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Articles

Synthesis of Chelate-Supported Dialkyl and Alkylidene Complexes of Molybdenum(VI)

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The use of chelating diamide $[o\text{-}(Me_3SiN)_2C_6H_4]^{2-}$ as a coligand for high-oxidation early transition metal complexes has been investigated. Reaction of $Mo(NPh)_2Cl_2DME$ with $Li_2[o\text{-}(Me_3SiN)_2C_6H_4]$ afforded green microcrystals of $[Mo(NPh)(\mu\text{-}NPh)(o\text{-}(Me_3SiN)_2C_6H_4)]_2$ (**1**), while reaction of $Mo(NPh)_2Cl_2DME$ with $H_2[o\text{-}(Me_3SiN)_2C_6H_4]$ gave $Mo(NPh)Cl_2(o\text{-}(Me_3SiN)_2C_6H_4)(NH_2Ph)$ (**2**). Two derivatives of **2** are reported, $Mo(NPh)Cl_2(o\text{-}(Me_3SiN)_2C_6H_4)(PMe_3)$ (**3**) and $Mo(NPh)Cl_2(o\text{-}(Me_3SiN)_2C_6H_4)(THF)$ (**4**). Structural studies of **3** are reported. Reaction of **3** or **4** with RMgX (X = Cl or Br) gave $Mo(NPh)R_2(o\text{-}(Me_3SiN)_2C_6H_4)$ (R = Me **5**, Ph **6**, CH_2CMe_3 **7**, CH_2Ph **8**, CH_2SiMe_3 **9**). Reaction of **2** with RMgCl (R = CH_2CMe_3, CH_2SiMe_3) gave mixtures of $Mo(NPh)R_2(o\text{-}(Me_3SiN)_2C_6H_4)$ and $Mo(NPh)_2R_2$. Both $Mo(NPh)_2(CH_2CMe_3)_2$ (**10**) and $Mo(NPh)_2(CH_2SiMe_3)_2$ (**11**) were isolated form the reaction of $Mo(NPh)_2Cl_2DME$ and RMgCl (R = CH_2CMe_3, CH_2SiMe_3). The alkylidene, $Mo(NPh)(C(H)CMe_3)(o\text{-}(Me_3SiN)_2C_6H_4)(PMe_3)$ (**13**), was isolated from the reaction of **7** and an excess of PMe_3 at 80 °C, while $Mo(NPh)(C(H)SiMe_3)(o\text{-}(Me_3SiN)_2C_6H_4)(PMe_3)$ (**14**) was only observed by ^1H NMR under similar conditions.

Introduction

For several decades the study of high oxidation state, early transition metal compounds and their derivatives has been the focus of intense research due to their use in organic synthesis and in catalysis.[1] Among the most studied derivatives of high oxidation state early transition metal compounds are metal alkyls and alkylidenes. High oxidation state alkyls have been extensively used as catalysts for the polymerization of olefins, as exemplified by the large number of reports using group 4 metallocene type systems.[2] Likewise, the importance of alkylidenes is demonstrated by the comprehensive study of the olefin metathesis reactions that they are able to catalyze.[3,4] Through this reaction, alkylidenes have been shown to catalyze the polymerization of strained olefinic ring systems in ring opening metathesis polymerization (ROMP) and the polymerization of acyclic dienes (ADMET).[5]

Previous reports from our group have focused on the chemistry of W(VI) imido dichloride, dialkyl, and alkylidene compounds supported by ligands derived from *N*,*N*′-bis(trimethylsilyl)-*o*-phenylenediamine ($H_2\text{-}o\text{-}(Me_3SiN)_2C_6H_4$).[6] By using this chelating ligand, we achieved the syntheses of thermally stable, coordinatively unsaturated dialkyl species.[7] These complexes display insertion chemistry with alkyl isocyanides[8] and undergo β-hydride abstraction in the presence of Lewis bases.[9] In addition, the thermally stable neopentylidene com-

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plex $\mathrm{W(NPh)(C(H)CMe_3)}$($o$-$\mathrm{(Me_3SiN)_2C_6H_4}$)($\mathrm{PMe_3}$) was shown to catalyze the ROMP of norbornene and cyclooctene and catalyze the ADMET oligomerization of 1,9-decadiene.[10]

For some time, we have been interested in using *N*,*N′*-disubstituted-*o*-phenylenediamides (*o*-pda) as ancillary ligands for other high oxidation state early transition metal systems. While disubstituted-pda compounds have already been reported for Zr(IV), Ti(IV),[11] and recently Ta(V),[12] our efforts with other members of group 6 have, until now, been unsuccessful. We now wish to report the syntheses and characterization of Mo(VI) complexes supported by imido and chelating-diamide coligands. Included in this work are the syntheses of dichloride and dialkyl species, the synthesis of alkylidene species, and the isolation of a dimeric Mo(VI) complex.

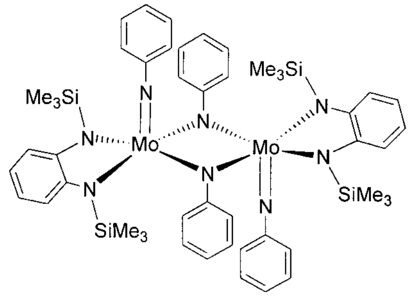
Results and Discussion

Synthesis of Imido-Bridged Dimer. Since our bidentate diamide ligand was bound to W(VI) through the reaction of dilithiated $\mathrm{Li_2}$-o-$\mathrm{(Me_3SiN)_2C_6H_4}$ with $\mathrm{W(NPh)Cl_4(OEt_2)}$,[6] the reaction of $\mathrm{Li_2}$-o-$\mathrm{(Me_3SiN)_2C_6H_4}$ with $\mathrm{Mo(NPh)_2Cl_2DME}$[13] was investigated.

When $\mathrm{Li_2}$-o-$\mathrm{(Me_3SiN)_2C_6H_4}$ was prepared in situ in $\mathrm{Et_2O}$, cooled to −78 °C, and then added to an −78 °C $\mathrm{Et_2O}$ solution of $\mathrm{Mo(NPh)_2Cl_2DME}$, a rapid color change from orange to green occurred as the reaction mixture returned to room temperature. Filtration of the reaction mixture followed by extraction of the remaining solids with toluene and removal of the solvent in vacuo produced low yields of forest-green, microcrystalline [$\mathrm{Mo(NPh)}$(μ-NPh)(o-$\mathrm{(Me_3SiN)_2C_6H_4}$)]$_2$ (**1**).

$$\mathrm{Mo(NPh)_2Cl_2(DME)} + \mathrm{Li_2}\text{-}o\text{-}\mathrm{(Me_3SiN)_2C_6H_4} \xrightarrow{\mathrm{Et_2O},\ -78^{\circ}\mathrm{C}}$$

