(CH₂CH₂)(MesPyr)₂ (**5b**) in 71% isolated yield (eq 5). The higher reactivity



of Mo(NAr)(CHCMe₂Ph)(η^1 -MesPyr)₂ toward ethylene can be ascribed to the fact that it is a 14-electron species, in contrast to **5a**. One ethylene carbon resonance was found at 54.2 ppm with $J_{\text{CH}} = 160$ Hz. Proton NMR spectra reveal multiplets at 2.45 and 1.96 ppm for the ethylene protons, consistent with the 2-mesitylpyrrolide ligands in **5b** being bound in an η^1 manner, as found in Mo(NAr)(CHCMe₂Ph)(η^1 -MesPyr)₂.⁶ As a demonstration that **5b** can be employed as a precursor to other bisalkoxide ethylene complexes, **5b** was treated with 2 equiv of HOCH(CF₃)₂ in ether to yield Mo(NAr)(CH₂CH₂)[OCH(CF₃)₂]₂(Et₂O) (**6**) in 41% isolated yield after recrystallization. As judged from the proton NMR spectrum, **6** contains a mirror plane of symmetry on the NMR time scale, the equivalent alkoxides each contain two inequivalent CF₃ groups, and two ethylene proton resonances are observed at 2.64 ppm and 1.83 ppm. An ether adduct of the bishexafluoroisopropoxide imido alkylidene complex is formed as a consequence of the relatively small size of the hexafluoroisopropoxide ligand.^{17,18}



The structure of Mo(NAr)(CH₂CH₂)(O-*i*-PrF₆)₂(Et₂O) is best described as a distorted trigonal bipyramid in which the alkoxide and the imido ligands are in equatorial positions (Figure 3). The sum of the angles between the equatorial ligands is 351.6°, and they are all displaced slightly toward

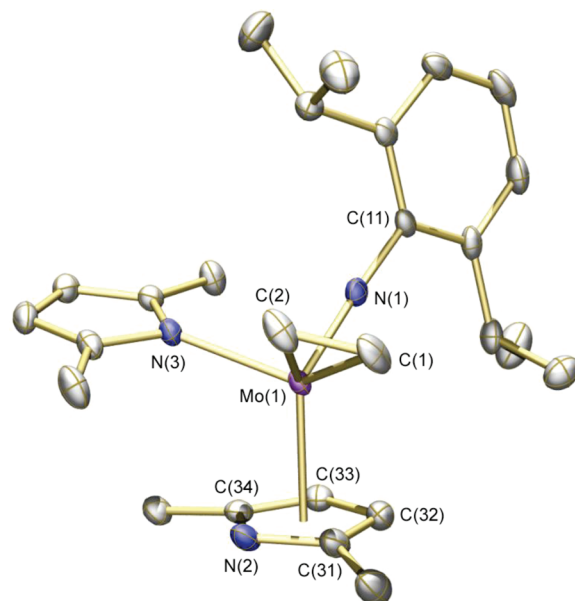


Figure 2. POV-ray drawing of **5a**. Thermal ellipsoids are displayed at 50% probability level. Hydrogen atoms are omitted. Selected distances (Å) and angles (deg): Mo(1)–C(1) = 2.215(2) Å, Mo(1)–C(2) = 2.199(2) Å, Mo(1)–N(1) = 1.7423(17) Å, Mo(1)–N(2) = 2.3785(17) Å, Mo(1)–N(3) = 2.1444(17) Å, C(1)–C(2) = 1.404(4) Å, Mo(1)–C(31) = 2.396(2) Å, Mo(1)–C(32) = 2.407(2) Å, Mo(1)–C(33) = 2.420(2) Å, Mo(1)–C(34) = 2.396(2) Å, Mo(1)–N(1)–C(11) = 174.88(14)°, N(1)–Mo(1)–C(1) = 87.32(8)°, N(1)–Mo(1)–C(2) = 101.17(8)°.

the ether oxygen as a consequence of the long Mo–O_{ether} bond length (2.3071(14) Å) relative to Mo–C_{ethylene} bond lengths (2.181(2) and 2.178(2) Å). The C(1)–C(2) distance is 1.409(3) Å, which is characteristic of other ethylene complexes discussed here. The *trans* relationship of the ether and ethylene might suggest that a five-coordinate intermediate in which (especially large) imido and alkoxide ligands occupy equatorial positions is the most facile mechanism of displacing one two electron ligand by another, including one olefin by another (vide infra). It should be noted that the planar three-coordinate monomeric species, W(N-*t*-Bu)[OSi(*t*-Bu)₃]₂, which is analogous to the central core of **6**, is known.¹⁹

When a sample of **6** in benzene-*d*₆ was degassed and exposed to 1 atm of ¹³C-ethylene, a ¹³C NMR spectrum suggested that a metallacyclopentane complex is formed on the basis of a C_α resonance at 78.54 ppm ($J_{\text{CH}} = 134$ Hz) and a C_β resonance at 39.21 ppm ($J_{\text{CH}} = 127$ Hz). In a proton NMR spectrum employing unlabeled ethylene at room temperature, only broad resonances were observed for the metallacycle and ethylene protons. When all volatile components were removed from the sample the residue was found to consist of **6**. An X-ray structural study of an isolated molybdacyclopentane complex is reported later in this paper.

In the interest of isolating other olefin complexes we treated **2c** with neat styrene. Dry styrene was vacuum transferred to a Schlenk flask charged with solid Mo(NAr)(CH₂CH₂)(Me₂Pyr)(OSiPh₃) (**2c**). Removal of all volatiles in

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(18) Anders, U.; Nuyken, O.; Buchmeiser, M. R.; Wurst, K. *Macromolecules* **2002**, *35*, 9029.

(19) Epley, D. F.; Wolczanski, P. T.; Vanduyne, G. D. *Angew. Chem., Int. Ed.* **1991**, *30*, 584.

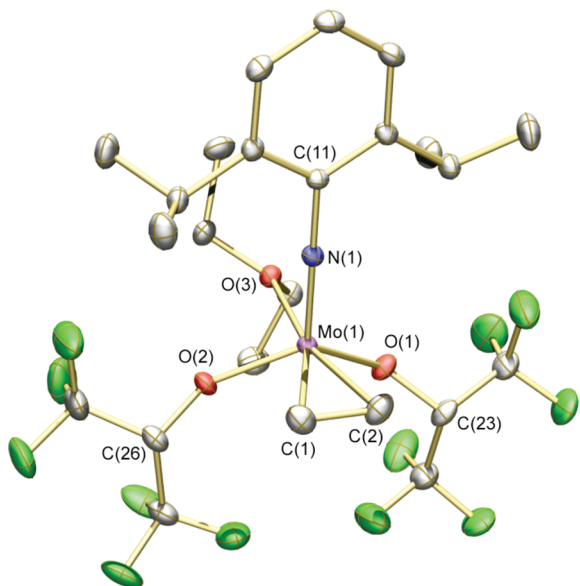
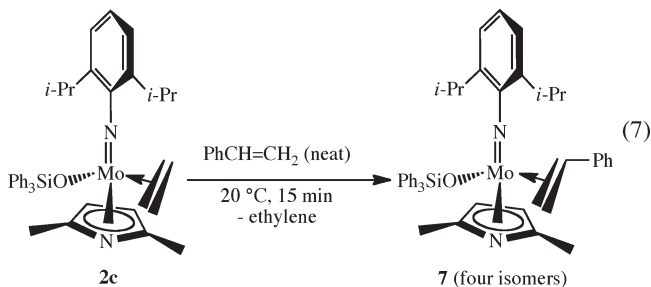


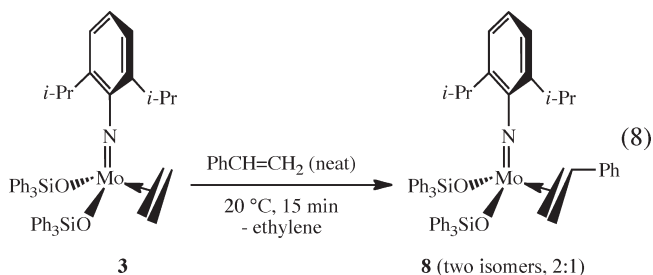
Figure 3. POV-ray drawing of **6**. Thermal ellipsoids are displayed at 50% probability level. Hydrogen atoms are omitted. Selected distances (Å) and angles (deg): Mo(1)–C(1) = 2.181(2) Å, Mo(1)–C(2) = 2.178(2) Å, C(1)–C(2) = 1.409(3) Å, Mo(1)–O(1) = 1.9792(14) Å, Mo(1)–O(2) = 1.9888(14) Å, Mo(1)–O(3) = 2.3071(14) Å, Mo(1)–N(1) = 1.7148(16) Å, Mo(1)–N(1)–C(11) = 178.18(14)°, Mo(1)–O(1)–C(23) = 138.89(13)°, Mo(1)–O(2)–C(26) = 137.50(13)°, O(1)–Mo(1)–O(2) = 118.18(6)°, O(1)–Mo(1)–N(1) = 117.77(7)°, N(1)–Mo(1)–O(2) = 115.60(7)°.

vacuo after 15 min gave a gray residue whose proton NMR spectrum in C_6D_6 suggested that the product, Mo(NAr)(CH₂CHPh)(Me₂Pyr)(OSiPh₃) (**7**), was a mixture of four isomers. Four isomers of **7** can be rationalized in view of the presence of a stereogenic metal center, enantiotopic styrene faces, and no rotation of styrene on the NMR time scale. The major isomer (~30%) displays olefinic proton resonances at 4.23 (t, 1H), 3.08 (dd, 1H), and 2.40 (dd, 1H) ppm. We were not able to obtain a crystalline sample of **7** suitable for an X-ray study.



