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Synthesis and Reactivity of Molybdenum(IV) Olefin Complexes Supported by a Chelating Ancillary Ligand

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The reactivity of $[Mo(NPh)Cl_2(o\text{-}(Me_3SiN)_2C_6H_4{\cdot}THF)]$ (**1**) with β-hydrogen-containing Grignard reagents was examined. Reaction of **1** with 2 equiv of RMgCl ($R = CH_2CH_2Ph$, $CH_2CH_2CH_3$, $CH_2CH(CH_3)_2$, $CH_2CH_2CH_2CH_3$, and $CH(CH_3)CH_2CH_3$) gave Mo(IV) olefin complexes of the type $[Mo(NPh)(\eta^2\text{-olefin})(o\text{-}(Me_3SiN)_2C_6H_4)]$ (olefin = styrene (**2a**), propene (**2b**), isobutene (**2c**), 1-butene (**2d**), and 2-butene (**2e**)). The crystal structure of **2a** is reported. Reaction of **1** with 2 equiv of ethylmagnesium chloride afforded a mixture of metallacyclopentane $[Mo(NPh)(CH_2CH_2CH_2CH_2)(o\text{-}(Me_3SiN)_2C_6H_4)]$ (**3a**) and an oligomeric molybdenum species having the empirical formula $[Mo(NPh)(o\text{-}(Me_3SiN)_2C_6H_4)]_x$ (**3b**). Pure **3a** was obtained by reaction of **1** with 2 equiv of EtMgCl under an atmosphere of ethylene. Treatment of **3a** with excess PMe_3 in benzene at 80 °C afforded $[Mo(NPh)(\eta^2\text{-ethylene})(o\text{-}(Me_3SiN)_2C_6H_4)(PMe_3)_2]$ (**3c**). Compounds **2c** and **2a** react with acetone to yield the oxametalacyclopentanes $[(Mo(NPh)(C(CH_3)_2CH_2C(CH_3)_2O)(o\text{-}(Me_3SiN)_2C_6H_4)]$ (**4a**) and $[(Mo(NPh)(C(H)PhCH_2C(CH_3)_2O)(o\text{-}(Me_3SiN)_2C_6H_4)]$ (**4b**), respectively. An X-ray crystallographic study on a single crystal of **4a** was performed. Only one diasteriomer of **4b** was formed and isolated. Its structure was assigned by NMR spectroscopy (ghmbc, ghmqc, and NOESY).

Introduction

β-Hydride transfer from transition metal centers is a key step in many stoichiometric and catalytic reactions. For example, β-hydride transfer is one important chain termination step in transition metal-catalyzed olefin polymerization and oligomerization.[1] In addition, β-hydride elimination is also the major decomposition pathway for transition metal alkyls.[2] This pathway often gives transition metal olefin complexes, which have been widely used in unusual organic transformations as well as in the construction of complex organic molecules from simple precursors.[3] Although various cyclopentadienyl (Cp) and derivative ring systems have overwhelmingly dominated as the ancillary ligand of choice for most early transition metal organometallic chemistry,[4] researchers have also focused on the use of non-Cp coligands in the study of chemical reactions performed by high oxidation state early transition metal complexes.[5−7]

In recent years we have concentrated our efforts on the study of W(IV) and W(VI) complexes that contain the dianionic, diamide ligand $[o\text{-}(Me_3SiN)_2C_6H_4]^{2-}$ ($(Me_3Si)_2$-pda).[8] This bidentate ligand has proven to be

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(1) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, 1987. (b) Parshall, G. W. *Homogeneous Catalysis*; John Wiley & Sons: New York, 1980; Chapter 3. (c) Cross, R. J. *The Chemistry of the Metal−Carbon Bond*; Hartley, F. R., Patai, S., Eds.; John Wiley & Sons: New York, 1985; Vol. 2, Chapter 8.

(2) Negishi, E.; Takahashi, T. *Acc. Chem. Res.* **1994**, *21*, 1277. (b) Buchwald, S. L.; Nielsen, R. B. *Chem. Rev.* **1988**, *88*, 1047. (c) Dyer, P. W.; Gibson, V. C.; Howard, J. A. K.; Whittle, B.; Wilson, C. *Polyhedron* **1995**, *14*, 103. (d) Dyer, P. W.; Gibson, V. C.; Clegg, W. *J. Chem. Soc., Dalton Trans.* **1995**, 3313. (e) Grubbs, R. H.; Miyashita, A. *J. Am. Chem. Soc.* **1978**, *100*, 1300. (f) Buchwald, S. L.; Watson, B. T.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 2544. (g) Buchwald, S. L.; Kreutzer, K. A.; Fisher, R. A. *J. Am. Chem. Soc.* **1990**, *112*, 4600. (h) Fernandez, F. J.; Gomez-Sal, P.; Manzanero, A.; Royo, P.; Jacobsen, H.; Berke, H. *Organometallics* **1997**, *16*, 1553. (i) Buijink, J. K. F.; Kloestra, R.; Meetsma, A.; Teuben, J. H.; Smeets, W. J. J.; Spek, A. L. *Oranometallics* **1996**, *15*, 2523. (j) Rietveld, M. H. P.; Teunisen, W.; Hagen, H.; van der Water, L.; Grove, D. M.; van der Schaff, P. A.; Mühlebach, A.; Kooijman, H.; Smeets, W. J. J.; Veldman, N.; Spek, A. L.; van Koten, G. *Organometalics* **1997**, *16*, 1674. (k) Kondakov, D.; Negishi, E. *J. Chem. Soc., Chem. Commun.* **1996**, 963. (l) Soleil, F.; Choukroun, R. *J. A. Chem. Soc.* **1997**, *119*, 2938.

(3) Millward, D. B.; Waymouth, R. M. *Organometallics* **1997**, *16*, 1153. (b) Takahashi, T.; Kotora, M.; Fischer, R.; Nishihara, Y.; Nakajima, K. *J. Am. Chem. Soc.* **1995**, *117*, 11039. (c) Knight, K. S.; Wang, D.; Waymouth, R. M.; Ziller, J. *J. Am. Chem. Soc.* **1994**, *116*, 1845. (d) Nugent, W. A.; Taber, D. F. *J. Am. Chem. Soc.* **1989**, *111*, 6435. (e) Taber, D. F.; Lovey, J. P.; Wang, Y.; Nugent, W. A.; Dixon, D. A.; Harlow, R. L. *J. Am. Chem. Soc.* **1994**, *116*, 9457. (f) Dyer, D. W.; Gibson, V. C.; Howard, J. A. K.; Whittle, B.; Wilson, C. *J. Chem. Soc., Chem. Commun.* **1992**, 1666. (g) Proulx, G.; Bergman, R. G. *J. Am. Chem. Soc.* **1994**, *116*, 7953.

(4) Crowe, W. E.; Vu, A. T. *J. Am. Chem. Soc.* **1996**, *118*, 5508.

(5) Aoyagi, K.; Kalai, K.; Gantzel, P. K.; Tilley, T. D. *Organometallics* **1996**, *15*, 923. (b) Aoyagi, K.; Kalai, K.; Gantzel, P. K.; Tilley, T. D. *Polyhedron* **1996**, *15*, 4299. (c) Pinado, G. J.; Thorton-Pett, M.; Bochman, M. J. *J. Chem. Soc., Dalton Trans.* **1998**, 393. (d) Lee, R. A.; Lachicotte, R. J.; Bazan, G. C. *J. Am. Chem. Soc.* **1998**, *120*, 6037. (e) Armistead, L. T.; White, D. S.; Gagné, M. R. *Organometallics* **1998**, *17*, 216. (f) Shah, A. A.; Dorn, H.; Voigt, A.; Roesky, H. W.; Parisini, E.; Schmidt, H. G.; Noltemeyer, M. *Organometallics* **1996**, *15*, 3176. (g) Shah, A. A.; Dorn, H.; Roesky, H. W.; Parisini, E.; Schmidt, H. G.; Noltemeyer, M. *J. Chem. Soc., Dalton Trans.* **1996**, 4143. (h) Guérin, F.; McConville, D. H.; Vittal, J. J.; Yap, G. A. P. *Organometallics* **1998**, *17*, 1290. (i) Gountchev, T.; Tilley, T. D. *J. Am. Chem. Soc.* **1997**, *119*, 12831. (j) Scollard, J. D.; McConville, D. H.; Rettig, S. J. *Organometallics* **1997**, *16*, 1810. (k) Lee, C. H.; La, Y. H.; Park, S. J.; Park, J. W. *Organometallics* **1998**, *17*, 3648. (l) Jeon, Y. M.; Park, S. J.; Heo, J.; Kim, K. *Organometallics* **1998**, *17*, 3161. (m) Guérin, F.; McConville, D. H.; Vittal, J. J. *Organometallics* **1995**, *14*, 3154. (n) Johnson, A. R.; Davis, W. M.; Cummins, C. C. *Organometallics* **1996**, *15*, 3825. (o) Horton, A. D.; de With, J.; van der Linden, A. J.; van de Weg, H. *Organometallics* **1996**, *15*, 2672. (p) Dyer, P. W.; Gibson, V. C.; Howard, J. A. K.; Wilson, C. *J. Organomet. Chem.* **1993**, *462*, C15. (q) Guérin, F.; McConville, D. H.; Vittal, J. J. *Organometallics* **1997**, *16*, 1491.