1



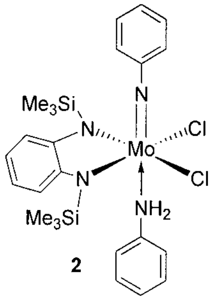
(1)

The ^{1}H NMR spectra are consistent with the dimeric structure shown in eq 1. A sharp singlet was observed at −0.04 ppm (36H) and is assigned to equivalent $\mathrm{Me_3Si}$ methyl groups. Signals corresponding to the phenylimido *ortho*-protons were observed as two doublets at 6.55 ppm (4H) and 6.74 ppm, which arise from the inequivalent phenylimido groups. This inequivalency was also confirmed by the observation of a triplet at 6.87 ppm (2H) and a triplet overlapping with the doublet at 6.74 ppm (together integrating to 6H), with both triplets corresponding to the *para*-phenylimido hydrogens. A triplet for a *meta*-phenyl imido hydrogen was observed at 7.00 ppm, with its inequivalent counterpart overlapping with one of the pda-ring resonances from 7.07 to 7.12 ppm. The other pda-ring resonance was clearly observed at 7.26 ppm (4H).

Further proof of the formulation of **1** was obtained from a single-crystal X-ray diffraction study. Unfortunately, a structure refinement suitable for publication was not obtained. However, the data were sufficient to confirm the identity of **1** as an imido-bridged dimer supported by the chelating-diamide group. Efforts to grow higher quality single crystals for X-ray diffraction are continuing. It is noted that several examples of imido-bridged dimers have been reported; thus the structure of **1** is precedented.[14]

Synthesis of Chelate-Supported Dichloride Species. When a suspension of brick-red $\mathrm{Mo(NPh)_2Cl_2DME}$ in hexanes was mixed with a hexanes solution containing 2 equiv of $\mathrm{H_2}$-o-$\mathrm{(Me_3SiN)_2C_6H_4}$ and stirred overnight, a slow reaction occurred giving a dark green solution along with the formation of a blue precipitate. Filtration of the reaction mixture gave a nearly quantitative yield of a hexanes-insoluble blue-purple powder, **2**.

$$\mathrm{Mo(NPh)_2Cl_2(DME)} + 2\ \mathrm{H_2}\text{-}o\text{-}\mathrm{(Me_3SiN)_2C_6H_4} \xrightarrow{\text{hexanes, RT}}$$



(2)

2

The NMR spectra of **2** were consistent with the structure shown in eq 2. Proton NMR ($\mathrm{C_6D_6}$) spectra of **2** displayed one resonance due to equivalent $\mathrm{Me_3Si}$ groups at 0.40 ppm (18H) and a broad singlet at 3.92 ppm (2H) corresponding to the coordinated aniline N−H protons. Although the aromatic region in the ^{1}H NMR of **2** was rather complex (three different phenyl rings), the presence of the *o*-phenylenediamide ring was con-

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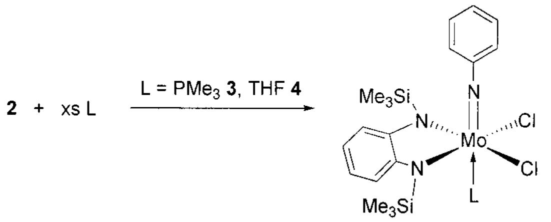
firmed by its two distinct resonances centered at 6.6 ppm (m, 4H). Slightly lower yields of **2** were obtained by refluxing $Mo(NPh)_2Cl_2DME$ and 1 equiv of H_2-*o*-$(Me_3SiN)_2C_6H_4$ in hexanes for 7 h followed by cooling to room temperature and filtration. Alternatively, **2** was also isolated by stirring equimolar quantities of starting materials in hexanes at room temperature for 2 days.

A possible pathway for the formation of **2** involves loss of DME from the starting material followed by coordination of the Mo atom to H_2-*o*-$(Me_3SiN)_2C_6H_4$. Diamine protons are then either both transferred to an imido nitrogen or form a dianilide complex followed by α abstraction of an NH proton by one of the anilide groups. These types of proton-transfer reactions have been postulated to be part of the formation of multiply bonded ligands in related complexes.[15] For example, Wilkinson et al.[16] reported that the reaction of $Cr(NBu^t)_2Cl_2$ and excess NH_2Bu^t resulted in the formation of $Cr(NBu^t)_2(NHBu^t)Cl$ with loss of Bu^tNH_3Cl. Nugent and Chan[17] have reported that $W(N\text{-}t\text{-}Bu)_2(HN\text{-}t\text{-}Bu)_2$ reacts with substituted vicinal diols to form chelated-glycolate compounds $W(N\text{-}t\text{-}Bu)_2(X)(NH_2\text{-}t\text{-}Bu)$ (X = pinacolate, benzopinacolate, and perfluoropinacolate) with loss of aniline. In addition, Wigley et al. have reported that $[Mo(NAr)_3Cl]^-$ is converted to $Mo(NAr)_2(NH_2Ar)_2$ in the presence of NH_2Ar.[18]

Because of possible side reactions with coordinated aniline during alkylation reactions, species of the type $Mo(NPh)Cl_2(o\text{-}(Me_3SiN)_2C_6H_4)L$ (L = PMe_3 **3**, THF **4**) were prepared from **2**. Compound **3** was prepared by dissolving **2** in Et_2O at room temperature followed by addition of excess PMe_3 with stirring. Blue-purple microcrystals of **3** were obtained by concentrating the reaction mixture and cooling to −78 °C. Proton and ^{13}C NMR spectra suggest that **3** has pseudo-octahedral coordination geometry, with the phenylimido and PMe_3 ligands occupying mutually *trans* positions. Proton NMR spectra showed equivalent Me_3Si groups, which give rise to one resonance at 0.44 ppm (18H). A doublet centered at 0.73 ppm (9H, J_{PH} = 8.7 Hz) was assigned to the PMe_3 methyl groups. The pda ligand showed its characteristic set of resonances centered around 6.90 ppm (m, 4H). In addition, two triplets and a doublet corresponding to the imido ligand were also observed (6.77 ppm (t), 7.04 ppm (t), and 7.83 ppm (d)).



