Carbonylation of ['Bu₃SiNH]₃ZrH and X-ray Structural Study of ['Bu₃SiNH]₃ZrCH₃

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Treatment of $ZrCl_4$ with 3 equiv of 'Bu₃SiNHLi afforded ('Bu₃SiNH)₃ZrCl (1); alkylation of 1 with MeMgBr gave ('Bu₃SiNH)₃ZrMe (2), whose structure was determined via X-ray crystallography. Crystal data: monoclinic, $P2_1/c$, $a = 22.052$ (3) Å, $b = 12.943$ (2) Å, $c = 17.320$ (2) Å, $\beta = 108.93$ (1)°, $Z = 4$, $T = 25$ °C. The methyl derivative 2 exhibits near-tetrahedral coordination with a normal Zr–C distance (2.231 (7) Å) and virtually indistinguishable amido groups (d(Zr–N)$_{av}$ = 2.039 (7) Å, ∠(Zr–N–Si)$_{av}$ = 151.4 (8)°). Upon thermolysis of 2 in cyclohexane (95 °C, 8 h), CH₄ was eliminated via abstraction of an amido hydrogen, generating the transient [('Bu₃SiNH)₂Zr=NSi'Bu₃] (3), which was scavenged by H₂ (3 atm) to produce ('Bu₃SiNH)₃ZrH (4). The monohydride 4 was shown to reduce CO to provide [('Bu₃SiNH)₃Zr]₂(μ-OCH₂) (6), presumably via monohydride (4) reduction of undetected [('Bu₃SiNH)₃Zr(CHO)] (5). Further carbonylation yielded the spectroscopically observable [('Bu₃SiNH)₃Zr]₂(μ-η¹:η²-OCH₂C=O) (7) and, ultimately, [('Bu₃SiNH)₃Zr]₂(cis-μ-O(H)C=C(H)O) (8). Thermolysis of 6 in THF resulted in the elimination of ('Bu₃SiNH)₃ZrOMe (10), leaving the transient 3, which was trapped by solvent to give ('Bu₃SiNH)₂(THF)Zr=NSi'Bu₃ (9). The addition of LiOMe to 1 provided an alternate route to 10. The mechanism of CO reduction is discussed in relation to other group 4 and actinide mono- and dihydride systems.

Introduction

The past two decades of organometallic research have manifested a renewed interest in homogeneous chemistry pertinent to the Fischer–Tropsch (F-T) reaction, the conversion of dihydrogen and carbon monoxide (syngas) to hydrocarbons and oxygenates.[1,2] During the course of these studies, the emergence of early-transition-metal chemistry, in particular the observation of CO reduction by group 4 hydrides, played a historical and important role. Of critical interest was the observation of C–C-coupled products upon stoichiometric reduction of CO, which suggested that the selective conversion of syngas to desirable C₂-oxygenates could be achieved. Central to these studies was the formation of cis and trans enediolates. Scheme I shows a mechanism proposed by Bercaw et al.[3] (A) for the formation of Cp*₂HM(trans-μ-O(H)C=C(H)-O)MHCp*₂ (Cp* = η⁵-C₅Me₅; M = Zr, Hf);[3-5] curiously, the trans orientation only occurs in cases where the product-forming step is a β-H elimination from a sterically favorable conformation of an intermediate η²-aldehyde.[4,6] In the Cp*₂M system, the cis enediolate results from a zirconoxycarbene coupling with CO, followed by stereospecific hydrogenation of a bound ketene.[7,8] In all other cases involving carbonylation of μ-CH₂O intermediates, cis-O(H)C=C(H)O bridges are ultimately formed. Typically the bridging formaldehyde group binds as an μ-η¹:η²-CH₂O unit or metallaoxirane, where the oxygen binds to two metals.[9] For example, [Cp₂Zr(μ-η¹:η²-CH₂O)]₂[10] and [Cp₂Zr(μ-η¹:η²-CH₂O)]₃ have been synthesized, the latter via treatment of [Cp₂ZrH₂]ₙ with CO,[11] but further carbonylation studies have not been reported. However, Floriani et al.[12] have shown that carbonylation of Cp₂ClZr(μ-η¹:η²-CH₂O)ZrClCp₂ affords [Cp₂Zr(μ-η¹:η²-cis-O(H)C=C(H)O)]₂ upon elimination of Cp₂ZrCl₂ (B), and a similar treatment of [Cp₂Zr]₂(μ-η¹:η²-CH₂O)(μ-η¹:η²-CHPhO) produces [Cp₂Zr]₂(μ-η¹:η²-cis-O(H)C=C(H)O)-(μ-η¹:η²-CHPhO) via the acyl intermediate [Cp₂Zr]₂(μ-η²:η¹-OCH₂C=O)(μ-η¹:η²-CHPhO) (C), according to Erker et al.[13] In these instances, the crucial transformation of an η²-acyl[14,15] (e.g., μ-η²:η¹-OCH₂C=O) into the cis-O(H)-C=C(H)O fragment is considered to occur via a 1,2-hy-

drogen shift. In neither example is an additional Zr–H functionality present; thus, the aforementioned pathway to a trans enediolate is obviated.

In an intriguing study, Marks et al. have spectroscopically observed the long-sought formyl Cp*₂Th-(OCH'Bu₂)(CHO),[16] prepared from Cp*₂Th(OCH'Bu₂)(H)

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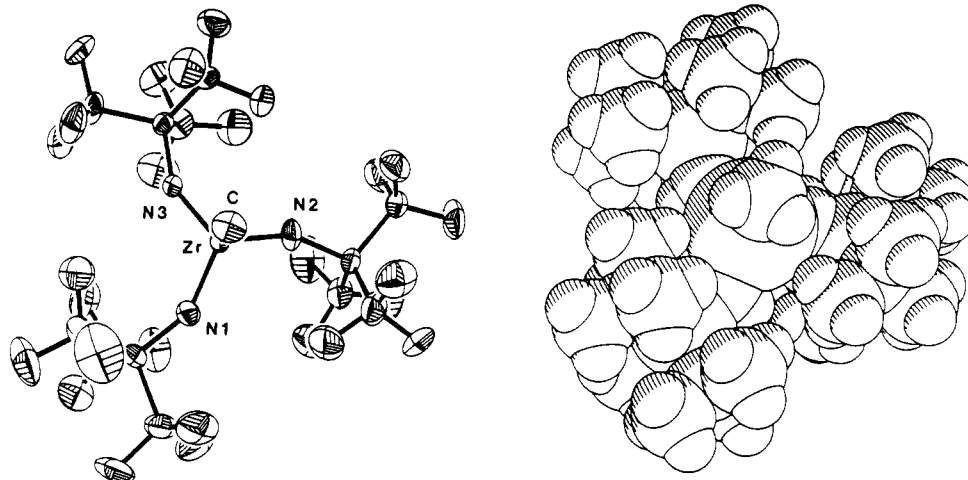