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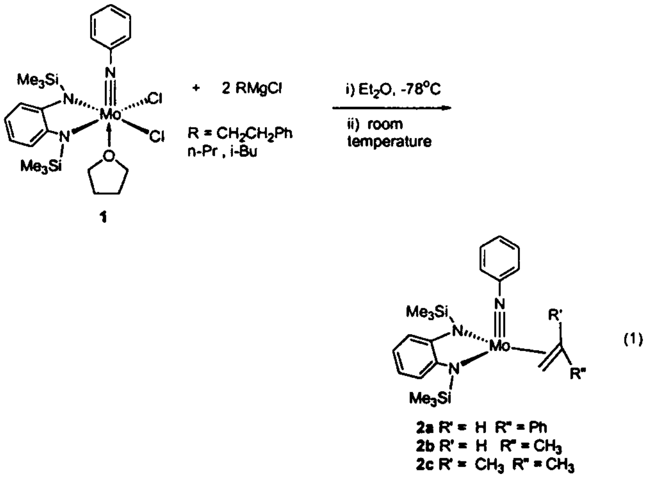
very useful in the isolation of dialkyl and alkylidene species of W(VI). It has also allowed us to convert some of the β-hydrogen-containing dialkyls into olefin complexes upon treatment with PMe_3.[9] These W(VI) β-hydrogen-containing dialkyls were otherwise stable to β-hydrogen transfer reactions. Extension of this chemistry to molybdenum has resulted in the synthesis of the analogous non β-hydrogen containing Mo(VI) dialkyls.[10] The β-hydrogen-containing Mo(VI) dialkyls, which are not as stable as their tungsten counterparts, decompose to afford the corresponding molybdenum olefin complexes. The synthesis, structure, and initial reactivity studies of these olefin complexes are reported herein.

Results and Discussion

Synthesis and Characterization of η^2-Olefin Complexes and Structure of [Mo(NPh)(η^2-styrene)(*o*-$(Me_3SiN)_2C_6H_4$)]. The reaction of [Mo(NPh)Cl_2(*o*-$(Me_3SiN)_2C_6H_4$)·THF] (**1**)[10] in Et_2O at −78 °C with 2 equiv of RMgCl (R = CH_2CH_2Ph, *n*-Pr, and *i*-Bu) gave bright red solutions that turned deep green when they were warmed to 25 °C and stirred for several hours. Upon workup, these reactions afforded the η^2-olefin complexes **2a**−**c** as emerald green crystals or oils (eq 1). Complex **2a** is stable in the solid state, while **2b** and **2c** decompose over the course of 1 day at room temperature. Typically, **2b** and **2c** were generated and used immediately for subsequent reaction chemistry.



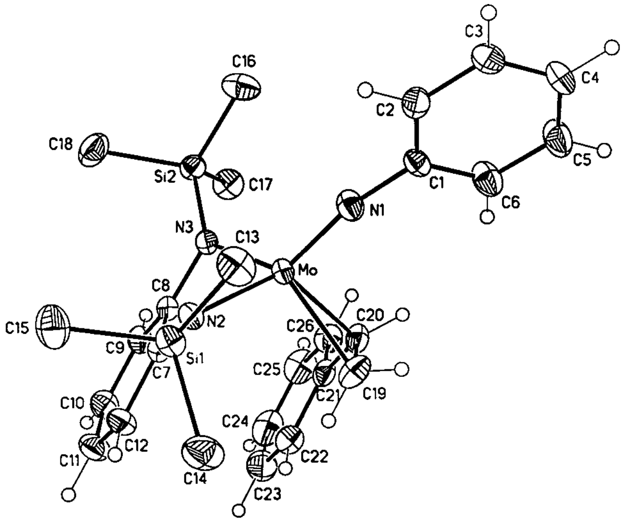


Figure 1. Molecular structure of **2a** (50% probability thermal ellipsoids). Selected bond lengths (Å) and angles (deg): Mo−N(1), 1.7366(17); Mo−N(2), 2.0098(16); Mo−N(3), 2.0184(16); Mo−C(19), 2.145(2); Mo−C(20), 2.190(2); C(19)−C(20), 1.452(3); C(19)−C(20)−C(21), 123.1(2).

Single crystals of **2a** were grown from a concentrated pentane solution at room temperature overnight. A single-crystal X-ray diffraction experiment revealed that **2a** is a pseudo-four-coordinate η^2-styrene complex, this particular isomer having the styrene phenyl ring oriented *anti* with respect to the phenyl imido ligand (Figure 1). The Mo−N(1) bond length of 1.7366(17) Å is consistent with a molybdenum−nitrogen triple bond interaction,[2c,d,3f,11] while the Mo−N(2) and N(3) amide bond lengths of 2.0098(16) and 2.0184(16) Å are within the range expected for Mo−N single bonds.[12] The Mo−C(19) and Mo−C(20) bond distances are 2.145(2) and 2.190(2) Å, respectively. The small difference in these bond lengths is attributed to steric interactions of the styrene phenyl ring with the phenyl ring of the $(Me_3Si)_2$-pda functionality. The C(19)−C(20) bond length of 1.452(3) Å is at the upper end of olefin bond lengths in metal olefin complexes and supports a considerable amount of metallacyclopropane character in **2a**.[13,14] The crystal and refinement data for **2a** are summarized in Table 1.

NMR experiments revealed that the structure of **2a** in solution is consistent with that determined by X-ray crystallography. There are, however, two isomers present in solution in a 1:1 ratio. The ^1H NMR spectrum of **2a** showed four singlets, corresponding to two sets of

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[6] Cummins, C. C.; Schrock, R. R.; Davis, W. M. *Organometallics* **1992**, *11*, 1452. (b) Freundlich, J. S.; Schrock, R. R.; Davis, W. M. *Organometallics* **1996**, *15*, 2777. (c) Cai, S.; Schrock, R. R. *Inorg. Chem.* **1991**, *30*, 4105. (d) Cummins, C. C.; Lee, J.; Schrock, R. R.; Davis, W. D. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1501. (e) Schrock, R. R.; Seidel, S. W.; Mösch-Zanetti, N. C.; Dobbs, D. A.; Shih, K.-Y.; Davis, W. M. *Organometallics* **1997**, *16*, 5195.

[7] Hill, J. E.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1990**, *9*, 2211. (b) Kriley, C. E.; Kechener, J. L.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1993**, *12*, 2051. (c) Fanwick, P. E.; Rothwell, I. P.; Kriley, C. E. *Polyhedron* **1996**, *15*, 2403. (d) Thorn, M. G.; Hill, J. E.; Waratuke, S. A.; Johnson, E. S.; Fanwick, P. E.; Rothwell, I. P. *J. Am. Chem. Soc.* **1997**, *119*, 8630. (e) Vilardo, J. S.; Lockwood, M. A.; Hanson, L. G.; Clark, J. R.; Parkin, B. C.; Fanwick, P. E.; Rothwell, I. P. *J. Chem. Soc., Dalton Trans.* **1997**, 3353.