(3)

Table 1. Crystal Data and Structure Refinement for 3

empirical formula	$C_{25}H_{46}Cl_2MoN_3OPSi_2$
fw	658.64
temperature	173(2) K
wavelength	0.71073 Å
crystal system	monoclinic
space group	*P*2(1)/*c*
unit cell dimens	a = 9.7269(2) Å, α = 90° b = 17.7600(4) Å, β = 94.237(1)° c = 18.9629(4) Å, γ = 90°
volume, *Z*	3266.88(12) Å^3, 4
density (calcd)	1.339 Mg/m^3
abs coeff	0.709 mm^{-1}
F(000)	1376
crystal size	0.28 × 0.16 × 0.14 mm
θ range for data collection	2.10−27.50°
limiting indices	$-12 \leq h \leq 11$, $-21 \leq k \leq 22$, $-22 \leq l \leq 24$
no. of reflns collected	21565
no. of indep reflns	7435 [*R*(int) = 0.0308]
abs corr	empirical
max. and min. transmn	0.928 and 0.712
refinement method	full-matrix least-squares on F^2
no. of data/restraints/params	7435/0/461
goodness-of-fit on F^2	1.027
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0283, wR2 = 0.0676 [6045]
R indices (all data)	R1 = 0.0409, wR2 = 0.0734
extinction coeff	0.0010(2)
largest diff peak and hole	0.492 and −0.702 e Å^{-3}

The THF adduct $Mo(NPh)Cl_2(o\text{-}(Me_3SiN)_2C_6H_4)THF$, **4**, was prepared by stirring **2** in THF for 1 h followed by precipitation with pentane and filtration. Proton NMR spectra in C_6D_6 confirmed the presence of coordinated THF as two multiplets at 1.06 ppm (4H) and 3.56 ppm (4H). In addition, the singlet at 0.44 ppm corresponding to the equivalent Me_3Si methyl groups was consistent with octahedral coordination geometry.

Crystals of **3** were obtained by cooling a concentrated Et_2O solution to −20 °C for several days. Data collection and refinement parameters are listed in Table 1. As Figure 1 shows, **3** has a distorted octahedral geometry with the PMe_3 and phenylimido ligands in mutually *trans* positions. The molybdenum metal center is raised 0.307(1) Å above the plane containing the chloride and amido N atoms. A long Mo−P(1) bond length of 2.7240(6) Å[19,20] is indicative of a weak interaction between the metal center and the phosphorus atom. The Mo−N3 bond length of 1.745(2) Å is consistent with a Mo≡N triple bond.[21] The Mo−N1 [2.018(2) Å] and Mo−N2 [2.017(2) Å] bond lengths are within normal values for Mo−N single bonds as are the Mo−Cl1 and Mo−Cl2 distances.

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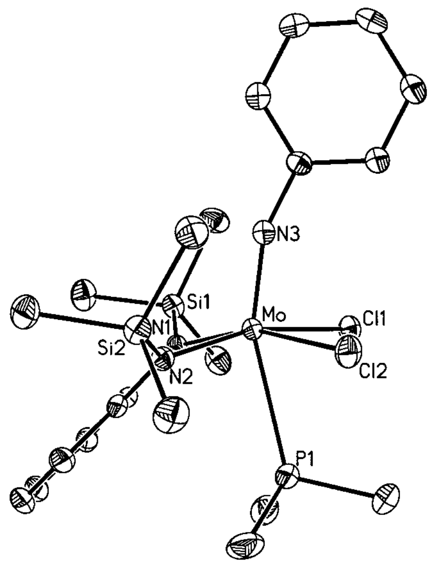
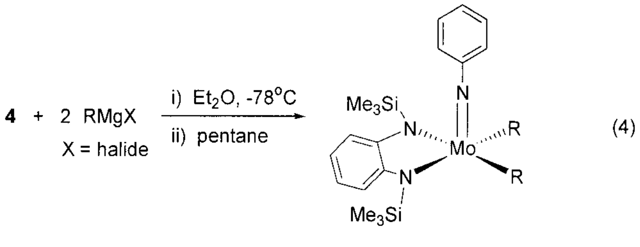


Figure 1. Thermal ellipsoid drawing of **3**. Thermal ellipsoids are drawn to 40% probability.

Synthesis of Dialkyl Complexes. The reaction of **4** with 2 equiv of RMgCl (R = Me **5**, R = Me_3CCH_2 **7**, $PhCH_2$ **8**, Me_3SiCH_2 **9**) in Et_2O at −78 °C gave orange-red mixtures within 1 h, and the reaction of **4** with 2 equiv of RMgBr (R = Ph **6**) produced a purple mixture within 1 h. Removal of the solvent followed by extraction with pentane or toluene separated the desired dialkyl products $Mo(NPh)R_2(o\text{-}(Me_3SiN)_2C_6H_4)$ from the magnesium salts. Complexes **5**, **7**, and **9** were crystallized by cooling concentrated acetonitrile solutions to 0 °C, while compounds **6** and **8** were recrystallized from toluene and pentane solutions cooled to −78 °C, respectively.

Proton NMR spectra of **5** in C_6D_6 revealed the presence of two methyl groups as a singlet at 1.13 ppm (6H). Both the methyl and Me_3Si groups, respectively, were equivalent at room temperature. This suggests that the coordination geometry of this compound is square pyramidal with the phenylimido group occupying the apical position (eq 4). Carbon-13 NMR spectra in $CDCl_3$ show the methyl carbons to be at 31.28 ppm with a coupling constant of $^1J_{CH}$ = 126.4 Hz. This coupling constant indicates that agostic interactions[22] between the methyl hydrogens and the metal center in **5** are unlikely, at least at room temperature, despite the $16e^-$ formal electron count at the metal center.



(4)

R = Me **5**, Ph **6**, Me_3CCH_2 **7**, $PhCH_2$ **8**, Me_3SiCH_2 **9**

Proton NMR spectra of **6** in C_6D_6 solution showed equivalent Me_3Si groups at 0.11 ppm (18H), which suggested the symmetric square pyramidal structure shown in eq 4. There are two triplets in a 2:1 ratio at 6.82 ppm (2H) and 6.90 ppm (1H), which were assigned to the phenyl group hydrogens *para* to the metal center and *para* to the imido nitrogen, respectively. Another set of resonances that confirmed the identity of **6** are two doublets in a 4:2 ratio at 7.40 and 7.61 ppm, which are assigned to the phenyl group protons *ortho* to the metal center and *ortho* to the imido nitrogen, respectively. One of the resonances attributed to the pda-ring protons was observed, but it is partially overlapping with the doublet at 7.40 ppm. However, these two resonances integrate to six total hydrogens.

The ^1H spectra of **7**−**9** are similar in that they display resonances that are assigned to equivalent Me_3Si groups as well as doublets (or in the case of **8** an AB quartet) for the methylene protons of the alkyl groups. Although these spectra are consistent with a square pyramidal structure, they are also consistent with rapidly equilibrating square pyramidal and trigonal bipyramidal structures at room temperature. Given that the solid-state structure of $W(NPh)(CH_2CMe_3)_2(o\text{-}(Me_3SiN)_2C_6H_4)$ is a trigonal bipyramid[7] and that the compound is fluxional at room temperature, we investigated the ^1H spectra of **7**−**9** at low temperatures.

