Silyl Hydrides of Tantalum Supported by Cyclopentadienyl-imido Ligand Sets: Syntheses, X-ray, NMR, and DFT Studies

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Reactions of the imido complex $Cp(ArN)Ta(PMe_3)_2$ (**1**, Ar = 2,6-diisopropylphenyl) with silanes afford the silyl hydrides $Cp(ArN)Ta(PMe_3)(H)(SiR_nCl_{3-n})$ (**2b**−**e**) and $Cp(ArN)Ta(PMe_3)(H)(SiPhMeH)$ (**2a**) as the first kinetic products. However, the hydride compounds $Cp(ArN)Ta(PMe_3)(H)(SiR_nCl_{3-n})$ are metastable and, first, rearrange in the presence of phosphine to the chlorides $Cp(ArN)Ta(PMe_3)(Cl)(SiHR_nCl_{2-n})$ (**5**) and then decompose to $Cp(ArN)Ta(PMe_3)(Cl)(H)$ (**4**) and eventually to $Cp(ArN)Ta(PMe_3)Cl_2$ (**3**). Complexes with a smaller Ar′ substituent at nitrogen (Ar′ = 2,6-dimethylphenyl) react faster, as do more Lewis acidic silanes. The occurrence of interligand hypervalent interactions in the tantalum complexes $Cp(ArN)Ta(PMe_3)(H)(SiR_nCl_{3-n})$ has been revealed by X-ray structure analysis, DFT calculations, and the experimental determination of the sign of the coupling constant J(Si−H). The J(Si−H) was found to be negative for $Cp(ArN)Ta(PMe_3)(H)(SiMe_nCl_{3-n})$ (J(Si−H) = −40 Hz for n = 1; J(Si−H) = −50 Hz for n = 0), indicative of the presence of Si−H bonding, but positive for $Cp(ArN)Ta(PMe_3)(H)(SiMeHPh)$ (J(Si−H) = +14 Hz), suggesting the absence of direct Si−H interactions. A DFT study of the mechanism of silane coupling with the model imido complex $Cp(MeN)Ta(PMe_3)_2$ established the feasibility of the direct addition of silanes $HSiMe_nCl_{3-n}$ (n = 1−3) to the imido group to give the adduct $Cp(MeN\{\rightarrow SiR_3\text{-}H\})Ta(PMe_3)_2$, as previously found in the related niobium chemistry.

Introduction

Early transition metal silyl complexes in nonmetallocene environments[1] have recently received significant attention. Most of this interest stems from their relevance to catalytic transformations of organosilanes[2] such as dehydrogenative polymerization, and uses as potential precursors to M/N/Si ceramics, which have useful applications in microelectronics as diffusion barriers.[3]

We[4,5] and others[6] have been studying the application of the imido ligand $(RN)^{2-}$, which is isolobal to the ubiquitous cyclopentadienide ligand Cp^-,[7] to the design of metallocene-

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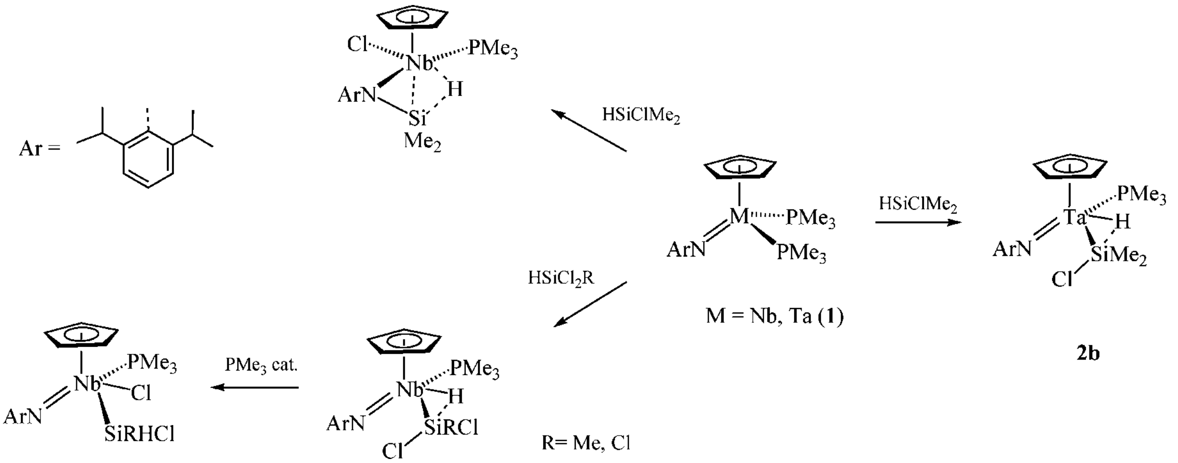
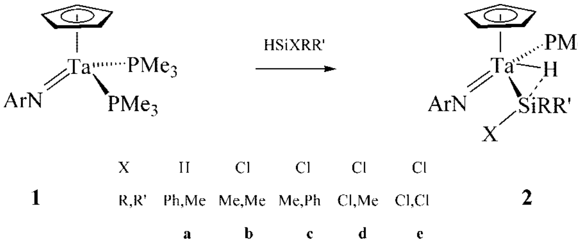
Scheme 1. Reactions of $\mathrm{Cp(ArN)M(PMe_3)_2}$ (M = Nb, Ta) with Hydrosilanes



like ligand platforms. In particular, we are interested in studying the effect of supporting ligand sets on the extent of interligand hypervalent interactions (IHI) between silyl and hydride ligands, which were originally discovered for group 5[8] and 4[9] metallocene complexes. We have previously established[5] that $\mathrm{Cp(ArN)Ta(PMe_3)_2}$ (**1**, Ar = 2,6-diisopropylphenyl) reacts with $\mathrm{HSiClMe_2}$ to afford the silylhydrido complex $\mathrm{Cp(ArN)Ta(PMe_3)(H)(SiClMe_2)}$ (**2b**), whereas the corresponding reaction of $\mathrm{Cp(ArN)Nb(PMe_3)_2}$ gives the β-agostic silylamido compound $\mathrm{Cp\{\eta^3\text{-}N(Ar)SiMe_2\text{-}H\}NbCl(PMe_3)}$ (Scheme 1).[10] The silyl hydride **2b**, like its isolobal niobocene analogues $\mathrm{Cp_2Nb(SiClMe_2)(H)(X)}$ (X = H, $\mathrm{SiMe_2Cl}$),[11] was shown to have IHI according to X-ray analysis and DFT calculations. By applying more Lewis acidic silanes $\mathrm{HSiCl_2R}$ (R = Me, Cl), we prepared metastable niobium complexes $\mathrm{Cp(ArN)Nb(PMe_3)(H)(SiCl_2R)}$, which rearrange/decompose *upon phosphine catalysis* into silyl chlorides $\mathrm{Cp(ArN)Nb(PMe_3)(Cl)(SiClHR)}$ and/or to the hydride $\mathrm{Cp(ArN)Nb(PMe_3)(Cl)(H)}$.[12] Mechanistic studies established that silane addition to $\mathrm{Cp(RN)Nb(PMe_3)_2}$ goes via an unusual coupling of silane with the nitrogen center rather than via the common Si−H bond oxidative addition to the metal. We then set out to investigate the effect of varying the ligand substituents on the extent of interligand interactions[13] in the corresponding tantalum chemistry. Preliminary results[14] for the complexes $\mathrm{Cp(ArN)Ta(PMe_3)(H)(SiXR_2)}$ revealed an unusual dependence of silicon−hydrogen coupling constants upon the substituents at silicon. Full details of this research and insights into the mechanism of formation of the complexes $\mathrm{Cp(ArN)Ta(PMe_3)(H)(SiR_3)}$ are reported herein.