Figure 1. Molecular structure and space-filling view of (ᵗBu₃SiNH)₃ZrMe (2).

via the migratory insertion of CO (D).[17,18] Again, the final, isolable carbonylation product in this system is [Cp*₂Th-(OCHᵗBu₂)]₂(cis-μ-O(H)C=C(H)O). An accompanying kinetic study[19] of this process implicates a reduction of the formyl[20,21] by Cp*₂Th(OCHᵗBu₂)(H), subsequent CO insertion into the [Cp*₂Th(OCHᵗBu₂)]₂(μ-CH₂O) intermediate, forming an η²-acyl, and a final 1,2-hydrogen shift to give the cis enediolate (D).[18] With the reasoning that hard, electrophilic metal centers should encourage the breakdown of CO, carbonylation studies in these laboratories have centered around complexes containing the bulky silox (ᵗBu₃SiO⁻)[22,23] and ᵗBu₃SiNH⁻ [24] ligands. Recent investigations of C–H and H–H activation by the transient (ᵗBu₃SiNH)₂Zr=NSiᵗBu₃ have made possible the carbonylation studies of a group 4 monohydride, (ᵗBu₃SiNH)₃ZrH.[24] Herein are reported these investigations, which parallel those of the Cp*₂Th system, including the isolation of μ-CH₂O and spectroscopic detection of μ-OCH₂C=O intermediates.

Results and Discussion

(ᵗBu₃SiNH)₃ZrH Synthesis. Treatment of ZrCl₄ with 3 equiv of ᵗBu₃SiNHLi,[25] prepared from ⁿBuLi and

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Table I. Crystallographic Data for (ᵗBu₃SiNH)₃ZrMe (2)

formula: C₃₇H₈₇N₃Si₃Zr	$a = 22.052 (3)$ Å
fw: 749.60	$b = 12.943 (2)$ Å
space group: $P2_1/c$ (No. 14)	$c = 17.320 (2)$ Å
cryst dimens: 0.3 × 0.3 × 0.3 mm	$\beta = 108.93 (1)°$
$\mu = 3.30$ cm⁻¹ (no abs cor)	$V = 4676.1 (2)$ Å³
Nicolet R3m/V: 2θ range 0–50°	$Z = 4$
(±h,−k,l)	
no. of rflns: 8491	$T - 25$ °C
no. of indep rflns: 7813 ($R_{int} = 2.24\%$)	$\lambda = 0.71069$ Å (Mo Kα)
no. of rflns ($|F_o| \geq 3\sigma|F_o|$): 6083	$\rho_{calc} = 1.065$ g/cm³
$R = 6.05\%$; $R_w = 7.84\%$ (6083 rflns)	
$w^{-1} = \sigma^2(F) + 0.0008F^2$	GOF = 1.66 (6083 rflns)

ᵗBu₃SiNH₂,[26] resulted in the formation of (ᵗBu₃SiNH)₃ZrCl (**1**, eq 1) in 88% yield. Alkylation of **1** with MeMgBr in

$$ZrCl_4 + 3^tBu_3SiNHLi \xrightarrow[-3LiCl]{Et_2O} (^tBu_3SiNH)_3ZrCl \quad (1)$$
$$\mathbf{1}$$
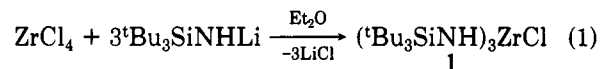
Et₂O yielded white crystals of the methyl derivative (ᵗBu₃SiNH)₃ZrMe (**2**, eq 2). Thermolysis of **2** in cyclo-

$$(^tBu_3SiNH)_3ZrCl + MeMgBr \xrightarrow[-MgClBr]{Et_2O}$$
$$\mathbf{1}$$
$$(^tBu_3SiNH)_3ZrMe \quad (2)$$
$$\mathbf{2}$$
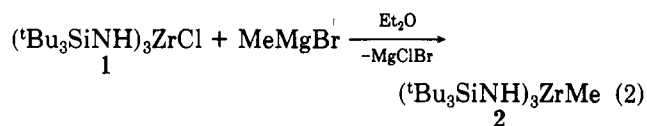
hexane at 95 °C (8 h) resulted in the elimination of methane,[24] generating the transient bis(amido) imido complex (ᵗBu₃SiNH)₂Zr=NSiᵗBu₃ (**3**). If dihydrogen was present (3 atm), **3** added H₂ across the imido linkage to afford (ᵗBu₃SiNH)₃ZrH (**4**, eq 3). When similarly treated

$$(^tBu_3SiNH)_3ZrMe \xrightarrow[C_6H_{12}, -MeH]{95\ °C,\ 8\ h}$$
$$\mathbf{2}$$
$$[(^tBu_3SiNH)_2Zr=NSi^tBu_3] \xrightarrow[3\ atm]{H_2} (^tBu_3SiNH)_3ZrH \quad (3)$$
$$\mathbf{3} \qquad\qquad\qquad\qquad \mathbf{4}$$
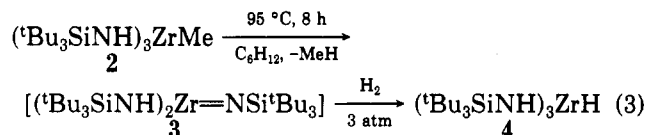
with D₂, **2** released CH₄ upon conversion to (ᵗBu₃SiNH)₂(ᵗBu₃SiND)ZrD (4-(ND)-d), which exhibited further deuteration of its amido sites upon extended thermolysis.[24] Examination of crude reaction mixtures by ¹H NMR spectroscopy revealed that **4** formed cleanly (>95%), but its high solubility in hydrocarbon solvents limited the isolated yields (40–60%).

The hydride resonance for (ᵗBu₃SiNH)₃ZrH (**4**) is shifted significantly downfield (δ 9.60, C₆D₆), consistent with a

(26) Nowakowski, P. M.; Sommer, L. H. *J. Organomet. Chem.* **1979**, *178*, 95–103.

