The mechanism of oxidative addition of Pd(0) to Si–H bonds: electronic effects, reaction mechanism, and hydrosilylation†

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The oxidative addition of Pd to Si–H bonds is a crucial step in a variety of catalytic applications, and many aspects of this reaction are poorly understood. One important yet underexplored aspect is the electronic effect of silane substituents on reactivity. Herein we describe a systematic investigation of the formation of silyl palladium hydride complexes as a function of silane identity, focusing on electronic influence of the silanes. Using [μ-dcpe]Pd₂ (dcpe = dicyclohexylphosphino)ethane and tertiary silanes, data show that equilibrium strongly favours products formed from electron-deficient silanes, and is fully dynamic with respect to both temperature and product distribution. A notable kinetic isotope effect (KIE) of 1.21 is observed with H/DSiPhMe₂ at 233 K, and the reaction is shown to be 0.50 order in [μ-dcpe]Pd₂ and 1.10 order in silane. Formed complexes exhibit temperature-dependent intramolecular H/Si ligand exchange on the NMR timescale, allowing determination of the energetic barrier to reversible oxidative addition.

Taken together, these results give unique insight into the individual steps of oxidative addition and suggest the initial formation of a σ-complex intermediate to be rate-limiting. The insight gained from these mechanistic studies was applied to hydrosilylation of alkynes, which shows parallel trends in the effect of the silanes’ substituents. Importantly, this work highlights the relevance of in-depth mechanistic studies of fundamental steps to catalysis.

Introduction

Palladium hydrides are a unique class of organometallic compounds which are invoked as key intermediates in a variety of catalytic reactions, including the Mizoroki–Heck reaction, alcohol and alkene oxidation, nucleocarbonylation reactions, hydrofunctionalization reactions, (co)polymerization reactions and alkene and alkyne (cyclo)isomerization reactions. However, despite the fact that these species are often proposed as intermediates, the direct observation or isolation of complexes containing a formal Pd–H bond is uncommon, and fundamental study of their behaviour has largely been precluded.

Organosilicon compounds are broadly significant, since they are used as monomers to synthesize polysiloxanes (silicones) and have also recently gained attention for their use as bio compatible yet non-natural carbon isosteres in the synthesis of bioactive molecules. Transition metal-catalysed hydrosilylation of alkynes and alkenes is the primary method for synthesizing organosilanes, with most development and mechanistic work focusing primarily on Pt catalysts. On the other hand, Pd catalysts show complementary and modular regioselectivity and are more useful in enantioselective hydrosilylation.

A key step in the mechanism of transition metal-catalysed hydrosilylation is the oxidative addition of the metal to the Si–H bond. While this fundamental step of organometallic chemistry, to form (silyl)M(H) complexes, has been well-studied for Pd’s neighbouring elements Rh, Pt, and most other transition metals, it is much less understood for Pd. The oxidative addition of Rh and Pt to Si–H is facile, and complexes have been reported with a variety of ligand scaffolds and silanes. In addition to hydrosilylation (Fig. 1b), the oxidative addition of Pd to Si–H bonds (Fig. 1a) is a vital step of carbene insertion reactions (Fig. 1c) and C-Si cross-coupling reactions (Fig. 1d) and hydrodehalogenation reactions (Fig. 1e) amongst others. A key limitation that unifies all of these reactions is the dependence on silane identity; most reactions are heavily dependent on the number of substituents (primary vs. secondary silanes, etc.) on silicon, and most protocols do not investigate the electronic and/or steric effects of the silane substituents. Notably, the electronic effects of the silane substituents have been experimentally investigated for Rh and Pt, but remain unexplored for Pd. Because of the importance of this step in many Pd-catalysed reactions, we
Fig. 1  (a) Oxidative addition to form silyl palladium hydride species implicated in (b) hydrosilylation (only one isomer shown for clarity), (c) carbene insertion, (d) C–Si cross-coupling, and (e) hydro-dehalogenation reactions.

sought to determine the mechanism of Si–H oxidative addition to Pd(0) with a focus on elucidating the effect of silane substituents.

Despite being implicated as catalytic intermediates for more than half of a century, it was not until the early 2000's that the Fink group reported the isolation of the first (silyl)Pd(H) complex. Since this seminal work, Ishii and Iluc have both also published related work. Importantly, the effect of silane substituent has not been systematically explored; the complex.

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exerting an electronic influence on the reactivity. These results are then shown to be relevant in the hydrosilylation of alkenes and provide mechanistic rational behind observed changes in reactivity.

Results and discussion

Initial reactivity studies of [(μ-depe)Pd]₂ (1) with silanes

We began by investigating the reactivity of a library of tertiary silanes with [(μ-depe)Pd]₂ (1) by ¹H and ³¹P NMR (Fig. 3). These reactions proceed cleanly to afford a new product, as initially observed by NMR, and only the reactants and the product are observed. For silanes with at least one phenyl ring or alkoxide substituent (3–6), the reactions proceed in good to excellent yields.

