The Versatility of Lithium Reagents in Synthetic Organometallic Chemistry: Their Differing Reactions with [Cp*Mo(NO)(CH₂SiMe₃)₂]

Peter Legzdins* and Stephen F. Sayers

Abstract: [Cp*Mo(NO)(CH₂SiMe₃)₂] exhibits three principal types of reaction with the various lithium reagents investigated during this study, namely: regioselective deprotonation, reduction, and addition. Deprotonation of the reactant, achieved by treatment with lithium amide reagents, leads ultimately to the formation of the alkylidene "ate" complex [Cp*Mo(NO)(CH₂SiMe₃)(=CHSiMe₃)]₂-[Li₂(thf)₃] (1). While LiN(SiMe₃)₂ effects this conversion directly with no detectable intermediates, reaction with 1 equiv of LDA in THF for 15 min deprotonates the Cp* ligand to form the lithium salt of the "tucked-in" ate complex [(η⁵,η¹-C₅Me₄CH₂)Mo(NO)(CH₂SiMe₃)₂]-[Li(thf)₃] (2) in 40% isolated yield. Complex 2 slowly converts to the thermodynamically more stable 1 when left as a THF or C₆D₆ solution at ambient tem-

perature for 48 h. Reaction of the dialkyl starting material with either *t*BuLi or PhLi leads to the production of the alkylidene complex 1 in irreproducible yields (10–50% NMR; not isolable). A kinetic analysis of the reaction of [Cp*Mo(NO)(CH₂SiMe₃)₂] with LiN(SiMe₃)₂ indicated that the reaction was first-order in both the lithium and molybdenum reagents, and the activation parameters of $\Delta H^{\ddagger} = 7.3 \pm 1.0 \, \text{kcal mol}^{-1}$ and $\Delta S^{\ddagger} = -34 \pm 3$ e.u. suggest an associative process. Treatment of the neutral dialkyl with 1 equiv of LiPPh₂ in THF results in a

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one-electron reduction and production of {[Cp*Mo(NO)(CH₂SiMe₃)₂][Li(thf)]}₂ (3). If left in solution, the 17e⁻ dialkyl anion 3 is converted to the 18e⁻ alkylidene anion 1 by the Ph₂P–PPh₂ coproduct, which effects the requisite hydrogen-atom abstraction. Finally, addition of a sterically undemanding alkyllithium reagent such as MeLi to the 16e⁻ dialkyl reactant leads to the formation of the 18e⁻ trialkyl anionic complex [Cp*Mo(NO)(CH₂SiMe₃)₂(Me)][Li(thf)₃] (4). Warming of 4 in a C₆D₆ solution results in loss of methane and production of 1. In most cases, the chemistry exhibited by the Mo system is duplicated by the analogous W congener, [Cp*W(NO)(CH₂SiMe₃)₂]. The solid-state molecular structures of complexes 1 and 4 have been established by single-crystal X-ray crystallographic analyses.

Introduction

The ubiquitous use of lithium reagents in synthetic organic chemistry attests to their widespread utility in this field.[1] The considerable versatility of these reagents is demonstrated by the wide variety of reaction types that they undergo and by the regio- and stereoselectivity of the transformations that may be achieved by their use.[2] The utilization of lithium reagents in synthetic organometallic chemistry is equally extensive,[3] and the range of reactions of a single organometallic substrate with different lithium reagents may, in principle, be greater than that which can be achieved with a single organic substrate. A striking illustration of this fact is provided by the chemistry presented in this paper, in which we describe how a single organometallic molecule, namely [Cp*Mo(NO)(CH₂SiMe₃)₂], reacts in a range

of ways with a variety of lithium reagents. The eventual thermodynamic product of most of these transformations is the lithium salt of the alkylidene anion, [Cp*Mo(NO)(=CHSiMe₃)-(CH₂SiMe₃)]⁻. Nevertheless, careful choice of the lithium reagent can effect the kinetically controlled regioselective deprotonation, reduction, or addition reactions of the organometallic reactant to produce isolable intermediate complexes. In most cases, the chemistry exhibited by the Mo system may also be carried out with the analogous W congener, [Cp*W(NO)-(CH₂SiMe₃)₂]. A portion of this work has been previously communicated.[4]

Experimental Section

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All reactions and subsequent manipulations involving organometallic reagents were performed under anaerobic and anhydrous conditions. The general procedures routinely employed in these laboratories have been described previously.[5] ⁷Li NMR spectra were recorded on a Varian XL300 spectrometer tuned to 116.59 Hz and referenced to a solution of LiCl (1 M) in D₂O. [Cp*Mo(NO)(CH₂SiMe₃)₂] was prepared according to literature methods.[6] The analogous [Cp*W(NO)(CH₂SiMe₃)₂] was prepared in a

Table 1. Numbering scheme, colors, yields, elemental analyses, and infrared data for complexes 1–5.

Complex	No.	Color (yield, %)	Anal. found (calcd) C	H	N	IR (Nujol) (v_{NO}, cm^{-1})
$\{[Cp^*Mo(NO)(CH_2SiMe_3)(=CHSiMe_3)]\}_2\{[Li_2(thf)_3]\}$	1	yellow (62)	48.62 [a] (48.99)	8.46 (8.16)	2.94 (3.17)	1352
$\{[Cp^*W(NO)(CH_2SiMe_3)(=CHSiMe_3)][Li(thf)]\}_2$	1′	yellow (76)	43.64 (43.95)	7.04 (7.32)	3.00 (2.33)	1370
$[(\eta^5,\eta^1\text{-}C_5Me_4CH_2)Mo(NO)(CH_2SiMe_3)_2][Li(thf)_3]$	2	yellow (40)	54.66 (54.81)	9.26 (9.13)	2.33 (2.13)	1478
$\{[Cp^*Mo(NO)(CH_2SiMe_3)_2][Li(thf)]\}_2$	3	red (25)	[b]			1350
$[Cp^*Mo(NO)(CH_2SiMe_3)_2(Me)][Li(thf)_3]$	4	yellow (85)	53.34 (53.12)	8.94 (9.20)	2.20 (2.48)	1463
$[Cp^*W(NO)(CH_2SiMe_3)_2(Me)][Li(thf)]$	4′	yellow (37)	42.03 [c] (42.72)	8.00 (7.45)	2.02 (2.35)	1388

[a] Desolvated. [b] Satisfactory elemental analysis not obtained. [c] Anal. calcd for 1.5 THF.

Table 2. ^{1}H, ^{13}C, and ^{7}Li NMR data (recorded in C_6D_6).