Results and Discussion

1. Reactions of $\mathrm{Cp(ArN)Ta(PMe_3)_2}$ (1) with Silanes. The tantalum complex **1** (Ar = 2,6-diisopropylphenyl) readily reacts with a series of silanes $\mathrm{HSiXR_2}$ to give the silyl hydride derivatives **2** (eq 1). In none of the reactions were agostic compounds similar to the niobium complex $\mathrm{Cp\{\eta^3\text{-}N(Ar)SiMe_2\text{-}H\}NbCl(PMe_3)}$ (Scheme 1) observed. The products **2a**−**e** were characterized by spectroscopic methods (multinuclear NMR and IR) and by X-ray diffraction studies of $\mathrm{Cp(ArN)Ta(PMe_3)(H)(SiClMe_2)}$[5a] (**2b**) and $\mathrm{Cp(ArN)Ta(PMe_3)(H)(SiCl_2Me)}$ (**2d**).[14] In particular, the hydride signals appear as characteristic doublets due to the coupling with the phosphine at rather low field (about 5 ppm), apparently as a result of the anisotropy of the M−N multiple bond.[2a,15]



1 **2** (1)

Among the different silanes used in eq 1, chlorosilanes react with **1** within a few minutes, whereas the reaction with $\mathrm{H_2SiMePh}$ was complete only after 14 h, the products being two isomers of **2a** (ratio 7:1).[16] Heating an NMR sample of this mixture in $\mathrm{C_6D_6}$ at 60 °C for 1 h results in a rearrangement, changing the ratio to 3:2 without decomposition. Further heating at 110 °C for 5 h does not change the composition of the

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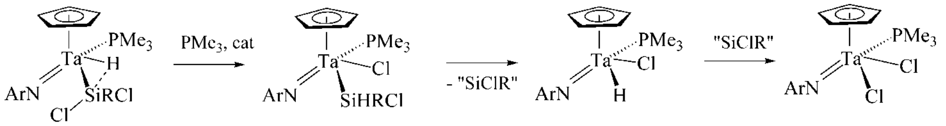
Scheme 2. Decomposition Pathway for Complexes 2d and 2e in Mother Liquor



2d,e **5d,e** **4** **3**

R Me Cl

d **e**

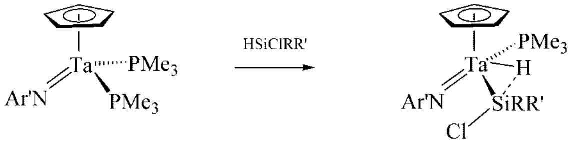
mixture, thus establishing the presence of equilibrium.[17] An NMR tube reaction of **1** with $HSiPh_2Cl$ showed an intractable mixture of products; thus a preparative scale reaction was not pursued. No reaction occurs with the bulkier silane HSi^iPr_2Cl over the course of several weeks.

Complexes **2a**–**e** are stable in the solid state and in solutions containing the pure complex. However, keeping the chlorosilyl complexes **2b**–**e** in the mother liquor leads to decomposition (Scheme 2). Thus, monitoring the reaction of **1** with $HSiCl_3$ at room temperature by NMR in C_6D_6 reveals, in addition to **2e**, a *very slow* formation of two more products, Cp(ArN)Ta$(PMe_3)Cl_2$ (**3**, Ar = 2,6-diisopropylphenyl) and a new hydridochloride derivative, Cp(ArN)Ta(PMe_3)(H)Cl (**4**).[18] Complex **4** exhibits a low-field hydride signal at 10.26 coupled to phosphorus with J(P–H)= 69.1 Hz, the large value of coupling constant being indicative of a cis arrangement of the hydride and phosphine ligands. Another intermediate, having a hydride signal at 7.91 (d, J(P–H)= 5.6 Hz) and a Cp signal at 5.86 (d, J(P–H) = 1.8 Hz), is tentatively assigned to the rearranged structure Cp(ArN)Ta(PMe_3)(Cl)$(SiHCl_2)$ (**5e**).[19] A similar rearrangement of complexes Cp(ArN)Nb(PMe_3)(H)$(SiCl_2R)$ to Cp(ArN)Nb(PMe_3)(Cl)(SiHClR) has been found in related niobium chemistry.[5c,12] Heating a sample of *pure* **2e** in C_6D_6 in a sealed NMR tube results in the formation of **3** after 12 h at 80 °C. However, in the presence of 3 equiv of PMe_3 a 40% decomposition of **2e** occurred within 2 h at 80 °C, the major products being **3** and the rearranged complex **5**, formed in a 4:3 ratio. In the presence of 3 equiv of PMe_3, complete transformation of **2e** to **3** at room temperature requires several days.

The compound **2d** slowly rearranges to **5d** in the mother liquor at room temperature so that after 2 days 35% conversion is achieved, with the yield of **5d** amounting to 22%. For comparison, the analogous rearrangement of Cp(ArN)Nb(PMe_3)(H)$(SiCl_2Me)$ takes several hours. Heating an NMR sample of pure **2d** at 50 °C for 21 h does not result in any significant decomposition, whereas an increase in temperature to 60 °C leads to a noticeable reaction, so that after 1.5 h the rearranged product **5d** contributes to about 30% intensity of the Cp-containing products in ^{1}H NMR. However, this transformation is not clean and several other coproducts are formed. One of them was identified as Cp(ArN)Ta(PMe_3)(H)(Cl) (**4**) (vide supra), a likely product of net silylene (:SiClMe) extrusion from **5d**. Further increasing the temperature to 90 °C results in decomposition to Cp(ArN)Ta$(PMe_3)Cl_2$ (**3**) after 2.5 h. Complete decomposition was achieved after heating the reaction mixture at 110 °C for 2 h. In contrast, when **2d** is heated in the presence of 15 equiv of PMe_3, the reaction occurs at *a noticeable rate already at 50 °C* and in 2.5 h the rearranged product **5d** is formed in 50% yield, the second major product being **3**. Further heating at this temperature results in a clean transformation of **5d** into **3**. Moreover, with 9 equiv of PMe_3 added, the compound **2d** rearranges *even at room temperature* over the course of several days into a mixture of **5d**, **3**, and **4**, achieving a 1:0.54: 0.20 ratio after 3 days, with the starting **2d** and other minor coproducts contributing to about 35% of the intensity in the Cp region. In the absence of phosphine, pure **2d** is stable in solutions at least for several weeks.

In contrast, thermal decomposition of Cp(ArN)Ta(PMe_3)-(H)$(SiMe_2Cl)$ (**2b**) is slow in both the presence and absence of PMe_3. A significant reaction is observed only at temperatures above 70 °C and requires 1.5 days to reach 50% conversion. Among various Cp and silane products formed, only H_2SiMe_2 was identified (by its characteristic ^{1}H NMR signals). Finally we note that attempted reactions of Cp(ArN)Ta$(PMe_2Ph)_2$ with $HSiMe_2Cl$ and $HSiMeCl_2$ gave Cp(ArN)Ta$(PMe_2Ph)Cl_2$ as the only tantalum-containing product.

2. Reactions of Cp(Ar′N)Ta$(PMe_3)_2$ with Silanes. The compound Cp(Ar′N)Ta$(PMe_3)_2$ (**6**, Ar′ = 2,6-dimethylphenyl), featuring a less bulky 2,6-dimethylphenyl substituent at nitrogen, is analogous to **1** and exhibits similar reactivity toward silanes $HSiClR_2$ (eq 2). The only difference is that in this case the reaction with $HSiClPh_2$ does give high yields of the derivative Cp(Ar′N)Ta(PMe_3)(H)$(SiClPh_2)$ (**7f**). The attempted reaction with HSi^iPr_2Cl does not afford an isolable silyl or agostic derivative, but instead slowly produces a complex reaction mixture of yet unidentified products over a period of several days. The compounds **7** were characterized by NMR and IR spectroscopy and by an X-ray diffraction study of **7d**.



6 **7**

R,R' Me,Me Me,Ph Cl,Me Ph,Ph

b c d f (2)

The molecular structure of **7d** is shown in Figure 1. This compound is analogous to the previously reported complex **2d**[14] and exhibits very similar molecular parameters (e.g., the Ta–Si bond is 2.569(2) Å in **2d** vs 2.570(6) Å in **7d**). Complex **7d** appears to have two different Si–Cl bond lengths (2.116(7) Å to the chloride lying trans to hydride and 2.109(9) Å to the cis Cl), although due to the relatively large esd's, the difference is not statistically significant. In the closely related compound **2d** two types of Si–Cl distances were observed, which was

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[17] The composition of the mixture was established by NMR experiments that were run at room temperature *after* the thermal experiments. Since the ratio of two diastereomers does not change with temperature, it suggests that their interconversion occurs with a relatively small barrier. No high-temperature NMR experiments were attempted.

[18] This compound has been prepared by an independent method and fully characterized. G. I. Nikonov, unpublished.

[19] We could not confirm this structure by the ^{29}Si NMR due to the low content of this species in the sample, but its niobium analogue has been previously described (ref 12).

