

**Direct hydrosilylation by a zirconacycle with β -hydrogen**

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ARTICLE

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Azasilazirconacycle $\text{Cp}_2\text{Zr}\{\kappa^2\text{-N}(\text{SiHMe}_2)\text{SiHMeCH}_2\}$ (**1**) and formaldehyde react through an uncatalyzed addition reaction (hydrosilylation) to form an exocyclic methoxysilyl-substituted zirconacycle. Although **1** contains 2-center-2-electron SiH groups, this transformation parallels the reactions of non-classical $[\text{Cp}_2\text{ZrN}(\text{SiHMe}_2)_2]^+$ (**[2]⁺**) with carbonyls. Reactions of **1** with a series of nucleophilic and electrophilic agents were explored, as well as reactions of related β -SiH-containing silazidozirconium compounds, to develop a rationale for the unexpected hydrosilylation. For example, carbon monoxide and **1** react at the Zr–C bond to form $\text{Cp}_2\text{Zr}\{\kappa^2\text{-OC}(\text{=CH}_2)\text{SiHMeN}(\text{SiHMe}_2)\}$ (**7**), as does $\text{B}(\text{C}_6\text{F}_5)_3$ to give $\text{Cp}_2\text{Zr}\{\text{N}(\text{SiHMe}_2)\text{SiHMeCH}_2\text{B}(\text{C}_6\text{F}_5)_3\}$ (**8**). OPe_3 and *N,N*-dimethylamidopyridine (DMAP) do not appear to interact with **1**. In contrast, OPe_3 and DMAP react with non-classical compounds **[2]⁺** and zwitterionic **8**.

Introduction

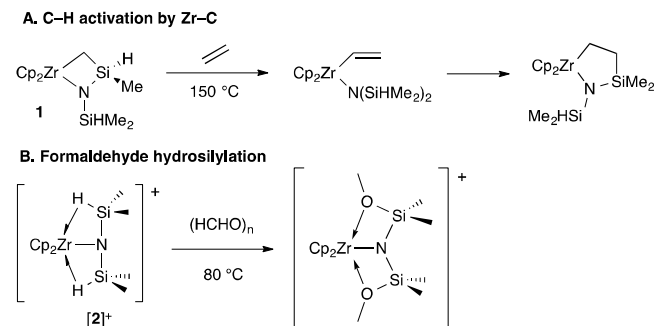
The β position in organometallic compounds is well-known as a reactive site involved in intramolecular abstraction and elimination processes.^{1, 2} In metal alkyl systems lacking the appropriate vacant metal orbitals, β -H elimination processes can be slow. As a result, alternative reaction pathways may become accessible. Similarly, d^0 metal amido compounds containing β -H are reluctant to undergo β -elimination. This inertness is proposed to be related to the geometric and electronic structure of β -agostic amides, which contain features that are generally dissimilar to those of the expected transition state of β -elimination.³ Notably, the structural distortion and spectroscopy of β -agostic amides are distinguished from those of alkyl ligands (that readily β -eliminate) by larger M–N–C angles and downfield ¹H NMR chemical shifts for the β -H.

In the absence of intramolecular elimination processes, alkyl and amide ligands containing β hydrogen are still reactive at that position. For example, rare earth and main group compounds of the tris(dimethylsilyl)methide or bis(dimethylsilyl)amido ligand react with Lewis acids via β -H abstraction.^{4–6} $\text{Cp}_2\text{Zr}\{\text{N}(\text{SiHMe}_2)_2\}\text{Et}$ reacts with $\text{B}(\text{C}_6\text{F}_5)_3$ via β -H abstraction from the amide or ethyl ligands.⁷ Other main group alkyls, such as ZnEt_2 and $[\text{Al}]\text{CH}_2\text{CHMe}_2$, also react with $\text{B}(\text{C}_6\text{F}_5)_3$ via β -H abstraction.^{8, 9} In some of these cases, the compounds display features associated with non-classical or agostic β -H interactions, but not always. Often non-classical structures are fluxional, and therefore it is difficult to experimentally assess if the intermolecular reactions of the β -H containing ligand occur from non-classical structures or molecular configurations in which the β -E–H is a classical 2-center-2-electron bond.

Therefore, we sought to compare the reactivity of classical and non-classical β -hydrogen-containing compounds. The

recently reported azasilazirconacyclobutane compound $\text{Cp}_2\text{Zr}\{\kappa^2\text{-N}(\text{SiHMe}_2)\text{SiHMeCH}_2\}$ (**1**) with a pendent β -SiHMe₂ group and an endocyclic β -SiH provides such an opportunity.¹⁰ The rigid cyclic structure of the molecule results in classical bonding for both Si–H groups. In contrast, the cationic compound $[\text{Cp}_2\text{ZrN}(\text{SiHMe}_2)_2][\text{HB}(\text{C}_6\text{F}_5)_3]$ (**[2]⁺**) is characterized by unusual spectroscopic and geometric features supporting the presence of two non-classical Zr–H–Si structures.⁷ Related diagnostic structures were previously reported for rare earth tetramethyldisilazido compounds,^{11–14} but before that only molybdenum, niobium, tantalum and zirconium tetramethyldisilazido compounds were reported.^{15–17}

Moreover, studies of these two zirconium compounds reveal unusual reactivity. The Zr–C bond of **1** reacts with ethylene through a sequence involving C–H bond activation (Scheme 1A), whereas a β -hydrogen-free analog was unchanged after treatment with C_2H_4 under forcing conditions.¹⁰



Scheme 1. A. C–H bond activation by a classical β -SiH containing zirconacycle **1**. B. Hydrosilylation of formaldehyde by non-classical SiH in **[2]⁺**.

Interestingly, the non-classical compound $[2]^+$ and carbonyls react by addition of the Si–H bonds to the C=O (Scheme 1B). Compound $[2]^+$ also reacts with *N,N*-dimethylaminopyridine (DMAP) via attack at a silicon center to give Si–N bond formation and a new zirconium hydride.⁷ In order to understand the effect of classical and non-classical β -hydrogen on reactivity, we decided to investigate the reactions of **1** with two-electron donors and carbonyls to compare with the reactivity of $[2]^+$. The results of those studies are described in the present disclosure. Unexpectedly, **1** and formaldehyde react to give a methoxysilyl, and we describe a number of combinations of related SiH-containing zirconium silazidos and carbonyls that provide some insight into the unusual addition reaction. We also compare the reactivity of **1**, $[2]^+$, and a zwitterionic analog of $[2]^+$ prepared by the reaction of **1** and $B(C_6F_5)_3$.

Experimental

All manipulations were performed under a dry argon atmosphere using standard Schlenk techniques or under a nitrogen atmosphere in a glovebox unless otherwise indicated. Water and oxygen were removed from benzene and pentane solvents using an IT PureSolv system. Benzene- d_6 was heated to reflux over Na/K alloy and vacuum-transferred. Methylene chloride- d_2 was vacuum transferred from CaH_2 and stored under N_2 in the glovebox. PMe_3 , triethylphosphine oxide, DMAP, benzophenone, paraformaldehyde and paraformaldehyde- d_2 were purchased from Aldrich and were used as received. Acetone, acetophenone, and cyclohexanecarbaldehyde were degassed and stored over 4 Å molecular sieves before use. The compounds $Cp_2Zr\{\kappa^2-N(SiHMe_2)SiHMeCH_2\}$ (**1**),¹⁰ $Cp_2Zr\{N(SiHMe_2)_2\}Et$,⁷ $Cp_2Zr\{N(SiHMe_2)_2\}H$,¹⁸ $Cp_2Zr\{\kappa^2-NSiMe_2(SiHMe_2)\}PMe_3$ (**6-PMe₃**),¹⁰ and $B(C_6F_5)_3$ ¹⁹ were prepared following literature procedures.

1H , $^{13}C\{^1H\}$, ^{11}B and $^{29}Si\{^1H\}$ NMR spectra were collected on a Bruker DRX-400 spectrometer, a Bruker Avance III-600 spectrometer, or an Agilent MR 400 spectrometer. ^{11}B NMR spectra were referenced to an external sample of $BF_3 \cdot Et_2O$. ^{15}N chemical shifts were determined either by 1H - ^{15}N HMBC experiments on a Bruker Avance II 700 spectrometer with a Bruker Z-gradient inverse TXI $^1H/^{13}C/^{15}N$ 5mm cryoprobe or by 1H - ^{15}N CIGARAD experiments on an Agilent MR400 spectrometer; ^{15}N chemical shifts were originally referenced to liquid NH_3 and recalculated to the CH_3NO_2 chemical shift scale by adding -381.9 ppm. Assignments of NMR resonances are supported by 1H - 1H and heteronuclear correlation experiments. Infrared spectra were measured on a Bruker IFS66v FTIR. Elemental analyses were performed using a Perkin-Elmer 2400 Series II CHN/S. X-ray diffraction data was collected on a Bruker APEX II diffractometer.