Compd no.	^{1}H NMR, δ	^{13}C {^{1}H} NMR, δ	^{7}Li NMR, δ
1	11.7 (s, 1H, =CHSiMe$_3$), 3.76 (br, 4H, thf), 1.89 (s, 15H, C$_5$Me$_5$), 1.54 (br, 4H, thf), 0.49 (s, 9H, SiMe$_3$), 0.35 (s, 9H, SiMe$_3$), −0.74 (s, 2H, CH_2SiMe$_3$)	257.1 (=CHSiMe$_3$, $^1J_{CH}$ = 143 Hz), 107.2 (C$_5$Me$_5$), 68.6 (thf), 25.9 (thf), 10.9 (C$_5Me_5$), 7.6 (CH$_2$SiMe$_3$), 3.1 (SiMe$_3$), 2.4 (SiMe$_3$)	−3.0
1′	9.32 (s, 1H, =CHSiMe$_3$), 3.72 (br, 4H, thf), 1.88 (s, 15H, C$_5$Me$_5$), 1.51 (br, 4H, thf), 0.45 (s, 9H, SiMe$_3$), 0.34 (s, 9H, SiMe$_3$), −0.65 (s, 2H, CH_2SiMe$_3$)	223.1 (=CHSiMe$_3$, $^1J_{CH}$ = 107 Hz), 108 (C$_5$Me$_5$), 68.5 (thf), 25.6 (thf), 10.8 (C$_5Me_5$), 7.8 (CH$_2$SiMe$_3$), 3.7 (SiMe$_3$), 2.3 (SiMe$_3$)	−2.7
2	3.53 (br, 12H, thf), 3.08 (s, 1H, C$_5$CH$_2$), 3.07 (s, 1H, C$_5$CH$_2$), 1.88 (s, 3H, C$_5$Me$_4$), 1.74 (s, 3H, C$_5$Me$_4$), 1.63 (s, 3H, C$_5$Me$_4$), 1.44 (br, 12H, thf), 1.42 (s, 3H, C$_5$Me$_4$), 0.51 (s, 9H, SiMe$_3$), 0.47 (s, 9H, SiMe$_3$), 0.32 (d, $^2J_{HH}$ = 12.0 Hz, 1H, CH_2SiMe$_3$), −0.32 (d, $^2J_{HH}$ = 12.0 Hz, 1H, CH_2SiMe$_3$), −0.51 (d, $^2J_{HH}$ = 12.0 Hz, 1H, CH_2SiMe$_3$), −0.76 (d, $^2J_{HH}$ = 12.0 Hz, 1H, CH_2SiMe$_3$)	132.0 (C$_5$Me$_4$), 114.5 (C$_5$Me$_4$), 105.3 (C$_5$Me$_4$), 104.1 (C$_5$Me$_4$), 101.0 (C$_5$Me$_4$), 68.3 (thf), 60.4 (C$_5$CH$_2$), 25.5 (thf), 16.9 (CH$_2$SiMe$_3$), 16.5 (CH$_2$SiMe$_3$), 10.8 (C$_5Me_4$), 10.4 (C$_5Me_4$), 9.6 (C$_5Me_4$), 9.3 (C$_5Me_4$), 5.1 (SiMe$_3$), 4.6 (SiMe$_3$)	−3.5
4	3.54 (br, 12H, thf), 1.70 (s, 15H, C$_5$Me$_5$), 1.41 (br, 12H, thf), 0.48 (s, 18H, SiMe$_3$), 0.26 (s, 3H, Me), −0.27 (s, 4H, CH_2SiMe$_3$)	107.0 (C$_5$Me$_5$), 68.4 (thf), 25.5 (thf), 22.0 (CH$_2$SiMe$_3$), 15.5 (Me), 10.2 (C$_5Me_5$), 5.1 (SiMe$_3$)	−3.5
4′	3.67 (br, 4H, thf), 1.64 (s, 15H, C$_5$Me$_5$), 1.42 (br, 4H, thf), 0.43 (s, 18H, SiMe$_3$), 0.29 (s, 3H, Me), −0.33 (d, $^2J_{HH}$ = 10.5 Hz, 2H, CH_2SiMe$_3$), −0.40 (d, $^2J_{HH}$ = 10.5 Hz, 2H, CH_2SiMe$_3$)	108.1 (C$_5$Me$_5$), 68.7 (thf), 25.5 (thf), 22.5 (CH$_2$SiMe$_3$), 19.5 (Me), 10.3 (C$_5Me_5$), 5.1 (SiMe$_3$)	

similar fashion. PHPh$_2$, PH$_2$Ph, HN(C$_3$H$_7$)$_2$, tBuLi, MeLi, PhCCH, and LiN(SiMe$_3$)$_2$ (all from Aldrich) were used as received. Compounds LiPRPh [R = H, Ph] and LDA [(Me$_2$CH)$_2$NLi] were prepared by deprotonation of the parent phosphine or amine with nBuLi. Attempts to obtain mass spectra of all new compounds prepared during this work were unsuccessful because of their extreme air sensitivity. For the kinetic analyses, LiN(SiMe$_3$)$_2$ was purified by sublimation at 80 °C under a static vacuum, [Cp*Mo(NO)-(CH$_2$SiMe$_3$)$_2$] was twice recrystallized from pentane, and THF was vacuum-transferred from Na/benzophenone prior to use.

In all cases the molybdenum and tungsten congeners of the complexes described below were synthesized in an analogous manner. The preparations of the molybdenum complexes are described in detail, with any variants for the tungsten analogues being noted where appropriate. The numbering scheme, colors, isolated yields, analytical, and IR data for all new products are listed in Table 1. ^{1}H, ^{13}C, and ^{7}Li NMR data are collected in Table 2, and the results of X-ray diffraction analyses of complexes 1 and 4 are presented in Tables 3 and 6.

Reaction of [Cp*Mo(NO)(CH$_2$SiMe$_3$)$_2$] with LiN(SiMe$_3$)$_2$: [Cp*Mo(NO)-(CH$_2$SiMe$_3$)$_2$] (200 mg, 0.46 mmol) and LiN(SiMe$_3$)$_2$ (90 mg, 0.46 mmol) were intimately mixed and cooled to −100 °C in a small flask. THF (2 mL) was slowly poured down the sides of the flask and allowed to freeze onto the solid mixture. The mixture was then stirred while being allowed to warm slowly to room temperature. Over the course of 4 h a color change from purple to red occurred; the final mixture was taken to dryness in vacuo. The red solid remaining was extracted into pentane (2 mL), and the extracts were filtered through a plug of Celite (1 × 1 cm) supported on a medium-porosity glass frit. Slow evaporation of the pentane filtrate resulted in the deposition of pale red crystals, which were recrystallized from pentane to obtain pale yellow crystals (143 mg, 62% yield) of [Cp*Mo(NO)(CH$_2$SiMe$_3$)-(=CHSiMe$_3$)]$_2$[Li$_2$(thf)$_3$] (1). The tungsten analogue $\{$[Cp*W(NO)-(CH$_2$SiMe$_3$)(=CHSiMe$_3$)][Li(thf)]$\}_2$ (1′) was isolated similarly (196 mg, 76% yield).

Reaction of [Cp*Mo(NO)(CH$_2$SiMe$_3$)$_2$] with LDA: [Cp*Mo(NO)-(CH$_2$SiMe$_3$)$_2$] (200 mg, 0.46 mmol) and LDA (50 mg, 0.46 mmol) were intimately mixed and cooled (−100 °C) in a small flask. THF (2 mL) was slowly added down the sides of the flask and was allowed to freeze onto the mixture. The mixture was stirred as it warmed to room temperature. After 15 min a color change from purple to yellow occurred. The mixture was subsequently taken to dryness in vacuo. The remaining yellow solid was washed with pentane (2 × 1 mL) and dried in vacuo to obtain [(η^5,η^1-C$_5$Me$_4$CH$_2$)-Mo(NO)(CH$_2$SiMe$_3$)$_2$][Li(thf)$_3$] (2) (106 mg, 40% yield). The corresponding tungsten complex [(η^5,η^1-C$_5$Me$_4$CH$_2$)W(NO)(CH$_2$SiMe$_3$)$_2$][Li(thf)$_3$] (2′) was not sufficiently thermally stable to permit its isolation, but it was observed by ^{1}H NMR spectroscopy to decompose rapidly to 1′ in C$_6$D$_6$. Complex 2′: ^{1}H NMR (C$_6$D$_6$): δ = 3.66 (br, 12H, thf), 2.88 (s, 1H, C$_5$CH_2), 2.82 (s, 1H, C$_5$CH_2), 1.85 (s, 3H, C$_5$Me$_4$), 1.50 (s, 3H, C$_5$Me$_4$), 1.46 (s, 3H, C$_5$Me$_4$), 1.44 (br, 12H, thf), 1.38 (s, 3H, C$_5$Me$_4$), 0.46 (s, 9H, SiMe$_3$), 0.39 (s, 9H, SiMe$_3$), 0.95 (d, $^2J_{HH}$ = 12.5 Hz, 1H, CH_2SiMe$_3$), 0.01 (d. $^2J_{HH}$ = 12.5 Hz, 1H, CH_2SiMe$_3$), −0.45 (d, $^2J_{HH}$ = 12.5 Hz, 1H, CH_2SiMe$_3$), −0.50 (d, $^2J_{HH}$ = 12.5 Hz, 1H, CH_2SiMe$_3$).

