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Silane–Isocyanide Coupling Involving 1,1-Insertion of XylNC into the Si–H Bond of a σ-Silane Ligand

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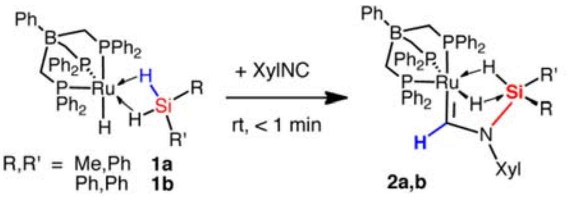
Supporting Information

ABSTRACT: Complexes $[PhBP^{Ph}{}_3]RuH(\eta^3\text{-}H_2SiRR')$ (R,R′ = Me,Ph, **1a**; RR′ = Ph$_2$, **1b**) react with XylNC (Xyl = 2,6-dimethylphenyl) to form Fischer carbene complexes $[PhBP^{Ph}{}_3]Ru(H){=}[C(H)(N(Xyl)(\eta^2\text{-}H{-}SiRR'))]$ (**2a**,**b**) that feature a γ-agostic Si–H bond. The ruthenium isocyanide complexes $[PhBP^{Ph}{}_3]Ru(H)(CNXyl)(\eta^2\text{-}HSiHRR')$ (**6a**,**b**) are not intermediates as they do not convert to **2a**,**b**. Experimental and theoretical investigations indicate that XylNC is activated by initial coordination to the silicon center in **1a**,**b**, followed by 1,1-insertion into an Si–H bond of the coordinated silane and then rearrangement to **2a**,**b**.

A number of novel transformations have been identified for transition metal complexes possessing a silicon center that is activated toward nucleophilic attack.[1−4] Silylene complexes[1] exhibit this property and engage in a variety of stoichiometric and catalytic Si—X (X = C, N, O) bond-forming reactions that involve binding of a Lewis basic substrate to silicon to form intermediates of the type $L_nMSiR_2[base]$.[1,2] Cationic ruthenium and iridium Si–H σ-complexes may also exhibit high electrophilicity at silicon,[3,4] and this appears to play a role in hydrosilations of ketones[3c,4a] and challenging substrates such as nitriles[4b] and pyridines.[4c] For these reactions, the key Si–O and Si–N bond-forming steps appear to involve nucleophilic attack of the substrate onto the silicon center of an η^1- or η^2-H–SiR$_3$ ligand with simultaneous cleavage of the Si–H bond.[3,4] It might also be possible for Si–H σ-complexes to bind substrates at silicon without Si–H bond cleavage, and this was suggested by our recent discovery that η^3-H$_2$SiRR′ σ-complexes $[PhBP^{Ph}{}_3]$-RuH(η^3-H$_2$SiRR′) (R,R′ = Me,Ph **1a**; R,R′ = Ph$_2$ **1b**, eq 1) add Lewis bases to form stable adducts of the type $\{[PhBP^{Ph}{}_3]Ru[(\mu\text{-}H)_3SiRR'(base)]\}$ (base = THF, PMe$_3$, 4-dimethylaminopyridine).[5] In these adducts, the donor atom of the base is in close proximity to the hydride ligands, and in principle this could favor uncommon 1,1-hydrosilation reactions. Thus, it is important to examine the role that **1a**,**b** might play in activations of unusual substrates and in new hydrosilation reactions.



(1)

Carbon monoxide and isocyanides are potentially interesting 1,1-insertion substrates for hydrosilations, but little is known concerning this possibility. Silylformylations, involving the coupling of a silane, CO, and an alkene or alkyne, are known,[6] and the catalytic 1,1-hydrosilation of isocyanides has only been reported for the reaction of CyNC with Et$_3$SiH using Cu(acac)$_2$ as a catalyst.[7] Furthermore, the formyl and iminoformyl silane products that might result from insertions into an Si–H bond are attractive synthetic targets as useful chemical intermediates[8] that are difficult to prepare by other methods.[9] Herein we describe an unusual 1,2-hydrosilation reaction involving XylNC (Xyl = 2,6-Me$_2$C$_6$H$_3$) and **1a**,**b** that procedes by coordination of XylNC to silicon followed by 1,1-insertion of the isocyanide into a coordinated Si–H bond. This novel 1,1-hydrosilation step is followed by rearrangement to 1,2-hydrosilation products that feature a ruthenium carbene ligand with a γ-agostic Si–H bond (**2a**,**b**, eq 1).

