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Nonclassical β-Hydrogen Elimination of Hydrosilazido Zirconium Compounds via Direct Hydrogen Transfer

KaKing Yan, Arkady Ellern, and Aaron D. Sadow*

Department of Chemistry, Iowa State University, Ames, Iowa 50011, United States

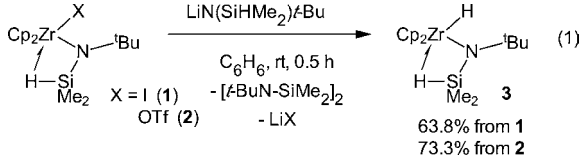
Supporting Information

ABSTRACT: Salt metathesis reactions of $Cp_2(NR_2)ZrX$ (X = Cl, I, OTf) and lithium hydrosilazides ultimately afford hydride products $Cp_2(NR_2)ZrH$ that suggest unusual β-hydrogen elimination processes. A likely intermediate in one of these reactions, $Cp_2Zr[N(SiHMe_2)t\text{-Bu}][N(SiHMe_2)_2]$, is isolated under controlled synthetic conditions. Addition of alkali metal salts to this zirconium hydrosilazide compound produces the corresponding zirconium hydride. However as conditions are varied, a number of other pathways are also accessible, including C−H/Si−H dehydrocoupling, γ-abstraction of a CH, and β-abstraction of a SiH. Our observations suggest that the conversion of (hydrosilazido)zirconocene to zirconium hydride and silanimine does not follow the classical four-center mechanism for β-elimination.

β-Elimination reactions are central to the stoichiometric and catalytic chemistry of organometallic compounds. However, the corresponding elimination of a metal amide (MNR_2) to form a metal hydride (M−H) and an imine is considerably less facile and less common.[1] For example, a few highly reactive three-coordinate tris(anilido) d^2 group 5 and d^3 group 6 complexes are masked as metallaziridine hydride compounds by a rare, reversible β-elimination while β-eliminations of d^0 metal amides are virtually unknown.[2] Instead, d^0 metal amide compounds undergo α-, β-, and γ-abstraction processes to give metal imido,[3,4] azometallacyclopropane (η^2-imine),[5] and azametallacyclobutane products.[6] Recently, the distinct reactivity of alkyl and amide ligands was suggested to be related to their dissimilar β-agostic structures.[7] In short, β-agostic amides generally contain long N−C bonds, large (ca. ∼120°) ∠M−N−C angles, and short β-C−H distances,[7] whereas β-agostic alkyls contain short C−C bonds, acute ∠M−C−C angles, and long β-CH bonds.[8] In the analysis of alkyl and amide reactivity, the relationship between β-agostic structures and β-elimination is tied to the idea that agostic alkyls represent arrested intermediates on the reaction coordinate for elimination. Because β-agostic amides do not give those features, β-elimination is not the favored pathway for amides.

Interestingly, hydrosilazide ligands [$N(SiHR_2)R$] have the typical reactivity associated with early metal amides, undergoing α-abstraction,[9] β-abstraction,[10] and γ-abstraction,[6] even though the structural features of β-agostic hydrosilazides (small ∠M−N−Si angles, short N−Si distances) are closer to those of alkyl ligands rather than aliphatic amides.[11] Thus, 'β-hydridic' silazides might be more reactive toward β-elimination. In fact, examples from the main group, where β-eliminations (even of alkyls) are typically uncommon, hint at this reactivity. Reaction of a diketinimate zinc chloride and $LiNR_2BH_3$ gives a zinc hydride,[12] and a four-coordinate zinc tetramethyldisilazide is converted to a zinc hydride in the presence of LiCl.[13] Furthermore, dehydrogenation of hydrosilazanes occurs upon addition of *n*-butyllithium followed by chlorosilanes.[14]

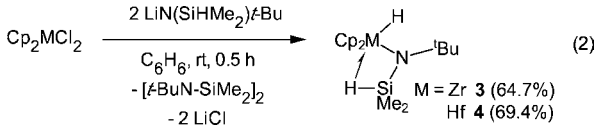
Thus, we were intrigued by the reaction of $LiN(SiHMe_2)t\text{-Bu}$ and $Cp_2Zr[N(SiHMe_2)t\text{-Bu}]X$ [X = I (**1**), OTf (**2**)] that provides $Cp_2Zr[N(SiHMe_2)t\text{-Bu}]H$ (**3**), LiX, and $[t\text{-BuN-SiMe}_2]_2$ (eq 1). The products suggest a sequence involving salt



metathesis followed by β-hydrogen elimination, where $[t\text{-BuN-SiMe}_2]_2$ likely forms via head-to-tail dimerization of the silanimine $t\text{-BuN}{=}SiMe_2$.