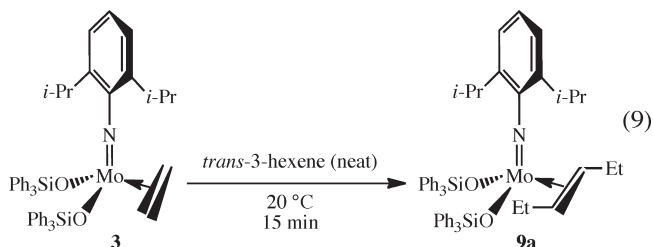
The reaction between purple Mo(NAr)(CH₂CH₂)(OSiPh₃)₂ (**3**) and neat, freshly dried styrene immediately yielded a green solution from which a green product could be obtained upon removal of all volatiles in vacuo. Recrystallization of the residue from pentane yielded green crystals of Mo(NAr)(CH₂CHPh)(OSiPh₃)₂ (**8**, eq 8), the proton NMR spectrum of which in C_6D_6 showed two isomers to be present in the ratio of 2:1. The major isomer displays olefinic proton resonances at 3.58 (t, 1H), 3.28 (dd, 1H), and 2.44 (dd, 1H) ppm for the bound styrene, while olefinic proton resonances for the minor isomer are found at 4.64 (t, 1H), 2.99 (dd, 1H), and 2.26 (dd, 1H) ppm.

Compound **8** also can be prepared by treating Mo(NAr)(CH₂CHPh)(Me₂Pyr)(OSiPh₃) (**7**) with 1 equiv of Ph₃SiOH.



An X-ray structural study of a single crystal of **8** showed it to be the isomer in which the phenyl ring points toward the imido ligand (Figure 4). The styrene is oriented perpendicular to the Mo(1)–N(1) axis (N(1)–Mo(1)–C(1) = 98.49(10)° and N(1)–Mo(1)–C(2) = 98.76(10)°) with C(1)–C(2) = 1.433(4) Å.

A reaction between Mo(NAr)(CH₂CH₂)(OSiPh₃)₂ (**3**) and neat *trans*-3-hexene immediately produced an indigo colored hexene complex (eq 9) whose NMR spectrum in C_6D_6 revealed the presence of 2 isomers in the ratio of 4:1. The major isomer displays two olefinic multiplets between 3.5 and 2 ppm, consistent with the formation of Mo(NAr)(OSiPh₃)₂(*trans*-3-hexene) (**9a**, eq 9). Crystals of **9a** could be obtained through recrystallization of crude **9**. An X-ray structural study of the major isomer reveals it to have the expected structure (Figure 5).



The most logical proposal is for the second isomer of **9** to be Mo(NAr)(*cis*-3-hexene)(OSiPh₃)₂ (**9b**). Treatment of **3** with neat *cis*-3-hexene led to a 1:1 mixture of **9a** and what we propose to be Mo(NAr)(*cis*-3-hexene)(OSiPh₃)₂ (**9b**) on the basis of its mirror symmetry. Over a period of 5 h, the mixture evolved into approximately the same 4:1 mixture of **9a** and **9b** formed upon treatment of **3** with *trans*-3-hexene. Therefore, **9a** and **9b** are in slow equilibrium with the position of that equilibrium being approximately what one would predict on the basis of the relative energies of the free olefins. After 12 h, the ¹H NMR spectrum reveals other olefinic resonances that correspond to the initial resonances in the spectrum of Mo(NAr)(2-hexene)(OSiPh₃)₂, which is prepared independently from **3** and neat *trans*-2-hexene. Therefore, we propose that **9a** and **9b** slowly are converted into a complex mixture that contain Mo(NAr)(*trans*-2-hexene)(OSiPh₃)₂ (**9c**) (2 isomers) and Mo(NAr)(*cis*-2-hexene)(OSiPh₃)₂ (**9d**) (2 isomers). An even more complex mixture (up to eight isomers eventually) is formed when **3** is treated with neat 1-hexene; we propose that Mo(NAr)(1-hexene)(OSiPh₃)₂ forms initially and is then converted into isomers of Mo(NAr)(2-hexene)(OSiPh₃)₂ and Mo(NAr)(3-hexene)(OSiPh₃)₂.

When a sample of **3** in toluene-*d*₈ was degassed and exposed to 1 atm of ethylene, the color changed from purple to red–orange. At 20 °C, two broad resonances were observed at ~3.1 and ~2.5 ppm, which integrate to four

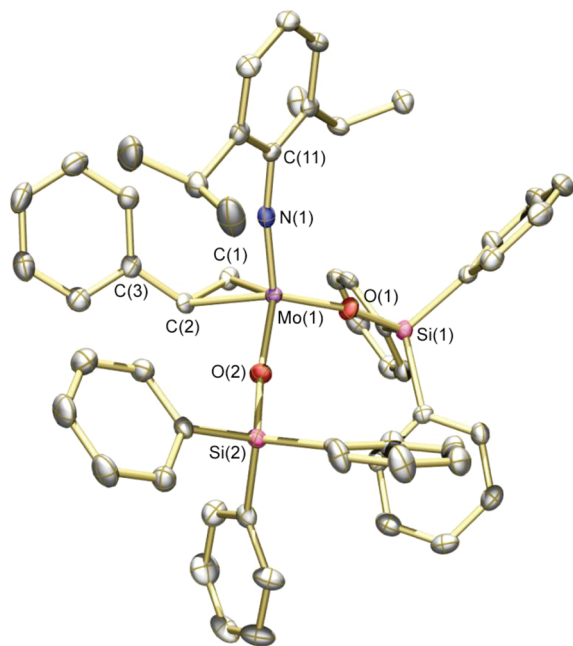


Figure 4. POV-ray drawing of **8**. Thermal ellipsoids are displayed at 50% probability level. Hydrogen atoms are omitted. Selected distances (Å) and angles (deg): Mo(1)–N(1) = 1.738(2) Å, Mo(1)–O(1) = 1.9116(15) Å, Mo(1)–O(2) = 1.9176(16) Å, Mo(1)–C(1) = 2.121(3) Å, Mo(1)–C(2) = 2.159(2) Å, C(1)–C(2) = 1.433(4) Å, Mo(1)–N(1)–C(11) = 169.78(17)°, N(1)–Mo(1)–C(1) = 98.49(10)°, N(1)–Mo(1)–C(2) = 98.76(9)°.

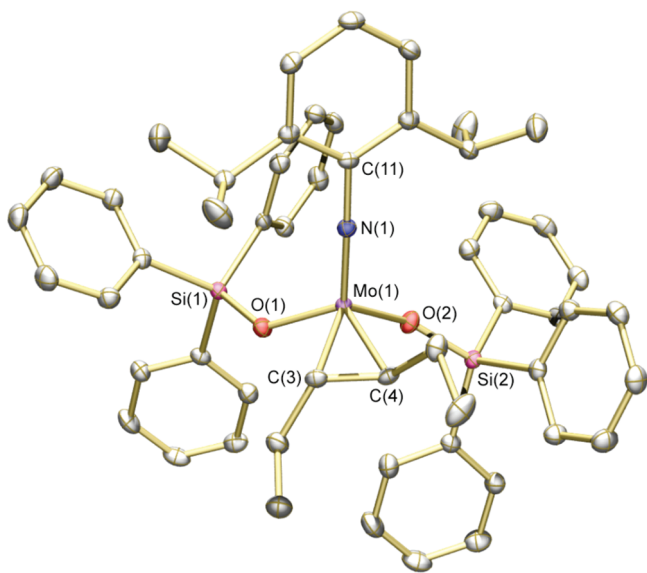
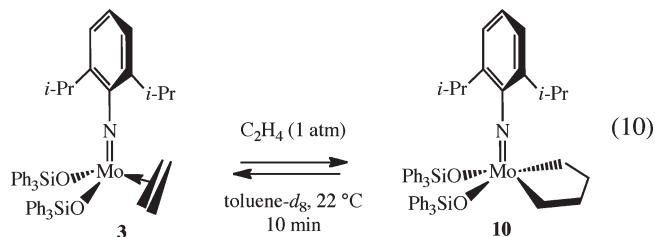


Figure 5. POV-ray drawing of **9a**. Thermal ellipsoids are displayed at 50% probability level. Hydrogen atoms are omitted. Selected distances (Å) and angles (deg): Mo(1)–N(1) = 1.7337(13) Å, Mo(1)–O(1) = 1.9381(11) Å, Mo(1)–O(2) = 1.9197(11) Å, Mo(1)–C(3) = 2.1509(15) Å, Mo(1)–C(4) = 2.1350(15) Å, C(3)–C(4) = 1.440(2) Å, Mo(1)–N(1)–C(11) = 174.15(11)°, N(1)–Mo(1)–C(3) = 98.17(6)°, N(1)–Mo(1)–C(4) = 97.88(6)°.

protons each (Figure 6). At -20 °C, four resonances are observed at 3.11, 3.06, 2.58, and 2.41 ppm integrating as two protons each, consistent with formation of the metallacyclopentane species, Mo(NAr)(C₄H₈)(OSiPh₃)₂ (**10**) (eq 10). When

3 was exposed to ¹³C-ethylene (~0.5 atm) at 20 °C, two resonances are observed in the ¹³C NMR spectrum at 72.4 and 37.5 ppm that can be assigned to C_α and C_β, respectively, along with a resonance for the ¹³C-labeled ethylene complex (at 55.2 ppm). Although ethylene exchange is facile on the chemical time scale, this exchange is not rapid on the NMR time scale because a small amount of **3** can be observed throughout the temperature range shown in Figure 6. It appears that the fluxional process shown in Figure 6 leads to equilibration of the two types of CH_α resonances (“upper” and “lower”) and the two types of CH_β resonances (“upper” and “lower”) but *not* to interconversion of CH_α and CH_β resonances or equilibration of **10** with **3** on the NMR time scale. Compound **10** clearly must



form from an intermediate bis ethylene complex in which the ethylenes are approximately *cis* to one another, perhaps through rearrangement of an initial species that has some other structure, even an initial TBP species that contains ethylenes *trans* to one another. The fluxional process observed for **10** is proposed to consist of a five-coordinate rearrangement of either the intact metallacyclopentane or a Mo(VI) alkenyl hydride species formed from the metallacyclopentane through reversible β hydride elimination. The fact that CH_α and CH_β resonances do not exchange eliminates the possibility of formation of a bisethylene species in which one or both ethylenes can rotate about the Mo–(ethylene) bond axis. The fluxional process has been investigated by line-shape analyses of the β -protons (see Supporting Information). The activation parameters for the exchange of the β -protons were obtained from the Eyring plot: $\Delta H^\ddagger = 18.0(0.3)$ kcal/mol and $\Delta S^\ddagger = 15.6(1.2)$ eu. The large and positive entropy of activation is consistent with significant disorder in the transition state and therefore would favor formation of an alkenyl hydride intermediate.

