Reversible C(sp^3)-Si Oxidative Addition of Unsupported Organosilanes: Effects of Silicon Substituents on Kinetics and Thermodynamics

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ABSTRACT: The intermolecular oxidative addition of unactivated C(sp^3)-Si bonds is reported for a family of organosilanes at a cationic pincer-supported iridium complex. To our knowledge, no examples of oxidative addition to give analogous unsupported (alkyl)metal silyl complexes have been previously reported. The generality of this transformation is excellent, with successful examples demonstrated for tetraorganosilanes, mono- and poly-alkoxysilanes, and two siloxysilanes. Oxidative addition is found to be completely reversible, with the product of reductive elimination being subject to trapping by triethylsilane. The successful isolation of these metal silyl complexes has allowed for an in-depth kinetic analysis of C(sp^3)-Si reductive elimination, a process with strong implications in both catalytic C-H silylation and olefin hydrosilylation. The apparent order of reactivity is: $SiMe_3$ > $SiMe_2(CF_3)$ > $SiMe_2OSiMe_3$ > $SiMe_2OSiMe_2OSiMe_3$ > $SiMe_2(OMe)$ > $SiMe_2(OEt)$ > $SiMe(OMe)_2$. A DFT analysis of the oxidative addition products shows that the thermodynamic stability of the (alkyl)metal silyl complexes span a range of *ca.* 10 kcal·mol^{-1}, which relate closely with the experimentally-determined rates of C(sp^3)-Si reductive elimination and trapping, though a clear kinetic distinction exists between methoxy- and siloxysilyl complexes.

INTRODUCTION

Organosilanes are an important and versatile class of compounds which have found diverse applications in materials, fine chemicals, and as building blocks for the synthesis of complex molecules. For instance, alkoxysilanes are prepared and used on industrial scales including in residential plumbing systems where vinylalkoxysilanes are employed in the synthesis of cross-linked polyethylene (PEX) tubing.[1-2] A variety of organosilane derivatives have found applications as partners in cross-coupling chemistry, with organosilanes bearing electron withdrawing groups (alkoxy, siloxy, fluoro) being favored in Hiyama-type reactions.[3-4]

Although organosilanes can be prepared in stoichiometric fashion from alkyl, aryl, or vinyl halides, their preparation by catalytic methods including olefin hydrosilylation or direct C-H silylation offers the opportunity to avoid the formation of stoichiometric byproducts. Of these two catalytic approaches, olefin hydrosilylation represents the more mature process, with established catalytic systems having been demonstrated for many transition metals.[5] For instance, Pt and Ir hydrosilylation catalysts are typically highly active, and thought to operate through the Chalk-Harrod mechanism (Figure 1, top left) with C-Si bond-formation occurring through a concerted reductive elimination.[5-6] Conversely, direct C-H silylation is a challenging process which has been largely limited to a few catalyst systems.[7] In one example, the Hartwig group proposed that phenanthroline-supported iridium complexes catalyze the C-H silylation of arenes through an Ir(III)/(V) cycle (Figure 1, top right).[8] $HSi(OSiMe_3)_2(CH_3)$ serves as the silylating reagent with C-Si bond-formation presumably occurring from an iridium(V)disilyldihydrido σ-aryl. In the case of electron deficient arenes, C-Si reductive elimination appears to represent the turnover limiting step.[8] Other notable examples of sp^2 C-H silylation include diimine/Ir catalysts examined by Miyaura[9], a Rh-catalyzed process developed by Hartwig[10], as well as a recent pincer-supported iridium system reported by Esteruelas.[11]

