Articles

Conventional Lithium Bases as Unconventional Sources of Methyl Anion: Facile Me−Si and Me−C Bond Cleavage in RLi, R_2NLi, and BR_4^- by an Electrophilic Osmium Dihydride

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cis,trans-$Os(H)_2(OTf)(NO)(P^iPr_3)_2$ (**1-OTf**) and several other precursors (**1-X**) to $Os(H)_2(NO)(P^iPr_3)_2^+$ (**1**$^+$) react with $(Me_3Si)_2NLi$, $(Me_3Si)_2CHLi$, lithium 2,2,6,6-tetramethylpiperidide (TMPLi), Me_3SiCH_2Li, and $B(CH_2SiMe_3)_4^-$ by a highly unusual, facile β-Me^- transfer, the exclusive reaction pathway for the first two in nonpolar solvents. A series of lithium alkyls and alkylamides and organoborate reagents have been examined to reveal widespread occurrence of the direct β-R'^- transfer (R′ = H, Me) to the Os electrophile, being completely selective for β-H^- over β-Me^-, with the sole (surprising) exception of NpLi. The β-R′ elimination was ruled out as the mechanism of the net β-R'^- transfer for two representative RLi cases with R′ = H, Me, and a single-electron-transfer mechanism was shown to be inoperative for tetraalkylborates. The mechanistic studies also uncovered the important role of Li in RLi and R_2NLi, which acts as a potent Lewis acid to abstract the halide/pseudohalide X from **1-X** in generating the unsaturated Os species. The proposed intimate mechanism of Me−C and Me−Si bond cleavage is a direct S_E2 substitution at carbon with inversion of the Me group, supported by DFT calculations. While the imines formed in the process of C−H and C−Me cleavage are lithiated by, and compete for the Os with, the original base, the unsaturated silicon species formed by Si−Me cleavage react with the remaining base by 1,2-addition of (N,C)-Li, forming intermediates that are also reactive by β-Me^- transfer. A complex mixture of Os-free coproducts is obtained in both cases. The structural features of **1**$^+$ responsible for its unusual reactivity are discussed.

Introduction

Lithium alkyls[1−3] (RLi) and alkylamides[4] (R_2NLi) are invaluable synthetic tools[5] in organic[1,2] and inorganic chemistry,[4,6,7] including anionic olefin polymerization processes.[8,9] Bulky amides, such as hexaalkyldisilazides, are widely used to stabilize transition-metal complexes[10,11] and main-group compounds[12] with low coordination numbers, and 2,2,6,6-tetramethylpiperidide has found increasing use in a similar fashion.[11,13] The

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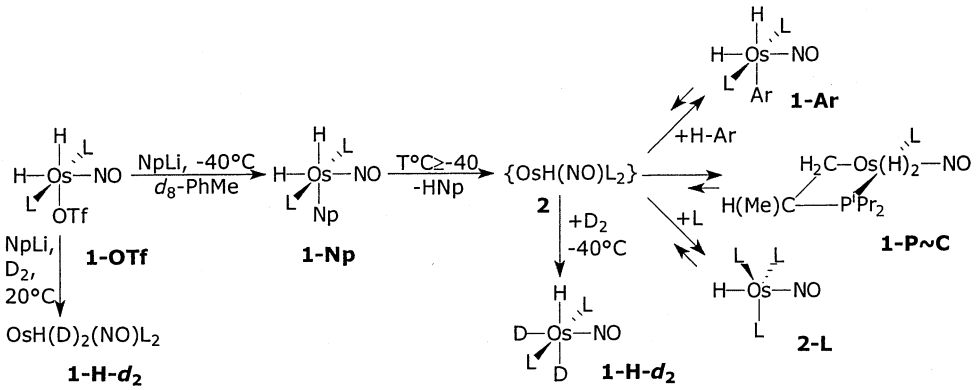
Scheme 1. Generation and Reactivity of 2



typical modes of reactivity of RLi and R_2NLi, as a nucleophile or as a base, are often complicated by single-electron-transfer reduction[14] and β-hydride-tansfer[15−17] processes.

Tetraorganylborates (BR_4^-)[18] are gaining increased attention as mild but selective synthetic alternatives to organolithium reagents.[19−22] In comparison to RLi and R_2NLi, the SET reactivity is much more widespread with BR_4^-,[23,24] commonly used as free-radical initiators of olefin polymerization.[25] The direct transfer of the nucleophilic R^- from BR_4^- can also proceed in competition with transfer of an α-[19] or β-substituent[26] (to boron), including hydride.

Full substitution of the β-positions in RLi and R_2NLi solves the β-H^- transfer problem, and β-Me^- transfer does not typically take place. We are aware of only a few precedents of an organolithium base serving as a source of MeLi: Shiner and co-workers obtained the β-Me^- transfer product in 33% yield in the thermal reaction of lithium 2,2,6,6-tetramethylpiperidide (TMPLi) with a nonenolizable ketone,[27] and Pines et al. have implicated loss of RNa from a cyclohexadienyl intermediate, driven by achieving aromaticity, in a sodium/benzylsodium-catalyzed thermal dehydromethylation of several cyclohexadienes.[28]

This study describes facile β-Me^- transfer from $(Me_3Si)_2NLi$, $(Me_3Si)_2CHLi$, Me_3SiCH_2Li, TMPLi, and $B(CH_2SiMe_3)_4^-$ to an osmium electrophile under ambient conditions, the exclusive reaction pathway for the former two reagents in nonpolar solvents, which represents rare examples of intermolecular sp^3 C−Si[29−31] and C−C[32] bond cleavage.

Results

I. General Remarks on the "Dehydrohalogenation" of $Os(H)_2(OTf)(NO)L_2$. The main focus of this study is the mechanism of HOTf removal from *cis*,*trans*-$Os(H)_2(OTf)(NO)L_2$ (L = P^iPr_3; **1-OTf**), accomplished with a variety of organolithium reagents. As detailed in a separate report,[33] this reaction affords the highly reactive 16-electron Os intermediate {$OsH(NO)L_2$} (**2**), which, eluding direct observation even at low temperatures, scavenges an additional phosphine ligand and reacts by intra- and intermolecular C−H activation with phosphine alkyls and aromatic solvents, respectively, with progressively larger $\Delta G^{\ddagger}$ and $-\Delta G°$ values (Scheme 1). Mechanistic studies[33] revealed the involvement of **2** as the true reaction intermediate and C−H bond-

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breaking and -forming reactions proceeding by oxidative-addition/reductive-elimination mechanisms. Generation of **2** under ambient conditions effectively leads to the formation of the metalated isomers **1-P∼C**, which in C_6D_6 solvent convert to the products of aromatic C−D oxidative addition $Os(H)(D)(C_6D_5)(NO)(P^iPr_3)_2$ (**1-Ph-*d*,*d*$_5$**) on the time scale of hours; integration of hydride or ^{31}P resonances of **1-P∼C** and **1-Ph-*d*,*d*$_5$** can be reliably used to evaluate the extent of formation of **2**. Of additional importance to the mechanistic studies presented here, generation of **2** often yields the trihydride **1-H**[34] and free L, in a decomposition fashion, the yields of which vary, although both typically constitute at most a trace amount, with the exception of the reaction with NpLi.[33]

II. Reactivity of Organolithium Bases with 1-OTf. (a) RLi and R_2NLi. Originally, it was found that $(Me_3Si)_2NLi$ instantaneously reacts with **1-OTf** under ambient conditions in a variety of solvents via an unprecedented methyl anion transfer to quantitatively yield **1-Me**, thus serving as a formal source of MeLi. A number of other lithium alkyls and alkylamides were then examined to determine the scope and generality of such an unusual process. Indeed, in several other cases, $(Me_3Si)_2CHLi$, Me_3SiCH_2Li, and lithium 2,2,6,6-tetramethylpiperidide (TMPLi), β-Me^- transfer was found to be at least a significant reaction pathway. To the best of our knowledge, such reactivity is unprecedented for the above reagents, with the exception of TMPLi.[27] Distantly related examples of similar reactivity include β-Me^- abstraction from $Cp'_2ZrCl(CH(SiMe_3)_2)$ by $AlCl_3$,[30] from $(Cp^*{\sim}O)Ti(CH_2SiMe_3)_2$ by $B(C_6F_5)_3$,[31] and from (η^5-cyclohexadienyl)ruthenium complexes by Brønsted acidic catalysts.[35]

The reactivity of **1-OTf** with all organolithium reagents examined was found to generally conform to three independent pathways, as shown in Scheme 2: β-R'^- transfer (A), triflate

metathesis (B), and deprotonation (C), all of which eventually lead to **2** (with the exception of A with R′ = H, as the trihydride **1-H** is stable to H_2 reductive elimination[34]). The independence of pathways A and B is discussed below.

In C_6D_6, the reactivity of **1-OTf** with all organolithium reagents examined predominantly follows pathways A and B. The starting material **1-OTf** is fully consumed at 20 °C within 15 min of mixing the reagents[36] (essentially instantaneously), giving the products corresponding to pathways A and B in yields summarized in Table 1. The surprising result is that only NpLi does not react via pathway A, as inferred from the −40 °C reaction in d_8-PhMe,[33] while all other bases studied transfer the β-R'^- substituent (Me or H) to a significant extent. Although all **1-R** (R ≠ H) species formed via either of the pathways A and B reductively eliminate

Scheme 2. Observed Pathways of Reactivity of 1-OTf with RLi and BR_4^-

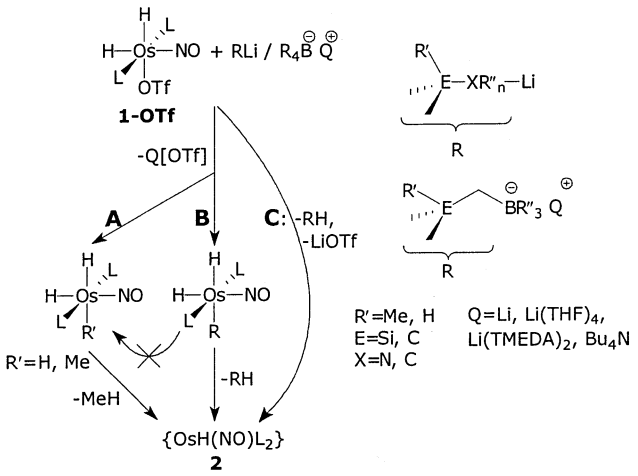

Table 1. Reactivity of 1-OTf with RLi: Yields of the Reaction Products in C_6D_6 at 20 °C Obtained by ^1H NMR Integration within 15 Min, According to Pathways A and B (Scheme 2)

	yield, %	
R(Li)	pathway A (R′)	pathway B
$(Me_3Si)_2N$	100 (Me)	
$(Me_3Si)_2CH$	100 (Me)	
Me_3SiCH_2	40 (Me)	60
TMP	50 (Me)	13[a]
Np	− (Me)	100
$^iPr_2N$	96 (H), 0 (Me)	
^tBu	100 (H)	
^nBu	53 (H)	47
Et	81 (H)	19

[a] Pathway B or C, see text.

R−H under ambient conditions, these subsequent reactions are only marginally developed after 15 min at 20 °C (except for **1-Np**). With the latter exception, a significant amount of secondary products was observed only in ^{n}BuLi and EtLi reactions, in which case **2** was trapped by the olefins released in the β-H^- transfer as adducts **2-C_4H_8** (6%) and **2-C_2H_4** (5%), respectively. The two reaction pathways, A and B, account for all of the observed products in all but two cases, TMPLi and LDA, in which case **1-OTf** undergoes additional reactions with the imines released in pathway A. Additionally, small amounts of **1-H**, **1-Ph-*d*,*d*$_5$**, and **1-P∼C** (13%), indicative of the intermediate formation of **2**, were invariably observed in the case of TMPLi and, although consistent with formation of a highly reactive **1-TMP** intermediate (not observed at 20 °C) via pathway B, these could also result from the deprotonation pathway C.

The syntheses of the four RLi reagents exhibiting the β-Me^- transfer did not employ MeLi, and therefore their reactivity via pathway A (with R′ = Me) involves genuine cleavage of Me−Si and Me−C bonds by $Os(H)_2(NO)(P^iPr_3)_2^+$ (**1**$^+$) at 25 °C. While for bulky $(Me_3Si)_2NLi$, $(Me_3Si)_2CHLi$, and TMPLi triflate metathesis (pathway B) is likely severely impeded by the steric bulk of the P^iPr_3 phosphines in **1**$^+$, the reactivity of Me_3SiCH_2Li reveals a considerable kinetic preference for the β-Me^- transfer (A) over transfer of Me_3SiCH_2 (B) (the product of B, **1-CH_2SiMe_3**, is quite stable at T < 20 °C). In comparison to the β-H^- transfer, however, β-Me^- transfer is observed experimentally to be strongly disfavored,

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(36) RLi and R_2NLi were typically used in 20−50% molar excess.

Table 2. Reactivity of 1-OTf with BR_4^-: Yields of the Reaction Products in C_6D_6 at 20 °C Obtained by ^1H NMR Integration within 15 Min, According to Pathways A and B (Scheme 2)

	yield, %	
$Q^+BR_4^-$	pathway A (R′)	pathway B (R)
$LiBMe_4$		100
$[Bu_4N][Ph_3BMe]$		100 (Me), 0 (Ph)
$LiBEt_4$	23 (H)	77[a]
$[Li(TMEDA)_2][^iPr_3BMe]$	39 (H)	61 (Me), 0 (^{i}Pr)
$[Li(THF)_4][B(CH_2SiMe_3)_4]$	59 (Me)	41

[a] With **2-C_2H_4** included.

at least kinetically, as the reaction with LDA reveals no trace of **1-Me**.

(b) BR_4^-. Several tetraorganylborates were examined for reactivity with **1-OTf** under analogous conditions, and similar reactivity pathways, consisting of β-R′$^-$ transfer (i.e. β to boron) (pathway A) and triflate metathesis with R^- (pathway B), were found, again involving both H^- and Me^- transfer in A (Table 2, Scheme 2). While cases of β-H^- transfer from BR_4^- have been documented,[26] β-Me^- transfer from $B(CH_2SiMe_3)_4^-$ is unprecedented, to the best of our knowledge.[37] On the basis of the following observations, the products in Table 2 are attributed to the reactivity of intact $LiBR_4$ rather than the corresponding RLi, possibly formed from the former in a preequilibrium fashion together with BR_3. The solution ^1H NMR studies of $LiBMe_4$ revealed no evidence for such an equilibrium, as the B−H coupling was resolved at temperatures of up to 100 °C in PhMe[38] and 55 °C in Et_2O.[39] The $LiBEt_4$ reaction gives a product distribution (A vs B) considerably different from that obtained with EtLi (Table 1), while the reaction of $[Li(THF)_4][B(CH_2SiMe_3)_4]$ leads to organic products dramatically different from those obtained in the reaction of Me_3SiCH_2Li in the presence of $B(CH_2SiMe_3)_3$ and the Bu_4N^+ salt of $B(CH_2SiMe_3)_4^-$ exhibits reactivity very similar to that of $[Li(THF)_4][B(CH_2SiMe_3)_4]$, with a related Os compound. The reactions of $LiBEt_4$ with **1-OTf** in d_4-MeOH and THF give very similar product ratios, both with an increased proportion of B relative to that obtained in C_6D_6, while pure $LiBEt_4$ shows no significant hydrolysis in d_4-MeOH on the time scale of the reaction with **1-OTf** (10−15 min at 20 °C). However, the reaction of **1-OTf** with a d_4-MeOH solution of $LiOCD_3$, prepared by quenching with 1.2 equiv of EtLi and containing 1.5 equiv of BEt_3, gave products very similar to those obtained with $LiBEt_4$. In view of the fact that BEt_3 is inert to **1-OTf** in d_4-MeOH, this result suggests that $BEt_3(OMe)^-$ may exhibit similar reactivity.[40]

(c) Characterization and Intrinsic Reactivity of 1-R. The identity of the β-Me^- transfer product, **1-Me**, was confirmed by independent synthesis from **1-OTf** and MeLi. However, the borates Ph_3BMe^- and BEt_4^- are the reagents of choice for the preparation of the corresponding **1-Me** and **1-Et**, because the reactions (quantitative for **1-Me**) can be carried out in MeOH at low temperature to yield crystalline but temperature-sensitive products, isolated in moderate to good yields. While isolation of **1-^{n}Bu** and **1-Np**[33] was not attempted, due to their limited thermal stability, **1-CH_2SiMe_3** is highly soluble and could be isolated only in low yields and as a ca. 15:85 mixture with **1-Me**.

All dihydrido alkyl complexes **1-R** exhibit NMR data sufficient for unambiguous assignments of the *cis*,*trans*-$Os(H)_2(R)(NO)(P^iPr_3)_2$ octahedral structures. The α-CH ^1H NMR resonances of the alkyl groups reveal moderate couplings to P (4−5 Hz) and the *cis*-hydride (1−2 Hz),[41] while the differences of the hydride ^1H NMR chemical shifts, $\Delta\delta = \delta(H_A) - \delta(H_M)$, for all **1-R** are distinctly lower than the values of halide/pseudohalide derivatives **1-X**.[33]

The main reactivity mode characteristic of all **1-R** compounds is the reductive elimination of the corresponding RH to yield **2** and its subsequent products. Scheme 3 shows the order of stability of the complexes observed in aromatic solvents,[33] which ranges from a $t_{1/2}$(−20 °C) value of about 1 h for **1-Np** to a $t_{1/2}$(+60 °C) value of about 10 h for the most thermodynamically stable **1-Ph** ($t_{1/2}$(25 °C) ≈ 24 h for **1-Me**). Consideration of the relative stability of the alkyl complexes (R = Me, Et, ^{n}Bu, Np), with reasonably similar electronic properties, clearly shows that increasing steric bulk of R[42] accelerates the reductive elimination of RH.