In the ¹H NMR spectrum, the peak corresponding to silane Si–H (4–6 ppm) is consumed during the reaction, along with a concomitant appearance of a new resonance below 0 ppm (−1.23 to −2.34 ppm), which is consistent with the Pd centre interacting with the silane Si–H bond to form a (silyl)Pd(H), a Pd(η²-H–SiR₃) complex, or some structure in between these extremes. In addition to the ¹H NMR signal, a new band in the IR spectrum (1838 to 1881 cm⁻¹) is observed, consistent with known analogous Ni and Pd complexes.
showing that there is only one phosphorus environment. At low signals between 57 ppm and in the $^{31}$P-{1H} NMR spectra, the upfield signal is a doublet due to trans coupling to the 1H signal in the $^{1}$H NMR spectrum for most products appears as a doublet (2$^{\text{J_{H-P}}}$ = 119 Hz). The hydride peak in the $^{1}$H NMR shifts from 5.71 ppm in 5a to $-1.74$ ppm upon coordination/oxidative addition to Pd and changes from a singlet with $^{29}$Si satellites ($J_{\text{HH-Si}}$ = 198 Hz) to a triplet ($J_{\text{HH-P}}$ = 78 Hz) with $^{29}$Si satellites ($J_{\text{HH-Si}}$ = 30 Hz; see ESI, Table S1†). In related Ni,⁶¹,⁹¹ and Pt,⁶¹ and Rh complexes, the $J_{\text{HH-Si}}$ values of our complexes are in between these markers yet are closer to values known for (silyl)M(H) complexes of group 10 metals¹⁶,⁸²,⁹¹,⁹² than for their σ-complexes.⁶²,¹⁰⁰–¹⁰³ Therefore, our data support the formation of the (silyl)Pd(H) complexes, as drawn in Fig. 3.

A comparison of the data shown in Fig. 3 reveals that higher conversions are obtained with increasing number of aryl substituents and alkoxide substituents on the silane. This trend correlates well with the electronegativity of the atoms attached to Si (11 > 10a > 9 > 8a > 7).¹⁰⁴ While this trend is revealing, we sought to decouple the kinetic effects from the thermodynamic effects and systematically investigate the electronic influence on each parameter of the reaction.

**Electronic effects in oxidative addition of Pd(0) to silanes**

To probe our hypothesis that the oxidative addition of silanes to Pd(0) is more facile with electron-poor silanes, a library of electronically diverse triaryl silanes were synthesized and evaluated in the reaction. The targeted silanes span a gradient of electronic character, with substituents in the para position ranging from electron-donating (X = NMe₂, OMe, Me) to electron-withdrawing (X = F, CF₃). Reactions of these silanes 5 with 1 cleanly yield the expected (dcpe)Pd(H)(SiAr₃) complexes 10a-f (Fig. 3c), all in excellent NMR conversions except for the reaction with the electron-rich 4-dimethylaminophenyl-substituted silane (5b $\rightarrow$ 10b, mass balance is remaining starting material).

A translucent, off-white crystal of (dcpe)Pd(H)(Si(4-CF₃-Ph)₃) (10f) suitable for single crystal diffraction was grown from a reaction mixture of 1 and HSi(4-CF₃-Ph)₃ (5f) in benzene/hexane (Fig. 4). Product 10f displays nearly ideal square planar geometry around the palladium atom, with the summed total of bond angles equal to 360°. To get a more precise measure of the structure’s geometry, the structural parameter $\tau_4$ was calculated from crystallographic data.¹⁰⁵,¹⁰⁶ Analysis of 10f gives $\tau_4$ = 0.15, where $\tau_4$ = 0 indicates an ideally square planar complex, and $\tau_4$ = 1 represents a tetrahedral complex. The $\tau_4$ value in the $^{1}$H NMR spectrum for most products appears as a triplet at room temperature with $^{3}$J_{H-P} values of 75–80 Hz, which is the average of the cis and trans coupling constants. Only one signal in the $^{31}$P($^{1}$H) NMR spectrum is observed (55–60 ppm, corresponding to a downfield shift from 1 at 23 ppm), showing that there is only one phosphorus environment. At low temperatures, the hydride signal in the $^{1}$H NMR resolves into a doublet ($^{3}$J_{H-P} (trans) = ~160 Hz), the $^{31}$P($^{1}$H) spectra show two signals between 57–64 ppm, and in the $^{1}$H-coupled $^{31}$P spectra, the upfield signal is a doublet due to trans coupling to the
Fig. 4 Molecular structure of (dcpe)Pd(H)(Si(4-CF3-Ph)3) (10f). Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms except for Pd–H are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd1–H1 1.59(3), Pd1–Si1 2.3413(5), Pd1–P1 2.3422(5), Pd1–P2 2.3584(5), H1–Pd1–Si1 67(1), H1–Pd1–P2 96(1), P1–Pd1–P2 86.46(2), P1–Pd1–Si1 111.01(2). One Cf1 group is highly disordered and was refined as being located in three positions with an occupation factor of 0.33 each.

value of 10f can be compared to similar complexes whose characterization includes the Pd–H bond length (allowing calculation of τ4): Ishii’s (dcpe)Pd(H)(SiH2Trip) (Trip = 9-trip-tcyl)m complex gives τ4 = 0.11 and fluc’s (P–P)Pd(H)(SiHPh2) complex gives τ4 = 0.39 (Table S44). 10f is therefore comparable to known square planar silyl palladium hydride complexes. Deviation from square planarity is likely due to steric repulsion between the cyclohexyl substituents of dcpe and the aryl groups of the silane. Solid-state geometry also gives information on the strength of each ligand’s trans influence. Silyl ligands are known for being among the strongest trans-influencing ligands. Therefore, we expect that the Pd–P bond trans to the silyl ligand will be longer than the Pd–P bond trans to the H; indeed, this is the case for complex 10f, which has Pd–P bond lengths of 2.3584(5) Å and 2.3422(5) Å, respectively.