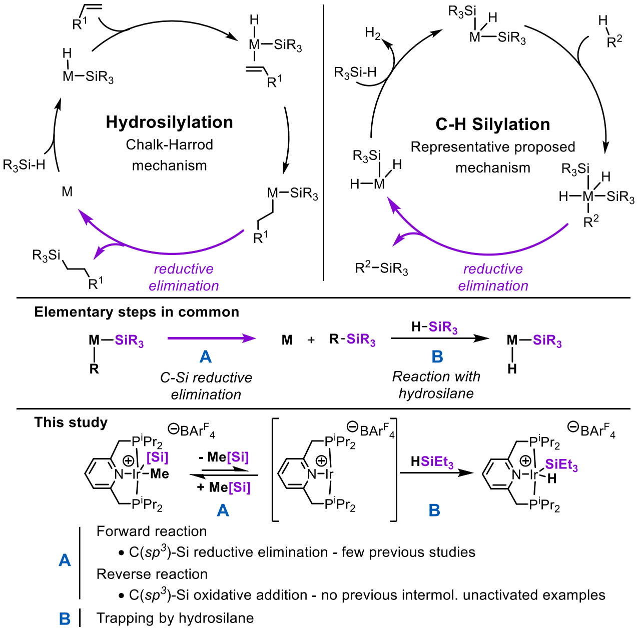
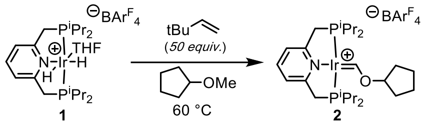


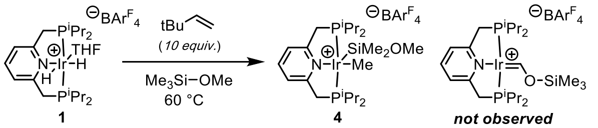
Figure 1. Proposed mechanisms for olefin hydrosilylation and C-H silylation and relationship to this study.

Although olefin hydrosilylation and alkane/arene C-H silylation are distinct processes, both feature a C-Si reductive elimination step prior to product formation. Despite the importance of this transformation, few reports have examined C-Si reductive elimination in detail. The Ozawa group showed that C-Si reductive elimination occurs from (alkyl)Pt(II) silyl complexes in the presence of π-acidic ligands including olefins and acetylenes, with the rate of reductive elimination showing first order dependence on the alkyne.[12] Further studies examined the effect of the Pt-R (R=Me, Et, Pr, Bu, Ph) on the rate of C-Si reductive elimination and showed Me-Si reductive elimination to be the fastest.[13] By comparison, to our knowledge only a single example of an isolable Ir silyl complex bearing an unsupported Ir-C bond has been reported. The Tilley group demonstrated that this complex undergoes reductive elimination after rate-limiting phosphine dissociation, precluding an in-depth analysis of other factors that control the rate of C-Si reductive elimination in cases where ligand dissociation is not rate determining.[14]



(1)

Recently our group has been studying the conversion of ethers to alkoxycarbenes via the α,α-dehydrogenation at cationic iridium complexes.[15-16] We reported the synthesis of the cationic PNP pincer-supported Ir(I) alkoxycarbene complex **2** derived from cyclopentyl methyl ether (eqn. 1) and demonstrated its reactivity in atom- and group-transfer reactions.[17]



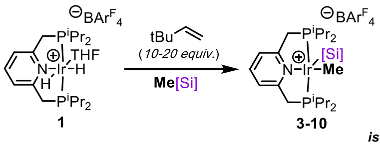
(2)

During the course of our studies, we found that methoxytrimethylsilane does not undergo α,α-dehydrogenation to form a siloxymethylidene, but instead reacts via Si-CH_3 oxidative addition to give the (methyl)Ir(III)silyl complex **4** (eqn. 2). This outcome is unexpected given the paucity of examples of direct C(*sp*^{3})-Si oxidative addition. To our knowledge, no examples of an analogous oxidative addition to give an isolable, unsupported alkyl of a metal silyl have been reported except in cases involving strained silicon-containing rings,[18] though this reaction has been explored computationally.[19-21] The product (alkyl)metal silyl would be a plausible intermediate in the catalytic *sp*^{3} C-H silylation of unactivated alkanes, but there are no reports of undirected, intermolecular catalytic *sp*^{3} C-H silylation[7, 22] except for one that operates through a σ-bond metathesis mechanism.[23] Thus this seemingly simple oxidative addition is apparently exceptionally uncommon.

