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Silicon-hydrogen bonds are shown to add to a nickel carbon double bond to yield nickel α-silylalkyl hydrido complexes. Kinetic and isotope labeling studies suggest that a concerted 4-centred addition across the Ni=C bond is operative rather than a mechanisms involving Si-H oxidative addition. This constitutes an example of Si-H bond activation via ligand cooperativity.

The homogeneously catalysed hydrosilation of unsaturated functions is a commercially important process that relies on the facile activation of Si-H bonds. While mechanisms that rely on sigma bond metathesis or heterolytic hydride abstraction pathways are operative in early transition metal and main group element catalysts, respectively, for late metals this activation typically takes place via oxidative addition. Activation mechanisms that involve a ligand engaging cooperatively in the Si-H bond cleavage step are less common.

Recently, we described a family of nickel PC carbene Pincer complexes which rapidly added protic E-H bonds (E = RCC-, R2N- and RO-) across the anchoring C=Ni linkage such that the nucleophilic E group ends up bonded to nickel (Scheme 1). In this system, the Ni carbene adopts a nucleophilic, “Schrock-like” character and likely acts to deprotonate E-H in the key step leading to product. We were interested in how these compounds would interact with E-H bonds in which the polarity is reversed and the hydrogen is more hydridic in character. Accordingly, we have explored the reactivity of this system with various tertiary silanes and describe evidence for direct, concerted addition of Si-H across the Ni=C bond such that the silicon is delivered to the nucleophilic carbene carbon. The tert-butyl nitrile stabilized PC carbene P complex reacts with triphenylsilane in benzene or THF to yield a yellow solution of a nickel hydrido product with a characteristic upfield triplet resonance at -13.56 ppm (2JHP = 62 Hz). The disappearance of the carbene carbon signal at 110.2 ppm in the 13C NMR is consistent with a concerted addition of Si-H to Ni=C.

Scheme 1. Addition of protic E-H bonds to Ni=C.
spectrum for 1, and detection of a $^{29}$Si signal at -4.2 ppm via a $^1$H-$^{29}$Si HMBC experiment suggested the Ph$_3$Si group is attached to anchoring carbon of the PC$_{\text{aryl}}$P ligand as depicted for 3$_{\text{Ph}}$ in Scheme 2. Purification of 3$_{\text{Ph}}$ from these reactions was complicated by the nitrile byproduct, so a second protocol for the preparation of 3$_{\text{Ph}}$ was developed, wherein the PC$_{\text{aryl}}$P nickel (II) bromide $^2$ was dehydrohalogenated using KHDMDS in the presence of triphenylsilane. Here, the presumed THF solvated PC$_{\text{aryl}}$P intermediate I shown in Scheme 2 is rapidly trapped by the silane rather than the nitrile ligand as in the synthesis of 1. We propose I as the intermediate in this process because the known compound (PC$_{\text{aryl}}$P)Ni(N(SiMe$_3$)$_2$)$_2$ does not form when 2 is treated with KHDMDS in THF solvent; $^9$ furthermore, separately prepared amido complex does not react with silane under the conditions of this experiment. Since the preformed carbene complex 1 also engages in this reactivity, it seems likely that I is the key species in the formation of 3$_{\text{Ph}}$. Thus, as I is generated through dehydrohalogenation of 2 in THF, it reacts rapidly with the silane present to yield the observed product. By the dehydrohalogenation method, 3$_{\text{Ph}}$ is easily isolated from the non-basic HN(SiMe$_3$)$_2$ byproduct in 80% yield as analytically pure yellow crystals; its structure was confirmed by X-ray crystallography.

The molecular structure of 3$_{\text{Ph}}$ is shown in Figure 1, along with selected metrical data. The Ni(1)-(C(1)) distance of 2.043(4)Å is elongated by 0.04-0.06Å in comparison to related PC$_{\text{aryl}}$P compounds $^5$, $^6$ due to the strong trans influencing hydrido donor and the steric presence of the Ph$_3$Si group, which also causes the phenyl group linking C(1) and P(1) to tilt 44.2(6)$^\circ$ out of the plane defined by the aryl group connecting P(2) and C(1). Although the plane of one of the phenyl rings on the silicon atom lies closely along the C(1)-Ni(1) vector, there does not appear to be an agostic interaction present between the C-H bond on C(39) and the Ni(1) center based on the long Ni(1)-C(39) distance of 3.051Å. Furthermore, the open C(1)-Si(1)-C(38) angle of 116.5(2)$^\circ$ is suggestive of a repulsive rather than an attractive interaction.

As depicted in Scheme 2, this dehydrohalogenative protocol can be used to prepare the related derivatives 3$_{\text{PhMe}}$, 3$_{\text{OMe-PH}}$, and 3$_{\text{PhMe-Ni}}$ in moderate to good yields. Each was fully characterized by multinuclear NMR spectroscopy and X-ray crystallography; details can be found in the ESI (Figures S1-3).