Scheme I

highly electrophilic zirconium center surrounded by hard nitrogen donors (cf. Cp*$_2$ZrH(CH$_2$CHMe$_2$), δ 6.43; Cp*$_2$ZrH$_2$, δ 7.46).[4] In addition, the NH shift for **4** (δ 4.87) experiences a downfield shift relative to those of the hydrocarbyl derivatives (^{t}Bu$_3$SiNH)$_3$ZrMe (**3**, δ 4.10),

(^{t}Bu$_3$SiNH)$_3$ZrCy (δ 3.89), and (^{t}Bu$_3$SiNH)$_3$ZrPh (δ 4.50 ppm),[24] a possible indication of increased electrophilicity in this system. The infrared spectrum of **4** exhibits ν(Zr–H) at 1553 cm^{-1}, which shifts to 1117 cm^{-1} upon deuteration of the hydride position. Highly soluble in

Table II. Selected Interatomic Distances (Å) and Angles (deg) for (^{t}Bu$_3$SiNH)$_3$ZrMe (2)

Zr–C(Me)	2.231 (7)	Zr–N1	2.046 (5)	Zr–N2	2.040 (4)
Zr–N3	2.032 (4)	N1–Si1	1.735 (5)	N2–Si2	1.737 (4)
N3–Si3	1.749 (4)	Si–C (av)	1.924 (12)	C–C (av)	1.527 (14)
C–Zr–N1	108.0 (2)	C–Zr–N2	107.5 (2)	C–Zr–N3	107.2 (2)
N1–Zr–N2	110.4 (2)	N1–Zr–N3	112.2 (2)	N2–Zr–N3	111.3 (2)
Zr–N1–Si1	151.5 (3)	Zr–N2–Si2	150.6 (2)	Zr–N3–Si3	152.1 (3)
N–Si–C (av)	107.1 (5)	Si–C–C	112.0 (14)	C–Si–C (av)	111.7 (10)
C–C–C (av)	106.8 (18)				

common aromatic or aliphatic hydrocarbon solvents, 4 is formulated as a pseudotetrahedral monomer by analogy to the methyl complex 3, whose structure has been determined via X-ray crystallography. Closely related to 4 are the actinide hydrides [(Me$_3$Si)$_2$N]$_3$MH (M = U, Th, Hf), prepared by Andersen et al.[27]

Structure of (^{t}Bu$_3$SiNH)$_3$ZrMe (2). A single-crystal X-ray structure determination (Mo Kα, monoclinic, *P*2$_1$/*c* of (^{t}Bu$_3$SiNH)$_3$ZrMe (2) confirmed its pseudotetrahedral geometry. Figure 1 reveals the *C$_3$* symmetry of 2 resulting from the array of ^{t}Bu$_3$SiNH groups that spiral out from the Zr–Me axis. The C–Zr–N angles (107.6 (4)° average) are slightly less than the N–Zr–N angles (111.3 (9)° average) in accord with greater steric repulsion between the silamide ligands (Table II). Molecular views show that the bent Zr–N–Si linkages (151.4 (8)° average) serve to keep the silamide ligands far apart, thereby obviating significant deviations from tetrahedral geometry. In addition, each Zr–N(H)–Si plane is canted such that the amide hydrogens are directed slightly away from the Zr–Me group. The three planes generated by the sp^2 nitrogens resemble the blades of a pyramidal propeller, comparable to the (Me$_3$Si)$_2$N ligands of [(Me$_3$Si)$_2$N]$_3$MCl (M = Ti, Zr, Hf).[28] The virtually indistinguishable amido ligands display short Zr–N distances (d(Zr–N)$_{av}$ = 2.039 (7) Å) that are characteristic of strong N(pπ)→Zr(dπ) donation in low-coordinate group 4 complexes,[28-30] complementing a similarly short 2.231 (8) Å zirconium–carbon bond. As espoused by Andersen et al.,[29] the short bond lengths can in part be attributed to the smaller covalent radius of four-coordinate Zr(IV). The remaining distances and angles that describe the ^{t}Bu$_3$SiNH ligands (Table II) reflect the subtle steric influences of the ^{t}Bu group, as has been observed previously for the analogous siloxide ^{t}Bu$_3$SiO$^-$ (silox).[22,31]

Carbonylation Studies. Exposure of (^{t}Bu$_3$SiNH)$_3$ZrH (4) to 1 atm of CO in benzene at 25 °C produced a turbid solution that became homogeneous over ~5–10 min, resulting in [(^{t}Bu$_3$SiNH)$_3$Zr]$_2$(*cis*-μ-O(H)C=C(H)O) (8, Scheme II) as the sole product. Cis enediolate 8 exhibits a vinylic singlet at δ 5.62 in the ^{1}H NMR spectrum (C$_6$D$_{12}$) with an accompanying vinylic carbon resonance at δ 127.94 in the ^{13}C{^{1}H} NMR spectrum. The corresponding resonances of the isotopomer [(^{t}Bu$_3$SiNH)$_3$Zr]$_2$(cis-μ-O-(H)^{13}C=^{13}C(H)O (8-^{13}C$_2$), obtained from 4 and 90% ^{13}CO, split into a diagnostic, 10-line AA'XX' pattern[32] ($^1J_{CH}$ =

Scheme II
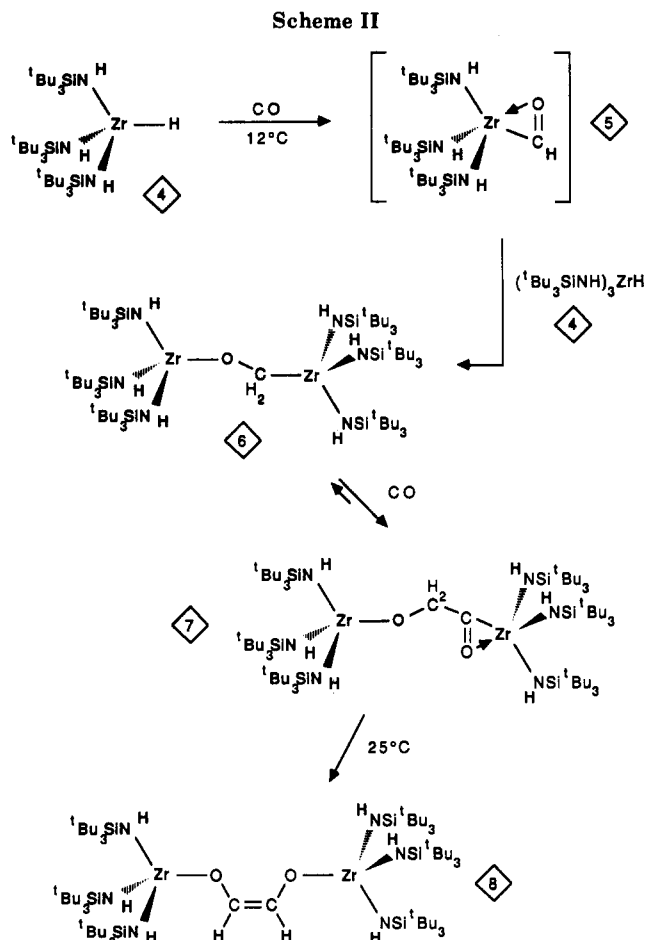
178, $^2J_{CH}$ = 21, $^1J_{CC}$ = 91, $^3J_{HH}$ = 3 Hz), consistent with the atom connectivity and cis geometry proposed.