Scheme 3. Relative Order of Stability of 1-R Complexes toward Reductive Elimination of RH

$$R = Np \ll {}^nBu \approx CH_2SiMe_3 \approx Et < Me \ll Ph$$

(d) Evidence for the Deprotonation Pathway (C). Under conditions that favor minimal aggregation of organolithium bases, with strong solvation of Li, the reactivity of **1-OTf** with selected RLi can follow neither of the pathways dominating the reactivity in aromatic solvents and available spectroscopic data point to deprotonation mechanism C. Thus, reaction of **1-OTf** with 5 equiv of Me_3SiCH_2Li in d_8-THF at −40 °C proceeds on the time scale of minutes to yield a new major product; only a trace of **1-CH_2SiMe_3** was observed at −20 °C, after complete conversion. The ^1H NMR spectrum of this new species, tentatively assigned as the osmate $OsH(CH_2SiMe_3)(NO)L_2^-$ (**2-$CH_2SiMe_3^-$**), formed via pathway C as shown below, at −40 °C shows all of the signals expected for a TBP structure with *trans*-L, in the correct intensity ratio. The hydride appears as a 32.8 Hz triplet at −10.38 ppm, while the α-CH_2 protons at 0.60 ppm exhibit a P−(C)H coupling of 5.4 Hz, and (PCH)Me signals are diastereotopically shifted. Most importantly, the selectively decoupled $^{31}P\{^1H\}$ signal[43] is a doublet, confirming the presence of a single hydride ligand.

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(41) Such coupling probably results from through-space interactions and is not unusual: analogous observations were made for *cis*,*trans*-$OsH(Me)(CO)_2L_2$ complexes: Esteruelas, M. A.; Lahoz, F. J.; Lopez, J. A.; Oro, L. A.; Schlünken, C.; Valero, C.; Werner, H. *Organometallics* **1992**, *11*, 2034.

(42) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

(43) Hydride-only coupled ^{31}P signal.

Since the product of pathway **B**, **1-CH$_2$SiMe$_3$**, is stable for hours at temperatures of up to 0 °C, formation of **2-CH$_2$SiMe$_3^-$** cannot be explained by the intermediate formation of **1-CH$_2$SiMe$_3$** undergoing reductive elimination to give **2**, which then reacts with Me_3SiCH_2-Li to form the observed Os product. Therefore, **2** is formed via deprotonation of **1-OTf** and is promptly complexed by the remaining Me_3SiCH_2Li, with loss of OTf^-. An alternative mechanism for the formation of **2-CH$_2$SiMe$_3^-$**, deprotonation of **1-CH$_2$SiMe$_3$**, is plausible; however, the hydrides are expected to be considerably more acidic in **1-OTf**, due to the greater electronegativity of OTf, compared to that of CH_2SiMe_3. Indeed, using [*cis*,*trans*-Os(H)$_2$(THF)(NO)L$_2$][B(C$_6$H$_3$-3,5-(CF$_3$)$_2$)$_4$], **1-THF$^+$**(BAr′$_4^-$), one of the most reactive forms of **1$^+$**, under conditions analogous to those of the **1-OTf** reaction yields the identical product, **2-CH$_2$SiMe$_3^-$**, but much faster: the reaction is complete in minutes at −80 °C, consistent with greater hydride acidity in the cationic species. Additionally, reaction of **1-OTf** with 15 equiv of Me_3SiCH_2Li and 20 equiv of TMEDA in d_8-PhMe at −60 °C gives predominantly **1-CH$_2$SiMe$_3$** and 22% of **2-CH$_2$SiMe$_3^-$**, identified by a similar −10.05 ppm (32 Hz) hydride triplet in the ^{1}H NMR spectrum and a ^{31}P NMR chemical shift similar to that observed in d_8-THF (also a doublet with selective decoupling). However, both products evolve with the same rates and, therefore, are being formed via independent processes (B and C), which rules out the intermediacy of **1-CH$_2$SiMe$_3$** in the formation of **2-CH$_2$SiMe$_3^-$**. Notably, the analogous reaction in d_8-PhMe *in the absence of TMEDA* yields no observable trace of the osmate species, which shows that solvation of Li is necessary for the operation of the deprotonation mechanism.

Further characterization of the osmate **2-CH$_2$SiMe$_3^-$** was hampered by its very limited thermal stability. In all cases where its formation was established by low-temperature NMR, the complex decomposed within minutes at room temperature, producing mainly free L. Attempts to convert it to **1-CH$_2$SiMe$_3$** by protonation failed: reacting **2-CH$_2$SiMe$_3^-$** with excess MeOH even at −80 °C gave several new species, but with no appreciable amount of the desired product. In the case of NpLi, a similar hydride signal was observed in the **1-OTf**/NpLi reaction in d_8-PhMe,[33] assignable to the analogous **2-Np$^-$** osmate, although in trace yield, and it also did not persist at ambient temperature.

In sharp contrast to the Me_3SiCH_2Li results, using a much weaker base,[44] $(Me_3Si)_2NLi$, in a reaction with **1-THF$^+$** in d_8-THF at −60 °C, gave no observable amount of **2** or related products but cleanly and quantitatively produced **1-Me** on the time scale of hours, with no intermediates. Additionally, the reaction of **1-OTf** with 1.5 equiv of Me_3SiCH_2Li in d_8-THF at *room temperature* gave products of pathways A and B in ca. 60% total yield. Therefore, while pathway C in principle can be operational, it requires a very strong base, such as highly disaggregated alkyllithium, and yet still may not be the kinetically preferred reactivity pathway, apparently due to the high strength of the Os−H bonds and limited steric accessibility of (Os)H.

III. Independence of Pathways A and B: Direct β-R′$^-$ Transfer vs β-R′ Elimination. The widespread occurrence of β-hydride elimination reactions of transition-metal alkyl[45] and, to a lesser extent, alkylamide[46] complexes suggests that formation of the products of pathway A, with R′ = H, may be the result of β-hydride elimination from the products of pathway B. While numerous examples of analogous β-methyl elimination reactions, involving C−C and C−Si bond cleavage, have been documented,[47−49] these are by far much less common and often require fairly high activation energies.[47] Nevertheless, several early-metal metallocene complexes have been shown to undergo facile β-methyl elimination,[48] which demonstrates the possibility of such a mechanism with R′ = Me.

Since all possible products of pathway B are saturated complexes, some transformation is necessary to generate a vacant Os orbital, in order for the β-R′ elimination to proceed.[50,51] We have considered a nondissociative β-R′ elimination mechanism, such as bending of NO[52] or migration of a ligand to the NO nitrogen,[52] and two dissociative mechanisms, reversible loss of L and reversible loss of H_2. While reversible loss of NO is a possibility,[52] it was not considered, since **1-H**, a representative of **1-R** complexes in this regard, is quite stable at 90 °C in MeOH under H_2 for 24 h.[34] We have studied two pairs of complexes, **1-H**/**1-Et** and **1-Me**/**1-CH$_2$SiMe$_3$**, to evaluate the possibility of the β-R′ elimination mechanism for β-R′ = H, Me, as opposed to a direct β-R′$^-$ transfer from RLi that does not involve intermediate formation of the products of pathway **B**.

(a) β-R′ = H. Monitoring the evolution of the rapidly formed initial products of the reaction of **1-OTf** with $LiBEt_4$ in C_6D_6 at 28 °C by ^{1}H NMR for 11 h showed only a slight increase in the amount of **1-H**, from 23% of all observed Os products measured initially to a maximum of 27%, comparable to the experimental integration error. At the same time, the **1-Et** complex fully decayed in a first-order reaction via reductive elimination of ethane, forming **1-P∼C**, which subsequently converted into **1-Ph-*d*,*d*$_5$**.[33] The amount of the **2-C$_2$H$_4$** adduct slightly increased, from 19 to 24%. Following the evolution of pure **1-Et**, devoid of an observable trace of **1-H**, under analogous conditions revealed a ca. 1% trace of **1-H** appearing after 95% conversion of **1-Et**. This amount of the trihydride is attributable to the reactivity of **2** (Scheme 1), since decay

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of, for example, **1-Me** often generates similar traces of **1-H**. These results rule out a nondissociative β-hydride elimination mechanism. However, a dissociative mechanism may be responsible for the suspected conversion of **1-Et** to **1-H**, if the product is more prone to the loss of either L or H_2 and, due to some fortuitous combination of rates, the formation of the product effectively stops the transformation. This possibility is clearly inconsistent with the fact that pure **1-Et** in solution produces no observable trace of **1-H** after 15 min. Nevertheless, reaction of **1-OTf** with a C_6D_6 solution of EtLi, also containing 10 equiv of P^iPr_3, gave 79% of **1-H**, while the analogous reaction under an H_2 atmosphere produced 78% of **1-H** (cf. Table 1). In the latter case, the small amount of **2-C_2H_4** typically formed in the absence of H_2 (ca. 5% yield) was absent, indicating that **2** that was produced was trapped by the added H_2 as **1-H** and therefore increasing the observed yield of the latter. Such variations between the yields obtained in the presence of H_2 and L and in their absence (Table 1) are insignificantly small. Thus, these results rule out a β-hydride elimination mechanism as the source of **1-H** in the reaction of **1-OTf** with EtLi, which therefore proceeds via direct β-hydride transfer.

(b) β-R′ = Me. Having established the β-hydride elimination mechanism inoperative in **1-Et** suggests that the analogous β-Me^- elimination is unlikely in principle, in light of the much more frequent occurrence of the former. Indeed, experiments analogous to those performed for the β-H^- case lead to the same conclusions. Monitoring the reaction of **1-OTf** with 2 equiv of Me_3SiCH_2Li in d_8-PhMe by ^1H NMR at −40 °C shows the reaction proceeding to completion within minutes at this temperature. A 50:50 mixture of **1-CH_2SiMe_3** and **1-Me**, generated in a separate experiment with 4 equiv of Me_3SiCH_2Li at the same temperature, remained unchanged after several hours at that temperature and temperatures of up to 0 °C. In the reaction of **1-OTf** with 15 equiv of Me_3SiCH_2Li and 20 equiv of TMEDA in d_8-PhMe at −60 °C, a 94:6 mixture of the above products was produced on the time scale of hours and again remained unchanged on warming to room temperature. Under ambient conditions in C_6D_6 both **1-CH_2SiMe_3** and **1-Me** reductively eliminate Me_4Si and CH_4, respectively, with the former reaction proceeding ca. 10 times faster. While it was impossible to isolate pure **1-CH_2SiMe_3**, the low-temperature generation results clearly rule out a nondissociative β-Me^- elimination mechanism, since **1-CH_2SiMe_3** does not convert to **1-Me** once its formation is complete (i.e. once **1-OTf** is consumed). When the two dissociative mechanisms were tested, **1-OTf** was reacted with a C_6D_6 solution of Me_3SiCH_2Li, also containing 10 equiv of P^iPr_3, to give a 56:44 mixture of **1-CH_2SiMe_3** and **1-Me**, while reaction under an H_2 atmosphere led to a 54:46 ratio of the products. Notably, the latter reaction also gave 23% of **1-H**. However, the analogous reaction under D_2 gave ca. 10% of each of the **1-H-*d*** and **1-H-d_2** isotopomers,[34] together with a 55:45 ratio of **1-CH_2SiMe_3** and **1-Me**; for comparison, exposing the reaction mixture generated from **1-OTf** and Me_3SiCH_2Li to an atmosphere of H_2 2 min after mixing of the reagents showed only 10% of **1-H** with a 60:40 ratio of the major products, after 10 min. While these results indicate that H_2 can react with

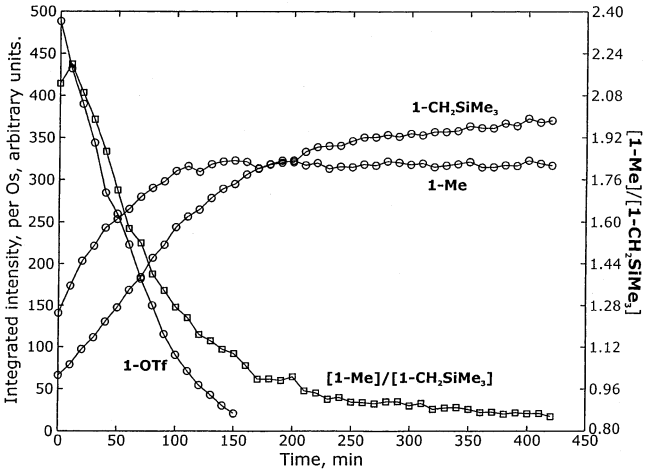


Figure 1. Time evolution of **1-Y** (circles) and [**1-Me**]/[**1-CH_2SiMe_3**] ratio (squares) in the reaction of **1-OTf** with 15 equiv of Me_3SiCH_2Li, monitored by ^1H NMR at −70 °C in d_8-PhMe.

1-OTf and Me_3SiCH_2Li to give **1-H**, bypassing the **1-CH_2SiMe_3** intermediate (to give **1-H-*d*** in the D_2 reaction),[53] they also show that within 10 min up to 10% of the latter can be converted to **1-H**, via intermediate **2** (to give **1-H-d_2** in the D_2 reaction). In the absence of added H_2, this amount of **2** probably converts to **1-P∼C**, not observed by ^1H NMR presumably due to the broadness of its hydride signals.[33] Thus, the attempted suppression of either dissociative mechanism gives a negligible effect.

Finally, following the evolution of the products **1-CH_2SiMe_3** and **1-Me** by ^1H NMR in a reaction of **1-OTf** with 15 equiv of Me_3SiCH_2Li in d_8-PhMe at −70 °C (Figure 1) provides direct evidence against the intermediacy of **1-CH_2SiMe_3** in the formation of **1-Me**.[54] While the formation of **1-Me** follows pseudo-first-order kinetics, with k(**1-Me**) = [3.8(1)] × 10^{-4} s^{-1}, the evolution of **1-CH_2SiMe_3** has an induction period, effectively leading to a smaller k(**1-CH_2SiMe_3**) = [1.5(1)] × 10^{-4} s^{-1}, as does the decay of **1-OTf**, such that the plot of ln([**1-OTf**]) vs time is curved upward and its loss is described by a lowered k(**1-OTf**) = [1.6(1)] × 10^{-4} s^{-1}. Since the growth of **1-Me** levels off, rather than decaying, if it somehow were an intermediate for the formation of **1-CH_2SiMe_3**, the acceleration of pathway B is apparently caused by the release of LiOTf, presumably due to the formation of mixed aggregates of LiOTf with Me_3SiCH_2Li that exhibit reactivity different from that

(53) Me_3SiCH_2Li possibly undergoes hydrogenolysis prior to the reaction with **1-OTf**, giving LiH, the source of **1-H-*d*** in the D_2 reaction: Gilman, H.; Jacoby, A. L.; Ludeman, H. *J. Am. Chem. Soc.* **1938**, *60*, 2336. Screttas, C. G.; Eastham, J. F.; Kamienski, C. W. *Chimia* **1970**, *24*, 109. Screttas, C. G.; Eastham, J. F. *J. Am. Chem. Soc.* **1966**, *88*, 5668.

(54) (a) The presence of a large excess (>5 equiv) of RLi or $LiBR_4$ in solutions of dihydrido alkyl/aryl complexes **1-R** with poor solvation of Li causes a considerable increase in the difference of the hydride signals $\Delta\delta = \delta(H_A) - \delta(H_M)$ due to the formation of "lithium bonding" interactions[54b] with the nitrosyl oxygen, and not due to the presence of paramagnetic species. These intermolecular interactions are temperature-dependent, and formation of soluble RLi/LiOTf aggregates effects a greater increase in the $\Delta\delta$ parameter. Strong acceleration of the reductive elimination of RH results from such lithium bonding interactions, as detailed elsewhere. Analogous lithium bonding interactions with the X ligand of halide/pseudohalide complexes **1-X** lead to a similar increase in the $\Delta\delta$ value. (b) Scheiner, S. In *Lithium Chemistry: Theoretical and Experimental Overview*; Sapse, A.-M., Schleyer, P. v. R., Eds.; Wiley: New York, 1995; Chapter 3.

of the pure Me_3SiCH_2Li. These results clearly demonstrate that the ratio of **1-Me** to **1-CH_2SiMe_3** *decreases* with time (Figure 1), thus ruling out the intermediacy of the latter in the formation of the former.

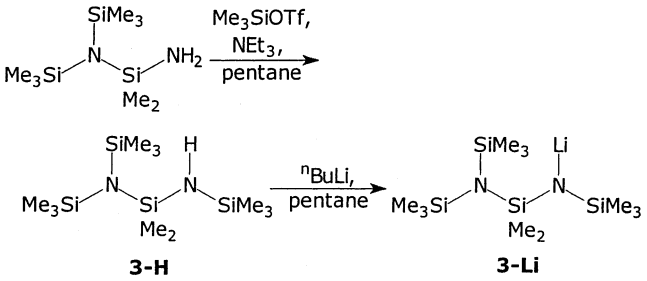
Therefore, these results rule out β-Me^- elimination from **1-CH_2SiMe_3** as a mechanism for formation of **1-Me** in the reaction of **1-OTf** with Me_3SiCH_2Li, which thus proceeds via direct β-Me^- transfer.