Furthermore, we have found that this transformation is remarkably general and now report a kinetic and thermodynamic analysis of a family of organoiridium silyls formed by C(*sp*^{3})-Si oxidative addition. Kinetic analyses show that C(*sp*^{3})-Si activation is a facile and reversible process and supplemental studies using DFT suggest a difference in driving force of *ca.* 10 kcal·mol^{-1} across the series of complexes.

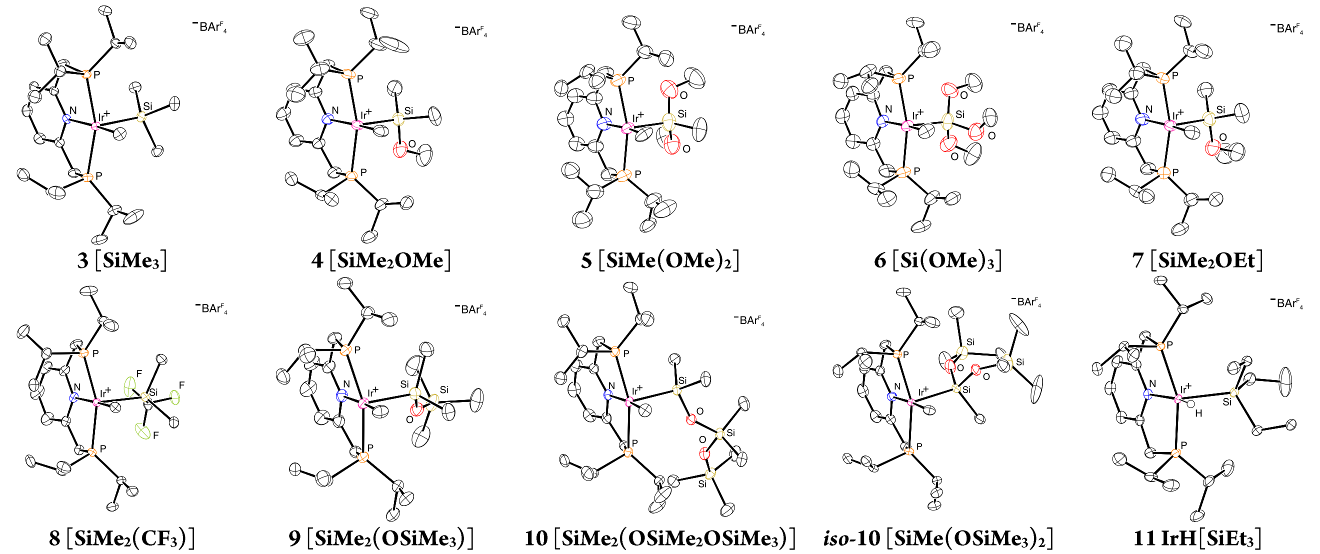
RESULTS AND DISCUSSION

Dehydrogenation of complex **1** with excess *tert*-butylethylene (10 *equiv.*) in neat methoxytrimethylsilane yields complex **4**, which gives a $^{31}P\{^1H\}$ NMR signal at 32.6 ppm and an upfield triplet $^{13}C\{^1H\}$ resonance at -20.8 ppm corresponding to the Ir-CH_3. Complex **4** was characterized by X-ray diffraction, (Figure 2) confirming its structure as an unprecedented example of a 5-coordinate silyl methyl complex resulting from intermolecular C(*sp*^{3})-Si activation. Analogous reactivity was found for a large family of methyl organosilanes including tetramethylsilane, dimethoxydimethylsilane, trimethoxymethylsilane, ethoxytrimethylsilane, trifluoromethyltrimethylsilane, hexamethyldisiloxane and octamethyltrisiloxane. In all cases, intermolecular C(*sp*^{3})-Si activation was observed, giving complexes **3-10** in analytically pure form after crystallization (eqn. 3). These complexes were characterized in solution by ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR and in the solid state by single-crystal X-ray diffraction (Figure 2). Thus we have been able to achieve intermolecular C(*sp*^{3})-Si oxidative addition in tetraorganosilanes, as well as mono-, di- and trialkoxysilanes and two siloxysilanes (Table 1).