X-ray quality crystals of **10** were grown from a pentane:toluene (10:1) solution of **10** at -35 °C under 1 atm of ethylene. A drawing of the structure of **10** is shown in Figure 7. Complex **10** has an approximate square pyramidal coordination geometry, with the imido ligand occupying the apical position. It is similar to the structure of a molybdacyclopentane reported by Boncella.²⁰ The Mo(1)–C(1) and Mo(1)–C(4) bonds (2.176(3) and 2.200(3) Å) are typical of Mo–C single bonds and the C(1)–C(2), C(2)–C(3), and C(3)–C(4) bond lengths (1.513(5), 1.526(5), and 1.524(5) Å, respectively) are typical of C–C single bonds.

When a sample of Mo(NAr)(CHCMe₂Ph)(OSiPh₃)₂²¹ in toluene-*d*₈ was degassed and exposed to 1 atm of ethylene, four broad peaks were observed at 3.38, 2.86, 2.23, and 1.24 ppm in the ratio of 1:1:2:2 (see Supporting Information), consistent with the formation of the square pyramidal

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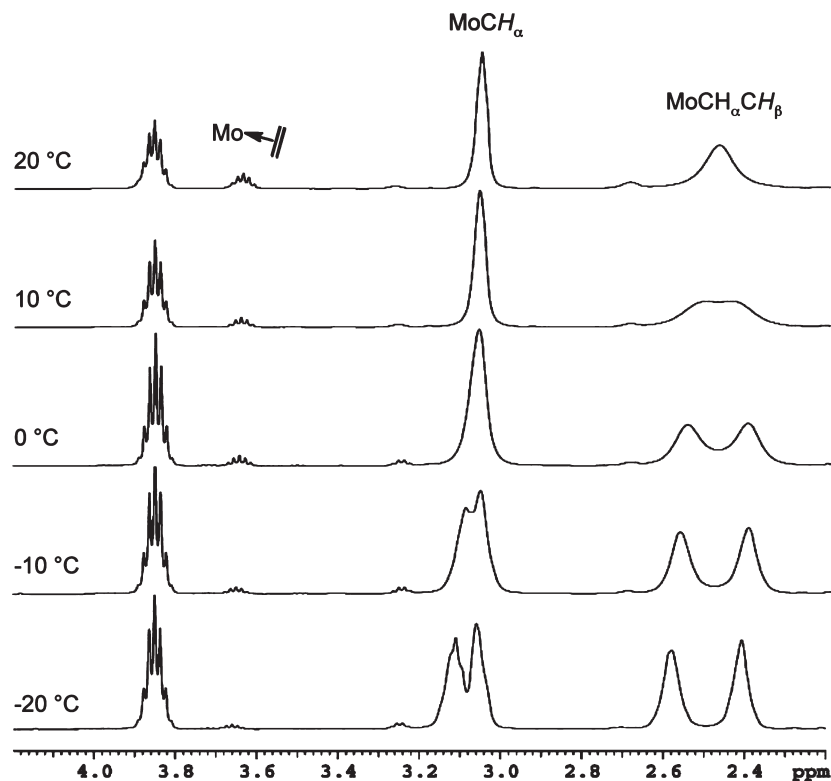


Figure 6. Variable-temperature ^1H NMR spectroscopic studies of $\text{Mo}(\text{NAr})(\text{OSiPh}_3)_2(\text{C}_4\text{H}_8)$ (**10**) in toluene- d_8 under 1 atm of ethylene.

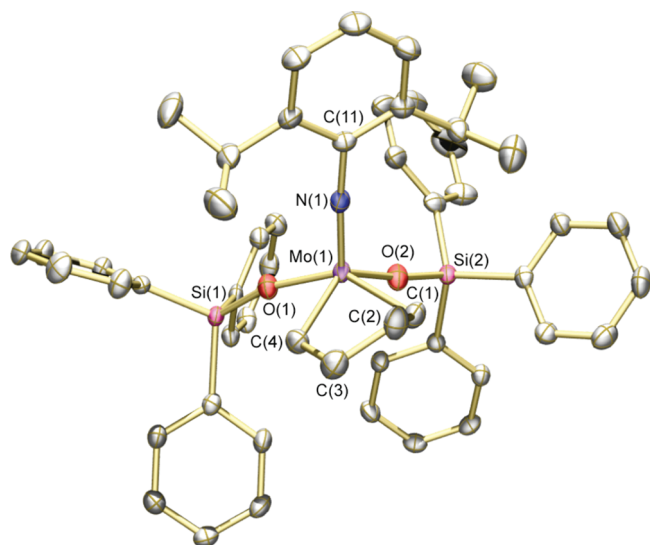
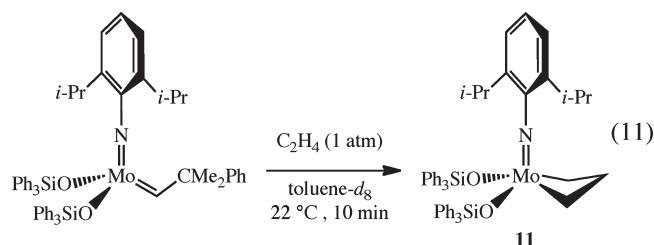


Figure 7. POV-ray drawing of **10**. Thermal ellipsoids are displayed at 50% probability level. Hydrogen atoms are omitted. Selected distances (Å) and angles (deg): Mo(1)–N(1) = 1.719(2) Å, Mo(1)–O(1) = 1.911(2) Å, Mo(1)–O(2) = 1.880(2) Å, Mo(1)–C(1) = 2.176(3) Å, Mo(1)–C(4) = 2.200(3) Å, C(1)–C(2) = 1.513(5) Å, C(2)–C(3) = 1.526(5) Å, C(3)–C(4) = 1.524(5) Å, Mo(1)–N(1)–C(11) = 175.2(2)°, C(1)–Mo(1)–C(4) = 71.86(13)°.

molybdacyclobutane species, $\text{Mo}(\text{NAr})(\text{C}_3\text{H}_6)(\text{OSiPh}_3)_2$ (**11**) (eq 11). When $\text{Mo}(\text{NAr})(\text{CHCMe}_2\text{Ph})(\text{OSiPh}_3)_2$ was exposed to ^{13}C -ethylene (~ 0.5 atm) at 20 °C, two doublet resonances were observed in the ^{13}C NMR spectrum at 37.6 ppm ($J_{\text{CC}} = 33$ Hz, $J_{\text{CH}} = 138$ Hz) and 27.8 ppm ($J_{\text{CC}} = 33$ Hz, $J_{\text{CH}} = 132$ Hz), corresponding to C_α and C_β ,

respectively, in a square pyramidal metallacyclobutane species.²² Although **11** can be isolated, after 1 day at room temperature $\text{Mo}(\text{NAr})(\text{CH}_2\text{CH}_2)(\text{OSiPh}_3)_2$ (**3**) and $\text{Mo}(\text{NAr})(\text{C}_4\text{H}_8)(\text{OSiPh}_3)_2$ (**10**) are also found in a solution of **11** as a consequence of decomposition of unobserved $\text{Mo}(\text{NAr})(\text{CH}_2)(\text{OSiPh}_3)_2$.



Olefin exchange and double bond isomerization would suggest that linear olefins can be isomerized catalytically. In fact, treatment of **2c** with 20 equiv of 1-decene in C_6D_6 (15 mM) at room temperature led to resonances near 5.5 ppm characteristic of internal olefins. Upon heating the sample for a period of two days at 85 °C, the 1-decene was converted almost completely to internal olefins according to ^1H NMR spectroscopic studies shown in Figure 8.

When **6** was treated with 20 equiv of 1-hexene in C_6D_6 , trace amounts of internal olefins were observed after 20 min at room temperature. After one day at 22 °C, the sample contained 52% internal olefins. At 60 °C over a period of

(22) (a) Feldman, J.; Davis, W. M.; Schrock, R. R. *Organometallics* **1989**, *8*, 2266. (b) Feldman, J.; Davis, W. M.; Thomas, J. K.; Schrock, R. R. *Organometallics* **1990**, *9*, 2535. (c) Feldman, J.; Schrock, R. R. *Prog. Inorg. Chem.* **1991**, *39*, 1. (d) Bazan, G. C.; Oskam, J. H.; Cho, H.-N.; Park, L. Y.; Schrock, R. R. *J. Am. Chem. Soc.* **1991**, *113*, 6899.

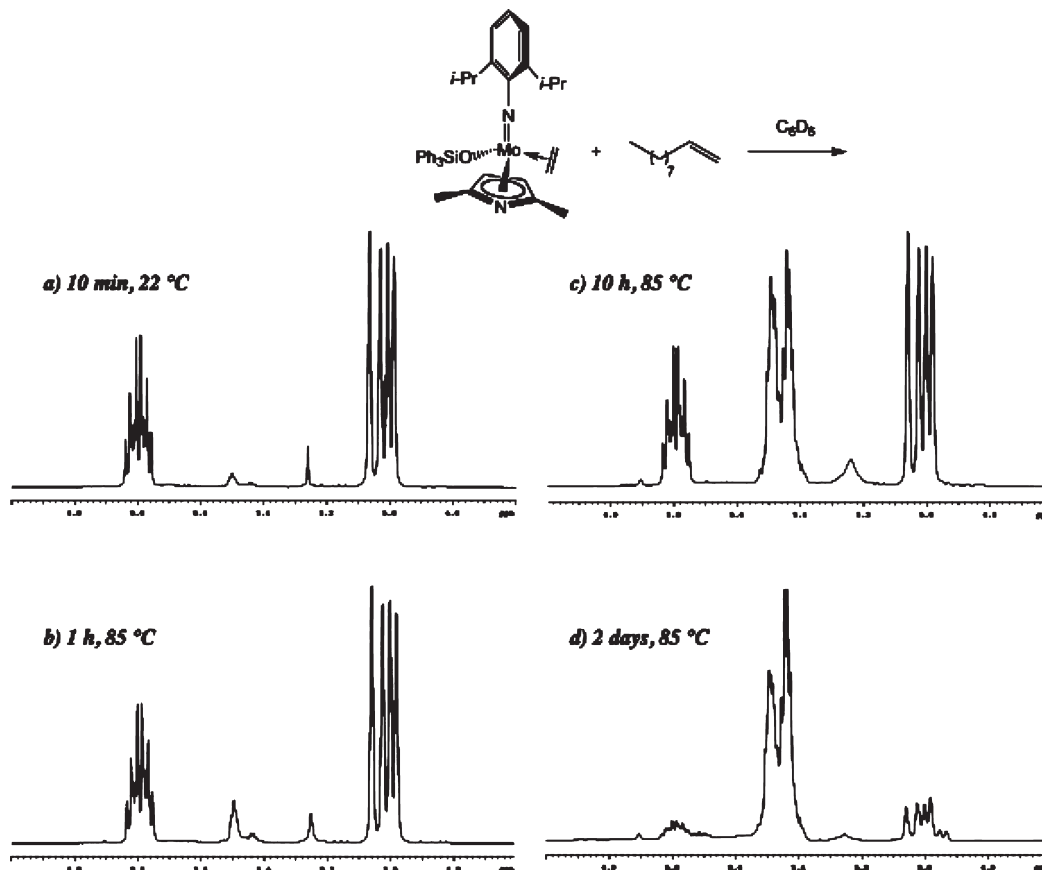


Figure 8. ^1H NMR spectroscopic studies to monitor the reaction between $\text{Mo}(\text{NAr})(\text{CH}_2\text{CH}_2)(\text{Me}_2\text{Pyr})(\text{OSiPh}_3)$ (**2c**) (5 mol %) and 1-decene.