When the carbonylation of (^{t}Bu$_3$SiNH)$_3$ZrH (4) was conducted in C$_6$D$_{12}$, the turbidity characteristic of the aforementioned benzene experiment was eliminated. Resonances attributable to two intermediates en route to cis enediolate 8 appeared during the 5–10 min required for complete reaction. The observation period could be significantly prolonged to ~45–50 min by immediate transfer of the freshly thawed cyclohexane solution to a 12 °C NMR spectrometer probe. The initial intermediate (6) displayed a singlet at δ 4.38 in the ^{1}H NMR spectrum accompanied by a carbon peak at δ 84.83 in the ^{13}C{^{1}H} NMR spectrum; use of ^{13}CO caused the proton resonance to split into a doublet ($^1J_{CH}$ = 133 Hz), while the coincident methylene carbon became a triplet. These features implied a bridging oxymethylene structure, [(^{t}Bu$_3$SiNH)$_3$Zr]$_2$(μ-OCH$_2$) (6), as shown in Scheme II. In 6, both (^{t}Bu$_3$SiNH)$_3$Zr units are equivalent by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy, presumably due to a rapid 1,2-dyotropic rearrangement[33] common to aldehyde bridges of this type.[34] Attempts to observe

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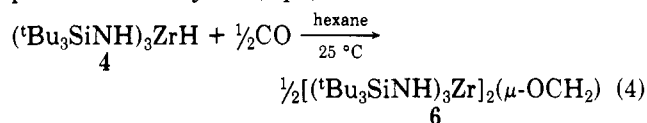
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this process at low temperatures were hampered by the insolubility of the binuclear species at temperatures below 12 °C. It is likely that $[({}^{t}Bu_{3}SiNH)_{3}Zr]_{2}(\mu\text{-}OCH_{2})$ (6) is formed from reduction of a transient formyl, $({}^{t}Bu_{3}SiNH)_{3}Zr(\eta^{2}\text{-}CHO)$ (5), by 1 equiv of 4.[20,21] Although a $\mu\text{-}\eta^{1}:\eta^{2}\text{-}CH_{2}O$ bridging group cannot be ruled out, model studies suggest that the steric interactions are severe enough to prohibit this ground-state structure.

The second intermediate was identified as $[({}^{t}Bu_{3}SiNH)_{3}Zr]_{2}(\mu\text{-}\eta^{1}:\eta^{2}\text{-}OCH_{2}C{=}O)$ (7), the acyl obtained from insertion of CO into the Zr–C bond of 6. The methylene of 7-${}^{13}C_{2}$ is observed as a doublet in the ${}^{1}H$ NMR spectrum ($C_{6}D_{12}$, δ 5.77, ${}^{1}J_{CH}$ = 141 Hz) and a doublet of triplets in the ${}^{13}C$ NMR spectrum (δ 84.05, ${}^{1}J_{CH}$ = 141, ${}^{1}J_{CC}$ = 13 Hz). No coupling is observed between the methylene protons and the acyl carbon, which resonates at δ 323.4 (d, ${}^{1}J_{CC}$ = 13 Hz) in the ${}^{13}C$ NMR spectrum, a position diagnostic for η^{2}-bound early-metal acyls.[6,17,18] The ${}^{1}J_{CC}$ value of 13 Hz is conspicuously low,[35] but those of related titanium acyls (cf. Cp_{2}-$\overline{TiCMe{=}CMeCH_{2}}{}^{13}C{=}O$, ${}^{1}J_{CC}$ = 12 Hz; $Cp_{2}ClTi{}^{13}COMe$, ${}^{1}J_{CC}$ = 19 Hz) possess similar values.[36]

Having identified the intermediates spectroscopically, we reasoned that $[({}^{t}Bu_{3}SiNH)_{3}Zr]_{2}(\mu\text{-}OCH_{2})$ (6) might be isolable upon stoichiometric carbonylation of $({}^{t}Bu_{3}SiNH)_{3}ZrH$ (4). Treatment of the hydride 4 with 0.5 equiv of CO in hexane precipitated 6 as a pure white powder in 79% yield (eq 4). The filtrate was examined
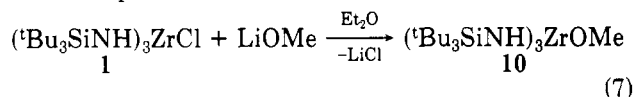
$$({}^{t}Bu_{3}SiNH)_{3}ZrH + \tfrac{1}{2}CO \xrightarrow[25\ °C]{hexane}$$
$$\underset{4}{}$$
$$\tfrac{1}{2}[({}^{t}Bu_{3}SiNH)_{3}Zr]_{2}(\mu\text{-}OCH_{2}) \quad (4)$$
$$\underset{6}{}$$

by ${}^{1}H$ NMR spectroscopy and found to contain both 4 and cis enediolate 8 in approximately a 2:1 ratio. The formation of 6 is apparently irreversible, since exposure of 6 to 1 atm of 90% ${}^{13}CO$ provided $[({}^{t}Bu_{3}SiNH)_{3}Zr]_{2}(\mu\text{-}\eta^{1}:\eta^{2}\text{-}OCH_{2}{}^{13}C{=}O)$ (7-${}^{13}C{=}O$) as the primary product. When it was warmed, the latter cleanly converted to $[({}^{t}Bu_{3}SiNH)_{3}Zr]_{2}(cis\text{-}\mu\text{-}O(H)C{=}{}^{13}C(H)O)$ (8-${}^{13}C$), whose ${}^{1}H$ NMR spectrum exhibited an eight-line pattern for the vinylic protons, having coupling constants identical with those extracted for 8-${}^{13}C_{2}$ (i.e. ${}^{1}J_{CH}$ = 178, ${}^{2}J_{CH}$ = 21, ${}^{3}J_{HH}$ = 3 Hz).