$Cp_2Zr\{\kappa^2-N(SiMe_2OMe)SiHMeCH_2\}$ (3**)**. Metallacycle **1** (0.115 g, 0.326 mmol) and paraformaldehyde (0.010 g, 0.33 mmol) were suspended in benzene (2 mL) and heated to 80 °C for 5.5 h. The reaction mixture was filtered, and the volatile components of the soluble portion were evaporated under reduced pressure to give a yellow oil. Extraction with pentane and evaporation of the pentane provided **3** as a viscous yellow oil (0.119 g, 0.31 mmol, 95%). 1H NMR (benzene- d_6 , 600 MHz, 25 °C): δ 5.91 (s, 5 H, C_5H_5), 5.87 (s, 5 H, C_5H_5), 4.50 (m, $^1J_{SiH} = 202$ Hz, 1 H, $NSiHMe$), 3.29 (s, 3 H, $SiMe_2OMe$), 1.90 (dd, $^2J_{HH} = 12.4$ Hz, $^3J_{HH} = 4.0$ Hz, 1 H, CH_2), 1.55 (dd, $^2J_{HH} = 12.4$ Hz, $^3J_{HH} = 2.2$ Hz, 1 H, CH_2), 0.32 (d, $^3J_{HH} = 2.4$

Hz, 3 H, CH_2SiHMe), 0.12 (s, 3 H, $SiMe_2OMe$), 0.10 (s, 3 H, $SiMe_2OMe$). $^{13}C\{^1H\}$ NMR (benzene- d_6 , 150 MHz, 25 °C): δ 112.32 (C_5H_5), 112.29 (C_5H_5), 50.02 ($SiMe_2OMe$), 35.56 ($ZrCH_2$), 2.14 (CH_2SiHMe), 1.26 ($SiMe_2OMe$), 0.80 ($SiMe_2OMe$). $^{15}N\{^1H\}$ NMR (benzene- d_6 , 61 MHz, 25 °C): δ -246.8 . $^{29}Si\{^1H\}$ NMR (benzene- d_6 , 119.3 MHz, 25 °C): δ -6.4 ($SiMe_2OMe$), -65.9 ($SiHMe$). IR (KBr, cm^{-1}): 2952 m, 2827 w, 2072 m br (ν_{SiH}), 1597 w, 1443 w, 1249 s, 1087 s, 1016 s, 900 s, 796 s br, 720 s. Anal. Calcd for $C_{15}H_{25}Si_2NOZr$: C, 47.07; H, 6.58; N, 3.66. Found: C, 47.37; H, 6.59; N, 3.44.

$Cp_2Zr\{N(SiHMe_2)t-Bu\}OMe$ (4**)**. Paraformaldehyde (0.008 g, 0.255 mmol) and $Cp_2Zr\{N(SiHMe_2)t-Bu\}H$ (0.090 g, 0.255 mmol) were suspended in benzene (5 mL) at room temperature, and the mixture was heated at 60 °C for 7 h. The resulting yellow solution was filtered, and the benzene supernatant was evaporated to dryness under reduced pressure to afford compound **4** as an analytically and spectroscopically pure yellow solid (0.075 g, 0.195 mmol, 87%). 1H NMR (benzene- d_6 , 600 MHz, 25 °C): δ 6.00 (s, 10 H, C_5H_5), 4.10 (m, $^1J_{SiH} = 164$ Hz, 1 H, $SiHMe_2$), 3.69 (s, 3 H, OMe), 1.27 (s, 9 H, CMe_3), 0.33 (d, $^3J_{HH} = 3.6$ Hz, 6 H, $SiHMe_2$). $^{13}C\{^1H\}$ NMR (benzene- d_6 , 150 MHz, 25 °C): δ 112.37 (C_5H_5), 61.89 (OMe), 57.66 (CMe_3), 35.10 (CMe_3), 3.07 ($SiHMe_2$). $^{15}N\{^1H\}$ NMR (benzene- d_6 , 61 MHz, 25 °C): δ -263 . $^{29}Si\{^1H\}$ NMR (benzene- d_6 , 119.3 MHz, 25 °C): δ -34.9 . IR (KBr, cm^{-1}): 2950 w, 2908 s, 2801 s, 2085 s (ν_{SiH}), 1600 w, 1456 m, 1382 s, 1354 s, 1244 s, 1189 s, 1144 s br, 1015 s, br, 921 s br, 794 s br, 687 s. Anal. Calcd for $C_{15}H_{27}Si_2NOZr$: C, 53.35; H, 7.64; N, 3.66. Found: C, 53.05; H, 7.60; N, 3.47. mp 82–84 °C.

$Cp_2Zr\{\kappa^2-O,N-OCMe_2SiMe_2N(SiHMe_2)\}$ (5**)**. A benzene solution (2 mL) of $Cp_2Zr\{N(SiHMe_2)_2\}Et$ (0.063 g, 0.165 mmol) and acetone (14.5 mL, 0.197 mmol) was heated at 60 °C for 4 h. The volatiles were evaporated under reduced pressure, and the product was extracted with pentane (2 × 3 mL) to give **5** (0.059 g, 0.144 mmol, 87%) as a yellow solid. X-ray quality crystals were grown from a concentrated pentane solution at -30 °C. 1H NMR (benzene- d_6 , 600 MHz, 25 °C): δ 6.10 (s, 10 H, C_5H_5), 4.30 (m, $^1J_{SiH} = 188.4$ Hz, 1 H, SiH), 1.25 (s, 6 H, $ZrOCMe_2$), 0.25 (d, $^3J_{HH} = 3.2$ Hz, 6 H, $SiHMe_2$), 0.22 (s, 6 H, $CSiMe_2$). $^{13}C\{^1H\}$ NMR (benzene- d_6 , 150 MHz, 25 °C): δ 114.27 (C_5H_5), 83.88 ($OCMe_2$), 29.01 ($ZrOCMe_2$), 2.90 ($CSiMe_2$), 2.25 ($SiHMe_2$). $^{29}Si\{^1H\}$ NMR (benzene- d_6 , 119.3 MHz, 25 °C): δ 24.6 ($CSiMe_2$), -23.6 ($SiHMe_2$). IR (KBr, cm^{-1}): 3104 w, 3070 w, 2961 s, 2897 m, 2851 m, 2085 m br (ν_{SiH}), 1443 m, 1369 m, 1352 m, 1246 s, 1163 m, 1148 m, 1113 s, 1015 s, 993 s, 946 s, 916 s br, 795 s br, 764 s. Anal. Calcd for $C_{17}H_{29}NOSi_2Zr$: C, 49.70; H, 7.12; N, 3.40. Found: C, 50.01; H, 6.81; N, 2.84. mp 82–90 °C.

$Cp_2Zr\{\kappa^2-NSiMe_2(SiHMe_2)\}PMe_3$ (6-PMe₃**)**. The synthesis and NMR characterization data of **6-PMe₃** was previously reported in reference 10. A benzene solution of $Cp_2Zr\{N(SiHMe_2)_2\}Et$ (0.028 g, 0.073 mmol) and 1.1 equiv of PMe_3 were heated at 65 °C for 2.5 h to give a deep red solution. The volatiles were removed under reduced pressure and the product was extracted with pentane (0.019 g, 0.044 mmol, 61 %). Red X-ray quality needle crystals were grown from a concentrated pentane solution at -30 °C. 1H NMR (benzene- d_6 , 600 MHz, 25 °C): δ 5.40 (s, 10 H, C_5H_5), 5.18 (br, 1 H, SiH), 0.93 (d, $^2J_{PH} = 9$ Hz, 9 H, PMe), 0.42 (d, $^3J_{HH} = 4.8$ Hz, 6 H, $SiHMe_2$), 0.40 (s, 6 H, $SiMe_2$). $^{13}C\{^1H\}$ NMR (benzene- d_6 , 150 MHz, 25 °C): δ 104.72 (C_5H_5), 20.98 (d, $^1J_{PC} = 21.8$ Hz, PMe), 3.62 ($SiMe_2$ and $SiHMe$ overlapped). $^{15}N\{^1H\}$ NMR (benzene- d_6 , 61 MHz, 25 °C): δ -331.1 . ^{31}P NMR (benzene- d_6 , 243 MHz, 25 °C): δ 18.67. $^{29}Si\{^1H\}$ NMR (benzene- d_6 , 119.3 MHz, 25 °C): δ 18.67.

°C): δ -12.9 ($^1J_{\text{SiH}} = 177.0$ Hz, SiHMe₂), -26.9 ($^2J_{\text{PSi}} = 74.0$ Hz, SiMe₂).

Cp₂Zr{κ²-OC(=CH₂)SiHMeN(SiHMe₂)} (7). Compound **1** (0.116 g, 0.329 mmol) was dissolved in benzene (15 mL), the solution was placed in a flask with a resealable teflon valve, and the reaction mixture was degassed with freeze-pump-thaw cycles (3×). The vessel was charged with CO (1 atm), and the reaction mixture was heated to 85 °C for 9 h. Evaporation of the volatile components, extraction of the resulting yellow residue with pentane, and evaporation of the pentane provided **7** as yellow microcrystalline solid (0.045 g, 0.12 mmol, 36%). ¹H NMR (benzene-*d*₆, 400 MHz, 25 °C): δ 6.09 (s, 5 H, C₅H₅), 6.06 (s, 5 H, C₅H₅), 5.43 (m, $^1J_{\text{SiH}} = 207$ Hz, 1 H, NSiHMe), 4.91 (s br, 1 H, C=CH₂), 4.48 (s br, 1 H, C=CH₂), 4.27 (m, $^1J_{\text{SiH}} = 190$ Hz, 1 H, NSiHMe₂), 0.41 (d, $^3J_{\text{HH}} = 3.2$ Hz, 3 H, OCNSiHMe) 0.24 (d, $^3J_{\text{HH}} = 3.1$ Hz, 3 H, ZrNSiHMe₂), 0.18 (d, $^3J_{\text{HH}} = 3.2$ Hz, 3 H, ZrNSiHMe₂). ¹³C{¹H} NMR (benzene-*d*₆, 125 MHz, 25 °C): δ 173.42 (OCCH₂), 115.31 (C₅H₅), 115.27 (C₅H₅), 98.41 (OCCH₂), 3.35 (OCSiHMe), 2.27 (SiMe₂), 0.73 (SiMe₂). ²⁹Si{¹H} NMR (benzene-*d*₆, 119.3 MHz, 25 °C): δ -10.5 (SiHMe), -24.6 (SiHMe₂). IR (KBr, cm⁻¹): 3083 w, 2953 s, 2075 s br (ν_{SiH}), 1609 m, 1576 s (ν_{C=C}), 1442 s, 1361 m, 1249 s, 1176 s, 1015 s, 916 s br, 796 s br. Anal. Calcd for C₁₅H₂₃Si₂NOZr: C, 47.32; H, 6.09; N, 3.68. Found: C, 47.73; H, 5.85; N, 3.28. mp 120 °C (decomp).