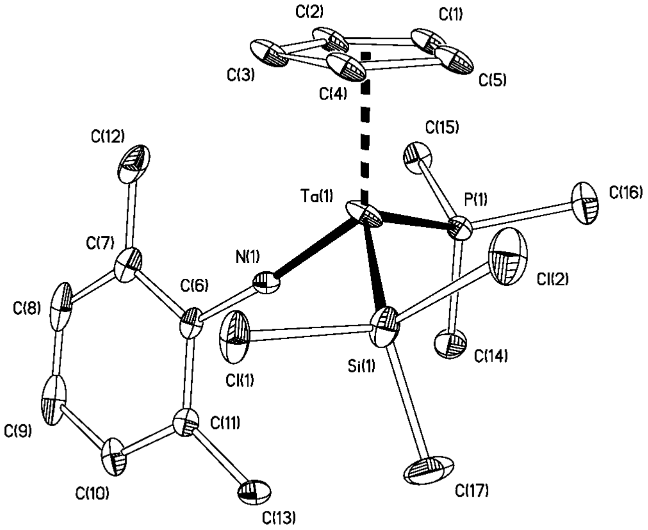

Figure 1. Molecular structure of **7d**. Hydrogen atoms are omitted for clarity. The hydride atom has not been determined. Selected bond distances (Å) and bond angles (deg): Ta1−P1 2.542(5), Ta1−Si1 2.570(6), Ta1−N1 1.794(14), Si1−Cl1 2.116(7), Si1−Cl2 2.109(9), Si1−C17 1.84(2), P1−Ta1−Si1 127.54(18), P1−Ta1−N1 90.7(4), Si1−Ta1−N1 97.7(4), Ta1−Si1−Cl1 114.3(3), Ta1−Si1−Cl2 110.8(3), Cl1−Si1−Cl2 101.9(4), Ta1−Si1−C17 121.6(11), Cl1−Si1−C17 103.4(12), Cl2−Si1−C17 102.6(10), Ta1−N1−C6 173.2(12).

attributed to the involvement of the trans Si−Cl bond in IHI with the Ta−H bond.[8−14]

Heating an NMR sample of pure **7b** in C_6D_6 at 60 °C for several hours produces a complex reaction mixture containing the silanes $HSiMe_2Cl$ and H_2SiMe_2 among other, as yet uncharacterized, products. No signals attributable to the putative agostic compound Cp(Ar′NSiMe$_2$-H)TaCl(PMe$_3$) or the rearranged product Cp(Ar′N)Ta(PMe$_3$)(Cl)(SiMe$_2$H) were observed in the ^{1}H NMR spectrum. Thermolysis of **7d** in C_6D_6 at 60 °C for several hours also gives a mixture of unidentified products. By way of contrast, heating **7c** (mixture of two isomers) in C_6D_6 at 65 °C in a sealed NMR tube does produce the rearranged product Cp(Ar′N)Ta(PMe$_3$)(Cl)(SiMePhH) (**8**, two isomers) identified by the characteristic pattern for the SiMePhH group. Due to the complexity of the reaction mixture and the presence of decomposition products, a preparative scale reaction was not pursued.

3. Spectroscopic Studies of Complexes Cp(RN)Ta(PMe$_3$)(H)(SiMe$_n$Cl$_{3-n}$) (R = Ar, Ar′). The silyl hydride complexes **2** (Ar = 2,6-diisopropylphenyl) and **7** (Ar′ = 2,6-dimethylphenyl) show an unusual trend in that the absolute values of the experimentally determined J(P−H) and J(Si−H) constants *increase* (by up to 50 Hz for the J(Si−H) in **2e**) upon increasing electronegativity of the substituents at Si (Table 1). This observation is of interest in view of the fact that most of the previously reported complexes with nonclassical Si−H interactions were characterized by J(Si−H) values larger than 20 Hz, with the coupling constant *decreasing* with increasing electronegativity of substituents at Si.[13,20] Surprisingly enough, our preliminary DFT and X-ray data for complexes **2** showed that *larger* J(Si−H) values correspond to weaker Si−H interactions in the more chlorinated members of this series.[14] Specifically, introduction of a chlorine group on silicon on going from **2a** to **2b** leads to the "switching on" of the interligand hypervalent interaction,[14b] but further chloride substitution at silicon results in the weakening of the Si−H bonding. Such behavior appears to be mirrored in the variation of the hydride signals in the ^{1}H NMR spectra (Table 1), which shift to a higher field from **2a** to **2b** but progressively move to a lower field from **2b** to **2e**.[21] An analogous "V"-type dependence on the number of Cl groups on Si was also observed for the Ta−H stretches in the IR spectra (Table 1). The high-field shift of the hydride resonance in the ^{1}H NMR spectra and the reduced frequency of the M−H band in the IR spectra serve as independent (although still indirect) indicators of the participation of the tantalum-bound hydride in a nonclassical bonding with the silicon atom ligand.[13e]

It is interesting to compare this result with silane σ-complexes, in which electron-withdrawing groups at silicon tend to promote more advanced Si−H addition (i.e., less residual Si−H interaction) to the metal,[13] although relatively large values of J(Si−H) can be still observed.[20] In contrast, chloride substitution in the agostic complex (Ar′N)(η^3-Ar′NSiMe$_2$-H···)Mo(Cl)(PMe$_3$)$_2$ (Ar′ = 2,6-dimethylphenyl) to give the analogue (Ar′N)(η^3-Ar′NSiMeCl-H···)Mo(Cl)(PMe$_3$)$_2$ results in slight strengthening of the Si−H interaction, although the value of J(Si−H) increases quite substantially (from 97 to 129 Hz).[5c] In all three cases (IHI, silane σ-complexes, and silylamido β-agostic complexes) the origin for the abnormal behavior of silicon−hydride coupling constants is the same: it stems from the relative increase of Si 3s character in the Si−H bond, caused by the chlorine substitution at silicon.[13e]

We have previously argued that the *sign* of the coupling constant, rather than its absolute value, serves as a more reliable signature of the presence of nonclassical bonding.[9] Namely, a negative sign of J(Si−H) indicates the presence of *direct* Si−H bonding due to the fact that silicon has a negative gyromagnetic ratio.[22] Indeed, negative values for J(Si−H) were measured or calculated for complexes for which the presence of interligand Si−H interactions was independently invoked from X-ray and/or DFT data.[9,23] We have now succeeded in the experimental determination of the sign of J(Si−H) in some complexes of type **2** (Table 1). In the compound Cp(ArN)Ta(PMe$_3$)(H)(SiMePhH) (**2a**, Ar = 2,6-diisopropylphenyl) the J(Si−H) was found to be positive, consistent with its classical silyl−hydride formulation. In contrast, in the chloro-substituted complexes Cp(ArN)Ta(PMe$_3$)(H)(SiMeCl$_2$) (**2d**) and Cp(ArN)Ta(PMe$_3$)(H)(SiCl$_3$) (**2e**) the signs of the Si−H coupling constants are *negative*, thus providing *ultimate experimental confirmation of the presence of significant interligand Si−H interactions*, in accord with the results of our X-ray studies and DFT calculations (vide infra).

4. Mechanism of Silane Addition. Our previous kinetic and DFT study of the reactions of Cp(ArN)Nb(PR′$_3$)$_2$ (Ar = 2,6-diisopropylphenyl) with silanes established the possibility of a

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(20) See, however, an exception of this trend: (a) Nikonov, G. I. *Organometallics* **2003**, *22*, 1597. (b) Lichtenberger, D. L. *Organometallics* **2003**, *22*, 1599. (c) Bader, R. F. W.; Matta, C. F.; Cortés-Guzmán, F. *Organometallics* **2004**, *23*, 66253. (d) Also see the comment on page 227 of ref 13e for the summary of the debate.

(21) The chemical shift of monochloro-substituted complex **2c** (5.82 and 5.68 ppm for two isomers) are downfield shifted relative to the chlorine free complex **2a**. However, given the fact that the phenyl group is a π-donor, which may result in descreased IHI, the origin of this shift is difficult to rationalize unequivocally.

(22) A negative J(Si−H) of −201.3 Hz was measured in SiH_4: (a) Jackowski, K. *Int. J. Mol. Sci.* **2003**, *4*, 135. (b) Sauer, S. P. A.; Raynes, W. T.; Nicholls, R. A. *J. Chem. Phys.* **2001**, *115*, 5994.

(23) Osipov, A. L.; Vyboishchikov, S. F.; Dorogov, K. Y; Kuzmina, L. G.; Howard, J. A. K.; Lemenovskii, D. A.; Nikonov, G. I. *Chem. Commun.* **2005**, 3349. (b) Vyboishchikov, S. F.; Nikonov, G. I. *Chem.−Eur. J.* **2006**, *12*, 8518. (c) Vyboishchikov, S. F.; Nikonov, G. I. *Organometallics* **2007**, *26*, 4160.

Table 1. Selected NMR (in C_6D_6) and IR (in Nujol) Parameters of Complexes 2 and 7

compound	^1H, δ	J(P−H), Hz	^{29}Si, δ	J(P−Si), Hz	J(Si−H), Hz	ν(Ta−H), cm^{-1}
2a	5.68 (dd, J(H−H) = 4.7 Hz)[a]	63.5	18.8	8.0	−179 (terminal Si−H) + 14 (Si−H−Ta)	1674
2b	5.13 (d)	64.2	91.7	15.0	|33.3|[b]	1650[c]
2c (two isomers)	5.82	64.5	87.4	14.6	−41	1660
	5.68	64.5	87.0	12.2		
2d	6.14 (d)	67.2	104.9	15	−41.5	1660
2e	6.74 (d)	70.5	83.5	14	−50	1668
7b	5.03 (d)	61.5	91.6	[d]	|30|[b]	1650
7c (two isomers)	5.60	55.0	87.4	[d]		1652
	5.65 (d)	63.1	90.0			
7d	6.00 (d)	64.8	106.1	15	−41	1650
7f	6.32 (d)	63.3	85.5	11.4		1676

[a] An erroneous value of 5.87 ppm was given in ref 14. The SiH signal is observed at 6.18 ppm corresponding to the IR stretch at 2062 cm^{-1}. [b] The sign cannot be determined because of insufficient separation of the ^{29}Si satellites from the main signal. [c] An erroneous value of 1736 cm^{-1} is given in the earlier paper (ref 5). [d] The value of J(Si−P) is absent because the ^{29}Si NMR was not recorded. The silicon signal was determined from a $^1H-^{29}Si$ HMQC; the J(Si−H) was measured from silicon satellites in the ^1H NMR spectrum.