24 h, the amount of internal olefins increased to 85% of the mixture, according to NMR spectra similar to those shown in Figure 8. A GC-mass spectrum of the reaction mixture revealed the presence of C_7H_{14} , C_8H_{16} , C_9H_{18} , $\text{C}_{10}\text{H}_{20}$, $\text{C}_{11}\text{H}_{22}$, and $\text{C}_{12}\text{H}_{24}$ species. The shorter chains (C_7 and C_8) clearly consist of more than one isomer. When the reaction between **6** and 1-hexene was attempted in diethyl ether under similar conditions, no internal olefins were found after one day. This experiment suggests that diethyl ether blocks any reaction that produces internal olefins. When **6** in C_6D_6 was treated with *trans*-3-hexene under similar conditions to those employed for 1-hexene, ^1H NMR and GCMS results were analogous to those observed for reactions involving 1-hexene.

When **6** was treated with 20 equiv of 1-octene, conversion to 90% internal olefins was observed after heating the reaction mixture to 100 °C for 18 h. When a similar experiment was carried out in ether, no internal olefins were observed. A GC-mass spectrum of the internal olefins (Figure 9a) revealed that olefins from C_8H_{16} to $\text{C}_{20}\text{H}_{40}$ are present, with C_{13} and C_{14} being the most abundant; chains longer than C_{15} constitute a relatively small portion of the mixture. Hydrogenation of the olefins in this mixture (Pd/C catalyst; Figure 9b) converted all olefin isomers to a single linear alkane, which suggests that all internal olefins are linear. A GC-mass spectrum of a standard of linear alkanes C_8H_{18} to $\text{C}_{14}\text{H}_{30}$ matched the GC-mass spectrum obtained for the hydrogenated mixture in retention time, peak shape, and fragmentation patterns for each alkane.

Mixtures of linear olefins most likely form through metathesis reactions. When **9** was treated with 1 atm of ethylene,

the molybdacyclopentane species **10** was observed immediately, along with free *trans*-3-hexene. After 2 weeks at room temperature, 1-butene was observed in the ^1H NMR spectrum of the reaction mixture. When ^{13}C -ethylene was employed, a singlet at 113.4 ppm for $^{13}\text{CH}_2=\text{CHCH}_2\text{CH}_3$ was observed in the ^{13}C NMR spectrum of the reaction mixture, consistent with its formation through a metathesis reaction of *trans*-3-hexene with $^{13}\text{CH}_2^{13}\text{CH}_2$. After another week at room temperature, $^{13}\text{CH}_2=\text{CHCH}_3$ (115.9 ppm), $^{13}\text{CH}_3\text{CH}=\text{CHCH}_3$, and $^{13}\text{CH}_2=\text{CH}^{13}\text{CH}_3$ (19.3 and 18.0 ppm) were observed in the reaction mixture, all of which are consistent with isomerization of 1-butene to 2-butene, followed by reaction of 2-butene with $^{13}\text{CH}_2^{13}\text{CH}_2$. All observations are consistent with very slow metathesis of olefins over a period of weeks.

A benzene solution of **6** was placed under 1 atm of $\text{CD}_3\text{CH}=\text{CH}_2$, and the sample was heated to 60 °C for 1 day. A ^2H NMR spectrum (Figure 10) showed resonances at 4.8 and 5.8 ppm, consistent with scrambling of deuterium into all three propylene sites through a process that must involve more than reversible CH or CD activation of $\text{CD}_3\text{CH}=\text{CH}_2$ to give allyl intermediates. (See Discussion Section.)

When **6** was treated with 100 equiv of cyclooctene in C_6D_6 , polycyclooctene was formed and could be isolated in 38% yield after 24 h through precipitation with methanol. The polycyclooctene sample contained 88% *trans* double bonds according to ^{13}C NMR spectra.

Discussion

It is clear from the work reported here that molybdenum ethylene complexes can be the product of “reduction” of the

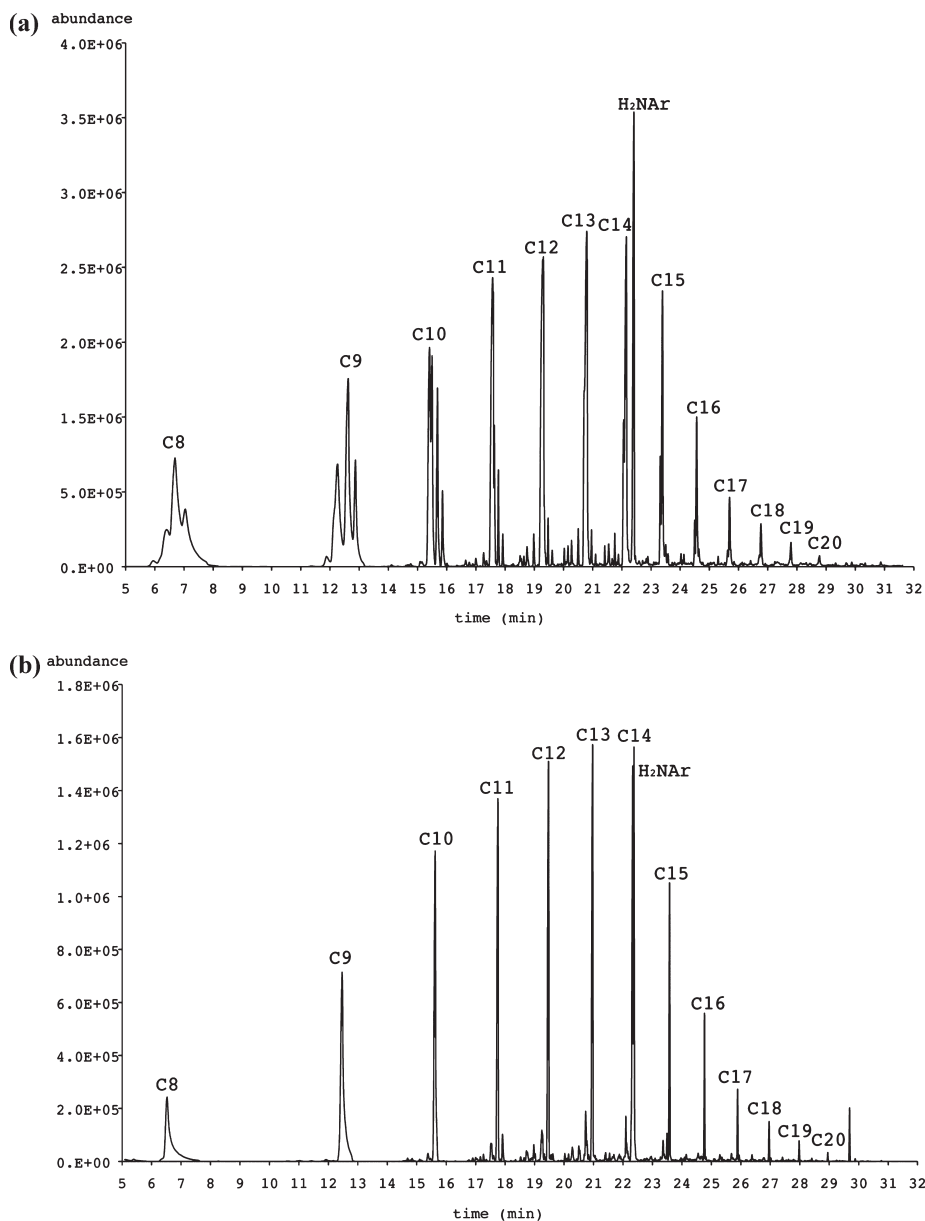
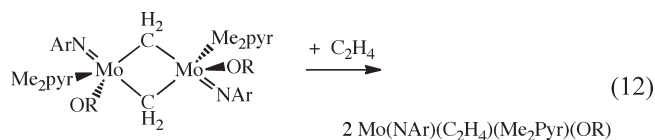


Figure 9. Reaction of 20 equiv of 1-octene with $\text{Mo}(\text{NAr})(\text{CH}_2\text{CH}_2)[\text{OCH}(\text{CF}_3)_2]_2(\text{Et}_2\text{O})$ after one day at 100 °C. (a) GC trace of the reaction mixture prior to hydrogenation. (b) GC trace of the reaction mixture after hydrogenation.

metal upon exposure of MAP species, or bisalkoxides, to ethylene. These results are similar to what has been observed in solution in Mo or W biphenolate or binaphtholate systems.^{3,4,5} The two most likely mechanisms for reduction are rearrangement of a molybdacyclobutane complex to an olefin (e.g., rearrangement of the unsubstituted metallacyclobutane to propylene) or bimolecular coupling of methylenide species. Both experimental³ and theoretical evidence (for high oxidation state Re, Mo, and W systems on silica^{10,23}) suggest that ethylene assists metallacycle rearrangement. Calculations suggest that the mechanism consists of ethylene accepting a β hydride from the metallacyclobutane ring and donating it back to an α carbon of the allyl intermediate. Because bis- μ -methylidene species and a bis- μ -ethylene species have been structurally characterized in one high

oxidation state tungsten system,⁵ formation of the final ethylene complex is likely to involve ethylene attack on the bis- μ -ethylene



species to give 2 equiv of the ethylene species (eq 12) rather than formation of 1 equiv of the ethylene species and a high energy three-coordinate intermediate that is then captured by ethylene. Restricting ethylene from the coordination sphere at the point where it is required for the last step (shown in eq 12) could be one of the reasons why MAP methylidene species that contain relatively bulky aryloxides are relatively stable toward decomposition reactions and lead to long-lived methylidene complexes and long-lived catalysts in the presence of ethylene.^{9g}