The addition of XylNC (1 equiv in benzene-d_6) to a yellow solution of **1a**,**b** resulted in immediate loss of color and quantitative formation of the carbene complexes **2a**,**b** (by ^{1}H NMR spectroscopy). The ^{1}H NMR spectra for **2a**,**b** (benzene-d_6) display a downfield resonance (doublet of triplets) for the carbene α-protons (**2a**, 10.41 ppm; **2b**, 10.28 ppm). Similarly, the $^{13}C\{^1H\}$ NMR spectra exhibit a downfield doublet of triplets resonance for the carbene carbons (**2a**, 263.4 ppm; **2b**, δ 264.6 ppm).[10] The room temperature ^{1}H NMR spectra contain only one hydride resonance for the two Ru–H ligands in each complex (**2a**, −6.64 ppm; **2b**, −6.32 ppm), which on the basis of ^{29}Si-filtered $^1H\{^{31}P\}$ and ^{1}H–^{29}Si HMBC spectra exhibit moderate J_{SiH} coupling constants (**2a**, J_{SiH} = 46 Hz; **2b**, J_{SiH} = 49 Hz). These values indicate Si–H interactions that are weaker than those in **1a**,**b**[5] but consistent with the presence of at least one Ru–H–Si 3c 2e bond.[11,12] At −70 °C, the ^{1}H NMR spectrum for **2a** (toluene-d_8) displays a resonance for each hydride ligand (−6.52 ppm, J_{SiH} = 36 Hz; −6.59 ppm, J_{SiH} = 56 Hz), and this indicates the existence of chemically inequivalent Ru–H–Si interactions.

The solid-state structure of **2a**, determined by single crystal X-ray diffraction, is consistent with the low-temperature NMR data for this complex (Figure 1). Both hydride ligands were located and refined, to provide Si–H distances consistent with the presence of inequivalent Ru–H–Si interactions (d(Si–H) 1.71(3), 1.95(5) Å).[13] The silicon atom is also bound to nitrogen and two carbon atoms, for a total coordination number of five. The Ru–C distance (2.034(4) Å) is longer than those of

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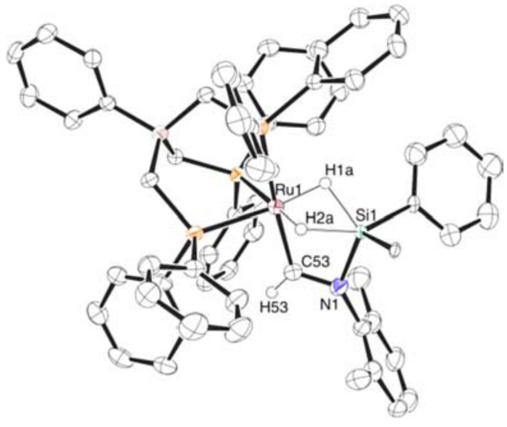
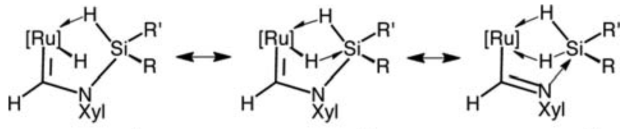


Figure 1. Solid state structure of **2a**. Thermal ellipsoids set to 50% probability. Only hydridic hydrogens and the carbene α-hydrogen are shown.