(c) Other RLi and BR_4^-. Despite the above conclusions, one can envision a β-R'^- elimination mechanism operating for the products of pathway B for the *other* reagents: $(Me_3Si)_2NLi$, $(Me_3Si)_2CHLi$, TMPLi, LDA, ^{t}BuLi, and $^iPr_3BMe^-$ (R = ^{i}Pr), since any such transient intermediates, not observed at 20 °C and even at −60 °C in the case of $(Me_3Si)_2NLi$, very likely would experience a considerable steric repulsion with P^iPr_3 ligands, thus encouraging their loss, or any other transformation considered above, to generate an unsaturated species necessary for the migration. However, such steric repulsion would also facilitate the reductive elimination of RH/R_2NH, as is clearly evident from the relative stability of **1-R** alkyls (Scheme 3). Since only a small amount of the products derived from **2** is observed, and only for TMPLi, the products of **B** likely never form for all of the other RLi and BR_4^- reagents (except possibly TMPLi). Therefore, we conclude that pathway A, followed with all reagents considered except NpLi and possibly TMPLi, is independent of pathway B and the β-R'^- transfer occurs in a direct fashion from RLi and BR_4^-.

IV. Fate of the Organic Products in Pathway A. The expected organic products were identified by ^{1}H NMR (not quantified) in the C_6D_6 reactions of **1-OTf** with ^{t}BuLi (isobutylene), ^{n}BuLi (1-butene), EtLi (ethylene), $LiBEt_4$ (ethylene and BEt_3 as the only volatile products), and $[Li(TMEDA)_2][^iPr_3BMe]$ (propylene; BR_3 not analyzed). When β-R'^- transfer leads to the formation of unsaturated silicon compounds (formally), silenes ($(Me_3Si)_2CHLi$, Me_3SiCH_2Li, and $[Li(THF)_4][B(CH_2SiMe_3)_4]$) and silanimine ($(Me_3Si)_2NLi$), and imines (TMPLi and LDA), the organic products of pathway A underwent subsequent transformations, described in detail below.

(a) Silanimines and Silenes. The C_6D_6 reactions of **1-OTf** with $(Me_3Si)_2NLi$ and Me_3SiCH_2Li produce highly complex mixtures of organic products, as evidenced by observation of numerous sharp signals in the (−0.5 to 0.8 ppm) (Si)Me region of ^{1}H NMR spectra, while several broad features are observed in that region in the case of $(Me_3Si)_2CHLi$. However, using 4 equiv of $(Me_3Si)_2NLi$ in a d_8-THF reaction with **1-THF^+** at −60 °C (conditions under which $(Me_3Si)_2NLi$ exists as a solvated monomer to a significant extent[55]) gave very different results. On the time scale of hours at −60 °C, this reaction produces the trisilazide **3-Li** (Scheme 4) in an equilibrium mixture with trisilazane **3-H**, $(Me_3Si)_2NLi$, and $(Me_3Si)_2NH$, due to hydrolysis by trace water, as essentially the only organic products (>90% total yield of **3-Li** + **3-H** by ^{1}H NMR integration vs **1-Me**) accompanying the quantitative formation of **1-Me**. The trisilazane derivatives were characterized by independent synthesis (Scheme 4), ^{1}H (**3-H**, **3-Li**) and ^{29}Si NMR (**3-H**), EI-MS

Scheme 4. Synthesis of 3-H and 3-Li



3-H **3-Li**

(**3-H**), and EA (**3-Li**).[56] The formation of **3-Li** in the above reaction likely proceeds via 1,2-addition of $(Me_3Si)_2N-Li$ to the transient $Me_3SiN{=}SiMe_2$, either as a true intermediate or not (i.e., β-Me^- transfer may occur concurrently with $(Me_3Si)_2N^-$ attack at the Si that donates Me^-). Silanimines are highly reactive species,[57−60] becoming isolable only with heavy substitution at both Si and N,[61] that undergo a variety of transformations,[57−59,62] such as adduct formation at Si, 1,2-addition and cycloaddition of a number of reagents, and oligomerization. Because 1,2-addition to a Si=N double bond is symmetry-forbidden, such reactions proceed via a polar mechanism,[57,59] in which a nucleophile (e.g., O in ROH) first attacks Si, followed by migration of an electrophile (H in ROH) to N. Although we are not aware of studies of 1,2-addition of lithium alkylamides to silanimines, such reactions are expected to be facile, considering the high nucleophilicity of N in R_2N-Li and the fact that the N−Li bond is easily ionizable, provided the addition of the R_2N^- nucleophile is not sterically prohibitive. In fact, Wiberg and co-workers have reported on analogous 1,2-addition of alkyllithium reagents to silanimines[63] and silenes.[64,65] This reasoning also suggests that **3-Li**, always observed in the −60 °C d_8-THF reaction above together with **3-H**, is not formed via 1,2-addition of $(Me_3Si)_2N-H$ to $Me_3SiN{=}SiMe_2$ and subsequent lithiation by $(Me_3Si)_2NLi$ but rather via 1,2-addition of $(Me_3Si)_2N-Li$, due to the lower nucleophilicity of $(Me_3Si)_2NH$ compared to that of $(Me_3Si)_2NLi$.

Notably, **3-Li** also exhibits β-Me^- transfer reactivity, quantitatively forming **1-Me** in a C_6D_6 reaction with

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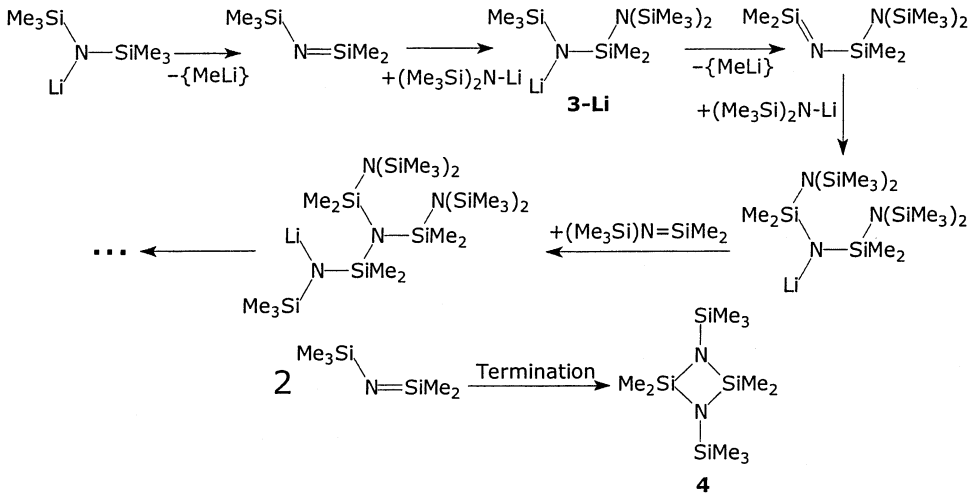
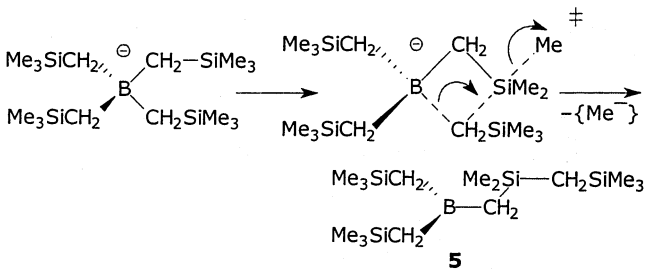
Scheme 5. Proposed Mechanism for Oligomerization of Silazanes in the Reaction of 1-OTf with $(Me_3Si)_2NLi$



1-OTf within 10 min at 20 °C, in addition to a mixture of organic products even more intractable than that obtained with $(Me_3Si)_2NLi$. In view of the above results it appears likely that the complex mixture of organic products formed in a 20 °C C_6D_6 reaction of $(Me_3Si)_2NLi$ with **1-OTf** is composed of branched oligo- and cyclosilazanes. The latter are produced in a cascade fashion via successive β-Me^- transfer from R_2NLi and 1,2-addition of R_2N-Li to putative $R_2Si{=}NR$ intermediates; cyclodimerization of these terminates the reaction sequence (Scheme 5). Although neither **3-Li** nor **3-H** is observed in the C_6D_6 reaction of **1-OTf** with $(Me_3Si)_2NLi$, 1,2-addition of R_2N-Li is likely to compete with dimerization of $R_2Si{=}NR$ in C_6D_6, at least at the initial stages of the reaction, since the presence of only a 4-fold excess of $(Me_3Si)_2NLi$ in a d_8-THF reaction with **1-THF**$^+$ at −60 °C already leads to a nearly quantitative yield of **3-Li**, which, in turn, reacts with **1-OTf** in C_6D_6 quantitatively via β-Me^- transfer. The reaction sequence proposed in Scheme 5 should yield branched products, i.e., containing $N(SiMe_2R)_3$ centers, that are not accessible via oligomerization of $Me_3SiN{=}SiMe_2$. It is also notable that ^1H NMR signals reported[66] for cyclodisilazane **4** (Scheme 5) were not observed in the reactions of **1-OTf** with either $(Me_3Si)_2NLi$ or **3-Li**, suggesting that **4** is at least not the major reaction product in either case. In contrast, the corresponding cyclodisilazane was the predominant product in an analogous type of reaction, formal transfer of β-H^- from lithium tetramethyldisilazide to organic electrophiles, investigated by Seyferth et al.[67]

In close analogy to silanimines, silenes are also highly reactive species, exhibiting similar reactivity.[57−59,68−69] Although $Me_3SiCH_2SiMe_2CH_2Li$, the analogue of **3-Li**, could not be clearly identified in the reaction of **1-OTf** with 15 equiv of Me_3SiCH_2Li in d_8-PhMe at −70 °C, 20 °C reactions of **1-OTf** with Me_3SiCH_2Li invariably gave small amounts of $(Me_3Si)_2CH_2$, the analogue of **3-H**, which suggests that a reaction sequence analogous to

Scheme 6. Proposed Mechanism for the Formation of 5



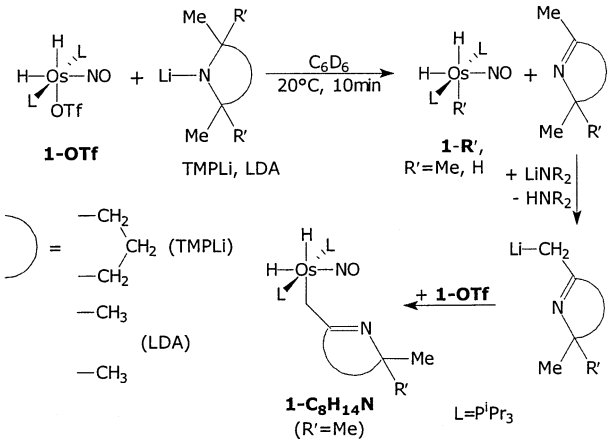
that outlined for $Me_3SiN{=}SiMe_2$ in Scheme 5 operates in the case of $H_2C{=}SiMe_2$ as well, and likely for $(Me_3Si)HC{=}SiMe_2$, the formal product of $(Me_3Si)_2CHLi$ in pathway A, also. Notably, all ^1H and ^{31}P NMR signals of **1-CH_2SiMe_3**, formed from **1-OTf** and Me_3SiCH_2Li, often overlapped a set of analogous, very closely situated signals, possibly corresponding to the product of reaction of **1-OTf** and $Me_3SiCH_2SiMe_2CH_2Li$ via pathway B: i.e., **1-$CH_2SiMe_2CH_2SiMe_3$**. The NMR signals of the latter were integrated up to 10% of the main product, **1-CH_2SiMe_3**, and both were always summed together in reporting the yield in Table 1 according to pathway B in the Me_3SiCH_2Li reactions.

In contrast to the complex mixtures of organic products obtained from the above RLi and R_2NLi reagents in the reactions with **1-OTf** in C_6D_6, β-Me^- transfer from $[Li(THF)_4][B(CH_2SiMe_3)_4]$ under analogous conditions gave the novel borane $(Me_3SiCH_2)_2B(CH_2SiMe_2CH_2SiMe_3)$ (**5**) together with $B(CH_2SiMe_3)_3$, the product of B, as essentially the only organic products. The formation of **5**, characterized by ^1H NMR[70] and EI-MS (M^+ at m/z 344), may proceed via β-Me^- transfer concurrent with attack of another alkyl group at the Si that donates Me^- (Scheme 6).[26] The reaction of **1-OTf** with a C_6D_6 solution containing Me_3SiCH_2Li and 1.6 equiv of $B(CH_2SiMe_3)_3$ (which do not react to an observable extent) gave no trace of **5**. While this result shows that reactivity of $[Li(THF)_4][B(CH_2SiMe_3)_4]$ via pathway A involves genuine borate rather than Me_3SiCH_2Li, it

(66) Wiberg, N.; Preiner, G.; Schieda, O. *Chem. Ber.* **1981**, *114*, 3518.
(67) Wiseman, G. H.; Wheeler, D. R.; Seyferth, D. *Organometallics* **1986**, *5*, 146.
(68) Wiberg, N.; Wagner, G. *Chem. Ber.* **1986**, *119*, 1467.
(69) Brook, A. G.; Baines, K. M. *Adv. Organomet. Chem.* **1986**, *25*, 1.

(70) A ^{11}B NMR spectrum recorded on a 89:11 mixture of **5** and $B(CH_2SiMe_3)_3$ in C_6D_6 showed a several ppm broad signal at 78.6 ppm, indistinguishable from that of pure $B(CH_2SiMe_3)_3$.

Scheme 7. Reactivity of Imines Formed in the Reactions of TMPLi and LDA with 1-OTf



does not rule out formation of free $H_2C{=}SiMe_2$ in the $B(CH_2SiMe_3)_4^-$ reaction, which subsequently reacts with $B(CH_2SiMe_3)_3$ via 1,2-addition of a B−C bond, because the silene may react much faster with Me_3SiCH_2Li. However, it is notable that the reaction of BEt_4^- via **A** does not follow the mechanism of Scheme 6, producing exclusively ethylene and BEt_3 instead.

(b) Imines. In contrast to the unsaturated silicon transients, which react via 1,2-addition as discussed above, the imines formed from TMPLi and LDA in pathway A undergo deprotonation of the α-CH_3 group and the resulting Li azaallyls react with remaining **1-OTf** via OTf^- metathesis, competing for **1-OTf** with the primary reaction pathways (Scheme 7).[71] Thus, as described earlier,[72] reaction of **1-OTf** with a C_6D_6 solution of TMPLi gives **1-C_8H_{14}N** in 33% yield, in addition to **1-Me** (50%), as well as products derived from **2** (13%) and **1-Cl** (2%) and **1-OH** (2%), which result from LiX impurities in TMPLi. While using a solution of 6 equiv of TMPLi does not significantly decrease the ratio **1-C_8H_{14}N**:**1-Me**, it can be increased essentially to the theoretical maximum of 50:50 if the steady-state concentration of TMPLi is limited by reacting **1-OTf** with large crystals of TMPLi instead of a homogeneous solution. Furthermore, the reaction of solid **1-OTf** and TMPLi with a C_6D_6 solution of 1.4 equiv of the corresponding imine, 1,2-dehydro-2,6,6-trimethylpiperidine, gives **1-C_8H_{14}N** in 90−95% yield, in addition to trace **1-H** and free L. Formation of **1-Me** is completely suppressed in this reaction, demonstrating that imine lithiation and subsequent OTf^- metathesis with **1-OTf** are both considerably faster than β-Me^- transfer from TMPLi.

The dihydride **1-C_8H_{14}N**, isolated in 69% yield from the reaction of **1-OTf** with TMPLi in the presence of the imine, and fully characterized[72] by NMR and X-ray diffraction, reductively eliminates 1,2-dehydro-2,6,6-trimethylpiperidine in C_6D_6 on the time scale of hours with a rate intermediate between that of **1-Me** and **1-Et**, in close analogy to the other **1-R** complexes. The crystal structure determination of **1-C_8H_{14}N** (Figure 2, Tables 3 and 4) revealed an octahedral geometry significantly

(71) Analogous subsequent transformations of these or closely related imines takes place with organic electrophiles.[16,27]

(72) Yandulov, D. V.; Huffman, J. C.; Caulton, K. G. *New J. Chem.* **2000**, *24*, 649.

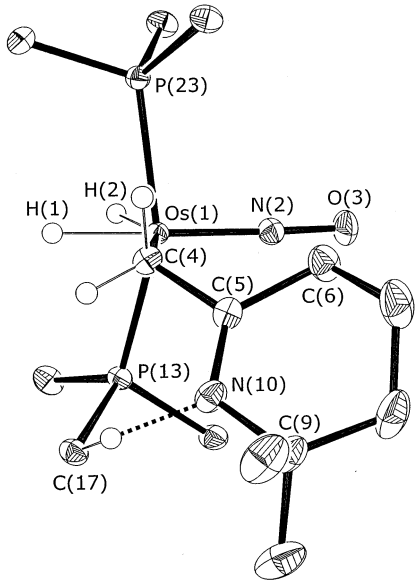


Figure 2. ORTEP representation of *cis,trans*-$Os(H)_2(C_8H_{14}N)(NO)(P^iPr_3)_2$ (**1-C_8H_{14}N**) with phosphine methyl groups and selected hydrogens omitted, showing the atom labeling and a N(10)···H−C(17) hydrogen bond. Thermal ellipsoids are drawn at the 50% probability level.