Variable-temperature ^1H NMR studies showed that **7** and **9** are fluxional in solution and that decoalescence of the Me_3Si peak occurs at −18 and −30 °C, respectively. The two-site exchange approximation gives $\Delta G^{\ddagger}$ = 12.6 kcal/mol for this process for **7** and $\Delta G^{\ddagger}$ = 11.9 kcal/mol for **9**.[23] Thus, the NMR spectra of both **7** and **9** are consistent with trigonal bipyramidal structures in which the imido group and one Me_3SiN group occupy the axial positions. It appears that this geometry is preferred over the square pyramid with an apical imido group for steric reasons. The ^1H NMR spectrum of **8** was invariant from room temperature to −78 °C.

Reactivity of 2 with Alkylating Agents. When **2** was allowed to react with 2 equiv of RMgCl (R = Me_3CCH_2 or Me_3SiCH_2) in diethyl ether at −78 °C, an unexpected mixture of products was obtained. The mixture contained **7** and **9** as well as the bis-imido species of the type $Mo(NPh)_2R_2$ (**10**, and **11**, respectively). Formation of dimeric **1** was not observed.

$$\begin{aligned}&Mo(NPh)Cl_2(o\text{-}(SiMe_3N)_2C_6H_4)(NH_2Ph) + \\ &2RMgCl \xrightarrow{Et_2O,\ -78\ ^\circ C} Mo(NPh)R_2(o\text{-}(SiMe_3N)_2C_6H_4) \\ &\qquad R = CH_2CMe_3,\ \mathbf{7}\text{ and }\mathbf{10} \\ &\qquad CH_2SiMe_3,\ \mathbf{9}\text{ and }\mathbf{11} \\ &\qquad + Mo(NPh)_2R_2 \quad (5)\end{aligned}$$

We have independently prepared **10** and **11** by reaction of $Mo(NPh)_2Cl_2DME$ with 2 equiv of RMgCl (R =

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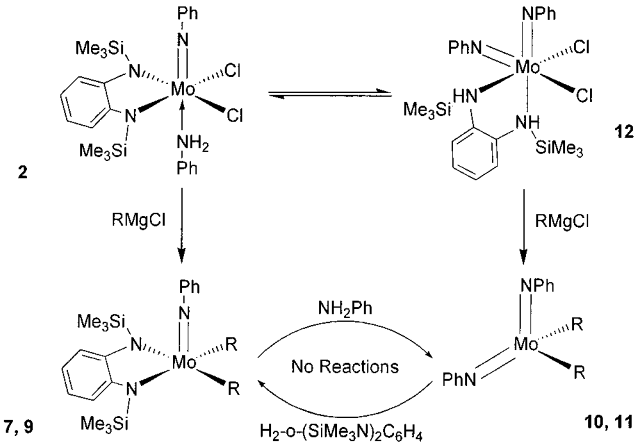
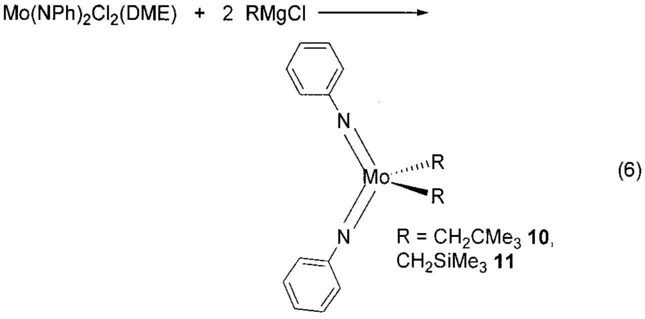
(22) For review of agostic interactions: Brookhart, M.; Green, M. L. H.; Wang, L. *Prog. Inorg. Chem.* **1988**, *36*, 1. More recent examples: (a) Coles, M. P.; Gibson, V. C.; Clegg, W.; Elsewood, M. R. J. *Polyhedron* **1998**, *17*, 2483. (b) Jaffart, J.; Mathier, R.; Etienne, M.; McGrady, J. E.; Eisenstein, O.; Maseras, F. *J. Chem. Soc., Chem. Commun.* **1998**, 2011. (c) Cole, J. M.; Gibson, V. C.; Howard, J. A. K.; McIntyre, G. J.; Walker, G. L. P. *J. Chem. Soc., Chem. Commun.* **1998**, 1829. (d) Rietveld, M. H. P.; Teunissen, W.; Hagen, H.; van de Water, L.; Grove, D. M.; van der Schaaf, P. A.; Mühlebach, A. L.; van Koten, G. *Organomentallics* **1997**, *16*, 1674. (e) Haaland, A.; Scherer, W.; Ruud, K.; McGarrady, G. C.; Downs, A. J.; Swang, O. *J. Am. Chem. Soc.* **1998**, *120*, 3762. (f) Jordan, R. F.; Bradley, P. K.; Baenziger, N. C.; LaPointe, R. E. *J. Am. Chem. Soc.* **1990**, *112*, 1289.

(23) Sandström, J. *Dynamic NMR Spectroscopy*; Academic Press: New York, 1982.

Scheme 1



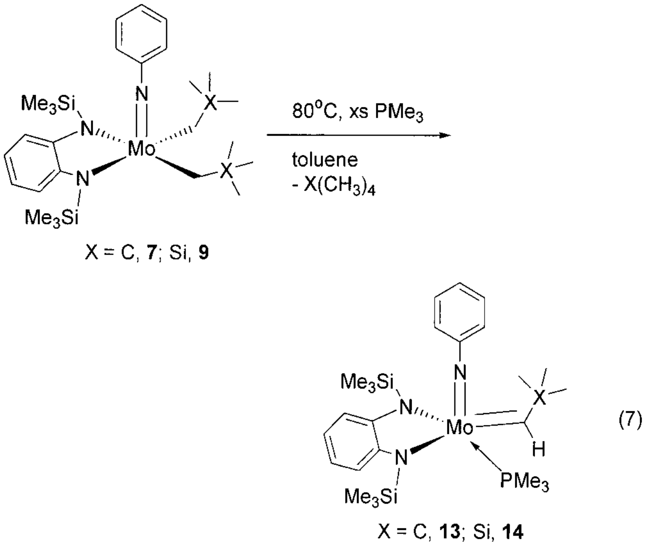
Me$_3$CCH$_2$ and Me$_3$SiCH$_2$) in Et$_2$O at −78 °C. Both **10** and **11** were obtained in high yields and purity in this manner. Similar compounds have been reported by Schrock[24] and Osborn[25] as intermediates in the syntheses of molybdenum(VI) alkylidenes with alkoxide or triflate ancillary ligands. However, they did not report these complexes (presumably because of the unexpected insolubility of **10** and **11** in aliphatic hydrocarbon solvents). Proton NMR (C_6D_6) spectra of **10** showed the neopentyl methyl resonance as a sharp singlet at 1.19 ppm (18H) and the methylene protons as a singlet at 2.06 ppm (4H). Proton NMR (C_6D_6) of **11** showed a sharp singlet at 0.17 ppm (18H) corresponding to the Me$_3$Si methyl protons and a singlet at 1.58 ppm (4H) for the methylene protons. The aromatic region showed the normal resonances for equivalent phenyl imido groups.