[8] VanderLende, D. D.; Abboud, K. A.; Boncella, J. M. *Polym. Prepr.* **1994**, *35*, 691. (b) VanderLende, D. D.; Abboud, K. A.; Boncella, J. M. *Organometallics* **1994**, *13*, 3378. (c) Boncella, J. M.; Wang, S.-Y. S.; VanderLende, D. D.; Huff, R. L.; Vaughan, W. M.; Abboud, K. A. *J. Organomet. Chem.* **1996**, *530*, 59. (d) Huff, R. L.; Wang, S.-Y. S.; Abboud, K. A.; Boncella, J. M. *Organometallics* **1997**, *16*, 1779. (e) Wang, S.-Y. S.; VanderLende, D. D.; Abboud, K. A.; Boncella, J. M. *Organometallics* **1998**, *17*, 2628.

[9] Wang, S.-Y. S.; Abboud, K. A.; Boncella, J. M. *J. Am. Chem. Soc.* **1997**, *119*, 11990. (b) Boncella, J. M.; Wang, S.-Y. S.; VanderLende, D. D. *J. Organomet. Chem.* **1999**, *591*, 8.

[10] Ortiz, C. G.; Abboud, K. A.; Boncella, J. M. *Organometallics* **1999**, *18*, 4253.

[11] Bryson, N.; Youinou, M. T.; Osborn, J. A. *Organometallics* **1991**, *10*, 3389.

[12] O'Donoghue, M. B.; Davis, W. M.; Schrock, R. R. *Inorg. Chem.* **1998**, *37*, 5149. (b) Duan, Z.; Verkade, J. G. *Inorg. Chem.* **1995**, *34*, 1576. (c) Mösch-Zanetti, N. C.; Schrock, R. R.; Davis, W. M.; Wanninger, K.; Siedel, S. W.; O'Donoghue, M. B. *J. Am. Chem. Soc.* **1997**, *119*, 11037.

[13] Burger, B. J.; Santarsiero, B. D.; Trimmer, M. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 3134. (b) Clark, J. R.; Fanwick, I. P.; Rothwell, I. P. *J. Chem. Soc., Chem. Commun.* **1995**, 553.

[14] The average C−C bond length for metal-coordinated styrene is 1.41(9) Å. A search of the October 1998 release of the Cambridge Database. Allen, F. H.; Kenward, O. *Chem. Des. Autom. News* **1993**, *8*, 31.

Table 1. Crystal Data, Data Collection, and Structure Refinement for 2a

empirical formula	$C_{26}H_{35}MoN_3Si_2$
fw	541.69
temperature	173(2) K
wavelength	0.71073 Å
cryst syst	monoclinic
space group	$P2(1)/c$
unit cell dimens	$a = 12.4996(1)$ Å, $\alpha = 90°$ $b = 11.1300(1)$ Å, $\beta = 91.25°$ $c = 19.1658(2)$ Å, $\gamma = 90°$
volume	2665.72(4) Å^3
Z	4
density (calcd)	1.350 Mg/m^3
abs coeff	0.600 mm^{-1}
$F(000)$	1128
cryst size	$0.22 \times 0.17 \times 0.057$ mm^3
θ range for data collection	1.63−27.50°
limiting indices	$-11 \le h \le 16, -13 \le k \le 14, -24 \le l \le 23$
no. of reflns collected	18 247
no. of indep reflns	6091 [R(int) = 0.0261]
completeness to $\theta = 27.50°$	99.4%
abs corr	empirical (SADABS, Blessing 1995)
max. and min. transmn	0.949 and 0.824
refinement method	full-matrix least-squares on F^2
no. of data/restraints/params	6091/0/296
goodness-of-fit on F^2	1.051
final R indices $[I > 2\sigma(I)]^a$	R1 = 0.0278, wR2 = 0.0642 [5129]
R indices (all data)	R1 = 0.0387, wR2 = 0.0697
extinction coeff	0.00005(15)
largest diff peak and hole	0.831 and −0.487 e Å^{-3}

[a] $R1 = \sum(||F_o| - |F_c||)/\sum|F_o|$; $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[wF_o^{2\,2}]]^{1/2}$; $S = [\sum[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.0370p)^2 + 0.31p]$; $p = [\max(F_o^2,0) + 2F_c^2]/3$.

inequivalent trimethylsilyl groups. Other resonances, due to the coordinated styrene, were observed in the region spanning 1−5 ppm. Through a COSY 2D NMR experiment two sets of olefinic resonances were identified for **2a**. Isomer A had resonances at 1.16 ppm (m, 1H), 3.38 ppm (m, 1H), and 4.90 ppm (t, 1H). Isomer B showed signals at 1.05 ppm (m, 1H), 2.22 ppm (t, 1H), and 3.54 ppm (m, 1H). Furthermore, four resonances due to coordinated styrene carbons were present in the $^{13}C\{^1H\}$ NMR spectrum.

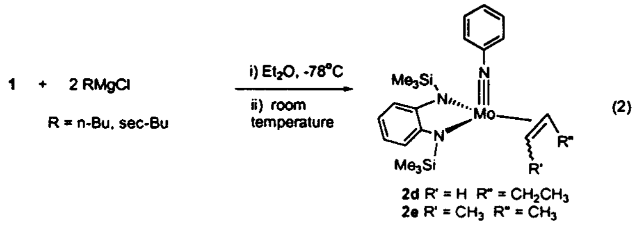
We propose that the isomers differ only by the position of the styrene phenyl group in relation to the imido phenyl group. One isomer is depicted in Figure 1, and in the other isomer (a diasteriomer) the styrene phenyl group is *syn* to the imido phenyl group. This type of isomerism for transition metal olefin complexes is well precedented in the literature.[2c,d,3f,15] It is possible to assign each set of the above resonances in the ^{1}H NMR spectrum to their respective isomer in an NOE difference experiment. An ortho proton belonging to the coordinated styrene fragment in the isomer of **2a** shown in Figure 1 is positioned directly over the phenyl ring of the *o*-$(Me_3Si)_2$-pda functionality *syn* to it. These ortho protons are shifted significantly upfield in the ^{1}H NMR spectrum as a result of the pda ring current and are assigned to the resonance at 5.94 ppm (d, 2H). Irradiation of these protons, in an NOE difference experiment, produced positive NOES at 1.16 ppm (5.7%) and 4.90 ppm (6.4%) and a negative NOE at 3.38 ppm (1.7%). This confirms the olefinic resonances of isomer A as corresponding to the isomer shown in Figure 1.

We have also observed that the diasteriomers of **2a** do not interconvert on the NMR time scale up to 80 °C. This large barrier for rotation of the olefin along the metal−olefin axis is consistent with a large degree of back-bonding from the d^2 metal center to the styrene fragment and is again consistent with the suggestion that **2a** has a considerable degree of metallacylopropane character.[16]

Propene complex **2b** also exists in two isomeric forms. Although the ^{1}H NMR spectrum of **2b** showed only two singlets due to the trimethylsilyl groups, two doublets, assigned to the propene-methyl groups were observed. Six multiplets, corresponding to olefinic protons, were also observed.

The ^{1}H NMR spectrum of the isobutene complex (**2c**) displayed upfield resonances assigned to inequivalent trimethylsilyl groups. In addition, two singlets assigned to the isobutene-methyl groups were observed. However, one of the doublets due to an olefinic proton was obscured by the methyl resonance at 0.73 ppm. The remaining olefinic proton was observed at 2.99 ppm (1H). The isolation of **2c** represents a rare example of an early transition metal isobutene complex.[2g,15a]

Reaction of **1** with 2 equiv of *n*-BuMgCl, 2 equiv of *sec*-BuMgCl, or 1 equiv of *n*-Bu_2Mg afforded, after appropriate workup, identical product mixtures, as determined by ^{1}H and ^{13}C NMR spectroscopy. As a result of the complexity of the ^{1}H NMR spectra of these products, ^{13}C (APT) spectroscopy was used to confirm the identities of the complexes in this mixture as various isomers of the η^2-1-butene and η^2-2-butene complexes **2d** and **2e**, respectively (eq 2). Five different resonances, assigned to ═C(H) groups, were observed in this mixture, supporting the existence of at least four different olefin complexes. The 1-butene isomers were easily identified in this mixture, because they have terminal ═CH_2 olefin and methylene groups. We observed two methylene resonances and two terminal ═CH_2 olefin resonances, and these results support the existence of two distinct 1-butene complexes. Of the five observed ═C(H) resonances, two must be attributed to the internal olefin carbons of these 1-butene isomers. The other three ═C(H) resonances must be assigned to 2-butene isomers. These three ═C(H) resonances can be most easily explained by proposing the existence of two 2-butene isomers: one cis and one trans. Unfortunately, only three resonances corresponding to methyl groups were observed. As five distinct methyl resonances are expected, we can only assume that some of