Cp₂Zr{N(SiHMe₂)SiHMeCH₂B(C₆F₅)₃} (8). Compound **1** (0.082 g, 0.232 mmol) and B(C₆F₅)₃ (0.125 g, 0.244 mmol) were allowed to react in benzene (5 mL). A light-yellow oil precipitated from the benzene solution. The benzene was separated from the oil with a pipet. The oil was washed with benzene (2 × 5 mL), extracted with methylene chloride (1 × 5 mL), and evaporated to dryness to give a pale yellow solid. This solid was washed with pentane (2 × 5 mL) and dried under vacuum to give **8** as a white solid (0.159 g, 0.184 mmol, 79 %). ¹H NMR (bromobenzene-*d*₅, 600 MHz, 25 °C): δ 5.54 (s, 5 H, C₅H₅), 5.46 (s, 5 H, C₅H₅), 1.64 (br d, $^2J_{\text{HH}} = 15$ Hz, 1 H, CH₂), 0.61 (br d, $^2J_{\text{HH}} = 13.0$ Hz, 1 H, CH₂), 0.02 (br overlapping signal, $^1J_{\text{SiH}} = 81$ Hz, 4 H, SiHMe₂ and SiHMeCH₂B(C₆F₅)₃), -0.04 (br s, 3 H, SiHMe₂), -0.07 (br s, 3 H, SiHMeCH₂B(C₆F₅)₃), -0.54 (br s, $^1J_{\text{SiH}} = 83$ Hz, 1 H, SiHMe₂). ¹³C{¹H} NMR (bromobenzene-*d*₅, 150 MHz, 25 °C): δ 148.23 (C₆F₅), 146.65 (C₆F₅), 138.08 (C₆F₅), 136.49 (C₆F₅), 134.90 (C₆F₅), 108.17 (C₅H₅), 107.74 (C₅H₅), 8.87 (CH₂B(C₆F₅)₃), -2.05 (SiMe₂), -2.80 (CH₂SiHMe), -2.88 (SiMe₂). ¹¹B NMR (bromobenzene-*d*₅, 119.3 MHz, 25 °C): δ -14.4. ¹⁹F NMR (bromobenzene-*d*₅, 564 MHz, 25 °C): δ -131.9 (d, $^3J_{\text{FF}} = 21.3$ Hz, 6 F, *o*-F), -162.2 (t, $^3J_{\text{FF}} = 21.5$ Hz, 3 F, *p*-F), -165.7 (t, $^3J_{\text{FF}} = 19.9$ Hz, 6 F, *m*-F). ²⁹Si{¹H} NMR (bromobenzene-*d*₅, 119.3 MHz, 25 °C): δ -36.2 (SiMe), -47.3 (SiMe₂). IR (KBr, cm⁻¹): 3125 w, 2963 w, 2905 w, 1737 m (ν_{SiH}), 1641 s, 1579 m br, 1512 s, 1456 vs br, 1257 s, 1169 s, 1101 s, 1081 s, 1017 s, 972 s, 925 s, 860 s, 811 s, 778 s, 750 m. Anal. Calcd for BC₃₂F₁₅H₂₃Si₂NZr: C, 44.45; H, 2.68; N, 1.62. Found: C, 44.01; H, 2.51; N, 1.51. mp 113-120 °C.

Cp₂ZrN{SiMe₂(OCHMe₂)}{SiMe(OCHMe₂)CH₂B(C₆F₅)₃} (9). Acetone (32.5 mL, 0.444 mmol) was added to a methylene chloride solution (10 mL) of **8** (0.128 g, 0.148 mmol), and the mixture was stirred for 20 min. All volatile substances were removed under reduced pressure. The residue was washed with pentane (2 × 2 mL). The solid was dried in *vacuo* to give **9** as a yellow solid (0.141 g, 0.144 mmol, 97%). X-ray quality crystals were grown from a concentrated methylene chloride solution at -30 °C. ¹H NMR (methylene chloride-*d*₂, 600 MHz, 25 °C):

δ 6.47 (s, 5 H, C₅H₅), 6.32 (s, 5 H, C₅H₅), 4.13 (m, 1 H, Me₂SiOCH), 3.95 (m, 1 H, BCH₂SiOCH), 1.53 (d, $^3J_{\text{HH}} = 6.3$ Hz, 3 H, BCH₂SiOCH(CH₃)₂), 1.52 (d, $^3J_{\text{HH}} = 6.2$ Hz, 3 H, Me₂SiOCH(CH₃)₂), 1.49 (d, $^3J_{\text{HH}} = 6.5$ Hz, 3 H, Me₂SiOCH(CH₃)₂), 1.29 (d, $^3J_{\text{HH}} = 6.5$ Hz, 3 H, BCH₂SiOCH(CH₃)₂), 0.31 (s br, 3 H, SiMe₂), 0.13 (s br, 3 H, SiMe₂), -0.21 (s br, 3 H, SiMe). ¹³C{¹H} NMR (methylene chloride-*d*₂, 150 MHz, 25 °C): δ 149.54 (br, C₆F₅), 147.95 (br, C₆F₅), 139.36 (br, C₆F₅), 137.90 (br, C₆F₅), 136.39 (br, C₆F₅), 116.26 (C₅H₅), 115.29 (C₅H₅), 75.07 (Me₂SiOCH), 74.91 (BCH₂SiOCH), 25.44 (Me₂SiOCH(CH₃)₂), 25.15 (BCH₂SiOCH(CH₃)₂), 24.77 (Me₂SiOCH(CH₃)₂), 24.29 (BCH₂SiOCH(CH₃)₂), 4.29 (SiMe₂), 4.20 (SiMeCH), 4.15 (SiMe₂). ²⁹Si{¹H} NMR (methylene chloride-*d*₂, 119.3 MHz, 25 °C): δ 13.8 (SiMe₂), 5.7 (SiMeCH₂). ¹⁹F NMR (methylene chloride-*d*₂, 376 MHz, 25 °C): δ -133.1 (d, $^3J_{\text{FF}} = 22.1$ Hz, 6 F, *o*-F), -165.2 (t, $^3J_{\text{FF}} = 20.4$ Hz, 3 F, *p*-F), -168.3 (t, $^3J_{\text{FF}} = 20.5$ Hz, 6 F, *m*-F). ¹¹B NMR (methylene chloride-*d*₂, 79.5 MHz, 25 °C): δ -15.1. Anal. Calcd for BC₃₈F₁₅H₃₅Si₂NO₂Zr: C, 46.53; H, 3.60; N, 1.43. Found: C, 46.34; H, 4.00; N, 1.14. mp 77-85 °C.

Cp₂ZrN{(SiMe₂DMAP)SiHMeCH₂B(C₆F₅)₃}H (10a) and **Cp₂ZrN{(SiHMe₂)SiMe(DMAP)CH₂B(C₆F₅)₃}H** (10b).