(6)

One possible explanation for the reactivity observed in the reaction of **2** with alkylating agents is shown in Scheme 1. If **2** is equilibrating with **12**, alkylation of **12** would lead to **10** and **11**, while alkylation of **2** would give **7** and **9**. In separate NMR-scale experiments, samples of **7** and **10** were combined with aniline and H$_2$-*o*-(Me$_3$SiN)$_2$C$_6$H$_4$, respectively. No reaction was observed in either case. This eliminates the possibility that in the presence of aniline or H$_2$-*o*-(Me$_3$SiN)$_2$C$_6$H$_4$ the dialkyl species interconvert. We were, however, unable to detect further evidence for the equilibrium between **12** and **2** other than the reactivity observed with the alkylating agents. Proton NMR samples of **2** (toluene-d_8) do not show evidence for proton exchange even when cooled to −85 °C.

Synthesis of Chelate-Supported Alkylidenes. The alkylidene complex **13** was obtained when a toluene solution of **7** was heated to 80 °C for 0.5 h in the presence of excess PMe$_3$. Proton NMR spectra of this purple solid revealed a singlet at 0.37 ppm (18H) assigned to Me$_3$Si methyl groups, a broadened doublet at 0.85 ppm corresponding to coordinated PMe$_3$, and a singlet at 1.32 ppm (9H), which was assigned to the alkylidene *tert*-butyl group. A small, broad singlet was observed at 12.13 ppm (1H) and is assigned to the alkylidene hydrogen.



(7)

Alkylidene **13** demonstrated fluxional behavior while in solution. A coalesced resonance was observed at room temperature for the Me$_3$Si groups, which decoalesced at −37 °C ($\Delta G^{\ddagger} = 12.51$ kcal/mol). The mechanism for this equilibration is proposed to involve the reversible dissociation of phosphine from the metal center. The dissociation induces a plane of symmetry in the molecule, which makes the Me$_3$Si groups equivalent. A similar mechanism is observed in the analogous tungsten complex.[6b]

In a similar reaction, when bis(trimethylsilylmethyl) **9** was heated to 85 °C in toluene-d_8 in the presence of excess PMe$_3$, formation of the corresponding alkylidene was observed. The formation of alkylidene **14** was confirmed by a singlet at 13.62 ppm attributed to the alkylidene proton and a singlet near 0.0 ppm for TMS. This alkylidene, however, has proven difficult to isolate in pure form.

Polymerization Reactions. The activity of several of the compounds described above toward olefin polymerization was examined. Dimethyl **5** was added to an ethylene-saturated MAO solution in toluene. After 10 min no polyethylene was obtained. However, the polymerization of norbornene was achieved by preparing alkylidenes in situ. In separate experiments, small samples of the dialkyls **7**, **8**, and **9** were heated to 85 °C in toluene for 0.5 h. To these reaction mixtures, toluene solutions of freshly sublimed norbornene were added and stirred without heat for 1 h. Moderate quantities of polynorbornene were isolated in both cases as white solids. Further study of these polymerization reactions

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[24] Oskam, J. H.; Fox, H. H.; Yap, K. B.; Mcconville, D. H.; O'Dell, R.; Lichtenstein, B. J.; Schrock, R. R. *J. Organomet. Chem.* **1993**, *459*, 185.

[25] Schoettel, G.; Kress, J.; Osborn, J. A. *J. Chem Soc., Chem. Commun.* **1989**, 1962.

and of the isolated polymers is underway and will be reported in the future.

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. Diethyl ether, dimethoxyethane, tetrahydrofuran, toluene, pentane, hexane, and hexamethyldisiloxane were distilled under nitrogen from sodium or sodium benzophenone ketyl and degassed prior to use. Acetonitrile was dried over P_2O_5, vacuum-transferred into a storage flask, and stored over molecular sieves prior to use.

NMR spectra were obtained on a Varian Gemini 300 or VXR 300 instrument in C_6D_6 or $CDCl_3$ solutions, referenced to residual solvent peaks, and reported relative to TMS. ^{31}P NMR spectra were referenced to external H_3PO_4.

The compounds $Mo(NPh)_2Cl_2DME$[13] and bis(trimethylsilyl)-*o*-phenylenediamine[6,26] were prepared according to literature procedures. All other reagents were obtained from Aldrich Chemicals and used as received.

Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA. Despite repeated recrystallizations, we were unable to obtain satisfactory elemental analyses for compounds **5**–**13**, with the results usually being 1–2% low in carbon with satisfactory results for N and H. Given the propensity for Mo alkyls to form metal carbides on pyrolysis, this is not unexpected.

High-resolution mass spectra were obtained in FAB mode on samples of the compounds dissolved in NPOE (*para*-nitrophenyl octyl ether) and were performed in the Mass Spectrometry Laboratory at the Department of Chemistry, University of Florida.

$[Mo(NPh)_2(o\text{-}(Me_3SiN)_2C_6H_4)]_2$, 1. A sample of bis(trimethylsilyl)-*o*-phenylenediamine (0.574 g, 2.27 mmol) was dissolved in 20 mL of diethyl ether and cooled to −78 °C. With stirring, 2 equiv of n-BuLi (1.82 mL, 4.55 mmol) was added. The yellow solution was stirred at −78 °C for 20 min and then at room temperature for 30 min. This yellow solution was then combined with a slurry of $Mo(NPh)_2Cl_2(DME)$ (1.0 g, 2.27 mmol) in Et_2O (20 mL) at −78 °C. The reaction mixture turned to a forest-green color within a few minutes and was then stirred at room temperature for 1 h. The solution was then filtered and the precipitate dried under reduced pressure. Extraction with toluene (30 mL) produced a green solution that was then pumped to dryness, giving **1** as green microcrystals in low yield (0.27 g, 23% yield). Washing the product four times with cold ether and twice with pentane provided analytically pure **1**. Anal. Calcd for $C_{48}H_{64}N_8Si_4Mo_2$: C, 54.52; H, 6.10; N, 10.60. Found: C, 54.37; H, 6.16; N, 10.44. ^1H NMR (C_6D_6): δ −0.04 (s, 36H, NSi*Me*$_3$), 6.55 (d, 4H, aromatic), 6.75 (m, 6H, aromatic), 6.87 (t, 2H, aromatic), 7.01 (t, 4H, aromatic), 7.1 (m, 8H, aromatic), 7.26 (m, 4H, aromatic). ^{13}C NMR ($CDCl_3$): δ 1.273, 122.03, 122.27, 122.53, 123.71, 124.20, 125.67, 128.22, 128.84, 141.76, 156.28, 171.96.

