ORGANOMETALLICS

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From Unsymmetrically Substituted Benzamidinato and Guanidinato Dichlorohydridosilanes to Novel Hydrido N-Heterocyclic Silylene Iron Complexes

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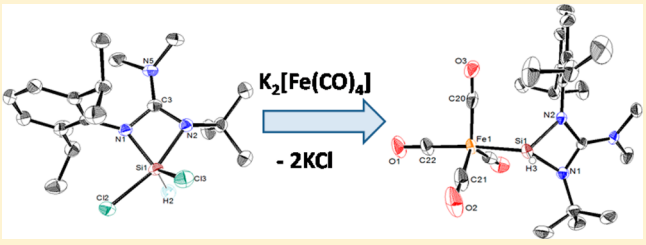
Supporting Information

ABSTRACT: Starting from the unsymmetric N,N′-substituted thiourea compounds (R)N(H)C(=S)N(H)(^{t}Bu) (**1**, R = Dipp: 2,6-^{i}Pr$_2$-C$_6$H$_3$; **2**, R = 1-adamantyl), the corresponding asymmetric carbodiimines (R)N=C=N(^{t}Bu) (**3**, R = Dipp; **4**, R = 1-adamantyl) are readily accessible in high yields upon reduction with LiHMDS (Li[N(SiMe$_3$)$_2$]). The reaction of compound **3** with PhLi followed by $SiCl_4$ afforded, in a one-pot reaction, the asymmetric benzamidinato-stabilized trichlorosilane [PhC{(N^{t}Bu)(NDipp)}]$SiCl_3$ (**5**). Similarly, silanes [PhC{(N^{t}Bu)(NDipp)}]$SiHCl_2$ (**6**), [(NMe$_2$)C{(N^{t}Bu)(NDipp)}]$SiHCl_2$ (**7**), and [PhC{(N^{t}Bu)(NAd)}]$SiHCl_2$ (**8**) could also be isolated. All novel trichloro- or dichlorohydridosilanes were fully spectroscopically characterized and studied by single-crystal X-ray diffraction analyses, the latter revealing in all cases a distorted-trigonal bipyramidal five-coordinate silicon center. The reactions of silanes **5**−**8** with $K_2[Fe(CO)_4]$ were also explored: In the case of the reaction of silane **5** with $K_2[Fe(CO)_4]$, no reaction was observed even after prolonged heating. However, in the case of the silanes **6**−**8**, the selective formation of the corresponding hydrido Si^{II}:→Fe^0 complexes [[R^{1}C{(N^{t}Bu)(NR^2)}](H)Si:→Fe(CO)$_4$] (**9**, R^1 = Ph, R^2 = Dipp; **10**, R^1 = NMe$_2$, R^2 = Dipp; **11**, R^1 = Ph, R^2 = 1-adamantyl) could be achieved. Complexes **9**−**11** represent unprecedented hydrido-N-heterocyclic silylene complexes, bearing asymmetric ligand backbones. Complexes **9**−**11** were fully spectroscopically characterized, and in addition the single-crystal X-ray structure analysis of compound **10** is reported.



INTRODUCTION

One of our key research objectives in the preceding years has been to investigate N-heterocyclic silylene (NHSi) transition metal complexes as possible precatalysts for a variety of transformations, which, given the ready abundance of silicon in the earth's crust, precipitated our early interest in this direction.[1] In general, NHSi complexes are accessible by reactions of isolable "free" NHSis with a suitable transition metal complex, which then affords the corresponding NHSi complex.[2] One of the most useful NHSis for this purpose, used in our group and others in recent times, is Roesky's chlorosilylene, PhC(N^{t}Bu)$_2$SiCl.[3] Taking advantage of the facile coordination this chlorosilylene offers, a plethora of its complexes (Chart 1) across the transition metals: titanium,[4] vanadium,[5] chromium, molybdenum or tungsten,[6] rhenium or manganese,[7] iron,[8] and even copper[9] have been isolated and studied to date.

In preceding studies it was found that the robust nature of this chlorosilylene, upon coordination to transition metals, enables further functionalization of the Si^{II}−Cl bond, and even reactive Si^{II} hydrides could be isolated in this manner.[10] Previously it was also found that the hydrido Si^{II} complex [LHSi:→Fe(dmpe)$_2$] (L = PhC(N^{t}Bu)$_2$; dmpe = 1,2-bis-(dimethylphosphino)ethane) is also catalytically active in the hydrosilylation of ketones, affording high yields of the corresponding alcohols after workup.[11] In the latter case, the Si^{II} center appears to act in a cooperative way with the iron center, thereby facilitating the catalytic process (Scheme 1). Although this is the first example whereby a hydrido-NHSi complex successfully engages a catalytic transformation, the prochiral ketones employed in this study did not in any instance afford enantiomeric excesses (ee), due to the lack of chiral induction. This would be highly desirable and represents a major advance in using low-valent silicon chemistry in homogeneous catalysis.

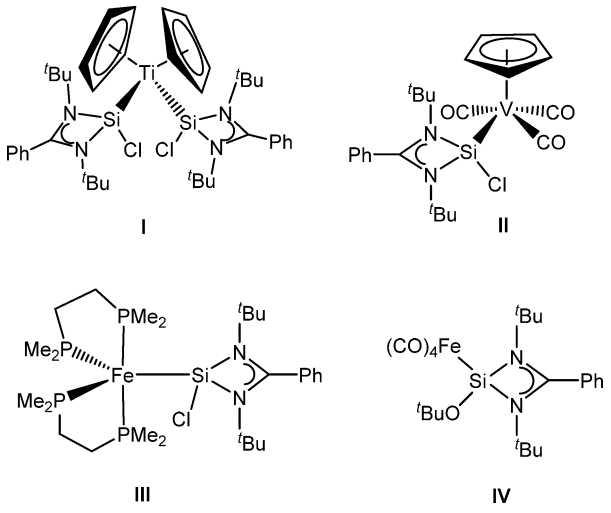
We therefore became interested in whether it might be possible to prepare "asymmetric" benzamidinato-[12] or related guanidinato-stabilized NHSi complexes,[13] which are not known to date,[14] since their isolation could enable asymmetric catalysis.

Access to NHSi transition metal complexes relies almost exclusively on the isolation of the "free" NHSi and then coordination thereof to a transition metal center, usually by ligand elimination.[15] The isolation of the reactive free NHSi can be experimentally difficult due to their intrinsic high reactivity, particularly to moisture and oxygen.[16] Accordingly, access to hydrido-NHSi complexes involves isolation of the free

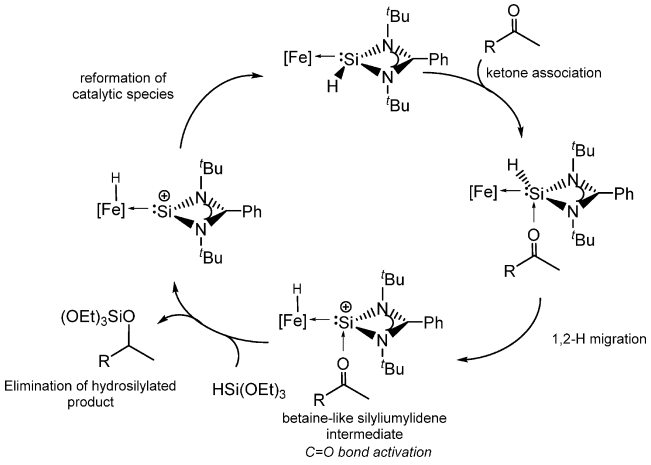
Received: June 3, 2014
Published: September 19, 2014

   dx.doi.org/10.1021/om5005918 | Organometallics 2014, 33, 5272−5282

Chart 1. Some Examples of N-Heterocyclic Silylene Complexes Based on the Chlorosilylene Ligand PhC(N^{t}Bu)SiCl and the Related Derivative IV



Scheme 1. Proposed Mechanism for the Hydrosilylation of Ketones Mediated by [LHSi:→[Fe]],[a] Showing Cooperative Behavior between the NHSi and Iron Center[11]



[a] L = PhC(N^{t}Bu)$_2$; [Fe] = Fe(dmpe)$_2$, dmpe = bis-(dimethylphosphino)ethane.

halo-NHSi in a first synthetic step, subsequent coordination to the metal center as a second step, followed by a halide−hydride exchange reaction, typically by "superhydride" ($HBEt_3$ anion) or similar reagent (Scheme 2). All presently reported hydrido-NHSi complexes, in themselves very rare, generally follow this somewhat cumbersome and time-consuming three-step synthetic route.[17]

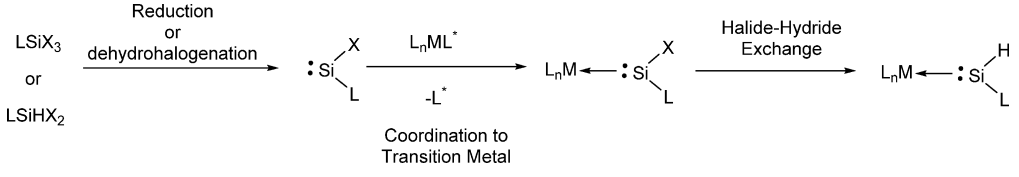
In the present study we report our progress in this direction, particularly a facile and new *direct* route to asymmetric benzamidinato- or guanidinato-stabilized hydrido-NHSi complexes of iron, which are readily accessible from a double metathesis route using $K_2[Fe(CO)_4]$ from the corresponding dichlorohydridosilanes as Si^{IV} precursors bearing asymmetric ligands. This new route effectively saves two synthetic steps (i.e., the isolation of the free NHSi and its coordination to a transition metal) and, given the increasing interest these complexes have attracted recently, might be of considerable practical importance.