Table 3. Details of X-ray Structure Determinations of *cis,trans*-$Os(H)_2(C_8H_{14}N)(NO)(P^iPr_3)_2$ (1-C_8H_{14}N) and [*cis,trans*-$Os(H)_2((THF)(NO)(P^iPr_3)_2]$-$[B(C_6H_3\text{-}3,5\text{-}(CF_3)_2)_4]\cdot$THF (1-$THF^+$)

	1-C_8H_{14}N	1-THF^+
formula	$C_{26}H_{56}N_2OOsP_2$	$C_{58}H_{70}BF_{24}NO_3OsP_2$
fw	666.94	1550.16
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
color of cryst	pale yellow	yellow
a, Å	8.8330(2)	15.183(2)
b, Å	11.5202(3)	17.785(2)
c, Å	16.0550(4)	24.578(4)
α, deg	103.704(1)	
β, deg	99.448(1)	97.41(1)
γ, deg	98.890(1)	
T, °C	−160	−160
Z	2	4
$R(F_o)^a$	0.0159	0.0627
$R_w(F_o)^b$	0.0134	0.0487
GOF for the last cycle	0.549	1.082
max Δ/*σ* for last cycle	0.002	0.03

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, where $w = 1/\sigma^2(|F_o|)$.

distorted by compression of the *cis*-C−Os−H and *cis*-H−Os−H angles to 80.7(8) and 72.9(11)°, respectively, most reliably identified by the increase in the *cis*-C−Os−N angle from 90 to 104.15(7)°. This type of distortion, which allows the ligands with strong trans influence, hydride and alkyl, to avoid being perfectly trans to any other ligand in the molecule, has been identified previously[34] in the structures of *mer,trans*-$M(H)_3(NO)L_2$ (M = Ru, Os, L = PR_3) and **1-Cl** and rationalized on the grounds of strengthening M−H *σ*-bonds at the expense of increased M→NO *π*-back-bonding. The distortion in **1-C_8H_{14}N** explains the conformation of the $C_8H_{14}N$ ligand around the Os(1)−C(4) bond, in which the C_5N ring is oriented away from the smaller H(1) and toward the bulkier NO ligand (dihedral ∠N(2)−Os(1)−C(4)−C(5) = 26.5°) and also takes place for the

Table 4. Selected Interatomic Distances (Å) and Angles (deg) for *cis,trans*-Os(H)$_2$(C$_8$H$_{14}$N)(NO)(P^{i}Pr$_3$)$_2$ (1-C$_8$H$_{14}$N)

Os(1)−P(13)	2.3673(5)	Os(1)−P(23)	2.3706(5)
Os(1)−N(2)	1.7748(16)	Os(1)−C(4)	2.2396(19)
Os(1)−H(1)	1.599(22)	Os(1)−H(2)	1.668(25)
N(2)−O(3)	1.1940(20)	N(10)−C(5)	1.2804(25)
N(10)−C(9)	1.4840(26)	N(10)···C(17)	3.368(3)
P(13)−Os(1)−N(2)	101.98(5)	P(23)−Os(1)−N(2)	97.73(5)
P(13)−Os(1)−C(4)	92.57(5)	P(23)−Os(1)−C(4)	92.46(5)
P(13)−Os(1)−H(1)	77.6(8)	P(23)−Os(1)−H(1)	81.9(8)
P(13)−Os(1)−H(2)	83.2(9)	P(23)−Os(1)−H(2)	82.7(9)
P(13)−Os(1)−P(23)	157.782(17)	H(1)−Os(1)−H(2)	72.9(11)
Os(1)−N(2)−O(3)	177.15(15)	Os(1)−C(4)−C(5)	118.25(13)
C(4)−Os(1)−H(1)	80.7(8)	C(4)−Os(1)−H(2)	153.5(9)
N(2)−Os(1)−H(1)	175.2(8)	N(2)−Os(1)−H(2)	102.3(9)
N(2)−Os(1)−C(4)	104.15(7)	C(5)−N(10)−C(9)	121.53(18)
N(10)−C(5)−C(4)	118.93(18)	N(10)−C(5)−C(6)	124.53(18)

phosphines,[34] such that *cis*-P−Os−N angles, 101.98(5) and 97.73(5)°, are considerably greater than 90°. All hydrogens of the C$_5$N ring were located, and the C=N double bond was unambiguously identified as N(10)−C(5) (1.2804(25) Å, as compared to the single N(10)−C(9) bond of 1.4840(26) Å). Notably, the imine nitrogen points toward a phosphine methine C−H bond, possibly forming a weak hydrogen bond (N(10)···C(17) = 3.368(3) Å) that may lock the alkyl group in this position, preventing a disorder.

The imine released via pathway A of the **1-OTf** reaction with a C$_6$D$_6$ solution of LiN^{i}Pr$_2$ (LDA) underwent subsequent transformation analogous to that found in the case of TMPLi. Two products were observed in the case of LDA, in unequal ratio: the minor product with −7.21 and −8.35 ppm hydride signals, essentially identical with those of **1-C$_8$H$_{14}$N** (−7.23 and −8.37), and the major product with hydride signals at −6.86 and −8.24 ppm, both with similar ^{31}P chemical shifts of 30.0 (30.1 for **1-C$_8$H$_{14}$N**) and 28.3 ppm, respectively. On the basis of the similarity of the spectroscopic data of the dihydrides formed in the LDA reaction and those of **1-C$_8$H$_{14}$N**, the former species likely correspond to the isomers of *cis,trans*-Os(H)$_2$(CH$_2$C(Me)=N^{i}Pr)(NO)L$_2$, with *cis* and *trans* configurations around the C=N double bond. Indeed, subjecting the reaction mixture to a 60 °C thermolysis for 14 h quantitatively transformed both compounds into **1-Ph-*d*,*d*$_5$** isomers via the intermediacy of **2**,[33] while ^{1}H NMR analysis of the volatile components revealed the presence of only HN^{i}Pr$_2$, ^{i}PrN=CMe$_2$, and trace P^{i}Pr$_3$. In contrast to the TMPLi reaction, the metalated derivatives of ^{i}PrN=CMe$_2$ were formed in only 4% yield, comprising all of the observed products together with the product of A, **1-H** (96%). The decreased yield of the metalated imine products formed with LDA relative to that formed with TMPLi is consistent with β-H$^-$ transfer being inherently faster than β-Me$^-$ transfer, as determined from the strong kinetic preference for the former in the LDA reaction (Table 1). In analogy to TMPLi, the yield of metalated imines also increases, up to 20%, if large crystals of LDA are used in the reaction with **1-OTf** instead of a homogeneous solution.

V. Mechanistic Insights. (a) Influence of the Os Leaving Group. The rates of **A** and **B** in the reactions of **1-X** with organolithium bases and borates strongly depend on the nature of X *and* the electrophilicity of Li. A series of **1-X** complexes with X = **Cl**, **F**, **OTf**, **THF**$^+$ (BAr′$_4^-$) and no ligand (BAr′$_4^-$) were used to evaluate their reactivity toward X-ligand substitution with selected reagents in various solvents (the qualitative rate dependence is shown in Table 5). Aside from the product distribution, all of these reactions led to products (via A and B) identical with those discussed for **1-OTf** above.

The primary precursor to all of the **1-Y** complexes, the chloride **1-Cl**, is very inert toward organolithium reagents in general. Reactions with MeLi, ^{n}BuLi, and ^{t}BuLi in C$_6$D$_6$ or C$_6$D$_{12}$ proceed slowly, on the time scale of hours at 20 °C, producing considerable amounts of free L in addition to the **1-R** products formed in the corresponding **1-OTf** reactions (Table 1), while (Me$_3$Si)$_2$NLi·OEt$_2$ shows no reaction after 18 h (entry 1). The formation of substantial amounts of free L in these reactions is suggestive of a competitive operation of a single-electron-transfer mechanism, although it could also implicate the deprotonation mechanism C. The unsolvated lithium borates (entries 2 and 4) are among the few reagents that afford clean conversion of **1-Cl** on reasonable time scales.

The fluoride derivative **1-F** is substantially more reactive than **1-Cl**, affording **1-Me** in a C$_6$D$_6$ reaction with (Me$_3$Si)$_2$NLi·OEt$_2$ on the time scale of minutes (entries 1 and 5). The fluoride complex, generated in situ from **1-OTf** and [Bu$_4$N][Ph$_3$SiF$_2$], is unstable toward H$_2$ loss, producing OsF(NO)L$_2$ in solution on the time scale of hours, which, together with H$_2$, exists in a kinetically slow equilibrium with **1-F**, such that both Os complexes are observed in a constant ratio after prolonged periods of time in a closed system, and this ratio can be reversibly perturbed by raising the temperature to 90 °C.[33] This inherent reactivity of **1-F** leads to the formation of a trace amount of **1-H** in the entry 5 reaction and illustrates *one of the pathways* **1-H** is formed in the reactions generating **2**. Adventitious water or trace methanol of crystallization may afford the corresponding **1-OR** species by oxidative addition, which, in close analogy to **1-F**, slowly lose H$_2$ (as established for **1-OH**[33]) scavenged by the remaining **2** to give comparable amounts of **1-H** and Os(OR)(NO)L$_2$. The latter is not always observed by ^{31}P NMR, indicating that hydride ligand scavenging is also operative in the formation of **1-H**.[73]

The triflate derivative **1-OTf** reacts with all reagents listed in Tables 1 and 2 in C$_6$D$_6$ essentially instantaneously at 20 °C. The reaction with (Me$_3$Si)$_2$NLi·OEt$_2$ is also instantaneous in alkanes, Et$_2$O, and neat (Me$_3$Si)$_2$NH (entry 6) but proceeds slowly in d_8-THF, requiring over 2 h for full conversion. This allows us to compare the reactivity of **1-OTf** and **1-THF**$^+$, and the latter reacts instantly at 20 °C, thus demonstrating that OTf$^-$ inhibits the β-Me$^-$ transfer. Using the least reactive reagent, B(CH$_2$SiMe$_3$)$_4^-$, allows evaluation of the influence of the coordinated THF in **1-THF**$^+$, and entries 11 and 12 show that THF suppresses the reactivity of **1**$^+$, the most reactive form of osmium species abstracting β-Me$^-$. The reaction in entry 12

(73) Dehydrogenation of an ^{i}Pr group of P^{i}Pr$_3$ via β-hydride elimination from the metalated **1-P∼C** intermediate as a route to **1-H** is inconsistent with the ^{31}P chemical shift being essentially identical with that of the authentic **1-H**; additionally, **1-H** is often formed in the analogous reactions with L = P^{t}Bu$_2$Me, also with a ^{31}P chemical shift identical with that of the authentic trihydride, in which case β-hydride elimination from the metalated species is not possible.

Table 5. Qualitative Dependence of the X-Substitution Rates in 1-X by Selected RLi, R_2NLi, and $Q^+BR_4^-$ on the Nature of X and Solvent at RT

entry	X	RLi/R_2NLi/$Q^+BR_4^-$	solvent	time	conversn, %
1	Cl	Me_3SiCH_2Li; $(Me_3Si)_2NLi{\cdot}OEt_2$	C_6D_{12}	15 min; 18 h	0
2	Cl	$LiBMe_4$	C_6D_6	20 min	73
3	Cl	$LiBMe_4$	Et_2O	15 min	0
4	Cl	$LiBEt_4$	C_6D_6	35 min; 2 h	25; 41
5	F	$(Me_3Si)_2NLi{\cdot}OEt_2$	C_6D_6	10 min; 1 h	10; 71
6	OTf	$(Me_3Si)_2NLi{\cdot}OEt_2$	Et_2O, C_6D_6, C_6D_{12}, $(Me_3Si)_2NH$	10 min	100
7	OTf	$[Bu_4N][B(CH_2SiMe_3)_4]$	C_6D_6	10 min; 2 h	38; 77
8	OTf	$[Li(THF)_4][B(CH_2SiMe_3)_4]$	C_6D_6	10 min	100
9	OTf	$(Me_3Si)_2NLi{\cdot}OEt_2$	d_8-THF	15 min	73
10	THF^+	$(Me_3Si)_2NLi{\cdot}OEt_2$	d_8-THF	10 min	100
11	THF^+	$[Li(THF)_4][B(CH_2SiMe_3)_4]$	d_8-THF	10 min	14
12	THF^+	$[Bu_4N][B(CH_2SiMe_3)_4]$	d_8-PhMe/PhF	10 min	100

proceeds via A (63%) and B (37%), similar to that of $[Li(THF)_4][B(CH_2SiMe_3)_4]$ with **1-OTf** in C_6D_6 (Table 2).

The highly electrophilic *five-coordinate* [*cis*,*trans*-$Os(H)_2(NO)L_2][B(C_6H_3\text{-}3,5\text{-}(CF_3)_2)_4]$ ($\mathbf{1}^+(BAr'_4{}^-)$), originally prepared in PhF from **1-BF$_4$** and $NaBAr'_4$,[74] can be conveniently generated via hydride abstraction from **1-H** by $[Ph_3C][BAr'_4]$.[34] While $\mathbf{1}^+$ invariably forms oils, largely precluding its isolation, the THF adduct **1-THF**$^+$ is crystalline and was isolated in 81% yield. The X-ray structure determination of **1-THF**$^+$ (Table 3; Figure S2, Supporting Information) revealed the presence of a *coordinated* THF molecule; however, extensive disorder precluded meaningful analysis of geometric parameters. A second THF molecule is present in the lattice but is not involved in hydrogen bonding to the hydride ligands (not located), as the closest lattice THF oxygen is 7.13 Å from Os and THF is pointing away from the metal, toward $BAr'_4{}^-$ aromatic hydrogens. The absence of hydrogen-bonding interactions is consistent with low acidity of the hydrides in **1-THF**$^+$. The coordinated THF is labile, and a single, exchange-averaged set of THF resonances is observed by ^{1}H NMR in CD_2Cl_2 solution at 20 °C for the total of 1.9 equiv of THF (the lattice THF was partly lost under vacuum), while the H_M hydride signal is sharp (H_A is obscured by (PC)Me resonances). However, THF coordination is preferred to that of CD_2Cl_2, as hydride signals of **1-CD_2Cl_2**$^+$-$(BAr'_4{}^-)$[74] are strongly exchange-broadened at 20 °C. The weak coordination of THF allows for a significant population of the five-coordinate form in a 50:50 solvent mixture of d_8-PhMe and PhF (Table 5, entry 12), as opposed to THF solvent (Table 5, entry 11), which determines the substantial difference in reactivity toward $B(CH_2SiMe_3)_4^-$ between the two cases.

The above results, summarized in Scheme 8, show a clear trend in that X-substitution reactivity of **1-X** follows the leaving group ability of X, with the exception of F (rationalized below). Therefore, loss of X^- from **1-X** is a crucial step in the mechanisms of both **A** and **B**, consistent with the five-coordinate cation $\mathbf{1}^+$ exhibiting the highest reactivity. Additionally, this leaving-group dependence explains the marked difference in product yields in the reaction of **1-OTf** with Me_3SiCH_2Li in d_8-THF, which proceeds with over 90% preference via C at −40 °C, but gives 60% yield of A and B products at 20 °C: the accessibility of $\mathbf{1}^+$ via dissociation of OTf^- increases with temperature, making pathways A and B operative.

Scheme 8. Relative Order of the Reactivity of 1-X by X Substitution

$$X = Cl < F < OTf < THF^+ (BAr'_4{}^-) < - (BAr'_4{}^-)$$

(b) The Role of Lithium. In addition to the X-ligand dependence, the rates of X^- substitution are strongly influenced by the extent of solvation of Li. Entries 7 and 8 in Table 5 show that $Li(THF)_4^+$ imparts higher reactivity to $B(CH_2SiMe_3)_4^-$ than does Bu_4N^+, while entries 6 and 9 reveal strong suppression of the rate of reaction with $(Me_3Si)_2NLi{\cdot}OEt_2$ by THF. Analogous suppression of the rate by solvation of Li is evident in the $LiBEt_4$ reactions in entries 3 and 4. Overall, the unsolvated lithium borates are much more reactive toward **1-Cl** than any RLi or R_2NLi compound studied, consistent with the minimal stabilization of Li^+ possible in $LiBR_4$ via interactions with the C−H bonds.[39,75] These results demonstrate the electrophilic role that lithium plays in assisting the loss of the X^- in the reactions with **1-X** studied here. Thus, the higher reactivity of **1-F** (vs **1-Cl**) is caused by the stronger Li···X interaction with the harder Lewis base, F.