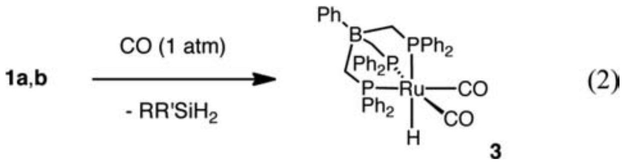
most related ruthenium carbene complexes,[14] and this may be due to the strong *trans* influence of the phosphine ligands. The C−N distance (1.314(4) Å) is consistent with such single bonds in related carbene complexes. The (η^2-H−Si)−N−C−Ru framework in **2a** is similar to that of an iminoacyl complex $[Cp^*(CO)Ru\{C(R){=}N(\eta^2\text{-H}{-}SiHC(SiMe_3)_3)\}]$ possessing a γ-agostic Si−H bond.[15] The Ru−Si distance for **2a** (2.362(3) Å) is shorter than that for the iminoacyl complex $[Cp^*(CO)Ru\{C(R){=}N(\eta^2\text{-H}{-}SiH_2C(SiMe_3)_3)\}]$ (2.5563(7) Å) and this may be due to the presence of two Ru−H−Si interactions in **2a**.[16]



A **B** **C**

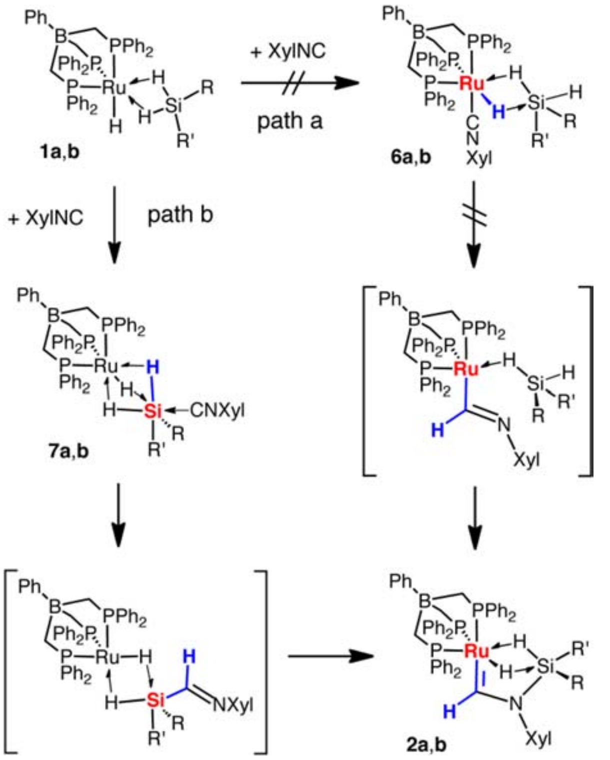
Although **2a** appears to have considerable carbene character, it may also be described as an iminoformyl complex with a dative N→Si bond that expands the coordination sphere of silicon in an η^3-$H_2SiMePh$ ligand (structure **C**). Similar intramolecular O→M (M = Zn,[17a] Ca, Sr[17b]) interactions have recently been identified as key factors in the transformation of carbonyl ligands to acyl ligands at rhenium. However, the iminoformyl description for **2a**,**b** implies the presence of two strong Si−H interactions, which is not in agreement with the NMR data for **2a**. The structure of **2a** was examined by DFT calculations, which provided an optimized structure (**2a-DFT**) with Si−H distances that differ considerably (1.854, 2.177 Å).[18] This provides further support for the description of **2a**,**b** as carbene complexes featuring a γ-agostic Si−H bond and a weaker Ru−H→Si interaction (hybrid of structures **A** and **B**).[12a,19]