$Mo(NPh)Cl_2(o\text{-}(Me_3SiN)_2C_6H_4)(NH_2Ph)$, 2. Using 2 equiv of Diamine. A hexanes solution (30 mL) of bis(trimethylsilyl)-*o*-phenylenediamine (5.74 g, 22.7 mmol) was added to a slurry of $Mo(NPh)_2Cl_2(DME)$ (5.0 g, 11.3 mmol) in hexanes (40 mL). The dark red mixture was stirred for 24 h and filtered, giving a blue-purple powder. Washing the powder twice with hexanes (20 mL) followed by washing with cold diethyl ether (20 mL) gave pure compound in 91% yield (6.23 g). Analytically pure **2** was obtained by washing twice with cold diethyl ether. Anal. Calcd for $C_{24}H_{34}Si_2N_4Cl_2Mo$: C, 47.91; H, 5.69; N, 9.31. Found: C, 47.89; H, 5.66; N, 9.24. ^1H NMR (C_6D_6): δ 0.39 (s, 18H, NSi*Me*$_3$), 3.95 (s, 2H, N*H*$_2$Ph), 6.24 (m, 2H, aromatic), 6.54–6.80 (m, 8H, aromatic), 6.98 (t, 2H, aromatic), 7.82 (d, 2H, aromatic). ^{13}C NMR ($CDCl_3$): δ 1.28, 119.75, 120.99, 122.93, 125.08, 126.91, 128.49, 128.56, 129.47, 140.57, 146.03, 155.63.

Using 1 equiv of Diamine. The above procedure was repeated using 0.5 g (1.13 mmol) of $Mo(NPh)_2Cl_2(DME)$ and 0.287 g (1.13 mmol) of bis(trimethylsylil)-*o*-phenylenediamine. The reaction mixture was allowed to stir for ca. 2 days at room temperature or refluxed in hexanes for 7 h. From either procedure blue-purple $Mo(NPh)Cl_2(o\text{-}(Me_3SiN)_2C_6H_4)(NH_2Ph)$ was obtained in high yield and purity.

$Mo(NPh)Cl_2(o\text{-}(Me_3SiN)_2C_6H_4)(PMe_3)$, 3. A sample of **2** (3.0 g, 4.98 mmol) was slurried in diethyl ether (25 mL) and stirred at room temperature. A small excess of PMe_3 (0.417 g, 5.48 mmol) was added via syringe. The reaction mixture immediately formed a royal blue solution, which was stirred for 1 h. Concentration (ca. 15 mL) followed by cooling (−78 °C) and filtration gave 2.7 g of microcrystalline **3** (92%). Recrystallization of **3** from diethyl ether provided analytically pure compound. Anal. Calcd for $C_{21}H_{36}Si_2N_3Cl_2PMo$: C, 43.15; H, 6.21; N, 7.19. Found: C, 43.03; H, 6.14; N, 7.23. ^1H NMR (C_6D_6): δ 0.44 (s, 18H, NSi*Me*$_3$), 0.74 (d, 9H, J_{P-H} = 8.7 Hz, P*Me*$_3$), 6.77 (t, 1H, phenylimido *para*-proton), 6.83 (m, 2H, diamine ring *meta*-protons), 6.99 (m, 2H, diamine ring *ortho*-protons), 7.04 (t, 2H, phenylimido *meta*-protons), 7.83 (m, 2H, phenylimido *ortho*-protons). ^{13}C NMR ($CDCl_3$): δ 1.41, 11.50 (d, 18.17 Hz), 120.70, 125.55, 128.34, 128.77, 129.11, 129.47. ^{31}P NMR (C_6D_6): δ −22.48.

$Mo(NPh)Cl_2(o\text{-}(Me_3SiN)_2C_6H_4)(THF)$, 4. At room temperature a sample (5.0 g, 8.31 mmol) of **2** was dissolved in tetrahydrofuran (30 mL) and stirred for 1 h. Upon addition of THF, the reaction mixture acquired a royal blue color. Concentration (ca. 20 mL) followed by addition of pentane (ca. 150 mL) caused precipitation of **4**, which was isolated by filtration and dried in vacuo (5.21 g, 76%). Analytically pure **4** was obtained after washing the product with cold pentane (ca. 20 mL) three times. Anal. Calcd for $C_{22}H_{35}ON_3Si_2Cl_2Mo$: C, 45.51; H, 6.08; N, 7.24. Found: C, 45.53; H, 6.10; N, 7.18. ^1H NMR (C_6D_6): δ 0.44 (s, 18H, NSi*Me*$_3$), 1.07 (m, 4H, $-OCH_2CH_2CH_2CH_2-$), 3.56 (m, 4H, $-OCH_2CH_2CH_2CH_2-$), 6.74 (t, 1H, phenylimido *para*-proton), 6.82 (m, 2H, diamine ring *meta*-protons), 6.94 (t, 2H, phenylimido *meta*-protons), 7.01 (m, 2H, diamine ring *ortho*-protons), 7.73 (d, 2H, phenylimido *ortho*-protons). ^{13}C NMR ($CDCl_3$): δ 1.18, 25.34, 68.58, 120.07, 120.92, 125.02, 127.26, 128.41, 128.59, 129.44.

$Mo(NPh)Me_2(o\text{-}(Me_3SiN)_2C_6H_4)$, 5. A diethyl ether solution (25 mL) of **4** (1.0 g, 1.72 mmol) was cooled to −78 °C. Two equivalents of 3.0 M MeMgCl (1.15 mL, 3.45 mol) in Et_2O was added in a dropwise fashion, and the mixture was allowed to warm to room temperature. The blue solution quickly turned to an orange-red solution. After 1 h of stirring, the mixture was pumped to dryness and extracted with pentane once (50 mL). The volume of the filtrate was then reduced ca. 10 mL. Acetonitrile was then added (30 mL) to precipitate the product, which was isolated by filtration at 0 °C (0.59 g, 74%). Further purification of **5** was attained by recrystallization (five times) from concentrated pentane/acetonitrile (20:80) solutions cooled to 0 °C. Melting point: 96–100 °C. Anal. Calcd for $C_{20}H_{33}N_3Si_2Mo$: C, 51.36; H, 7.11; N, 8.98. Found: C, 49.11; H, 7.02; N, 8.34. ^1H NMR (C_6D_6): δ 0.36 (s, 18H, NSi*Me*$_3$), 1.14 (s, 6H, Mo*Me*$_2$), 6.84 (t, 1H, phenylimido *para*-proton), 6.98 (m, 2H, diamine ring *meta*-protons), 7.02 (t, 2H, phenylimido *meta*-protons), 7.34 (m, 2H, diamine ring *ortho*-protons), 7.42 (d, 2H, phenylimido *ortho*-protons). ^{13}C NMR ($CDCl_3$): δ 1.22, 31.29 (s, Mo-Me$_2$, J_{C-H} = 126.4 Hz), 122.05, 124.38, 124.83, 124.91, 128.45, 134.77, 156.45. MS Calcd for $[M - CH_3]^+$: 454.1035 *m/e*. Found (FAB): 454.1096 *m/e*.