(c) Lithium Bonding Interactions with X(Os). While no strong evidence for intermediates in pathways A and B have been obtained, monitoring slow reactions of organolithium reagents with several **1-X** compounds by ^{1}H NMR revealed lithium bonding interactions with the X ligand. Remarkably similar to the lithium bonding interactions with NO oxygen[54] in their effect on the hydride chemical shifts, the interactions with the X ligand also cause a substantial increase in the $\Delta\delta$ parameter ($\delta(H_A) - \delta(H_M)$), by effectively reducing the trans influence of X. Thus, the $\Delta\delta$ value of **1-Cl** was found to be 0.62 ppm greater than normal during the reaction with $LiBMe_4$ (Table 5, entry 2), while in the case of $LiBEt_4$, this increase was 1.13 ppm at 25% conversion and decreased to 0.90 ppm at 41% conversion, due to the consumption of $LiBEt_4$ and precipitation of LiCl. In the case of **1-F** (entry 5), the increase in $\Delta\delta$ amounted to 0.55 ppm after 10 min and also decreased to 0.15 ppm at 71% conversion. In neither case were the $\Delta\delta$ values of the **1-R** products significantly affected, thus ruling out interactions with NO oxygen for **1-X**. The latter can be expected to be more pronounced for **1-R** than for **1-X**, since ν(N−O) of **1-Me** is 26 cm^{-1} lower than that of **1-Cl**, for example. Although the trans J_{F-H} coupling in **1-F** of 69.3 Hz was not significantly affected

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(75) Rhine, W. E.; Stucky, G.; Peterson, S. W. *J. Am. Chem. Soc.* **1975**, *97*, 6401. Clegg, W.; Lamb, E.; Liddle, S. T.; Snaith, R. *J. Organomet. Chem.* **1999**, *573*, 305.

by the presence of $(Me_3Si)_2NLi{\cdot}OEt_2$, the hydride signals were strongly broadened, concealing J_{P-H} and J_{H-H} couplings. Similar broadening, concealing all couplings and consistent with reversible formation of a lithium-bonded adduct, was always observed in the low-temperature (≤−40 °C) reactions of **1-OTf** in d_8-PhMe with $(Me_3Si)_2NLi{\cdot}OEt_2$, NpLi, Me_3SiCH_2Li, and Me_3SiCH_2Li (15 equiv) in the presence of TMEDA (20 equiv), but not with Me_3SiCH_2Li in d_8-THF at −80 °C, consistent with solvation of Li precluding such interactions in the latter case. While the fact that the hydride signals of **1-OTf** are sufficiently sharp to resolve all couplings in d_8-THF at −80 °C rules out hindered rotation of the phosphines[76] as the cause of the line broadening, the hydride signals of **1-R** complexes, comparable in size to **1-OTf**, were not broadened under identical conditions, thus ruling out typical T_2 broadening. Finally, an IR spectrum of **1-Cl** in heptane in the presence of 1 equiv of $(Me_3Si)_2NLi$ showed a new ν(N−O) band, blue-shifted by 20 cm^{-1}, which, fully consistent with lithium bonding to Cl reducing the back-bonding to NO, rules out an interaction with NO oxygen; the latter causes a 60 cm^{-1} red shift in the case of **1-R** complexes,[33] in close analogy to the effect of hydrogen bonding[77,78] and to formation of a number of other Lewis acid adducts.[52] The $\Delta\delta$ value of **1-Cl** is increased by 0.79 ppm in C_6D_6 in the presence of 2 equiv of $(Me_3Si)_2NLi$. No low-frequency ν(N−O) band was found for **1-Cl** in the presence of 1 equiv of $(Me_3Si)_2NLi$, which indicates that lithium bonding to the Cl is stronger than that to the NO oxygen.

(d) Possible Mechanisms of Substitution of X. The Li···X interactions are crucial to the thermodynamic driving force for β-Me^- transfer *from organolithium* reagents. An attempt to deprive the reactants of reasonable nucleophiles, in the reaction of $\mathbf{1}^+$ with $(Me_3Si)_2NLi$ in a 50:50 solvent mixture of d_8-PhMe and PhF at 20 °C, resulted in a slow reaction proceeding on a time scale of minutes (cf. entries 6 and 10) to yield none of the products representative of either β-Me^- transfer or deprotonation of $\mathbf{1}^+$. No **1-Me**, no **1-P∼C**, no products of oxidative addition of aromatic solvent C−H bonds, and no free L were observed. Thus, sequestering Li^+ with nucleophiles is integral to pathway A being kinetically facile, while entries 9 and 10 of Table 6 show that solvent THF is as efficient as a coordinating X^-. Overall, these results implicate the loss of *nucleophile-stabilized* Li^+ as an important mechanistic feature of A, obviously not essential to the reaction of $[Bu_4N][B(CH_2SiMe_3)_4]$ (entry 12), and reveal that the facility with which β-Me^- transfer from organolithium reagents to **1-OTf** occurs stems from the combination of good leaving-group properties of OTf^- and large interaction energy between the hard Li^+ and OTf^-.

The results described in parts a−d of section V show that reactions of **1-X** (X = F, Cl, OTf) with organolithium reagents in noncoordinating solvents begin with formation of a lithium bond to the X ligand and the subsequent abstraction of X^- by Li^+ is involved in the rate-determining step. These observations are consistent with (a) an associative mechanism, in which a nucleophile (R or β-R′ of Scheme 2) coordinates to Os with concomitant bending of NO,[79] (b) an interchange mechanism, with the seven-coordinate intermediate of (a) being a transition state, which additionally may or may not require NO bending, or (c) a dissociative mechanism, in which X^- first migrates onto Li to generate the five-coordinate $\mathbf{1}^+$ and the resulting ion pair collapses via either A or B and loss of LiX. These mechanisms do not specify the sequence of R/β-R′ transfer and loss of free LiX. In the absence of direct observation of either (a) or (c) intermediates neither mechanism can be ruled out. However, (c) appears to be most likely, since the reactions that do not involve abstraction of X^- by Li^+ (entries 12 and 11), or at least not to the extent possible in noncoordinating solvents (entries 10 and 9), clearly proceed via a dissociative mechanism, analogous to (c) except for the formation of solid LiX, because excess X^- (OTf^- or THF, respectively) suppresses the rate.

Table 6. Dependence of Yields via A vs B on the Extent of Solvation of Li in the Reactions of 1-OTf with $Q^+BR_4^-$ and Me_3SiCH_2Li[a]

			yield, %	
entry	$Q^+BR_4^-$/RLi	solvent	pathway A	pathway B
1	$LiBEt_4$	C_6D_6	23	77
2	$LiBEt_4$	THF	10	90
3	$LiBEt_4$	d_4-MeOH	11	89
4	$[Li(THF)_4][B(CH_2SiMe_3)]$	C_6D_6	59	41
5[b,c]	$[Li(THF)_4][B(CH_2SiMe_3)]$	d_8-THF	24	76
6[d]	15 Me_3SiCH_2Li	d_8-PhMe (−70 °C)	46	54
7[c,e]	15 Me_3SiCH_2Li + 20 TMEDA	d_8-PhMe (−60 °C)	5	73
8	2 Me_3SiCH_2Li + 20 TMEDA	C_6D_6	46	54
9	Me_3SiCH_2Li	C_6D_{12}	45	55
10[c,f]	3 Me_3SiCH_2Li	d_8-THF	60	40
11[c,f]	Me_3SiCH_2Li	Et_2O	80	20

[a] Unless otherwise indicated, all reactions were carried out at 20 °C with a slight excess of $Q^+BR_4^-$/RLi, and yields were determined by ^1H or ^{31}P NMR integration within 10−15 min with quantitative conversion of **1-OTf** into the products of pathways A and B. [b] 18% conversion after 15 min. [c] **1-Me** and **1-CH_2SiMe_3** are major products. [d] 100% conversion after 7 h. [e] 100% conversion after 4 h. [f] Me_3SiCH_2Li dissolved 30 s prior to the addition of **1-OTf**.

(e) Viability of the SET Mechanism. An important mechanistic possibility within either of the above mechanisms involves a single-electron transfer to Os, followed by R•/β-R′• abstraction, as opposed to transfer of the anionic fragments. Kochi and co-workers have thoroughly examined the reactivity of BR_4^- with organic[20] and organometallic[21] electrophiles, demonstrating the viability of both SET and nucleophilic mechanisms. The selectivity of R group transfer from mixed $R'BR''_3^-$ borates was diagnostic of the specific pathway followed.[20] A more substituted R group is transferred preferentially in a SET mechanism due to both the weaker B−C bond and the greater stability of the R• radical, both of which correlate with the C−H bond strength in the corresponding RH;[23,80] a less substituted,

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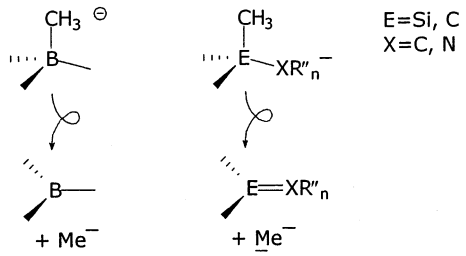
Scheme 9. Relationship among R⁻, R_2N^-, and BR_4^-



more accessible fragment is predominantly transferred via a nucleophilic attack at the substrate.

The reactivity of the mixed $[Li(TMEDA)_2][^iPr_3BMe]$ borate (Table 2) clearly shows that, at least with the borate reagents, pathway B does not involve single-electron transfer, since the Me group is transferred exclusively.[81] The more substituted ^{i}Pr group is not transferred to an observable extent, and **1-H** is formed via direct β-H^- transfer from the (B)^{i}Pr group. However, even if all of the observed **1-H** were produced via β-H elimination from the unobserved product of $^iPr^-$ transfer, the yield of the Me^- transfer product would still be greater, as the former would have been formed with 3-fold statistical preference.

The trihydride **1-H** undergoes instantaneous electron-transfer reduction by $[Li(TMEDA)_2][naphthalene]^\bullet$ in C_6D_6, resulting in the formation of free L and development of a brown, from pale yellow, color. No other new species are detected by either ^{1}H or ^{31}P NMR, except for, perhaps, a very broad background in the (PC)Me region. Notably, reactions of **1-Cl** with several RLi gave very similar results, in that partial conversion into the corresponding **1-R** products was invariably accompanied by formation of substantial amounts of free L and development of a brown color. Therefore, it is possible that the SET pathway is operative with **1-Cl**, because the substitution of Cl is the slowest; i.e., the reactivity pathways available to **1-OTf** are strongly inhibited, but they do not necessarily lead to formation of **1-R** but, rather, to decomposition. All other combinations of **1-X** and RLi/R_2NLi did not give any strong evidence for the involvement of SET, as, for example, **1-H** formed in C_6D_6, C_6D_{12}, or d_8-THF as a result of decomposition (section I) was typically free of partially deuterated isotopomers, easily distinguishable by ^{1}H NMR.[34]

(f) Proposed Intimate Mechanism of the β-Me^- Transfer. The carbanionic fragments of RLi and R_2-NLi containing β-Me^- are closely related to methyltrialkylborates in that both are adducts of unsaturated compounds (olefins or imines and boranes) with Me^- (Scheme 9). Such borates, most commonly exemplified by $MeB(C_6F_5)_3^-$, are well-known to interact with electrophilic transition-metal centers via the bridging methyl group.[82] The structures of such charge-assisted adducts may be considered as snapshots along the Me^- transfer pathway, from B to M, proceeding with inversion of the methyl group in an S_E2 mechanism.[83] While in the case of $MeBR_3^-$ the methyl group bears a portion of the delocalized negative overall charge and is therefore nucleophilic, in the carbanionic fragments of RLi and R_2NLi the negative charge is largely localized at the lithiated center and only a small fraction of it is delocalized over to the β-substituents, through mesomeric forms. Nevertheless, this similarity suggests that analogous S_E2 with Me^- inversion may be the intimate mechanism of C−Si and C−C bond cleavage in the reactions of **1-X** with RLi and R_2NLi.

The DFT calculations (B3LYP/LANL2DZ) on the simplified models $[Os(H)_2(NO)(PH_3)_2][Me_3ECH_n]$ (E = C, Si, n = 2; E = B, n = 3) show that the Me^- transfer from free anions via backside electrophilic attack by Os is facile (Figure 3). Analogous to the structurally characterized $MeBR_3^-$ adducts, charge-assisted agostic minima were located for $Me_3ECH_2^-$ (E = Si, C), bound primarily through a CH_3 hydrogen. The activation energies (with ZPE) for the β-Me^- transfer with inversion relative to these agostic structures are only 7.7 (C) and 3.2 (Si) kcal/mol, which correlate with the E−CH_3 bond strengths[84] and approach the inversion barrier of free CH_3^- of 2.1 kcal/mol calculated at the same level. Neither the agostic adduct nor the transition state for the Me^- transfer could be located for BMe_4^-; the PES for the $[Os(H)_2(NO)(PH_3)_2][Me_3BCH_3]$ system is very flat in the region of B−C and Os−C distances estimated from the $Me_3ECH_2^-$ results, which indicates that, if the agostic minimum exists at the current level, the activation energy relative to it is below 2 kcal/mol. Although a transition state for β-Me^- transfer with retention of configuration, known to be relevant for relatively small electrophiles,[85] has not been located, such a mechanism is highly unlikely here in view of the limited steric accessibility of Os in $[Os(H)_2(NO)(P^iPr_3)_2]^+$.

Thermodynamically, for the reaction of $[Os(H)_2(NO)(PH_3)_2]^+$ with $Me_3ECH_2^-$, pathway B, giving $Os(H)_2(CH_2EMe_3)(NO)(PH_3)_2$, is favored over A, giving $Os(H)_2(CH_3)(NO)(PH_3)_2$ and $Me_2E{=}CH_2$, for both E = Si (by 43.7 kcal/mol) and E = C (by 7.2 kcal/mol). The large difference in thermodynamics of A and B between Si and C stems from the weakness of the Si=C double bond.[84,86] The value calculated for Si, although likely to be reduced in the experimental system due to subsequent 1,2-addition of Me_3SiCH_2Li, is sufficiently

(81) All attempts to prepare $MeB^nBu_3^-$ or $MeBEt_3^-$ via reactions of BR_3 with MeLi invariably gave considerable amounts of the other four $Me_nBR_{4-n}^-$ isomers, in contrast to B^iPr_3, as determined by observation of closely situated (B)CH_3 resonances in ^{1}H NMR spectra. Using such mixtures gave very similar results in that only small amounts of **1-H** and **1-^{n}Bu** accompanied the formation of **1-Me** in the C_6D_6 reaction with **1-OTf**.

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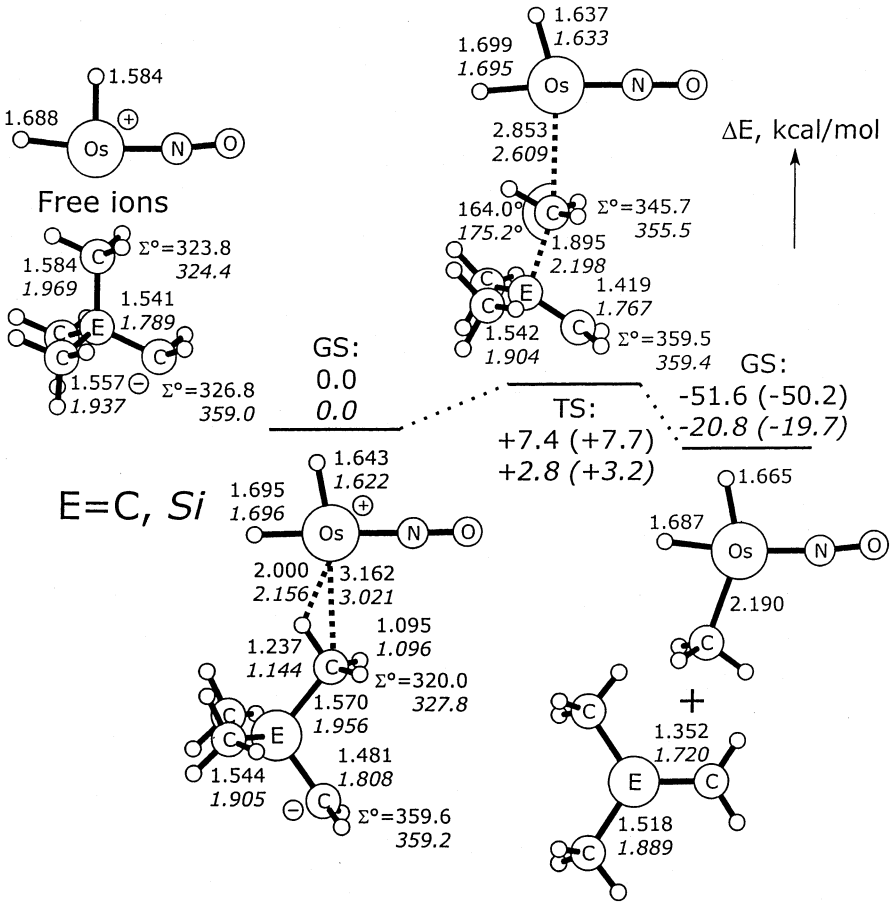

Figure 3. Selected geometrical parameters (Å, deg) and relative electronic energies (kcal/mol; corrected with ZPE in parentheses) of the structures involved in the intermolecular Me^- transfer from $Me_3ECH_2^-$ (E = C, *Si*) to $Os(H)_2(NO)(PH_3)_2^+$, as computed at the B3LYP/LANL2DZ level. *trans*-PH_3 groups were omitted for clarity. $\Sigma°$ denotes the sum of angles around the carbon of the transferred CH_3 and around ECH_2^-.

large to indicate that β-Me^- transfer from Me_3SiCH_2Li occurs under kinetic control. Conversely, pathway B appears to be kinetically favored over A for NpLi, as the yield via B increases from Me_3SiCH_2Li to NpLi (Table 1) despite decreasing thermodynamic preference and consistent with the calculated higher activation energy for the β-Me^- transfer from C than from Si. Thus, inhibiting pathway B sterically, in the case of TMPLi, results in the predominant operation of A with C−C bond cleavage (Table 1).