RESULTS AND DISCUSSION

The seminal work of Roesky showed that the carbodiimine ^{t}Bu-N=C=N-^{t}Bu is the key building block to access benzamidinato-stabilized trichloro- or dichlorohydridosilanes, upon its reaction with PhLi, then the silane ($SiCl_4$ or $SiHCl_3$), in a one-pot synthesis affording $LSiCl_3$ or $LSiHCl_2$ (L = PhC(N^{t}Bu)$_2$), respectively.[3] Using a dehydrohalogenation reaction with the latter precursor, the chlorosilylene LSiCl can be accessed in higher yields than through reductive dechlorination of $LSiCl_3$. Tacke and co-workers[12] have very recently employed a similar strategy to access the first guanidinato-stabilized[18] silanes, using the symmetrical carbodiimine Dipp-N=C=N-Dipp (Dipp = 2,6-diisopropylphenyl). Its reaction with $LiNMe_2$, followed by trichlorosilane addition, affords selectively L′$SiCl_2H$ (L′ = $(NMe_2)C(NDipp)_2$). The latter also then serves as a key starting material to access the NHSi L′Si(Ntms$_2$) (tms = $SiMe_3$). On the basis of these seminal efforts, we reasoned that starting from an asymmetric carbodiimine, of the type R^1-N=C=N-R^2 (R^1 ≠ R^2, R^1, R^2 = aliphatic or aromatic substituents), a similar reaction sequence could afford asymmetric benzamidinato- or guanidinato-stabilized silanes of the type L*$SiCl_3$ and L*$SiHCl_2$ (L* = PhC(NR^1)(NR^2) or $(Me_2N)C(NR^1)(NR^2)$), respectively. Hence the starting point in our investigation was targeting the asymmetric carbodiimines Dipp-N=C=N-^{t}Bu (**3**) and Ad-N=C=N-^{t}Bu (**4**) (Ad = 1-adamantyl), since they bear substantially different substituents on the N atoms in both cases. Both carbodiimines **3** and **4** are known, but their hitherto reported syntheses are less convenient and require metal (Zr, Fe, Ta, Sn)-mediated routes[19] and/or workup procedures involving distillation.[20] In our hands, we found that carbodiimine **3** or **4** can readily be accessed upon reduction with LiHMDS (Li[N(SiMe$_3$)$_2$]) starting from the thiourea precursors (Dipp)N(H)C(=S)N(H)(^{t}Bu) (**1**)[21] and (1-adamantyl)N(H)C(=S)N(H)(^{t}Bu) (**2**),[22] respectively (Scheme 3). This novel reductive route to carbodiimines **3** and **4** is clean and selective, and both can be isolated in high yields (**3**, 72%; **4**, 100%) without any additional purification (distillation) steps necessary.

Having succeeded in the facile isolation of the asymmetric carbodiimines, we next turned our attention to the synthesis of

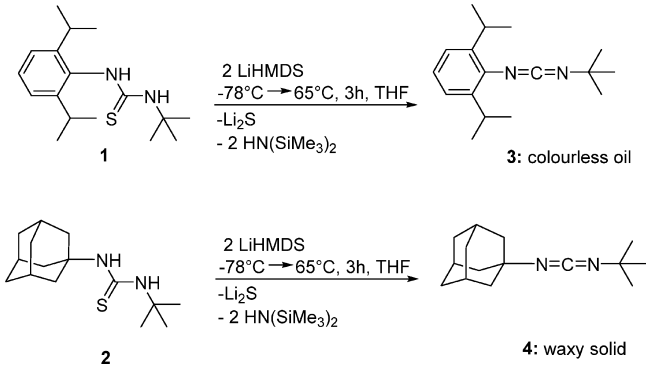
Scheme 2. Schematic Representation of the Hitherto Employed Synthetic Strategy for Access to Hydrido NHSi Complexes[a]



[a] X = halogen; L = PhC(N^{t}Bu)$_2$; L* = ligand capable of elimination e.g., PMe_3, CO, NHC.

dx.doi.org/10.1021/om5005918 | Organometallics 2014, 33, 5272−5282

Scheme 3. Novel Route to Asymmetric Carbodiimines 3 and 4 upon Reduction of Thioureas 1 and 2 with LiHMDS



the corresponding Si^{IV} compounds using them as initial building blocks to construct the ligand backbone. By employing a similar reaction strategy to that of Tacke and Roesky,[12,13] it was indeed possible to isolate several novel Si^{IV} compounds[23] in a similar fashion (Scheme 4).

Reacting carbodiimine **3** or **4** with $LiNMe_2$ or LiPh in an initial step and subsequently with either tetrachlorosilane or trichlorosilane afforded the desired asymmetric silanes (**5**–**8**) in moderate to high yields (**5**, 84%; **6**, 89%; **7**, 83%; **8**, 63%) as colorless solids. This synthetic procedure seems to work in a rather general fashion, as evidenced by the facile isolation of these silanes, which represent only the second set of isolable asymmetric silanes stabilized by benzamidinato or guanidinato ligands.[14] The silanes **5**–**8** are thermally robust, and all exhibit melting points without decomposition (**5**, 175–178 °C; **6**, 103–106 °C; **7**, 123–128 °C; **8**, 115–116 °C).

In the $^{29}Si\{^1H\}$ NMR spectra, the silanes **5**–**8** exhibit strongly shielded singlet resonance signals, comparable to each other within narrow limits, typical for Si^{IV} complexes of this type, in the range δ = −92.9 to −102.3 ppm (Table 1). The

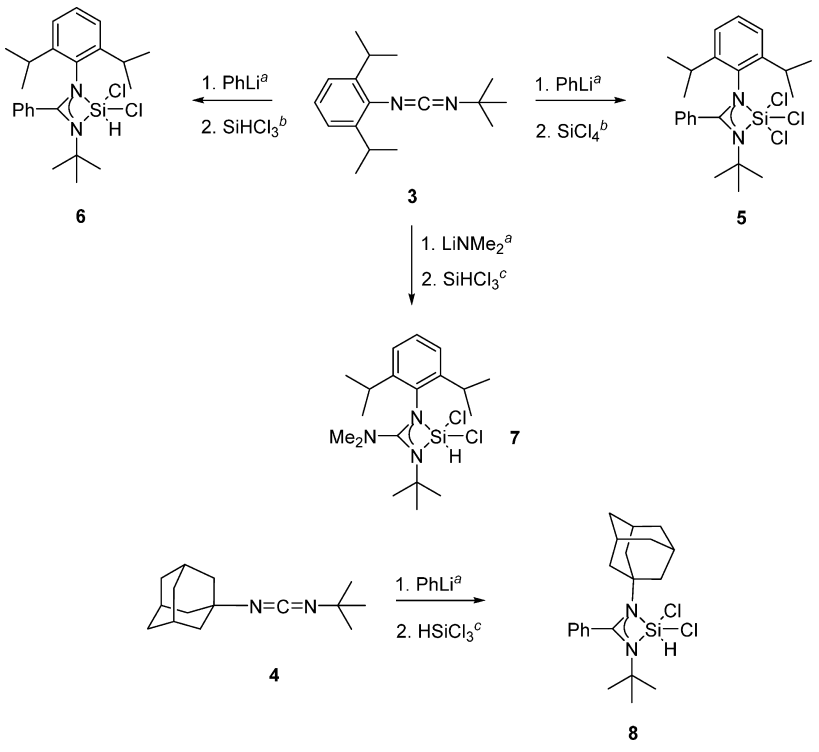
Table 1. Summary of Some Key NMR Spectral Parameters (in ppm, spectra recorded in C_6D_6 at 298 K) Observed for Silanes 5–8

complex	$^{29}Si\{^1H\}$	^1J (^{29}Si,H)/Hz	$^{13}C\{^1H\}$ of NCN
5	−93.8		171.2
6	−92.9	353	170.5
7	−102.3	346	171.2
8	−97.3	332	171.3

similarity in the chemical shifts suggests that the steric and/or electronic changes in the ligand backbone do not affect the ^{29}Si NMR shift for this series of compounds. It is interesting to note that silanes **5** and **6**, both featuring the identical ligand arrangement, reveal very similar chemical shifts, despite compound **5** being a trichlorosilane and compound **6** a dichlorohydridosilane. The most shielded in this series is silane **7**, bearing the guanidinato ligand backbone, which exhibits a chemical shift at δ = −102.3 ppm, ca. 10 ppm upfield shifted from its benzamidinato analogue, compound **6**, clearly due to the increased electron-donating capacity of Me_2N (in **7**) vs Ph (in **6**).

The asymmetry of the bidentate benzamidinato or guanidinato ligands should conceivably give rise to two stereoisomers in the case of the silanes **6**–**8** (Figure 1). The ^1H NMR spectra of all four silanes exhibit sharp lines and reflect a symmetric pattern, consistent with only one

Scheme 4. Synthesis of Asymmetric Benzamidinato- Or Guanidinato-Stabilized Silanes from Asymmetric Carbodiimines 3 and 4[a]



[a]Reactions were carried out in diethyl ether under the following conditions: (a) −78 °C → rt, 3 h; (b) rt, 12 h; (c) −78 °C → rt, 12 h.

dx.doi.org/10.1021/om5005918 | Organometallics 2014, 33, 5272–5282

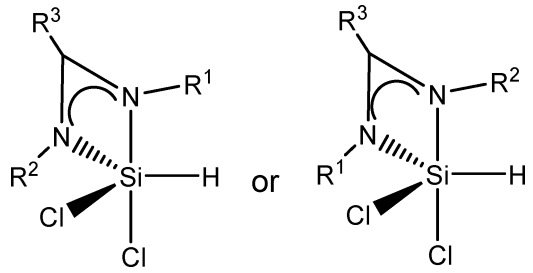


Figure 1. Stereoisomerism in the case of the silanes **6**–**8** derived from the asymmetry of the ligands. R^1, R^2 = Dipp, ^{t}Bu, Ad; R^3 = Ph or NMe_2. (Ideal trigonal-bipyramidal geometry is shown for clarity.)

component present on the NMR time scale; this includes the silanes **6**–**8**, where stereoisomerism is expected. This observation indicates that either there is rapid interconversion between the two possible stereoisomeric forms for the silanes **6**–**8** on the time scale of the measurement, and the time-averaged symmetric spectrum is observed, or one stereoisomer is energetically preferred and the spectra reflect its presence alone. The former scenario is more likely, since IR and single-crystal X-ray diffraction data (*vide infra*) indeed provide evidence for the coexistence of two stereoisomeric forms in the solid state. The interconversion between the stereosiomers in the case of compounds **6**–**8** most likely follows Berry pseudorotation,[24] typical for five-coordinate systems, which is often very rapid on the NMR time scale.[25] In fact, variable-temperature NMR experiments (in THF-d_8) were conducted for compounds **6** and **7**, but even at −80 °C, in both cases, this exchange process could not be frozen out, and the spectra in both compounds were analogous to those at room temperature.

Particularly diagnostic in silanes **6**–**8** is the presence of a Si-*H* signal in the ^{1}H NMR spectrum, which in all three cases shows up as a sharp singlet resonance signal at δ = **6**, 6.60; **7**, 6.56; **8**, 6.87 ppm. In all cases the presence of low-intensity ^{29}Si satellites derived from $^1J(^{29}Si,H)$ is detectable, with coupling constants ranging from 332 Hz (**8**) to 353 Hz (**6**) (Table 1). The most characteristic resonance signal in the $^{13}C\{^1H\}$ NMR spectrum of compounds featuring benzamidinato or guanidinato ligands is that of the NCN in the backbone of the four-membered chelate ring. This signal is clearly visible in all of the silanes **5**–**8** (Table 1) and exhibits a remarkably similar chemical shift position. Also in the ^{13}C NMR spectrum, a highly symmetric pattern is observed for all the silanes.