$Mo(NPh)Ph_2(o\text{-}(Me_3SiN)_2C_6H_4)$, 6. A diethyl ether solution (25 mL) of **4** (0.5 g, 0.862 mmol) was cooled to −78 °C and charged with 2 equiv of PhMgBr in Et_2O (0.86 mL, 1.72 mmol). After 1 h of stirring at room temperature the mixture

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(26) Birkofer, L.; Kuhlthau, H. P.; Ritter, A. *Chem. Ber.* **1960**, *93*, 2810.

was stripped of solvent and dried (in vacuo). Extraction with toluene (25 mL) followed by concentration (10 mL) and cooling (−78 °C) produced red-purple microcrystals in good yield (0.35 g, 70%). Further purification of the product was attained after washing the crude product with cold pentane three times. The compound may be recrystallized from Et_2O at −78 °C. Melting point: 114−117 °C. Anal. Calcd for $C_{30}H_{37}N_3Si_2Mo$: C, 60.89; H, 6.30; N, 7.10. Found: C, 58.54; H, 6.33; N, 6.87. ^1H NMR (C_6D_6): δ 0.12 (s, 18H, NSi*Me*$_3$), 6.78−6.98 (m, aromatics), 7.06−7.12 (m, aromatics), 7.34−7.43(m, 6H, aromatics), 7.60 (d, 2H, phenylimido *ortho*-protons). ^{13}C NMR ($CDCl_3$): δ 0.46, 123.23−134.784 (aromatic, overlapping). MS Calcd for $[M + H]^+$: 594.1664 *m*/*e*. Found (FAB): 594.1669 *m*/*e*.

Mo(NPh)(CH$_2$CMe$_3$)$_2$(*o*-(Me$_3$SiN)$_2$C$_6$H$_4$), 7. A diethyl ether (40 mL) solution of **4** (0.5 g, 0.862 mmol) was cooled to −78 °C. Two equivalents of 0.54 M neopentylmagnesium chloride (3.19 mL, 1.72 mmol) in Et_2O was added in a dropwise fashion, and the reaction mixture was allowed to warm to room temperature. The blue solution quickly turned to a red-brown solution. After 1 h of stirring, the mixture was pumped to dryness and extracted with pentane (50 mL). The filtrate was stripped of solvent in vacuo, and **7** was isolated as a viscous oil. Recrystallization from acetonitrile (15 mL) at 0 °C yielded **7** as a red solid in high yield (0.41 g, 79%). Further recrystallization from acetonitrile gave red crystals. Anal. Calcd for $C_{28}H_{49}N_3Si_2Mo$: C, 58.00; H, 8.52; N, 7.25. Found: C, 57.10; H, 8.61; N, 7.17. ^1H NMR (C_6D_6): δ 0.56 (s, 18H, NSi*Me*$_3$), 0.95 (s, 18H, CH$_2$C*Me*$_3$), 2.57 (d, 2H, C*H*$_2$CMe$_3$), 2.77 (d, 2H, C*H*$_2$CMe$_3$), 6.90 (t, 1H, phenylimido *para*-proton), 6.96 (m, 2H, diamine ring *meta*-protons), 7.09 (t, 2H, phenylimido *meta*-protons), 7.30 (m, 2H, diamine ring *ortho*-protons), 7.75 (d, 2H, phenylimido *ortho*-protons). ^{13}C NMR ($CDCl_3$): δ 4.17, 33.66, 38.58, 82.52, 117.97, 126.43, 128.60, 145.17, 154.44.

Mo(NPh)(CH$_2$Ph)$_2$(*o*-(Me$_3$SiN)$_2$C$_6$H$_4$), 8. Two equivalents of a 1 M benzylmagnesium chloride solution in THF (1.72 mL, 1.72 mmol) was added to a stirring diethyl ether (30 mL) solution of **4** (0.5 g, 0.862 mmol) at −78 °C. After 1 h of stirring at room temperature, the mixture was pumped to dryness and extracted with pentane (50 mL). The filtrate was then concentrated (ca. 10 mL), cooled to −78 °C, and filtered, giving red-orange crystals of **8** (0.37 g, 69%). Further purification of **8** was attained by recrystallization (five times) from concentrated pentane solutions cooled to −78 °C. Melting point: 112−116 °C. Anal. Calcd for $C_{32}H_{41}N_3Si_2Mo$: C, 62.01; H, 6.67; N, 6.78. Found: C, 61.17; H, 6.59; N, 6.63. ^1H NMR (C_6D_6): δ 0.09 (s, 18H, NSi*Me*$_3$), 2.87 (m, 4H, C*H*$_2$Ph), 6.86 (m, 3H, aromatics), 7.07 (m, 4H, aromatics), 7.09 (m, 8H, aromatics), 7.35 (m, 4H, aromatics). ^{13}C NMR ($CDCl_3$): δ 1.083, 54.43, 122.32, 123.34, 125.56, 126.47, 127.53, 127.80, 128.57, 134.31, 152.79, 156.33. MS Calcd for $[M + H]^+$: 622.1995 *m*/*e*. Found (FAB): 622.2 *m*/*e*.

Mo(NPh)(CH$_2$SiMe$_3$)$_2$(*o*-(Me$_3$SiN)$_2$C$_6$H$_4$), 9. A diethyl ether solution (30 mL) of **4** (0.5 g, 0.862 mmol) was cooled to −78 °C with stirring. Two equivalents of 1.28 M trimethylsilylmethylmagnesium chloride (1.34 mL, 1.72 mmol) in Et_2O was added in a dropwise fashion, and the reaction mixture was allowed to warm to room temperature. The blue solution quickly turned to a red-orange solution. After 1 h of stirring, the mixture was pumped to dryness and extracted with pentane (40 mL). The pentane filtrate was then pumped to dryness to yield **9** as a green solid in good yield (0.42 g, 80%). The compound may be purified by recrystallization from acetonitrile (0 °C). Anal. Calcd for $C_{26}H_{49}N_3Si_4Mo$: C, 51.03; H, 8.07; N, 6.87. Found: C, 49.95; H, 7.91; N, 6.82. ^1H NMR (C_6D_6): δ 0.03 (s, 18H, CH$_2$Si*Me*$_3$), 0.47 (s, 18H, NSi*Me*$_3$), 1.82 (d, 2H, C*H*$_2$SiMe$_3$), 2.19 (br, 2H, C*H*$_2$SiMe$_3$), 6.87 (t, 1H, phenylimido *para*-proton), 6.81 (m, 2H, diamine ring *meta*-protons), 7.08 (t, 2H, phenylimido *meta*-protons), 7.27 (m, 2H, diamine ring *ortho*-protons), 7.71 (d, 2H, phenylimido *ortho*-protons). ^{13}C NMR ($CDCl_3$): δ 2.27, 3.73, 58.01, 118.83, 126.81, 127.60, 128.72, 154.50.