The model systems in Figure 3 closely represent the experiment only for BMe_4^- but are oversimplified in the case of $Me_3ECH_2^-$, as the loss of solvated Li^+ from C may occur concomitantly with or following the β-Me^- transfer and is not modeled here. Therefore, these model studies are not intended to represent the actual mechanism of A with RLi and R_2NLi but, rather, to demonstrate that a backside electrophilic attack at the β-Me group by Os is a viable intimate mechanism of Si−Me and C−Me bond cleavage established experimentally. The use of such model systems for the pathway B of BR_4^- reagents is justified by the rate-suppression data, which demonstrate the involvement of the five-coordinate $\mathbf{1}^+$, and the S_E2 mechanism with inversion is corroborated by calculations. A detailed description of the sequence of Os−X, Li−XR''_n (Scheme 2), and (Si,C)−CH_3 bond cleavage events in the reactions of **1-X** with RLi and R_2NLi, while certainly integral to the mechanism, is beyond the scope of this study.

(g) Influence of Solvation of Li on the Distribution of Products via A vs B. Tight ion pairing of the borate reagents enhances the β-R'^- transfer relative to the R^- transfer to **1-OTf** in the reactions with $LiBEt_4$ (Table 6, entries 1−3), and a similar effect is seen for $[Li(THF)_4][B(CH_2SiMe_3)_4]$ (entries 4 and 5). This is consistent with the presence of the cation in a tight ion pair inhibiting the access of the Os electrophile to the B−C bonds. An analogous effect of aggregation on the product distribution is observed for Me_3SiCH_2Li, such that pathway B is accelerated when the nucleophilic CH_2Li site is more accessible, in lesser-aggregated structures. Thus, while reaction of **1-OTf** with 15 equiv of Me_3SiCH_2Li in d_8-PhMe at −70 °C gives a 46:54 ratio of A and B at complete conversion (entry 6), similar to that obtained with a slight excess of RLi in C_6D_6 at 20 °C (Table 1), the analogous low-temperature reaction in the presence of an additional 20 equiv of TMEDA (entry 7) proceeds via B in an overwhelming preference to A. The highly disaggregated form of Me_3SiCH_2Li in fact reacts exclusively via C at low temperatures in d_8-THF, and this reactivity preference is reflected in the formation of 22% of **2-$CH_2SiMe_3^-$** in the low-temperature reaction in d_8-PhMe in the presence of TMEDA. A similar effect on the product distribution can be inferred from the acceleration of pathway B by the formation of LiOTf (Figure 1) in the −70 °C reaction of base-free Me_3SiCH_2Li: the nucleophilic CH_2Li site may be more sterically accessible in the mixed aggregates[87] of Me_3-

$SiCH_2Li$ and LiOTf, which would facilitate the access of the Os electrophile.

Discussion

(a) Reasons for the Unusual Reactivity of 1^+. The organolithium reagents studied here have been used for several decades in a variety of settings, and yet little to no evidence has been reported for the β-Me^- transfer reactivity, the exclusive reaction pathway of **1-OTf** with $(Me_3Si)_2NLi$ and $(Me_3Si)_2CHLi$ in nonpolar solvents. Why?

The dihydride $Os(H)_2(NO)(P^iPr_3)_2^+$ is a highly unsaturated complex. The high electrophilicity of $\mathbf{1}^+$ results in *reversible* OTf^- abstraction from **1-OTf** by $NaBAr'_4$, unless the product is stabilized by coordination of CD_2Cl_2, and requires the use of a better leaving group (**1-BF_4**) or a very potent electrophile (Ph_3C^+) for generation in the five-coordinate form in solution and only with PhF as a polar cosolvent.[74] The absence of π-donor ligands, the positive charge, and the presence of a very strong π-acid, linear NO^+, all contribute to maximize the Lewis acidity of Os in $\mathbf{1}^+$. The presence of the π-acidic NO compatible with a high degree of unsaturation is a rare combination that may be the key feature of the electronic structure of $\mathbf{1}^+$ responsible for the facile Me^- abstraction. Additionally, the presence of a 5d metal Os is beneficial to the Me^- transfer via backside electrophilic attack, as the LUMO of $\mathbf{1}^+$, extended trans to the apical hydride in the square-based pyramid,[88] is quite diffuse. It is the high electrophilicity of Os in $\mathbf{1}^+$ that determines the facility with which the Me^- transfer occurs, while several other factors serve to inhibit the other reactivity pathways.

A typical reaction course of an M−X fragment with an RLi reagent, halide metathesis to yield M−R and LiX, is kinetically inhibited in the case of $\mathbf{1}^+$ by the two bulky P^iPr_3 ligands. A P^iPr_3 adduct of $\mathbf{1}^+$, *cis,mer*-$Os(H)_2(NO)(P^iPr_3)_3^+(BAr'_4{}^-)$, appears to test the steric limits of the vacant coordination site, as the ^{31}P signals are slightly exchange broadened at 20 °C. It is important to note that the steric discrimination, imparted by the bulky phosphines to the Os center, is primarily kinetic in origin in the reactions with organolithium reagents. In fact, the products of X-metathesis with a bulky Y can be stabilized via either a reductive elimination of H-Y, as in the case of Y = Np,[33] or a loss of free L. Therefore, the role of steric factors in the reactivity of $\mathbf{1}^+$ is best described as impeding the access of Os to the congested nucleophilic sites in the aggregated structures of organolithium reagents, thus kinetically favoring abstraction of an "outside" R'^- group. Using increasingly disaggregated forms of RLi indeed accelerates the metathesis pathway B under certain conditions. Nevertheless, the sterically driven kinetic preference for A is quite pronounced, as the reaction with Me_3SiCH_2Li with rare exceptions yields substantial amounts of **1-Me** (Table 6), yet the corresponding product of B is only slightly less stable toward reductive elimination of RH and is greatly favored thermodynamically. This kinetic preference, however, is insufficient to overcome a higher barrier for Me−C bond cleavage, as compared to Me−Si, in NpLi, such that only with additional steric congestion of the nucleophilic site, in the case of TMPLi, does the cleavage of Me−C bond become the major pathway.

While the absence of π-donor ligands in $\mathbf{1}^+$ is essential to the high electrophilicity of Os, the presence of hydrides would seem to suggest deprotonation (C) as a favored reactivity pathway of $\mathbf{1}^+$. Cationic metal hydrides are known to be hydrogen-bond donors[78] and can be Brønsted acidic.[89] Although indeed operational, this reaction mode is quite unfavorable, at least kinetically, requiring very strong bases. The weak kinetic acidity of the hydrides exemplifies the strength of Os−H bonds, a structural feature shown to be central to the stabilization of an isoelectronic ruthenium complex.[88] Notably, substitution of a Cl ligand for a hydride in $\mathbf{1}^+$, while predictably lowering the electrophilicity of Os,[74] also activates the deprotonation mechanism, and $OsHCl(NO)L_2^+(BAr'_4{}^-)$ is rapidly deprotonated by NEt_3 at 20 °C to yield the stable d^8 square-planar species $OsCl(NO)L_2$.[90] The analogous thermodynamic stability of the deprotonation product is lacking in the case of $\mathbf{1}^+$, as **2** suffers from the combination of high unsaturation and the strong reducing power of Os(0), both increased relative to $OsCl(NO)L_2$ due to the absence of a π-donor, halide. Stabilization of **2** via simple adduct formation, possible in the case of the precursor **1-OTf**, is also not very favorable, as the presumed primary product of deprotonation, the adduct of **2** with OTf^-, is not observed, and even the observed species, **2-$CH_2SiMe_3^-$**, is only stable at low temperatures. Thus, the absence of π-donors and the presence of pure σ-donors, hydrides, in $\mathbf{1}^+$ makes the complex quite resistant to deprotonation, both kinetically, due to the strong σ-bonding of the hydrides, and thermodynamically, as **2** is highly unstable.

The high degree of unsaturation of Os in $\mathbf{1}^+$ might have triggered electron transfer to metal, but this reaction mode was found to be at most a minor pathway. The +2 oxidation state for Os is not characteristic of particularly strong oxidative behavior, and while the most electron-rich Os(II) species studied here, **1-H**, according to the lowest ν(N−O),[34,74] does undergo facile reduction with Li[naphthalene]$^\bullet$, this pathway must be slow relative to the two X-substitution pathways and can only be activated, to a limited extent, by suppressing the last two.

Finally, the product of Me^- transfer, **1-Me**, is sufficiently stable to be isolated and identified. The propensity of the Me^- transfer product for further reactivity is increased by the presence of hydride ligands, essential for high electrophilicity of the metal center, as the cis arrangement of H and Me in late-transition-metal complexes is typically unstable,[91] although several examples stable to MeH reductive elimination are

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(89) Reference 45, p 91.

(90) The reaction of $[OsHCl(NO)(P^iPr_3)_2][BAr'_4]$ with 2 equiv of NEt_3 in C_6D_6 within seconds gave a dark brown-green solution containing *trans*-$OsCl(NO)(P^iPr_3)_2$ as the only Os product, identified by ^1H and ^{31}P NMR: Werner, H.; Flügel, R.; Windmüller, B.; Michenfelder, A.; Wolf, J. *Organometallics* **1995**, *14*, 612.

(91) Reference 51, p 154.

known.[41,92] *If the primary product of Me^- transfer is not sufficiently stable to CH_4 elimination, the metal-containing reaction products would be identical with those resulting from a deprotonation reaction*, while the (diagnostic) organic products can be quite complex. This rapid subsequent reactivity may therefore mask the original reaction pathway.

(b) Scope of the Reaction. The Me^- transfer reactivity investigated here requires the reagent to contain a strongly nucleophilic center, as essentially no reaction occurred between **1-OTf** and $SnMe_4$ in C_6D_6 even on prolonged heating (18 h at 60 °C). The isoelectronic series of the organolithium species that exhibited Me^- transfer reactivity, $Me(ER_2)XR''_n{}^-$ (Scheme 9) with E = C, Si and X = C, N, could not be extended to alkoxides (X = O), as the increasing electronegativity of X strongly diminished the nucleophilicity of the β-Me groups. Neither of the Me_3EOM' (E = C, Si; M′ = Li, K) reagents reacted with **1-OTf** or **1-THF**$^+$ via A, instead giving complex mixtures of products of B and, possibly, C; lithium reagents were particularly inert, requiring long reaction times and/or thermal activation. In addition to the decreased nucleophilicity of the β-Me groups, the alkoxides lack the steric hindrance of the nucleophilic site present in lithium alkyls and alkylamides. However, the borate $B(CH_2SiMe_3)_4^-$, in which the Me_3SiCH_2 group is substantially less nucleophilic than in Me_3SiCH_2Li, was found to be reactive via A, although less so than the amide $(Me_3Si)_2NLi$.

Overall, the β-Me^- transfer reactivity described here requires primarily a highly electrophilic metal center with appropriate steric protection, which is resistant to deprotonation and SET reduction.

Conclusions

This study demonstrates how an attempted substitution at a sterically congested M−X with lithium alkyls and alkylamides devoid of β-hydrogens can follow a pathway dramatically different from that expected and result in a net transfer of a β-Me^- group to M. The electrophile studied here, $Os(H)_2(NO)(P^iPr_3)_2^+$, is highly potent and abstracts β-Me^- not only from the very bulky $(Me_3Si)_2NLi$, $(Me_3Si)_2CHLi$, and TMPLi but also from the relatively unhindered Me_3SiCH_2Li, which transfers the intact $Me_3SiCH_2^-$ to Os at a rate competitive with the β-Me^- transfer. The latter example reveals a considerable kinetic preference for the abstraction of the β-R′$^-$ group, also evident from widespread abstraction of β-hydrides from conventional unhindered nucleophiles, such as EtLi and ^{n}BuLi. Out of an extensive series of RLi and R_2NLi examined, only NpLi is completely resistant to the β-R′$^-$ transfer; in comparison to Me_3SiCH_2Li, this surprisingly different behavior is suggested by DFT calculations to be due to kinetic control. While this unusual reactivity of $Os(H)_2(NO)(P^iPr_3)_2^+$ includes the abstraction of the β-Me^- from a weakly nucleophilic R in $B(CH_2SiMe_3)_4^-$, neutral substrates ($SnMe_4$) or even alkali-metal alkoxides (Me_3EOM', E = Si, C) were found to be inert to the transfer of Me^-, evidently due to insufficient nucleophilicity of the Me groups and/or lack of steric protection at the nucleophilic center. This reactivity is also completely selective for the transfer of β-H^- over that of β-Me^-, as $^iPr_2NLi$ transfers β-H^- exclusively.

Mechanistic studies reveal that substitution reactions of halide/pseudohalide X at **1-X** begin by coordination of electrophilic Li in RLi/R_2NLi to the X ligand, forming a "lithium bond". The electrophilicity of Li is of considerable importance to the substitution rates, which shows that in the absence of external donor ligands Li acts as a potent Lewis acid, abstracting X^- to produce the unsaturated Os species. Coordination of intact R^- to Os is a pathway unrelated to the transfer of β-R′$^-$ via β-R′ elimination, as the resulting **1-R** complexes react overwhelmingly by reductive elimination of RH. Single-electron-transfer reduction from a substrate to Os, followed by abstraction of R′$^\bullet$, was ruled out for BR_4^- reagents as the mechanism of net β-R′$^-$ transfer, on the basis of the reactivity of mixed borate $^iPr_3BMe^-$. The proposed intimate mechanism of the intermolecular Me−C/Si bond cleavage is a direct S_E2 substitution at the methyl carbon with inversion of the Me group, supported by DFT calculations. For the systems exhibiting competitive transfer of β-R′$^-$ and intact R^-, increasingly disaggregated forms of RLi react preferentially by the latter pathway, which establishes the transfer of easily accessible, "outside" β-R′$^-$ as being kinetically driven. However, this dependence is not strongly pronounced, likely due to indiscriminately high electrophilicity of Os in $Os(H)_2(NO)(P^iPr_3)_2^+$.

While imines formed in the β-R′$^-$ transfer reaction are lithiated by and compete with the original base for the Os, unsaturated silicon species appear to react by 1,2-insertion with remaining RLi/R_2NLi, generating species that are also active β-Me^- donors. In both cases, a rather complex mixture of final organic products is obtained. Of several factors identified as responsible for the unusual reactivity of $Os(H)_2(NO)(P^iPr_3)_2^+$, high electrophilicity, augmented by the presence of the very strong π-acid NO, and steric protection of the metal center are of utmost importance. In view of the common occurrence of these conditions in transition-metal chemistry, it is reasonable to anticipate the β-Me^- transfer reactivity to be rather widespread.

Experimental Section

General Considerations. All manipulations were carried out using standard Schlenk, high-vacuum, and glovebox techniques under argon, with flame- or oven-dried glassware. Bulk solvents were purified by appropriate methods, distilled, and stored under Ar in gastight solvent bulbs with Teflon closures. Deuterated solvents were dried and deoxygenated accordingly, vacuum-transferred, degassed, and stored in Teflon-stoppered bulbs in an argon-filled glovebox. ^1H, ^{19}F, ^{31}P, ^{11}B, and ^{29}Si NMR spectra were recorded on a Varian Gemini 2000 (^1H, 300 MHz; ^{31}P, 122 MHz; ^{19}F, 282 MHz) or a Varian Inova 400 (^1H, 400 MHz; ^{19}F, 376 MHz; ^{31}P, 162 MHz; ^{11}B, 128 MHz; ^{29}Si, 80 MHz) spectrometer and referenced to the residual protio solvent peaks (^1H), internal Me_4Si standard (^{29}Si), or external 85% H_3PO_4 (^{31}P), neat $BF_3{\cdot}OEt_2$ (^{11}B), and neat CF_3COOH (^{19}F, −78.5 ppm relative to $CFCl_3$). Chemical shifts are reported in ppm relative to tetramethylsilane (^1H, ^{29}Si), 85% H_3PO_4 (^{31}P), $BF_3{\cdot}OEt_2$ (^{11}B), and $CFCl_3$ (^{19}F). NMR probe temperatures were calibrated with a methanol standard. During variable-temperature (VT) measurements, samples were allowed at least 10 min to equilibrate at each temperature, which was maintained to ±0.5 °C. Infrared spectra were

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recorded on a Nicolet 510P FT-IR spectrometer in a KBr solution cell.