The bridged formaldehyde complex $[({}^{t}Bu_{3}SiNH)_{3}Zr]_{2}\text{-}(\mu\text{-}OCH_{2})$ (6) also correlated with known derivatives upon thermolysis. It was previously shown that the transient $({}^{t}Bu_{3}SiNH)_{2}Zr{=}NSi{}^{t}Bu_{3}$ (3), generated upon elimination of MeH from $({}^{t}Bu_{3}SiNH)_{3}ZrMe$ (2, eq 3), could be trapped by THF.[24] In accord with precedent, thermolysis of $[({}^{t}Bu_{3}SiNH)_{3}Zr]_{2}(\mu\text{-}OCH_{2})$ (6) in THF afforded equimolar amounts of $({}^{t}Bu_{3}SiNH)_{2}(THF)Zr{=}NSi{}^{t}Bu_{3}$ (9) and $({}^{t}Bu_{3}SiNH)_{3}ZrOMe$ (10) as indicated by eqs 5 and 6.

$$[({}^{t}Bu_{3}SiNH)_{3}Zr]_{2}(\mu\text{-}OCH_{2}) \xrightarrow[110\ °C,\ 3\ h]{THF}$$
$$\underset{6}{}$$
$$({}^{t}Bu_{3}SiNH)_{3}ZrOMe + [({}^{t}Bu_{3}SiNH)_{2}Zr{=}NSi{}^{t}Bu_{3}] \quad (5)$$
$$\underset{10}{}\qquad\qquad\qquad \underset{3}{}$$

$$3 \rightarrow ({}^{t}Bu_{3}SiNH)_{2}(THF)Zr{=}NSi{}^{t}Bu_{3} \quad (6)$$
$$\underset{9}{}$$
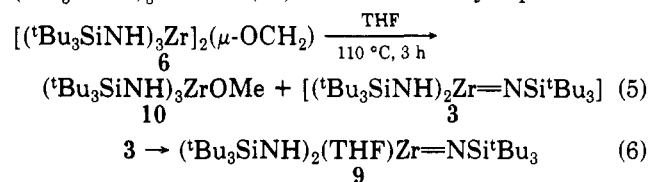
While 9 was characterized via spectral comparison with

an authentic sample, the methoxy derivative 10 displayed resonances at δ 3.82 in the ${}^{1}H$ and δ 59.55 in the ${}^{13}C\{{}^{1}H\}$ NMR spectra, thereby establishing the methoxy functionality. A sample of 10 prepared independently from $({}^{t}Bu_{3}SiNH)_{3}ZrCl$ (1) and LiOMe in ether (eq 7) exhibited identical spectral features.

$$({}^{t}Bu_{3}SiNH)_{3}ZrCl + LiOMe \xrightarrow[-LiCl]{Et_{2}O} ({}^{t}Bu_{3}SiNH)_{3}ZrOMe$$
$$\underset{1}{}\qquad\qquad\qquad\qquad\qquad\qquad \underset{10}{}$$
$$(7)$$

Conclusions

A cis stereochemistry is found for the enediolate product $[({}^{t}Bu_{3}SiNH)_{3}Zr]_{2}(cis\text{-}\mu\text{-}O(H)C{=}C(H)O)$ (8), obtained from treatment of the monohydride $({}^{t}Bu_{3}SiNH)_{3}ZrH$ (4) with CO. The observation of $[({}^{t}Bu_{3}SiNH)_{3}Zr]_{2}(\mu\text{-}OCH_{2})$ (6) and the penultimate acyl $[({}^{t}Bu_{3}SiNH)_{3}Zr]_{2}(\mu\text{-}\eta^{1}:\eta^{2}\text{-}OCH_{2}C{=}O)$ (7) give credence to the generality of this sequence, as it pertains to monohydrides of the early metals and actinides. Unfortunately, despite the utilization of hard, electronegative, ancillary ligands, spectroscopic detection of an intermediate formyl akin to $Cp^{*}{}_{2}Th(OCH{}^{t}Bu_{2})(CHO)^{16}$ has not been realized. Related early-transition-metal CO migratory insertions are considered thermodynamically unfavorable; hence, $[({}^{t}Bu_{3}SiNH)_{3}Zr(CHO)]$ (5) is presumed to be kinetically accessible. While this interpretation is favored, it is also conceivable that formation of a transient formyl (5) is slow relative to its ensuing reduction by another monohydride (4) molecule.[20,21] In support of this proposition are the aforementioned spectroscopically equivalent $({}^{t}Bu_{3}SiNH)_{3}Zr$ moieties in the μ-formaldehyde 6. An accidental degeneracy of the ${}^{1}H$ and ${}^{13}C\{{}^{1}H\}$ NMR resonances is considered highly unlikely, since different solvents (e.g. $C_{6}D_{6}$, $C_{6}D_{12}$) gave similar results; thus, a 1,2-dyotropic shift is probably operative.[33,34] The steric interactions associated with this unimolecular rearrangement are effectively the same as those pertaining to the bimolecular reduction of presumed formyl 5 by hydride 4; therefore, the latter process may still be relatively swift.

Oxymethylene complexes such as $[({}^{t}Bu_{3}SiNH)_{3}Zr]_{2}(\mu\text{-}OCH_{2})$ (6) may undergo hydrogenolysis, generating hydride and methoxide fragments, making these species a branch point between CO hydrogenation and C–C coupling processes.[3] Under mild conditions, 6 does not react with H_{2}, but $({}^{t}Bu_{3}SiNH)_{3}ZrOMe$ (10) is formed via a thermolytic elimination pathway in THF. Formally a 1,2-elimination, the process is nonetheless reminiscent of a hydrogenolysis or alkyl/hydride reductive elimination.

One phenomenon common to several systems concerns the sole formation of cis enediolate from proposed 1,2-hydrogen shift pathways. Theoretical studies suggest that the η^{2}-acyl possesses carbenium ion character,[6,15] rather than the oxycarbene depiction previously favored.[3,21] The hydrogen migration can be regarded as a 1,2-hydride shift to an acyl acceptor orbital (LUMO) that consists primarily of an empty p orbital situated on the acyl carbon. Similar alkyl shifts are thought to be operative in generating $M(cis\text{-}O(R)C{=}C(R)O)$ fragments upon carbonylation of $MR(\eta^{2}\text{-}COR)$ complexes,[6,15,37,38] although CO attack at the

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acyl and subsequent rearrangement is also plausible,[17,39-41] and Rothwell et al. have noted the coupling of η^2-acyl and isoelectronic η^2-iminoacyl functionalities.[42] The geometry of bridging cis enediolate ligands is thought to be dictated by a sterically favorable conformer in which the hydride shift occurs. In the [('Bu₃SiNH)₃Zr]₂(μ-η^1:η^2-OCH₂C=O) (7) to [('Bu₃SiNH)₃Zr]₂(cis-μ-O(H)C=C(H)O) (8) conversion, a similar case can be made. Specific orientations of precursor acyls may lead to the cis enediolate products, as in the examples of Floriani (B, Scheme I), Erker (C), Tilley[41] (Cp*Cl₃(py)Ta(η^2-O=CCH₂'Bu) → Cp*Cl₃(py)-Ta(cis-O(H)C=CH'Bu)), and Marks[18] (M(η^2-O=CCH₂'Bu) → M(cis-O(H)C=CH'Bu), M = Cp₃Th, Cp*₂ThCl). However, in both the Cp₂*Th(OR)H system of Marks et al.[16] and the ('Bu₃SiNH)₃Zr sequence discussed herein, the steric arguments for cis products are not indisputable; thus, it is possible that this configuration may result from stereoelectronic control of the hydride shift pathway.