Comparing the Pd–P bond lengths in related complexes gives insight into the trans-influencing ability of the 4-CF3-phenyl substituents of the silane. The Pd–P bond length trans to the silyl ligand in complex 10a (ref. 82) and Ishii’s complex** are 2.350(2) Å and 2.3319(14) Å, respectively. With no change in ancillary ligand (dcpe) across all three cases, these results indicate that the –Si(4-CF3-Ph)3 group has a stronger trans influence than the –SiPh3 group, which in turn is stronger than –SiH2Trip.

Returning to our hypothesis on the effect of electronic character of the silane on oxidative addition, no useful distinctions could be made using the data in Fig. 3c, as most triaryl silanes exhibit similar reactivity. We thus turned to less reactive dimethylaryl silanes to further probe the influence of silane electronics on oxidative addition. The reaction of each dimethylaryl silane with 1 yielded the desired products (8a–f) (Fig. 3b), though to lower conversion than with triaryl silanes. The formed (silyl)Pd(H) complexes exhibit similar spectroscopic characteristics as described for their triaryl counterparts. The data in Fig. 3b show a clear trend with respect to the electronic nature of the silane: more electron-poor silanes give higher conversions to the silyl palladium hydrides 8.

Reaction equilibrium
To embark upon mechanistic studies, we first sought to determine if this oxidative addition reaction is reversible or irreversible. 1 and 3a were reacted in an NMR tube at 298 K and allowed to reach equilibrium (Fig. S10†). The reaction was then cooled to 253 K, and the conversion of 8a was measured to be 88%. Warming the reaction to 293 K and then 333 K resulted in concomitant decreases in conversion to 8a (44% and 17%, respectively). Subsequent cooling back to 298 K resulted in a conversion of 41%, which is consistent with the data in Fig. 3. Because the conversion is consistently ~42% at ambient temperature independent of whether the reaction had previously been heated or cooled, we deemed this reaction to be reversible.

We also tested reversibility by taking advantage of the differential reactivity of electron-rich and -poor silanes: if the reaction is indeed reversible, then we expect that a silyl palladium hydride formed from an electron-rich silane should convert to the corresponding product of oxidative addition of an electron-poor silane if one is added. This reaction is expected to occur through reductive elimination of the electron-rich silane, followed by preferential oxidative addition of the electron-poor silane. (dcpe)Pd(H)(Si(tolyl)3) (10d, formed in situ from 1 and 5d) was reacted with triphenyl silane (5a), and conversion to an equilibrium mixture of 1 : 3.3 (10d/10a) was observed (Scheme 1). An analogous experiment with tris(4-fluorophenyl)silane (5e) added to a solution of pre-formed 10a shows an equilibrium ratio of 1 : 2.8 (10a/10e) (Table S16†). The formation of H2 or bis-silyl by-products was not observed, and mass balance is consistently 100% against an internal standard. These data imply that the formation of silyl palladium hydrides is completely reversible with respect to product distribution.

To quantify the trend imparted by silane electronic character, we measured the equilibrium constants (Keq) for the reactions of 1 with each silane 3a-f and constructed a Hammett plot. This analysis gave a sensitivity constant, pK (eq indicates that this value is derived from equilibrium constants, as

Scheme 1 Conversion of 10d into 10a via reversible oxidative addition. Experiment was performed in C7D8 and relative conversions were determined by 31P{1H} NMR integration; Reaction conditions: 1.00 equiv. of 1, 2.05 equiv. each of 5a and 5d, 13.33 mM in C7D8, and 3 h.
opposed to rates of reaction) of 3.5 ± 0.5 (Fig. 5), consistent with the data in Fig. 3b showing that the reaction is more favourable with electron-poor silanes.

We hypothesized that this observed trend in $K_{\text{eq}}$ and thus $\Delta G_{\text{OA}}$ (OA, oxidative addition), of the reaction is dictated by the varying bond strengths of the Pd–Si bonds, where stronger Pd–Si bonds are formed with electron-poor silanes. To deconvolute the enthalpic and entropic contributions to $\Delta G_{\text{OA}}$, the equilibrium constants as a function of temperature were measured. van’t Hoff analysis was carried out (Fig. 6) for the reactions of 1 with 3a ($X = \text{H}$), 3c ($X = \text{OMe}$), and 3f ($X = \text{CF}_3$). These particular silanes were chosen to represent a breadth of electronic character. The $\Delta S_{\text{OA}}$ values are all large and negative, reflecting the loss of entropy in this reaction between three reactants to form two products. $\Delta H_{\text{OA}}$ is negative for all three substrates, but more importantly, a clear trend is observed: $8f < 8a < 8c$ (CF$_3$ < H < OMe) in $\Delta H_{\text{OA}}$. These data show that the reaction between 1 and silanes 3 is more favourable with electron-poor silanes, which we interpret to mean that there is an increased strength of the Pd–Si bond in products $8$.