Transformation of 2 into 1: Complex 2 (30 mg, 0.07 mmol) was dissolved in C$_6$D$_6$ (0.7 mL) in an NMR tube, and the progress of its transformation to 1 was monitored at room temperature by ^{1}H NMR spectroscopy. Over the course of 48 h the signals characteristic of 2 diminished and disappeared,

while signals due to 1 appeared and increased in intensity. Consistently, the transformation of 2 to 1 also occurred when a reaction mixture of [Cp*Mo(NO)(CH$_2$SiMe$_3$)$_2$] with LDA (vide supra) was stirred for 2 d before the products were isolated.

Kinetic study of the reaction of [Cp*Mo(NO)(CH$_2$SiMe$_3$)$_2$] with LiN(SiMe$_3$)$_2$: The progress of the reaction was monitored by the decrease of the starting material by UV/visible spectroscopy on a Hewlett–Packard HP 8452 diode array spectrophotometer by following the disappearance of an absorption maximum at 528 nm for [Cp*Mo(NO)(CH$_2$SiMe$_3$)$_2$]. The linear relationship between absorbance at 528 nm and the concentration of [Cp*Mo(NO)(CH$_2$SiMe$_3$)$_2$] was confirmed by a Beer's Law plot. Solutions of the reagents were made by syringing exact quantities of stock solutions into a UV cell such that the volume of the solution in the cell was always 3 mL and the concentration of the molybdenum reagent remained at 3.0 mM. The experiments were performed at 50 °C under pseudo-first-order conditions, with approximately 6-, 12-, 16-, 24-, 42-, 84-, and 120-fold excesses of the lithium reagent and with each point being duplicated by a completely independent run. Run times varied over the range of 30 min to 2 h, depending on the concentration of the lithium reagent. In all cases a minimum of 5 half-lives were used in the data analyses. A_∞ (the absorbance at $t = \infty$) was an optimized value that varied over the range 0.08 to 0.12, depending largely on the concentration of the lithium reagent. The temperature dependence of the reaction was studied using a 100-fold excess of the lithium reagent at 30, 40, 50, and 60 °C. Results of the kinetic analyses are collected in Tables 4 and 5.

Reaction of [Cp*Mo(NO)(CH$_2$SiMe$_3$)$_2$] with LiPPh$_2$: [Cp*Mo(NO)-(CH$_2$SiMe$_3$)$_2$] (200 mg, 0.46 mmol) and LiPPh$_2$ (88 mg, 0.46 mmol) were intimately mixed and cooled to −100 °C in a small flask. THF (2 mL) was slowly poured down the sides of the flask and allowed to freeze onto the powders. The mixture was stirred and allowed to warm to room temperature, whereupon a color change from purple to red occurred. The mixture was stirred for a further 10 min at ambient temperature and was then taken to dryness in vacuo. The resulting red solid was extracted with pentane (2 mL) and filtered through a plug of Celite (1 × 1 cm) supported on a medium-porosity glass frit. Slow evaporation of the pentane filtrate resulted in the deposition of red crystals (30 mg, 15% yield) of {[Cp*Mo(NO)-(CH$_2$SiMe$_3$)$_2$][Li(thf)]}$_2$ (3). Attempts to obtain the analogous tungsten complex in the same manner were unsuccessful and resulted in no isolable products.

Transformation of 3 into 1: [Cp*Mo(NO)(CH$_2$SiMe$_3$)$_2$] (30 mg, 0.07 mmol) and LiPPh$_2$ (13 mg, 0.07 mmol) were intimately mixed and cooled to below −100 °C in an NMR tube. [D$_8$]THF (0.7 mL) was slowly added down the sides of the tube and allowed to freeze onto the mixture. The tube was sealed, and the mixture was allowed to warm to room temperature, during which time a color change from purple to red occurred. Spectra obtained immediately after warming exhibited signals due to Ph$_2$P–PPh$_2$ in both the ^{31}P and ^{1}H NMR spectra. These signals diminished over the course of several hours, and signals due to the phosphine Ph$_2$PH and 1 appeared and increased in intensity. A C$_6$D$_6$ solution of isolated 3 showed no evidence for the formation of 1 in its NMR spectrum over the course of several weeks at ambient temperature in the absence of air.

Reduction of [Cp*Mo(NO)(CH$_2$SiMe$_3$)$_2$] with Na/Hg amalgam: [Cp*Mo(NO)(CH$_2$SiMe$_3$)$_2$] (180 mg, 0.41 mmol), Na/Hg (1.3 mmol Na) amalgam, and LiBF$_4$ (200 mg, 2.1 mmol) were mixed in a small vial, and THF (2 mL) was added at room temperature. The mixture was stirred for 2 h, during which time a color change from purple to red occurred. Solvent was removed from the final mixture in vacuo, and the remaining red solid was extracted into pentane (2 mL). The extracts were filtered through Celite and were allowed to evaporate slowly to cause the deposition of small red crystals of 3 (50 mg, 25% yield). The same experiment was repeated in the absence of the lithium salt to obtain a red oily solid (v_{NO} = 1363 cm^{-1}), which defied all attempts at crystallization. A similar experiment was performed in the presence of an excess of [Ph$_3$PNPPh$_3$]Cl, but no product could be isolated from the oily brown solid that resulted.

Reaction of [Cp*Mo(NO)(CH$_2$SiMe$_3$)$_2$] with MeLi: A solution of [Cp*Mo(NO)(CH$_2$SiMe$_3$)$_2$] (200 mg, 0.46 mmol) in THF (1 mL) was cooled to −100 °C in a small flask. MeLi (0.4 mL, 1.4 M in Et$_2$O) was slowly added down the sides of the flask and allowed to freeze onto the mixture. The

mixture was then stirred and allowed to warm to room temperature. After 15 min, a color change from purple to yellow had occurred. The final mixture was taken to dryness in vacuo, and the remaining yellow powder was dissolved in pentane (ca. 2 mL). The solution was filtered through Celite; slow evaporation of the solvent from the filtrate resulted in deposition of yellow crystals (265 mg, 85% yield) of [Cp*Mo(NO)(CH$_2$SiMe$_3$)$_2$(Me)][Li(thf)$_3$] (4). The tungsten congener, [Cp*W(NO)(CH$_2$SiMe$_3$)$_2$(Me)][Li(thf)$_3$] (4′), was likewise isolated as yellow crystals (81 mg, 37% yield).

Reactions of [Cp*Mo(NO)(CH$_2$SiMe$_3$)$_2$] with *t*BuLi or PhLi: These reactions were effected identically. To a cold (−100 °C) solution of [Cp*Mo(NO)-(CH$_2$SiMe$_3$)$_2$] (50 mg, 0.12 mmol) in THF (2 mL) was added approximately 1 equiv of the organolithium reagent (*t*BuLi as a 1.7 M solution in pentane, PhLi as a 1.8 M solution in Et$_2$O/cyclohexane, 30/70). The reaction mixture was stirred while being warmed to room temperature, whereupon a color change from purple to red occurred over the course of 15 min. After this time the reaction mixture was taken to dryness, and the resulting powder was dissolved in C$_6$D$_6$ (0.75 mL). In both cases only signals due to the alkylidene complex 1 were evident in the ^{1}H NMR spectra of these samples.

**Electrochemical analysis of 4**: A solution of 4 (9.6 mg) and Bu$_4$NPF$_6$ (0.1 M) in THF (4.0 mL) at 22 °C was analysed by cyclic voltammetry with a polished glassy carbon disk (1.5 mm diameter) as the working electrode, Pt wire as the auxiliary electrode, and an Ag wire as a pseudo-reference electrode.

Results and Discussion

Discussion of the reactions of [Cp*Mo(NO)(CH$_2$SiMe$_3$)$_2$] with the various lithium reagents investigated during the current study is ordered by their three principal reaction types, regioselective deprotonation, reduction, and addition. For the majority of cases the tungsten analogues of the molybdenum complexes presented have been synthesized and react in exactly the same manner. Consequently, only the molybdenum species are discussed in detail, with any differences for the tungsten congeners being highlighted when appropriate.