IR spectroscopy proved to be a very useful tool in the characterization of the silanes **6** and **7** in the solid state. In the case of compound **6**, comparison of its IR spectrum with compound **5** showed a virtually identical spectrum with the exception of two very strong absorption bands for compound **6** at ν = 2214 and 2193 cm^{-1}, assignable to two ν(Si–*H*) stretching vibrations (Figure 2). The existence of two bands is expected if two stereoisomers are present. The stretching vibration at ν = 2214 cm^{-1} is of lower intensity than that at 2193 cm^{-1}. In close analogy with silane **7**, two strong stretching vibrations are also observed at ν = 2221 and 2141 cm^{-1}, respectively, again reflecting the coexistence of the two stereoisomers in the solid state. In compound **7** the band at ν = 2221 cm^{-1} is of higher intensity.

Additionally, all four silanes were the subject of single-crystal X-ray diffraction analyses, and crystals suitable for this purpose were obtained from concentrated *n*-hexane (**5**–**7**) or toluene (**8**) solutions upon slow cooling to 5 or −30 °C. Figure 3

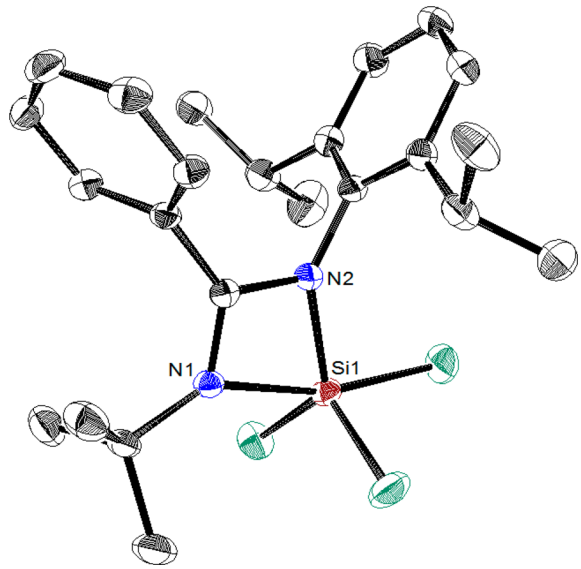


Figure 3. ORTEP representation of the molecular structure of silane **5** in the solid state at the 50% probability level. H atoms are omitted for clarity. Cl atoms are shaded green.

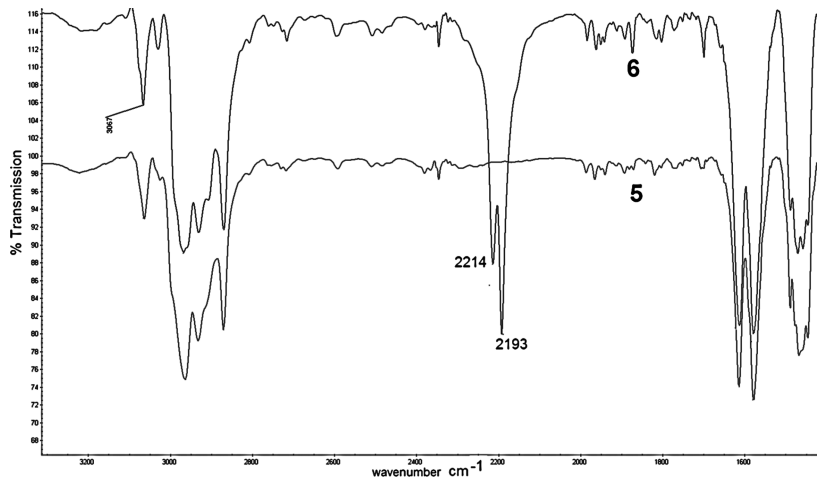


Figure 2. Comparative IR spectra of silanes **5** and **6** clearly showing two Si–H stretching vibrations for the latter in the range 1450–3400 cm^{-1}.

dx.doi.org/10.1021/om5005918 | *Organometallics* 2014, 33, 5272–5282

shows the solid-state structure of silane **5** (the structure of **7** is presented in the SI). A comparison among silanes **5**−**7** is presented in Table 2 since they have the same N-substitution pattern, making their structural comparison possible.

Table 2. Summary of Selected Bond Lengths (Å) and Angles [deg] of Silanes 5−7

metric parameter	5/Å or deg	6/Å or deg[b]	7/Å or deg
Bond Lengths			
N1−C1	1.370(2)	1.370(2)	1.374(2)
N2−C1	1.301(2)	1.297(2)	1.342(2)
N1−Si1	1.771(1)	1.781(2)	1.788(1)
N2−Si1	1.988(1)	2.018(2)	1.921(1)
Cl1−Si1	2.1314(6)	2.1427(7)	2.1922(5)
Cl2−Si1	2.0714(6)	2.0636(7)	2.0922(5)
Cl3−Si1	2.0540(6)		
C1−Si1	2.345(2)	2.369(2)	2.335(1)
Bond Angles			
N1−Si1−N2	69.2(6)	68.20(7)	71.03(5)
C1−N1−Si1[a]	95.7(1)	96.7(1)	94.24(8)
C1−N2−Si1	88.4(1)	88.5(1)	89.57(8)
N1−C1−N2	106.6(1)	106.6(2)	105.2(1)
N2−C1−C2	130.5(1)	129.8(2)	130.3(1)
N1−C1−C2	122.9(1)	123.7(2)	124.6(1)
N2−Si1−Cl2	165.00(5)	164.44(5)	164.52(4)
N1−Si1−Cl1	120.92(5)	118.68(6)	125.30(4)
N2−Si1−Cl1	93.67(4)	93.02(5)	93.19(4)
Cl2−Si1−Cl1	95.08(3)	96.68(3)	92.73(2)
Cl2−Si1−N1	96.05(5)	96.41(5)	93.93(4)

[a]C1 refers to the NCN atom in the backbone of the ligand in all cases. [b]Two molecules (stereoisomers) were found in the asymmetric unit, and the metric parameters reported here reflect one of these.

The related silanes **5**, **6**, and **7** exhibit very similar metric parameters, in terms of both bond lengths and angles, which are comparable to each other within narrow margins (Table 2). These parameters are also akin to those of the related but symmetric silane L′SiHCl$_2$ (L′ = (NMe$_2$)C(NDipp)$_2$)[13] reported by Tacke and co-workers. In the case of silanes **6** and **7**, the H atom residing on the Si^{IV} centers could be located. In silanes **5**−**7** each Si^{IV} center is five coordinate and exhibits a distorted trigonal-bipyramidal geometry. The source of this distortion is the ring strain associated with the benzamidinato or guanidinato ligand system featuring an acute bite angle of approximately 70° in all cases. The degree of distortion from ideal trigonal-bipyramidal geometry can be computed by the τ value[26] and reveals that silane **7** deviates most notably from idealized trigonal-bipyramidal geometry: **5**, τ = 0.75; **6**, τ = 0.76; τ = **7**, 0.65. In the structure solution of silane **6**, fortunately, two molecules were found in the asymmetric unit, which correspond to two stereoisomeric forms of compound **6** (Figure 4). This provides additional evidence for their existence and also provides some rationale for the IR spectrum (*vide supra*) where two Si−H stretching vibrations were observed, corresponding to these two stereoisomers. Their mutual presence in the asymmetric unit suggests they are energetically very close on the potential energy hypersurface. In the case of the silane **7**, only one molecule is found in the asymmetric unit, representing one of the possible stereoisomers, which might suggest there is a greater energy difference between the two stereoisomers in compound **7** and that only one preferentially crystallized.

The silane **8**, bearing the 1-adamantyl residue, is structurally similar to the aforementioned silanes **5**−**7**, and its structure is presented in Figure 5 along with some key metric parameters. The silicon-bound hydride could also be located in the Fourier difference map and refined. Only one of the possible stereoisomers is found in the asymmetric unit, akin to compound **7**. The computed τ value is comparable to those of compounds **5** and **6** (τ = 0.73), suggesting that no major geometric distortions around the silicon center arise from the dramatic increase in steric bulk of the 1-adamantyl residue.

The availability of the silanes **5**−**8** initially prompted us to explore their ability to undergo reduction/dehydrohalogenation reactions to access the corresponding asymmetric mononuclear NHSis. Therefore, we employed a range of reducing agents for **5** (K mirror, KC$_8$, Na-naphthalenide) and dehydrohalogenation

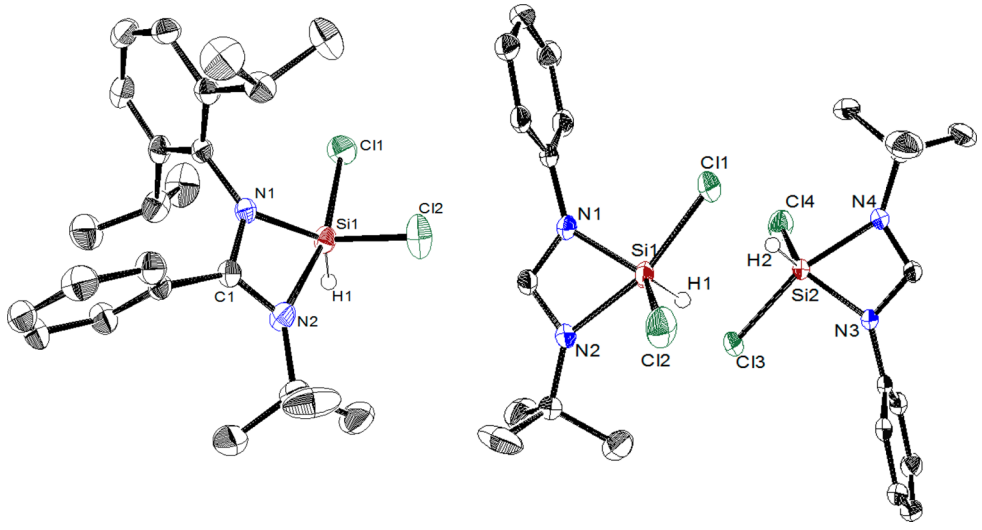


Figure 4. ORTEP representation of the molecular structure of one of the independent molecules (stereoisomers) in silane **6** in the solid state at the 50% probability level (left). All H atoms are omitted for clarity, except H1. ORTEP representation of the two stereoisomers of compound **6** in the asymmetric unit (right). Thermal ellipsoids are set at 50% probability. All H atoms are omitted for clarity, except H1 and H2. ^{i}Pr groups of Dipp substituents and the Ph group in the backbone are omitted for clarity (right).