Compound **8** (0.049 g, 0.056 mmol) and DMAP (0.125 g, 0.057 mmol) were allowed to react in methylene chloride (2 mL) to form a yellow solution. The solution was stirred for 5 min., and then the solvent was evaporated. The resulting material was washed with pentane (2 × 5 mL) and then dried to give a mixture of Cp₂ZrN{(SiMe₂DMAP)SiHMeCH₂B(C₆F₅)₃}H (10a) and Cp₂ZrN{(SiHMe₂)SiMe(DMAP)CH₂B(C₆F₅)₃}H (10b) (0.055 g, 0.056 mmol, 99%) as a yellow crystalline solid in a 1.65:1 ratio as determined by integration of the ¹H NMR spectrum. ¹⁹F NMR resonances were assigned based on the ratio of 10a:10b, but ¹³C{¹H} NMR signals associated with the C₆F₅ groups were broad and not assigned to 10a or 10b. 10a: ¹H NMR (methylene chloride-*d*₂, 600 MHz, -53 °C): δ □□□(d, $^3J_{\text{HH}} = 7.3$ Hz, 2 H, α-NC₅H₄NMe₂), 6.72 (d, $^3J_{\text{HH}} = 7.2$ Hz, 2 H, β-NC₅H₄NMe₂), 5.61 (s, 5 H, C₅H₅), 5.60 (s, 5 H, C₅H₅), 3.93 (br s, 1 H, ZrH), 3.17 (s, 6 H, NMe₂), 1.17 (br d, $^2J_{\text{HH}} = 8.2$ Hz, 2 H, BCH₂), 0.53 (s, 3 H, SiMe₂), 0.48 (s, 3 H, SiMe₂), 0.28 (overlapped with SiHMe₂ resonance, assigned by ¹H-¹H COSY experiment, SiH), 0.25 (br s, 6 H, SiHMe₂). ¹³C{¹H} NMR (methylene chloride-*d*₂, 125 MHz, -53 °C): δ 155.28 (*ipso*-NC₅H₄NMe₂), 142.31 (α-NC₅H₄NMe₂), 106.92 (β-NC₅H₄NMe₂), 105.39 (C₅H₅), 105.01 (C₅H₅), 40.13 (NC₅H₄NMe₂), 8.30 (br, BCH₂), 1.05 (SiMe₂), 1.03 (SiMe₂), -1.96 (SiHMe₂). ¹¹B NMR (methylene chloride-*d*₂, 119.3 MHz, -53 °C): δ -14.7. ¹⁵N{¹H} NMR (methylene chloride-*d*₂, 61 MHz, -53 °C): δ -193.8 (NC₅H₄NMe₂), -295.8 (NC₅H₄NMe₂), -317.7 (ZrN). ¹⁹F NMR (methylene chloride-*d*₂, 564 MHz, -53 °C): δ -133.3 (br, 6 F, *o*-F), -164.4 (t, $^3J_{\text{FF}} = 20.2$ Hz, 3 F, *p*-F), -167.7 (d, $^3J_{\text{FF}} = 21.1$ Hz, 6 F, *m*-F). ²⁹Si{¹H} NMR (methylene chloride-*d*₂, 119.3 MHz, -53 °C): δ -4.6 (SiMe₂DMAP), -63.9 (d, $^1J_{\text{SiH}} = 112.3$ Hz, SiHMe₂). 10b: ¹H NMR (methylene chloride-*d*₂, 600 MHz, -53 °C): δ □□□(d, $^3J_{\text{HH}} = 6.8$ Hz, 2 H, α-NC₅H₄NMe₂), 6.53 (d, $^3J_{\text{HH}} = 6.5$ Hz, 2 H, β-NC₅H₄NMe₂), 5.86 (s, 5 H, C₅H₅), 5.47 (s, 5 H, C₅H₅), 3.99 (br s, 1 H, ZrH), 3.17 (s, 6 H, NMe₂), 1.33 (br d, $^2J_{\text{HH}} = 14.1$ Hz, 2 H, BCH₂), 1.29 (br, 1 H, SiH), 0.39 (br s, 6 H, SiMe and SiHMe₂), 0.27 (br s, 3 H, SiHMe₂). ¹³C{¹H} NMR (methylene chloride-*d*₂, 125 MHz, -53 °C): δ 156.08 (*ipso*-NC₅H₄NMe₂), 142.47 (α-NC₅H₄NMe₂), 105.81 (C₅H₅), 105.73 (β-NC₅H₄NMe₂), 105.21 (C₅H₅), 40.20 (NC₅H₄NMe₂), 10.50 (br, BCH₂), -0.47 (SiMe₂), -1.20 (SiMe₂), -1.96 (SiHMe₂). ¹¹B NMR (methylene chloride-

d_2 , 119.3 MHz, $-53\text{ }^\circ\text{C}$): δ -14.7 . $^{15}\text{N}\{^1\text{H}\}$ NMR (methylene chloride- d_2 , 61 MHz, $25\text{ }^\circ\text{C}$): δ -192.3 ($\text{NC}_5\text{H}_4\text{NMe}_2$), -295.8 ($\text{NC}_5\text{H}_4\text{NMe}_2$), -311.8 (ZrN). ^{19}F NMR (methylene chloride- d_2 , 564 MHz, $-53\text{ }^\circ\text{C}$): δ -135.3 (d, $^3J_{\text{FF}} = 22.3$ Hz, 6 F, *o*-F), -164.7 (t, $^3J_{\text{FF}} = 20.2$ Hz, 3 F, *p*-F), -167.5 (br, 6 F, *m*-F). $^{29}\text{Si}\{^1\text{H}\}$ NMR (methylene chloride- d_2 , 119.3 MHz, $-53\text{ }^\circ\text{C}$): δ 11.4 (SiMe_2DMAP), -61.1 (d, $^1J_{\text{SiH}} = 115.0$ Hz, SiHMe_2). IR (KBr, cm^{-1}): 2959 m br, 1845 m vbr (ν_{SiH}), 1641 m ($\nu_{\text{C}_6\text{F}_5}$), 1601 m, 1565 s, 1511 s ($\nu_{\text{C}_6\text{F}_5}$), 1458 s br ($\nu_{\text{C}_6\text{F}_5}$), 1403 m, 1309 m, 1255 m, 1233 m, 1102 s br, 1069 s br, 1030 m, 972 s, 846 m, 804 s br, 681 m. Anal. Calcd for $\text{BC}_{39}\text{F}_{15}\text{H}_{33}\text{Si}_2\text{N}_3\text{Zr}$: C, 47.46; H, 3.37; N, 4.26. Found: C, 47.06; H, 3.84; N, 4.40.

Cp₂Zr{N(SiHMe₂)SiHMeCH₂B(C₆F₅)₃}OPe_t₃ (11). Compound **8** (0.053 g, 0.061 mmol) and OPe_t₃ (0.008 g, 0.061 mmol) react in methylene chloride (2 mL) to form a yellow solution. The solution was stirred for 5 min., the volatile materials were removed under reduced pressure, and the solid was washed with pentane (2 × 5 mL). The resulting material was then dried under vacuum to give **11** (0.057 g, 0.057 mmol, 93%) as a yellow crystalline solid. ^1H NMR (methylene chloride- d_2 , 600 MHz, $25\text{ }^\circ\text{C}$): δ 6.37 (s, 5 H, C₅H₅), 6.24 (s, 5

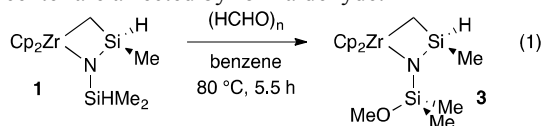
H, C₅H₅), 4.09 (m, $^1J_{\text{SiH}} = 169.4$ Hz, 1 H, SiHMe_2), 3.82 (m, $^1J_{\text{SiH}} = 177$ Hz, 1 H, SiHMe), 1.98 (m, 6 H, PCH₂), 1.19 (m, 9 H, PCH₂CH₃), 0.47 (d, $^3J_{\text{HH}} = 2.8$ Hz, 3 H, SiHMe_2), 0.37 (br, 2 H, CH₂), 0.27 (d, $^3J_{\text{HH}} = 3.0$ Hz, 3 H, SiHMe_2), -0.45 (d, $^3J_{\text{HH}} = 2.3$ Hz, 3 H, SiHMe). $^{13}\text{C}\{^1\text{H}\}$ NMR (methylene chloride- d_2 , 150 MHz, $25\text{ }^\circ\text{C}$): δ 149.65 (C₆F₅), 148.05 (C₆F₅), 139.17 (C₆F₅), 137.82 (C₆F₅), 137.48 (C₆F₅), 136.26 (C₆F₅), 115.13 (C₅H₅), 114.96 (C₅H₅), 18.79 (d, $^1J_{\text{PC}} = 65.5$ Hz, PCH₂CH₃), 11.57 (br, BCH₂), 5.94 (d, $^2J_{\text{PC}} = 4.7$ Hz, PCH₂CH₃), 2.79 (SiHMe), 2.06 (SiHMe₂), 1.34 (SiHMe₂). ^{11}B NMR (methylene chloride- d_2 , 119.3 MHz, $25\text{ }^\circ\text{C}$): δ -14.7 . ^{19}F NMR (methylene chloride- d_2 , 564 MHz, $25\text{ }^\circ\text{C}$): δ -133.5 (br, 6 F, *o*-F), -165.9 (t, $^3J_{\text{FF}} = 19.9$ Hz, 3 F, *p*-F), -168.8 (br, 6 F, *m*-F). ^{31}P NMR (methylene chloride- d_2 , 243 MHz, $25\text{ }^\circ\text{C}$): δ 101.9. $^{29}\text{Si}\{^1\text{H}\}$ NMR (methylene chloride- d_2 , 119.3 MHz, $25\text{ }^\circ\text{C}$): δ -7.7 (SiHMe), -26.3 (SiHMe₂). IR (KBr, cm^{-1}): 2956 m, 2914 w, 2890 w, 2135 m br (ν_{SiH}), 2099 m br (ν_{SiH}), 1641 m ($\nu_{\text{C}_6\text{F}_5}$), 1511 s ($\nu_{\text{C}_6\text{F}_5}$), 1457 s br ($\nu_{\text{C}_6\text{F}_5}$), 1271 m, 1250 m, 1166 m, 1082 s br, 1016 m, 973 s, 930 s, 861 s, 804 s, 681 m. Anal. Calcd for $\text{BC}_{38}\text{F}_{15}\text{H}_{38}\text{Si}_2\text{NOPZr}$: C, 45.69; H, 3.83; N, 1.40. Found: C, 45.81; H, 3.81; N, 1.36. mp 95–98 °C.

Table 1. Crystallographic Data for compounds 4, 5, 6-PMe₃, and 9.