Deprotonation of [Cp*Mo(NO)(CH$_2$SiMe$_3$)$_2$]: Deprotonation of [Cp*Mo(NO)(CH$_2$SiMe$_3$)$_2$] may be achieved by treatment with lithium amide reagents, which lead ultimately to the formation of the alkylidene "ate" complex [Cp*Mo(NO)(CH$_2$SiMe$_3$)-(=CHSiMe$_3$)]$_2$[Li$_2$(thf)$_3$] (1). Interestingly, despite the similarities between LiN(SiMe$_3$)$_2$ and LDA, the reactions of [Cp*Mo(NO)(CH$_2$SiMe$_3$)$_2$] with these two lithium amide reagents follow quite different reaction paths.

a) With LiN(SiMe$_3$)$_2$: Treatment of [Cp*Mo(NO)-(CH$_2$SiMe$_3$)$_2$] with 1 equiv of LiN(SiMe$_3$)$_2$ in THF effects a net deprotonation at the α-carbon of one of the alkyl ligands and forms the alkylidene "ate" complex 1. This complex is isolable from a red solution (probably resulting from incomplete deprotonation) as analytically pure, yellow plates in 62% yield from pentane [Eq. (1)]. Once isolated, 1 is not easily redissolved in

R = SiMe$_3$ 1

(1)
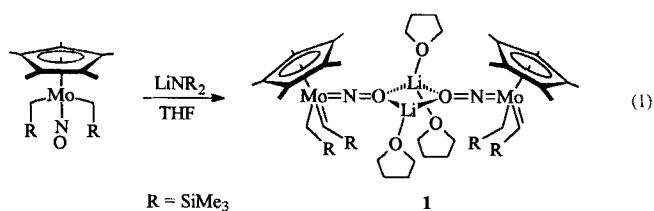
pentane, but is readily soluble in Et_2O. Not surprisingly, dissolution of the complex in chlorinated solvents such as $CDCl_3$ results in immediate decomposition to a plethora of products as indicated by ^1H NMR spectroscopy. A C_6D_6 solution of **1** exhibits signals diagnostic of an alkylidene complex in both its ^1H (at $\delta = 11.7$) and ^{13}C (at $\delta = 257$, $^1J_{CH} = 143$ Hz) NMR spectra, in addition to other signals consistent with its formulation (see Table 2). The IR spectrum of **1** as a Nujol mull displays a very low nitrosyl stretching frequency of 1352 cm^{-1}. This value is 243 cm^{-1} lower than the neutral precursor ($\nu_{NO} = 1595$ cm^{-1}). Such a decrease is indicative of lithium being coordinated to the nitrosyl oxygen atom and has been observed previously in similar Lewis-acid isonitrosyl adducts. For example, Gladysz and coworkers reported a similar reduction in nitrosyl stretching frequency (261 cm^{-1}) upon coordination of BCl_3 to $[CpRe(NO)(PPh_3)(SiMe_2Cl)]$ ($\nu_{NO} = 1656$ cm^{-1}) to afford $[CpRe(NOBCl_3)(PPh_3)(SiMe_2Cl)]$ ($\nu_{NO} = 1395$ cm^{-1}).[7] Monitoring the reaction of $[Cp^*Mo(NO)(CH_2SiMe_3)_2]$ and LiN-$(SiMe_3)_2$ ($[D_8]THF$) over the course of 4 h at 20 °C revealed no detectable intermediate complexes.

The solid-state molecular structure of **1** has been established by a single-crystal X-ray crystallographic analysis,[8] and an ORTEP plot is shown in Figure 1. Two molecules of **1** are
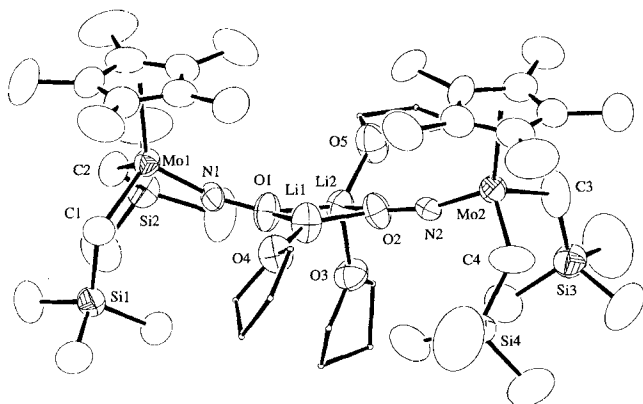

Figure 1. ORTEP diagram of $[Cp^*Mo(NO)(CH_2SiMe_3)(=CHSiMe_3)]_2[Li_2(thf)_3]$ (**1**) at 208 K. Thermal ellipsoids of 50% probability are shown for the non-hydrogen atoms; for clarity the THF C atoms are represented as small spheres of arbitrary radius.

present in the asymmetric unit of the crystal, forming a nearly dimeric structure. The two halves of the structure are similar, though not identical, and are linked through a lithium–isonitrosyl bridge. The alkyl and alkylidene carbon atoms are clearly differentiated by their Mo–C bond lengths (Mo(1)–C(1) = 2.207(9), Mo(2)–C(3) = 2.208(11), Mo(1)–C(2) = 1.960(11), Mo(2)–C(4) = 1.940(11) Å; Table 3) and by their Mo-C-Si bond angles (Mo(1)-C(1)-Si(1) = 117.6(5)°, Mo(2)-C(3)-Si(3) = 122.4(6), Mo(1)-C(2)-Si(2) = 132.9(5), Mo(2)-C(4)-Si(4) = 136.3(8)°). The distortion of the bond angles from their ideal values (120° for the alkylidene and 109° for the alkyl) is almost certainly due to the steric bulk of the $SiMe_3$ fragment.

The Mo-N-O bond angles in **1** are Mo(1)-N(1)-O(1) = 164.0(5), Mo(2)-N(2)-O(2) = 165.7 (5), and the bond lengths within the Mo–NO fragment (Mo(1)–N(1) = 1.711(8),

Table 3. Selected bond lengths (Å) and angles (°) for $[Cp^*Mo(NO)(CH_2SiMe_3)$-$(=CHSiMe_3)]_2[Li_2(thf)_3]$ (**1**).

Mo(1)–N(1)	1.711(8)	Mo(2)–N(2)	1.738(8)
Mo(1)–C(1)	2.207(9)	Mo(2)–C(3)	2.208(11)
Mo(1)–C(2)	1.960(11)	Mo(2)–C(4)	1.940(11)
Mo(1)–Cp1	2.08	Mo(2)–Cp2	2.09
O(1)–N(1)	1.314(12)	O(2)–N(2)	1.282(11)
O(1)–Li(1)	1.849(22)	O(2)–Li(1)	1.824(21)
O(1)–Li(2)	1.937(18)	O(2)–Li(2)	1.973(19)
O(3)–Li(2)	1.894(13)	O(5)–Li(2)	1.912(15)
O(4)–Li(1)	1.874(19)	Li(1)–Li(2)	2.708(23)
N(1)-Mo(1)-C(1)	99.8(4)	N(2)-Mo(2)-C(3)	100.4(4)
N(1)-Mo(1)-C(2)	103.6(4)	N(2)-Mo(2)-C(4)	102.7(4)
C(1)-Mo(1)-C(2)	101.4(4)	C(3)-Mo(2)-C(4)	101.4(6)
N(1)-Mo(1)-Cp1	121.1	N(2)-Mo(2)-Cp2	121.5
C(1)-Mo(1)-Cp1	111.7	C(3)-Mo(2)-Cp2	110.3
C(2)-Mo(1)-Cp1	116.3	C(4)-Mo(2)-Cp2	117.4
N(1)-O(1)-Li(1)	126.8(8)	N(2)-O(2)-Li(1)	131.7(9)
N(1)-O(1)-Li(2)	138.2(8)	N(2)-O(2)-Li(2)	137.3(7)
Li(1)-O(1)-Li(2)	91.3(9)	Li(1)-O(2)-Li(2)	90.9(9)
Mo(1)-N(1)-O(1)	164.0(5)	Mo(2)-N(2)-O(2)	165.7(5)
Mo(1)-C(1)-Si(1)	117.6(5)	Mo(2)-C(3)-Si(3)	122.4(6)
Mo(1)-C(2)-Si(2)	132.9(7)	Mo(2)-C(4)-Si(4)	136.3(8)
O(1)-Li(1)-O(2)	92.2(9)	O(1)-Li(2)-O(5)	130.9(9)
O(1)-Li(1)-O(4)	127.1(12)	O(2)-Li(2)-O(3)	112.0(9)
O(2)-Li(1)-O(4)	138.7(13)	O(2)-Li(2)-O(5)	111.1(8)
O(1)-Li(2)-O(2)	85.2(7)	O(3)-Li(2)-O(5)	106.6(8)
O(1)-Li(2)-O(3)	109.1(7)		