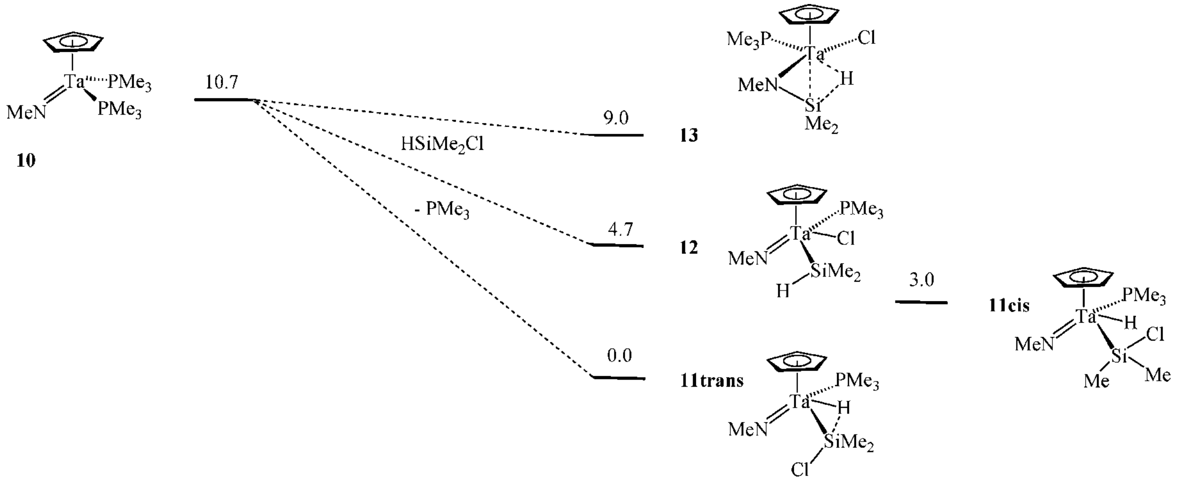

Figure 2. Relative free energies of the products in the reaction between complex **10** and $HSiMe_2Cl$ (in kcal/mol).

new mechanism of silane activation.[12] This pathway includes direct addition of silanes to the imido moiety to give an intermediate structure, Cp(ArN→SiR_2Cl−H···)Nb(PR'_3)$_2$ (**9**), with a pentacoordinate silicon center and an additional agostic Si−H···Nb interaction. The Si−H activation products Cp(ArN)Nb(PR'_3)(H)(SiR_2Cl) were found to be kinetic products of silane addition. However, in the presence of phosphine, they rearrange, likely via the same intermediate **9**, into the products of Si−Cl bond activation, such as complexes Cp(ArN-SiR_2-H···)Nb(PR'_3)(Cl) (R_2 = Me_2, MePh) and Cp(ArN)Nb(PMe_3)(Cl)(SiR_2H) (R_2 = MeCl, Cl_2).[12]

A very similar scenario appears to be happening for the tantalum complexes Cp(RN)Ta(PMe_3)$_2$ (R = Ar, Ar′). The initially formed products Cp(ArN)Ta(PMe_3)(H)($SiXR_2$) are metastable and decompose in the presence of phosphine into Cp(ArN)Ta(PMe_3)(Cl)($SiHR_2$), Cp(ArN)Ta(PMe_3)(Cl)(H), and eventually Cp(ArN)Ta(PMe_3)Cl_2, but the rate of this decomposition is noticeably slower than for niobium analogues. Like for the Nb complexes, the presence of phosphine accelerates the reactions significantly, suggesting that a diphosphine intermediate akin to **9** is involved. But in contrast to the Nb chemistry, in none of the reactions was an agostic complex of tantalum, such as Cp(ArN-SiR_2-H···)Ta(PMe_3)(Cl), observed.

To understand better the factors controlling the outcome of these very complex transformations, we carried out DFT calculations on model complexes **10**−**19** (Figures 2−4, Tables 2, 3). For computational simplicity we used a methyl substituent at nitrogen. However, exact modeling of substituents at phosphorus and silicon was applied because our previous studies showed that this was important.[5a] A good agreement between the calculated and experimental geometries is observed, when the latter are available from X-ray analyses.

In accord with our experimental findings, the most thermodynamically stable product of $HSiClMe_2$ addition to the diphosphine complex **10** is the silyl hydride **11trans** (Figure 2). A rotamer of **11trans**, the complex **11cis**, having the chloride substituent at Si in the cis position to the hydride is 3.0 kcal/mol less stable (free energy scale), due to the loss of Si−H interligand hypervalent interactions (IHI). This is seen from a noticeable elongation of the Ta−Si bond from 2.583 Å in **11trans** to 2.594 Å in **11cis**, accompanied by a shortening of the Si−Cl bond from 2.171 Å to 2.148 Å and the contraction of the Ta−H bond from 1.812 Å to 1.798 Å.[24]

A structural isomer of **11**, the silyl chloride complex Cp(MeN)Ta(PMe_3)(Cl)($SiHMe_2$) (**12**), is further destabilized by 1.7 kcal/mol (Figure 2). A structure of this type is possibly formed at high temperature in the course of thermal decomposition of compounds **2** to the dichloride **3**. The agostic compound **13** is the least stable product of silane addition. Although it is thermodynamically feasible (ΔG_r = −1.7 kcal/mol), it lies 9.0 kcal/mol (free energy scale) above **11trans**, thus accounting for our inability to observe such a structure experimentally. As

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(24) Structurally, IHI is characterized by elongated Si−X bonds, elongated M−H bonds, shortened M−Si bonds, and shortened Si−H contacts. The presence of an electron-withdrawing group X trans to the metal-bound hydride is a prerequisite of IHI, well documented in previous structural and theoretical studies (refs 5a, 5b, 8, 9, 12, and 14).

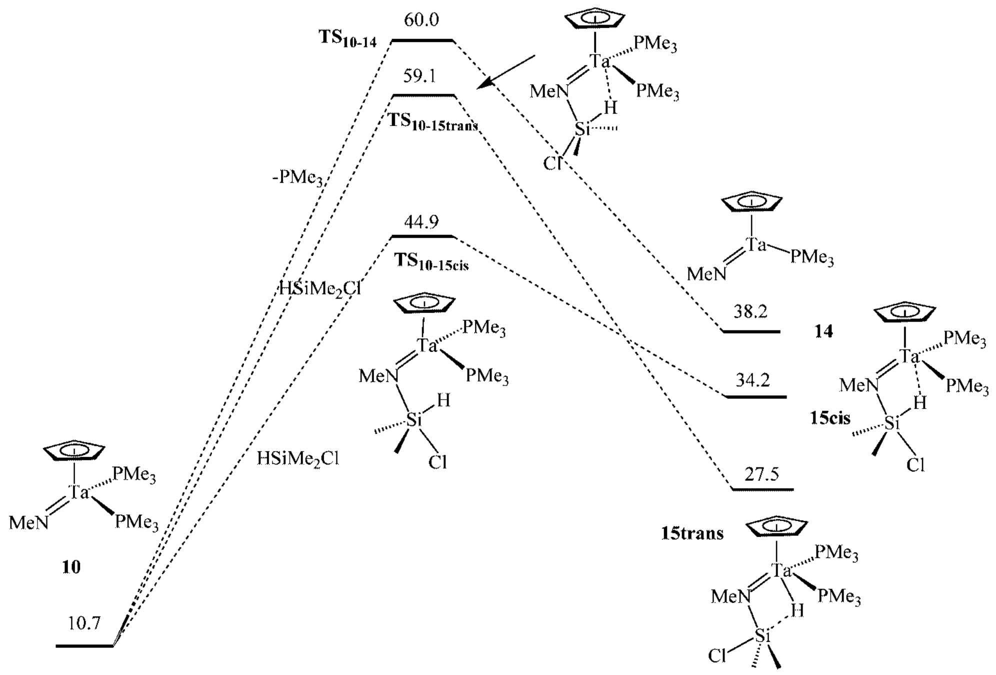

Figure 3. Possible reaction pathways in the reaction between complex **10** and $HSiMe_2Cl$. Free energies (in kcal/mol) are taken relative to **11trans**.