To determine if this trend in the electronic influence of silanes is more general, we returned to triaryl silanes 5. Because the equilibrium constants are too large to measure at room temperature under our standard conditions, we took advantage of the reaction’s full reversibility in product distribution by performing competition experiments. In these experiments, 2.05 equivalents of each HSiPh$_3$ (5a) and HSi(4-X–Ph)$_3$ (5b–f, $X = \text{NMMe}_2, \text{OMe}, \text{Me}, \text{F}, \text{CF}_3$) were added to one equivalent of 1 (Fig. 7).

As with the non-competitive oxidative addition reactions of dimethylaryl silanes 3a–f (Fig. 5), these data show that oxidative addition occurs preferentially with the more electron-poor silane. For example, when 5a (a comparatively electron-neutral...
silane) and 5e (an electron-poor silane) compete over the reaction with 1, oxidative addition preferentially occurs with 5e over 5a, forming 10e in larger concentrations than 10a. Because the relative ratios of products are proportional to the ratios of equilibrium constants (see ESI Section 5f for derivation), a Hammett plot was constructed to quantify the effect of electronic factors on the equilibrium constant of oxidative addition (Fig. 7). For triaryl silanes, Hammett analysis gives \( \rho_{eq(comp)} = 9.6 \pm 0.9 \), showing a more dramatic effect on \( K_{eq} \) than monoaryl silanes (non-competitive equilibrium data in Fig. 5, \( \rho_{eq} = 3.5 \pm 0.5 \)). However, to allow for a direct comparison of the two systems, we additionally performed the same competition studies with dimethylaryl silanes 3a-f (Table S18 and Fig. S16†). \( \rho_{eq(comp)} \) was found to be 3.4 ± 0.3 with these dimethylaryl silanes. Notably, these data trend proportionally to the number of changing substituents at silicon.

To conclude studies on the reaction equilibrium, we sought to determine the effect of deuterium substitution in the silane. Reaction of 1 and 3a-d1 proceeded as expected, affording product 8a-d1; the \(^{31}P^{1H}\) NMR spectrum at room temperature shows a 1 : 1 : 1 triplet (\( J_{D-P} = 11 \text{ Hz} \)) in 40% conversion. As with 3a, the coupling constant is an average of the cis and trans coupling due to dynamic exchange behaviour (vide infra). The equilibrium constants for the reactions of proto-silane 3a and deuterio-silane 3a-d1 were determined independently (Table S11†). The equilibrium isotope effect (EIE) was determined to be 3.7 ± 0.2 at 298 K. The room temperature IR stretching frequencies for the Si–H and Si–D bonds in 3a and 3a-d1 are 2116 cm\(^{-1}\) and 1539 cm\(^{-1}\), respectively. The EIE measured for this reaction is consistent with the fact that deuterium prefers to form the stronger bond;\(^{24-26,31,33}\) i.e., \( K_{eq(D)} \) is lower than \( K_{eq(H)} \) because the difference in energy between the Si–D and Pd–D bonds is larger than the difference in energy between the Si–H and Pd–H bonds.

**Reaction kinetics**

Having examined the ground state, we next turned our attention to understanding the kinetics and reaction mechanism. In probing the mechanism, three possible pathways for oxidative addition were considered: concerted, S_n2-like, or radical. A concerted pathway was deemed most reasonable as Si–H bonds are non-polar and have been shown to proceed via concerted pathways in related systems. We ruled out the S_n2-like pathway on the basis of relative acidities of Pd–H (\( pK_a \approx 24 \)) and Si–H (\( pK_a \approx 35 \)) bonds. Additionally, no by-products were observed that would result from a radical pathway (Si–Si bond coupling, \( H_3, etc. \)), so we shifted our attention from that pathway as well.

In line with a concerted pathway, the proposed mechanism for oxidative addition is seen in Fig. 8. Step i is dissociation of dimer 1 into monomers 12 in solution.\(^{24-26} \) The 14-electron complex 12 can then react with silane in step ii to form \( \sigma \)-complex 13, which then undergoes oxidative cleavage of the Si–H bond to form the product in step iii. These steps were taken as the basis for determination of the rate determining step (RDS) of the reaction.

If step i is rate-determining, then the rate law will show 0.5th order in 1, 0th order in silane, and there will be no effect of electronic or deuterium substitution in the silane on the rate of the reaction (\( \rho_i = 0 \) for a Hammett plot and KIE = 1, respectively (KIE, kinetic isotope effect)). If step ii or step iii is the RDS, then the reaction will be 0.5th order in 1 and 1st order in silane; electron poor-silanes are expected to react faster (\( \rho_i > 0 \) in a Hammett plot); additionally, a normal, primary KIE is predicted. We expect that a small KIE would point toward step ii being the RDS, since the Si–H bond is only weakened in the transition state (12 → 13). A large, primary KIE would point toward step iii being the RDS, since it is during that step that the Si–H bond is cleaved.

Initial attempts to collect kinetic data by monitoring the reaction of 1 with 5a by NMR proved unsuccessful, since the reaction was complete within a minute at room temperature. We thus set out to determine conditions that are amenable to reaction monitoring by NMR; however, even at low reagent concentrations (1.67 mM 1, 3.42 mM 5a) and low temperature (233 K), the formation of 10a was too rapid to obtain reliable kinetic data. In line with our findings on reaction equilibria, we reasoned that \( \text{Me}_2\text{PhSiH} \) 3a may also react more slowly in oxidative addition, yet still would have the advantage of allowing for electronic modulation via substitution on the aryl ring. Indeed, the gradual formation of a silyl palladium hydride 8a is observable via \(^{31}P^{1H}\) and \(^1H\) NMR at 233 K.