Mo(2)–N(2) = 1.738(8), N(1)–O(1) = 1.314(12), N(2)–O(2) = 1.282(11) Å) indicate a considerable degree of Mo → NO backbonding (i.e., a relatively short Mo–N bond and a relatively long N–O bond) consistent with the electron-rich nature of the metal center. For comparison, the neutral $[Cp^*Mo(NO)(CH_2SiMe_3)(CH_2Ph)]$ exhibits bond lengths of Mo–N = 1.760(2) and N–O = 1.217(2) Å.[9] Finally, an important feature of the molecular structure of **1** is the orientation of the alkylidene ligand such that its principal constituents and the Mo–NO fragment are virtually coplanar. The low N–Mo=C–Si torsion angle of 5.1° is consistent with the π-orbital overlap requirement for the nitrosyl and alkylidene ligands to be mutually orthogonal.[10]

The deprotonation of an alkyl ligand to form an alkylidene ligand necessarily results in a formal increase of two valence electrons at the metal center. Consequently, for such a conversion to be successful, it is imperative that the starting complex be either electronically unsaturated or contain labile ligands which may readily be lost during the transformation. The metal center in $[Cp^*Mo(NO)(CH_2SiMe_3)_2]$ is ideally suited for such chemistry since it has a 16-valence-electron configuration. Stabilization of the final product is aided by the presence of the strongly π-acidic nitrosyl ligand which can also interact with the cationic counterion. Deprotonation of an alkyl ligand has been used successfully to create neutral alkylidene complexes from cationic precursor complexes,[11] but has not been utilized previously to form anionic complexes from neutral precursors. In fact, complex **1** joins a very small group of formally anionic alkylidene-containing complexes. The only other example of a similar "ate" complex is $[Mo(NAd)(CHCMe_2Ph)$-$(OCH(CF_3)_2)_3][Li(DME)]$ synthesized very recently by Schrock and his coworkers by treatment of $[Mo(NAd)(CHCMe_2Ph)$-$(OTF)_2(DME)]$ with 3 equiv of $LiOCH(CF_3)_2$.[12] Other anionic alkylidene complexes have been claimed, but their characterization data are far from complete.[13]

Complex **1** is isoelectronic with neutral alkylidene nitrosyl compounds of the type [CpMo(NO)(=CHR)(L)], which have been reported previously by our group.[14] In these latter compounds, however, the alkylidene-containing fragment is stabilized by a neutral Lewis base rather than a formally anionic alkyl ligand.

b) With LDA: Reaction of [Cp*Mo(NO)(CH$_2$SiMe$_3$)$_2$] with 1 equiv of LDA in THF for 15 min at ambient temperature results in deprotonation of the Cp* ligand and formation of the lithium salt of the "tucked-in" anionic complex [(η^5,η^1-C$_5$Me$_4$CH$_2$)Mo(NO)(CH$_2$SiMe$_3$)$_2$][Li(thf)$_3$] (**2**) in 40% isolated yield [Eq. (2)]. The identity of **2** is readily established by its

$$\text{(structure)} + \text{LDA} \xrightarrow[\text{THF}]{15 \text{ min}} \text{(structure)} \qquad (2)$$
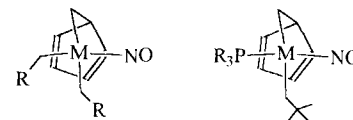
2
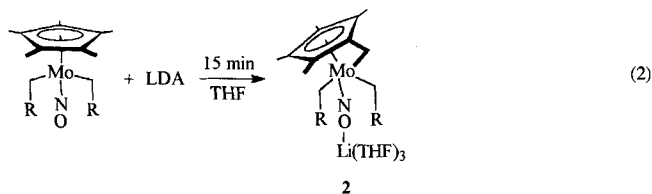
NMR spectra, which display six different methylene-proton resonances and four inequivalent Cp* methyl group signals (Table 2). This also indicates that the arrangement of ligands is *cis* at the metal center. The IR spectrum of **2** (Nujol mull) exhibits a ν_{NO} at 1478 cm^{-1}; this indicates that the Li$^+$ counterion is coordinated to the nitrosyl ligand of **2** but in a manner different from that in **1**. Elemental analysis, ^{1}H NMR, and IR spectral data indicate a four-coordinate Li$^+$ ion coordinated to the nitrosyl ligand with the other coordination sites of the lithium being occupied by three THF molecules, similar to the coordination sphere of the lithium ion in [Cp*Mo(NO)(CH$_2$SiMe$_3$)$_2$-(Me)][Li(thf)$_3$] (**4**) (vide infra).

An alternative bonding mode possible for the Cp* ligand of complex **2** is as an η^6-fulvene ligand. However, the relevant ^{13}C NMR shift of the signal due to the methylene carbon in **2** ($\delta = 60.4$) falls well within the range expected for "tucked-in" complexes (generally lower than $\delta = 80$),[15] and so the complex should be considered as exhibiting little fulvene character. Many examples of (η^5,η^1-C$_5$Me$_4$CH$_2$) and η^6-fulvene-containing complexes are known,[16] including a related 18e$^-$ neutral complex, [(η^5,η^1-C$_5$Me$_4$CH$_2$)Mo(NO)(CH$_2$CMe$_3$)(PMe$_3$)], which was isolated previously by our group.[17]

Complex **2** slowly converts to the thermodynamically more stable **1** when left in THF or C$_6$D$_6$ solution at ambient temperature for 48 h. In the case of the tungsten analogue, the conversion from **2′** to **1′** is much faster. In fact, it has proven impossible to isolate the tungsten "tucked-in" complex in pure form since it converts to the alkylidene isomer within 1 h, and so considerable conversion to the alkylidene product occurs before the reaction to form the "tucked-in" complex is complete. Bercaw and coworkers have previously invoked the reverse conversion of a neutral alkylidene complex ([Cp$_2^*$Hf=CHPh]) to its "tucked-in" isomer by thermolysis.[18] Interestingly, our neutral "tucked-in" complex (namely [(η^5,η^1-C$_5$Me$_4$CH$_2$)Mo(NO)-(CH$_2$CMe$_3$)(PMe$_3$)]) does not convert to an alkylidene complex thermally.[17] The probable reason for this can be found in the coordination geometry at the metal center. In the case of the

neutral complex, the alkyl ligand and the methylene carbon atom of the tucked-in Cp* ligand are *trans* to each other across the metal center and are separated by the phosphine and nitrosyl ligands. In anionic complex **2** the methylene carbon is *cis* to an alkyl ligand and so has a facile route for effecting the requisite proton transfer (Scheme 1).