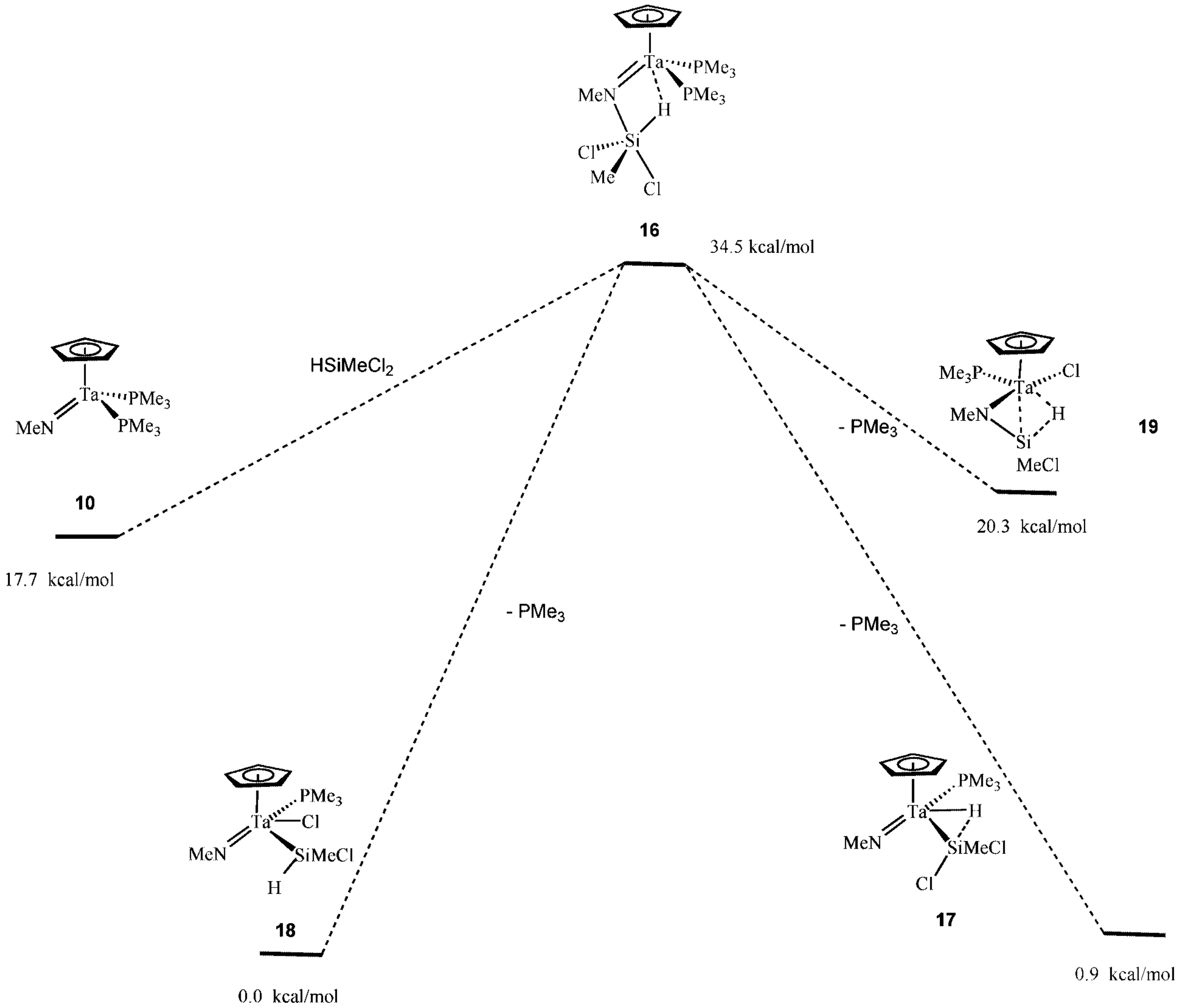

Figure 4. Relative free energies of stable intermediates in the preparation of **17** and **18**.

Table 2. Selected Interatomic Distances (Å) of the Ta Structures 11−13 and 15

	structures					
	11cis	**11trans**	**12**	**13**	**15cis**	**15trans**
Ta−H	1.798	1.812		2.008	1.924	1.805
Ta−N	1.789	1.788	1.782	2.020	1.987	2.062
Ta−P4, P5	2.527	2.533	2.633	2.560	2.557,2.536	2.523,2.523
Ta−Si	2.594	2.583	2.661	2.721	2.910	3.199
Ta−Cl	3.879	3.920	2.538	2.496	4.439	5.080
Si−N	3.116	3.166		1.728	1.805	1.753
Si−H	2.243	2.174	1.502	1.570	1.635	2.223
Si−Cl	2.148	2.171		3.869	2.410	2.174

Table 3. Selected Interatomic Distances (Å) of the Ta Structures 10, 14, 17−19

	10	**14**	**16**	**17**	**18**	**19**
Ta−H			1.903	1.808		2.156
Ta−N	1.802	1.793	1.991	1.786	1.780	2.016
Ta−P4, P5	2.500, 2.490	2.507	2.532, 2.556	2.531	2.625	2.531
Ta−Si			2.900	2.562	2.629	2.758
Ta−Cl					2.541	2.492
Si−N			1.779			1.723
Si−H			1. 635	2.197	1.497	1.512
Si−Cl			2.286, 2.146	2.144,2.124	2.155	2.101

mentioned above, in the analogous niobium chemistry the Nb(V) silyl hydride complex was a kinetic product of silane addition, whereas the Nb(III) silylamido agostic complex was the thermodynamic product. Structural parameters of the Ta complexes **11**−**13** (Table 2) are very close to those of their Nb analogues,[12] which does not suggest an obvious reason why the agostic complex **13** is so much destabilized relative to other products. Taking into account that lower oxidation states become less stable down the group, one can expect destabilization of the Ta(III) agostic d^2 structure relative to the Ta(V) silylhydrido d^0 form. Another possible factor could be the increased stability of the metal−ligand multiple bonds down the group, which tend to retain the Ta=NR functionality in the product.

Supporting this idea is the observation that Ta(V) complexes **11** and **12** are much more stable relative to the Ta(III) complex **10** than their Nb analogues relative to Cp(MeN)Nb$(PMe_3)_2$: $\Delta G_r(\mathbf{11}) = -10.7$ kcal/mol versus $\Delta G_r = -3.7$ kcal/mol for Cp(MeN)Nb$(SiMe_2Cl)$(H)(PMe_3) and $\Delta G_r(\mathbf{12}) = -6.0$ kcal/mol versus $\Delta G_r = 2.1$ kcal/mol for Cp(MeN)Nb$(SiMe_2H)$(Cl)(PMe_3).

As for the previously studied Nb complexes,[12] we considered two mechanisms of silane addition to the starting diphosphine **10**. A dissociative mechanism goes via the transition state $\mathbf{TS_{10-14}}$[25] to afford a monophosphine intermediate **14** amenable for Si−H bond activation at the metal center to afford the complex **11** (Figure 3).

An alternative, associative pathway discussed here includes silane addition to the metal−nitrogen multiple bond. We considered two directions of such an attack. Addition of silane in such an orientation that chloride is trans to nitrogen but cis to the hydride gives the species **15cis**, which features a pentacoordinate silicon center and a Si−H···M agostic bonding (the Si−H bond is 1.635 Å, the Ta−H bond is 1.924 Å). This addition requires overcoming a barrier of 34.2 kcal/mol ($\mathbf{TS_{10-15cis}}$), which is much below the barrier of phosphine dissociation from **10** (49.3 kcal/mol). Another adduct, **15trans**, emerges when silane adds to **10** with the chlorine lying trans to the hydride and cis to the nitrogen center. In this case, a more stable structure is obtained (27.5 vs 34.2 kcal/mol for **15cis**), but the required barrier $\mathbf{TS_{10-15trans}}$ is prohibitively high (48.4 kcal/mol) (Figure 3).

In contrast to the agostic complex **15cis**, **15trans** is essentially a silylamido hydride derivative characterized by a shorter Si−N bond length (1.753 vs 1.805 Å in **15cis**), a longer Ta−N bond (2.062 vs 1.987 Å in **15cis**), a shorter Ta−H bond (1.805 vs 1.924 Å in **15cis**), and a significantly longer Si−H distance (2.223 vs 1.635 Å in **15cis**). The corresponding transition state $\mathbf{TS_{10-15trans}}$ features the silicon atom in a distorted trigonal -bipyramidal geometry with an unusual trans disposition of the methyl groups.[26] The Si−Cl bond is significantly elongated to 2.509 Å, whereas the Si−N distance is shortened to 1.875 Å. The Si−H bond is stretched to 1.603 Å, whereas the incipient Ta−H bond is still rather long (2.045 Å). The occupation of apical sites by electron-donating methyl groups and the stretching of Si−Cl and Si−H bonds suggests a possible origin of such a high barrier.