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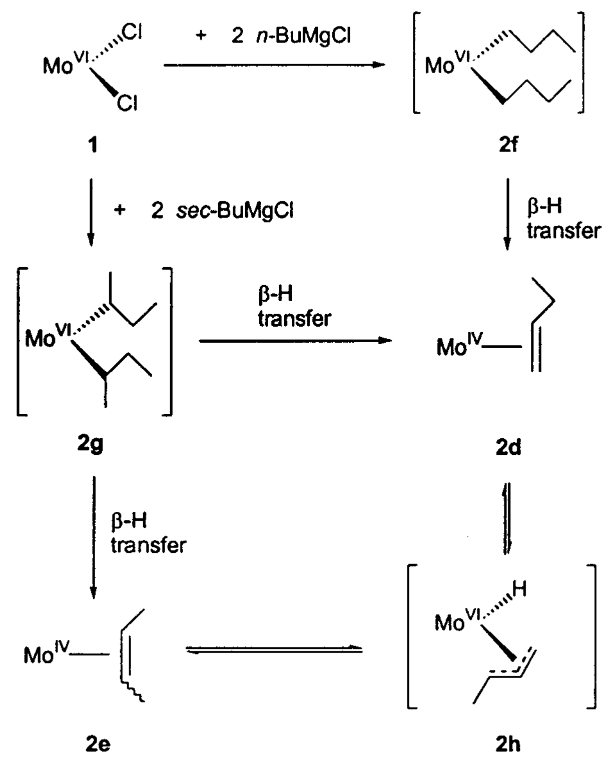
(15) Clark, G. R.; Nielson, A. J.; Richard, C. E. F.; Ware, D. C. *J. Chem. Soc., Dalton Trans.* **1995**, 1907. (b) Clark, G. R.; Nielson, A. J.; Richard, C. E. F. *J. Chem. Soc., Dalton Trans.* **1990**, 1173.

(16) Su, F. M.; Cooper, C.; Geib, S. J.; Rheingold, A. L.; Mayer, J. M. *J. Am. Chem. Soc.* **1986**, *108*, 3545.

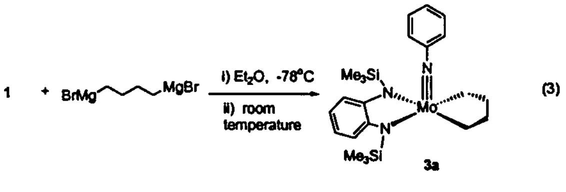
Scheme 1



these signals overlap. The signals due to trimethylsilyl groups are observed near 1.32 ppm.

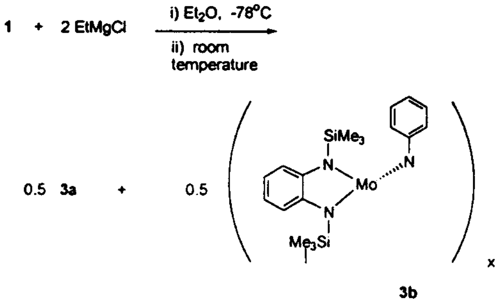
As depicted in Scheme 1, we propose that 1-butene and 2-butene complexes present in these mixtures result from isomerization of the coordinated olefin through allylic C−H activation. The reaction of **1** with *sec*-BuMgCl should yield the di-*sec*-butyl complex **2g**, which, through β-hydride transfer, forms both 1-butene and 2-butene complexes **2d** and **2e**, respectively. However, the di-*n*-butyl complex can only decompose to the 1-butene complex. At this point, allylic activation would produce an allyl hydride intermediate (**2h**), which can reversibly be converted into a 2-butene complex by insertion/migration into the opposite carbon. This allyl mechanism is very common for transition metal-mediated olefin isomerization.[17−19]

Formation of Mo(VI) Metallacyclopentane [Mo-(NPh)($CH_2CH_2CH_2CH_2$)(o-($Me_3SiN)_2C_6H_4$)] (3a). The reaction of **1** and 1 equiv of $BrMgCH_2CH_2CH_2CH_2MgBr$ in Et_2O (−78 °C) resulted in the formation of red-orange metallacyclopentane **3a** (eq 3). We propose that **3a** adopts a square pyramidal geometry similar to the tungsten analogue.[8e] Four multiplets are observed for the metallacycle protons in the ^1H NMR spectrum. The o-($Me_3Si)_2$-pda nitrogens and the two α-carbons occupy the basal plane of **3a**. A plane of symmetry that bisects the N−Mo−N and C_α−Mo−C_α angles makes each α- and β-carbon equivalent to the other. However, as protons sitting above and below the plane are inequivalent, each α-hydrogen couples to its geminal α-hydrogen and to both vicinal β-hydrogens. Likewise, each β-hydrogen couples to its geminal β-hydrogen and to both α-hydrogens. A single Me_3Si resonance in the ^1H NMR spectrum of **3a** was observed, as is consistent with the proposed structure.

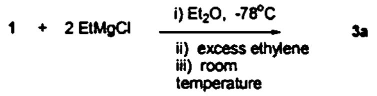


(3)

Metallacyclopentane **3a** was also obtained after **1** was allowed to react with 2 equiv of EtMgCl (Et_2O, −78 °C) and then warmed to room temperature (eq 4). The yield of this reaction was much lower, as 1 equiv of "Mo" was lost when two ethylene molecules coupled to make the metallacycle. We propose that this material is best described as an oligomeric molybdenum species having the empirical formula $[Mo(NPh)(o\text{-}(Me_3SiN)_2C_6H_4)]_x$ (**3b**). A high-yielding procedure for the generation of **3a** involved treatment of **1** with 2 equiv of EtMgCl (Et_2O, −78 °C) in the presence of excess dry ethylene (eq 5).



(4)



(5)

We propose that the formation of **3a** occurs via the pathway shown in Scheme 2. Upon addition of EtMgCl to **1**, the bright orange-red color of the dialkyl complex appears. Upon warming, the solution darkens and becomes the color of **3a**. β-Hydride transfer from a Mo(VI) diethyl complex would afford a Mo(IV) ethylene complex. This ethylene complex could then disproportionate in the absence of excess ethylene to yield **3a** and three-coordinate $[Mo(NPh)(o\text{-}(Me_3SiN)_2C_6H_4)]$. This three-coordinate, coordinatively unsaturated, and electron-deficient intermediate then oligomerizes to generate **3b**. However, in the presence of excess ethylene coupling of the coordinated ethylene molecule and a free ethylene molecule gives **3a** in essentially quantitative yield.

The oligomeric molybdenum species **3b** can be synthesized by treatment of a pentane solution of **2b** with excess lutidine. When **3b** is synthesized in such a manner it forms as a black precipitate that can be isolated by filtration and purified by successive washings with pentane. Once pure, the solubility of **3b**, in conventional solvents ($CHCl_3$, CH_2Cl_2, THF, Et_2O,

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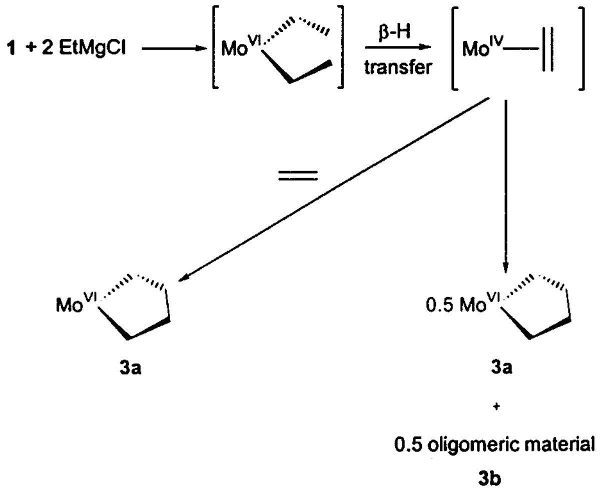
[17] Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*; John Wiley and Sons: New York, 1984.