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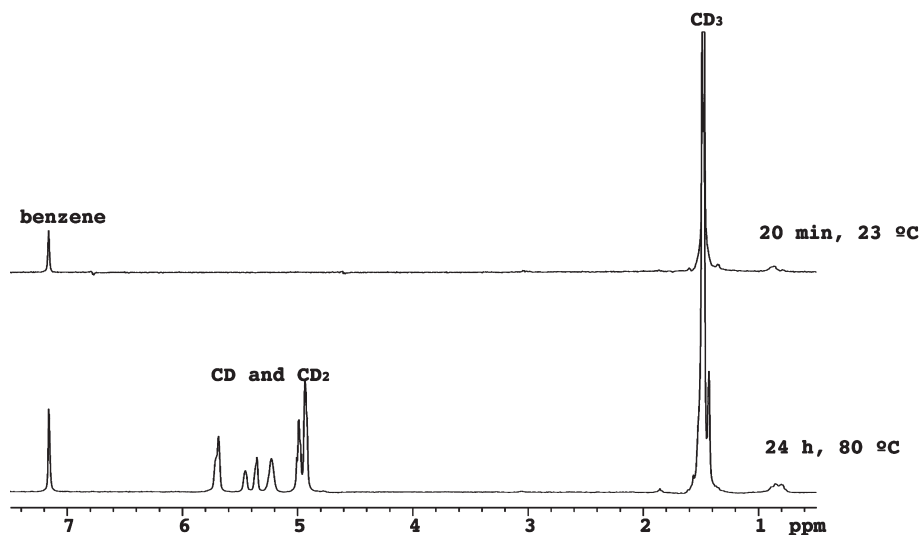
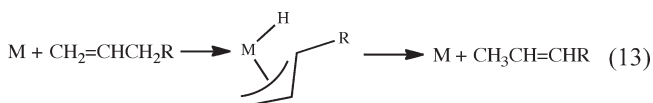


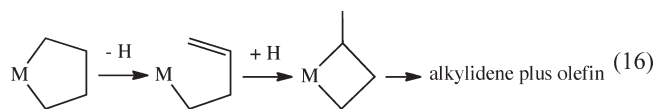
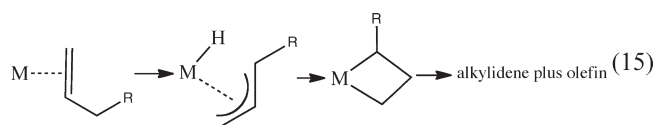
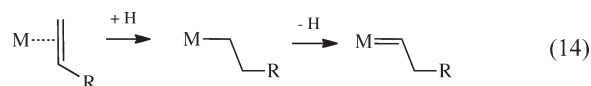
Figure 10. ^2H NMR spectrum of $\text{Mo}(\text{NAr})(\text{CH}_2\text{CH}_2)[\text{OCH}(\text{CF}_3)_2](\text{Et}_2\text{O})$ in benzene under 1 atm of $\text{CD}_3\text{CH}(\text{CH}_2)$. From left to right: 7.16 (benzene), 5.69 (1 H), 5.45 (0.33 H), 5.35 (0.46 H), 5.23 (0.71 H), 4.99 (1.05 H), 4.93 (1.45 H), 1.47 (7.68 H), 1.43 (1.21 H), 0.85 (0.41 H).

Other important findings reported here include facile catalytic isomerization of olefins. We propose that olefins are isomerized via allylic CH activation to give an allyl intermediate (σ or π). However, it is not necessarily true that the H is transferred to the metal, as shown in eq 13. Another possibility is for H to be transferred to the imido nitrogen to yield an intermediate $\text{Mo}(\text{IV})$ allyl *amido* species. However, for the purposes of discussion, we will choose the proposal shown in eq 13. This oxidative addition mechanism of isomerizing olefins is one of the classic methods that has been documented for decades.²⁴



An important question is how an alkyldiene, albeit only traces of it, is formed. Some of the leading candidates for forming an alkyldiene from an ordinary olefin at a single metal center include addition of H from an external or internal source (e.g., through CH activation in a ligand) to the olefin to give an alkyl followed by α abstraction of H from the alkyl, e.g., as shown in eq 14.^{14–16} (For convenience, the “+H” and “–H” nomenclature is meant to encompass reactions that involve $\text{M}-\text{H}$ species and other possible mechanistic variations, e.g., transfer of H to and from another ligand through CH activations, etc.) A second possible general mechanism of forming an alkyldiene is to form an allyl hydride complex followed by a metallacyclobutane ring; an example is shown in eq 15. Formation of a metallacyclobutane could be an alternative consequence of formation of an olefin isomer from an allyl hydride intermediate (eq 13). The third possibility is to form and contract a metallacyclopentane ring to a metallacyclobutane ring and then lose an olefin to form an alkyldiene, e.g., as shown in eq 16.^{25,26} Unfortunately, we have not been able to think of a means of determining exactly which process is (or processes

are) responsible for formation of alkyldienes in the systems reported here or confirming that they are imido alkyldienes.



The results presented here are related to others we have uncovered in which $\text{Mo}(\text{IV})$ or $\text{W}(\text{IV})$ compounds slowly catalyze typical metathesis reactions. As mentioned in the Introduction, one is a homologation of a vinyl tin species to an allyl tin species in the presence of ethylene and $\text{Mo}(\text{NAr})(\text{CH}_2\text{CH}_2)(\text{Biphen})$ ⁷ as a catalyst. A mechanism was proposed that involved contraction of a “mixed” metallacyclopentane ring containing ethylene and the vinyl tin species to a metallacyclobutane ring. Complexes that contain an unsupported $\text{M}=\text{M}$ double bond ($\text{M} = \text{Mo}$ or W) such as $[\text{Mo}(\text{NAr})(\text{CH}_2-t\text{-Bu})(\text{OC}_6\text{F}_5)_2]$ ($\text{Ar} = 2,6-i\text{-Pr}_2\text{C}_6\text{H}_3$) or $\{\text{W}(\text{NAr}')[\text{OCMe}_2(\text{CF}_3)_2]_2\}$ ($\text{Ar}' = 2,6-\text{Me}_2\text{C}_6\text{H}_3$) also will slowly catalyze olefin metathesis reactions.⁸ However, it was estimated that only a relatively small amount ($\sim 2\%$) of the $\text{M}=\text{M}$ species was “activated” by the olefin. Finally, an ethylene complex mentioned earlier in this paper, $\text{Mo}(\text{N}-2,6-\text{Cl}_2\text{C}_6\text{H}_3)(\text{CH}_2\text{CH}_2)(\text{rac-Biphen})(\text{ether})$, is inactive for ring-closing of diallyl ether over a period of 10 days at 22°C , but when 10 equiv of norbornene were added to a benzene solution of 5 mol % $\text{Mo}(\text{NAr}^{\text{Cl}})(\text{CH}_2\text{CH}_2)(\text{rac-Biphen})(\text{ether})$ and diallyl ether, a 56% yield of 2,4-dihydrofuran was obtained in 10 days.

(24) *Organotransition Metal Chemistry: From Bonding to Catalysis*; Hartwig, J., Ed.; University Science Books: Sausalito, CA, 2010.

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The results reported here also suggest that formation of Mo(IV) species as products of decomposition of metathesis catalysts could lead to isomerization of double bonds in metathesis substrates or products. Fortunately, metathesis usually is several orders of magnitude faster than olefin isomerization. Yet there may be some circumstances in which “reformation” of alkylidenes from olefins contributes to catalyst activity over the long-term, e.g., “alkane metathesis,” which is usually carried out at temperatures of 125° or more.²⁷ Eventually, however, decomposition processes that involve destruction of the basic structure of an imido alkylidene catalyst will lead to irreversible loss of metathesis activity.

Conclusions

All of our observations suggest that (i) olefin complexes of the type M(NAr)(X)(Y)(olefin) can form readily, (ii) exchange of olefins at Mo(IV) centers is facile, (iii) isomerization of olefins at Mo(IV) centers is facile, and (iv) traces of metathesis catalysts are formed. We propose that the metathesis catalysts are of the type M(NAr)(X)(Y)(alkylidene) but that the amounts present are in the undetectable range (< 1%).

Experimental Section

General synthetic procedures can be found in earlier papers that concern MAP catalysts.⁹ Compounds **1a** and **1b** were prepared as described in the literature.^{9a}

Mo(NAr)(CHCMe₂Ph)(2,5-Me₂NC₄H₂)(OSiPh₃) (1c). A cold solution of Ph₃SiOH (149 mg, 0.54 mmol, 1 equiv) in 5 mL of diethyl ether was added dropwise to a cold solution of Mo(NAr)-(CHCMe₂Ph)(2,5-Me₂NC₄H₂)₂ (319 mg, 0.54 mmol, 1 equiv) in 5 mL of diethyl ether. The reaction mixture was stirred at room temperature for 30 min, and the volatile components were removed in vacuo. The resulting orange solid was recrystallized from diethyl ether to give 259 mg of orange crystals; yield 62%. ¹H NMR (500 MHz, CD₂Cl₂) δ 11.85 (s, 1H, *syn* Mo=CH, *J*_{CH} = 120.4 Hz), 7.54–7.08 (m, 23H, *Ar*), 5.79 (s, 2H, NC₄H₂), 3.72 (sept, 2H, MeCHMe, *J* = 7.0 Hz), 2.11 (s, 6H, CH₃), 1.62 (s, 3H, CH₃), 1.52 (s, 3H, CH₃), 1.06 (app d, 6H, MeCHMe), 0.96 (br, 6H, MeCHMe). ¹³C NMR (125 MHz, CD₂Cl₂) δ 286.7, 153.4, 148.6, 147.5, 136.4, 135.7, 135.5, 130.6, 130.4, 128.6, 128.4, 126.5, 126.3, 123.5, 109.7, 108.9, 108.1, 54.9, 31.9, 30.6, 30.4, 29.1, 23.8 (br), 17.3 (br). Anal. Calcd for C₄₆H₅₂MoN₂OSi: C, 71.48; H, 6.78; N, 3.62. Found: C, 71.44; H, 6.69; N, 3.75.