With regard to the 1,2-hydride shift pathway proposed for the transformation of 7 to 8, another plausible mechanism that invokes a transient Zr=N linkage must be considered. Abstraction of an amido proton by the acyl carbon would produce an intermediate aldehyde adduct of 3 (i.e., ('Bu₃SiNH)₂(RCHO)Zr=NSi'Bu₃, 3·OHCR). The subsequent transfer of a methylene hydrogen from the aldehyde would generate [('Bu₃SiNH)₃Zr]₂(cis-μ-O(H)C=C(H)O) (8). Several factors mitigate against this process: (1) the imido-forming abstraction reactions are prohibitively slow at 25 °C, (2) from the standpoint of sterics, the best transition-state conformation leads to the trans product, and (3) exposure of ('Bu₃SiNH)₂(THF)Zr=NSi'Bu₃ (9) to aldehydes appears to yield products derived from deoxygenation of the carbonyl functionality, not hydrogen transfer.[24] A full investigation of the reactivity of 9 with aldehydic and related substrates is currently underway.

Experimental Section

General Considerations. All manipulations were performed with use of either glovebox or high-vacuum-line techniques. Hydrocarbon solvents containing 1-2 mL of added tetraglyme were distilled under nitrogen from purple benzophenone ketyl and vacuum-transferred from the same prior to use. Benzene-d_6 and cyclohexane-d_{12} were dried over activated 4-Å molecular sieves, vacuum-transferred, and stored under N₂; toluene-d_8 was dried over sodium benzophenone ketyl. All glassware was oven-dried, and NMR tubes were additionally flamed under dynamic vacuum. Carbon monoxide (Matheson) and ¹³CO (Cambridge) were used as received. Purification of ZrCl₄ (Aldrich) was accomplished via sublimation (10⁻⁴ Torr, 180 °C), and 'Bu₃SiNH₂[26] was prepared according to published procedures.

NMR spectra were obtained with Varian XL-200 and XL-400 spectrometers. Chemical shifts are reported relative to TMS, and all couplings are in Hz. Infrared spectra, recorded on a Mattson FT-IR instrument interfaced to an AT&T PC7300 computer, were used as fingerprints and are not reported. Analyses were performed by Analytische Laboratorien, Elbach, West Germany, or Oneida Research Services, Whitesboro, NY. Satisfactory C, H, and N analyses of the methyl (2) and hydride (1) derivatives could not be obtained from either firm on various samples. For complexes of the ('Bu₃SiNH)₃ZrX type, it has been noted that for

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X = hydride or alkyl, elemental analyses are consistently low in all elements. When X = OR or halide, the species give satisfactory combustion analyses. From inspection of the data, it is possible that the former substituents may encourage the formation of SiN or SiC during the combustion process.

Procedures. 1. 'Bu₃SiNHLi.[25] To a flask containing 10.0 g of 'Bu₃SiNH₂ (46.4 mmol) in 40 mL of hexane at -78 °C was added 34 mL of "BuLi (55 mmol, 1.6 M in hexane). The reaction mixture was slowly warmed to 25 °C and then stirred for an additional 1.5 h. The solvent volume was reduced by half and the resulting slurry stirred for 30 min at -78 °C. The product was obtained as a white powder after filtration and vacuum drying (6.99 g). A second crop yielded an additional 2.73 g (94% total). ¹H NMR (C₆D₆): δ -1.99 (s, NH, 1 H), 1.15 (s, 'Bu, 27 H).

2. ('Bu₃SiNH)₃ZrCl (1). To a flask containing ZrCl₄ (2.77 g, 11.89 mmol) and 'Bu₃SiNHLi (7.90 g, 35.69 mmol) was added 125 mL of diethyl ether via vacuum transfer. The mixture was warmed from -78 to 25 °C over 1.5 h and subsequently stirred for 8 h. The volatiles were then removed in vacuo, the residue was extracted with hexane (6 × 120 mL), and the extracts were and filtered. Concentrating the solution volume to 70 mL and cooling to -10 °C resulted in the formation of colorless crystals that were collected by filtration and dried in vacuo to yield colorless 1 (8.09 g, 88%). ¹H NMR (C₆D₆): δ 1.24 (s, 'Bu, 81 H), 4.89 (s, NH, 3 H). ¹³C{¹H} NMR: δ 23.32 (SiC), 30.93 (CH₃). Anal. Calcd for ZrSi₃ClN₃C₃₆H₈₄: C, 56.15; H, 11.00; N, 5.46. Found: C, 55.91; H, 10.93; N, 5.36.

3. ('Bu₃SiNH)₃ZrCH₃ (2). To a 100-mL flask containing 1 (3.647 g, 4.74 mmol) slurried in 50 mL of Et₂O at -78 °C was added 1.78 mL of MeMgBr (4.97 mmol, 2.8 M in Et₂O) via syringe. After the mixture was slowly warmed to 25 °C (1.5 h) and stirred for a total of 9.5 h, the ether was removed by vacuum transfer and replaced with 30 mL of hexane. Filtration and extraction (3 × 30 mL) gave a filtrate that was concentrated and cooled to yield 3.22 g (91%) of 2 as white microcrystals. ¹H NMR (C₆D₆): δ 0.63 (s, ZrCH₃, 3 H), 1.24 (s, 'Bu, 81 H), 4.10 (s, NH, 3 H). ¹³C{¹H} NMR: δ 23.24 (SiC), 28.68 (ZrC), 30.92 (CH₃).

4. ('Bu₃SiNH)₃ZrH (4). To a 200-mL glass bomb containing 2 (2.30 g, 3.07 mmol) was added 40 mL of cyclohexane via vacuum distillation. The bomb was immersed in liquid N₂, dihydrogen was admitted (1 atm), and the mixture was warmed to 25 °C (~7 equiv of H₂, ~3 atm). The vessel was placed in a 95 °C bath for 8 h and cooled to 25 °C and the solvent and H₂/MeH were removed, leaving an off-white crystalline solid. The solid was dissolved in 25 mL of hexane and the solution filtered, concentrated, and cooled to -78 °C. The white crystalline 4 collected by filtration (1.40 g, 62%) contained ~1-2% impurities (primarily 'Bu₃SiNH)₄Zr) by ¹H NMR spectroscopy. Recrystallization from hexane gave 930 mg (41%) containing <1% impurities (¹H NMR). ¹H NMR (C₆D₆): δ 1.25 (s, 'Bu, 81 H), 4.87 (s, NH, 3 H), 9.60 (s, ZrH, 1 H). ¹³C{¹H} NMR: δ 22.91 (SiC), 30.84 (CH₃). IR (C₆H₁₂): ν(ZrH/ZrD) = 1553/1117 cm⁻¹.