3	$SiMe_3$	37%
4	$SiMe_2(OMe)$	54%
5	$SiMe(OMe)_2$	20%
6	$Si(OMe)_3$	16%
7	$SiMe_2(OEt)$	85%
8	$SiMe_2(CF_3)$	60%
9	$SiMe_2(OSiMe_3)$	49%
10	$SiMe_2(OSiMe_2OSiMe_3)$	33%
***iso*-10**	$SiMe(OSiMe_3)_2$	-

(3)



3 [$SiMe_3$] **4** [$SiMe_2OMe$] **5** [$SiMe(OMe)_2$] **6** [$Si(OMe)_3$] **7** [$SiMe_2OEt$]

8 [$SiMe_2(CF_3)$] **9** [$SiMe_2(OSiMe_3)$] **10** [$SiMe_2(OSiMe_2OSiMe_3)$] ***iso*-10** [$SiMe(OSiMe_3)_2$] **11** IrH[$SiEt_3$]

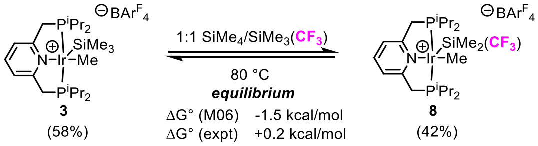
Figure 2. ORTEPs of Complexes **3-11** shown at 50% probability. Full disorder models and anions are omitted for clarity.

When octamethyltrisiloxane is used, complex **10** is obtained as the major product, however this silane differs from the other members of the family (**3**-**9**) by virtue of having both internal and terminal methylsilane groups. Although the major product obtained is the one resulting from terminal activation (**10**), a minor component resulting from C(sp^3)-Si activation of an internal methyl group can be separated in impure form through successive, fractional crystallizations (***iso*-10**). Although this minor isomer could not be obtained in sufficient quantities for further studies, it represents a silyl complex analogous to that derived from $HSi(OSiMe_3)_2(CH_3)$, the most–common silane reagent employed in C-H silylation catalysis.[8, 10, 24-31]

Table 1. Experimental and Computed Metrics of Ir Complexes

Complex	Si-Ir-C (DFT)[a]	Si-Ir-C (XRD)	Ir-Si (XRD)	$^{31}P\{^1H\}$ (ppm)[b]	$^{13}C\{^1H\}$ (ppm)[b]
3	88.2	93.1(1)	2.334(1)	28.8	-21.3
4	95.4	98.2(1)	2.298(1)	32.6	-20.8
5[c]	96.9	97.8(3)	2.235(4)	35.1	-20.8
6[c]	99.0	94.5(2)	2.247(2)	35.2	-21.6
7[c]	95.1	96.9(2)	2.273(2)	32.5	-20.6
8	83.3	84.1(1)	2.290(1)	28.1	-22.4
9	94.3	94.2(1)	2.312(1)	31.6	-20.7
10	95.8	95.1(1)	2.306(1)	31.9	-20.7
***iso*-10**	88.6	92.6(1)	2.291(1)	31.3	-21.6

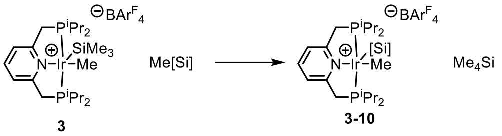
[a] See the supporting information for details. [b] NMR in CD_2Cl_2. [c] Extensive disorder in the X-ray structure may decrease the accuracy of the experimental structural metrics.