As detailed above (Fig. 8), the rate law distinguishes between step i and steps ii or iii being the RDS; therefore, we first embarked on measuring the orders in the reactants. We utilized the method of initial rates to ensure that the rate of the backward reaction (from 8 to 1 and 3) is negligible. Data was

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*Fig. 8 Proposed mechanism for the oxidative addition of silanes to 1.*

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collected on samples of varied concentrations of 1 (1.67–13.3 mM) or 3a (3.42–27.3 mM) while the concentration of the unexamined reagent was kept constant. The observed rate of each reaction (Fig. S17 and S19†) was then plotted against initial reagent concentration to determine the reaction order.

As shown in Fig. 9, the reaction was determined to be 0.5th order (0.57 \pm 0.09) in dimer 1. This result is consistent with any of the three steps in the mechanism of Fig. 8 being the RDS, and supports the hypothesis that the dimer 1 dissociates into two [(dipe)Pd] fragments (12) prior to or during the RDS.

We next determined the order in silane (Fig. 10). A plot of the initial rate versus the concentration of 3a shows that the reaction is 1st order (0.9 \pm 0.1) in silane. This suggests the silane is involved in or before the RDS, and thus dimer dissociation (step i) of the mechanism in Fig. 8 can be ruled out as the RDS. With these data, the simplified rate law of the reaction can be written (eqn (1)), showing an overall 1.5th order reaction.

\[
\text{Rate} = k_\text{obs}[1]^{0.5}[3a]^1
\]  

(1)

Having ruled out dimer dissociation as the RDS in the mechanism, we next examined the effect of electronic substitution at silicon on rates of reaction via a Hammett analysis. Rates of reaction were measured using dimethylaryl silanes 3a, 3c, and 3f, and these experiments reveal a marked influence of silane electronics on the initial rates of product formation (Fig. S21–S24†). Analysis of kinetic trials for each silane gives a trend in \(k_\text{obs} \) of \(X = CF_3 > H > OMe\), which follows the same trend as in equilibrium studies: strongly electron-withdrawing substituents at silicon favour rapid oxidative addition, while electron-donating substituents hinder the reaction rate.

A Hammett plot was constructed from these data (Fig. 11), which shows \(\rho^* = 1.2 \pm 0.3\) († notation is used to distinguish this sensitivity constant obtained from rates of reaction from the sensitivity constant obtained from reaction equilibrium constants \(\rho_{\text{eq}}\)). Comparing the \(\rho\) value obtained for the reaction equilibrium \(\rho_{\text{eq}} = 3.5 \pm 0.5\) with that obtained for rates \(\rho^* = 1.2 \pm 0.3\) reveals that the observed rate of oxidative addition is approximately three times less sensitive to changes in electronics as the equilibrium constant \(K_{\text{eq}}\). The result of this Hammett analysis provides further evidence that either silane coordination (Fig. 8, step ii) or Si–H oxidative cleavage (Fig. 8, step iii) is the RDS of oxidative addition.
To help differentiate between these two steps being the RDS, the KIE of the reaction was determined. Recognizing the convoluted nature of KIEs and EIEs, we continued using the method of initial rates to discount any equilibria involving reaction of the Si–H bond, and therefore measured rates of reaction are approximately independent of equilibrium effects. The initial rate of reaction for Me2PhSiD (3a–d1) was measured, and it was found to react more slowly than 3a, with a KIE of 1.21 ± 0.04 (Fig. 12). The maximum primary KIE possible for Si–H/Si–D without invoking tunnelling is ~4 (see ESI, Section 9f for details). Therefore, a KIE of 1.21 is large enough to be considered a primary isotope effect, but the magnitude is small and challenging to interpret. Either step ii is the RDS, in which a smaller magnitude KIE is rationalized by the Si–H bond not being formally broken in the transition state; or step iii is the RDS, in which a very early transition state (which is expected due to the high energy of the σ-complex) would lead to a lower magnitude KIE. Notably, the KIE reported here is consistent with those of other oxidative addition studies and catalytic reactions involving Si–H and C–H bond cleavage.117

We next sought to measure the barrier (∆G‡OA) for the overall reaction by performing an Eyring analysis. The rate of reaction was measured as a function of temperature, and the results are seen in Fig. 13. ∆H‡OA and ∆S‡OA are obtained from the equation of the fit of the data, and as a result, ∆G‡OA at a given temperature can be calculated. From the data in Fig. 13, ∆H‡OA was determined to be 6.0 ± 0.3 kcal mol⁻¹, ∆S‡OA was determined to be −40 ± 20 cal mol⁻¹ K⁻¹, and therefore ∆G‡OA at 233 K was calculated to be 16.3 ± 0.3 kcal mol⁻¹. This large, negative value for ∆S‡OA supports the proposed mechanism in Fig. 8. The transition state of the RDS is highly ordered relative to the ground state, consistent with step ii or iii being the RDS. These kinetic data have been compiled, and the observed rate constants (kobs) have been determined using the rate law in eqn (1) (Table 1).