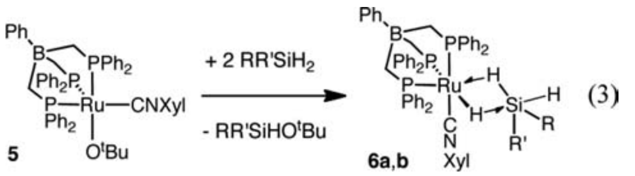
It seemed possible that **1a**,**b** might react with carbon monoxide to form carbene complexes analogous to **2a**,**b**. However, the addition of 1 atm of CO to solutions of **1a**,**b** in benzene-d_6 resulted in displacement of the silane and quantitative formation of the dicarbonyl complex $[PhBP^{Ph}_3]RuH(CO)_2$ (**3**, eq 2). The formation of **3** demonstrates that the ruthenium center of **1a**,**b** is readily accessible to appropriate incoming nucleophiles. Thus, it seems possible that formation of **2a**,**b** results from coordination of XylNC to ruthenium, followed by migratory insertion into a Ru−H bond (Scheme 1, path a).[20] To examine this possibility, a monoisocyanide complex was sought as an alternate starting material for the synthesis of **2a**,**b**. For this purpose, the alkoxide complex $[PhBP^{Ph}_3]RuO^tBu$ (**4**) was obtained by metathesis of $\{[PhBP^{Ph}_3]Ru(\mu\text{-}Cl)\}_2$ with KO^tBu in benzene. Treatment of **4** with 1 equiv of XylNC resulted in immediate formation of $[PhBP^{Ph}_3]Ru(O^tBu)(CNXyl)$ (**5**). The presence of one isocyanide ligand in **5** was evident from FTIR data (ν_{CN} = 2074 cm^{-1}), ^{1}H NMR data (one xylyl group), and elemental analysis. Complex **5** was treated with 2 equiv of $RR'SiH_2$ to form $RR'HSiO^tBu$ and $[PhBP^{Ph}_3]Ru(H)(CNXyl)(\eta^2\text{-}HSiHRR')$ (RR′ = MePh, **6a**; RR′ = Ph_2, **6b**, eq 3). Complexes **6a**,**b** are stable at room temperature for at least a week in benzene-d_6 solution and do not react further under these conditions to form **2a**,**b**.



(2)

Scheme 1. Potential Mechanisms for the Formation of 2a,b from 1a,b and XylNC





(3)

Characterization of **6a**,**b** by FTIR and multinuclear NMR experiments indicated the presence of the XylNC ligand, two Ru−H ligands, and the SiRR′H fragment (see Supporting Information). Moderate J_{SiH} values for the Ru−H ligands (^{1}H δ −6.73 ppm (2 H), J_{SiH} = 32 Hz, **6a**; ^{1}H δ −6.31 ppm (2 H), J_{SiH} = 34 Hz, **6b**) suggested that **6a**,**b** feature Ru−H−Si 3c 2e bonding, but the nature of these interactions was not evident from these data. The structure of **6b** was determined by single crystal XRD, but the hydride positions could not be located (see Supporting Information). This structure was used as a starting point for geometry optimization calculations, which revealed distinct Si—H distances for **6a,b-DFT** (1.885, 2.152 Å for **6a-DFT**; 1.840, 2.174 Å for **6b-DFT**).[18] Thus, **6a,b** appear to be η^2-H—SiHRR′ complexes that feature an additional, weak Ru—H→Si interaction.[12a,19]

The stability of **6a,b** clearly rules out a typical migratory insertion pathway to form **2a,b**, and an alternate mechanism must be considered. To obtain more information about the formation of **2a,b**, the reaction of **1a,b** with XylNC was examined by NMR spectroscopy at low temperatures in toluene-d_8. At temperatures below −30 °C, the XylNC adducts $\{[PhBP^{Ph}_3]Ru[(\mu\text{-}H)_3SiRR'(CNXyl)]\}$ (RR′ = MePh, **7a**; RR′ = Ph$_2$, **7b**, Scheme 1, path b) were observed by ^{1}H, ^{31}P{^{1}H}, and ^{1}H−^{29}Si HMBC NMR spectroscopy. The ^{1}H NMR spectrum of **7a** at −65 °C displays three Ru−H resonances (at −8.18, −8.49, and −8.61 ppm), that couple to a ^{29}Si resonance at 4 ppm (as shown by a ^{1}H−^{29}Si HMBC NMR experiment). A ^{29}Si-filtered ^{1}H{^{31}P} NMR spectrum of **7a** had an insufficient signal-to-noise ratio to allow accurate determination of J_{SiH} values, but these data could be obtained for complex **7b** at −65 °C (^{1}H δ −8.06 ppm, J_{SiH} = 42 Hz, 2 H; δ −8.32 ppm, J_{SiH} = 46 Hz, 1 H; ^{29}Si δ 8 ppm). The NMR data for **7a,b** at −65 °C are very similar to those of the DMAP adducts of **1a,b** at −60 °C.[5] Notably, silicon−isocyanide adducts are uncommon, and **7a,b** are the first examples in which the isocyanide is bound to a hypercoordinate silicon center. The two previously known isocyanide-silicon adducts involve three- and four-coordinate silicon centers resulting from the binding of an isocyanide to a free silylene ({MesTbtSi:}←CNAr),[21] or to the silylene ligand of a transition metal complex ($\{(\sigma\text{-}Cp)_2(RNC\rightarrow)Si\}$—AuCl).[22]