	4	5	6-PMe₃	9
Chemical Formula	C ₁₇ H ₂₉ NOSiZr	C ₁₇ H ₂₉ NOSi ₂ Zr	C ₁₇ H ₃₂ NPSi ₂ Zr	C ₃₈ H ₃₅ BF ₁₅ NO ₂ Si ₂ Zr
Formula Weight	382.72	410.82	428.81	980.88
Crystal System	orthorhombic	monoclinic	monoclinic	orthorhombic
Unit-cell dimensions	$a = 8.586(1)\text{ \AA}$ $b = 13.622(2)\text{ \AA}$ $c = 32.542(5)\text{ \AA}$ $\alpha = \beta = \gamma = 90^\circ$	$a = 17.1498(14)\text{ \AA}$ $b = 8.7333(7)\text{ \AA}$ $c = 15.0209(13)\text{ \AA}$ $\alpha = \gamma = 90^\circ$; $\beta = 114.845(1)^\circ$	$a = 9.947(3)\text{ \AA}$ $b = 8.477(2)\text{ \AA}$ $c = 12.816(3)\text{ \AA}$ $\alpha = \gamma = 90^\circ$; $\beta = 97.646(4)^\circ$	$a = 17.6574(16)\text{ \AA}$ $b = 19.6319(18)\text{ \AA}$ $c = 22.653(2)\text{ \AA}$ $\alpha = \beta = \gamma = 90^\circ$
Volume	3805.8(10) Å ³	2041.5(3) Å ³	1071.0(5) Å ³	7852.6(12) Å ³
Space Group	P 2 ₁ 2 ₁ 2 ₁	P 2 ₁ /c	P 2 ₁	P b c a
Z	8	4	2	8
Reflections collected	36156	17916	9483	53924
Independent reflections	8690	4179	4374	10942
R _{int}	0.0888	0.0436	0.0408	0.0882
R I > 2σ(I)	R ₁ = 0.1220 wR ₂ = 0.2888	R ₁ = 0.0491 wR ₂ = 0.1260	R ₁ = 0.0369 wR ₂ = 0.0999	R ₁ = 0.0443 wR ₂ = 0.0911
R _{all}	R ₁ = 0.1324 wR ₂ = 0.2940	R ₁ = 0.0621 wR ₂ = 0.1345	R ₁ = 0.0377 wR ₂ = 0.1009	R ₁ = 0.0954 wR ₂ = 0.1114

Results and Discussion

The metallacycle Cp₂Zr{κ²-N(SiHMe₂)SiHMeCH₂} (**1**) and paraformaldehyde (H₂CO)_n react in benzene at 80 °C over 5.5 h to give Cp₂Zr{κ²-N(SiMe₂OMe)SiHMeCH₂} (**3**) in 95% yield (eqn (1)). In this transformation, a β-methoxy group is formed from the addition of formaldehyde to the exocyclic β-SiH. Neither the Zr–C bond nor the β-SiH on the endocyclic silicon center are affected by formaldehyde.



A singlet resonance at 3.29 ppm in the ^1H NMR spectrum of **3** was assigned to the methoxy group, and only one SiH signal was detected at 4.50 ppm. That signal was assigned by ^1H - ^{29}Si HMQC and COSY experiments; the latter showed scalar coupling to the ZrCH₂ proving that the SiH is part of the cyclic

structure. As in **1**, the (C₅H₅)₂, CH₂, and SiMe₂ groups are diastereotopic. The transformation of the exocyclic β-SiH is supported by observation of two SiMe resonances (3 H each) assigned to the SiMe₂OMe group that appeared as singlets rather than doublets as in **1**. The product and approximate rate of conversion are not affected when the reaction is performed in acetonitrile or in the presence of donor ligands such as PMe₃, OPe_t₃ or *para*-dimethylaminopyridine (DMAP).

In addition, only starting materials are observed upon treatment of **1** with excess benzophenone, acetophenone, or cyclohexanecarbaldehyde even for 12 h at 80 °C. Reaction with acetone (2 equiv.) at 80 °C overnight in benzene provides multiple unidentified products. Benzaldehyde gives a mixture of at least three products, one of which is tentatively assigned as a Zr–C insertion product based on the observation of a new resonance for the benzylic CH₂ in the ^1H NMR spectrum. Upon thermolysis of **1** with excess benzaldehyde at 60 °C, a small amount of toluene is generated (<5%) among unidentified zirconium-containing products. Compound **3** is inert toward further formaldehyde insertions under the conditions of eqn (1).

Apparently, the pendant β -SiH in **1** is essential for its reaction with formaldehyde because 2 equiv. of paraformaldehyde and $\text{Cp}_2\text{Zr}\{\kappa^2\text{-N,C-N}(t\text{-Bu})\text{SiHMeCH}_2\}$ (which contains only an endocyclic SiH)¹⁸ are unchanged after heating in benzene- d_6 at 120 °C for 12 h. Note that $\text{Cp}_2\text{Zr}\{\kappa^2\text{-N,C-N}(t\text{-Bu})\text{SiHMeCH}_2\}$ is available only as a mixture with $\{\text{Cp}_2\text{ZrN}(\text{SiHMe}_2)\}_2$. These experiments strongly suggest that the reaction of compound **1** and formaldehyde is unlikely to involve insertion into the Zr–C bond followed by a rearrangement. Such a pathway was considered because $\text{Cp}_2\text{Zr}\{\kappa^2\text{-CH}_2\text{SiMe}_2\text{CH}_2\}$ and formaldehyde react through insertion into the Zr–C bond to give $\text{Cp}_2\text{Zr}\{\kappa^2\text{-OCH}_2\text{CH}_2\text{SiMe}_2\text{CH}_2\}$.²⁰ In addition, it is worth noting that the β -SiH in **1** are classically bonded (2-center-2-electron bonding) based on its signals in the infrared spectrum (2074 cm^{-1}) and ^1H NMR spectrum (4.84 ppm, $^1J_{\text{SiH}} = 193$ Hz).¹⁰ Thus, there is no evidence for a side-on Zr–H–Si interaction that might enhance reactivity toward formaldehyde. In addition, the rigid cyclic structure of **1** likely inhibits non-classical bonding. Still, the cationic compound $[\mathbf{2}]^+$ that contains two non-classical Zr–H–Si interaction also reacts with formaldehyde to give $[\text{Cp}_2\text{ZrN}(\text{SiMe}_2\text{OMe})_2]^+$.⁷

Reactions of related zirconium hydrosilazido compounds with carbonyl compounds were explored based on this unusual insertion reaction; however, in many cases the reactions provide the expected chemistry at Zr–R site (X = H, Me, Et) rather than at the β -SiH. For instance, the acyclic hydrido disilazido zirconium compounds $\text{Cp}_2\text{Zr}\{\text{N}(\text{SiHMe}_2)_2\}\text{H}$ reacts with formaldehyde or acetone at the Zr–H bond rather than the β -SiH to afford the zirconium methoxide $\text{Cp}_2\text{Zr}\{\text{N}(\text{SiHMe}_2)_2\}\text{OMe}$ or isopropoxide $\text{Cp}_2\text{Zr}\{\text{N}(\text{SiHMe}_2)_2\}\text{Oi-C}_3\text{H}_7$.⁷ The reactions with excess carbonyl molecules under these conditions do not result in further conversion of the $\text{N}(\text{SiHMe}_2)_2$ group.⁷ Similarly, hydrido zirconium silazide containing one β -SiH group $\text{Cp}_2\text{Zr}\{\text{N}(\text{SiHMe}_2)t\text{-Bu}\}\text{H}$ also undergoes insertion with paraformaldehyde exclusively into the Zr–H bond to give $\text{Cp}_2\text{Zr}\{\text{N}(\text{SiHMe}_2)t\text{-Bu}\}\text{OMe}$ (**4**). This compound is isolated and fully characterized by spectroscopic methods, and its connectivity is confirmed by a single crystal X-ray diffraction study (Figure 1).

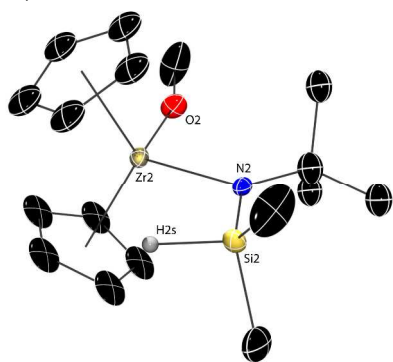


Figure 1. Thermal ellipsoid plot of one of two crystallographically independent molecules of $\text{Cp}_2\text{Zr}\{\text{N}(\text{SiHMe}_2)t\text{-Bu}\}\text{OMe}$ (**4**).

In contrast to the reactivity of hydrido zirconium silazides, the alkyl compound $\text{Cp}_2\text{Zr}\{\text{N}(\text{SiHMe}_2)_2\}\text{Me}$ and formaldehyde react to give a complex mixture after 9 h at 85 °C in benzene- d_6 . The combination of $\text{Cp}_2\text{Zr}\{\text{N}(\text{SiHMe}_2)_2\}\text{Et}$ and acetone affords a zirconacyclopentane product $\text{Cp}_2\text{Zr}\{\kappa^2\text{-O,N-}$

$\text{OCMe}_2\text{SiMe}_2\text{N}(\text{SiHMe}_2)\}$ (**5**) and ethane (Scheme 2). The latter byproduct was detected in ^1H NMR spectra of micromolar scale experiments performed in Teflon-sealed NMR tubes. Compound **5** was structurally characterized by a single crystal X-ray diffraction study (Figure 2) that proves Zr–O bond formation. In addition, the ^1H NMR spectrum clearly showed the two C_5H_5 , the SiMe_2 , and CMe_2 were equivalent, contrasting the diastereotopic groups present in **1** and **3**. A signal at 4.30 ppm ($^1J_{\text{SiH}} = 188$ Hz) was assigned to a single, terminal SiH moiety.