5. [('Bu₃SiNH)₃Zr]₂(μ-OCH₂) (6). To a flask containing 4 (0.510 g, 0.693 mmol) and 12 mL of hexane at ~10 °C was admitted 0.5 equiv of CO via a gas bulb. The white formaldehyde complex precipitated over 20 min, and the reaction mixture was subsequently stirred for 1 h. Colorless 6 was collected by filtration, washed once with 12 mL of hexane, and dried under vacuum (0.413 g, 79%). ¹H NMR (C₆D₁₂): δ 1.18 (s, 'Bu, 162 H), 3.67 (s, NH, 6 H), 4.38 (s, CH₂, 2 H). ¹³C{¹H} NMR: δ 23.71 (SiC), 31.70 (CH₃), 84.83 (CH₂, J_{CH} = 133 (6-¹³C)). IR (6 (6-¹³C), Nujol, cm⁻¹): 3236 (w, ν(NH)), 1385 (m), 1365 (m), 1068 (1053, s br, ν(CO)), 1010 (m), 1006 (w sh), 930 (m, br), 870 (m, br), 818 (vs), 809 (vs), 618 (s). Anal. Calcd for Zr₂Si₆ON₆C₇₃H₁₇₀: C, 58.49; H, 11.43; N, 5.61. Found: C, 58.65; H, 10.84; N, 5.66.

6. [('Bu₃SiNH)₃Zr]₂(cis-μ-O(H)C=C(H)O) (8). To a flask containing [('Bu₃SiNH)₃Zr]₂(μ-OCH₂) (0.315 g, 0.210 mmol) was added hexane (12 mL) by vacuum transfer. The slurry was brought to ~12 °C and exposed to 1 atm of CO for a period of 0.5 h. A pale yellow color was observed as the slightly soluble starting material dissolved and reacted. The result was a colorless, homogeneous solution, which was filtered and concentrated. Colorless microcrystals of 8 were collected by filtration at -10 °C and dried in vacuo (0.177 g, 55%). ¹H NMR (C₆D₁₂): δ 1.17 (s, 'Bu, 162 H), 3.66 (s, NH, 6 H), 5.62 (s, O(H)C=, 2 H). ¹³C{¹H} and ¹³C NMR: δ 23.71 (SiC), 31.39 (CH₃), 127.94 (O(H)C=,

Table III. Atomic Coordinates (×10⁴) and Equivalent Isotropic U's^a (Å² × 10⁴) for (^{t}Bu₃SiNH)₃ZrMe (2)

atom	x	y	z	U(eq)
Zr	2687 (1)	5420 (1)	9412 (1)	34 (1)
C	3086 (3)	4890 (5)	8450 (4)	61 (3)
Si1	2414 (1)	3028 (1)	10382 (1)	43 (1)
C11	2363 (4)	3400 (5)	11422 (4)	70 (3)
C111	2252 (5)	2486 (7)	11926 (5)	156 (7)
C112	1818 (3)	4164 (7)	11349 (6)	118 (5)
C113	2954 (4)	3972 (7)	11928 (5)	119 (5)
N1	2320 (2)	4161 (3)	9820 (3)	47 (2)
C12	1720 (3)	2115 (4)	9823 (4)	57 (3)
C121	1616 (4)	2065 (6)	8912 (4)	87 (4)
C122	1806 (4)	995 (5)	10132 (5)	83 (3)
C123	1066 (3)	2498 (4)	9842 (5)	99 (4)
C13	3223 (3)	2457 (5)	10436 (5)	72 (3)
C131	3731 (3)	3313 (6)	10619 (6)	114 (5)
C132	3445 (4)	1614 (6)	11107 (5)	104 (4)
C133	3206 (4)	1962 (6)	9607 (5)	105 (4)
N2	1978 (2)	6461 (3)	8886 (3)	44 (2)
Si2	1210 (1)	6741 (1)	8243 (1)	39 (1)
C21	1245 (3)	8076 (4)	7766 (4)	52 (2)
C211	1347 (4)	8934 (5)	8390 (5)	86 (3)
C212	1823 (3)	8134 (5)	7463 (5)	80 (3)
C213	652 (3)	8354 (5)	7048 (4)	75 (3)
C22	968 (3)	5684 (4)	7418 (4)	56 (2)
C221	274 (3)	5662 (5)	6959 (5)	86 (3)
C222	1303 (4)	5815 (6)	6789 (4)	88 (4)
C223	1161 (3)	4614 (5)	7786 (4)	74 (3)
C23	661 (3)	6759 (6)	8918 (4)	63 (3)
C231	12 (3)	7267 (7)	8505 (5)	101 (4)
C232	987 (4)	7326 (8)	9701 (5)	101 (4)
C233	544 (3)	5657 (6)	9171 (5)	95 (4)
N3	3417 (2)	6087 (3)	10310 (3)	48 (2)
Si3	3935 (1)	7118 (1)	10717 (1)	42 (1)
C31	3513 (3)	7958 (5)	11311 (4)	54 (2)
C311	2954 (3)	8565 (6)	10755 (5)	89 (4)
C312	3969 (4)	8725 (6)	11891 (5)	96 (4)
C313	3204 (4)	7279 (7)	11781 (5)	97 (4)
C32	4727 (3)	6527 (5)	11425 (4)	66 (3)
C321	5281 (3)	7286 (7)	11665 (5)	104 (4)
C322	4930 (4)	5605 (6)	11012 (6)	107 (4)
C323	4649 (4)	6097 (7)	12202 (5)	100 (4)
C33	4053 (3)	7864 (5)	9814 (4)	65 (3)
C331	4362 (4)	8932 (7)	10058 (5)	104 (4)
C332	3421 (3)	7984 (6)	9117 (4)	85 (4)
C333	4493 (4)	7264 (8)	9455 (5)	120 (5)

^{a}Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

AA'XX' pattern,[32] $^1J_{CH} = 178$, $^2J_{CH} = 21$, $^1J_{CC} = 91$, $^3J_{HH} = 3$ (8-$^{13}C_2$)). IR (8 (8-$^{13}C_2$), Nujol, cm^{-1}): 3245 (w, ν(NH)), 1600 (vw, br), 1385 (m), 1365 (m), 1158 (1139, s, ν(CO)), 1068 (1055, s, ν(CO)), 1010 (m), 1002 (w), 930 (m), 875 (m, br), 820 (vs), 805 (vs), 615 (s). Anal. Calcd for Zr₂Si₆O₂N₆C₇₄H₁₇₀: C, 58.20; H, 11.22; N, 5.50. Found: C, 57.82; H, 11.52; N, 5.39.