In the case of the more Lewis acidic dichlorosilane $HSiCl_2Me$, the enthalpy of its addition to **10** to give the initial adduct **16** is negative (−1.2 kcal/mol), but **16** is still less stable by 16.8 kcal/mol on the free energy scale than the starting diphosphine complex **10** due to the loss of entropy (Figure 4). Complex **16** is further stabilized relative to the unsaturated complex Cp(MeN)Ta(PMe_3) (**14**) in comparison with the related adduct **15cis** in the case of $HSiMe_2Cl$ addition (by 10.7 vs 4.0 kcal/mol, respectively). This extra stabilization can be traced to shorter Si−N and Si−Ta bonds in **16** (Tables 2 and 3), but other structural features are very similar in both compounds.

The formation of the silyl hydride complex **17** from **10** is thermodynamically allowed ($\Delta G_r = -16.8$ kcal/mol), but the most stable product is the "rearranged" chloride silyl derivative Cp(MeN)Ta(PMe_3)(Cl)(SiHClMe) (**18**) (Figure 4). This result agrees well with the observed phosphine-induced decompositions of the real silyl hydride complexes **2d** and **2e** to Cp(ArN)Ta(PMe_3)(Cl)(SiHClX) (X = Me or Cl), Cp(ArN)Ta(PMe_3)(Cl)(H), and Cp(ArN)Ta$(PMe_3)Cl_2$. Interestingly, the formation of the agostic complex **19** from **10** is in fact thermodynamically unfavorable (Figure 4).

In the related niobium chemistry, kinetic studies suggested that the rearrangement of initial silyl hydride products into agostic or chloride silyl products goes via an Nb analogue of complex **16**.[12] In this context, it is rewarding that our calculations predict a greater free energy gap between the tantalum intermediate **16** and the kinetic product **17** ($\Delta G = 33.6$ kcal/mol) than the previously found difference for their niobium analogues ($\Delta G = 26.0$ kcal/mol).[12] This is in accord with our experimental observation that niobium derivatives rearrange

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(25) The electronic potential surface around complex **14** is very shallow, which does allow for the determination of a transition state for the dissociative pathway by the standard methods. For the methodology of estimation of the barrier of phosphine dissociation from **10**, see the Supporting Information.

(26) In hypervalent compounds, such as pentacoordinate silanes, the apical sites are preferentially occupied by the most electron-withdrawing groups. See: Corriu, R. J. P.; Young, J. C. Hypervalent Silicon Compounds. In *Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.;Wiley: New York, 1989; pp 1242−1288.

qualitatively faster than their tantalum congeners, thus further supporting our inference that rearrangement of the silyl hydride species **2** into chloride silyl products goes via bis(phosphine) structures similar to **15** and **16**.

Like **11trans**, the complex **17** exhibits interligand hypervalent interactions between the silyl and hydride ligands, as evidenced by comparing two types of Si−Cl bonds in **17**.[24] Thus, the Si−Cl bond lying trans to the hydride is longer than the cis Si−Cl bond(s): 2.144 vs 2.124 Å. An analogous effect was observed in other complexes with IHI and in the X-ray structure of **8d** discussed above. IHI also results in the elongation of the Ta−H bonds, and in comparison with **17**, the presumably stronger Si−H interaction in **11trans** leads to a longer Ta−H bond in the latter (1.812 Å in **11trans** vs 1.808 Å in **17**). The calculated Si−H distance increases from 2.174 Å in **11trans** to 2.197 Å in **17**, further signifying the weakening of IHI. These observations are in accord with our earlier conclusion that IHI is the strongest in monochloro-substituted derivatives, which have the most electron-depleted and hence the longest metal−hydride bond.

Conclusions

The silyl hydrides $\mathrm{Cp(ArN)Ta(PMe_3)(H)(SiR_3)}$ (**2**, Ar = 2,6-diisopropylphenyl) and $\mathrm{Cp(Ar'N)Ta(PMe_3)(H)(SiR_3)}$ (**7**, Ar′ = 2,6-dimethylphenyl) were found to be intermediates in the reactions between diphosphine complexes $\mathrm{Cp(R'N)Ta(PMe_3)_2}$ (R′ = Ar or Ar′) with silanes H-SiR$_3$. In the presence of PMe$_3$ they sequentially rearrange/decompose into $\mathrm{Cp(R'N)Ta(PMe_3)(Cl)(SiHR}_n\mathrm{Cl}_{2-n})$ (**5** for R′ = Ar and **8** for R′ = Ar′), $\mathrm{Cp(R'N)Ta(PMe_3)(Cl)(H)}$, and eventually $\mathrm{Cp(R'N)Ta(PMe_3)Cl_2}$. As in related niobium chemistry, DFT calculations suggest that complexes $\mathrm{Cp(R'N)Ta(PMe_3)(H)(SiR_3)}$ and $\mathrm{Cp(R'N)Ta(PMe_3)(Cl)(SiHR}_n\mathrm{Cl}_{2-n})$ are formed from the same key intermediate, the imido/silane adduct $\mathrm{Cp(R'N{\rightarrow}SiR_3)Ta(PMe_3)_2}$ (**15** for the model complex with R′ = Me, R$_3$ = Me$_2$Cl; **16** for R′ = Me, R$_3$ = MeCl$_2$), as a result of Si−H and Si−Cl bond activation, respectively. We studied two ways how this key intermediate could be formed and found that although addition of a chlorosilane with its Si−Cl bond oriented cis to the imido group gives a more stable product, its reaction barrier is energetically too demanding. Silane addition with the Si−Cl bond trans to imido group is kinetically preferred and affords a pentacoordinate silicon structure $\mathrm{Cp(R'N{\rightarrow}SiR_2Cl{-}H{\cdots})Ta(PMe_3)_2}$ supported by an additional agostic Si−H···Ta interaction.

An important advance in our investigation of interligand hypervalent interactions in Cp/imido complexes has been achieved in the experimental determination of the sign of the coupling constants between the hydride and silyl ligands in complexes $\mathrm{Cp(ArN)Ta(PMe_3)(H)(SiR_3)}$ (**2**). The observed *J*(Si−H) was found to be positive for the classical compound $\mathrm{Cp(ArN)Ta(PMe_3)(H)(SiMeHPh)}$ (**2a**) and negative for the chloro-substituted complexes $\mathrm{Cp(ArN)Ta(PMe_3)(H)(SiR}_n\mathrm{Cl}_{3-n})$ (**2b**−**e**, *n* = 1−3). The latter fact conclusively proves the existence of direct Si−H interactions. Interestingly, the Si−H bonding diminishes when the *absolute* value of the *J*(Si−H) in $\mathrm{Cp(ArN)Ta(PMe_3)(H)(SiR}_n\mathrm{Cl}_{3-n})$ (*n* = 1−3) increases. This trend contradicts the previously accepted view that hydride−silyl coupling constants should decrease when the strength of nonclassical bonding decreases. Recent studies indicate that this "abnormal behavior" of *J*(Si−H) is general and can be found also in silane σ-complexes and agostic complexes.[5c,20a] Its rationalization in terms of Bent's rule effects and rehybridization of the silicon center can be found in a recent review.[13e]

Experimental Section

All manipulations were carried out using conventional glovebox and Schlenk techniques. Solvents were dried over sodium or sodium benzophenone ketyl. NMR spectra were recorded on a Varian Mercury-*vx* (^{1}H, 300 MHz; ^{13}C, 75.4 MHz) and Unity-Plus (^{1}H, 500 MHz; ^{13}C, 125.7 MHz) spectrometers. IR spectra were obtained as Nujol mulls with a FTIR Perkin-Elmer 1600 series spectrometer. Silanes were obtained from Sigma-Aldrich and Lancaster and distilled over CaH$_2$. Starting complexes $\mathrm{Cp(RN)TaCl_2}$ and $\mathrm{Cp(RN)Ta(PMe_3)_2}$ (R = Ar, Ar′) were prepared by literature methods (see Supporting Information for details). Compound **2b** was previously reported.[5a] Syntheses and characterization of complexes **2a**,**d**,**e** are reported in the Supporting Information of the preliminary communication to this paper.[14]