Presumably, compound **5** is formed through a two-step β -SiH abstraction and carbonyl insertion sequence. Abstraction gives a zirconium silanimine $\text{Cp}_2\text{Zr}\{\kappa^2\text{-N}(\text{SiHMe}_2)\text{SiMe}_2\}$ intermediate. Subsequent insertion of acetone into the Zr–Si

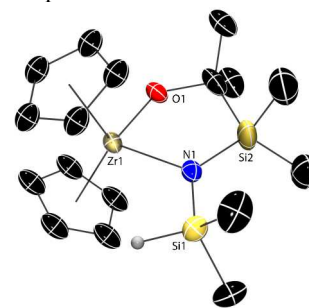
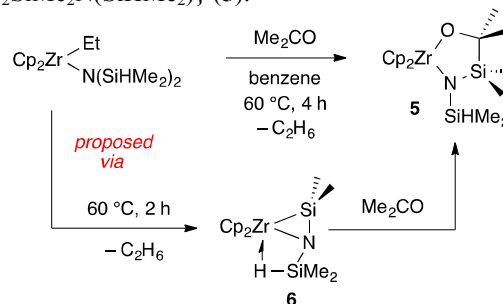


Figure 2. Rendered thermal ellipsoid plot of $\text{Cp}_2\text{Zr}\{\kappa^2\text{-O,N-OCMe}_2\text{SiMe}_2\text{N}(\text{SiHMe}_2)\}$ (**5**).



Scheme 2. Proposed pathway for the formation of **5**.

bond provides **5**. In support of this pathway, thermolysis of $\text{Cp}_2\text{Zr}\{\text{N}(\text{SiHMe}_2)_2\}\text{Et}$ in the absence of acetone provides the proposed silanimine intermediate $\text{Cp}_2\text{Zr}\{\kappa^2\text{-N}(\text{SiHMe}_2)\text{SiMe}_2\}$ (**6**).¹⁰ Notably, the proposed silanimine species contains a non-classical Zr–H–Si feature ($\delta_{\text{SiH}} = -2.23$ ppm, $^1J_{\text{SiH}} = 89$ Hz); however, we have not yet obtained X-ray quality crystals of **6**. Further evidence that $\text{Cp}_2\text{Zr}\{\text{N}(\text{SiHMe}_2)_2\}\text{Et}$ reacts to give a zirconium silanimine is provided by a trapping experiment with PMe_3 . Previously, we reported the solution-phase characterization of the trapped product, $\text{Cp}_2\text{Zr}\{\kappa^2\text{-NSiMe}_2(\text{SiHMe}_2)\}\text{PMe}_3$ (**6-PMe}_3**). Recently, we obtained crystals of **6-PMe}_3**, and a single crystal X-ray diffraction study reported here provides unambiguous evidence for formation of the zirconium silanimine complex (Figure 3).

In this case, the non-classical β -SiH in **6** is not the site of reactivity with acetone, which instead inserts into the Zr–Si bond to form a Zr–O bond. Again, this contrasts the reactivity of non-classical β -SiH-containing $[\mathbf{2}]^+$, which reacts with acetone to give β -SiOCHMe₂ groups.

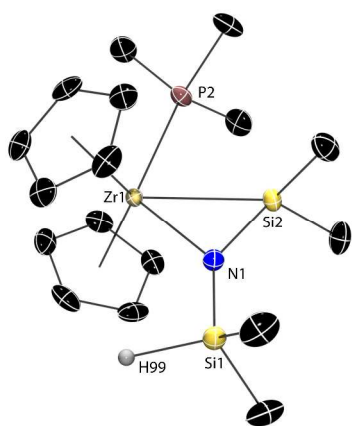
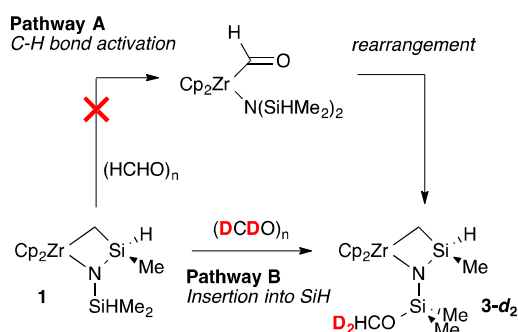


Figure 3. Thermal ellipsoid plot of $\text{Cp}_2\text{Zr}\{\kappa^2\text{-NSiMe}_2(\text{SiHMe}_2)\}\text{PMe}_3$ (**6-PMe₃**). Selected interatomic distances (Å): Zr1-N1, 2.195(2); Zr1-Si2, 2.660(1); Zr1-P2, 2.683(1); Zr1-Si1, 3.605(2); Zr1-H99, 3.7(2); Si1-N1, 1.680(3); Si1-N1, 1.693(3). Selected interatomic angles (°): Si1-N1-Si2, 138.1(2); Zr1-N1-Si1, 136.6(2); Zr1-N1-Si2, 85.3(1).

Thus, the interaction of formaldehyde and $\text{Cp}_2\text{Zr}\{\text{N}(\text{SiHMe}_2)_2\}\text{Et}$ apparently does not involve insertion into a Zr–C bond. This insertion pathway also seems unlikely for the reaction of **1** and formaldehyde. For this reason, we considered an alternative mechanism based on the reaction of compound **1** and ethylene. That reaction was proposed to involve vinylic C–H bond activation by the Zr–C moiety to give a $[\text{Zr}]\text{CH}=\text{CH}_2$ intermediate.¹⁰ Our next hypothesis, then, was that C–H bond activation of formaldehyde by **1** could give **3** via a Zr formyl intermediate followed by an isomerization (Pathway A, Scheme 3). Zirconium formyl compounds are exceedingly rare,²¹ and have been postulated as intermediates in zirconium models of Fisher-Tropsch chemistry.^{22–24} A rare isolated zirconium formyl is stabilized by interaction with a phosphine,²⁵ and such an intermediate might rearrange by an unanticipated pathway to give **3**.

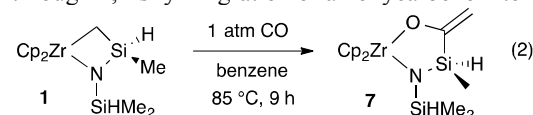


Scheme 3. A deuterium labeling experiment rules out CH bond activation as a first step in the conversion of **1** to **3**.

A deuterium labeling experiment tested this hypothesis: **1** and paraformaldehyde- d_2 react under the conditions of eqn (1) to give $\text{Cp}_2\text{Zr}\{\kappa^2\text{-N}(\text{SiMe}_2\text{OCHD}_2)\text{SiHMeCH}_2\}$ (**3-*d*₂**). ^1H NMR and ^2H NMR spectroscopy of this product indicated that deuterium was incorporated solely into the methoxy group, whereas a C–H bond activation would partly label the SiMe groups. Apparently, the reaction of **1** with paraformaldehyde occurs directly at the β -SiH without cleavage of the Zr–C bond.

Therefore, reactions of **1** and coordinating molecules, such as OPeEt_3 , PMe_3 , pyridine, and DMAP, were tested, but the ^1H

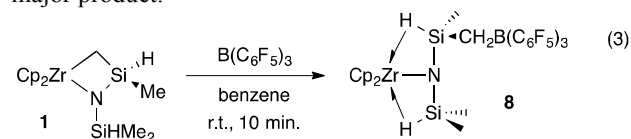
NMR spectrum of **1** was unchanged in the presence of these molecules. As noted above, these molecules apparently do not inhibit the reaction of **1** and formaldehyde. These experiments do not provide evidence for coordination of formaldehyde to the zirconium center in **1**, but that possibility is not unambiguously ruled out either. Therefore, other small-molecule reactivity was investigated to probe sites for coordination and reactivity. Reaction of **1** and CO at 85 °C for 3 h gives the five-membered cyclic insertion product containing a Zr–O bond and an exocyclic methylene group (**7**, eqn (2)). Carbon monoxide and azametallasilacyclobutanes (for group 4, Th and U centers) were previously suggested to involve 1,1-insertion of CO to give an acyl that rearranges to the product through 1,2-silyl migration of an oxycarbene intermediate.^{26–30}



Resonances in the ^1H NMR spectrum of **7** at 4.91 and 4.48 ppm were assigned to the exocyclic methylene. These signals showed correlations in ^1H - ^{13}C HMBC experiments to ^{13}C NMR signals at 173.4 and 98.4 ppm, which were assigned to the terminal and disubstituted unsaturated carbon centers.

Because hydrosilylation of CO would have been unexpected, we next attempted reactions of **1** and tris(perfluorophenyl)borane. This strong Lewis acid is known to activate organosilanes to give $[\text{R}_3\text{Si-H-B}(\text{C}_6\text{F}_5)_3]$ -type species,^{31–33} while organometallic alkyl and hydride compounds L_nMR react to form $[\text{L}_n\text{M-R-B}(\text{C}_6\text{F}_5)_3]$.³⁴ Recently, we have found that β -SiH-containing organometallic compounds such as $\text{M}[\text{C}(\text{SiHMe}_2)_3]_2(\text{THF})_2$ ($\text{M} = \text{Ca}, \text{Yb}$) react with $\text{B}(\text{C}_6\text{F}_5)_3$ by β -hydrogen abstraction.⁵ Interestingly, the reaction of $\text{B}(\text{C}_6\text{F}_5)_3$ and $\text{Cp}_2\text{Zr}\{\text{N}(\text{SiHMe}_2)_2\}\text{R}$ ($\text{R} = \text{Me}, \text{Et}, \text{CH}=\text{CHSiMe}_3$) involves competitive β -H abstraction and alkyl group abstraction.⁷ Thus, the interaction of **1** and $\text{B}(\text{C}_6\text{F}_5)_3$ should identify the most nucleophilic site in **1**.