The product is identical to authentic samples of **3** prepared by treatment of $[Cp_2ZrHCl]_n$ with $LiN(SiHMe_2)t\text{-Bu}$.[10,11a] Its ^1H NMR spectrum contained a ZrH (δ 5.53) and upfield SiH (δ 1.21, $^1J_{SiH}$ = 113 Hz) that is consistent with a β-agostic structure, as previously described by Berry and co-workers. The starting materials, $Cp_2Zr[N(SiHMe_2)t\text{-Bu}]X$ (X = I,[11a] OTf), also contain β-agostic hydrosilazides (δ_{SiH}: (**1**) 1.71 and (**2**) 1.29). Thus, both the starting and product zirconium hydrosilazido compounds contain β-agostic SiH structures.

Compound **3** is also conveniently obtained by treatment of Cp_2ZrCl_2 with 2 equiv of $LiN(SiHMe_2)t\text{-Bu}$ (eq 2). Additionally,



Cp_2HfCl_2 and 2 equiv of $LiN(SiHMe_2)t\text{-Bu}$ provide the congener $Cp_2Hf[N(SiHMe_2)t\text{-Bu}]H$ (**4**) and $[t\text{-BuN-SiMe}_2]_2$, while Cp_2TiCl_2 and 2 equiv of $LiN(SiHMe_2)t\text{-Bu}$ give paramagnetic titanium species as well as the elimination byproduct $[t\text{-BuN-SiMe}_2]_2$.

The SiH and HfH resonances in the ^1H NMR spectrum of $Cp_2Hf[N(SiHMe_2)t\text{-Bu}]H$ (δ_{SiH} 1.35, $^1J_{SiH}$ = 118 Hz; δ_{HfH}

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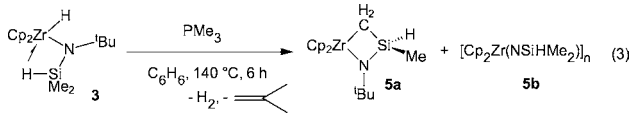
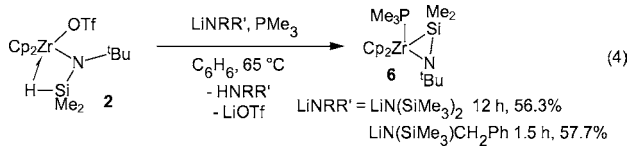
10.12) are downfield compared to the zirconium analog. In the IR spectrum (KBr), the ν_{SiH} (1907 cm^{-1}) and ν_{HfH} (1640 cm^{-1}) were observed.

Possible pathways for formation of **3** and **4** that avoids β-elimination might involve β- or γ-abstraction followed by hydrogenolysis by adventitious H_2. For example, $[Cp_2ZrHCl]_n$ and $LiN(SiMe_3)_2$ react at room temperature to give the azasilazirconacyclobutane $Cp_2Zr[\kappa^2\text{-}N,C\text{-}N(SiMe_3)\text{-}SiMe_2CH_2]$.[6b] In fact, thermolysis of **3** at 140 °C in a sealed flask forms H_2 and $Cp_2Zr[\kappa^2\text{-}N,C\text{-}N(t\text{-}Bu)SiHMeCH_2]$ (**5a**) showing that mechanism is viable. However, isobutylene and species assigned as imido $[Cp_2Zr(\mu\text{-}NSiHMe_2)]_n$ (**5b**) are also formed (eq 3). If γ-abstraction is involved in the formation of **3**,



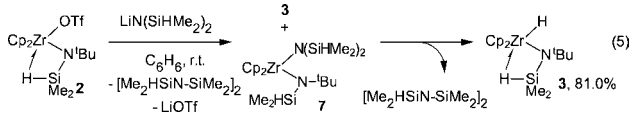
the metallacyclic intermediates will be the same for γ-abstraction from **3**. The irreversible formation of $[Cp_2Zr(\mu\text{-}NSiHMe_2)]_n$ thus suggests that γ-abstraction is not involved in the formation of **3**. Finally, that pathway does not account for $[t\text{-}BuN\text{-}SiMe_2]_2$ produced in the apparent β-elimination.