Mo(NAr)(CH₂CH₂)(OAr)(2,5-Me₂NC₄H₂) (2a). A Schlenk flask was charged with Mo(NAr)(CHCMe₂Ph)(OAr)(2,5-Me₂NC₄H₂) (60 mg, 0.090 mmol), a stir bar, and 2 mL of heptane. The solution was degassed by freeze–pump–thawing the solution (3 times), and 1 atm of ethylene was introduced. The reaction was stirred at room temperature for 15 min and set aside at –30 °C for 12 h. Removal of the volatiles in vacuo followed by addition of pentane to the residue afforded a dark-red precipitate of the product; yield 31 mg, 59%. ¹H NMR (300 MHz, C₆D₆) δ 7.22 (d, 2, *Ar*), 7.02 (t, 1, *Ar*), 6.89 (s, 3, *Ar*), 5.78 (br, 2, *Pyr*), 3.57 (sept, 2, CHMe₂), 3.25 (br, 2, CHMe₂), 2.95 (m, 2, ethylene), 2.60 (m, 1, ethylene), 2.16 (s, 6, Pyr_{Me}), 1.95 (m, 1, ethylene), 1.25–1.13 (m, 24, CHMe₂). ¹³C NMR (125 MHz, C₆D₆) δ 163.84, 155.02, 143.74, 139.41, 128.68, 128.40, 128.30, 127.22, 123.96, 123.75, 120.77, 107.65, 60.24, 56.29, 28.39, 25.97, 25.18, 24.70, 24.57, 16.02. Experiments employing ¹³C₂H₄ revealed

the resonances at 60.24 ppm and 56.29 ppm to be those for ethylene carbons (*J*_{CH} = 155 Hz and *J*_{CC} = 39 Hz). Anal. Calcd for C₃₂H₄₆MoN₂O: C, 67.35; H, 8.12; N, 4.91. Found: C, 67.56; H, 8.11; N, 4.97.

Mo(NAr)(CH₂CH₂)(OCCMe(CF₃)₂)(2,5-Me₂NC₄H₂) (2b). Compound **2b** was prepared in a manner analogous to **2a** by treating Mo(NAr)(CHCMe₂Ph)(OCMe(CF₃)₂)(2,5-Me₂NC₄H₂) (235 mg, 0.347 mmol) with ethylene in heptane. The complex was crystallized from pentane at –30 °C as dark-red crystals; yield 123 mg, 57%. ¹H NMR (300 MHz, C₆D₆) δ 6.19–6.81 (m, 3, *Ar*), 5.51 (br, 2, *Pyr*), 3.48 (sept, 2, CHMe₂), 2.77 (m, 2, ethylene), 2.45 (m, 1, ethylene), 2.16 (m, 1, ethylene), 2.10 (s, 6, Pyr_{Me}), 1.65 (s, 3, OMe), 1.10 (d, 6, CHMe₂), 1.06 (d, 6, CHMe₂). ¹⁹F NMR (282 MHz, C₆D₆) δ –75.20, –77.80. ¹³C NMR (125 MHz, C₆D₆) δ 154.24, 145.74, 128.68, 128.27, 123.79, 110.15, 105.39, 56.34, 54.12, 28.09, 25.35, 23.62, 20.37, 16.26. Anal. Calcd for C₂₄H₃₂F₆MoN₂O: C, 50.18; H, 5.61; N, 4.88. Found: C, 50.26; H, 5.31; N, 4.67.

Mo(NAr)(CH₂CH₂)(2,5-Me₂NC₄H₂)(OSiPh₃) (2c). Compound **2c** was prepared in a manner analogous to **2b** by treating Mo(NAr)(CHCMe₂Ph)(2,5-Me₂NC₄H₂)(OSiPh₃) (250 mg, 0.32 mmol) with ethylene in 5 mL of diethylether. The dark-red precipitate was collected and recrystallized from diethylether; yield 150 mg, 70%. ¹H NMR (500 MHz, C₆D₆) δ 7.89 (dd, 6H, *Ar*, *J* = 7.5 Hz, 2.0 Hz), 7.24–7.14 (m, 9H, *Ar*), 6.94–6.83 (m, 3H, *Ar*), 5.00–6.00 (br, 2H, NC₄H₂), 3.71 (sept, 2H, MeCHMe, *J* = 6.5 Hz), 2.87 (m, 1H, C₂H₄), 2.70 (m, 1H, C₂H₄), 2.20 (m, 2H, C₂H₄), 2.11 (br s, 6H, CH₃), 1.10 (d, 6H, MeCHMe, *J* = 7.0 Hz), 1.00 (d, 6H, MeCHMe, *J* = 7.0 Hz). ¹³C NMR (125 MHz, C₆D₆) δ 153.8, 145.8, 141.3, 136.3, 135.9, 129.5, 128.7, 128.1, 127.9, 57.9, 56.8, 28.3, 25.6, 23.2, 17.0. Experiments employing ¹³C₂H₄ revealed ethylene carbon resonances at 56.8 and 57.9 ppm (*J*_{CH} = 153 Hz and *J*_{CC} = 37 Hz). Anal. Calcd for C₃₈H₄₄MoN₂OSi: C, 68.24; H, 6.63; N, 4.19. Found: C, 68.18; H, 6.60; N, 3.84.

Mo(NAr)(CH₂CH₂)(OSiPh₃)₂ (3). Mo(NAr)(CH₂CH₂)(2,5-Me₂NC₄H₂)(OSiPh₃) (25.6 mg, 0.038 mmol, 1 equiv) and Ph₃SiOH (10.6 mg, 0.038, 1 equiv) were transferred to a 20 mL vial equipped with a magnetic stir bar. Pentane (7 mL) and diethyl ether (0.1 mL) were added. The color of the reaction mixture changed from red to purple. The reaction mixture was stirred at room temperature until triphenylsiloxide was completely consumed. The reaction mixture was stored at –35 °C, and 20 mg of purple crystals were obtained; yield = 61%. ¹H NMR (500 MHz, C₆D₆) δ 7.77 (d, 12H, *Ar*), 7.20–7.10 (m, 18H, *Ar*), 6.98–6.89 (m, 3H, *Ar*), 3.69 (sept, 2H, MeCHMe, *J* = 6.9 Hz), 2.74 (app q, 2H, C₂H₄, *J* = 6.2 Hz, 5.6 Hz), 1.99 (app q, 2H, C₂H₄, *J* = 6.2 Hz, 5.6 Hz), 1.00 (d, 12H, Me₂CHMe₂, *J* = 7.0 Hz). ¹³C NMR (125 MHz, C₆D₆) δ 154.6, 146.7, 137.6, 135.9, 130.3, 128.5, 123.4, 55.2, 29.7, 24.0. Experiments employing ¹³C₂H₄ revealed the resonance at 55.2 ppm to be that for ethylene carbons (*J*_{CH} = 155 Hz). Anal. Calcd for C₅₀H₅₁MoN₂O₂Si₂: C, 70.65; H, 6.05; N, 1.65. Found: C, 70.61; H, 6.14; N, 1.86.

Mo(NAr)(CH₂CH₂)(OTf)₂(dme) (4a). Ethylene (60 psi) was added to a solution of Mo(NAr)(CHCMe₂Ph)(OTf)₂(dme) (0.800 g, 1.1 mmol) in 10 mL of toluene. The reaction mixture was heated to 80 °C for two days under a 60 psi of ethylene. Red crystals (0.646 g, yield = 86%) were isolated directly from the reaction via filtration. The product is a mixture of *cis* and *trans* isomers in the ratio of ~2:1, as determined by ¹H and ¹⁹F NMR spectroscopy studies. ¹H NMR (500 MHz, C₆D₆) *cis*-**4** (selected resonances) δ 3.93–3.84 (m, 1H), 3.82–3.73 (m, 1H), 3.53 (s, 3H, OMe), 3.35 (s, 3H, OMe), 1.15 (d, 6H, Me₂CHMe₂, *J* = 7.0 Hz), 0.98 (d, 6H, Me₂CHMe₂, *J* = 7.0 Hz). ¹H NMR (500 MHz, C₆D₆) *trans*-**4** (selected resonances) δ 3.08 (s, 3H, OMe), 2.95 (s, 3H, OMe), 1.26 (d, 12H, Me₂CHMe₂, *J* = 7.0 Hz). ¹³C NMR (125 MHz, C₆D₆) δ 151.0, 139.4, 124.7, 124.3, 77.4, 72.3, 70.7, 70.2, 69.2, 64.2, 63.1, 28.6, 25.4, 24.9, 23.7. ¹⁹F NMR (282 MHz, C₆D₆) δ –78.3, –78.3, –78.6. Anal. Calcd for C₂₀H₃₁F₆MoNO₈S₂: C, 34.94; H, 4.54; N, 2.04. Found: C, 35.24; H, 4.58; N, 2.06.

Mo(NAd)(CH₂CH₂)(OTf)₂(dme) (4b). A 100 mL Schlenk round-bottom flask equipped with a side arm and a magnetic stir

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bar was charged with solid Mo(NAd)(OTf)₂(CH₂CH₂)(dme) (354 mg) and 10 mL of benzene. The reaction mixture was degassed (3×) and then exposed to 1 atm of ethylene. The reaction mixture was heated at 60 °C for 6 h. The volatiles were removed under vacuum, and the yellow solid generated was washed with diethyl ether; 155.4 mg of yellow solid were obtained (yield = 71%). The product obtained is a mixture of *cis* and *trans* isomers in the ratio of ~2:1, as determined by ¹H and ¹⁹F NMR spectroscopy studies. ¹H NMR (500 MHz, C₆D₆) δ 3.95–3.80 (m), 3.51 (s, *OMe*), 3.47 (s, *OMe*), 3.45–3.40 (m), 3.33 (s, *OMe*), 3.14 (s, *OMe*), 2.95–2.65 (m), 2.58–2.45 (m), 2.26–2.17 (m), 2.11 (br), 1.77 (br), 1.31 (br). ¹³C NMR (125 MHz, C₆D₆) δ 78.3, 77.4, 72.9, 72.6, 71.7, 69.9, 69.8, 67.6, 65.8, 64.2, 63.0, 60.9, 41.9, 41.1, 35.8, 35.7, 29.4, 29.3. ¹⁹F NMR (282 MHz, C₆D₆) δ -77.5, -77.8, -78.3. Anal. Calcd for C₁₈H₂₉F₆MoNO₈S₂: C, 32.68; H, 4.42; N, 2.12. Found: C, 33.26; H, 4.44; N, 2.00.