dx.doi.org/10.1021/om5005918 | *Organometallics* 2014, 33, 5272−5282

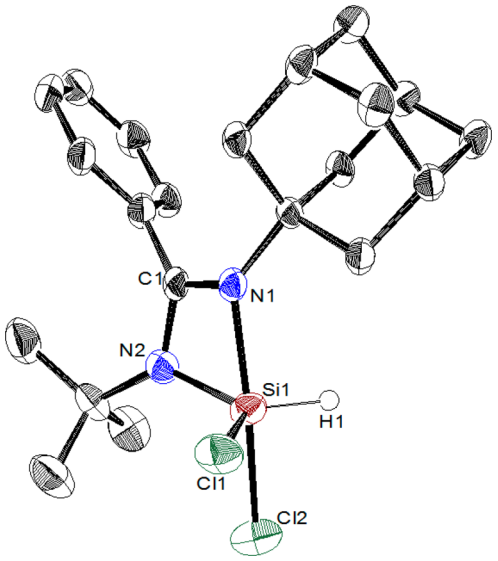


Figure 5. ORTEP representation of the molecular structure of silane **8** in the solid state. Thermal ellipsoids are set at the 50% probability level. All H atoms, with the exception of H1, are omitted for clarity. Selected bond lengths [Å]: Si1−N2 1.798(3), Si1−N1 1.941(3), Si1−Cl1 2.084(1), Si1−Cl2 2.172(1), Si1−C1 2.325(3), N1−C1 1.312(5). Selected bond angles [deg]: N2−Si1−N1 70.0(1), N2−Si1−Cl1 117.6(1), N1−Si1−Cl1 94.9(1), N2−Si1−Cl2 100.5(1), N1−Si1−Cl2 169.0(1), Cl1−Si1−Cl2 94.49(5), N2−Si1- C1 36.0(1), N1−Si1−C1 34.3(1), Cl1−Si1−C1 112.59(9), Cl2−Si1−C1 135.5(1), C1−N1−C12 130.1(3), C1−N1−Si1 89.1(2).

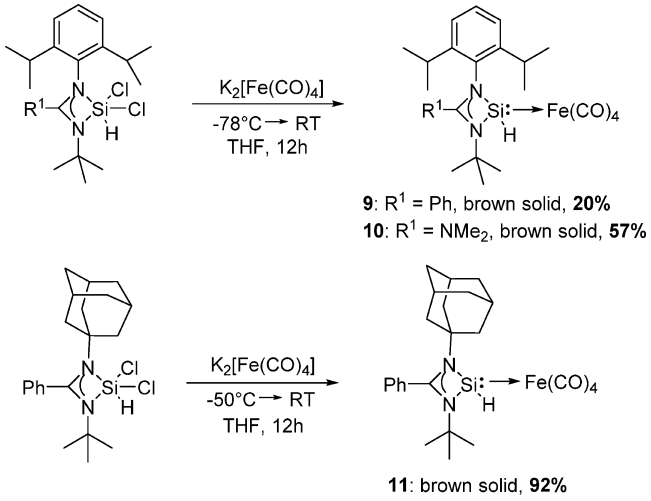
reagents (LiHMDS, NaHMDS, even ^{n}BuLi, ^{t}BuLi, etc.) for silanes **6**−**8**. Unfortunately, all experiments did not afford the desired NHSi.

We then considered an alternative possibility: that the silanes could, when reacted with a suitable metalate as reducing agent, form the targeted NHSi metal complexes, *directly* by a salt metathesis route. For this purpose we chose $K_2[Fe(CO)_4]$ given its ease of access and availability to probe this synthetic idea.

Initially we reacted silane **5** with $K_2[Fe(CO)_4]$, hoping to form the corresponding NHSi complex [{PhC(N^{t}Bu)(NDipp)}(Cl)Si:→Fe(CO)$_4$]. However, this reaction did not proceed to any extent, even under reflux in THF after 72 h. Strikingly, when the silanes **6**−**8** were reacted with $K_2[Fe(CO)_4]$, the envisaged reaction did occur, and the corresponding hydrido-NHSi iron(0) complexes [{R^{1}C(N^{t}Bu)(NR^2)}(H)Si:→Fe(CO)$_4$] (**9**, R^1 = Ph, R^2 = Dipp; **10**, R^1 = NMe$_2$, R^2 = Dipp; **11**, R^1 = Ph, R^2 = 1-adamantyl) could be isolated upon workup (Scheme 5). This represents a facile new route to access hydrido NHSi complexes, directly from the easily accessible dichlorohydridosilanes, without the need to isolate the "free" NHSi ligand.[27]

The hydrido Si^{II}:→Fe^0 complexes **9**−**11** were fully characterized spectroscopically. In all three cases the [M + H]$^+$ signal could clearly be detected in the high-resolution ESI-MS spectrum, with a fitting isotope distribution pattern confirming their constitution. The ^{29}Si{^{1}H} NMR spectra of all three complexes (in C_6D_6) reveal one sharp singlet, downfield shifted from the corresponding silane precursors **6**−**8** (Table 3). This provides further evidence of the coordination of the hydrido-NHSi to the iron center and additionally is indicative that the oxidation state of the silicon center is +2, since this is the typical spectral region for related

Scheme 5. Direct Synthesis of the Asymmetric Hydrido Si^{II}:→Fe Complexes 9−11 from the Respective Dichlorohydridosilanes, upon Reaction with $K_2[Fe(CO)_4]$



9: R^1 = Ph, brown solid, **20%**
10: R^1 = NMe$_2$, brown solid, **57%**
11: brown solid, **92%**

Table 3. Summary of Some Key Chemical Shifts (in ppm, spectra recorded in C_6D_6 at 298 K) Observed in Complexes 9−11

complex	^{29}Si{^{1}H}	^{1}H NMR shift of Si−*H*	^1J (^{29}Si,H)/Hz
9	99.6	7.05	200
10	83.6	7.04	205
11	86.5	6.91	204

Si^{II} group VIII metal complexes.[28] Moreover, in all three compounds, in the ^{1}H NMR spectra, the silicon-bound hydride atom is clearly detectable, flanked by ^{29}Si satellites (Table 3).

In the case of complexes **9** and **10**, IR spectroscopy in the solid state was also recorded, and in both cases three sharp bands are visible in the carbonyl region, in accordance with the expectations for the iron centers exhibiting local C_{3v} symmetry (**9**, ν = 2013, 1984, 1887 cm^{-1}; **10**, ν = 2022, 1944, 1909 cm^{-1}). This implies that the hydrido-NHsilylene ligands necessarily occupy the apical position in the trigonal-bipyramidal coordination sphere of the iron center in both complexes, as equatorial coordination would afford a local C_{2v} symmetry at the iron center and four bands in the CO region would be observed.[29] In contrast to the silanes **6** and **7**, only one stretching vibration for the Si−H bond is observed in the infrared spectra of the corresponding Fe^0 complexes **9** and **10**, at ν = 2059 cm^{-1} (**9**) and ν = 2100 cm^{-1} (**10**), respectively. Compared to the Si^{IV} precursors, these stretching vibrations are shifted to slightly lower wavenumbers in both cases, as would be expected for a decrease in the oxidation state at Si.[30] The presence of only one stretching vibration, in both cases, suggests a preference for formation of only one stereoisomer.

Efforts to obtain crystals suitable for single-crystal X-ray diffraction analysis of complexes **9** and **11** remained unsuccessful. In the case of complex **11**, likely as a result of the adamantyl residue, only amorphous wax-like blocks resulted, despite attempting numerous solvents and crystallization procedures. Fortunately, crystals suitable for X-ray diffraction analysis were obtained in the case of complex **10**, from dilute hexane solutions with slow cooling to 5 °C. The solid-state structure of complex **10** is depicted in Figure 6.

dx.doi.org/10.1021/om5005918 | *Organometallics* 2014, 33, 5272−5282

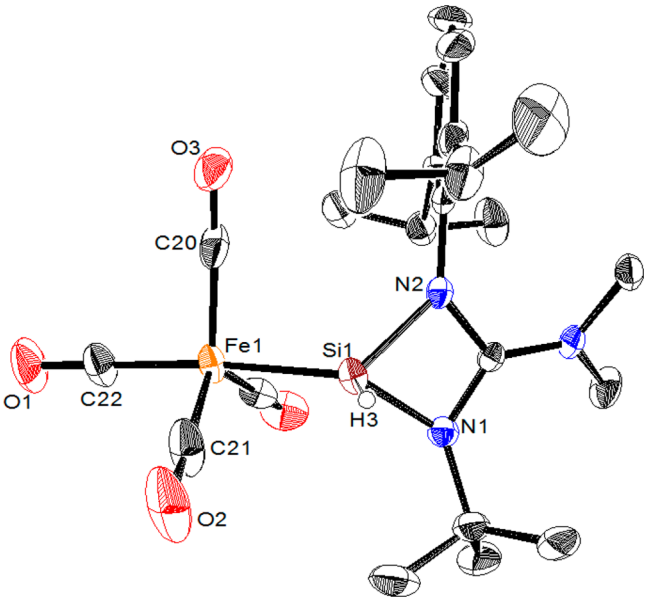


Figure 6. ORTEP representation of the molecular structure of complex **10** in the solid state. Thermal ellipsoids are set at the 50% probability level. All H atoms, with the exception of H3, are omitted for clarity. Selected bond lengths [Å]: Fe1−C20 1.779(6), Fe1−C21 1.780(6), Fe1−C22 1.787(5), Fe1−C23 1.770(5), O1−C22 1.139(7), O2−C21 1.134(8), O3−C20 1.151(8), O4−C23 1.144(6), Fe1−Si1 2.234(1), Si1−N2 1.811(4), Si1−N1 1.829(4), Si1−C1 2.284(4). Selected bond angles [deg]: N2−Si1−N1 72.7(2), N2−Si1−Fe1 124.1(1), N1−Si1−Fe1 126.0(1).