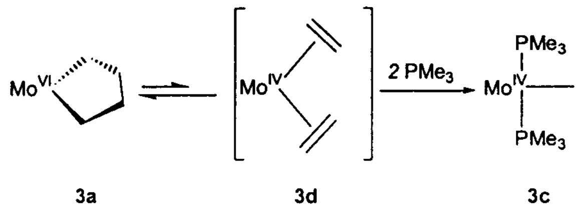
[18] Along these lines we have observed catalytic transformation of allylanisole to *trans*-β-methylstyrene.

[19] Although no hydride species are detected in solution, we have isolated hydride complexes of a closely related tungsten system[19b] and have spectroscopically observed a molybdenum $P(Me)_3$-stabilized dihydride of this system (manuscript in preparation). (b) Boncella, J. M.; Wang, S.-Y. S.; VanderLende, D. D. *J. Organomet. Chem.* **1999**, *591*, 8.

Scheme 2



Scheme 3

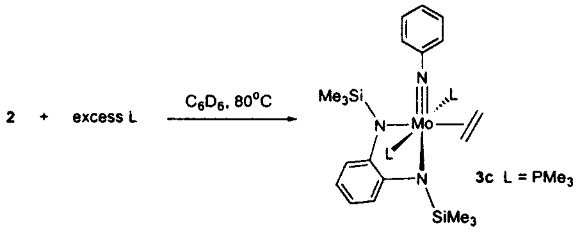


benzene, toluene, and CH_3CN), decreases substantially, making structural studies in solution difficult. All that can be concluded by NMR spectroscopy is that the formulation of **3b** is supported by integration and multiplicity of the aromatic proton resonances in the ^1H NMR spectrum. If **3b** is left under an inert atmosphere at room temperature, it begins to decompose within one month by ^1H NMR, affording an intractable mixture.

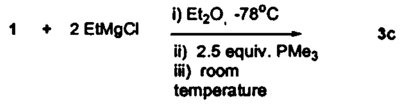
We came upon the synthesis of **3b** via treatment with lutidine by accident while we were exploring the chemistry of these olefin complexes with pyridine and pyridine derivatives. Reaction of **2b** with pyridine results in the formation of a five-coordinate, square pyramidal, bispyridine adduct, $[Mo(NPh)(Py)_2(o\text{-}(Me_3SiN)_2C_6H_4)]$.[20] We attribute the difference in reactivity of **2b** with pyridine and lutidine to the different steric environments around the Lewis basic nitrogen atoms in both molecules. Pyridine readily displaces propene from **2b** and remains bound to the metal center. Lutidine, however, can displace olefin from **2b** but is not involved in adduct formation. Effective displacement of propene from **2b,** by lutidine, would generate the three-coordinate, coordinatively unsaturated, and electron-deficient $[Mo(NPh)(o\text{-}(Me_3SiN)_2C_6H_4)]$, which then oligomerizes. In general, we observe the formation of **3b** whenever reaction conditions permit loss of the olefin ligand without replacement by another donor.

Significant interest has been shown in early transition metal metallacyclopentane species due to their role in the dimerization and trimerization of ethylene as a means for catalytically preparing butene[21] and hexene,[22] respectively. We did not observe formation of metallacycloheptane species nor the formation of hexene when **3a** was exposed to excess ethylene. When a C_6D_6 solution of **3a** was heated to 80 °C under ethylene pressure (1−2 atm), the only identifiable products were butene and free $H_2\text{-}o\text{-}(Me_3SiN)_2$-pda. The observation of $H_2\text{-}o\text{-}(Me_3Si)_2$-pda suggests that the butene formed was more likely a result of the decomposition of **3a** than from the catalytic dimerization of ethylene.

Formation of Mo(IV) Ethylene Complex $[Mo(NPh)(\eta^2\text{-ethylene})(o\text{-}(Me_3SiN)_2C_6H_4)(PMe_3)_2]$ (3c). When a small excess (2.2 equiv) of PMe_3 was added to a C_6D_6 solution of **3a** and heated to 80 °C, formation of $[Mo(NPh)(\eta^2\text{-ethylene})(o\text{-}(Me_3SiN)_2C_6H_4)(PMe_3)_2]$ (**3c**) was observed (eq 6). No **3c** was produced under identical conditions at room temperature. Alternatively, **3c** was prepared by reacting 2 equiv of EtMgCl with **1** (Et_2O, −78 °C) while in the presence of slightly more than 2 equiv of PMe_3 (eq 7).



(6)



(7)

A broad singlet assigned to the trimethylsilyl protons and a broadened singlet assigned to the trimethylphosphine methyl protons were observed in the ^1H NMR spectrum of **3c**. Two broadened doublets were assigned to the ethylene protons.[23] The equilibrium between metallacyclopentanes and bis-ethylene species has been extensively studied in the past.[3c,24] The need for heat in the preparation of **3c** from **3a** suggests that **3a** can be better described as a metallacyclopentane than as a bis-ethylene complex (Scheme 3). A bis-ethylene species such as **3d** could conceivably be part of an equilibrium that lies toward **3a**. Addition of PMe_3, accompanied by heat, could effectively trap **3d**, ultimately resulting in the formation of **3c**.

Synthesis of Oxametallacycles $[(Mo(NPh)(C(CH_3)_2CH_2C(CH_3)_2O)(o\text{-}(Me_3SiN)_2C_6H_4)]$ (4a) and $[(Mo(NPh)(C(H)PhCH_2C(CH_3)_2O)(o\text{-}(Me_3SiN)_2C_6H_4)]$ (4b). Addition of acetone to a solution of **2c** in pentane resulted in the exclusive formation of **4a**, as determined by ^1H and ^{13}C NMR spectroscopy. A single-crystal X-ray crystallographic study of **4a** reveals the square pyramidal geometry about molybdenum (Figure 2). The regioselectivity of this particular reaction, with

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(20) The synthesis, structure, and reactivity studies of this pyridine complex will be reported elsewhere (manuscript in preparation). We include it here only to offer insight into the formation of **3b** via treatment of **2b** with lutidine.

(21) McLain, S. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1978**, *100*, 1315. (b) McLain, S. J.; Sancho, J.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 5610.

(22) Encrich, R.; Heinemann, O.; Jolly, P. W.; Krüger, C.; Verhounik, G. P. J. *Organometallics* **1997**, *16*, 1511. (b) Meijboom, N.; Schaverien, C. J.; Orpen, A. G. *Organometallics* **1990**, *9*, 774. (c) Briggs, J. R. *J. Chem. Soc., Chem. Comm.* **1989**, 674.

(23) We have previously isolated and characterized the corresponding tungsten analogue of **3c**.[9]

(24) Cohen, S. A.; Auburn, P. R.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 1136. (b) Erker, G.; Dorf, U.; Rheingold, A. L. *Organometallics* **1988**, *7*, 138.

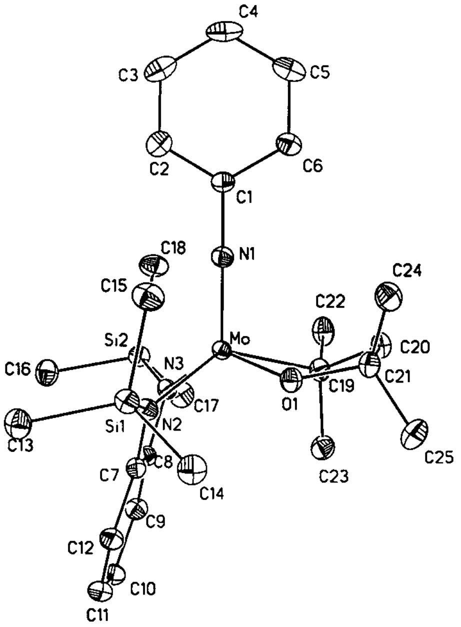

Figure 2. Structure of **4a** (50% probability thermal ellipsoids). Selected bond lengths (Å) and angles (deg): Mo−N(1), 1.7348(18); Mo−O(1), 1.9344(15); Mo−N(3), 2.0072(18); Mo−N(2), 2.0513(17); Mo−C(19), 2.209(2); O(1)−C(21), 1.432(3); C(19)−C(20), 1.541(3); C(20)−C(21), 1.534(3); Mo−C(19)−C(20), 103.80(14); Mo−O(1)−C(21), 122.89(13); C(22)−C(19)−C(23), 109.7(2); C(24)−C(21)−C(25), 109.7(2); C(19)−C(20)−C(21), 111.91(18).

respect to the formation of the metallacycle, became quite clear upon examination of **4a**. The methylene carbon (C(20)) has taken up position between both tertiary carbons, C(19) and C(21). The propensity for molybdenum to form M−O bonds along with the minimization of steric repulsion between the methyl groups of acetone and the isobutene ligand in **2c** during the reaction explains the observed regioselectivity. The Mo−N(1) distance of 1.7348(18) Å is consistent with a metal−nitrogen triple bond,[2c,d,3f,11] and the Mo−N(2) and N(3) amide distances are within the range expected for Mo−N single bonds.[12] The Mo−O(1) distance of 1.9344(15) Å and the Mo−C(19) distance of 2.209(2) Å are both consistent with metal−atom single bonds.[25] The crystal and refinement data for **4a** are summarized in Table 2.