(4)

Although complexes **3**-**10** are stable in solution at room temperature, C(sp^3)-Si oxidative addition is completely reversible in certain cases. For instance, heating a solution of the tetramethylsilane-derived complex **3** in an equimolar mixture of tetramethylsilane and trifluoromethyltrimethylsilane gives an equilibrium between complexes **3** and **8**. At equilibrium, the observed **3**:**8** ratio is found to be 58:42, corresponding to a ΔG° of *ca.* +0.2 kcal·mol^{-1}. On the other hand, attempts to equilibrate the methoxytrimethylsilane-derived complex **4** with trifluoromethyltrimethylsilane failed to show any reactivity, which inspired us to analyze the relative stability of the silyl complexes by DFT. A summary of computed relative free energies (M06/def2svp(CHNOF), def2tzvp(IrPSi)) is given in Table 2 and reveals a profound impact of the silicon substituents on the stability of the resulting silyl complexes. For instance, while the computed ΔG° for the **3**:**8** pair is -1.5 kcal·mol^{-1} (in good agreement with the experimentally determined value of +0.2 kcal·mol^{-1}), the formation of **4** is downhill from **3** by nearly 6 kcal·mol^{-1} and downhill from **8** by more than 4 kcal·mol^{-1}. This finding explains the lack of apparent reversibility of oxidative addition when **4** is heated in trifluoromethyltrimethylsilane solution, as this reaction would be substantially uphill. Indeed the reverse reaction between **8** and methoxytrimethylsilane proceeds to **4** as one would expect given the driving force.

Table 2. Predicted stability of (methyl)iridium silyl complexes.



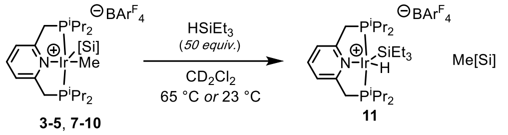
Complex	[Si]	ΔG°$_{calc}$ (kcal·mol^{-1})[a]
3	$SiMe_3$	0
4	$SiMe_2(OMe)$	-5.9
5	$SiMe(OMe)_2$	-9.0
6	$Si(OMe)_3$	-6.3
7	$SiMe_2(OEt)$	-4.3
8	$SiMe_2(CF_3)$	-1.5
9	$SiMe_2(OSiMe_3)$	-7.1
10	$SiMe_2(OSiMe_2OSiMe_3)$	-9.5
***iso*-10**	$SiMe(OSiMe_3)_2$	-11.0

[a] See the supporting information for details.

When considering the computed relative free energies of silyl exchange in complexes **3**-**10**, we find that formation of alkoxy- and siloxysilyl complexes is predicted to be the most downhill. These computations serve as a readout of the relative $Si\text{-}CH_3$/Ir-Si bond strengths,[32] the latter of which is expected to be strongly influenced by the π-accepting ability of the silyl ligand. Previous DFT experiments on a series of $Os(SiR_3)$ complexes showed that the Os-Si bond strength tracks with the π-accepting ability of the Si-X σ* orbitals.[33] This analysis argues for the π-accepting ability of alkoxy- and siloxysilanes in **4**-**7**, **9**, and **10** and suggests that the trifluoromethyldimethylsilyl group in **8** is a poor π-acceptor. Formation of complexes **10** and ***iso*-10** are predicted to be furthest downhill from **3**, with a predicted ΔG° of -9.5 kcal·mol^{-1} for **10** being slightly more negative than the value calculated for dimethoxysilyl complex **5** (Table 2).

Rates of reductive elimination and trapping. While the relative driving forces computed for C(sp^3)-Si oxidative addition in **3**-**10** served to illuminate our experiments demonstrating the reversibility of C(sp^3)-Si oxidative addition, our succesful isolation of these complexes provided a unique opportunity to experimentally examine the kinetics of the corresponding C(sp^3)-Si reductive elimination process. A previous report has examined the kinetics of C-Si reductive elimination from *cis*-$PtMe(SiPh_3)(PMePh_2)_2$ in the presence of diphenylacetylene, though in that case the reaction rate was found to be inversely dependent on phosphine, implicating rate-limiting ligand dissociation.[12-13] To our knowledge, no analogous study has been conducted for a family of silyl substituents despite the importance of C-Si reductive elimination in both olefin hydrosilylation and C-H silylation catalysis.

Table 3. Rates of reductive elimination and trapping by $HSiEt_3$.