$\mathrm{Cp(ArN)Ta(PMe_3)(H)(SiMePhCl)}$ (2c). A 0.15 mL amount of HSiMePhCl (1.0 mmol) was added to 20 mL of a hexane solution of $\mathrm{Cp(ArN)Ta(PMe_3)_2}$ (0.243 g, 0.424 mmol). The mixture was left for 2 days at room temperature. After that the purple solution was filtered and dried, producing a red oil. The oil was dissolved in 10 mL of hexane and cooled to −30 °C. A yellow deposit was formed on the walls in the course of several days. The solution was filtered and the residue was dried, giving 0.091 g of a yellow powder. The second crop was obtained in an analogous way. NMR spectra showed the formation of a mixture of two diastereomers of **2c**. Analytically pure material was not obtained even after multiple recrystallization. Total yield: 0.141 g (0.22 mmol, 51%). IR (Nujol): $\nu_{\mathrm{Ta-H}} = 1660\ \mathrm{cm^{-1}}$. ^{1}H NMR (C$_6D_6$): δ 8.23 (d, *J*(H−H) = 7.5 Hz, m-Ar), 8.09 (d, *J* = 8.1 Hz, m-Ar), 7.33 (t, *J* = 7.5 Hz, p-Ar), 7.27 (t, *J* = 7.7 Hz, p-Ph), 7.21−6.93 (m, Ph), 5.78 (d, *J*(P−H)= 22.2 Hz, 1, Ta−H), 5.61 (d, *J* = 1.5 Hz, 5, Cp), 5.34 (d, *J*(P−H)= 36.9 Hz, 1, Ta−H), 5.33 (d, *J* = 1.5 Hz, 5, Cp), 4.08 (q, *J*(H−H) = 6.7 Hz, 1, C*H*Me$_2$), 3.86 (q, *J*(H−H) = 6.8 Hz, 1, C*H*Me$_2$), 1.40 (s, SiMe), 1.10 (s, SiMe), 0.93 (d, *J*(P−H) = 8.7 Hz, 9, PMe), 0.92 (d, *J*(P−H) = 8.7 Hz, 9, PMe). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 143.1 (o-Ar), 142.9 (o-Ar), 135.1 (m-Ar), 134.2 (m-Ar), 127.8 (p-Ar), 127.6 (p-Ar), 127.5 (p-Ar), 122.9 and 122.7 and 119.9, 100.9 (Cp), 100.7 (Cp), 27.2 (C*H*Me$_2$), 27.1 (C*H*Me$_2$), 24.6 (CH*Me*$_2$), 24.3 (CH*Me*$_2$), 24.2 (CH*Me*$_2$), 22.5 (CH*Me*$_2$), 19.8 (d, *J*(P−C) = 20.5 Hz, PMe), 19.6 (d, *J*(P−C) = 19.5 Hz, PMe), 15.5 (s, SiMe), 14.1 5 (s, SiMe). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ −2.0. ^{29}Si NMR (C$_6$D$_6$): δ 88.3 (^{2}*J*(Si−P) = 15.9 Hz, *J*(Si−P) = 12.8 Hz).

Thermal Decomposition of $\mathrm{Cp(ArN)Ta(PMe_3)(H)(SiMeCl_2)}$ (2d). An NMR sample of **2d** was heated at 60 °C for 1.5 h to give a mixture of $\mathrm{Cp(ArN)Ta(PMe_3)(Cl)(SiClHMe)}$ (**5d**, 30%), $\mathrm{Cp(ArN)Ta(PMe_3)(H)(Cl)}$ (**4**), and other yet unidentified products. Further increase of the temperature to 90 °C resulted in decomposition into $\mathrm{Cp(ArN)Ta(PMe_3)Cl_2}$ (**3**) after 2.5 h. The complete decomposition was achieved after heating the reaction mixture at 110 °C for 2 h.

5d. IR (Nujol): $\nu_{\mathrm{Ta-H}} = 2122\ \mathrm{cm^{-1}}$. ^{1}H NMR (C$_6D_6$): δ 7.06 (d, *J*(H−H) = 8.0 Hz, 2, m-Ar), 6.87 (pt, *J*(H−H) = 8.0 Hz, 1, p-Ar), 6.75 (dq, *J*(H−H) = 4.0 Hz, 1, SiH), 5.72 (s, 5, Cp), 3.80 (sept, *J*(H−H) = 7.0 Hz, 1, $\mathrm{C}\underline{H}\mathrm{Me_2}$), 1.33 (d, *J*(H−H) = 7.5 Hz, 6, $\mathrm{CH}\underline{Me_2}$), 1.26 (br, 3, SiMe), 1.15 (d, *J*(H−H) = 7.0 Hz, 6, $\mathrm{CH}\underline{Me_2}$), 0.91 (d, *J*(P−H) = 8.7 Hz, 9, PMe). The position of the SiMe group was determined by a COSY experiment, which showed that the hydride on Si at 6.75 ppm is coupled to the broad signal at 1.26 ppm. ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ −10.7 ppm. ^{29}Si HMQC: δ 54.3 ppm; this signal is coupled to the hydride at 6.75 ppm and the methyl group at 1.26 ppm.

3. This compound was independently prepared by a literature procedure described for its Nb analogue.[7c] ^{1}H NMR (C$_6$D$_6$): δ 7.07 (d, *J*(H−H) = 7.5 Hz, 2, m-Ar), 6.87 (pt, *J*(H−H) = 7.7 Hz, 1, p-Ar), 5.95 (s, 5, Cp), 3.82 (sept, *J*(H−H) = 6.9 Hz, 1, $\mathrm{C}\underline{\mathrm{H}}\mathrm{Me_2}$), 1.32 (d, *J*(H−H) = 6.9 Hz, 6, $\mathrm{CH}\underline{Me_2}$), 1.27 (d, *J*(H−H) = 6.9 Hz, 6, $\mathrm{CH}\underline{Me_2}$). ^{31}P{^{1}H} NMR (C$_6D_6$): δ −1.3 ppm. Anal. Calcd for $C_{20}H_{31}Cl_2TaP$ (568.294): C, 42.27; H, 5.50, N 2.46. Found: C, 42.43; H, 5.57; N, 2.19

Cp(Ar′N)Ta(PMe$_3$)(H)(SiMe$_2$Cl) (7b). To a suspension of Cp(NAr′)Ta(PMe$_3$)$_2$ (0.22 g, 0.425 mmol) in a 2:1 mixture of ether/pentane (50 mL) was added 0.2 mL (1.7 mmol) of $HSiMe_2Cl$ to give after keeping overnight a yellow solution and a small amount of gray precipitate. The solution was filtered and cooled to −80 °C to produce yellow crystals. The crystals were filtered and dried. Yield: 0.05 g (0.093 mmol, 22%). IR (Nujol): $\nu_{Ta-H} = 1650\ cm^{-1}$. ^1H NMR (C_6D_6): δ 7.02 (d, J(H−H) = 7.2 Hz, 2 H, m-C_6H_3), 6.81 (pt, J = 7.8 Hz, 1 H, p-C_6H_3), 5.48 (d, J(P−H) = 1.8 Hz, 5 H, Cp), 5.03 (d, J(P−H) = 61.5 Hz, 1 H, Ta−H), 2.35 (s, 6 H, C_6H_3*Me*$_2$), 1.22 (s, 3, SiMe), 0.97 (s, 3, SiMe), 0.84 (d, J(P−H)= 8.7 Hz, 9 H, PMe). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 156.5, 132.5, 127.8, 121.67 (all Ar′), 100.2 (Cp), 21.3 (C_6H_3*Me*$_2$), 20.3 (SiMe), 19.9 (SiMe), 15.5 (bs, PMe). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −2.6 (s). ^{29}Si NMR (C_6D_6): δ 91.6 (J(Si−H) = 30 Hz). Anal. Calcd for $C_{18}H_{30}ClNTaPSi$ (535.905): C, 40.34; H, 5.64, N 2.61. Found: C, 40.15; H, 5.67; N, 2.59.

NMR Reaction of Cp(NAr′)Ta(PMe$_3$)$_2$ with HSiMePhCl. HSiMePhCl was added by syringe to an equivalent of Cp(NAr′)Ta(PMe$_3$)$_2$ dissolved in C_6D_6. The spectrum recorded in about 10 min showed clean formation of a mixture of two diastereomers of Cp(NAr′)Ta(PMe$_3$)(H)(SiMePhCl) (**7c**). IR (Nujol): $\nu_{Ta-H} = 1652\ cm^{-1}$. Upon heating for several hours at 65 °C, these products transform into other compounds, including two isomers of the rearranged product Cp(Ar′N)Ta(PMe$_3$)(Cl)-(SiMePhH) (**8**), characterized by their SiH quartets at 6.23 ppm (J(H−H) = 4.1 Hz) and 6.15 ppm (J(H−H) = 4.1 Hz) coupled to the methyl groups at 1.19 and 0.96 ppm, respectively. No signals that might be assigned to an agostic species were observed.

First Isomer of 7c. ^1H NMR (C_6D_6): δ 8.10 (d, J(H−H) = 7.2 Hz, 4, both isomers, o-Ph), 7.34 (pt, J(H−H) = 7.4 Hz, 2, p-Ph), 7.2−7.15 (m, both isomers, p-Ph), 7.02 (d, J(H−H) = 7.2 Hz, C_6H_3), 6.82 (pt, J(H−H) = 7.5 Hz, C_6H_3), 5.65 (d, J(H−P) = 63.1 Hz, 1, Ta-*H),* 5.30 (s, 5, Cp), 2.37 (s, 6, C_6H_3*Me*$_2$), 1.40 (s, 3, Me), 0.85 (d, J(H−P) = 4.5 Hz, both isomers and free PMe_3 are in exchange). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 156.4 (s, i-Ph), 150.4 (s, i-Ar′), 134.1 (s, o-Ph), 127.8 (s, m-Ar′), 127.5 (p, m-Ph), 121.8 (p-Ar′),100.8 (Cp), 21.2 (s, Ar′), 20.2 (d, J(P−C) = 2.9 Hz, PMe_3), 15.0 (d, J(P−C) = 2.0 Hz, SiMe). $^{31}P\{^1H\}$ NMR (C_6D_6.): δ −1.96 (s). ^{29}Si gHMQC NMR (C_6D_6): δ 90.0.