Table 2. Crystal Data, Data Collection, and Structure Refinement for 4a

empirical formula	$C_{25}H_{41}MoN_3OSi_2$
fw	551.73
temperature	173(2) K
wavelength	0.71073 Å
cryst syst	triclinic
space group	$P\bar{1}$
unit cell dimens	$a = 9.8841(7)$ Å, $\alpha = 101.370(1)°$ $b = 11.2646(7)$ Å, $\beta = 96.272(1)°$ $c = 14.766(1)$ Å, $\gamma = 115.921(1)°$
volume	1413.6(2) Å^3
Z	2
density (calcd)	1.296 Mg/m^3
abs coeff	0.569 mm^{-1}
F(000)	580
cryst size	0.27 × 0.25 × 0.16 mm^3
θ range for data collection	1.44−27.50°
limiting indices	$-12 \le h \le 10, -13 \le k \le 14, -16 \le l \le 19$
no. of reflns collected	9474
no. of indep reflns	6236 [R(int) = 0.0620]
completeness to θ = 27.50°	96.0%
abs corr	integration
max. and min. transmn	0.9639 and 0.8427
refinement method	full-matrix least-squares on F^2
no. of data/restraints/params	6236/0/300
goodness-of-fit on F^2	1.066
final R indices [$I > 2\sigma(I)$][a]	R1 = 0.0380, wR2 = 0.1071 [6002]
R indices (all data)	R1 = 0.0390, wR2 = 0.1090
extinction coeff	0.0002(10)
largest diff peak and hole	0.481 and −0.789 e Å^{-3}

[a] $R1 = \sum(||F_o| - |F_c||)/\sum|F_o|$; $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[wF_o^{2\,2}]]^{1/2}$; $S = [\sum[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.0370p)^2 + 0.31p]$, $p = [\max(F_o^2,0) + 2F_c^2]/3$.

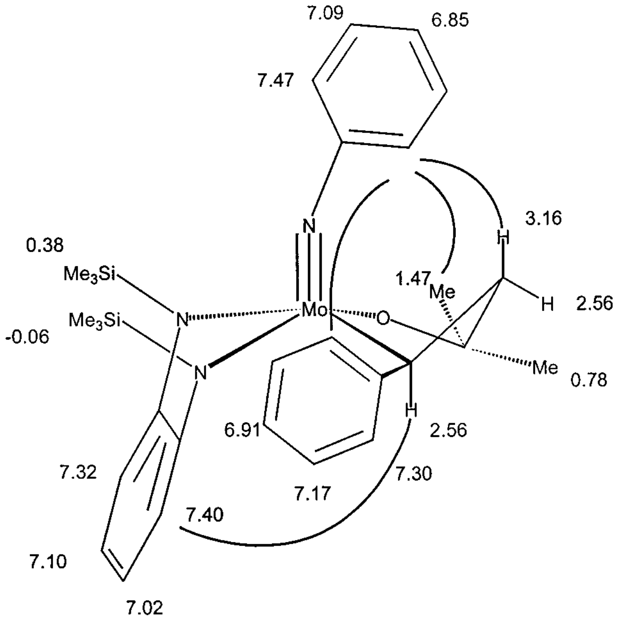

Figure 3. Proposed structure for **4b** assigned via ghmbc, ghmqc, and NOESY. Some of the observed NOES are shown with arced lines. The observed ^{1}H NMR resonances are assigned to their corresponding protons.

When acetone was added to a dark green solution of **2a** in pentane, the solution turned dark red in color. Concentration of the pentane solution under reduced pressure afforded a red solid. ^{1}H NMR spectroscopy of this product confirmed the existence of only one metallacycle-containing product. Pure **4b** was obtained via recrystallization from pentane at −30 °C, and the stereochemistry of **4b** was elucidated by 2-D NMR (ghmqc, ghmbc, and NOESY). The proposed structure for **4b** is illustrated in Figure 3. Complex **4b** adopts a five-coordinate square pyramidal geometry very similar to that of **4a**. Of interest in **4b** is the position of the C(H)Ph fragment, once part of the coordinated styrene in **2a**. The carbon atom of this fragment is bound to the molybdenum center, and the phenyl group occupies an equatorial position in reference to the metallacycle. Steric constraints during the reaction of **2a** with acetone most likely dictate the ultimate configuration of this metallacycle. Similar intramolecular coupling reactions with *in situ* generated early metal metallocenes (e.g., Cp_2Ti, Cp_2Zr, and Cp_2Hf) have been extensively

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(25) Cantrell, G. K.; Geib, S. J.; Meyer, T. Y. *Organometallics* **1999**, *18*, 4250. (b) Cantrell, G. K.; Geib, S. J.; Meyer, T. Y. *Organometallics* **2000**, *19*, 3562. (c) Schrock, R. R.; Luo, S.; Lee, J. C.; Zanetti, N. C.; Davis, W. M. *J. Am. Chem. Soc.* **1996**, *118*, 3883.

explored.[2b,26] Recent developments in this field involve the titanium-catalyzed cyclization of enones mediated by silanes[27] and titanium-based applications toward the synthesis of γ-butyrolactones.[28] We are currently in the process of examining the reactivity of these olefin complexes with various unsaturated organic substrates.

Experimental Section

General Methods. All reactions were conducted under a dry argon atmosphere using standard Schlenk techniques, and all compounds were handled in a nitrogen-filled drybox. All solvents were distilled under nitrogen from sodium or sodium benzophenone ketyl, stored over molecular sieves, and degassed prior to use.

NMR spectra were obtained on a Varian Gemini 300, VXR 300, or Mercury 300 instrument with C_6D_6 or $CDCl_3$ as solvents, as noted, and referenced to residual solvent peaks. An Inova 500 was used as indicated.

Compound **1**, $[\mathrm{Mo(NPh)Cl_2}(o\text{-}(\mathrm{Me_3SiN})_2\mathrm{C_6H_4})\cdot\mathrm{THF}]$, was synthesized following published procedures.[10] Ethylene was predried using 4 Å molecular sieves. All other reagents were obtained from Aldrich Chemicals and stored over 4 Å molecular sieves when necessary.

Complete Analysis Laboratories (Parsippany, NJ) performed elemental analyses. It was impossible to obtain satisfactory elemental analyses on these compounds, and typically results were ca. 1% lower than the theoretical values. Related compounds are known to form carbides and nitrides upon pyrolysis, and this may be responsible for the unsatisfactory results. The ^{1}H NMR spectra of **2a**−**c**, **3a**,**b**, and **4a**,**b** are included in the Supporting Information.

Preparation of η^2-Olefin Complexes. To an Et_2O solution of **1** (0.5 g, 0.86 mmol), cooled to −78 °C, was added dropwise 2 equiv of RMgCl (2.0 M in Et_2O, 1.72 mmol, 0.86 mL) (R = $CH_2CH_2C_6H_5$, $CH_2CH_2CH_3$, $CH_2CH(CH_3)_2$, $CH_2CH_2CH_2CH_3$, $CH(CH_3)CH_2CH_3$) or 1 equiv of Bu_2Mg (1.0 M in heptane, 0.86 mmol, 0.86 mL), with stirring. The mixture quickly turned from blue-purple to red. The reaction mixture was allowed to stir at room temperature for about 2 h, during which time the red solution changed to a forest-green-colored solution. After this time, the diethyl ether was removed under reduced pressure and the solids were dried for 1 h and then extracted with pentane (3 × 25 mL).