7. (^{t}Bu₃SiNH)₃ZrOMe (10). Into a flask containing (^{t}Bu₃SiNH)₃ZrCl (0.400 g, 0.520 mmol) and LiOMe (0.024 g, 0.623 mmol) was distilled THF (18 mL) at −78 °C. The reaction mixture was warmed slowly to 25 °C and stirred for 8 h, at which time the volatiles were removed in vacuo. The white solid residue was extracted with hexane (3 × 10 mL) and filtered. Concentration and cooling produced a crop of white microcrystals, which was collected by filtration and dried in vacuo (0.189 g, 48%). ^{1}H NMR (C₆D₆): δ 1.25 (s, ^{t}Bu, 81 H), 3.59 (s, NH, 3 H), 3.82 (s, ZrOCH₃, 3 H). ^{13}C{^{1}H} NMR: δ 23.22 (SiC), 30.95 (ZrC), 59.55 (OCH₃). IR (Nujol, cm^{-1}): 3259 (m, ν(NH)), 1385 (m), 1365 (m), 1151 (s), 1045 (s, br ν(CO)), 1007 (m), 1000 (m), 928 (m), 872 (m, br), 823 (vs), 815 (vs), 617 (s). Anal. Calcd for ZrSi₃ON₃C₃₇H₈₇: C, 58.05; H, 11.45; N, 5.49. Found: C, 58.16; H, 11.51; N, 5.69.

8. Thermolysis of 6 in THF. Into a small bomb containing 30 mg (0.020 mmol) of 6 was distilled 10 mL of THF at −78 °C. The bomb was placed in a bath at ∼110–115 °C for 3 h. The THF was replaced with hexane, in which the resulting white solid was slurried. After removal of the solvent, the white powder was dried in vacuo. The powder was extracted into C₆D₆, and a ^{1}H NMR spectrum revealed an approximate 1:1 ratio of (^{t}Bu₃SiNH)₂(THF)Zr=NSi^{t}Bu₃ (9)[24] and 10.

9. NMR-Tube Reactions. Oven- and flame-dried 5-mm NMR tubes sealed onto 14/20 ground glass joints were charged with reagents in the drybox, and brought out on needle valve adapters. The samples were freeze–pump–thaw degassed (−196 °C) and sealed off with a torch.

a. [(^{t}Bu₃SiNH)₃Zr]₂(μ-η^1:η^2-OCH₂C=O) (7). To an NMR tube containing 16 mg of 4 (0.022 mmol) was added 0.4 mL of C₆D₁₂. Approximately 3 atm of CO (^{13}CO) was condensed in at −196 °C. When the mixture was warmed to ∼12 °C in the NMR probe, 6 was observed to form, followed by 7. Within 45–50 min, only minor amounts of the intermediates could be seen and 8 dominated the spectrum. ^{1}H NMR (7, C₆D₁₂): δ 1.15, 1.14 (s, ^{t}Bu, 81 H), 3.66 (s, OZr(NH)₃, 3 H), 3.85 (s, H₂CZr(NH)₃, 3 H), 5.77 (s, CH₂, 2 H). ^{13}C{^{1}H} and ^{13}C NMR: δ 23.67, 23.79 (SiC), 31.19, 31.57 (CH₃), 84.05 (dt, CH₂, $J_{CC} = 13$, $J_{CH} = 141$ Hz (7-$^{13}C_2$)), 323.40 (d, C=O, $J_{CC} = 13$ Hz).

b. ^{13}CO Addition to 6 To Give 7-^{13}C=O and 8-^{13}C. To an NMR tube containing 16 mg of 6 (0.011 mmol) was added 0.4 mL of C₆D₁₂. Approximately 3 atm of ^{13}CO was condensed in at −196 °C. When the mixture was warmed to ∼12 °C in the NMR probe, 7-^{13}C=O was observed to form, followed by 8-^{13}C. Analysis of the ^{1}H NMR spectrum of 8-^{13}C revealed the expected vinylic couplings ($^1J_{CH} = 178$, $^2J_{CH} = 21$, $^3J_{HH} = 3$ Hz).

Single-Crystal X-ray Diffraction Analysis of (^{t}Bu₃SiNH)₃ZrMe (2). A colorless cube (0.3 × 0.3 × 0.3 mm) of (^{t}Bu₃SiNH)₃ZrMe (2), obtained from hexane solution, was sealed in a Lindemann capillary. Preliminary X-ray diffraction photographs displayed monoclinic symmetry. Precise lattice constants, determined from a least-squares fit of 15 diffractometer-measured 2θ values at 25 °C, were $a = 22.052$ (3) Å, $b = 12.943$ (2) Å, $c = 17.320$ (2) Å, and $\beta = 108.93$ (1)°. The cell volume was 4676.1 (2) Å³, with a calculated density of 1.065 g/cm³, where $Z = 4$. The space group was determined to be $P2_1/c$, and the asymmetric unit consisted of C₃₇H₈₇N₃Si₃Zr. All unique diffraction maxima ($\pm h, -k, l$) with $2\theta \leq 50°$ were measured on a four-circle automated diffractometer (Nicolet R3m/V), by a variable-speed, 2θ–θ scan (2.00–15°/min) with graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å) at 25 °C. After correction for Lorentz, polarization, and background effects, 6083 (77.9%) of the unique data (7813) were judged observed ($|F_o| \geq 3\sigma|F_o|$).[43] The structural solution proceeded with the SHELXTL PLUS system. The Zr was located via Patterson synthesis, and the non-hydrogen light atoms were revealed by successive Fourier syntheses. Full-matrix, least-squares refinements (minimization of $\sum w(F_o - F_c)^2$, where w is based on counting statistics modified by an ignorance factor ($w^{-1} = \sigma^2(F) + 0.0008F^2$)) with anisotropic heavy atoms and all hydrogens included at calculated positions (Riding model, fixed isotropic U) converged to $R = 6.05\%$ and $R_w = 7.84\%$ (6083 reflections), with GOF = 1.66.[44] No absorption correction was attempted ($\mu = 3.30$ cm^{-1}), and a final difference Fourier map revealed no peaks greater than 0.55 e/Å³.

Supplementary Material Available: Information pertaining to the X-ray structural investigation of (^{t}Bu₃SiNH)₃ZrMe (2), including a summary of crystal data encompassing data collection and solution/refinement, tables of hydrogen atom coordinates, isotropic and anisotropic temperature factors, bond lengths, and bond angles, and a fully labeled ORTEP drawing (9 pages); a table of observed and calculated structure factors (28 pages). Ordering information is given on any current masthead page.

(43) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A* **1968**, *A24*, 321–324.

(44) $R = \sum ||F_o| - |F_c||/(\sum |F_o|)$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(|F_o|)^2]^{1/2}$.