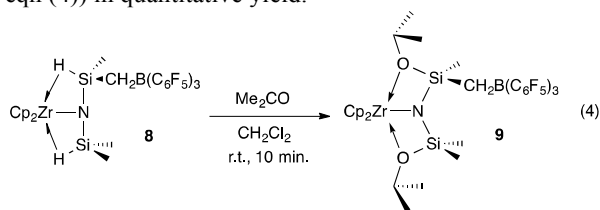
Alkyl group abstraction is observed to give the zwitterionic $\text{Cp}_2\text{Zr}\{\text{N}(\text{SiHMe}_2)\text{SiHMeCH}_2\text{B}(\text{C}_6\text{F}_5)_3\}$ (**8**; eqn (3)) as the major product.



A singlet resonance at -14.4 ppm in the ^{11}B NMR spectrum (acquired in bromobenzene- d_5) provided support for B–C bond formation, and a small signal at -25 ppm, assigned to $\text{HB}(\text{C}_6\text{F}_5)_3^-$ was also detected. The product precipitated as an oil from benzene, the oil was isolated and washed with more benzene to produce a solid, and methylene chloride extraction removes the trace borate signal to produce an off-white pure sample. As in compound **1**, the stereogenic silicon center resulted in diastereotopic C_5H_5 , CH_2 , and SiHMe_2 methyl groups, which each gave two signals in the ^1H NMR spectrum. In addition, two upfield ^1H NMR resonances at 0.02 and -0.54 ppm were assigned as silicon hydrides on the basis of strong coupling to the two silicon centers ($^1J_{\text{SiH}} = 81$ and 83 Hz). The far upfield chemical shifts and low silicon-hydrogen coupling constants are consistent with a rare multicenter non-classical interactions involving two side-on Zr–H–Si structures. Further support for this feature is provided by a low energy SiH stretch ($\nu_{\text{SiH}} = 1737 \text{ cm}^{-1}$) in IR spectrum. For comparison, the ν_{SiH} bands in **1** appear at 2074 cm^{-1} .¹⁰

Neutral diastereic d^0 amido compounds were previously reported for trivalent rare earth disilazido compounds, and these contain upfield SiH chemical shifts, low $^1J_{\text{SiH}}$ values, and low energy IR bands.^{11–14,35, 36} In addition, the reaction of $\text{B}(\text{C}_6\text{F}_5)_3$ and $\text{Cp}_2\text{Zr}\{\text{N}(\text{SiHMe}_2)_2\}\text{H}$ provides the cationic Zr amido complex $[\text{Cp}_2\text{ZrN}(\text{SiHMe}_2)_2]^+$, which contains two side-on Zr–H–Si interactions identified through a single crystal X-ray crystallographic study and distinct NMR and IR spectroscopic features.⁷ In that structure, the closest cation-anion contact is a long distance (3.27 Å) between one of the Si centers in $[\text{Cp}_2\text{ZrN}(\text{SiHMe}_2)_2]^+$ and a *meta*-F in the $[\text{HB}(\text{C}_6\text{F}_5)_3]^-$ anion. Thus, compound **8** represents the first zwitterionic complex of this type. Unfortunately, the material obtained proved recalcitrant toward forming X-ray quality crystals.

Further support for the proposed connectivity and zwitterionic nature of compound **8** was obtained through derivatization reactions. Following the reactivity of $[\text{Cp}_2\text{ZrN}(\text{SiHMe}_2)_2]^+$ ($[\text{2}]^+$),⁷ zwitterionic **8** reacts with two equiv. of acetone in methylene chloride to give the product $\text{Cp}_2\text{ZrN}\{\text{SiMe}_2(\text{OCHMe}_2)\}\{\text{SiMe}(\text{OCHMe}_2)\text{CH}_2\text{B}(\text{C}_6\text{F}_5)_3\}$ (**9**; eqn (4)) in quantitative yield.



The ^1H NMR spectrum of **9** contained four doublets at 1.53, 1.52, 1.49, and 1.29 ppm assigned to diastereotopic inequivalent isopropyl groups. Three singlets at 0.31, 0.13, and -0.21 ppm indicated that all three SiMe groups were inequivalent, as were the C_5H_5 ligands. X-ray quality crystals of **9** were grown from methylene chloride solution at room temperature. A single crystal X-ray diffraction study (Figure 4) confirms the Si– CH_2 – $\text{B}(\text{C}_6\text{F}_5)_3$ connectivity of **9** and supports the related assignment in **8**. The B1–C5 distance is 1.657(4) Å, and this distance is similar to the B–C distance in methyl-abstracted tris(pentafluorophenyl)borane compounds such as $(\text{C}_5\text{Me}_2\text{H}_3)_2\text{ZrMe}(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3$ (1.663(5) Å).³⁴

In addition, the X-ray diffraction study confirms the hydrosilylation of acetone by the β -SiH. The resulting isopropoxy groups bridge between the silicon and zirconium centers. The Zr1–O1 and Zr1–O2 distances of 2.319(2) and 2.321(2) Å are similar to the distances in cationic $[\text{Cp}_2\text{ZrN}(\text{SiMe}_2\text{OCHMe}_2)_2][\text{HB}(\text{C}_6\text{F}_5)_3]$. The oxygen in that cationic compound and in zwitterionic **9** are best described as silyl ethers that coordinate to the zirconium center.⁷ That is, the positive charge in the zwitterionic is located on zirconium rather than on the silicon centers. The methoxysilyl group on the silicon with the $\text{CH}_2\text{B}(\text{C}_6\text{F}_5)_3$ group is slightly twisted. Thus, the torsion angle Zr1–N1–Si2–O2 of $-9.8(1)^\circ$ is not planar, whereas the torsion angle associated with the SiMe_2OMe , Zr1–N1–Si1–O1 ($1.3(1)^\circ$) is nearly planar.

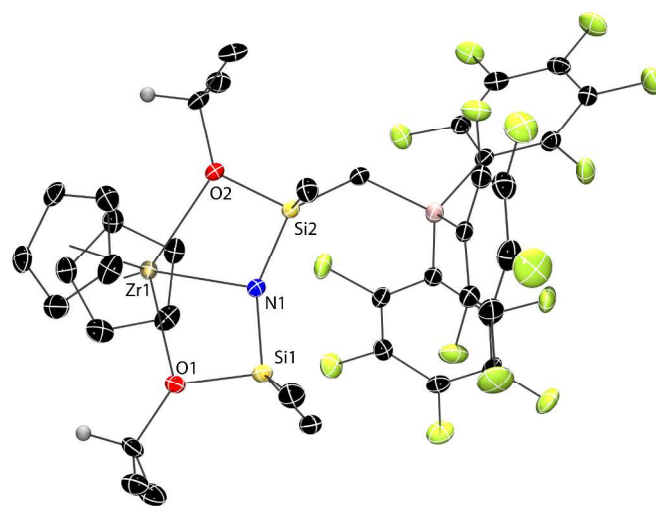
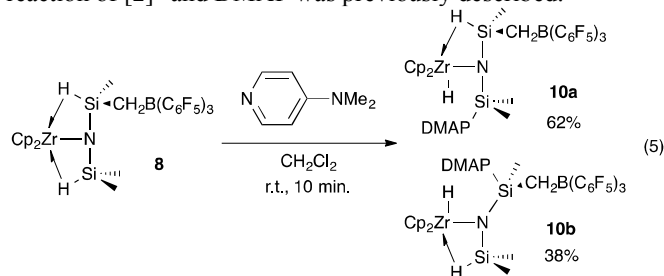


Figure 4. ORTEP diagram of $\text{Cp}_2\text{ZrN}\{\text{SiMe}_2(\text{OCHMe}_2)\}\{\text{SiMe}(\text{OCHMe}_2)\text{CH}_2\text{B}(\text{C}_6\text{F}_5)_3\}$ (**9**). Ellipsoids are drawn at 35% probability. All hydrogen atoms are not included for clarity. Significant interatomic distances (Å): Zr1–N1, 2.154(2); Zr1–O1, 2.319(2); Zr1–O2, 2.321(2); N1–Si1, 1.678(2); N1–Si2, 1.688(2); Si1–O2, 1.712(2); Si2–O1, 1.729(2); B1–C5, 1.657(4). Selected interatomic angles ($^\circ$): Zr1–N1–Si1, 105.1(1); Zr1–N1–Si2, 105.0(1); Si1–N1–Si2, 146.2(1); O1–Zr1–O2, 131.13(6); Zr1–N1–Si1–O2, 1.3(1); Zr1–N1–Si2–O1, $-9.8(1)$, O2–Si1–Si2–O1, $-9.0(1)$.

The reaction of formaldehyde and **8** provides a mixture of compounds. The ^1H NMR spectrum of the crude reaction mixture contains signals that may be assigned to SiOMe groups, but the product was not isolated.