R = $\mathbf{CH_2CH_2C_6H_5}$ (2a). The volume of the combined pentane extracts was reduced to 10 mL and then cooled to −78 °C for 2 h. Forest-green crystals appeared at the bottom of the flask, after which the mixture was filtered to yield $[\mathrm{Mo(NPh)}(\eta^2\text{-styrene})(o\text{-}(\mathrm{Me_3SiN})_2\mathrm{C_6H_4})]$ (**2a**) as a green crystalline solid. Additional crops (usually two) can be crystallized from the mother liquors, affording **2a** in 77% isolated yield. Anal. Calcd for $C_{26}H_{35}N_3Si_2Mo\cdot 0.32(CH_3(CH_2)_3CH_3)$: C, 58.49; H, 6.86; N, 7.42. Found: C, 57.46; H, 6.52; N, 8.05. ^{1}H NMR (C_6D_6): δ 0.09 (9H, NSi*Me*$_3$), 0.29 (9H, NSi*Me*$_3$), 0.36 (9H, NSi*Me*$_3$), 0.41 (9H, NSi*Me*$_3$), 1.05 (m, 1H, $\mathrm{C}\mathit{H}_2\mathrm{CHPh}$), 1.16 (m, 1H, $\mathrm{C}\mathit{H}_2\mathrm{CHPh}$), 2.22 (t, 1H, $\mathrm{CH_2C}\mathit{H}\mathrm{Ph}$), 3.38 (m, 1H, $\mathrm{C}\mathit{H}_2\mathrm{CHPh}$), 3.54 (m, 1H, $\mathrm{C}\mathit{H}_2\mathrm{CHPh}$), 4.90 (t, 1H, $\mathrm{CH_2C}\mathit{H}\mathrm{Ph}$), 5.94 (d, 2H, styrene ortho protons), 6.6−7.5 (aromatics). ^{13}C NMR (C_6D_6): δ 1.6, 1.6, 1.9, 2.0, 51.2, 53.1, 67.6, 74.5, 123.6, 123.8, 123.9, 124.0, 124.2, 124.3, 124.7, 125.1, 125.3 (ov), 125.5, 125.6, 125.8, 128.5, 129.0, 129.5, 130.8, 131.2, 144.5, 147.3, 158.1, 158.8, (six peaks are obscured by overlap with C_6D_6 and other aromatic resonances). HRMS calcd for $[M + H]^+$: 544.1506. Found (LSIMS): 544.1569.

R = $\mathbf{CH_2CH_2CH_3}$ (2b). The volume of the pentane extract was reduced to 10 mL and then cooled to −78 °C for 2 h. Dark-green microcrystals appeared, and after filtration, $[\mathrm{Mo(NPh)}(\eta^2\text{-propene})(o\text{-}(\mathrm{Me_3SiN})_2\mathrm{C_6H_4})]$ (**2b**) was obtained as microcrystals (isolated yield 68%). ^{1}H NMR (C_6D_6): δ 0.32 (27H, NSi*Me*$_3$), 0.36 (9H, NSi*Me*$_3$), 0.45 (m, 1H, $\mathrm{C}\mathit{H}_2\mathrm{CHCH_3}$), 0.90 (ov, m, 4H, $\mathrm{CH_2CHC}\mathit{H}_3$), 1.34 (m, 1H, $\mathrm{CH_2C}\mathit{H}\mathrm{CH_3}$), 2.40 (d, 3H, $\mathrm{CH_2CHC}\mathit{H}_3$), 2.81 (m, 1H, $\mathrm{C}\mathit{H}_2\mathrm{CHCH_3}$), 3.32 (m, 1H, $\mathrm{CH_2C}\mathit{H}\mathrm{CH_3}$), 4.01 (m, 1H, $\mathrm{C}\mathit{H}_2\mathrm{CHCH_3}$), 6.8−7.5 (aromatics). ^{13}C NMR (C_6D_6): δ 1.5, 1.5, 1.6, 1.9, 20.0, 26.3, 56.8, 57.9, 64.2, 73.6, 123.7, 123.8, 124.2, 124.4, 124.6, 124.7, 124.8, 125.0, 125.2, 129.4, 129.5, 129.8, 130.9, 140.0, 158.3, 158.6 (four peaks are obscured by overlap with C_6D_6 and other aromatic resonances).

R = $\mathbf{CH_2C(CH_3)_2}$ (2c). The pentane was removed from the mixture under reduced pressure. This allowed $[\mathrm{Mo(NPh)}(\eta^2\text{-isobutene})(o\text{-}(\mathrm{Me_3SiN})_2\mathrm{C_6H_4})]$ (**2c**) to be isolated as a thick, dark-green oil. Further attempts to obtain **2c** as a solid were not successful (isolated yield 72%). ^{1}H NMR (C_6D_6): δ 0.29 (9H, NSi*Me*$_3$), 0.36 (9H, NSi*Me*$_3$), 0.73 (ov, m, 4H, $\mathrm{C}\mathit{H}_2\mathrm{C(C}\mathit{H}_3)_2$), 2.60 (s, 3H, $\mathrm{CH_2C(C}\mathit{H}_3)_2$), 2.99 (d, 1H, $\mathrm{C}\mathit{H}_2\mathrm{C(CH_3)_2}$), 6.88 (t, 1H, N-Ph imido para proton), 7.00 (m, 2H, $(Me_3Si)_2$-pda aromatic protons), 7.07 (t, 2H, N-Ph imido meta protons), 7.41 (m, 4H, $(Me_3Si)_2$-pda aromatic protons and N-Ph imido ortho protons). ^{13}C NMR (C_6D_6): δ 1.4, 2.0, 27.9, 33.8, 59.3, 81.3, 123.5, 123.9, 124.4, 124.7, 125.0, 125.3, 129.4, 132.2, 133.1, 158.2.

R = $\mathbf{CH_2CH_2CH_2CH_3}$, $\mathbf{CH(CH_3)CH_2CH_3}$, or $\mathbf{(CH_3CH_2CH_2CH_2)_2Mg}$ (2d,e). The pentane was removed from the mixture under reduced pressure. This allowed a mixture of $[\mathrm{Mo(NPh)}(\eta^2\text{-1-butene})(o\text{-}(\mathrm{Me_3SiN})_2\mathrm{C_6H_4})]$ (**2d**) and $[\mathrm{Mo(NPh)}(\eta^2\text{-2-butene})(o\text{-}(\mathrm{Me_3SiN})_2\mathrm{C_6H_4})]$ (**2e**) to be isolated as a dark-green oil. Further attempts to obtain either of these compounds as solids and purify them were unsuccessful.

Preparation of $\mathbf{[Mo(NPh)(CH_2CH_2CH_2CH_2)(\mathit{o}\text{-}(Me_3SiN)_2C_6H_4]}$ (3a). Method 1. One equivalent of $BrMgCH_2CH_2CH_2CH_2MgBr$ (0.99 M in Et_2O, 0.86 mmol, 0.87 mL) was added to a diethyl ether solution of **1** (0.5 g, 0.86 mmol) cooled to −78 °C. The blue solution quickly turned to a purple solution upon addition of the alkylating agent. As the reaction mixture was allowed to warm up to room temperature, the color of the solution slowly turned red-orange. The red-orange solution was stirred for 1 h and pumped to dryness (in vacuo). The remaining solids were extracted with pentane and filtered. The red-orange filtrate was pumped to dryness and dried overnight (in vacuo). By ^{1}H NMR spectroscopy, metallacyclopentane **3a** was obtained in low purity and yield.

Method 2. To a cooled (−78 °C) diethyl ether solution of **1** (0.5 g, 0.86 mmol), was added 2 equiv of EtMgCl (2.0 M in Et_2O, 1.7 mmol, 0.86 mL). Reaction workup, similar to that described in method 1, provided both metallacyclopentane **3a** and oligomeric **3b** in low purity.