Complex **10** features an ideal trigonal-bipyramidal Fe^0 site and a distorted tetrahedral Si^{II} center. The hydrido-NHSi ligand occupies one of the apical positions of the coordination sphere of the iron atom, and the other sites are occupied by CO ligands, in accordance with the solid-state IR data (*vide supra*). The apical location of the NHSi ligand is akin to the complex $[Fe(CO)_4{\leftarrow}{:}Si(O^tBu)L]$ (L = $PhC(N^tBu)_2$) reported by Roesky and co-workers,[31] but contrasts our recently reported hydrido-NHSi iron complex $[LHSi{:}{\rightarrow}Fe(dmpe)_2]$ (L = $PhC(N^tBu)_2$; dmpe = 1,2-bis(dimethylphosphino)ethane),[11] in which the ligand is equatorially coordinated to iron. The explanation for this is that, in the latter complex, the presence of electron-rich alkyl phosphane ligands enhances the electron density at the Fe center and thereby increases its propensity for π-back-donation to the Si^{II} center. Moreover, as was shown by us previously, since the hydrido-NHSi ligand has the ability to behave as a π-acidic ligand, under these conditions, it preferentially adopts equatorial coordination. In complex **10**, the presence of π-acidic CO groups on the iron center substantially diminishes its π-density, thereby weakening its ability to form a π-back-donation and most likely accounts for the apical coordination of the ligand. The Fe1−Si1 bond length in complex **10** is 2.234(1) Å, which is comparable in magnitude to that observed in $[Fe(CO)_4{\leftarrow}{:}Si(O^tBu)L]$ (2.237(7) Å), but substantially longer than observed in $[LHSi{:}{\rightarrow}Fe(dmpe)_2]$: 2.184(2) Å. This is again due to the enhanced π-back-donation facilitated by the electron-rich phosphane ligands in the latter complex, increasing the electron density on the Fe(0) site.

Asymmetric iron complexes **9**−**11** were also screened for catalytic hydrosilylation of pro-chiral ketones, in the hope of observing enantiomeric excesses in the products. For all three complexes, even at a high (10 mol %) catalyst loading, employing $Si(OEt)_3H$ as silane, no catalytic activity was observed after 24 h at 70 °C heating. The inactivity of the catalysts contrasts with our previously reported electron-rich hydrido-NHSi Fe(0) system[11] and is likely due to the presence of the electron-withdrawing CO ligands, which impedes the reactivity of the system. In order to increase the electron density on the iron atom, we are currently exploring the possibility of inserting chelating electron-rich alkyl phosphanes (for example dmpe) by CO elimination using complexes **9**−**11** as starting materials. This should yield access to heteroleptic systems of the type $[[R^1C\{(N^tBu)(NR^2)\}](H)Si{:}{\rightarrow}Fe(CO)_n(\eta^2\text{-dmpe})_x]$ (x = 1, n = 2 or x = 2, n = 0),[32] which, due to an increase in electron density at the iron center, might then act as suitable catalysts for hydrosilylation reactions.

SUMMARY AND OUTLOOK

An improved route to asymmetric carbodiimines has been developed, and these precursor molecules were employed for the synthesis of corresponding asymmetric trichloro- and dichlorohydridosilanes in high yields. Due to the asymmetry of the carbodiimine, the resulting benzamidinato or guanidinato ligands induce stereoisomer formation in the corresponding silanes. Starting from the silanes, a new direct route to hydrido-NHSi iron(0) complexes could be achieved upon salt metathesis with $K_2[Fe(CO)_4]$. This represents a facile and general new route to hitherto unprecedented asymmetric hydrido-NHSi metal complexes, without the need to first isolate any "free" NHSi ligand. Further experiments are devoted to enabling entry to related iron(0) complexes capable of asymmetric catalytic transformations (e.g., hydrosilylation).

EXPERIMENTAL SECTION

General Considerations. All experiments and manipulations were carried out under a dry and oxygen-free atmosphere of nitrogen or argon, using standard Schlenk techniques, or in an MBraun inert atmosphere drybox containing an atmosphere of purified nitrogen. Solvents were dried by standard methods and stored over activated molecular sieves (4 Å). Prior to use, all solvents were degassed at least once *via* a freeze−pump−thaw cycle. C_6D_6 was dried by stirring it over KC_8 for 48 h and vacuum-transfer over activated molecular sieves (4 Å), where it was stored for use. The NMR spectra were recorded on a Bruker AV 200 or 400 spectrometer. Concentrated solutions of samples in C_6D_6 were sealed off in a Young-type NMR tube for measurements. The ^1H and $^{13}C\{^1H\}$ were referenced to the residual solvent signals as internal standards (δ_H = 7.15; δ_C = 128.00 ppm for C_6D_6). The $^{29}Si\{^1H\}$ NMR spectra were referenced to TMS (tetramethylsilane) as an external standard. Abbreviations: s = singlet; m = multiplet; br = broad, quint = quintet. Unambiguous signal assignments were made by employing a combination of DEPT-45 and 2D NMR H,C-COSY (HMQC/HMBC) experiments. Diastereotopic groups on the ^{i}Pr substituents are indicated with superscripts A, B, C, or D. High-resolution mass spectra (ESI or APCI) were recorded on a Thermo Fischer Scientific LTQ Orbitrap XL spectrometer. Electron impact (EI) spectra were recorded on a Finnigan MAT 95S Sectorfield spectrometer. The line of highest intensity in the isotope pattern is reported. For the single-crystal X-ray structure determinations, crystals were mounted on a glass capillary in perfluorinated oil and measured in a cold N_2 flow. The data for all compounds were collected on an Oxford Diffraction Supernova, single source at offset, Atlas at 150 K (Cu Kα radiation, λ = 1.5418 Å). The structures were solved by direct methods and refined on F^2 with the SHELX-97 software package. The positions of the H atoms were calculated and considered isotropically according to a riding model. $K_2[Fe(CO)_4]$ was synthesized according to a literature procedure,[33] (Dipp)N(H)C(=S)N(H)(^{t}Bu) (**1**)[21] and (1-Adamantyl)N(H)C(=O)N(H)(^{t}Bu) (**2**)[22] were prepared using different routes, and for compound **2** the NMR data are included here. For compounds **3** and **4** the NMR data are compared with literature.[19]

dx.doi.org/10.1021/om5005918 | *Organometallics* 2014, 33, 5272−5282

All other starting materials were obtained from commercial sources and used as received, unless otherwise stated.

***N*-(2,6-Diisopropylphenyl)-*N*′-(*tert*-butyl)thiourea (1).** In a 250 mL Schlenk flask, 100 mL of distilled water was added. Thiophosgene (7.50 g, 65.2 mmol) was added to the water, and then diisopropylphenylamine (9.64 g, 54.4 mmol) over a period of 30 min. A two-phase reaction follows, after which the organic phase was extracted and added to another 250 mL Schlenk flask together with *tert*-butylamine (19.9 g, 272.0 mmol), and the mixture was stirred at room temperature for 12 h. The reaction solution was then added to 200 mL of a dilute HCl solution, after which a precipitate was separated from a supernatant solution. The precipitate was washed with 5 mL of hexane, and the hexane washing discarded. The resulting residue was taken up in diethyl ether, dried over magnesium sulfate, and filtered. The clear filtrate was concentrated *in vacuo* until incipience and cooled to 5 °C overnight, affording colorless crystals of the desired product, which were separated from the supernatant solution and dried *in vacuo*. Yield: 9.39 g, 32.1 mmol (59%). Mp: 131−132 °C; lit.[21] 128−129 °C. ^{1}H NMR (200.13 MHz, $CDCl_3$, 25 °C, ppm): δ 1.17 (d, $^{3}J_{H-H}$ = 7.0 Hz, 6 H, 2 × CHCH^{A}_3), 1.21 (d, $^{3}J_{H-H}$ = 7.0 Hz, 6 H, 2 × CHCH^{B}_3), 1.41 (s, 9 H, 1 × C(CH_3)$_3$), 3.15 (sept, $^{3}J_{H-H}$ = 6.9 Hz, 2 H, 2 × CH(CH_3)$_2$), 5.19 (br s, 2 H, 2 × N-H), 7.20 (d, $^{4}J_{H-H}$ = 1.1 Hz, 1 H, C$^{3\text{ or }5}$-H, Dipp), 7.24 (br s, 1H, C$^{3\text{ or }5}$-H, Dipp), 7.37 (dd, $^{3}J_{H-H}$ = 6.8 Hz, $^{3}J_{H-H}$ = 8.6 Hz, 1H, C^{4}-H, Dipp). Lit.[21] (300 MHz, $CDCl_3$, ppm): δ 1.22 and 1.26 ($CHMe_2$), 1.42 (CMe_3), 3.15 ($CHMe_2$), 7.23 (Ar H-3 and -5), 7.37 (Ar H-4). ^{13}C{^{1}H} NMR (50.32 MHz, $CDCl_3$, 25 °C, ppm): δ 23.5 (s, 2 C, 2 × CHC^{A}H$_3$), 24.3 (s, 2 C, 2 × CHC^{B}H$_3$), 28.5 (s, 2 C, 2 × CH(CH_3)$_2$), 28.9 (s, 3 C, 1 × C(CH_3)$_3$), 53.7 (s, 1 C, 1 × −C(CH_3)$_3$), 124.5 (s, 2 C, 1 × $C^{3,5}$, Dipp), 130.0 (s, 1 C, 1 × C^{4}, Dipp), 130.0 (s, 1 C, 1 × C^{1}, Dipp), 148.0 (s, 2 C, 1 × $C^{2,6}$, Dipp), 180.0 (s, 1 C, 1 × −NH-C(S)-NH). ESI-MS, m/z: calcd for $C_{17}H_{28}N_2S$ [M + H]$^{+}$ 293.2041; found 293.2046. Anal. Calcd for $C_{17}H_{28}N_2S$: C 69.81, H 9.65, N 9.58, S 10.96. Found: C 69.89, H 9.93, N 9.45, S 10.75.

***N*-Adamantyl-*N*′-*tert*-butylthiourea (2).** A Schlenk tube was charged with 100 mL of hexane and 1-adamantylisothiocyanate (3.0 g, 15.5 mmol). Upon stirring at room temperature, 6 mL (54.4 mmol) of *tert*-butyl amine was added, and the reaction solution stirred at room temperature for 72 h. During the course of the reaction, a white precipitate formed. This precipitate was separated from the supernatant by cannula filtration, washed with a small amount of hexane, and dried *in vacuo* at room temperature for 1 h. Yield: 3.3 g, 13.3 mmol (86%). (NMR data not accessible in the literature.) ^{1}H NMR (200.13 MHz, $CDCl_3$, 25 °C, ppm): δ 1.47 (s, 9 H, 1 × C(CH_3)$_3$), 1.68 (br m, 12 H, 6 × CH_2, 1-adamantyl), 2.12 (m, 3 H, 3 × CH, 1-adamantyl), 8.28 (s, 2 H, 2 × NH). ^{13}C{^{1}H} NMR (50.32 MHz, C_6D_6, 25 °C, ppm): δ 29.2 (s, 6 C, 6 × CH_2, 1-adamantyl), 35.6 (s, 3 C, 1 × C(CH_3)$_3$), 43.8 (s, 6 C, 3 × CH, 1-adamantyl), 58.5 (s, 1 C, 1 × C(CH_3)$_3$), 115.0 (br s, 1 C, 1 × C^{1}, 1-adamantyl), 130.0 (s, 1 C, 1 × C═S).