Figure 1. Molecular structure of 3$_{\text{Ph}}$. Most hydrogen atoms are omitted for clarity. Selected bond and non-bonded distances (Å): Ni(1)-(C(1)) 2.043(4); Ni(1)-(P(1)) 2.1344(14); Ni(1)-(P(2)) 2.1079(14); Ni(1)-(H(1)) 1.32(5); C(1)-Si(1) 1.916(4); C(39)-Ni(1) 1.916(4); C(39)-C(1) 1.916(4); C(38)-Ni(1) 1.916(4); C(38)-C(1) 1.916(4).

Scheme 3. Kinetics of silane elimination from compounds 3$_{\text{Ph}}$.

These experiments show that conversion of compound 3$_{\text{Ph}}$ to 4 is first order in [3$_{\text{Ph}}$] (Figure S3) with a rate constant of 5.7(2) x 10$^{-4}$ s$^{-1}$. The rate of the reaction is dependent of the
amount of added phenol (2 – 10 equivalents), indicating that the reaction of phenol with the product of silane loss from 3

is rapid. Furthermore, the rate is not affected by the inclusion of additional excess triphenylsilane (0 – 6 equivalents), indicating that k₂ is also small relative to k₁. The first order rate constants, however, did vary slightly with the nature of the substitution on the silicon atom³ and the rate constants are shown in Scheme 3. Two labelling experiments were conducted. In the first, the rate of conversion of 3

(labelled in the nickel hydride position) to 4 was followed. The label was exclusively localized in the Ph

(P)Ni fragments.

(labelled in the Ph

P)Ni fragments.

is selective produced.

Treatment of 2 with in situ generated KSiPh

and both experiments and computations indicate that it is thermodynamically preferred over 3

Nickel silyl isomers 3

is characterized by a

NMR resonance at 52.8 ppm that exhibits

satellites (\(^{31}\)P-Si =

Figure 2. Molecular structure of 5

Most hydrogen atoms are omitted for clarity. Selected bond and non-bonded distances (Å): N(1)-C(13), 2.030(8); N(1)-P(1), 2.194(2); N(1)-P(2), 2.168(2); N(1)-Si(1), 2.338(2). Selected bond angles (°): P(1)-N(1)-P(2), 153.23(9); C(13)-N(1)-Si(1), 161.7(2); C(13)-N(1)-P(1), 84.1(2); C(13)-N(1)-P(2), 83.6(2); Si(1)-N(1)-P(2), 105.8(6); Si(1)-N(1)-P(1), 93.7(5).
forms reversibly under these conditions. In contrast, the elimination of RSiH/D product of this reaction (Figure S11); therefore, the reaction proceeds by a different (unknown) mechanism.

We thus conclude that the paths involving the 4-centred transition (B/C, Scheme 4) state are more consistent with our data, particularly path C. The substantially positive entropy of activation is indicative of a transition state in which the silane is well dissociated. The observed inverse KIE is also consistent with these mechanisms; in a rapid equilibrium between 3ph and I + HSIPh3, the right hand side should be slightly favoured when deuterium is incorporated since deuterium will be preferred in the Si-H position (\(\nu_{\text{SiH}} = 2119 \text{ cm}^{-1}\)) than the Ni-H position (\(\nu_{\text{NiH}} = 1781 \text{ cm}^{-1}\)). This would increase the concentration of I in the deuterated isotopologue leading to overall increased rates of production of 4 in the deuterated system. The involvement of a silane complex akin to II is an open question, but the lack of dependence on the rate of added silane and the positive activation entropy favour direct dissociation, i.e., path C.

In conclusion, we propose that the reaction of silanes with the \((\text{PC}_{3}\text{P})\text{Ni(THF)}\) intermediate occurs via a concerted Si-H addition across the Ni=C linkage to produce 3ph as the kinetically preferred product. This mode of silane activation is rare, having been proposed on the basis of kinetic and labelling data only for highly nucleophilic Schrock type carbenes, where oxidative addition paths were not available. Here, the high energy expected for an oxidative addition pathway involving Ni(IV) directs the reactivity to the concerted path in a late metal carbene system. This reactivity attests to the high nucleophility associated with the Ni=C linkage in these complexes. The reversibility of the silane activation disclosed here is potentially exploitable in catalytic cycles featuring ligand cooperativity.

Funding for this work was provided by NSERC of Canada in the form of a Discovery Grant and an Accelerator Supplement to W.E.P. W.E.P. also thanks the Canada Research Chair secretariat for a Tier I CRC (2013–2020) and the Alexander von Humboldt Stiftung for a Research Award. The authors would like to thank Lauren Doyle for performing the ground state energy computations on compounds 3ph and 5ph.

Notes and references

†The variation in rate constant with silane substituent does not correlate with the Hammett parameters. Rather, the rate variations appear to be related to slight changes in Si-H bond strength with changing substitution.


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