The reason for the striking difference in the regioselectivity of the two lithium amide reagents (LiN(SiMe$_3$)$_2$ and LDA) towards [Cp*Mo(NO)(CH$_2$SiMe$_3$)$_2$] despite the steric similarity between the two may be found in the pK_a of the corresponding free amine, which for LDA is much greater (HN(C$_3$H$_7$)$_2$ p$K_a = 35.7$, HN(SiMe$_3$)$_2$ p$K_a = 25.8$).[19] The LiN(SiMe$_3$)$_2$ reagent is simply not a strong enough base to remove a proton from the Cp* ring, and so is forced to deprotonate at a more acidic site on the organometallic reactant. The absence of visible intermediates for the reaction with LiN(SiMe$_3$)$_2$ raises the prospect that the reagent is removing the α-H atom directly from an alkyl ligand in the metal complex. The extended reaction time for the deprotonation lends support to this view, since these α-H atoms are sterically much less accessible. Furthermore, these protons are expected to be more acidic than those of the Cp* ring, and so the LiN(SiMe$_3$)$_2$ reagent could be capable of abstracting them.

Scheme 1. Arrangement of ligands in complexes **2** (left) and [(η^5,η^1-C$_5$Me$_4$CH$_2$)-Mo(NO)(CH$_2$CMe$_3$)(PMe$_3$)] (right).

Kinetic analysis of the reaction of [Cp*Mo(NO)(CH$_2$SiMe$_3$)$_2$] with LiN(SiMe$_3$)$_2$

: Plots of ln($A - A_\infty$) against time for the reactions of [Cp*Mo(NO)(CH$_2$SiMe$_3$)$_2$] with LiN(SiMe$_3$)$_2$ under pseudo-first-order conditions are linear; this linearity demonstrates that the reaction is first-order in the molybdenum reagent. A summary of the results obtained by this analysis is presented in Table 4. A plot of the observed rate constant against the concentration of the lithium reagent is a straight line (Figure 2), thereby demonstrating that the reaction is also first-order with respect to the lithium reagent. The reaction is evidently first-order in both the lithium and molybdenum reagents.

Table 4. Observed rate constants for the reaction of [Cp*Mo(NO)(CH$_2$SiMe$_3$)$_2$] with LiN(SiMe$_3$)$_2$ at 50 °C.

[Mo], mM	[Li], mM	Excess	k_{obs}, 10^{-4} s^{-1}
3.01	362.28	120.33	13.4
3.03	362.36	119.74	13.7
3.01	253.59	84.23	9.75
3.03	253.65	83.82	10.0
3.01	181.14	60.16	7.27
3.03	181.18	59.87	7.47
3.01	126.80	42.11	5.51
3.03	126.82	41.91	5.57
3.01	72.46	24.07	3.56
3.03	72.47	23.95	3.50
3.01	50.72	16.85	2.64
3.03	50.73	16.76	2.72
3.01	36.23	12.03	2.23
3.03	36.24	11.97	2.22
3.01	18.11	6.02	1.62
3.03	18.12	5.99	1.59
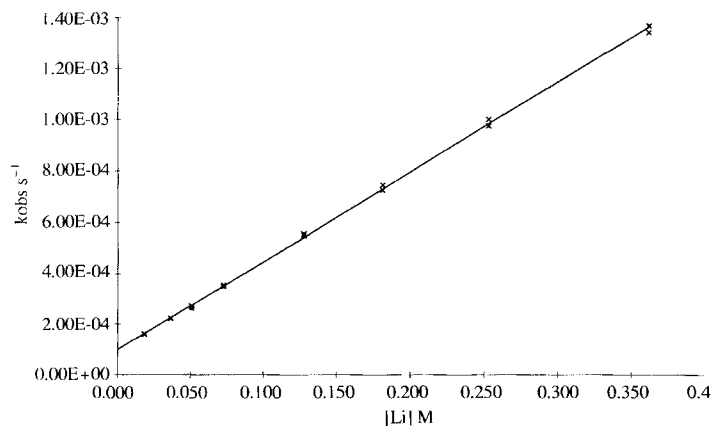
Figure 2. Plot of k_{obs} vs. [Li] for the reaction of [Cp*Mo(NO)(CH$_2$SiMe$_3$)$_2$] with LiN(SiMe$_3$)$_2$.

An interesting feature of the plot shown in Figure 2 is that the line does not pass through the origin. This may be a genuine effect, or it may be due to experimental error. Since the experiment monitors the disappearance of the starting material, then any cause contributing to its disappearance would cause deviant results. The experiment could not be monitored by the appearance of **1** because of its nearly colorless nature.

The effect of temperature on the reaction rate provides some insight into the nature of the transition state. Monitoring of the reaction at 30, 40, 50, and 60 °C (Table 5) and subsequent data analyses led to the linear Eyring plot shown in Figure 3. The linearity of the plot is confirmed by a regression which returns a residual value of 0.995; this indicates that there is only one

Table 5. Variation with temperature of the observed rate constant for the reaction of [Cp*Mo(NO)(CH$_2$SiMe$_3$)$_2$] with LiN(SiMe$_3$)$_2$.

T, K	[Mo], mM	[Li], M	k_{obs}, s^{-1}	k, M^{-1}s^{-1}
333.2	3.09	0.3015	0.001921	0.006371
333.2	3.07	0.3015	0.001806	0.00599
323.7	3.09	0.3015	0.00121	0.004013
323.7	3.07	0.3015	0.001185	0.00393
313.7	3.09	0.3015	0.000834	0.002766
313.7	3.07	0.3015	0.000828	0.002746
303.2	3.09	0.3015	0.000561	0.001861
303.2	3.07	0.3015	0.000564	0.001871
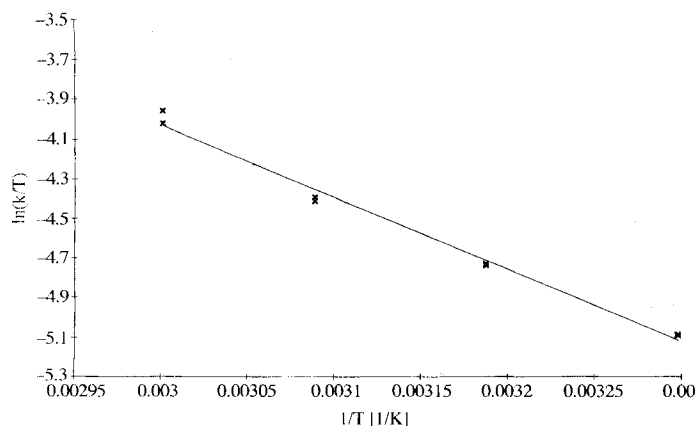
Figure 3. Eyring plot for the reaction of [Cp*Mo(NO)(CH$_2$SiMe$_3$)$_2$] with LiN(SiMe$_3$)$_2$.

mechanism operative during the deprotonation process. The activation parameters that may be extracted from the plot are $\Delta H^{\ddagger} = 30.5 \pm 3.0$ kJ mol^{-1} (7.3 $\pm$ 1.0 kcal mol^{-1}) and $\Delta S^{\ddagger} = -140 \pm 10$ J mol^{-1} K^{-1} (-34 ± 3 e.u.) (errors are 95% confidence limits of the regressed line). The small value of $\Delta H^{\ddagger}$ is indicative of a concerted transition state in which bonds are being broken and formed at the same time. During the reaction C–H, N–Li and Li–O(thf) bonds are broken, while Li–O(nitrosyl) and N–H bonds are formed, and an M–C single bond is converted to an M=C linkage.[20] Though the observed negative entropy of activation supports the view that this process occurs by an associative pathway, the possibility that salt effects are present cannot be ruled out.

In closing this section, we note that treatment of the dialkyl starting material with either *t*BuLi or PhLi leads to the production of the alkylidene complex **1** in irreproducible yields (NMR yield 10–50%; product not isolable). It is not clear by which routes the latter reactions occur, though it is likely that it is by one of the routes delineated for one of the other lithium reagents studied. However, no attempt has been made to discern the exact pathway of these reactions.