Reaction of 2 with Alkylating Agents. To a diethyl ether (30 mL) solution of **2** (0.45 g, 0.758 mmol) cooled to −78 °C was added 2 equiv of 0.54 M neopentylmagnesium chloride in Et_2O (2.80 mL, 1.51 mmol) with stirring. The solution was then allowed to stir at room temperature for 1 h. The solvent was removed in vacuo and pentane used to extract the product. The pentane was then removed in vacuo and the solid dried. Proton NMR spectra showed a mixture of **7** and **10** in a 1.18:1 ratio.

The 0.45 g of **2** was reacted with a 1.28 M solution of trimethylsilylmethylmagnesium chloride (1.18 mL, 1.51 mmol) following the same reaction procedure as described above. Proton NMR spectra revealed a 1.09:1 mixture of **9** and **11**.

Mo(NPh)$_2$(CH$_2$CMe$_3$)$_2$, 10. Two equivalents of 0.54 M neopentylmagnesium chloride in Et_2O (8.43 mL, 4.55 mmol) was added to a stirring slurry of Mo(NPh)$_2$Cl$_2$DME (1.0 g, 2.27 mmol) in Et_2O (40 mL) at −78 °C and stirred for 2 h at room temperature. The solvent was removed in vacuo and then toluene (30 mL) added to extract a light orange solution. After removal of the solvent in vacuo crystalline **10** was isolated in good yield (0.81 g, 85%) and high purity. Recrystallization from toluene/pentane gave crystals suitable for elemental analysis. Anal. Calcd for $C_{22}H_{32}N_2Mo$: C, 62.84; H, 7.67; N, 6.66. Found: C, 61.63; H, 7.54; N, 6.56. ^1H NMR (C_6D_6): δ 1.19 (s, 36H, CH$_2$C*Me*$_3$), 2.04 (s, 4H, C*H*$_2$CMe$_3$), 6.80 (t, 2H, phenylimido *para*-proton), 6.99 (t, 4H, phenylimido *meta*-protons), 7.28 (d, 4H, phenylimido *ortho*-protons). ^{13}C NMR (C_6D_6): δ 33.79, 81.99, 123.75, 125.24, 128.96, 157.20.

Mo(NPh)$_2$(CH$_2$SiMe$_3$)$_2$, 11. Two equivalents of 1.28 M trimethylsilylmethylmagnesium chloride in diethyl ether (2.54 mL, 3.26 mmol) was added to a stirring slurry of Mo(NPh)$_2$Cl$_2$-DME (0.72 g, 1.63 mmol) in Et_2O (40 mL) at −78 °C and stirred for 2 h at room temperature. The solvent was removed in vacuo, and then pentane (ca. 25 mL) was added to extract a dark orange solution, which after filtration and removal of the pentane in vacuo yielded crystalline **11** as a red solid in good yield (0.62 g, 84%). Recrystallization from pentane gave crystals suitable for analysis. Anal. Calcd for $C_{20}H_{32}N_2Si_2Mo$: C, 53.07; H, 7.12; N, 6.19. Found: C, 51.45; H, 7.10; N, 6.05. ^1H NMR (C_6D_6): δ 0.05 (s, 36H, CH$_2$Si*Me*$_3$), 1.62 (s, 4H, C*H*$_2$-SiMe$_3$), 7.06 (t, 2H, phenylimido *para*-proton), 7.13 (d, 4H, phenylimido *meta*-protons), 7.24 (t, 4H, phenylimido *ortho*-protons). ^{13}C NMR ($CDCl_3$): δ 1.96, 56.52, 123.58, 124.89, 128.54, 156.34.

Mo(NPh)(C(H)C(CH$_3$)$_3$)(*o*-(Me$_3$SiN)$_2$C$_6$H$_4$)(PMe$_3$), 13. In a resealable ampule a toluene (30 mL) solution of **7** (1.12 g, 1.92 mmol) was combined with an excess of trimethylphosphine (1.46 g, 19.2 mmol) and heated to 80 °C for 0.5 h. The color of the solution changed form red-orange to a dark purple color. The toluene was removed in vacuo. Microcrystals of **13** were obtained from a concentrated pentane (ca. 5 mL) solution. Compound **13** was recrystallized three times from pentane (ca. 5 mL) at −78 °C. Isolated yield: 0.70 g (63%). Anal. Calcd for $C_{26}H_{46}N_3Si_2PMo$: C, 53.49; H, 7.94; N, 7.19. Found: C, 51.11; H, 7.66; N, 7.23. ^1H NMR (C_6D_6): δ 0.378 (s, 18H, NSi*Me*$_3$), 0.871 (d, 9H, $J_{P-H} = 8.1$ Hz, P*Me*$_3$) 1.32 (s, 9H, C(C*H*$_3$)$_3$), 6.6−7.2 (m, aromatic), 12.14 (s, 1H, C(*H*)C(CH$_3$)$_3$). ^{13}C NMR (C_6D_6): δ 4.0, 17.5, 35.7, 43.4, 116.2, 120.8, 123.0, 124.6, 125.9, 128.6, 148.6, 275.3.

Mo(NPh)(CHSi(CH$_3$)$_3$)(*o*-(Me$_3$SiN)$_2$C$_6$H$_4$)(PMe$_3$), 14. In an NMR tube a toluene-d_8 solution of **9** was charged with an excess of PMe$_3$ and heated to 80 °C for 12 h. Formation of **14** was observed by NMR. Efforts to isolate this compound have proven difficult.

X-ray Experimental. Suitable crystals of **3** were obtained by cooling a concentrated Et_2O solution to −20 °C for several days. Data were collected at 173 K on a Siemens SMART PLATFORM equipped with a CCD area detector and a graphite monochromator utilizing Mo Kα radiation (λ =

0.71073 Å). Cell parameters were refined using 8192 reflections. A hemisphere of data (1381 frames) was collected using the ω-scan method (0.3° frame width). The first 50 frames were remeasured at the end of data collection to monitor instrument and crystal stability (maximum correction on I was $< 1\%$). ψ-scan absorption corrections were applied based on the entire data set.

The structure was solved by the direct methods in SHELXL-97[2727] and refined using full-matrix least squares. The non-H atoms were treated anisotropically, whereas the hydrogen atoms were calculated in ideal positions and were riding on their respective carbon atoms. A total of 461 parameters were refined in the final cycle of refinement using 6045 reflections with $I > 2\sigma(I)$ to yield R1 and wR2 of 2.83% and 6.76%, respectively. Refinement was done using F^2.

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Supporting Information Available: Tables of bond lengths and angles and positional and thermal parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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