**Dynamic exchange behaviour**

One interesting feature of these silyl metal hydride complexes is their fluxional behaviour in solution.33,35,118,119 We recognized

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Table 1: Summary of rate constants (kobs) obtaineda

| Entry | Pd complex | −H/D | −X | Temperature | kobs (mM⁻⁰·⁵ s⁻¹) |
|-------|------------|------|----|-------------|------------------|
| 1     | 8a         | −H   | −H | 233 K       | 9 × 10⁻⁵         |
| 2     | 8a         | −H   | −H | 243 K       | 1.4 × 10⁻⁴       |
| 3     | 8a         | −H   | −H | 253 K       | 2.1 × 10⁻⁴       |
| 4     | 8a         | −H   | −H | 273 K       | 5.9 × 10⁻⁴       |
| 5     | 8a–d1      | −D   | −H | 233 K       | 3.2 × 10⁻⁴       |
| 6     | 8c         | −H   | −OMe| 233 K       | 3.3 × 10⁻⁶       |
| 7     | 8f         | −H   | −CF₃| 233 K       | 1.4 × 10⁻⁴       |

a kobs for the formation of 8a at 233 K was determined from eight trials, and the value reported is the average (standard deviation is 1 × 10⁻⁵).
that investigating this dynamic exchange (DE) behaviour would provide insight into the overall reaction mechanism of oxidative addition because it offers a unique chance to probe the oxidative cleavage and reductive coupling steps \(k_1\) and \(k_{-1}\), respectively, in Fig. 8) independent of the overall oxidative addition process. Accordingly, solution \(^1\text{H}\) and \(^{31}\text{P}\{^1\text{H}\}\) NMR spectra of product 8a were recorded at multiple temperatures (Fig. 14). At very low temperatures, the \(^{31}\text{P}\{^1\text{H}\}\) NMR spectrum shows two singlets (\(\delta = 58.4\) and 57.4 ppm at 183 K) which undergo coalescence at 213 K, eventually forming a sharp singlet (\(\delta = 56.4\) ppm at 273 K (Fig. 14a). Similar behaviour is seen for the Pd–H peak in the \(^1\text{H}\) NMR spectra at low temperatures; a doublet of doublets (\(\delta = -1.39\) ppm, \(J_{\text{P}-\text{H}} = 192.6\) Hz, \(J_{\text{H}-\text{P}} = 7.9\) Hz at 183 K) proceeds through coalescence at 213 K to eventually form an apparent triplet, centring at \(-1.71\) ppm, \(J_{\text{P}-\text{H}} = 75.4\) Hz at 273 K (Fig. 14b). Line broadening analysis\(^{120,121}\) allows for the calculation of the barriers for this dynamic exchange (DE) process. \(\Delta H_{\text{DE}}, \Delta S_{\text{DE}}, \) and \(\Delta G_{\text{DE}}\) at 233 K were determined to be \(7.7 \pm 0.4\) kcal mol\(^{-1}\), \(-10.7 \pm 0.5\) cal mol\(^{-1}\) K, and \(10.2 \pm 0.4\) kcal mol\(^{-1}\), respectively.

In analogy to reported complexes and their dynamic exchange behaviour,\(^{62,63,64}\) we propose a mechanism in Scheme 2 that accounts for these NMR spectra. 8a and 8a’ are proposed to interconvert via the \(\sigma\)-complexes 13a and 13a’, which themselves interconvert by rotation around the Pd–(n\(^\text{H}\)-SiMe\(_2\)Ph) bond (\(k_3\) and \(k_{-3}\)). Conversion of 8a into 13a and 8a’ into 13a’ are reductive coupling steps (\(k_{-1}\)), the microscopic reverse of oxidative cleavage (\(k_1\)).

At elevated temperatures, exchange is rapid on the NMR timescale, and the Pd–H signal in the \(^1\text{H}\) NMR appears as a triplet due to coupling to both P nuclei, and the coupling constant is an average of the \(\text{trans}\) and \(\text{cis}\) \(J_{\text{H}-\text{P}}\) values. This interpretation is supported by the \(^{31}\text{P}\{^1\text{H}\}\) NMR data, which shows a singlet at elevated temperatures. Upon cooling, the Pd–H signal (\(^1\text{H}\) NMR) undergoes coalescence and gradually resolves into a doublet of doublets at sufficiently low temperatures. The splitting pattern is accounted for by the inequivalency of the P nuclei; at low temperature in the \(^{31}\text{P}\{^1\text{H}\}\) NMR, two distinct phosphorous environments are observed, as exchange is sufficiently slowed and both P nuclei environments (P and P’ in Scheme 2) are discrete. The tunability of this process from slow-exchange to fast-exchange over an accessible temperature range indicates a relatively small energy barrier for conversion between species, and is consistent with the measured barrier of 10.2 ± 0.4 kcal mol\(^{-1}\) at 233 K.

Important for the overall oxidative addition reaction (formation of 8a from 1 and 3a), the RDS of this dynamic exchange process is either the barrier for reductive coupling/oxidative cleavage (\(k_{-1}/k_1\)) or the barrier for rotation (\(k_3/k_{-3}\)). Therefore, the oxidative cleavage step \(k_1\) must be equal to or less than 10.2 ± 0.4 kcal mol\(^{-1}\) at 233 K.