Thus, β-abstraction products are not observed from hydride **3**, contrasting the mild conditions needed for β-abstraction from $Cp_2Zr[N(SiHMe_2)t\text{-}Bu](CH_2SiMe_3)$ (in the presence of PMe_3) to give $Cp_2Zr[\eta^2\text{-}N(t\text{-}Bu)SiMe_2](PMe_3)$ (**6**).[10] Interestingly, β-hydrogen abstraction occurs upon reaction of $Cp_2Zr[N(SiHMe_2)t\text{-}Bu]OTf$ and $LiN(SiMe_3)_2$ or $LiN(SiMe_3)CH_2Ph$ to give **6** and $HN(SiMe_3)_2$ or $HN(SiMe_3)CH_2Ph$ (eq 4). This



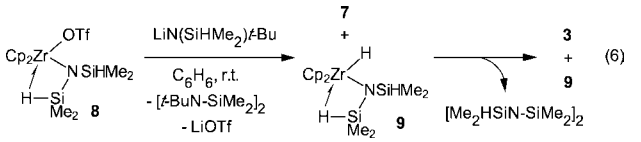
transformation is also not involved in the formation of **3**, because **6** and $HN(SiHMe_2)t\text{-}Bu$ do not provide **3** and $[t\text{-}BuN\text{-}SiMe_2]_2$ as would be expected if β-abstraction is the initial step on a pathway to form the zirconium hydride.

These experiments suggest that the SiH group in $LiN(SiHMe_2)t\text{-}Bu$ diverts the reaction from abstraction to elimination. The effect of the SiH in the lithium hydrosilazide was further explored by the reaction of **2** and $LiN(SiHMe_2)_2$. That interaction gives a mixture of **3** from elimination and the mixed diamide $Cp_2Zr[N(SiHMe_2)t\text{-}Bu][N(SiHMe_2)_2]$ (**7**; eq 5) from salt metathesis in a 1:1.4 ratio.



The formation of compound **7** was later verified by its independent preparation and characterization (see below). Micromolar scale reactions of **2** and $LiN(SiHMe_2)_2$ in toluene-d_8, monitored by ^1H NMR spectroscopy from −57 to 90 °C, showed signals consistent with **7** at −40 °C. Upon warming to 10 °C, this species rapidly but only partially converts to **3** (likely due to precipitation of LiOTf that occurs competitively with elimination; see below). Upon further thermolysis, **7** is converted to **3**.

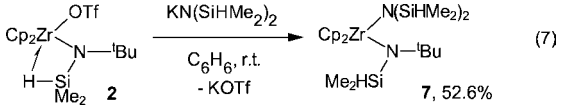
Similarly, $Cp_2Zr[N(SiHMe_2)_2]OTf$ (**8**) and $LiN(SiHMe_2)t\text{-}Bu$ react in benzene to give a mixture of **3**, **7**, and $Cp_2Zr[N(SiHMe_2)_2]H$ (**9**, eq 6) in a 1.0:10.4:0.7 ratio.



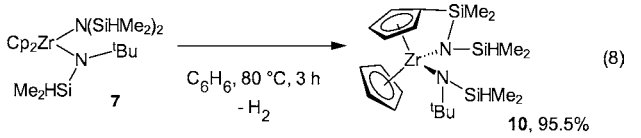
Interestingly, thermolysis of this mixture at 50 °C gives a mixture of **3** and **9** in a ratio of 11.4:0.7, derived from the intermediate mixture (**7** + **3**):**9**. Thus, **7** is an intermediate that affords zirconium hydride **3** but not hydride **9**.

These experiments suggest that two pathways provide zirconium hydride products. The first pathway involves the direct interaction of the metal triflate and lithium hydrosilazide (the first step of eqs 5 and 6 that provides **3** and **9**, respectively). In the second pathway, compound **7** appears to be a precursor to compound **3**. Thus, isolated zirconium bis(disilazide) was required to better study the conversion of **7** to **3**.

After a number of experiments, we found that compound **2** and the potassium disilazide $KN(SiHMe_2)_2$ react in benzene to form **7** (eq 7). The ^1H NMR spectrum of **7** contained two resonances assigned to SiH groups (δ 4.98, $^1J_{SiH}$ = 173 Hz; δ 4.90, $^1J_{SiH}$ = 185 Hz) in a 1:2 integrated ratio.