Materials. $KOSiMe_3$, $LiOSiMe_3$, KO^tBu, LiO^tBu, $[Bu_4N][Ph_3SiF_2]$, $Et_4NF{\cdot}nH_2O$, BEt_3 (1.0 M, hexanes), ^{t}BuLi (1.5 M, pentane), ^{n}BuLi (2.0 M, pentane) (Aldrich), and MeLi (1.6 M, Et_2O) (Acros) were used as received. $^iPr_2NLi$ (Aldrich)[93] and BPh_3 (Strem) were sublimed. **1-Cl**, **1-OTf**, **1-H**,[34] $[Bu_4N][Ph_3BMe]$,[40,94] $(Me_3Si)_2NLi{\cdot}OEt_2$,[95] $(Me_3Si)_2CHLi$,[96] NpLi[97] (Me_3SiCH_2Li analogously), TMPLi,[98] EtLi,[93] $LiBMe_4$,[99] $LiBEt_4$,[100] and $[Ph_3C][B(C_6H_3\text{-}3,5\text{-}(CF_3)_2)_4]$[101] were prepared according to the published procedures or slight modifications thereof. 1,2-Dehydro-2,6,6-trimethylpiperidine[102] was isolated and used as a mixture with 25% of 2,2,6,6-tetramethylpiperidine. The boranes B^iPr_3 and $B(CH_2SiMe_3)_3$[103] were prepared by the method of Brown.[104] $(Me_3Si)_2NLi$ was prepared from $(Me_3Si)_2NH$ (Aldrich) and ^{n}BuLi in pentane. $[Li(THF)_4][B(CH_2SiMe_3)_4]$[105] was prepared from Me_3SiCH_2Li and $B(CH_2SiMe_3)_3$ in THF at −78 °C and isolated by layering the THF solution with pentane at −20 °C; the Bu_4N^+ salt was prepared by adding a solution of the Li^+ salt in a minimal amount of THF to a water solution of 1.5 equiv of Bu_4NBr.[94] All organolithium and organoborate reagents were purified by crystallization and/or sublimation; with the exception of TMPLi, which invariably contained ca. 2% each of LiCl and LiOH, all were free of lithium halides/hydroxide that instantly react with **1-OTf** by halide metathesis. Preparation and characterization of **1-Ph**, **1-Np**, **1-P∼C**, and **2-L** will be reported separately.[33]

NMR Tube Reactions. Unless otherwise specified in the text, in a typical experiment 10 mg of solid **1-X** and 1.2−1.5 equiv of an appropriate organolithium/organoborate reagent were mixed in a flame-dried 5 mm NMR tube fitted with a Teflon stopcock (Young tube), followed by the solvent (0.5−0.6 mL), or a solution of RLi was added by syringe to a solution of **1-X**. The contents of the tube were vigorously shaken, the precipitate was centrifuged to the top, and the ^{1}H NMR spectrum was recorded within 10−15 min of the start of the reaction. In the reaction carried out under a gas atmosphere, C_6D_6 was vacuum-transferred onto the solids, the tube was pressurized while frozen, at ca. −20 °C, and the contents were vigorously shaken while the solvent was thawing.

Low-Temperature NMR Tube Reactions. Solid reagents, ground into fine powders, were placed in either a 5 mm NMR tube annealed to or a Young tube connected through a glass fitting to a short manifold. The flame-dried manifold was capped with a Teflon valve and led directly to the outlet of a 5 mL flask, capped with a Teflon valve, from which about 0.6 mL of an appropriate solvent was vacuum-transferred onto the solids, while maintaining the NMR tube maximally submerged in a −78 °C bath. The NMR tube was either sealed off under vacuum, while keeping the contents frozen at −198 °C, or refilled with Ar (Young tube). The mixture was homogenized at an appropriate temperature by applying an NMR tube mixer to the top of the tube, maximally submerged in a low-temperature bath, and the tube, cooled to a temperature of 10−20 °C lower than the probe temperature, was promptly transferred in the precooled NMR probe.

IR Measurements. In an argon-filled glovebox an appropriate amount of heptane, measured with a microliter syringe, was added to the mixture of solid reagents in an oven-dried vial equipped with a stirbar. IR spectra were recorded on homogeneous solutions within 5 min.

$[Li(TMEDA)_2][Ph_3BMe]$. A solution of BPh_3 (500 mg, 2.07 mmol) in 10 mL of Et_2O was treated with 0.9 equiv of MeLi (Et_2O solution, titrated immediately prior to use[106]). After the mixture was stirred for 3 min, TMEDA (600 mg, 5.16 mmol) was added, leading to immediate precipitation of a white solid, which was filtered off, washed with 3 × 10 mL of Et_2O, and dried in vacuo. Yield: 712 mg (1.43 mmol, 77%). ^{1}H NMR (d_5-pyridine, 20 °C): δ 8.11 (br. s, 6H, B(*o*-C_6H_5)), 7.33 (t, J_{H-H} = 7.4 Hz, 6H, B(*m*-C_6H_5)), 7.12 (t, J_{H-H} = 7.2 Hz, 3H, B(*p*-C_6H_5)), 2.36 (s, 8H, TMEDA), 2.15 (s, 24H, TMEDA), 1.21 (q, J_{B-H} = 3.7 Hz, 3H, BCH_3). Anal. Found (calcd) for $C_{31}H_{50}LiBN_4$: C, 75.54 (74.99); H, 9.83 (10.15); N, 10.89 (11.28).

$[Li(TMEDA)_2][^iPr_3BMe]$. A procedure analogous to that used for the Ph_3BMe^- salt, using B^iPr_3 (150 mg, 1.07 mmol) in 10 mL of Et_2O with 0.9 equiv of MeLi (Et_2O solution, titrated immediately prior to use) and TMEDA (311 mg, 2.68 mmol) gave a white solid, which was filtered off, washed with 3 × 5 mL of Et_2O, and dried in vacuo. Yield: 340 mg (0.86 mmol, 89%). ^{1}H NMR (d_4-MeOH, 20 °C): δ 2.46 (s, 8H, TMEDA), 2.25 (s, 24H, TMEDA), 0.69 (dq, J_{H-H} = 7.4 Hz, J_{B-H} = 2.5 Hz, 18H, B(CH(CH_3)$_2$)$_3$), 0.37 (m, 3H, B(CH(CH$_3$)$_2$)$_3$), −0.92 (q, J_{B-H} = 3.6 Hz, 3H, BCH_3) (hydrolysis becomes apparent after several hours at room temperature). Anal. Found (calcd) for $C_{22}H_{56}LiBN_4$: C, 66.64 (66.99); H, 13.75 (14.31); N, 14.08 (14.20).

***cis,trans*-Os(H)$_2$Me(NO)(P^{i}Pr$_3$)$_2$ (1-Me).** A MeOH solution (5 mL) of **1-OTf** (300 mg, 434 μmol) was treated with a MeOH solution (3 mL) of $[Li(TMEDA)_2][Ph_3BMe]$ (237 mg, 477 μmol) at room temperature, leading to precipitation of a yellow solid. The resulting mixture was stirred for 3 min and cooled to −40 °C to yield yellow crystalline material after several days, which was washed with 3 × 5 mL of MeOH at −40 °C, dried under full vacuum at room temperature for 30 min and stored under Ar at −20 °C. Yield: 206 mg (369 μmol, 85%) ^{1}H NMR (C_6D_{12}, 20 °C): δ 2.36 (m, 6H, P(CH(CH$_3$)$_2$)$_3$), 1.22 (dvt, J_{H-H} = 6.9 Hz, N = 13.8 Hz, 18H, P(CH(CH_3)$_2$)$_3$), 1.21 (dvt, J_{H-H} = 6.9 Hz, N = 13.8 Hz, 18H, P(CH(CH_3)$_2$)$_3$), 0.67 (td, J_{P-H} = 4.4 Hz, $J_{(C)H-(Os)H}$ = 2.1 Hz, 3H, (OsC)H_3), −7.99 (tdq, J_{P-H} = 25.4 Hz, J_{H-H} = 8.3 Hz, $J_{(C)H-(Os)H}$ = 2.1 Hz, 1H, ON−OsH[107]), −8.14 (td, J_{P-H} = 18.3 Hz, J_{H-H} = 8.3 Hz, 1H, Me−OsH). ^{31}P{^{1}H} NMR (C_6D_{12}, 20 °C): δ 30.7 (s). IR (C_6H_6): 1676 cm^{-1} (ν_{NO}). Anal. Found (calcd) for $C_{19}H_{47}NOOsP_2$: C, 40.54 (40.92); H, 8.11 (8.49); N, 2.53 (2.51).

***cis,trans*-Os(H)$_2$Et(NO)(P^{i}Pr$_3$)$_2$ (1-Et).** A MeOH solution (1.5 mL) of **1-OTf** (20 mg, 28.9 μmol) was treated with a MeOH solution (0.3 mL) of $LiBEt_4$ (6.2 mg, 46.3 μmol) at −78 °C with stirring and placed in a −40 °C freezer overnight. The yellow needles that formed were washed with 3 × 5 mL of MeOH at −40 °C and dried for 5 min under full vacuum at room temperature (crystals notably darkened). Yield: 8 mg (14.0 μmol, 48%). ^{1}H NMR (C_6D_6, 20 °C): δ 2.31 (m, 8H, P(CH(CH$_3$)$_2$)$_3$ and OsCH_2CH$_3$), 2.11 (approximately t, J_{H-H} = 7.4 Hz, 3H, OsCH$_2$CH_3), 1.18 (dvt, J_{H-H} = 7.0, N = 14.0 Hz, 18H, P(CH(CH_3)$_2$)$_3$), 1.13 (dvt, J_{H-H} = 7.0 Hz, N = 14.0 Hz, 18H, P(CH(CH_3)$_2$)$_3$), −7.80 (approximately td, J_{P-H} = 26.6 Hz, J_{H-H} = 8.0 Hz, 1H, ON−OsH), −7.94 (approximately td, J_{P-H} = 19.9 Hz, J_{H-H} = 8.0 Hz, 1H, Et−OsH). ^{31}P{^{1}H} NMR (C_6D_6, 20 °C): δ 29.1 (s).

***cis,trans*-Os(H)$_2$(CH$_2$SiMe$_3$)(NO)(P^{i}Pr$_3$)$_2$ (1-CH$_2$SiMe$_3$).** A pentane (3 mL) suspension of finely ground **1-OTf** (100 mg,

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(107) Signifies the hydride site trans to the specific ligand.

145 μmol) was treated with a pentane (1 mL) solution of Me_3SiCH_2Li (22 mg, 234 μmol), vigorously stirred for 5 min at room temperature, and concentrated to ca. 2 mL at −13 °C. Precooled methanol (10 mL) was added at −13 °C, and the mixture was filtered at −13 °C through a small frit attached to the end of a Teflon cannula and placed in a −40 °C freezer for several days to yield yellow crystalline material. The solid was washed with 3 × 5 mL of MeOH at −40 °C and dried for 20 min under full vacuum at room temperature. Yield: 18 mg of a 85:15 mixture of **1-Me** and **1-CH_2SiMe_3** (31.7 μmol, 22%). Selected ^{1}H NMR (C_6D_6, 20 °C): 0.94 (td, J_{P-H} = 5.8 Hz, $J_{(C)H-(Os)H}$ = 1.3 Hz, 2H, OsC*H*$_2$SiMe$_3$), 0.50 (s, 9H, $OsCH_2Si(CH_3)_3$), −7.39 (td, J_{P-H} = 27.0 Hz, J_{H-H} = 8.2 Hz, $J_{(C)H-(Os)H}$ not resolved, 1H, ON−Os*H*), −9.27 (td, J_{P-H} = 20.0 Hz, J_{H-H} = 8.1 Hz, 1H, H_2C−Os*H*). $^{31}P\{^1H\}$ NMR (C_6D_6, 20 °C): δ 28.0 (s).

***cis,trans*-Os(H)$_2$($C_8H_{14}N$)(NO)(P^iPr_3)$_2$ (1-$C_8H_{14}N$).** To a solid mixture of **1-OTf** (150 mg, 217 μmol) and TMPLi (63.8 mg, 434 μmol) was added a benzene solution (6 mL) of 1,2-dehydro-2,6,6-trimethylpiperidine (477 μmol) with stirring. The resulting dark brown homogeneous solution was stirred for 30 min at room temperature and brought to oil in vacuo. The residue was extracted with 4 × 5 mL of Me_4Si, and the combined extracts were filtered through Celite and concentrated to 5 mL to yield a brown crystalline material after standing at −40 °C for several days, which was washed with 3 × 5 mL of pentane at −40 °C, dried in vacuo, and stored under Ar at −20 °C. Yield: 100 mg (150 μmol, 69%). ^{1}H NMR (C_6D_6, 20 °C): δ 3.17 (td, J_{P-H} = 4.5 Hz, $J_{(C)H-(Os)H}$ = 1.3 Hz, 2H, OsC*H*$_2$), 2.49 (m, 6H, P(C*H*$(CH_3)_2)_3$), 2.37 (t, J_{H-H} = 6.7 Hz, 2H, (C^3)*H*$_2$), 1.80 (m, 2H, (C^4)*H*$_2$), 1.52 (m, 2H, (C^5)*H*$_2$), 1.38 (s, 6H, (C^6)(C*H*$_3)_2$), 1.15 (dvt, J_{H-H} = 7.0 Hz, N = 14.0 Hz, 18H, P(CH(C*H*$_3)_2)_3$), 1.14 (dvt, J_{H-H} = 7.0 Hz, N = 14.0 Hz, 18H, P(CH(C*H*$_3)_2)_3$), −7.23 (td, J_{P-H} = 28.1 Hz, J_{H-H} = 7.7 Hz, $J_{(C)H-(Os)H}$ not resolved, 1H, ON−Os*H*), −8.37 (td, J_{P-H} = 20.0 Hz, J_{H-H} = 7.7 Hz, 1H, H_2C−Os*H*). $^{31}P\{^1H\}$ NMR (C_6D_6, 20 °C): δ 30.1 (s). IR (C_6D_6): 1681 cm^{-1} (ν_{NO}).

[*cis,trans*-Os(H)$_2$(THF)(NO)(P^iPr_3)$_2$][B(C_6H_3-3,5-$(CF_3)_2)_4$]·THF (1-THF^+). THF (10 mL), precooled to −65 °C, was added via cannula to a mixture of solid **1-H** (221 mg, 407 μmol) and $[Ph_3C][B(C_6H_3\text{-}3,5\text{-}(CF_3)_2)_4]$ (441 mg, 399 μmol) at −65 °C. With stirring, the mixture was warmed to −45 °C within 45 min, as all $[Ph_3C]$ salt had dissolved. The resulting deep red homogeneous solution was concentrated to 5 mL at room temperature and layered with pentane (15 mL) to give large red crystals after standing at −20 °C overnight. The solid was washed with 4 × 5 mL of a 4:1 mixture of pentane and THF at −20 °C, briefly dried in vacuo (small crystals notably became pink, due to the loss of lattice THF), and stored under Ar at −20 °C. Yield: 508 mg (328 μmol, 82%). ^{1}H NMR revealed the presence of only 1.9 equiv of THF, and the complex was counted as a mono-THF adduct in all reactions, to ensure its complete conversion. ^{1}H NMR (CD_2Cl_2, 20 °C): δ 3.76 (m, THF), 2.42 (m, 6H, P(C*H*$(CH_3)_2)_3$), 1.88 (m, THF), 1.29 (dvt, J_{H-H} = 7.7 Hz, N = 15.4 Hz, 18H, P(CH(C*H*$_3)_2)_3$), 1.27 (dvt, J_{H-H} = 7.7 Hz, N = 15.4 Hz, 18H, P(CH(C*H*$_3)_2)_3$), −13.29 (td, J_{P-H} = 16.6 Hz, J_{H-H} = 6.8 Hz, THF−Os*H*) (ON−Os−*H* is completely obscured by the (PC)Me resonances; irradiation of that region collapses the visible hydride signal into a triplet). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ 41.5 (s). ^{19}F NMR (CD_2Cl_2, 20 °C): δ −63.6 (s). IR (CD_2Cl_2): 1761 cm^{-1} (ν_{NO}). Anal. Found (calcd) for $C_{58}H_{72}BF_{24}NO_3OsP_2$: C, 44.53 (44.94); H, 4.51 (4.68); N, 0.93 (0.90).

NMR Tube Reaction of 1-OTf with EtLi. Following the general procedure with C_6D_6 solvent gave a mixture of **1-H** (81%), **1-Et** (14%), and OsH(η^2-C_2H_4)(NO)(P^iPr_3)$_2$ (**2-C_2H_4**; 5%) (Table 1, part a of section II). **2-C_2H_4**: selected ^{1}H NMR (C_6D_6, 20 °C) δ −8.17 (t, J_{P-H} = 23.0 Hz, Os*H*); $^{31}P\{^1H\}$ NMR (C_6D_6, 20 °C): δ 17.0 (s), selectively decoupled, doublet. **2-C_2H_4** is stable for days at room temperature in C_6D_6 and can be quantitatively generated by the reaction of **1-OTf** with ($Me_3Si)_2NLi{\cdot}OEt_2$ in C_6D_6 under a C_2H_4 atmosphere for several days at 20 °C. **2-C_2H_4**: ^{1}H NMR (CD_2Cl_2, 20 °C) δ 2.14 (m, 6H, P(C*H*$(CH_3)_2)_3$), 1.56, (br t, J_{P-H} = 5.3 Hz, 4H, (Os)C_2H_4), 1.25 (dvt, J_{H-H} = 6.5 Hz, N = 13.0 Hz, 18H, P(CH(C*H*$_3)_2)_3$), 1.21 (dvt, J_{H-H} = 6.5 Hz, N = 13.0 Hz, 18H, P(CH(C*H*$_3)_2)_3$), −8.40 (t, J_{P-H} = 23.0 Hz, Os*H*); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ 17.0 (s).