Taking advantage of the line broadening observed for additional silyl palladium hydrides, we sought to investigate the effect of silane substitution on the barriers for DE. We focused on triaryl silanes 5 because not all products with dimethylsilyl silanes 3 reached the slow exchange regime at temperatures accessible in toluene-d\(_8\). The activation parameters (Table 2) show that there is no significant effect of electronic or isotopic substitution on the rate of dynamic exchange for triaryl silanes since the measured barriers are mostly within error of one another. \(\Delta H^1\) varies from 10–14 kcal mol\(^{-1}\), showing a trend of more electron-poor silanes having higher enthalpic barriers than electron-rich silanes, and \(\Delta S^1\) is close to zero. In this dynamic exchange process, \(\Delta H^1\) and \(\Delta S^1\) are opposing, and \(\Delta G^1\) for products 10a, 10c, and 10f are within error of one another, resulting in a net null electronic effect. Furthermore, the barriers for this dynamic exchange process for 10a–d, and 10a are also within error, implying a KIE of approximately 1 (within error). Measuring the rates of dynamic exchange at varying concentrations of 10f gave similar values; these data along with small values of \(\Delta S^1\) support our hypothesis that the process is
Table 2. Dynamic exchange (DE) barriers determined by linewidth analysis of $^{31}$P{H} NMR spectra at variable temperature. $\Delta H_{\text{DE}}$ and $\Delta G_{\text{DE}}$ are reported in kcal mol$^{-1}$ and $\Delta S_{\text{DE}}$ is reported in cal mol$^{-1}$ K$^{-1}$. $\Delta G_{\text{DE}}$ determined at 233 K

| Entry | Pd complex | –H/D | –X | $\Delta H_{\text{DE}}$ | $\Delta S_{\text{DE}}$ | $\Delta G_{\text{DE}}$ |
|-------|------------|------|----|---------------------|---------------------|---------------------|
| 1     | 10a        | –H   | –H | 12 + 1              | 3.5 + 0.3           | 11 + 1             |
| 2     | 10a-d1     | –D   | –H | 10.0 + 0.4          | –2.46 + 0.09        | 10.6 + 0.4         |
| 3     | 10c        | –H   | –OMe | 10.1 + 0.4          | –2.80 + 0.09        | 10.7 + 0.4         |
| 4     | 10f        | –H   | –CF$_3$ | 13.7 + 0.5          | 5.5 + 0.2           | 12.5 + 0.5         |

Constructing a reaction coordinate diagram

Taking our findings from equilibrium and kinetic studies, we have constructed a complete mechanistic picture for the oxidative addition of silanes to 1. With the bulk of the data obtained using dimethylphenyl silane 3a, we focus on those results in the discussion below (Fig. 15), but we expect the general trends to be analogous for the other silanes studied in this work.

$\Delta G_{\text{OA}}$ was determined in the course of studying the reaction equilibrium. $K_{\text{eq}}$ for the reaction between 3a and 1 at 233 K was determined to be 125, corresponding to $\Delta G_{\text{OA}} = -6 \pm 1$ kcal mol$^{-1}$ (Fig. 15, purple). Therefore, the silyl palladium hydride 8a is lower in energy by 6 kcal mol$^{-1}$ than the starting materials 1 and 3a. This energy difference is larger for electron-poor silanes than electron-rich silanes, as shown via Hammett plots (Fig. 5, 7 and S16$^\ddagger$).

The reaction was found to be 1$^\text{st}$ order in silane 3a (Fig. 10) and 0.5$^\text{th}$ order in palladium dimer 1 (Fig. 9). Because there is a dependence on the silane on the rate of reaction, dimer dissociation (1 → 12) is ruled out as the RDS. Therefore, either formation of the σ-complex 13a or oxidative cleavage of the Si–H bond must be the RDS, since both would account for the observed orders in reactants. Hammett analysis of the dependence of the rate of reaction on the electronic influence of the silane (Fig. 11) also does not differentiate between σ-complex formation and oxidative cleavage being the RDS, since the barriers for both steps are expected to be lowered with electron-poor silanes, in line with the observed trends. Based on the small, but primary KIE of 1.21 ± 0.04 (Fig. 12), we hypothesized that formation of the σ-complex 13a is the RDS, since cleavage of the Si–H bond is expected to result in a larger KIE value. However, this is not definitive evidence.

The reaction barrier for the full oxidative addition process (1 + 3a → 8a) was determined to be 16.3 ± 0.3 kcal mol$^{-1}$ by an Eyring analysis (Fig. 13). By linewidth analysis of the $^{31}$P{H} NMR spectra of product 8a, we determined that the barrier for the dynamic exchange process between 8a and 8a’ via 13a/13a’ is 10.2 ± 0.4 kcal mol$^{-1}$ (Fig. 14). Because no significant KIE or electronic effect was observed for the dynamic exchange process, we concluded that the RDS of dynamic exchange is likely rotation. Therefore, the maximum barrier of reductive coupling (the microscopic reverse of oxidative cleavage, or 8a → 13a) is equal to or lower than 10 kcal mol$^{-1}$. If oxidative cleavage (13a → 8a) was the RDS, then the maximum overall reaction barrier for oxidative addition would be the sum of $\Delta G_{\text{OA}}$ (6 ± 1 kcal mol$^{-1}$) and $\Delta G_{\text{DE}}$ (10.2 ± 0.4 kcal mol$^{-1}$). This sum (4 kcal mol$^{-1}$) is much less than the measured free energy barrier for oxidative addition (16.3 ± 0.3 kcal mol$^{-1}$). Therefore, formation of the σ-complex (step ii in Fig. 8) is deduced to be the RDS. As a consequence of step ii being the RDS, equilibria involving the silane and reaction of the Si–D/H bond are not included in the rate law, and the KIE can be considered separately from the EIE. Because of the importance in oxidative addition reactions in catalysis, we expect these findings to affect the design of silanes and catalysts for many catalytic reactions.