***N*-*tert*-Butyl-*N*′-2,6-diisopropylphenylcarbodiimine (3).** In a 250 mL two-necked round-bottom flask, LiHMDS (3.962 g, 16.411 mmol) was added, along with 100 mL of THF, and the resulting solution cooled to −78 °C. Dropwise, a solution of **1** (2.400 g, 8.205 mmol) in THF was added to the LiHMDS solution at −78 °C *via* dropping funnel. The resulting reaction solution was slowly warmed to room temperature over a period of 1 h and then refluxed for 2 h. During the course of reflux, the formation of a white precipitate was observed. The reaction was then allowed to cool to room temperature, and the volatile components were removed *in vacuo*. The residue was extracted with *n*-hexane and filtered *via* cannula, and the solvent from the filtrate was removed *in vacuo*. This afforded a colorless oil as product, which on the basis of NMR is completely pure, and no further distillation or purification step was required. Yield: 1.53 g, 5.91 mmol (72%). ^{1}H NMR (200.13 MHz, C_6D_6, 25 °C, ppm): δ 1.18 (s, 9 H, 1 × C(CH_3)$_3$), 1.23 (d, $^{3}J_{H-H}$ = 6.9 Hz, 12 H, 2 × CH(CH_3)$_2$), 3.63 (sept, $^{3}J_{H-H}$ = 6.9 Hz, 2 H, 2 × CH(CH_3)$_2$), 7.06 (s, 3 H, 3 × C-H, Dipp). Literature (300 MHz, C_6D_6, ppm): 1.18 (s, 9 H, 1 × C(CH_3)$_3$), 1.24 (d, 12 H, 2 × CH(CH_3)$_2$), 3.64 (sept, 2 H, CHMe$_2$), 7.07 (m, 3 H, *m*- and *p*-C_6H_3). ^{13}C{^{1}H} NMR (50.32 MHz, C_6D_6, 25 °C, ppm): δ 23.5 (s, 4 C, 2 × CH(CH_3)$_2$), 29.1 (s, 2 C, 2 × CH(CH_3)$_2$), 31.5 (s, 3 C, 1 × C(CH_3)$_3$), 55.8 (s, 1 C, 1 × C(CH_3)$_3$), 123.6 (s, 2 C, 2 × $C^{3,5}$, Dipp), 125.0 (s, 1 C, 1 × C^{4}, Dipp), 131.3 (s, 1 C, 1 × N═C═N), 135.1 (s, 1 C, 1 × C^{1}, Dipp), 142.5 (s, 2 C, 1 × $C^{2,6}$, Dipp).

***N*-Adamantyl-*N*′-*tert*-butylcarbodiimine (4).** In a 250 mL Schlenk flask, compound **2** (1.90 g, 7.60 mmol) and LiHMDS (2.50 g, 15.10 mmol) were added. The two solids were mixed thoroughly and cooled to −90 °C. Then 100 mL of precooled (−90 °C) THF was added rapidly *via* cannula to the solid mixture. The reaction was allowed to warm to room temperature over a period of several hours, during which a white precipitate formed. The supernatant solution was subsequently removed *in vacuo*, *n*-hexane (150 mL) was added to the residue, and the solution was stirred at room temperature for 0.5 h. The resulting suspension was filtered *via* a sintered glass frit, and the solvent from the filtrate was removed *in vacuo*. This afforded a wax-like solid in quantitative yields. ^{1}H NMR (200.13 MHz, C_6D_6, 25 °C, ppm): δ 1.22 (s, 9 H, 1 × C(CH_3)$_3$), 1.46 (m, 6 H, 3 × CH_2, 1-adamantyl), 1.86 (m, 9 H, 3 × CH_2 + 3 × CH, 1-adamantyl). ^{13}C{^{1}H} NMR (50.3 MHz, C_6D_6, 25 °C, ppm): δ 29.9 (s, 3 C, 3 × CH, adamantyl), 31.2 (s, 3 C, 3 × CH_3), 35.9 (s, 3 C, 3 × CH_2, 1-adamantyl), 45.0 (s, 3 C, 3 × CH_2, 1-adamantyl), 54.5 (s, 1 C, 1 × C^{1}, 1-adamantyl), 55.1 (s, 1 C, 1 × C(CH_3)$_3$), 138.9 (s, 1 C, 1 × N═C═N). ^{13}C shifts from literature[19f] in $CDCl_3$: δ 29.9, 31.3, 36.1, 44.9, 54.9, 55.0, 139.0.

(*N*-2,6-Diisopropylphenyl-*N*′-*tert*-butyl)benzamidinatotrichlorosilane (5). A Schlenk tube was charged with **3** (0.664 g, 2.570 mmol), and 20 mL of diethyl ether was added to the solid. The solution was cooled to −78 °C, and 1.45 mL of a 1.8 M solution of phenyllithium (0.220 g, 2.621 mmol) in dibutyl ether added dropwise. The yellow-colored reaction solution was stirred at −78 °C for 1 h, slowly warmed to room temperature, and then stirred for a further 3 h. Tetrachlorosilane (300 μL, 2.621 mmol) was added to the resulting solution rapidly *via* syringe upon which the formation of a white precipitate is observed. The reaction was stirred at room temperature for 12 h, and the resulting orange suspension filtered *via* cannula. The filtrate was concentrated *in vacuo* until the incipient point of crystallization and cooled to 5 °C overnight, affording colorless crystals of **5**. Yield: 1.208 g, 2.159 mmol (84%). Mp: 175−178 °C. ^{1}H NMR (200.13 MHz, C_6D_6, 25 °C, ppm): δ 1.13 (d, $^{3}J_{H-H}$ = 6.9 Hz, 6 H, 2 × CHCH^{A}_3), 1.24 (s, 9 H, 1 × C(CH_3)$_3$), 1.51 (d, $^{3}J_{H-H}$ = 6.7 Hz, 6 H, 2 × CHCH^{B}_3), 3.42 (sept, $^{3}J_{H-H}$ = 6.8 Hz, 2 H, 2 × CH(CH_3)$_2$), 6.66−6.72 (m, 1 H, 1 × C^{4}-H, Ph), 6.72−6.78 (m, 2 H, 1 × C^{3,5}-H, Ph), 6.81 (d, $^{4}J_{H-H}$ = 1.5 Hz, 1 H, 1 × C$^{3\text{ or }5}$-H, Dipp), 6.83 (br s, 1 H, 1 × C$^{3\text{ or }5}$-H, Dipp), 6.89 (dd, $^{3}J_{H-H}$ = 6.5 Hz, $^{3}J_{H-H}$ = 7.7 Hz, 1 H, 1 × C^{4}-H, Dipp), 7.07−7.11 (m, 2 H, 1 × C^{2,6}-H, Ph). ^{13}C{^{1}H} NMR (50.3 MHz, C_6D_6, 25 °C, ppm): δ 23.8 (s, 2 C, 2 × CHC^{A}H$_3$), 25.7 (s, 2 C, 2 × CHC^{B}H$_3$), 29.2 (s, 2 C, 2 × −CH(CH_3)$_2$), 31.0 (s, 3 C, 1 × C(CH_3)$_3$), 55.8 (s, 1 C, 1 × C(CH_3)$_3$), 123.9 (s, 2 C, 1 × $C^{3,5}$, Dipp), 127.1 (s, 2 C, 1 × $C^{2,6}$, Ph), 127.8 (s, 2 C, 1 × $C^{3,5}$, Ph (peak found by HMQC spectrum, hidden under solvent signal), 128.6 (s, 1 C, 1 × C^{1}, Ph), 129.0 (s, 1 C, 1 × C^{4}, Dipp), 130.7 (s, 1 C, 1 × C^{4}, Ph), 131.8 (s, 1 C, 1 × C^{1}, Dipp), 148.1 (s, 2 C, 1 × $C^{2,6}$, Dipp), 171.2 (s, 1 C, NC(Ph)N). ^{29}Si{^{1}H} NMR (50.3 MHz, C_6D_6, 25 °C, ppm): −93.8 (s, 1 Si, LSiCl$_3$). EI-MS, m/z: calcd for $C_{23}H_{31}N_2Cl_3Si$ [M]$^{+}$ 468 (100%); found 468. Anal. Calcd for $C_{23}H_{31}N_2Cl_3Si$: C 58.78, H 6.65, N 5.96. Found: C 58.94, H 6.80, N 6.00.