Reduction of [Cp*Mo(NO)(CH$_2$SiMe$_3$)$_2$]: Cyclic voltammetry studies have suggested that addition of electrons to [Cp'M(NO)R$_2$] compounds should afford the corresponding 17e$^-$ anions. However, treatment of the dialkyls with reducing agents (e.g. [CpFe(η^6-C$_6$Me$_6$)]) has previously resulted only in decomposition.[21] We have now found that treatment of [Cp*Mo(NO)(CH$_2$SiMe$_3$)$_2$] with 1 equiv of LiPPh$_2$ in THF results in a one-electron reduction of the starting material and production of $\{$[Cp*Mo(NO)(CH$_2$SiMe$_3$)$_2$][Li(thf)]$\}_2$ (**3**) [Eq. (3)]. The Ph$_2$P–PPh$_2$ coproduct can also be isolated from

$$+ \text{Ph}_2\text{P-PPh}_2$$
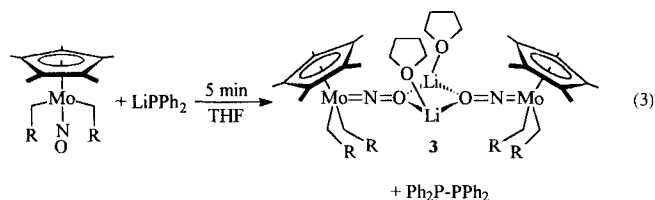
the final reaction mixture and is identifiable by its mass spectral and NMR spectroscopic data.[22] The isolation of **3** is dependent on the presence of Li$^+$ as a counterion that can bind to the nitrosyl and assist in delocalizing the extra electron density. Evidence for this can be found in the ESR spectrum of the compound, in which coupling to a lithium atom is evident (vide infra). Consistent with this view is the fact that reduction of [Cp*Mo(NO)(CH$_2$SiMe$_3$)$_2$] with Na/Hg amalgam in the presence of an excess of Li$^+$ (in the form of LiBF$_4$) does indeed afford **3**. This route results in only slightly improved isolated yields of the product, but the reaction is visibly cleaner than that with LiPPh$_2$ and the product is more stable under these experimental conditions. If the same reduction is performed without the Li$^+$ present, then a similar red product (presumably the sodium salt of the same anion) is formed which, as a Nujol mull, displays a nitrosyl stretching frequency of 1365 cm^{-1}. However, this product could not be isolated in pure form. All attempts at isolating the tungsten analogue of **3** have so far been unsuccess-

ful. This could perhaps be a demonstration of the lesser tendency of tungsten to form 17-valence-electron compounds.

The red crystals of **3** are extremely air sensitive, reconverting rapidly on exposure to air to purple [Cp*Mo(NO)(CH$_2$SiMe$_3$)$_2$] (v_{NO} (Nujol) = 1595 cm^{-1}). This characteristic property of the complex is not entirely surprising, since a simple one-electron oxidation will return the anion to its neutral state. Complex **3** has been subjected to an X-ray crystallographic analysis, full details of which were provided in an earlier report.[23] The complex displays no significant signals in its ^{1}H NMR spectra between $\delta = -30$ and $+40$ (relative to tetramethylsilane). The X-band ESR spectrum of **3** in C$_6$D$_6$ at 25 °C (shown in Figure 4)
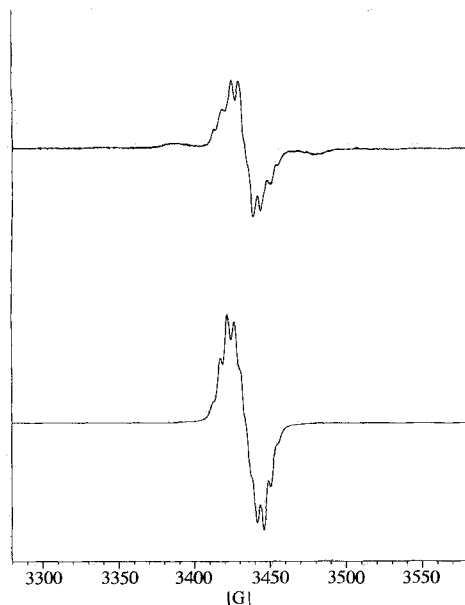

Figure 4. Observed (top) and simulated (bottom) X-band ESR spectra of complex **3** in C$_6$D$_6$ at room temperature.

exhibits coupling of the signal to the ^{14}N nucleus of the nitrosyl ligand (a_N = 5.9 G), the four ^{1}H nuclei of the methylene groups (a_{CH_2} = 5.5 G), the ^{7}Li nucleus (a_{Li} = 2.5 G), and the molybdenum center (g_{iso} = 1.99800). Hence, the unpaired electron density in **3** appears to be delocalized not only over the molybdenum atom and the atoms immediately surrounding it, but also over the lithium counterion. Since coupling of the signal to both lithium cations is not evident, it appears that the dimeric nature established for this complex in the solid state is not entirely maintained in solutions. It is more likely that the complex dissociates to some extent into its constituent monomers, the ready solubility of **3** in nonpolar solvents suggesting that each monomer exists as a tight ion pair (e.g., [Cp*Mo(NO → Li{thf}$_n$)(CH$_2$SiMe$_3$)$_2$]) in these media. Regrettably, attempts to measure the solid-state magnetic properties of **3** have been hampered by its extreme air-sensitivity.

Monitoring of the reaction between [Cp*Mo(NO)(CH$_2$SiMe$_3$)$_2$] and LiPPh$_2$ by ^{1}H and ^{31}P NMR spectroscopy reveals the immediate disappearance of signals due to the starting materials and appearance of signals attributable to the Ph$_2$P–PPh$_2$ coproduct. However, this reaction proceeds further, and over the course of 6 h at ambient temperature these

signals give way to resonances due to **1** and HPPh$_2$. In other words, the 17e$^-$ dialkyl anion **3** is converted into the 18e$^-$ alkylidene anion **1** by Ph$_2$P–PPh$_2$, which effects the requisite hydrogen-atom abstraction. The overall reaction may also be performed with LiPPhH, but the yield of product is much lower. Similar conversions of cationic 17c$^-$ alkyl complexes to cationic 18e$^-$ alkylidene complexes by hydrogen-atom abstraction have been documented by Cooper and coworkers. For example, they have invoked the phenylmethylidene complex [Cp$_2$W(CH$_2$)(Ph)]$^+$ as an intermediate following hydrogen-atom extraction from [Cp$_2$W(Me)(Ph)]$^+$.[24]

Addition reactions of [Cp*Mo(NO)(CH$_2$SiMe$_3$)$_2$]: Treatment of [Cp*Mo(NO)(CH$_2$SiMe$_3$)$_2$] with MeLi leads neither to deprotonation of the complex, as in the lithium amide cases, nor to reduction, as for lithium phosphides, but to direct attack of the metal center to form a trialkyl species, namely [Cp*Mo(NO)(CH$_2$SiMe$_3$)$_2$(Me)][Li(thf)$_3$] (**4**) [Eq. (4)]. This

$$(4)$$
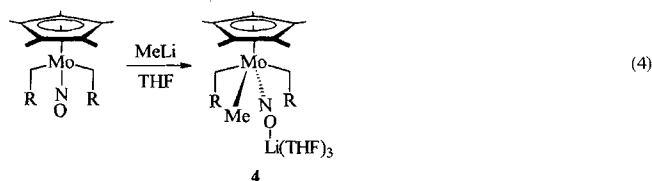
complex is isolable as yellow crystals from pentane in good yield (85%), though the crystals desolvate rapidly in a dry atmosphere to form an amorphous yellow powder. The complex is exceptionally air-sensitive (particularly as the desolvated powder), rapidly reconverting to purple [Cp*Mo(NO)(CH$_2$SiMe$_3$)$_2$] on exposure to air.