Mo(NAr)(CH₂CH₂)(η¹-2,5-Me₂NC₄H₂)(η⁵-2,5-Me₂NC₄H₂) (5a). A 25 mL Schlenk round-bottom flask equipped with a side arm and a magnetic stir bar was charged with solid Mo(NAr)(OTf)₂(CH₂CH₂)(dme) (156 mg, 0.23 mmol, 1 equiv) and lithium 2,5-dimethylpyrrolide (46 mg, 0.46 mmol, 2 equiv). The flask was degassed, and 5 mL of diethyl ether were vacuum transferred into it. The reaction mixture was allowed to warm up to room temperature and then immediately exposed to 1 atm of ethylene. The mixture was allowed to stir at room temperature for 3 h. The volatile materials were removed under vacuum. Benzene was added, and the reaction mixture was filtered through Celite. The volatile materials were removed, and the residue was recrystallized from pentane to give 58.3 mg of red crystals; yield = 52%. ¹H NMR (500 MHz, C₆D₆) δ 6.90–6.78 (m, 3H, *Ar*), 6.51 (s, 2H, NC₄H₂), 5.76 (s, 1H, NC₄H₂), 5.27 (s, 1H, NC₄H₂), 3.34 (sept, 2H, MeCHMe, *J* = 6.8 Hz), 3.06–2.96 (m, 1H, C₂H₄), 2.78–2.68 (m, 1H, C₂H₄), 2.66–2.56 (m, 1H, C₂H₄), 2.33–2.23 (m, 1H, C₂H₄), 2.52 (s, 3H, CH₃), 2.44 (s, 3H, CH₃), 1.88 (s, 3H, CH₃), 1.65 (s, 3H, CH₃), 1.05 (d, 6H, MeCHMe, *J* = 6.8 Hz), 1.00 (d, 6H, MeCHMe, *J* = 6.8 Hz). ¹³C NMR (125 MHz, C₆D₆) δ 152.0, 151.6, 147.9, 139.8, 139.1, 139.6, 123.9, 112.3, 110.9, 103.7, 100.7, 99.4, 51.3, 48.1, 28.0, 25.5, 23.3, 21.0, 20.1, 17.2, 14.6. Experiments employing ¹³C₂H₄ revealed the resonances at 51.3 ppm and 48.1 ppm to be those for ethylene carbons (*J*_{CH} = 157 Hz for each). Anal. Calcd for C₂₆H₃₇MoN₃: C, 64.05; H, 7.65; N, 8.62. Found: C, 63.47; H, 7.52; N, 8.44.

Mo(NAr)(CH₂CH₂)(2-MesitylNC₄H₃)₂ (5b). Benzene (10 mL) was added to a 25 mL Schlenk flask charged with a stir bar and Mo(NAr)(CHCMe₂Ph)(MesPyr)₂ (0.9243 g, 1.302 mmol). The solution was degassed via three freeze–pump–thaw cycles and then exposed to 1 atm of ethylene. The closed flask was heated at 60 °C for 4 days. The volatiles were removed in vacuo to give a brown residue. Pentane (~5 mL) and Et₂O (~1 mL) were added to the residue. The brown solids were collected and dried in vacuo for 1 h; yield 0.620 g (71%). ¹H NMR (500 MHz, C₆D₆) δ 6.88 (m, 3, *Ar-H*, *Pyr-H*), 6.82 (s, 1, *Ar-H*), 6.81 (s, 1, *Ar-H*), 6.77 (s, 4, *Ar-H*), 6.53 (m, 2, *Pyr-H*), 6.24 (m, 2, *Pyr-H*), 3.43 (sept, 2, CHMe₂), 2.65 (m, 2, C₂H₄), 2.16 (s, 6, *Pyr-Me*), 2.11 (s, 12, *Pyr-Me*), 1.96 (m, 2, C₂H₄), 1.00 (d, 12, CHMe₂, *J*_{HH} = 7 Hz). ¹³C NMR (125 MHz, C₆D₆) δ 154.71, 147.80, 140.50, 139.23, 138.28, 132.46, 129.39, 129.15, 128.96, 123.64 (NC₄H₃Mes), 111.92 (NC₄H₃Mes), 110.30 (NC₄H₃Mes), 54.22 (CH₂CH₂), 28.70, 24.45, 21.95, 21.52. Experiments employing ¹³C₂H₄ revealed that the 54.22 resonance is due to ethylene (*J*_{CH} = 160 Hz). Anal. Calcd for C₄₀H₄₉MoN₃: C, 71.94; H, 7.20; N, 6.29. Found: C, 72.24; H, 7.29; N, 6.05.

Mo(NAr)(CH₂CH₂)[OCH(CF₃)₂](Et₂O) (6). Mo(NAr)(CH₂CH₂)(MesPyr)₂ (0.201 g, 0.301 mmol) and 5 mL of diethyl ether were added to a 20 mL scintillation vial. Hexafluoroisopropanol (74 μL, 0.703 mmol, 2.33 equiv) was added in portions. The mixture was stirred for 30 min and filtered through glass wool. The filtrate was concentrated in vacuo to ~1 mL. After standing the solution at -27 °C for 1 day, red crystals were isolated; yield 0.088 g (41%). ¹H NMR (500 MHz, C₆D₆) δ 6.92 (m, 3, *Ar-H*), 4.68 (s, 2, OCH(CF₃)₂), 3.64 (q, 4, Et₂O), 3.54 (sept, 2, CHMe₂), 2.64 (m, 2,

C₂H₄), 1.83 (m, 2, C₂H₄), 1.13 (d, 12, CHMe₂, *J*_{HH} = 7 Hz), 0.88 (t, 6, Et₂O). ¹³C NMR (125 MHz, C₆D₆) δ 155.05, 148.33, 129.96, 128.58, 124.00, 78.75 (CF₃), 66.09 (O((CH₂)Me)₂), 63.17 (CH₂CH₂), 29.14 (CHMe₂), 24.44 (CHMe₂), 14.26 (O((CH₂)Me)₂). ¹⁹F NMR (282 MHz, C₆D₆) δ -75.56, -75.88. Anal. Calcd for C₂₄H₃₃F₁₂MoNO₃: C, 40.75; H, 4.70; N, 1.98. Found: C, 40.91; H, 4.67; N, 2.40.

Mo(NAr)(CH₂CHPh)(2,5-Me₂NC₄H₂)(OSiPh₃) (7). A 25 mL Schlenk round-bottom flask equipped with a side arm and a magnetic stir bar was charged with solid Mo(NAr)(CH₂CH₂)(2,5-Me₂NC₄H₂)(OSiPh₃) (306 mg, 0.458 mmol). Styrene, freshly dried over CaH₂, was vacuum transferred into the Schlenk flask. The reaction mixture was allowed to stir at room temperature for 15 min. The volatiles were removed in vacuo. Pentane (5 mL) was added, and the reaction mixture was placed at -35 °C; 252 mg of gray solid product was isolated (yield 74%). ¹H NMR (500 MHz, C₇D₈) (four isomers; selected peaks) δ 4.23 (t, 1H, CH₂=CHPh, *J* = 11.5 Hz), 4.16 (t, 1H, CH₂=CHPh, *J* = 11.5 Hz), 3.80 (br), 3.74–3.20 (m), 3.08 (dd, 1H, CH₂=CHPh, *J* = 11.5, 6.5 Hz), 2.97 (dd, 1H, CH₂=CHPh, *J* = 11.5, 6.0 Hz), 2.87–2.79 (m), 2.72 (dd, 1H, CH₂=CHPh, *J* = 12.2, 6.0 Hz), 2.63–2.56 (m), 2.40 (dd, 1H, CH₂=CHPh, *J* = 11.5, 6.5 Hz), 2.22 (s, *Me*), 2.09 (s, *Me*), 1.94 (s, *Me*), 1.89 (br), 1.83 (s, *Me*), 1.33 (d, 6H, MeCHMe, *J* = 6.5 Hz), 1.17 (d, 6H, MeCHMe, *J* = 6.5 Hz), 1.12 (d, 6H, MeCHMe, *J* = 6.5 Hz), 0.95 (d, 6H, MeCHMe, *J* = 6.5 Hz), 0.83 (d, 6H, MeCHMe, *J* = 6.5 Hz). ¹³C NMR (125 MHz, C₇D₈) δ 154.6, 154.0, 151.8, 147.0, 146.7, 146.5, 146.1, 146.0, 141.5, 141.0, 139.8, 138.4, 136.4, 136.3, 130.0, 129.8, 128.9, 128.3, 128.0, 127.0, 126.2, 124.0, 123.8, 123.6, 113.9, 109.2 (br), 104.1, 76.8, 73.7, 66.8, 60.0, 57.9, 57.7, 56.7, 54.6, 29.1, 28.7, 28.6, 26.2, 25.6, 25.3, 24.1, 23.6, 23.4, 17.4. Anal. Calcd for C₄₄H₄₈MoN₂OSi: C, 70.94; H, 6.49; N, 3.76. Found: C, 70.62; H, 6.67; N, 3.75.

Mo(NAr)(CH₂CHPh)(OSiPh₃)₂ (8). **Method A.** A 25 mL Schlenk round-bottom flask equipped with a side arm and a magnetic stir bar was charged with solid Mo(NAr)(CH₂CH₂)(OSiPh₃)₂ (60 mg, 0.0706 mmol). Styrene, freshly dried over CaH₂, was vacuum transferred to the Schlenk flask. The reaction mixture changed immediately from purple to green. The volatiles were then removed in vacuo and after recrystallization from pentane, 64 mg of green crystals were generated (yield = 98%).