We were further interested in the chemistry of **8** with 2-electron donors given the similar reactivity of **1** and $[\text{2}]^+$ with carbonyls, but the contrasting reactivity of the two compounds with 2-electron donors, as well as the unusual structure of zwitterionic **8** and its reactivity with acetone. Addition of DMAP to **8** results in Si–N bond formation and β -H migration to Zr to give the zwitterionic zirconium hydride $\text{Cp}_2\text{Zr}\{\text{N}(\text{SiMe}_2\text{DMAP})\text{SiHMeCH}_2\text{B}(\text{C}_6\text{F}_5)_3\}\text{H}$ (**10a**, 62%) and $\text{Cp}_2\text{Zr}\{\text{N}(\text{SiHMe}_2)\text{SiMe}(\text{DMAP})\text{CH}_2\text{B}(\text{C}_6\text{F}_5)_3\}\text{H}$ (**10b**, 38%) as a mixture of isomers (eqn (5)). As noted above, a similar reaction of $[\text{2}]^+$ and DMAP was previously described.⁷



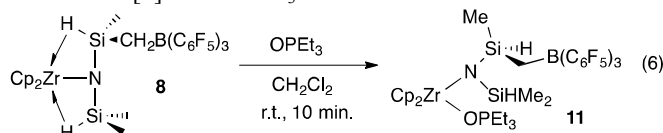
The formation of two isomers is due to the addition of DMAP to one of the two β -Si groups (SiHMe vs. SiHMe₂). DMAP coordination to the sterically less hindered Si position is favored (**10a**, 62%). The ^1H NMR spectrum acquired at room temperature in methylene chloride- d_2 was slightly broad, but the complete disappearance of **8** and the formation of two new species can be identified.

The low temperature NMR signals corresponding to **10** were sharper and better resolved. At 220 K, four ^{29}Si resonances were observed at 11.4, -4.6 , -61.1 and -63.9 ppm.

The signals at -61.1 ppm ($^1J_{\text{SiH}} = 115$ Hz) and -63.9 ppm ($^1J_{\text{SiH}} = 112$ Hz) were the only ones observed in a ^{29}Si INEPT experiment optimized for $J_{\text{SiH}} = 120$ Hz (~ 1 -bond coupling), and the signals at 11.4 ppm and -4.6 ppm were only detected in a ^{29}Si INEPT experiment optimized for $J_{\text{SiH}} = 7$ Hz (long range proton coupling). In a ^1H - ^{29}Si HMBSC experiment optimized for long range ^1H - ^{29}Si coupling ($J_{\text{SiH}} = 7$ Hz), the ^{29}Si resonance at -63.9 ppm correlated with the ^1H NMR signal at 0.25 ppm assigned to a SiHMe ; the ^{29}Si resonance at -61.1 ppm correlated with the ^1H NMR signals at 0.39 ppm and 0.27 ppm assigned to a SiHMe_2 . In that experiment, crosspeaks from the ^{29}Si signal of the major product at -4.6 ppm correlated to SiMe_2 singlet resonances (0.53 ppm and 0.48 ppm), the signal at 3.93 ppm (1 H) assigned to the ZrH , and the aromatic resonances assigned to DMAP (7.87 ppm) in the ^1H NMR spectrum. Similarly, crosspeaks from the ^{29}Si signal of the minor product at 11.4 ppm were correlated to a second SiMe resonance (0.39 ppm), the signal at 3.99 ppm (1 H) assigned to the ZrH , and the aromatic resonances assigned to DMAP (7.48 ppm). These long-range correlations between the silicon atom and the aromatic signals provide convincing evidence that DMAP is coordinated to silicon rather than zirconium.

The ^1H NMR signal at 3.93 ppm and 3.99 ppm were assigned as zirconium hydrides rather than silicon hydrides on the basis of their lack of 1-bond coupling to the silicon centers. In addition, a COSY experiment showed correlations between those signals and the non-classical SiH resonances at 0.28 and 1.29 ppm assigned to a $\text{Zr}-\text{H}-\text{Si}$. A broad band at 1845 cm^{-1} was observed in the crude mixture of **10a** and **10b** that suggested the non-classical nature of β - SiH groups in **10**.

The interaction of **8** and OPeEt_3 affords $\text{Cp}_2\text{Zr}\{\text{N}(\text{SiHMe}_2)\text{SiHMeCH}_2\text{B}(\text{C}_6\text{F}_5)_3\}\text{OPeEt}_3$ (**11**, eqn (6)). Although the coordination of OPeEt_3 to Zr distinguishes this reaction from that of **8** and DMAP, this result follows the reactions of $[2]^+$ with OPeEt_3 and DMAP.



The structure of **11** is dissimilar to that of the DMAP adducts **10a/b**, as demonstrated by NMR and IR spectroscopies. In the ^1H NMR spectrum of **11**, two doublet resonances at 0.27 ppm ($^3J_{\text{HH}} = 3.0$ Hz) and -0.45 ppm ($^3J_{\text{HH}} = 2.3$ Hz) were assigned to SiHMe_2 and SiHMe groups based on integration. Furthermore, two signals at 4.09 ppm ($^1J_{\text{SiH}} = 169$ Hz) and 3.82 ppm ($^1J_{\text{SiH}} = 177$ Hz) were assigned as SiHMe_2 and SiHMe groups, respectively, based on their correlation to the SiMe_2 and SiMe signals in a COSY experiment. The $^1J_{\text{SiH}}$ value suggests that **11** contains terminal silicon hydride groups. The observation of NMR signals assigned to SiHMe_2 and SiHMe groups provide evidence that OPeEt_3 is coordinated to Zr center instead of either β -Si positions. In addition, the ν_{SiH} at 2099 cm^{-1} in the infrared spectrum is consistent with classically bonded silicon hydrides.

Conclusion

The two β - SiH group in azasilazirconacycle **1** show NMR and IR spectroscopic features of classical 2-center-2-electron bonds. Neither spectral signatures of non-classical interactions nor intramolecular hydrogen elimination and abstraction pathways are observed. Nonetheless, the reactions of **1** with ethylene or formaldehyde diverge from the chemistry of β -H

free analogs. The reaction of **1** and formaldehyde at the exocyclic SiH gives a methoxysilyl moiety. A related reaction occurs with the highly non-classical β - SiH in cationic $[2]^+$ and zwitterionic **8**. In the latter reactions, nucleophilic attack of a carbonyl on silicon or zirconium centers is readily rationalized by interactions of OPeEt_3 or DMAP with $[2]^+$ or **8**. Similarly, a rhodium(I) catalyzed hydrosilylation was proposed to involve the coordination of a carbonyl to a silyl to give a five-coordinate silicon center that subsequently undergoes a 1,3-hydride shift,³⁷ although recently rhodium silylene complexes have been invoked as an alternative explanation.^{38, 39} In addition, the direct 1,1-insertion of isocyanide into an $\text{Si}-\text{H}$ of a six-coordinate silicon center was recently proposed.⁴⁰ The related transformation of **1**, however, cannot be explained by silylene intermediates, and reactions of **1** with donor ligands and the facile reaction of **1** and formaldehyde in the presence of donor ligands appears to rule out a pathway involving precoordination to the silicon center.

The reaction of **1** with $\text{B}(\text{C}_6\text{F}_5)_3$ or CO appears to involve the zirconium carbon bond. Coordination of CO prior to 1,1-insertion would occur on the distal side with respect to the SiHMe_2 group, and this reaction does not appear to provide evidence for coordination of formaldehyde to zirconium prior to hydrosilylation.

Notably, the metallacyclic structure of **1** appears to distinguish its reactivity from that of acyclic β - SiH containing silazidozirconium compounds. It may be that the strain associated with the 4-membered ring results in enhanced reactivity of the exocyclic β -hydrogen. Alternatively, the rigidity of the zirconacycle may limit even transient non-classical interactions that otherwise stabilize the reactive β -hydrogen.

Acknowledgements

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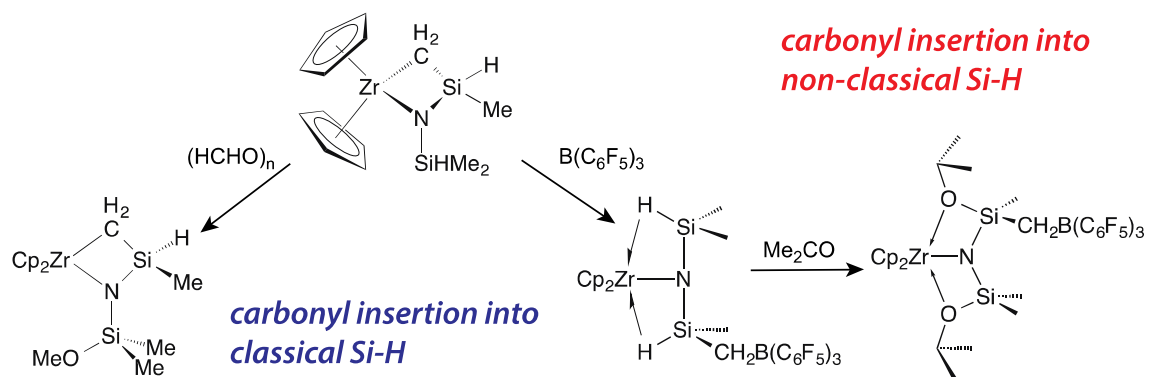
Notes and references

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[†] Electronic Supplementary Information (ESI) available: Crystallographic data files (988789-988792) are available from the CCDC. See DOI: 10.1039/b000000x/

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The pendent β -SiH-containing zirconacycle and formaldehyde react to give a direct hydrosilylation product, similarly to the reaction of the non-classical zwitterionic compound.