NMR Tube Reaction of 1-OTf with ^{n}BuLi. Following the general procedure with C_6D_6 solvent gave a mixture of **1-H** (53%), **1-^{n}Bu** (41%), and OsH(η^2-C_4H_8)(NO)(P^iPr_3)$_2$ (**2-C_4H_8**; 6%) (Table 1, part a of section II). **1-^{n}Bu**: selected ^{1}H NMR (C_6D_6, 20 °C) δ −7.82 (approximately td, J_{P-H} = 26.6 Hz, J_{H-H} = 8.2 Hz, 1H, ON−Os*H*), −7.94 (approximately td, J_{P-H} = 19.8 Hz, J_{H-H} = 8.2 Hz, 1H, ^{n}Bu-Os*H*); $^{31}P\{^1H\}$ NMR (C_6D_6, 20 °C) δ 28.9 (s). **2-C_4H_8**: selected ^{1}H NMR (C_6D_6, 20 °C) δ −10.06 (approximately t, J_{P-H} = 34 Hz, Os*H*); $^{31}P\{^1H\}$ NMR (C_6D_6, 20 °C) AB, δ(A) 28.6, δ(B) 25.9, J_{A-B} = 62 Hz. After 23 h at room temperature, both **1-^{n}Bu** and **2-C_4H_8** have fully converted into a mixture of **1-Ph-*d*,*d*$_5$** isomers.

NMR Tube Reaction of 1-OTf with LDA. Following the general procedure with C_6D_6 solvent gave a mixture of **1-H** and two new products, assigned as cis and trans isomers of *cis,trans*-Os(H)$_2$(CH_2C(Me)=N^{i}Pr)(NO)(P^iPr_3)$_2$ with respect to the C=N bond (Table 1, part b of section IV). Major product: selected ^{1}H NMR (C_6D_6, 20 °C) δ −6.86 (br td, J_{P-H} = 26 Hz, 1H, ON−Os*H*), −8.24 (td, J_{P-H} = 21.0 Hz, J_{H-H} = 7.8 Hz, 1H, H_2C−Os*H*); $^{31}P\{^1H\}$ NMR (C_6D_6, 20 °C) δ 28.2 (s). Minor product: selected ^{1}H NMR (C_6D_6, 20 °C) δ −7.21 (obscured), −8.35 (td, J_{P-H} = 20.1 Hz, J_{H-H} = 8.1 Hz, 1H, H_2C−Os*H*); $^{31}P\{^1H\}$ NMR (C_6D_6, 20 °C) δ 29.9 (s).

Low-Temperature NMR Tube Reaction of 1-OTf with Me_3SiCH_2Li in *d*$_8$-THF. Following the general procedure with d_8-THF solvent and 5 equiv of Me_3SiCH_2Li, starting at −80 °C, gave a new major product after minutes at −40 °C, assigned as OsH(CH_2SiMe_3)(NO)(P^iPr_3)$_2^-$ (**2-$CH_2SiMe_3^-$**). ^{1}H NMR (d_8-THF, −40 °C): δ 2.21 (m, 6H, P(C*H*$(CH_3)_2)_3$), 1.16 (dvt, J_{H-H} = 6.4 Hz, N = 12.8 Hz, 18H, P(CH(C*H*$_3)_2)_3$), 1.11 (dvt, J_{H-H} = 6.4 Hz, N = 12.8 Hz, 18H, P(CH(C*H*$_3)_2)_3$), 0.60 (t, J_{P-H} = 5.4 Hz, 2H, OsC*H*$_2$SiMe$_3$), −0.10 (s, 9H, $OsCH_2Si(CH_3)_3$), −10.38 (t, J_{P-H} = 32.8 Hz, Os*H*). $^{31}P\{^1H\}$ NMR (d_8-THF, −40 °C): δ 37.3 (s), selectively decoupled doublet. Using **1-THF^+** with 4 equiv of Me_3SiCH_2Li in an analogous reaction gave the identical product within minutes at −80 °C.

Low-Temperature NMR Tube Reaction of 1-OTf with Me_3SiCH_2Li in the Presence of TMEDA. Following the general procedure with d_8-PhMe solvent, 15 equiv of Me_3SiCH_2Li and 20 equiv of TMEDA gave complete conversion of **1-OTf** after several hours at −60 °C into **1-Me** (5%), **1-CH_2SiMe_3** (73%), and **2-$CH_2SiMe_3^-$** (22%). **2-$CH_2SiMe_3^-$**: selected ^{1}H NMR (d_8−PhMe, −60 °C) δ −10.05 (t, J_{P-H} = 32 Hz, Os*H*); $^{31}P\{^1H\}$ NMR (d_8−PhMe, −60 °C): δ 34.4 (s), selectively decoupled, doublet.

Generation of [Os(H)$_2$(NO)(P^iPr_3)$_2$][B(C_6H_3-3,5-$(CF_3)_2)_4$]. Following the general procedure with **1-H** and 0.8 equiv of $[Ph_3C][B(C_6H_3\text{-}3,5\text{-}(CF_3)_2)_4]$ in a 50:50 solvent mixture of d_8-PhMe and PhF gave a deep red solution of the title species, in addition to Ph_3CH, with the ^{1}H and ^{31}P NMR signals[74] considerably broadened due to the degenerate intermolecular hydride site exchange with the remaining **1-H**.

Generation of *cis,trans*-Os(H)$_2$X(NO)(P^iPr_3)$_2$ (1-X). X = F. Using **1-OTf** and 1.2 equiv of either $[Bu_4N][Ph_3SiF_2]$ or $Et_4NF{\cdot}nH_2O$ provided **1-F** quantitatively in C_6D_6 after 30 min. Selected ^{1}H NMR (C_6D_6, 20 °C): δ −0.70 (tt, J_{P-H} = 22.4 Hz, J_{F-H}(cis) = J_{H-H} = 8.9 Hz, 1H, ON−Os*H*), −11.52 (dtd, J_{F-H}(trans) = 69.3 Hz, J_{P-H} = 12.8 Hz, J_{H-H} = 8.1 Hz, 1H, F−Os-*H*). $^{31}P\{^1H\}$ NMR (C_6D_6, 20 °C): δ 36.4 (d, J_{P-F} = 20.5 Hz), selectively decoupled, doublet of triplets. ^{19}F NMR (C_6D_6, 20 °C): δ −345 (dtd, J_{F-H}(trans) = 71.0 Hz, J_{P-F} = 20.6 Hz, J_{F-H}(cis) = 9.6 Hz).

X = OH. Using **1-OTf**, 2 equiv of solid KOH (85%), and 1.5 equiv of 18-crown-6 in C_6D_6 gave **1-OH** after 29 h at room

temperature as the major hydride-containing species. Selected ^{1}H NMR (C_6D_6, 20 °C): δ −1.96 (td, J_{P-H} = 22.2 Hz, J_{H-H} = 8.4 Hz, 1H, ON−Os*H*), −10.38 (td, J_{P-H} = 14.0 Hz, J_{H-H} = 8.4 Hz, 1H, HO−Os-*H*). ^{31}P{^{1}H} NMR (C_6D_6, 20 °C): δ 32.8 (s).

X = Br. Using **1-OTf** and 3 equiv of Bu_4NBr in C_6D_6 gave **1-Br** quantitatively after 28 h at room temperature. Selected ^{1}H NMR (C_6D_6, 20 °C): δ −2.87 (td, J_{P-H} = 23.8 Hz, J_{H-H} = 7.6 Hz, 1H, ON−Os*H*), −10.27 (td, J_{P-H} = 14.9 Hz, J_{H-H} = 7.6 Hz, 1H, Br−Os−*H*). ^{31}P{^{1}H} NMR (C_6D_6, 20 °C): δ 29.8 (s).

X = I. Using **1-OTf** and 3 equiv of Bu_4NI in C_6D_6 gave **1-I** quantitatively after 1 h at room temperature. Selected ^{1}H NMR (C_6D_6, 20 °C): δ −4.44 (td, J_{P-H} = 24.3 Hz, J_{H-H} = 7.6 Hz, 1H, ON−Os*H*), −10.07 (td, J_{P-H} = 15.9 Hz, J_{H-H} = 7.6 Hz, 1H, I−Os-*H*). ^{31}P{^{1}H} NMR (C_6D_6, 20 °C): δ 26.7 (s).

Generation of [*cis,mer*-Os(H)$_2$(NO)(P^{i}Pr$_3$)$_3$][B(C$_6$H$_3$-3,5-(CF$_3$)$_2$)$_4$]. Using **1-THF**$^+$ and 1.5 equiv of P^{i}Pr$_3$ in a 50:50 solvent mixture of d_8-PhMe and PhF afforded the title complex quantitatively in seconds. Selected ^{1}H NMR (50:50 d_8-PhMe:PhF, 20 °C): δ −7.04 (approximately qd, J_{P-H} = 24.4 Hz, J_{H-H} = 6.8 Hz, 1H, ON−Os*H*), −7.21 (dtd, J_{P-H}(trans) = 61.6 Hz, J_{P-H}(cis) = 30.0 Hz, J_{H-H} = 6.8 Hz, 1H, P−Os−*H*). ^{31}P{^{1}H} NMR (50:50 d_8-PhMe:PhF, 20 °C): δ 19.6 (br. d, J_{P-P} = 7.3 Hz, 2P), 10.5 (br t, 1P).[108]

Generation of (Me$_3$SiCH$_2$)$_2$B(CH$_2$SiMe$_2$CH$_2$SiMe$_3$) (5). A mixture of **1-OTf** (20 mg) and 1.1 equiv of [Li(THF)$_4$][B(CH$_2$-SiMe$_3$)$_4$] in 0.5 mL of C_6H_6 was stirred for 5 min at room temperature and distilled onto a cold finger at 80 °C (bath)/ca. 10 mTorr. The condensed liquid was rinsed down with C_6H_6 and distilled again, to give a 89:11 mixture of **5** and B(CH$_2$-SiMe$_3$)$_3$, with a trace of **1-H**. ^{1}H NMR (C_6D_6, 20 °C): δ 1.01 (s, 2H, BC*H*$_2$SiMe$_2$), 0.97 (s, 4H, B(C*H*$_2$SiMe$_3$)$_2$), 0.20 (s, 6H, BCH$_2$Si(C*H*$_3$)$_2$), 0.15 (s, 18H, B(CH$_2$Si(C*H*$_3$)$_3$)$_2$), 0.12 (s, 9H, SiMe$_2$CH$_2$Si(C*H*$_3$)$_3$), −0.18 (s, 2H, SiMe$_2$C*H*$_2$SiMe$_3$). ^{11}B NMR (C_6D_6, 20 °C): δ 78.6 (br s), indistinguishable from the signal of pure B(CH$_2$SiMe$_3$)$_3$. EI-MS: 344 (M$^+$).

(Me$_3$Si)$_2$NSiMe$_2$N(H)SiMe$_3$ (3-H). (Me$_3$Si)$_2$NSiMe$_2$Cl[109] was prepared from (Me$_3$Si)$_2$NLi and Me$_2$SiCl$_2$ in THF for 90 min at 70 °C,[110] isolated and converted into (Me$_3$Si)$_2$NSiMe$_2$NH$_2$,[109] which was also isolated, by passing NH_3 through the solution in pentane at −15 °C for 30 min. A pentane (20 mL) solution of (Me$_3$Si)$_2$NSiMe$_2$NH$_2$ (2.187 g, 9.32 mmol) and NEt$_3$ (4.72 g, 46.64 mmol) was treated with Me$_3$SiOTf (2.28 g, 10.26 mmol) with stirring. The resulting mixture was stirred for 15 min, and the colorless solution was decanted off the heavy brown oil and filtered through Celite. Distillation at 133°/5 Torr gave **3-H** as a colorless liquid (bp 110 °C/9.5 Torr[110]). Yield: 2.432 g (7.93 mmol, 85%). ^{1}H NMR (C_6D_6, 20 °C): δ 0.31 (s, 6H, Si-(C*H*$_3$)$_2$), 0.28 (s, 18H, N(Si(C*H*$_3$)$_3$)$_2$), 0.13 (s, 9H, N(H)(Si-(C*H*$_3$)$_3$)). ^{1}H NMR (d_8-THF, 20 °C): δ 0.86 (br. s, 1H, N*H*), 0.24 (s, 6H, Si(C*H*$_3$)$_2$), 0.22 (s, 18H, N(Si(C*H*$_3$)$_3$)$_2$), 0.09 (s, 9H, N(H)-(Si(C*H*$_3$)$_3$)). ^{29}Si (C_6D_6, 20 °C): δ 1.85 (m, 2Si, N(*Si*Me$_3$)$_2$), 1.50 (m, 1Si, N(H)(*Si*Me$_3$)), −6.20 (m, 1Si, *Si*Me$_2$).[111] EI-MS: *m/z* 291.155 35 (M − Me)$^+$ (calcd. 291.156 44).

(Me$_3$Si)$_2$NSiMe$_2$N(Li)SiMe$_3$ (3-Li). 3-H (1.0 g, 3.26 mmol) in pentane (10 mL) was treated with 1.0 equiv of ^{n}BuLi (2.0 M, pentane) dropwise at 20 °C. The resulting mixture was filtered through Celite and brought to dryness in vacuo to give a slightly off-white waxy solid after prolonged evacuation. Yield: 0.76 g (2.43 mmol, 75%). A 200 mg amount of this material was distilled on a cold finger at 130 °C (bath)/0.2 mTorr to give 150 mg of analytically pure colorless, very viscous liquid that partially crystallized under Ar at room temperature after several weeks. At variance with a previous report, **3-Li** is quite stable thermally, showing no decomposition under 130 °C vacuum distillation. ^{1}H NMR (C_6D_6, 20 °C): δ 0.41 (s, 6H, Si(C*H*$_3$)$_2$), 0.35 (s, 18H, N(Si(C*H*$_3$)$_3$)$_2$), 0.27 (s, 9H, N(Li)(Si(C*H*$_3$)$_3$)). ^{1}H NMR (d_8-THF, 20 °C): δ 0.21 (s, 18H, N(Si(C*H*$_3$)$_3$)$_2$), 0.07 (s, 6H, Si(C*H*$_3$)$_2$), −0.1 (br s, 9H, N(Li)(Si-(C*H*$_3$)$_3$)). Anal. Found (calcd) for $C_{11}H_{33}LiN_2Si_4$: C, 42.03 (42.25); H, 10.31 (10.64); N, 8.86 (8.96).

X-ray Structure Determinations. General Considerations. The crystal was mounted under an inert atmosphere on a glass fiber using silicone grease and transferred to the goniostat, where it was cooled to −160 °C using a gas-flow cooling system of local design. The Bruker-AXS SMART6000 system was used for data collection. Data were corrected for Lorentz and polarization effects as well as absorption using the Bruker SAINT software.

(a) *cis,trans*-Os(H)$_2$(C$_8$H$_{14}$N)(NO)(P^{i}Pr$_3$)$_2$ (1-C$_8$H$_{14}$N). The data were collected using 5 s frames with an ω scan of 0.30°. The structure was readily solved using SHELXTL and Fourier techniques. All hydrogen atoms were visible in a difference Fourier phased on the non-hydrogen atoms and were refined isotropically in the final cycles of refinement. A final difference Fourier was essentially featureless. There was one peak of intensity 2.43 e/Å^3 at the metal site, and all other peaks were less than 0.5 e/Å^3.

(b) [*cis,trans*-Os(H)$_2$(THF)(NO)(P^{i}Pr$_3$)$_2$][B(C$_6$H$_3$-3,5-(CF$_3$)$_2$)$_4$]·THF (1-THF$^+$). The data were collected using 30 s frames with an ω scan of 0.30°. It was observed that the data decreased in intensity rapidly with increasing (sin θ)/λ. The structure was solved with some difficulty using SHELXTL and Fourier techniques. It was discovered that the cation suffered from disorder, the most serious being the presence of two possible positions for the metal atom. There was no evidence of a space group ambiguity. Many of the atoms in the THF solvent and the anion have large anisotropic thermal parameters. The disorder is such that there are two independent sets of Os−ligand distances present. The Os(91a)−O(24) distance is 2.62 Å, compared to 2.24 Å for Os(1)−O(24), while the remaining Os−ligand distances are similar for the two sites. A final difference Fourier still had several peaks of intensity up to 2.2 e/Å^3, mostly in the vicinity of the disordered metal atoms.

Computational Details. All calculations were performed with the Gaussian 98[112] suites of programs, using the hybrid density functional method B3LYP,[113] with LANL2DZ,[114−116] a valence double-ζ basis set with relativistic effective core potentials for Os,[115] Si,[116] and P[116] centers. Addition of polarization functions to H (hydrides and hydrogens of the transferred Me group, exponent 1.0), C (0.75), N (0.80), O (0.85), Si (0.284),[117] and P (0.387)[117] in the [Os(H)$_2$(NO)(PH$_3$)$_2$][Me$_3$-SiCH$_2$] model system increased the activation energy (Δ(E +

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ZPE)) for β-Me^- transfer by only 1.4 kcal/mol. All structures were fully optimized with standard convergence criteria without symmetry constraints, and all were confirmed to be real minima or transition states via frequency analysis, which was also used to calculate zero-point energies (ZPE) without scaling. In view of the essentially C_s-symmetric nature of both transition states in Figure 3, the PES for the $[Os(H)_2(NO)(PH_3)_2][Me_3BCH_3]$ model system was searched with C_s symmetry. For all transition states, motion corresponding to the imaginary frequency was visually checked and most structures were additionally optimized to the minima they connected after correspondingly perturbing the TS geometry.

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Supporting Information Available: Full X-ray structural information on **1-$C_8H_{14}N$** and **1-THF^+** as an X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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