In surprising contrast to the conversion of **7** to **3** in eq 5, thermolysis of isolated **7** in benzene results in H_2 elimination and interligand coupling between a Si−H bond of the $N(SiHMe_2)_2$ and the C−H bond of a C_5H_5 to form constrained-geometry-like $\{Me_2Si(C_5H_4)N(SiHMe_2)\}CpZrN(SiHMe_2)t\text{-}Bu$ (**10**, eq 8).



The C_5H_4 group appeared as four multiplets in the ^1H NMR spectrum of **10**. Two SiH signals (δ 5.16, $^1J_{SiH}$ = 196 Hz; δ 4.07, $^1J_{SiH}$ = 167 Hz) were observed in a 1:1 ratio. The monomeric structure of **10** was confirmed by X-ray crystallography (see Supporting Information (SI)). We considered a possible mechanism for the formation of **10** based on the thermolysis of $[Cp_2ZrHCl]_n$ that involves intermolecular activation of a C_5H_5 ligand to give $[Cp(Cl)Zr(\mu\text{-}\eta^1\text{:}\eta^5\text{-}C_5H_4)]_2$ and H_2.[15] However, that mechanism is ruled out by a plot of [**7**] vs time that follows an exponential decay for 3 half-lives (see SI), which is inconsistent with a dimeric intermediate. The same conversion of **7** into **10** occurs at room temperature in benzene (0.5 h; 52.5% based on a cyclooctane internal standard) in the presence of $Li[B(C_6F_5)_4](OEt_2)_{2.5}$ (1 or 0.5 equiv) suggesting that the transformation involves a Lewis acid activation.

However, LiCl or KOTf in a THF/benzene solvent mixture diverts the conversion of **7** from the C−H bond activation pathway, instead forming the β-hydrogen elimination products **3** and $[Me_2Si\text{-}NSiHMe_2]_2$ quantitatively. Thus, a sufficiently soluble salt containing both a cation (Li^+ or K^+) and a

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coordinating counteranion Cl^-, I^-, or OTf^- is required for hydrogen transfer to zirconium. Likely, the intermediate salt adduct that precedes the hydride transfer is also accessed upon treatment of [Zr]X with $LiN(SiHMe_2)_2$.

Interestingly, both the starting materials and products $Cp_2Zr[N(SiHMe_2)R]X$ (X = H, Cl, I, OTf; R = *t*-Bu, $SiHMe_2$) contain β-agostic SiH groups, yet the β-agostic silazide ligands in **1**, **2**, and **8** do not undergo elimination. Instead, the incoming lithium silazide transfers a SiH to zirconium and eliminates LiX and silanimine. This transfer appears to occur through a pathway that is sensitive to the nature of the incoming group and ancillary ligands. Thus, the most hindered of interactions, $LiN(SiHMe_2)t$-Bu with **1** or **2**, forms only hydride **3**, whereas the reaction of less hindered $LiN(SiHMe_2)_2$ and **1** or **2** gives a mixture of **3** and diamide **7**. The initial hydride to amide ratio is produced under kinetic control that reflects the relative (and sterically influenced) nucleophilicity of the nitrogen versus the β-H in a lithium hydrosilazide. Additionally, hydride transfer reactions are clearly facilitated under conditions where salt metathesis is reversible (i.e., the salt byproduct is soluble).

Direct hydride transfer, as an alternative to the classic β-elimination, was suggested for the reaction of Cp^*TaMe_3Cl and lithium diisopropylamide.[2] Additionally, side reduction products in late-metal-catalyzed Buchwald–Hartwig C–N cross-couplings are often attributed to β-elimination from a metal amide intermediate.[1,16] In those systems, the choice of base and solvent (i.e., the solubility of the salt) significantly influences the ratio of C–N to C–H bond formation, suggesting that a related direct hydride attack may be important.[1b] In the current hydrosilazide system, this direct hydrogen transfer may also be compared to reactions of transition metal amides and silanes that give metal hydrides and Si–N bonds.[17] The features of the reactions reported here, including the effect of a soluble salt on the favored pathway (among many transformations) and the observation that the β-elimination event does not involve the β-agostic SiH, provide strong evidence for the direct attack of the β-hydrogen of an amide on a metal center. Furthermore, the reactions described here provide an alternative strategy for the synthesis of catalytically important d^0 metal hydride compounds.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures, crystallographic information files (cif) for compounds **2**, **9**, **10**, and kinetics data. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

sadow@iastate.edu

Notes

The authors declare no competing financial interest.

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