Both the ^{1}H and ^{13}C NMR spectra of **4** display signals attributable to two equivalent Me$_3$SiCH$_2$ groups and a Me group, thereby implying that the geometry at the metal center is "*trans*" or "diagonal", that is, that the methyl group lies opposite the nitrosyl ligand. The solid-state molecular structure of **4**, established by an X-ray crystallographic analysis,[25] confirms this view; the ORTEP diagram of **4** is shown in Figure 5. The struc-

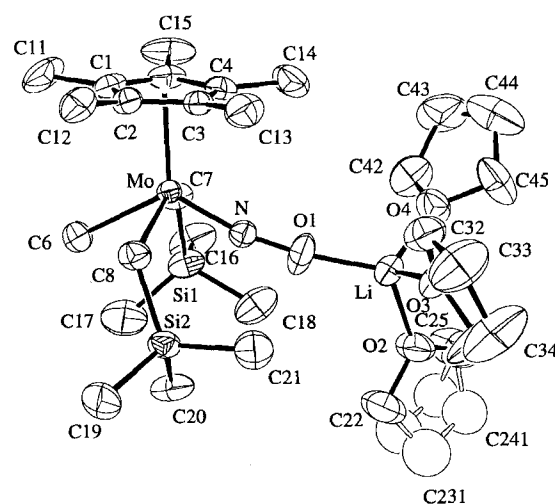

Figure 5. ORTEP diagram of [Cp*Mo(NO)(CH$_2$SiMe$_3$)$_2$(Me)][Li(thf)$_3$] (**4**) at 208 K. 50% probability ellipsoids (or spheres) are shown for all non-hydrogen atom sites. Disordered carbon-atom sites (50% occupancy) are C(231)–C(242).

ture is a regular four-legged "piano stool", with the Mo–C bond lengths for the three alkyl "legs" being essentially equal (Mo–C(6) = 2.241(7),   Mo–C(7) = 2.238(6),   Mo–C(8) = 2.275(6) Å; Table 6) and the Mo-N-O(1) angle of 169.1° being essentially linear. The Mo–N and N–O bond lengths (Mo–N =1.742(5), N–O(1) =1.254(7) Å) indicate a somewhat greater degree of Mo → NO backbonding, though not as great as that for **1** or **3**. The Nujol-mull nitrosyl stretching frequency of **4** (1463 cm^{-1}) is very similar to that of **2** (1478 cm^{-1}), indicating a similar type of binding of the transition-metal anion to the lithium counter-ion in both cases.

Table 6. Selected bond lengths (Å) and angles (°) for [Cp*Mo(NO)(CH$_2$SiMe$_3$)$_2$-Me][Li(thf)$_3$] (**4**).

Mo(1)–C(6)	2.241(7)	Mo(1)–C(8)	2.275(6)
Mo(1)–C(7)	2.238(6)	Mo(1)–N(1)	1.742(5)
Mo(1)–Cp	2.076	O(4)–Li(1)	1.917(12)
O(1)–N(1)	1.254(7)	O(2)–Li(1)	1.952(12)
O(1)–Li(1)	1.816(12)	O(3)–Li(1)	1.958(12)
C(6)-Mo(1)-C(7)	76.46(24)	C(7)-Mo(1)-N(1)	86.49(21)
C(6)-Mo(1)-C(8)	74.48(23)	C(7)-Mo(1)-Cp	107.6
C(6)-Mo(1)-N(1)	123.15(22)	C(8)-Mo(1)-N(1)	88.15(21)
C(6)-Mo(1)-Cp	115.9	C(8)-Mo(1)-Cp	108.2
C(7)-Mo(1)-C(8)	141.04(21)	N(1)-Mo(1)-Cp	121
Mo(1)-N(1)-O(1)	169.1(4)	N(1)-O(1)-Li(1)	170.6(5)
Mo(1)-C(7)-Si(1)	126.4(3)	Mo(1)-C(8)-Si(2)	120.3(3)
O(1)-Li(1)-O(2)	118.5(6)	O(2)-Li(1)-O(3)	103.6(5)
O(1)-Li(1)-O(3)	110.5(6)	O(2)-Li(1)-O(4)	101.5(6)
O(1)-Li(1)-O(4)	113.8(6)	O(3)-Li(1)-O(4)	107.9(6)

The discovery of the novel trialkyl anion in **4** immediately raised the possibility of generating a trialkyl neutral species. If such an entity were to be synthesized, it would be a 17-valence-electron species that would be expected to be quite reactive.[26] In order to determine whether the 17-electron neutral species would be stable, an electrochemical investigation of **4** was undertaken. Not surprisingly, the compound shows no reduction features other than a broad wave that corresponds to the reduction of the Li$^+$ counterion, which causes concomitant plating of the electrode. The principal oxidation feature of the complex appears at − 840 mV (vs [Cp$_2$Fe]) and is completely irreversible. This implies that under these conditions the neutral compound formed is inherently unstable and quickly decomposes to other species. At lower scan rates (below 600 mVs^{-1}) two other features become apparent (Figure 6), and these are attributed to subsequent redox reactions of the species formed by the initial oxidation.

Solutions of **4** in C$_6$D$_6$ are not thermally stable, but convert cleanly to the alkylidene complex **1** when warmed to 40 °C for a few hours, presumably with the concomitant loss of methane. This process is selective, with no production of the analogous methylidene complex being evident. This reactivity closely resembles the "classic" method of forming Schrock alkylidenes by thermolysis of an alkyl complex that is sterically overcrowded at the metal center.[27, 28]

Conclusion

This study has highlighted the range and versatility of reactions that may be performed by lithium reagents on a single chemical system. Direct attack at the metal center is possible, yielding, for
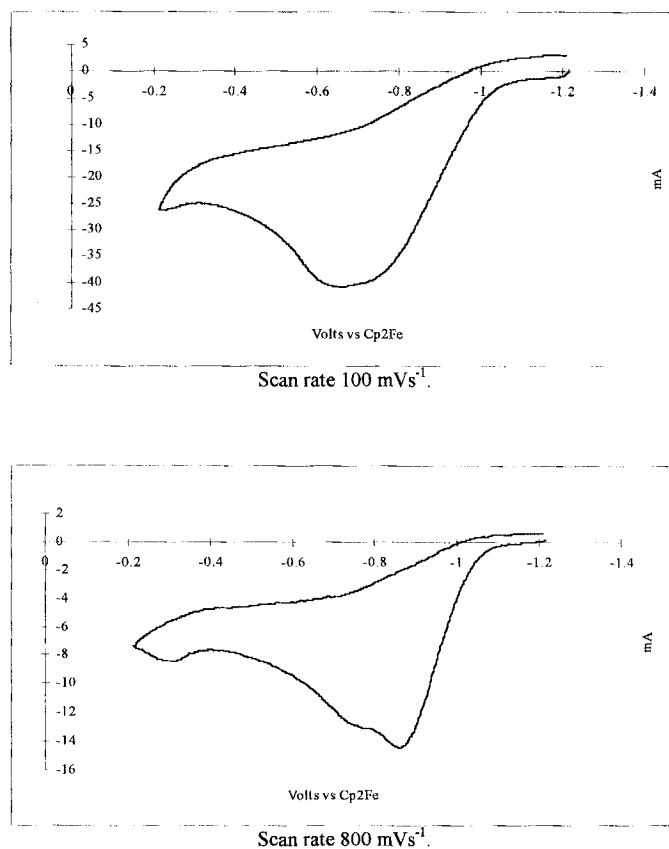

Scan rate $\overline{100}$ mVs^{-1}.

Scan rate 800 mVs^{-1}.

Figure 6. Cyclic voltammograms with differing scan rates for [Cp*Mo(NO)-(CH$_2$SiMe$_3$)$_2$(Me)][Li(thf)$_3$] (**4**) in THF.

example, the trialkyl complex **4**. When sterically bulky alkyl reagents or lithium amides are used, then deprotonation of a peripheral ligand with varying regioselectivities appears to be favored. Lithium phosphides cause an initial reduction of the starting organometallic complex. We are currently investigating whether methodology of the type outlined in this study may be utilized to synthesize other anionic alkylidene complexes, and we are continuing to study the reactivity of such complexes.

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