The isocyanide group in **7a,b** should be particularly electron deficient since π^*-backdonation to the isocyanide is not possible in **7a,b** as it is in **6a,b**.[23,24] Thus, a possible mechanism for the conversion of **7a,b** to **2a,b** involves transfer of a hydride ligand to the activated isocyanide to form an iminoformyl group bound to silicon (Scheme 1, path b). Rearrangement of the resulting $[PhBP^{Ph}_3]RuH[\eta^2\text{-}H{-}SiRR'(C(H){=}NXyl)]$ intermediate by Si−C bond cleavage and Ru−C and Si−N bond formations would provide **2a,b**. Note that the $[PhBP^{Ph}_3]$Ru fragment has previously been observed to mediate facile Si−C bond cleavage reactions.[25] At −24 °C, the conversion of **7a,b** to **2a,b** was observed over the course of 30 min, and no additional intermediates were detected (by ^{1}H NMR spectroscopy). Monitoring the disappearance of **7a** by ^{1}H NMR spectroscopy revealed that the conversion to **2a** was first order in **7a** (k = 3.67(8) × 10^{-3} s^{-1}, −24 °C). The rate of this conversion was compared with that for the deuterated sample **7a-d_3**, to give k_H/k_D = 1.74(9), which is consistent with a rate-determining step that involves transfer of a hydride ligand to the isocyanide carbon. This process would involve the unprecedented insertion of isocyanide into a Si−H bond (in this case, part of a Ru−H−Si 3c 2e interaction). Insertion of an isocyanide into an M—H bond is known for transition metal hydrides[20] and aluminum hydrides,[26] but has not been observed for any other molecular main-group hydride species. However, the insertion of an isocyanide into the Si—Mes bond of Cp*(Me$_3$Si)Mo(CO)$_2$═SiMes$_2$ has been reported.[27]

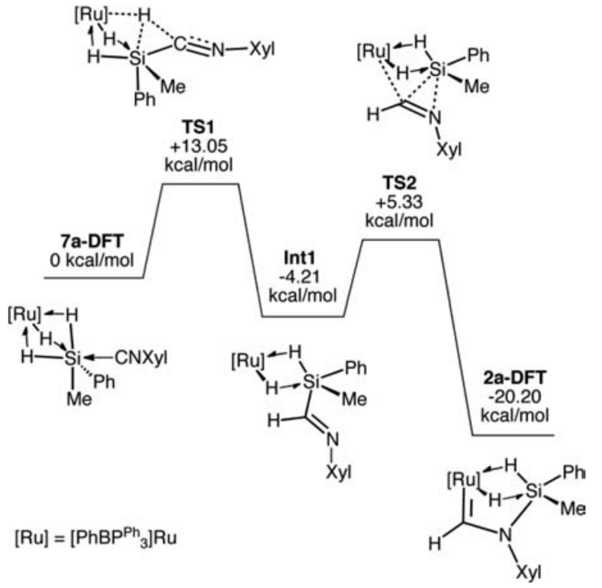


Figure 2. Mechanism for formation of **2a** from **7a** as determined using DFT calculations. Energies are gas phase free energies at 298 K relative to **7a-DFT** ($G_{7a\text{-}DFT}$ = 0 kcal/mol).