(*N*-2,6-Diisopropylphenyl-*N*′-*tert*-butyl)benzamidinatodichlorosilane (6). A Schlenk tube was charged with **3** (0.961 g, 3.719 mmol), and 30 mL of diethyl ether was added to the solid. The solution was cooled to −78 °C, and 2.10 mL of a 1.8 M solution of phenyllithium (0.319 g, 3.793 mmol) in dibutyl ether was added dropwise. The yellow-colored reaction solution was stirred at −78 °C for 1 h, slowly warmed to room temperature, and then stirred for a further 3 h. Trichlorosilane (400 μL, 3.793 mmol) was added to the resulting solution rapidly *via* syringe, upon which the formation of a white precipitate was observed. The reaction was then stirred at room temperature for 12 h, and the resulting orange suspension filtered *via* cannula. The filtrate was concentrated *in vacuo* until the incipient point

dx.doi.org/10.1021/om5005918 | *Organometallics* 2014, 33, 5272−5282

of crystallization and cooled to 5 °C overnight, affording colorless crystals of **6**. Yield: 1.446 g, 3.310 mmol (89%). Mp: 103−106 °C. ^{1}H NMR (200.13 MHz, C_6D_6, 25 °C, ppm): δ 1.12 (s, 9 H, 1 × C(CH_3)$_3$), 1.12 (d, $^{3}J_{H-H}$ = 6.9 Hz, 6 H, 2 × CHCH^{A}_3), 1.50 (d, $^{3}J_{H-H}$ = 6.8 Hz, 6 H, 2 × CHCH^{B}_3), 3.39 (sept, $^{3}J_{H-H}$ = 6.8 Hz, 2 H, 2 × $CH(CH_3)_2$), 6.60 (s, $^{1}J_{Si-H}$ = 353 Hz, 1 H, 1 × Si-*H*), 6.67−6.77 (m, 3 H, 1 × C^{3,4,5}-*H*, Ph), 6.84 (d, $^{4}J_{H-H}$ = 1.6 Hz, 1 H, 1 × C$^{3\text{ or }5}$-*H*, Dipp), 6.86 (br s, 1 H, 1 × C$^{3\text{ or }5}$-*H*, Dipp), 6.91 (dd, $^{3}J_{H-H}$ = 6.6 Hz, $^{3}J_{H-H}$ = 8.8 Hz, 1 H, 1 × C^{4}-*H*, Dipp), 7.06−7.10 (m, 2 H, 1× C^{2,6}-*H*, Ph). ^{13}C{^{1}H} NMR (50.32 MHz, C_6D_6, 25 °C, ppm): δ 23.7 (s, 2 C, 2 × CHC^{A}H$_3$), 25.7 (s, 2 C, 2 × CHC^{B}H$_3$), 29.1 (s, 2 C, 2 × $CH(CH_3)_2$), 30.8 (s, 3 C, 1 × C(CH_3)$_3$), 55.1 (s, 1 C, 1 × $C(CH_3)_3$), 123.8 (s, 2 C, 1 × C^{3,5}, Dipp), 127.3 (s, 2 C, 1 × C^{2,6}, Ph), 127.7 (s, 1 C, 1 × C^{4}, Ph (peak found by HMQC spectrum, hidden under solvent signal), 128.7 (s, 1 C, 1 × C^{4}, Dipp), 129.7 (s, 1 C, 1 × C^{1}, Ph), 130.5 (s, 2 C, 1 × C^{3,5}, Ph), 132.2 (s, 1 C, 1 × C^{1}, Dipp), 147.9 (s, 2 C, 1 × C^{2,6}, Dipp), 170.5 (s, 1 C, 1 × NC(Ph)N). ^{29}Si{^{1}H} NMR (50.32 MHz, C_6D_6, 25 °C, ppm): δ −92.8 (s, 1 Si, L*Si*HCl$_2$). ^{29}Si-INEPT NMR (200.13 MHz, C_6D_6, 25 °C, ppm): δ −92.9 (s, 1 Si, L*Si*HCl$_2$; $^{1}J_{Si-H}$ = 353 Hz). EI-MS, *m*/*z*: calcd for $C_{23}H_{32}N_2Cl_2Si$ [M]$^{+}$ 434 (100%); found 434. Anal. Calcd for $C_{23}H_{32}N_2Cl_2Si$: C 63.43, H 7.41, N 6.43. Found: C 63.13, H 7.66, N 6.28. IR (KBr, [cm^{-1}]): 2214 (s) (Si−H), 2193 (s) (Si−H).

(*N*-2,6-Diisopropylphenyl-*N*′-*tert*-butyl)guanidinato-dichlorosilane (7). A Schlenk tube was charged with compound **3** (1.726 g, 6.679 mmol), and 50 mL of THF was added to the solid. The solution was cooled to −78 °C, and a solution of $LiNMe_2$ (0.443 g, 8.683 mmol) in THF was added dropwise to it under rapid stirring. The yellow-colored reaction solution was stirred at −78 °C for 1 h, slowly warmed to room temperature, and then stirred for a further 2 h. Trichlorosilane (300 μL, 2.621 mmol) was added to the resulting solution rapidly *via* syringe (at −78 °C), upon which the formation of a white precipitate was observed. The reaction was stirred at room temperature for 12 h, and all volatiles were removed *in vacuo*. The resulting residue was extracted with 100 mL of CH_2Cl_2 and filtered *via* cannula, after which the CH_2Cl_2 was removed *in vacuo*. The residue was washed with 5 mL of *n*-hexane, the washing discarded, and the resulting solid dried *in vacuo* for 0.5 h, affording **7** as a white solid. Yield: 2.221 g, 5.544 mmol (83%). Mp: 123−128 °C. ^{1}H NMR (200.13 MHz, C_6D_6, 25 °C, ppm): δ 1.09 (d, $^{3}J_{H-H}$ = 6.8 Hz, 6 H, 2 × CHCH^{A}_3), 1.26 (s, 9 H, 1 × C(CH_3)$_3$), 1.46 (d, $^{3}J_{H-H}$ = 6.8 Hz, 6 H, 2 × CHCH^{B}_3), 2.12 (s, 6 H, 1 × N(CH_3)$_2$), 3.34 (sept, $^{3}J_{H-H}$ = 6.8 Hz, 2 H, 2 × $CH(CH_3)_2$), 6.56 (s, 1 H, $^{1}J_{Si-H}$ = 346 Hz, 1 × Si-*H*), 6.99−7.18 (m, 3 H, 1 × C^{3,4,5}-*H*, Dipp). ^{13}C{^{1}H} NMR (50.32 MHz, C_6D_6, 25 °C, ppm): δ 23.7 (s, 2 C, 2 × CHC^{A}H$_3$), 25.6 (s, 2 C, 2 × CHC^{B}H$_3$), 28.6 (s, 2 C, 2 × $CH(CH_3)_2$), 30.5 (s, 3 C, 1 × C(CH_3)$_3$), 40.8 (s, 2 C, 1 × N(CH_3)$_2$), 54.1 (s, 1 C, 1 × −$C(CH_3)_3$), 124.3 (s, 2 C, 1 × C^{3,5}, Dipp), 128.3 (s, 1 C, 1 × C^{4}, Dipp), 134.4 (s, 1 C, 1 × C^{1}, Dipp), 147.5 (s, 2 C, 1 × C^{2,6}, Dipp), 171.2 (s, 1 C, 1 × NC(Ph)N). ^{29}Si-INEPT NMR (200.13 MHz, C_6D_6, 25 °C, ppm): δ −102.3 (s, 1 Si, L*Si*HCl$_2$; $^{1}J_{Si-H}$ = 346 Hz). EI-MS, *m*/*z*: calcd for $C_{19}H_{33}N_3Cl_2Si$ [M]$^{+}$ 401 (100%); found 401. Anal. Calcd for $C_{19}H_{33}N_3Cl_2Si$: C 56.70, H 8.26, N 10.44. Found: C 56.81, H 8.70, N 10.46. IR (KBr, [cm^{-1}]): 2221 (s) (Si−H), 2141 (s) (Si−H).

(*N*-Adamantyl-*N*′-*tert*-butyl)benzamidinatodichlorosilane (8). A Schlenk tube was charged with carbodiimine **4** (1.00 g, 4.40 mmol), and 100 mL of diethyl ether was added to the solid. The solution was cooled to −78 °C, and 2.4 mL of a 1.8 M solution of phenyllithium in dibutyl ether was added dropwise. The light orange colored reaction solution was stirred at −78 °C for 1 h, slowly warmed to room temperature, and then stirred for a further 2.5 h. The reaction solution was then recooled to −50 °C, and trichlorosilane (0.44 mL, 4.40 mmol) was added to the resulting solution rapidly *via* syringe, upon which the formation of a white precipitate was observed with a yellow supernatant. The reaction was stirred at room temperature for 12 h, and the yellowish suspension was filtered *via* cannula. The filtrate was concentrated *in vacuo*, where upon a large amount of the product precipitated as a colorless solid. The remaining filtrate was decanted, and the solid dried *in vacuo* for 0.5 h, affording a pure colorless solid, **8**. Yield: 1.1 g, 2.7 mmol (61%). Mp: 115−116 °C. ^{1}H NMR (200.13 MHz, C_6D_6, 25 °C, ppm): δ 1.15 (s, 9 H, 1 × C(CH_3)$_3$), 1.33 (m, 6 H, 3 × CH_2, 1-adamantyl), 1.73 (m, 3 H, 3 × *CH*, 1-adamantyl), 1.90 (m, 6 H, 3 × CH_2, 1-adamantyl), 6.80−6.92 (m, 6 H, $^{1}J_{Si-H}$ = 332 Hz 1 × Si*H* + 5 × Ar-*H*). ^{13}C{^{1}H} NMR (50.32 MHz, C_6D_6, 25 °C, ppm): δ 29.9 (s, 3 C, 3 × CH_2, 1-adamantyl), 31.5 (s, 6 C, 6 × CH_3), 36.1 (s, 3 C, 3 × CH_2, 1-adamantyl), 43.5 (s, 3 C, 3 × *CH*, 1-adamantyl), 55.5 (s, 1 C, 1 × $C(CH_3)_3$), 57.2 (s, 3 C, C^{1}, 1-adamantyl), 128.0 (signals located by HMQC spectrum) (Ph-*C*), 128.2 (s, 1 C, 1 × Ph-*C*), 130.0 (s, 1 C, 1 × Ph-*C*), 133.2 (s, 1 C, 1 × C^{1}, Ph) 171.3 (s, 1 C, 1 × NCN). ^{29}Si{^{1}H} NMR (50.32 MHz, C_6D_6, 25 °C, ppm): δ −97.3. ESI-MS, *m*/*z*: calcd for $C_{21}H_{30}N_2ClSi$ [M − Cl]$^{+}$ 373.1861; found 373.1868.