Method B. Mo(NAr)(CH₂CHPh)(2,5-Me₂NC₄H₂)(OSiPh₃) (41.5 mg, 0.056 mmol, 1 equiv) and Ph₃SiOH (15.4 mg, 0.056, 1 equiv) were transferred to a 20 mL vial equipped with a magnetic stir bar. Pentane (5 mL) and 0.1 mL of diethyl ether were added. The color of the reaction mixture changed from red to green. The reaction mixture was stirred at room temperature until the starting material was completely consumed. The reaction mixture was placed at -35 °C, and 44.1 mg of green crystals were obtained (yield 85%). ¹H NMR (500 MHz, C₆D₆) (major isomer (67%)) δ 7.79 (d, 6H, *Ar*, *J* = 6.5 Hz), 7.73 (d, 6H, *Ar*, *J* = 6.5 Hz), 7.30–6.60 (m, 26H, *Ar*), 3.58 (t, 1H, CH₂=CHPh, *J* = 12.3 Hz), 3.41 (sept, 2H, MeCHMe, *J* = 6.8 Hz), 3.28 (dd, 1H, CH₂=CHPh, *J* = 12.3, 6.4 Hz), 2.44 (dd, 1H, CH₂=CHPh, *J* = 12.3, 6.4 Hz), 0.98 (d, 6H, MeCHMe, *J* = 6.8 Hz), 0.75 (d, 6H, MeCHMe, *J* = 6.8 Hz); (minor isomer (33%)) δ 7.75 (d, 6H, *Ar*, *J* = 6.5 Hz), 7.47 (d, 6H, *Ar*, *J* = 6.5 Hz), 7.30–6.60 (m, 26H, *Ar*), 4.64 (t, 1H, CH₂=CHPh, *J* = 10.9 Hz), 3.72 (sept, 2H, MeCHMe, *J* = 6.8 Hz), 2.99 (dd, 1H, CH₂=CHPh, *J* = 10.9, 6.7 Hz), 2.26 (dd, 1H, CH₂=CHPh, *J* = 10.9, 6.7 Hz), 1.02 (d, 6H, MeCHMe, *J* = 6.8 Hz), 0.96 (d, 6H, MeCHMe, *J* = 6.8 Hz). ¹³C NMR (125 MHz, C₆D₆) (major and minor isomers) δ 154.8, 154.0, 148.1, 147.1, 145.6, 144.7, 137.7, 137.5, 137.5, 137.2, 136.2, 136.1, 136.0, 135.9, 130.5, 130.4, 130.3, 130.0, 129.0, 128.7, 128.6, 128.5, 128.3, 128.0, 126.8, 126.2, 125.9, 125.7, 123.5, 123.3, 77.0, 73.0, 54.3, 52.1, 29.7, 29.4, 25.1, 24.7, 23.7, 23.0. Anal. Calcd for C₅₆H₅₅MoO₂Si₂: C, 72.62; H, 5.99; N, 1.51. Found: C, 72.71; H, 6.01; N, 1.47.

Mo(NAr)(*trans*-3-hexene)(OSiPh₃)₂ (9). A 1 dram vial was charged with solid Mo(NAr)(CH₂CH₂)(OSiPh₃)₂ (96 mg,

0.113 mmol). Addition of neat *trans*-3-hexene (100 μ L) led to a color change from purple to indigo. Pentane (0.1 mL) was added, and indigo crystals formed and were filtered off. The crystals were washed with pentane and dried in vacuo; yield 69 mg (67%). ^1H NMR (500 MHz, C_6D_6) (major isomer **9a** (80%)) selected peaks δ 7.79 (t, 12H, *Ar*, $J = 6.7$ Hz), 7.26–7.04 (m, 18H, *Ar*), 7.00–6.88 (m, 3H, *Ar*), 3.82 (sept, 2H, *MeCHMe*, $J = 6.8$ Hz), 3.49–3.32 (m, 1H), 2.42–2.30 (m, 1H), 2.20–2.03 (m, 1H), 2.03–1.91 (m, 1H), 1.75–1.62 (m, 1H), 1.42–1.32 (m, 1H), 1.11 (d, 6H, *MeCHMe*, $J = 6.8$ Hz), 0.97 (d, 6H, *MeCHMe*, $J = 6.8$ Hz), 0.94 (t, 3H, *MeCH₂CH=*, $J = 7.3$ Hz), 0.89 (t, 3H, *MeCH₂CH=*, $J = 7.3$ Hz); (minor isomer **9b** (20%)) selected peaks δ 3.75 (sept, 2H, *MeCHMe*, $J = 6.8$ Hz), 2.68 (m, 2H, *MeCH₂CH=*), 1.00 (d, 12H, *MeCHMe*, $J = 6.8$ Hz). ^{13}C NMR (125 MHz, C_6D_6) (major and minor isomers) δ 153.6, 147.3, 138.3, 137.4, 136.1, 136.0, 135.8, 130.4, 130.1, 128.7, 128.4, 128.3, 123.5, 78.1, 77.3, 33.8, 29.8, 28.4, 25.4, 23.0, 20.0, 18.6. Anal. Calcd for $\text{C}_{54}\text{H}_{59}\text{MoO}_2\text{Si}_2$: C, 71.57; H, 6.56; N, 1.55. Found: C, 71.67; H, 6.65; N, 1.59.

Mo(NAr)(C₄H₈)(OSiPh₃)₂ (10). A J-Young NMR tube was charged with a solution of Mo(NAr)(CH₂CH₂)(OSiPh₃)₂ (15 mg) in 0.6 mL of pentane and 0.1 mL of diethyl ether. The NMR tube was degassed three times and filled with 1 atm of ethylene. After 10 min at room temperature, the reaction mixture had changed from purple to red–orange. The NMR tube was stored at -35 °C to give orange crystals; 5.0 mg, 32% yield. X-ray quality crystals of **10** were grown from a pentane:toluene solution (10:1) of **10** at -35 °C under 1 atm of ethylene. ^1H NMR (500 MHz, C_7D_8 , -20 °C) δ 7.72 (d, 12H, *Ar*, $J = 7.3$ Hz), 7.16 (t, 6H, *Ar*, $J = 7.3$ Hz), 7.07 (t, 12H, *Ar*, $J = 7.3$ Hz), 7.02–6.91 (m, 3H, *Ar*), 3.85 (sept, 2H, *MeCHMe*, $J = 7.0$ Hz), 3.11 (br, 2H, *MoCH₂*), 3.06 (br, 2H, *MoCH₂*), 2.58 (br, 2H, *MoCH₂CH₂*), 2.41 (br, 2H, *MoCH₂CH₂*), 1.04 (d, 12H, *MeCHMe*, $J = 7.0$ Hz). Anal. Calcd for $\text{C}_{52}\text{H}_{55}\text{MoO}_2\text{Si}_2$: C, 71.12; H, 6.31; N, 1.60. Found: C, 71.50; H, 6.48; N, 1.40.

When $^{13}\text{C}_2\text{H}_4$ (~ 0.5 atm) was used, the following resonances were observed for the metallacyclopentane carbons. ^{13}C NMR (125 MHz, C_7D_8 , -20 °C) δ 72.4 (*MoC α*), 37.5 (*MoC α C β*).

Mo(NAr)(C₃H₆)(OSiPh₃)₂ (11). A J-Young NMR tube was charged with a suspension of Mo(NAr)(OSiPh₃)₂(CHCMe₂Ph)²¹ (9 mg) in 0.6 mL of pentane. The suspension was degassed (3 \times) and then exposed to 1 atm of ethylene. The reaction mixture was

placed at -35 °C. Red crystals (5.3 mg) were generated (yield = 65%). ^1H NMR (500 MHz, C_7D_8) (selected peaks) δ 3.73 (sept, 2H, *MeCHMe*, $J = 6.8$ Hz), 3.38 (br, 1H, *MoCH*), 2.86 (br, 1H, *MoCH*), 2.23 (br, 2H, *MoCH₂*), 1.24 (br, 2H, *MoCH₂CH₂*), 1.00 (d, 12H, *MeCHMe*, $J = 6.8$ Hz). When $^{13}\text{C}_2\text{H}_4$ (~ 0.5 atm) was used, the following peaks were observed corresponding to the square-pyramidal molybdacyclobutane carbons. ^{13}C NMR (125 MHz, C_7D_8) δ 37.6 (d, $J_{\text{CC}} = 33$ Hz, $J_{\text{CH}} = 138$ Hz, *MoC α*), 27.8 (d, $J_{\text{CC}} = 33$ Hz, $J_{\text{CH}} = 132$ Hz, *MoC α C β*). Anal. Calcd for $\text{C}_{51}\text{H}_{53}\text{MoO}_2\text{Si}_2$: C, 70.89; H, 6.18; N, 1.62. Found: C, 71.30; H, 6.48; N, 1.40.

Reaction Involving Cyclooctene. To a benzene-*d*₆ (0.6 mL) solution of Mo(NAr)(CH₂CH₂)(O-*i*-PrF₆)₂(Et₂O) (0.014 g, 0.0198 mmol) was added (260 μ L, 1.98 mmol) of cyclooctene via syringe. After 24 h at 23 °C, the mixture was dissolved in methylene chloride, and the solution was then added dropwise to methanol with vigorous stirring. A white precipitate of polycyclooctene was filtered off from the methanol solution; yield 0.082 g (38%). Both *trans* (88%) and *cis* (12%) CH=CH bonds were observed. ^1H NMR (500 MHz, CDCl_3) δ 5.38 (m, 1, *trans-CH*), 5.36 (m, 1, *cis-CH*), 2.01 (m, 2, *trans-CH₂*), 1.97 (m, 2, *cis-CH₂*), 1.31 (br m, 4, *trans-CH₂*), 1.29 (m, 2, *cis-CH₂*). ^{13}C NMR (125 MHz, CDCl_3) δ 130.54 (m, *trans-CH*), 130.08 (m, *cis-CH*), 32.83 (has a shoulder, *trans-* and *cis-CH₂*), 29.96 (*cis-CH₂*), 29.85 (*trans-CH₂*), 29.40 (*cis-CH₂*), 29.26 (*trans-CH₂*).

Crystal Structure Determinations. All structures were solved by direct methods using SHELXS²⁸ and refined against F₂ on all data by full-matrix least-squares with SHELXL-97²⁹ using established refinement techniques.³⁰ For details, see Supporting Information.

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Supporting Information Available: Experimental details for all NMR experiments and X-ray structural studies. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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