Further details of the isocyanide activation come from computational investigations starting with a geometry optimization calculation for the isocyanide adduct **7a** (Figure 2).[18] In the optimized structure (**7a-DFT**, $G_{7a\text{-}DFT}$ = 0 kcal/mol), the isocyanide carbon is near two of the hydride ligands (d_{C-H}: 2.67 Å, 2.80 Å). At the transition state (**TS1**, ΔG_{TS1} = +13.05 kcal/mol), one C−H distance is shortened (d_{C-H}: 1.62 Å, **TS1**) as a result of rotation of the SiMePh(CNXyl) fragment about the Ru−Si axis, elongation of the Ru−H bond (d_{Ru-H}: 1.65 Å, **7a-DFT**; 1.74 Å, **TS1**) and bending of the Si−C−N linkage (Si−C−N: 157.6°, **TS1**). This latter motion appears to give rise to the observed *cis*-configuration of the xylyl group and α-hydrogen in the final product. Notably, the resulting intermediate species (**Int1**, ΔG_{Int1} = −4.21 kcal/mol) is a σ-complex in which the Si−H bond of the iminoformylsilane PhMeHSiC(H)═NXyl is coordinated to the $[PhBP^{Ph}_3]$RuH fragment. The 1,1-hydrosilation of the isocyanide appears to be an important step in the formation of **2a,b**, and this type of transformation could be useful for 1,1-hydrosilation catalysis if the iminoformyl silane is displaced from the ruthenium complex. For **Int1**, the conversion to **2a-DFT** ($\Delta G_{2a\text{-}DFT}$ = −20.20 kcal/mol) occurs through a single transition state with a low barrier (**TS2**, ΔG_{TS2} = +5.33 kcal/mol) for the concerted formation of the Ru−C and Si−N bonds, and cleavage of the Si−C bond. This transition state is similar to those determined computationally for isomerization of isocyanides (E—NC) to cyanides (E—CN) via concerted E—N bond cleavage and E—C bond formation (E = alkyl$^+$, Me$_3$Si$^+$, (F$_3$C)$_3$B).[28] The energy barriers for **TS1** and **TS2** are consistent with the rapid formation of **2a** at room temperature and the inability to experimentally observe **Int1**.

In conclusion, the electrophilic η^3-H$_2$SiRR′ ligands in **1a,b** are directly involved in activation of XylNC to form Fischer carbene complexes **2a,b**. Experimental and computational results indicate that the reaction occurs *via* an unprecedented mechanism in which a hexacoordinate silicon center exhibits reactivity (insertion of XylNC into an Si−H bond) that is more typically observed at a transition metal center or, rarely, a low-coordinate main-group center. Notably, the cooperative activation of a substrate by a transition metal center and a hypercoordinate silicon center has not previously been observed. Electrophilic Si−

H σ-complexes have previously been reported for the activation and hydrosilation of nucleophilic substrates such as ketones, pyridines, and nitriles, but in these cases an adduct of the substrate with the σ-silane ligand was not observed (as for the formation of **2a**,**b**). Additionally, the reaction of **1a**,**b** with XylNC is the first example of an Si−H σ-complex activating a carbon nucleophile. Future work will focus on incorporation of isocyanide activations into new catalytic hydrosilations and discovery of additional substrate activations by η^3-H_2SiRR' complexes.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental, spectroscopic, and computational details and crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(13) Hydride H2a was located but required a restraint (DFIX 0.02 1.60 Ru1 H2a) in order to refine to a reasonable position.

(14) As of March 2013, a search of the Cambridge Structure database for related $Ru{=}C(H)NR_2$ species found 16 different structures. The Ru—C distances ranged from 1.828(4)[10b] to 2.046(15)[a] Å and all but the latter Ru—C distances were < 2 Å. The C—N distances for the 16 structures ranged from 1.263(20)[10b] to 1.374(3)[b] Å. (a) Clark, G. C. *J. Organomet. Chem.* **1977**, *134*, 51−65. (b) Rankin, M. A.; McDonald, R.; Ferguson, M. J.; Stradiotto, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 3603−3606.

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