Application to catalysis

Having fully elucidated the mechanism of the oxidative addition of silanes to palladium(0), we next demonstrate the relevance of this work to catalysis. Hydrosilylation was our first target because of its importance and industrial relevance. Subjecting complex 1 to HSiPh$_3$ (5a) and phenylacetylene (15) in toluene resulted in 66% yield of hydrosilylation products. Two regioisomers were observed: the branched product (E-16a) and the linear E-alkene (E-β-16a) in a 1 : 8 ratio. These results are consistent with related Pd(0)-catalysed hydrosilylation...
In this work, we have elucidated the mechanism of oxidative addition of Pd(0) to Si–H bonds and shown the relevance of this reaction in catalytic hydrosilylation. We evaluated the impact of silane electronics in the oxidative addition of Pd complexes. Notably, the effect of silane electronics on alkyne hydrosilylation has not been investigated in the literature. When compared to the neutral silane 5a, the rate of the reaction is faster with the electron-poor silane 5f and slower with the electron-rich silane 5d (Fig. 16). Reaction with 5f gives products 16f and E-β-16f in 98% yield in a 1 : 34 ratio, and reaction with 5d gives products 16d and E-β-16d in 40% yield in a 1 : 6 ratio. These results directly parallel the data obtained from oxidative addition and highlight the importance of studying this fundamental reaction in organometallic chemistry. Furthermore, using the isolated complex 10a as a catalyst in 5 mol% leads to a reaction profile nearly identical to that generated from 1/5a mixtures [see ESI Section 11†], further supporting the relevance of this oxidative addition to catalysis.

Conclusions

In this work, we have elucidated the mechanism of oxidative addition of Pd(0) to Si–H bonds and shown the relevance of this reaction in catalytic hydrosilylation. We evaluated the impact of silane electronic influence in the oxidative addition of [(μ-depe)Pd]2 to form well-defined, mononuclear silyl palladium hydrides. A library of electronically varied silanes have been synthesized and the corresponding silyl palladium hydrides characterized, including via single crystal diffraction of 10f. Extensive equilibrium and competition studies point to a pronounced effect of silane electronics in the oxidative addition reaction, quantified via Hammett analysis to show the reaction with triaryl silanes 5 to be approximately three times more sensitive to electronics than with dimethylsilyl silanes 3. Formation of (silyl)Pt(H) and (silyl)Rh(H) complexes via silane oxidative addition have shown a similar trend of being more favourable with electron-withdrawing substituents at silicon.44,49,61 van’t Hoff analysis suggests that this trend arises from the corresponding Pd–Si bond strength in products 10 and 8. Our conclusion that Pd–Si bond strength is related to the identity of the silicon substituents is supported by computational work of related Pd complexes.57 The formed silyl palladium hydrides exist in a dynamic equilibrium with 1 that is fully reversible with regard to both temperature and product distribution, which is similar to behaviour of (silyl)Pt(H) complexes.56 Kinetic studies further support the favourability of electron-poor silanes and show that the rate of reaction (kobs) is less sensitive to electronics than the equilibrium constant (Keq).

Further, this system is well-suited to answer long-standing questions in the oxidative addition of palladium to hydro-silanes via mechanism elucidation. The reaction is 0.5th order in starting dimer 1 and 1th order in silanes. The reaction barrier was determined to be 16.3 kcal mol−1 using Eyring analysis. This energy barrier far exceeds that of oxidative cleavage of the Si–H bond, (determined to be equal to or less than 10 kcal mol−1). The upper limit of the barrier for oxidative cleavage was determined by studying the dynamic behaviour of the (silyl)Pd(H) complexes on the NMR timescale. Analogous behaviour has been observed with (silyl)Pt(H) complexes, which was shown to be an intramolecular process involving reductive coupling of the hydride and silyl ligands.59,61,124,125 The barriers for dynamic exchange of these Pt complexes are approximately the same as the barriers reported here for (silyl)Pd(H) complexes. In conjunction with a small, primary KIE, we conclude that the RDS of oxidative addition is the formation of the σ-complex, not Si–H bond cleavage.

Lastly, we showed the relevance of our findings to catalysis, namely hydrosilylation. Electronic variation of the silane in catalysis directly parallels that of oxidative addition, which further supports the relevance and importance of in-depth mechanistic studies to catalysis.

Data availability

All data collected for this article, including experimental procedures, compound characterization, conversion values and graphical data, and NMR and IR spectra are available in the ESI.†

Author contributions

M. R. H. and A. K. C. are responsible for conceptualization, investigation, and manuscript writing. M. R. H. carried out all experimentation except crystallography. L. N. Z. performed all crystallography experimentation, data collection, and analysis. A. K. C. is responsible for supervision and project administration. All authors edited and reviewed the manuscript.

Conflicts of interest

There are no conflicts to declare.
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