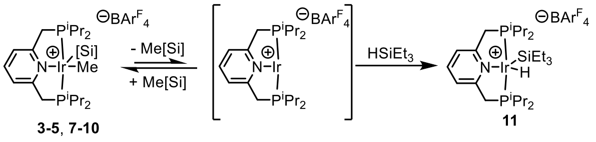


Complex	[Si]	Rate: 65 °C	23 °C, (s^{-1})
3	$SiMe_3$	-	$1.90(2) * 10^{-4}$
4	$SiMe_2(OMe)$	$1.01(9) * 10^{-4}$	-
5	$SiMe(OMe)_2$	$1.7(2) * 10^{-5}$	-
7	$SiMe_2(OEt)$	$5.4(3) * 10^{-5}$	-
8	$SiMe_2(CF_3)$	$1.34(3) * 10^{-3}$	$1.55(2) * 10^{-5}$
9	$SiMe_2(OSiMe_3)$	$9.7(3) * 10^{-4}$	-
10	$SiMe_2(OSiMe_2OSiMe_3)$	$1.40(2) * 10^{-4}$	-

Seven of the eight complexes tested (**3**-**5** and **7**-**10**) undergo C-Si reductive elimination on treatment with triethylsilane to give the free organosilane and a new iridium complex **11**. NMR analysis of **11** is consistent with a monohydride monosilyl complex, which we were able to confirm by single-crystal X-ray diffraction. With an excess of triethylsilane, all seven complexes undergo reductive elimination following pseudo first-order kinetics when conversion is monitored by $^{31}P\{^1H\}$ NMR spectroscopy. The use of a hydrosilane as the trapping reagent is highly relevant to both olefin hydrosilylation and C-H silylation mechanisms, since in both cases reaction with a hydrosilane follows the C-Si reductive elimination step.

Our kinetic findings are summarized in Table 3. The alkoxy- and siloxysilyl complexes **4**, **5**, **7**, **9** and **10** undergo reductive elimination and trapping over hours at 65 °C, while the triorganosilyl complexes **3** and **8** react rapidly even at 23 °C. The apparent order of reactivity follows $SiMe_3$ > $SiMe_2(CF_3)$ > $SiMe_2OSiMe_3$ > $SiMe_2OSiMe_2OSiMe_3$ > $SiMe_2(OMe)$ > $SiMe_2(OEt)$ > $SiMe(OMe)_2$. Thus the triorganosilyl complexes undergo reductive elimination and trapping more rapidly than the siloxylsilyl complexes, which are themselves significantly faster than the alkoxysilyl complexes. The rate of formation of **11** from siloxy- versus alkoxysilyl complexes argues that the relative thermodynamic stabilities of the silyl methyl complexes (Table 2) are not the only determinant of the rate of C(sp^3)-Si reductive elimination in this family of complexes. Instead, we hypothesize that the π-accepting ability of the silyl group contributes to the kinetics of reductive elimination, since the slowest rates of formation of complex **11** are observed for the mono and dialkoxysilyl complexes **4**, **7**, and **5**. Monomethoxysilyl complex **4** converts to **11** nearly an order of magnitude slower than monosiloxysilyl complex **9**, with the dialkoxysilyl **5** converting nearly two orders of magnitude slower. It may be the case that the success of siloxysilanes in arene C-H silylation stems from the increased stability of the iridium siloxysilyl intermediates relative to trialkylsilyl complexes, which does not appear to incur as significant a penalty to the rate of C(sp^3)-Si reductive elimination and trapping as alkoxysilyl derivatives.