Method 3. To a Schlenk tube containing a cooled (−78 °C) diethyl ether solution of **1** (1.0 g, 0.86 mmol) was added dropwise 2 equiv of EtMgCl (2.0 M in Et_2O, 1.7 mmol, 0.86 mL). The solution quickly changed color from blue to purple. This purple solution was frozen and the vessel evacuated. Subsequently, the solution was allowed to thaw, while the neck of the vessel was degassed for 5 min using dry ethylene. Ethylene was added to the Schlenk tube (1−2 atm) and the solution stirred for 1 h at room temperature. The resulting red-orange solution was pumped to dryness (in vacuo), followed by extraction with pentane. The volume of the filtrate was reduced and the concentrated solution cooled to −78 °C. This afforded dark-red crystals, which were isolated by filtration (0.58 g) in 69% isolated yield. Further purification of **3a** was done by recrystallization from pentane at −78 °C. Anal. Calcd for $C_{22}H_{35}N_3Si_2Mo$: C, 53.52; H, 7.14; N, 8.51. Found: C, 52.67;

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[26] Reviews: (a) Broene, R. D.; Buchwald, S. L. *Science* **1993**, *261*, 1696. (b) Negishi, E. *Chem. Scr.* **1989**, *29*, 457. (c) Negishi, E.; Takahashi, T. *Acc. Chem. Res.* **1994**, *27*, 124.

[27] Kablaoui, N. M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1995**, *117*, 6785. (b) Kablaoui, N. M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1996**, *118*, 3182. (c) Crowe, W. E.; Rachita, M. J. *J. Am. Chem. Soc.* **1995**, *117*, 6787.

[28] Kablaoui, N. M.; Hicks, F. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1996**, *118*, 5818. (b) Crowe, W. E.; Vu, A. T. *J. Am. Chem. Soc.* **1996**, 118, 1557.

H, 7.11; N, 8.44. ^{1}H NMR (C_6D_6): δ 0.32 (18H, NSi*Me*$_3$), 1.53 (m, 2H), 2.01 (m, 2H,), 2.64 (m, 2H), 3.13 (m, 2H), 6.90 (t, 1H, N-Ph imido para proton), 7.05 (m, 2H, $(Me_3Si)_2$-pda aromatic protons), 7.10 (t, 2H, N-Ph imido meta protons), 7.42 (m, 2H, $(Me_3Si)_2$-pda aromatic protons), 7.50 (m, 2H, N-Ph imido ortho protons). ^{13}C NMR (C_6D_6): δ 1.0, 36.3, 57.3, 123.3, 124.5, 125.1, 125.6, 129.0, 133.4.

Preparation of [Mo(NPh)(*o*-$(Me_3SiN)_2C_6H_4$)]$_x$ (3b). An excess of lutidine (5 equiv) was added to a stirring green pentane solution (20 mL) of **2b** (0.5 g, 1.0 mmol). After 2 h of stirring the solvents were removed under vacuum, affording a black solid. This black solid was washed with cold pentane and dried in vacuo (Isolated yield 68%). ^{1}H NMR (C_6D_6): δ 0.85 (18H, NSi*Me*$_3$), 6.30 (d, 2H), 7.60 (d, 2H), 7.99 (d, 2H), 8.12 (t, 1H), 8.43(d, 2H).

Preparation of [Mo(NPh)(η^2-ethylene)(*o*-$(Me_3SiN)_2$-C_6H_4)$(PMe_3)_2$] (3c). A small excess of PMe_3 (17 mg, 0.223 mmol) was added to a C_6D_6 solution of **3a** (50 mgs, 0.101 mmol) and heated to 80 °C, affording **3c** in low purity and yield. Alternatively, **3c** was prepared in low purity and yield by reacting 2 equiv of EtMgCl with **1** (Et_2O, −78 °C) while in the presence of slightly more than 2 equiv of PMe_3. Evidence for the formulation of **3c** comes from comparison of the ^{1}H NMR spectrum with that of the tungsten analogue.[9,23] Selected ^{1}H NMR (C_6D_6): δ 0.46 (br, 18H, Si*Me*$_3$), 0.95 (br, 18H, P*Me*$_3$), 2.22 (br, d, 2H), 2.66 (br, d, 2H).

Preparation of [Mo(NPh)$(C(CH_3)_2CH_2C(CH_3)_2O)$(*o*-$(Me_3SiN)_2C_6H_4$] (4a). Acetone (0.037 g, 0.65 mmol) was added to a stirring green solution of **2c** (0.32 g, 0.65 mmol) in 50 mL of pentane at room temperature. The color of the reaction mixture immediately changed from green to purple. The resulting pentane solution was concentrated in vacuo and cooled at −30 °C for 2 days, affording purple microcrystals, which were isolated by filtration and dried in vacuo. Additional crops can be crystallized from the mother liquors, affording **4a** in 78% isolated yield. Anal. Calcd for $C_{25}H_{41}N_3Si_2OMo$: C, 54.42; H, 7.49; N, 7.62. Found: C, 53.27; H, 8.01; N, 7.96. ^{1}H NMR ($CDCl_3$): δ 0.27 (9H, Si*Me*$_3$), 0.28 (9H, Si*Me*$_3$), 0.53 (*Me*), 0.95 (*Me*), 1.26 (*Me*), 1.86 (*Me*), 2.08 (d, 13 Hz, C(*H*)), 2.99 (d, 13 Hz, C(*H*)), 6.9−7.4 (aromatic protons, 9H). ^{13}C NMR: δ 0.5, 3.3, 30.8, 31.4, 34.4, 39.5, 67.8, 78.0, 83.8, 119.7, 120.9, 122.0, 125.4, 125.5, 125.8, 128.7, 139.5, 145.7, 156.7. HRMS calcd for $[M + H]^+$: 554.1926 *m*/*e*. Found (LSIMS): 554.1948 *m*/*e*.

Preparation of [Mo(NPh)$(C(H)PhCH_2C(CH_3)_2O)$(*o*-$(Me_3SiN)_2C_6H_4$] (4b). Acetone (0.022 g, 0.38 mmol) was added to a stirring green solution of **2a** (0.20 g, 0.38 mmol) in 50 mL of pentane at room temperature. The color of the reaction mixture immediately changed from green to red. The resulting pentane solution was concentrated in vacuo and cooled at −30 °C for 2 days, affording red microcrystals, which were isolated by filtration and dried in vacuo. Additional crops can be crystallized from the mother liquors, affording **4b** in 78% isolated yield. ^{1}H NMR (C_6D_6; 500 MHz; from ghmbc and ghmqc): δ −0.06 (9H, Si*Me*$_3$), 0.38 (9H, Si*Me*$_3$), 0.78 (*Me*), 1.47 (*Me*), 2.56 (m, 2H), 3.16 (“t”, 14.5 Hz, 1H), 6.85 (t of t, 7.5 Hz, 1.0 Hz, N-Ph imido para proton), 6.91 (t of t, 7.5 Hz, 1.0 Hz, metallacycle phenyl para proton), 7.02 (d of d of d, 8 Hz, 7 Hz, 1.5 Hz, $(Me_3Si)_2$-pda aromatic proton), 7.09 (t, 8 Hz, N-Ph imido meta protons), 7.10 (ov, $(Me_3Si)_2$-pda aromatic proton), 7.17 (t, 7.5 Hz, metallacycle phenyl meta protons), 7.30 (d of d, 8 Hz, 1 Hz, metallacycle phenyl ortho protons), 7.32 (d of d, 8.5 Hz, 1.0 Hz, $(Me_3Si)_2$-pda aromatic proton), 7.40 (d of d, $(Me_3Si)_2$-pda aromatic proton) 7.47 (d of d, 8.5 Hz, 1.0 Hz, N-Ph imido ortho protons). ^{13}C (C_6D_6; 500 MHz; from ghmbc and ghmqc): δ −0.1, 1.0, 28.0, 32.4, 56.2, 76.7, 86.4, 121.2, 123.6, 123.7, 123.8, 124.3, 125.6, 127.6, 128.0, 128.2, 128.9, 133.2, 140.3, 154.0, 156.2. HRMS calcd for $[M]^+$: 601.1844 *m*/*e*. Found (LSIMS): 601.1869.

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Supporting Information Available: Tables of atomic coordinates, anisotropic thermal parameters, and bond lengths and angles for **2a** and **4a** as well as ^{1}H NMR spectra of **2a**−**c**, **3a**,**b**, and **4a**,**b**. The NOE difference spectrum associated with **2a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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