Second Isomer of 7c. ^1H NMR (C_6D_6): δ 7.26 (pt, J(H−H) = 7.7 Hz, 2, m-Ph), 6.95 (d, J(H−H) = 7.3 Hz, C_6H_3), 6.77 (pt, J(H−H) = 7.3 Hz, C_6H_3), 5.60 (d, J(H−P) = 55.0 Hz, 1, Ta-*H),* 5.50 (s, 5, Cp), 2.07 (s, 6, C_6H_3*Me*$_2$), 1.16 (s, 3, Me). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 156.2 (s, i-Ph), 150.4 (s, i-Ar′), 134.5 (s, o-Ph), 127.8 (s, m-Ar′), 127.4 (p, m-Ph), 100.4 (Cp), 20.9 (s, Ar′), 19.8 (d, J(P−C) = 2.9 Hz, PMe_3), 15.2 (d, J(P−C) = 2.0 Hz, SiMe). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −2.03 (s). ^{29}Si gHMQC NMR (C_6D_6): δ 87.4 (s).

Cp(Ar′N)Ta(PMe$_3$)(H)(SiMeCl$_2$) (7d). To a solution of Cp(NAr′)Ta(PMe$_3$)$_2$ (0.275 g, 0.53 mmol) in 30 mL of ether was added 0.2 mL (1.9 mmol) of $HSiMeCl_2$. The color immediately changed to red. The solution was left at room temperature overnight to give a yellow solution and a small amount of gray precipitate. The solution was filtered and cooled to −80 °C to produce yellow crystals (0.096 g, 0.172 mmol). The crystals were filtered and dried. The second crop was obtained by keeping the concentrated mother liquor at −80 °C (0.04 g, 0.072 mmol). Total yield: 46%. IR (Nujol): $\nu_{Ta-H} = 1650\ cm^{-1}$. ^1H NMR (C_6D_6): δ 6.96 (d, J = 7.2 Hz, 2 H, C_6H_3), 6.78 (pt, J = 7.2 Hz, 1 H, C_6H_3), 6.00 (d, J(P−H) = 64.8 Hz, 1 H, Ta−H), 5.59 (d, J(P−H) = 1.5 Hz, 5 H, Cp), 2.27 (s, 6 H, C_6H_3*Me*$_2$), 1.52 (s, 3, SiMe), 0.81 (d, J(P−H) = 9.0 Hz, 9 H, PMe). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 132.5, 124.1, 122.3 (all Ar′), 101.5 (Cp), 21.0 (C_6H_3*Me*$_2$), 19.5 (d, J(P−C) = 31.5 Hz, PMe), 18.7 (SiMe). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −1.2 (s). ^{29}Si NMR (C_6D_6): δ 106.1 (J(Si−H) = 41 Hz). Anal. Calcd for $C_{17}H_{27}Cl_2TaPNSi$ (556.3203): C, 36.70; H, 4.89, N 2.52. Found: C, 36.60; H, 4.93; N, 2.50.

Table 4. X-ray Diffraction Crystal Data and Structure Refinement for 7d

formula	$C_{17}H_{27}Cl_2NPSiTa$
fw	556.31
color, habit	brown-red, block
cryst size, mm	0.24 × 0.24 × 0.40
cryst sys	monoclinic
space group	$P2_1/n$
a, Å	11.3952(3)
b, Å	14.8865(4)
c, Å	13.2074(5)
β, deg	106.379(1)
V, Å^3	2149.51(12)
Z	4
T, °C	150
ρ_{calc}, g/cm^3	1.716
F(000)	1088.000
radiation	Mo
μ, cm^{-1}	54.91
transmn factors	0.14 −0.27
$2\theta_{max}$, deg	54.97
total no. of reflns	8483
no. of unique reflns	4781
R_{merge}	0.02
no. with $I \geq \sigma(I)$	2326 (n = 2)
no. of variables	209
R	0.0789
R_w	0.0798
GOF	1.1289
max Δ/σ	0.0087

Cp(Ar′N)Ta(PMe$_3$)(H)(SiPh$_2$Cl) (7f). To a purple solution of Cp(Ar′N)Ta(PMe$_3$)$_2$ (0.082 g, 0.155 mmol) in 10 mL of ether was added 0.2 mL (1.02mmol) of $HSiPh_2Cl$. The solution was allowed to stand for 2 days at room temperature to produce well-shaped yellow crystals. The crystals were filtered, washed by 2 mL of ether, and dried. Yield: 0.039 g (0.059 mmol, 38%). IR (Nujol): $\nu_{Ta-H} = 1676\ cm^{-1}$. ^1H NMR (C_6D_6): δ 8.15 (d, J(H−H)= 8.1 Hz, 2, o-Ph), 8.11 (d, J(H−H) = 8.1 Hz, 2, o-Ph), 7.26 (pt, J(H−H) = 6.9 Hz, 4, m-Ph), 6.94 (d, J(H−H) = 7.2 Hz, C_6H_3), 6.77 (pt, J(H−H) = 7.3 Hz, C_6H_3), 6.32 (d, J(H−P) = 63.3 Hz, 1, Ta-*H),* 5.39 (d, J(H−P) = 1.5 Hz, 5, Cp), 2.07 (s, 6, C_6H_3*Me*$_2$), 0.91 (d, J(H−P) = 8.7 Hz, PMe_3). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 135.7, 135.3, 134.8, 134.7, 128.5, 127.7, 127.5, 121.9 (Ar and Ph), 100.9 (Cp), 20.9 (C_6H_3*Me*$_2$), 20.2 (d, J(H−P) = 30.9 Hz, PMe_3). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −2.0 (s). ^{28}Si NMR (C_6D_6): δ 85.5 (d, J(Si−P) = 11.4 Hz). Anal. Calcd for $C_{26}H_{34}ClNTaPSi$ (660.0466): C, 50.95; H, 5.19, N 2.12. Found: C, 49.68; H, 5.31; N, 2.15.

Experimental Determination of the Sign of *J*(Si−H). The silicon−hydride coupling constants were measured from the $^{29}Si-^1H$ satellites in the ^1H NMR spectra. The sign of the coupling constant was determined from a spin-tickling experiment where the ^{29}Si satellites in the ^1H spectrum of the proton terminally attached to silicon were irradiated and the effect on the ^{29}Si satellites of the nonclassically bonded hydride was observed. This showed that in Cp(ArN)Ta(PMe$_3$)(H^a)(SiMePhH^b) (**2a**) the signs of ^1J(Si−H^b) (known to be negative, i.e., ^1K(Si−H^b)[27] has a positive sign)[28] and J(Si−H) are opposite. This observation establishes the positive sign of the J(Si−H^a) in this compound: J(Si−H^a) = +14 Hz (i.e., K(Si−H^a) has a negative sign). From a similar spin-tickling experiment, by comparison to the negative sign of J(Si−H^a) in **2a**, the sign of ^2J(Si−P) was found to be negative. In this case, the proton NMR spectrum of the tantalum hydride was observed while

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low-power continuous irradiation was applied sequentially at the positions of the low- and high-frequency ^{29}Si satellites of the proton-coupled ^{31}P resonance. Given the negative sign of ^2J(Si−P), the negative sign of the J(Si−H) in **2d** and **2e** can be easily determined by a similar spin-tickling experiment, which shows that the sign of J(Si−H) is the same as that of ^2J(Si−P).

DFT Calculations. All calculations were carried out with the Gaussian 03 program package[29] using DFT applying Becke's three-parameter hybrid exchange functional in conjunction with gradient-corrected nonlocal correlation functional of Perdew and Wang (B3PW91).[30] The compound basis set used for the calculation consisted of the 6-31G(d) basis set for the Si, P, N, and Cl atoms, 6-31G for the carbon atoms and the silyl hydrogens, and the 3-21G basis set for the H atoms of Cp ring and Me groups. The basis set augmented by the p-polarization function (6-31G(d,p) basis set) was used for the hydride H atom. The Hay−Wadt effective core potentials (ECP) and the corresponding VDZ basis sets were used for the Ta atoms.[31]

X-ray Structure Analyses. The crystals of **7d** were grown from etherial solutions by cooling to −30 °C. The crystals were mounted in a film of perfluoropolyether oil on a glass fiber and transferred to a Siemens three-circle diffractometer with a CCD detector (SMART system). The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods and refined by full-matrix least-squares procedures (Table 4).[32] All non-hydrogen atoms were refined anisotropically; the hydrogen atoms except hydride were placed in calculated positions and refined in a "riding" model. The hydride position has not been determined.

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Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

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