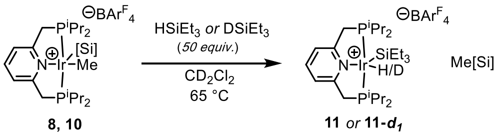
The decreased rates of reductive elimination and trapping of organometal silyls bearing electron-withdrawing substituents contrasts with the behavior observed for Si-H oxidative addition at late transition metals. In many cases, hydrosilanes bearing electron-withdrawing groups are found to react *more* rapidly, with triorganohydrosilanes undergoing Si-H oxidative addition slowly or not at all,[34-36] though at least one counter-example exists.[37] Both the increased rate of Si-H activation for electron-deficient silanes[35] and the increased stability of the resulting silyl complexes[38-40] have been attributed to the formation of stronger M-Si bonds with such silanes. Several studies on rhodium complexes show reduced rates of olefin hydrosilylation using electron-deficient silanes, which has also been attributed to the increased stability of the metal silyl intermediates.[41-43] By the same reasoning, the more-stable iridium silyl complexes in our study show decreased rates of C(sp^3)-Si reductive elimination and trapping, though the higher rates observed for siloxysilyl complexes relative to alkoxysilyl complexes is not reflected in the calculated metal silyl stabilities and likely stems from purely kinetic factors. This apparent distinction between the reactivity of methoxy and siloxysilyls is important since methoxy groups have been substituted for siloxy groups to simplify computations,[8] but our experimental findings indicate that this may not be a benign substitution.



(5)

Given our observation that C-Si reductive elimination can occur in the absence of triethylsilane, (eqn. 4) we propose that reductive elimination in the presence of triethylsilane occurs via the mechanism given in eqn. 5 where pre-equilibrium reductive elimination is followed by irreversible trapping by silane. An alternative mechanism involving triethylsilane-assisted C-Si reductive elimination (either through an Ir(V) complex or a σ-SiH complex) is difficult to rule out, but is not necessary given the evidence that reductive elimination can occur from the 5-coordinate iridium(III) complexes **3** and **8** in the absence of hydrosilane. A comparison of the rate of reductive elimination and trapping for **8** and **10** with $HSiEt_3$ and $DSiEt_3$ in separate experiments gives a small H/D isotope effect of 1.2 and 1.1 respectively, a value inconsistent with rate-limiting Si-H oxidative cleavage,[44-45] thus the mechanism given in eqn. 5 seems most probable (Table 4). The overall reaction scheme involving pre-equilibrium reductive elimination followed by trapping is distinct from the C(sp^3)-Si reductive elimination system studied by Ozawa, which proceeds via pre-equilibrium ligand exchange followed by irreversible reductive elimination.[13, 46]

Table 4. H/D isotope effect on the rate of reductive elimination and trapping by $HSiEt_3$.



Complex	Rate: **H**$SiEt_3$	**D**$SiEt_3$, (s^{-1})	H/D
8	$1.34(3) * 10^{-3}$	$1.09(2) * 10^{-3}$	1.2
10	$1.40(2) * 10^{-4}$	$1.27(6) * 10^{-4}$	1.1

CONCLUSION

In summary, we report a cationic pincer-supported iridium system capable of intermolecular C(sp^3)-Si oxidative addition. The generality of this manifold to activate C(sp^3)-Si bonds is shown for a large family of alkyl, alkoxy, and siloxysilanes. A thermodynamic analysis of these complexes by DFT shows a strong correlation of stability with the presence of electron withdrawing groups on the silyl ligand, providing a quantitative description of trends dating to early studies on olefin hydrosilylation. The predicted stabilities largely correspond with experimental rates observed for C(sp^3)-Si reductive elimination followed by trapping by silane, with an apparent order of reactivity following: $SiMe_3$ > $SiMe_2(CF_3)$ > $SiMe_2OSiMe_3$ > $SiMe_2OSiMe_2OSiMe_3$ > $SiMe_2(OMe)$ > $SiMe_2(OEt)$ > $SiMe(OMe)_2$. The significantly higher rate of RE/trapping for the siloxysilyl complexes versus the alkoxysilyl complexes does not correlate with the relative stability of the corresponding silyl complexes, hinting at an important kinetic distinction between these two classes of metal silyls. Given the importance of organometal silyl intermediates in catalytic C-H silylation and olefin hydrosilylation, we believe that our structural, thermodynamic, and kinetic analyses on the diverse family of iridium silyl complexes **3-11** will provide a strong basis for silyl-substituent selection in future catalytic method development.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at the ACS publications website at "http://pubs.acs.org."

Experimental procedures, summaries of computational and experimental results, and compound characterization data. (PDF)

Coordinates of computed species. (XYZ)

X-ray crystallographic data. (CIF)

CCDC 2062008–2062016 and 2068311 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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