(*N*-(2,6-Diisopropylphenyl-*N*′-*tert*-butyl)benzamidinato)-silylidene-irontetracarbonyl (9). A Schlenk tube was charged with **6** (0.546 g, 1.258 mmol) and K_2[Fe(CO)$_4$] (0.311 g, 1.258 mmol), and the two solids were cooled to −78 °C. Precooled THF (−78 °C, 50 mL) was added under stirring to the solid mixture *via* cannula. After completion of the addition of THF, the reaction mixture was slowly allowed to warm to room temperature and stirred for a further 12 h. The reaction solution turned light brown, and the formation of a white precipitate was observed. The volatile components were subsequently removed *in vacuo*, the remaining brown residue was extracted with toluene (50 mL), and the toluene was removed *in vacuo* (in the filtrate), affording a brown residue. This brown residue was then extracted with *n*-hexane (50 mL), concentrated to 5 mL *in vacuo*, and then stored at −30 °C. A light brown precipitate resulted, which was separated carefully at −30 °C from the supernatant *via* syringe, affording a light brown solid as product. Yield: 134 mg, 0.252 mmol (20%). ^{1}H NMR (200.13 MHz, C_6D_6, 25 °C, ppm): δ 1.09 (d, $^{3}J_{H-H}$ = 6.9 Hz, 6 H, 2 × CHCH^{A}_3), 1.28 (d, $^{3}J_{H-H}$ = 6.9 Hz, 6 H, 2 × CHCH^{B}_3), 1.46 (s, 9 H,1 × C(CH_3)$_3$), 3.29 (sept, $^{3}J_{H-H}$ = 6.9 Hz, 2 H, 2 × $CH(CH_3)_2$), 6.65−6.76 (m, 2 H, 2 × C-*H*, Ph), 6.80−6.93 (m, 3 H, 3 × C-*H*, Ph), 7.05 (s, $^{1}J_{Si-H}$ = 200 Hz, 1 H, 1 × Si-*H*), 6.94−7.11 (m, 3 H, 3 × C-*H*, Dipp). ^{13}C{^{1}H} NMR (50.32 MHz, C_6D_6, 25 °C, ppm): δ 22.4 (s, 2 C, 2 × CHC^{A}H$_3$), 24.8 (s, 2 C, 2 × CHC^{B}H$_3$), 28.7 (s, 3 C, 1 × C(CH_3)$_3$), 28.9 (s, 2 C, 2 × $CH(CH_3)_2$), 51.5 (s, 1 C, 1 × $C(CH_3)_3$), 123.0 (s, 2 C, 1 × C$^{3;5}$, Dipp), 124.7 (s, 1 C, 1 × C^{4}, Ph), 128.2 (s, 2 C, Ph (peak found by HMQC spectrum, hidden under solvent signal), 128.9 (s, 2 C, *C*, Ph), 136.7 (s, 1 C, 1 × C^{1}, Dipp), 138.5 (s, 2 C, 1 × C^{2,6}, Dipp), 146.4 (s, 1 C, 1 × C^{4}, Dipp), 153.3 (s, 1 C, 1 × NC(Ph)N), 213.1 (s, 2 C, 2 × Fe(CO)$^{A}_4$), 214.9 (s, 2 C, 2 × Fe(CO)$^{B}_4$). ^{29}Si{^{1}H} NMR (50.32 MHz, C_6D_6, 25 °C, ppm): δ 99.6 (s, 1 Si, L*Si*(H)-Fe(CO)$_4$). ^{29}Si-INEPT NMR (200.13 MHz, C_6D_6, 25 °C, ppm): δ 99.6 (s, 1 Si, L*Si*(H)-Fe(CO)$_4$; $^{1}J_{Si-H}$ = 200 Hz). ESI-MS, *m*/*z*: calcd for $C_{27}H_{32}N_2O_4SiFe$ [M + H]$^{+}$ 533.1509; found 533.1554. IR (KBr, [cm^{-1}]): 2059 (m) (Si−H), 2013 (s) (CO), 1984 (s) (CO), 1887 (s) (CO).

(*N*-(2,6-Diisopropylphenyl-*N*′-*tert*-butyl)guanidinato)-silylidene-irontetracarbonyl (10). A Schlenk tube was charged with **7** (0.287 g, 0.711 mmol) and K_2[Fe(CO)$_4$] (0.175 g, 0.712 mmol), and the two solids cooled to −78 °C. Precooled THF (−78 °C, 50 mL) was added under stirring to the solid mixture *via* cannula. After completion of the addition of the THF, the reaction mixture was slowly allowed to come to room temperature and stirred for a further 12 h. The reaction solution turned light brown, and the formation of a white precipitate was observed. The volatile components were subsequently removed *in vacuo*, the remaining brown residue was extracted with toluene (50 mL), and the toluene was removed *in vacuo* (in the filtrate), affording a brown residue. The brown residue was carefully washed with *n*-hexane (20 mL) at 0 °C, and the *n*-hexane washings were discarded. The remaining light brown residue was dried *in vacuo* for 0.5 h, affording the product. Yield: 88 mg, 0.178 mmol (25%). Mp: 60 °C (dec). ^{1}H NMR (200.13 MHz, C_6D_6, 25 °C ppm): δ 0.98 (d, $^{3}J_{H-H}$ = 6.8 Hz, 3 H, 1 × C^{6}CHCH^{D}_3), 1.11 (d, $^{3}J_{H-H}$ = 6.9 Hz, 3 H, 1 × C^{2}CHCH^{B}_3), 1.25 (s, 9 H, 1 × C(CH_3)$_3$), 1.31 (d, $^{3}J_{H-H}$ = 6.8 Hz, 3 H, 1 × C^{2}CHCH^{A}_3), 1.49 (d, $^{3}J_{H-H}$ = 6.9 Hz, 3 H, 1 × C^{6}CHCH^{C}_3), 2.04 (s, 6 H, 1 × −N(CH_3)$_2$), 2.91 (sept, $^{3}J_{H-H}$ = 6.7 Hz, 1 H, 1 × C^{6}CH(CH_3)$_2$), 3.49 (sept, $^{3}J_{H-H}$ = 6.9 Hz, 1 H, 1 × C^{2}*CH*(CH_3)$_2$), 6.96−7.02 (m, 2 H, 1 × C^{3,5}-*H*, Dipp), 7.04 (s, 1 H, 1 × Si-*H*, Si-satellites: $^{1}J_{Si-H}$ = 205 Hz), 7.06−7.13 (m, 1 H, 1 × C^{4}-*H*,

dx.doi.org/10.1021/om5005918 | *Organometallics* 2014, 33, 5272−5282

Dipp). $^{13}C\{^1H\}$ NMR (50.32 MHz, C_6D_6, 25 °C, ppm): δ 22.8 (s, 1 C, 1 × $C^2CHC^BH_3$), 24.6 (s, 1 C, 1 × $C^6CHC^DH_3$), 25.5 (s, 1 C, 1 × $C^2CHC^AH_3$), 26.0 (s, 1 C, 1 × $C^6CHC^CH_3$), 28.2 (s, 1 C, 1 × $C^6CH(CH_3)_2$), 28.9 (s, 1 C, 1 × $C^2CH(CH_3)_2$), 30.1 (s, 3 C, 1 × $C(CH_3)_3$), 39.9 (s, 2 C, 1 × $N(CH_3)_2$), 54.4 (s, 1 C, 1 × $-C(CH_3)_3$), 124.4 (s, 1 C, 1 × C^3, Dipp), 124.7 (s, 1 C, 1 × C^5, Dipp), 128.3 (s, 1 C, 1 × C^4, Dipp (peak found by HMQC spectrum, hidden under solvent signal), 133.3 (s, 1 C, 1 × C^1, Dipp), 145.5 (s, 1 C, 1 × C^2, Dipp), 146.0 (s, 1 C, 1 × C^6, Dipp), 161.4 (s, 1 C, 1 × −N-C(NMe_2)-N−), 215.7 (s, 4 C, 1 × Fe$(CO)_4$). ^{29}Si-INEPT NMR (200.13 MHz, C_6D_6, 25 °C, ppm): δ 83.6 (s, 1 Si, L*Si*(H)-Fe$(CO)_4$; $^1J_{Si-H}$ = 205 Hz). ESI-MS, *m/z*: calcd for $C_{23}H_{33}N_3O_4SiFe$ $[M + H]^+$ 500.1663; found 500.1660. Anal. Calcd for $C_{23}H_{33}N_3O_4SiFe$: C 55.31, H 6.66, N 8.41. Found: C 55.46, H 6.84, N 8.62. IR (KBr, [cm^{-1}]): ν = 2100 (br,w) (Si−H), 2022 (s) (CO), 1944 (s) (CO), 1909 (s) (CO).

(*N*-Adamantanyl-*N*′-*tert*-butyl)benzamidinato)silylidene-irontetracarbonyl (11). A Schlenk tube was charged with **8** (0.25 g, 0.61 mmol) and $K_2[Fe(CO)_4]$ (0.15 g, 0.61 mmol) and placed in a −50 °C cold bath. Precooled THF (60 mL) was added under rapid stirring to the solid mixture *via* cannula, and the reaction was left stirring in the cold bath over 12 h, with gradual warming to room temperature. During the course of the reaction, a white precipitate was observed, with a light brown supernatant solution. The solvent was removed *in vacuo*, and the remaining brown residue extracted with toluene (20 mL) and filtered *via* cannula. The toluene of the filtrate was removed *in vacuo*, affording a light brown solid, which was scratched into a powder by a freeze−pump−thaw cycle and dried for several hours at room temperature *in vacuo*. Yield: 0.23 g, 0.56 mmol (92%). Mp: 137−140 °C (dec). ^{1}H NMR (200.13 MHz, C_6D_6, 25 °C ppm): δ 1.05 (s, 9 H, 3 × CH_3), 1.31 (m, 9 H, 3 × CH_2, 1-adamantyl +3 × C*H*, 1-adamantyl), 1.77 (m, 6 H, 3 × CH_2, 1-adamantyl), 6.91 (s, 1 H, 1 × Si-*H*, Si-satellites: $^1J_{Si-H}$ = 204 Hz, 1 × Si*H*), 6.81−6.94 (m, 5 H, 5 × Ar-*H*) . $^{13}C\{^1H\}$ NMR (50.32 MHz, C_6D_6, 25 °C, ppm): δ 9.7 (s, 3 C, 3 × *C*H, 1-adamantyl), 31.1 (s, 3 C, 3 × CH_3), 35.7 (s, 3 C, 3 × CH_2, 1-adamantyl), 44.0 (s, 3 C, 3 × CH_2, 1-adamantyl), 54.9 (s, 1 C, 1 × $C(CH_3)_3$), 56.4 (s, 1 C, 1 × C^1, 1-adamantyl), 127.8 (s, 2 C, Ph), 128.0 (s, 2 C, Ph), 128.2 (s, 1 C, Ph), 130.7 (s, 1 C, Ph), 170.4 (s, 1 C, 1 × N═C(Ph)-N), 217.1, (s, 4 C, 4 × *CO*). $^{29}Si\{^1H\}$ NMR (50.32 MHz, C_6D_6, 25 °C, ppm): δ 86.5 ppm. ESI-MS, *m/z*: calcd for $C_{25}H_{30}FeN_2O_4Si$ $[M + H]^+$ 507.1397; found 507.1398.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Selected NMR and MS spectra of the compounds reported here as well as crystallographic details are available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors thank the Cluster of Excellence UniCat (financed by the Deutsche Forschungsgemeinschaft and administered by the TU Berlin). Alma Jäger is thanked for experimental assistance in the preparation of some of the compounds reported here as part of an internship under the supervision of B.B. Terry Brauer (University of South Africa) is gratefully acknowledged for proofreading the manuscript.

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