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Shuffle off the classic β-Si elimination by Ni-NHC cooperation: implication for C–C forming reactions involving Ni-alkyl-β-silanes†‡

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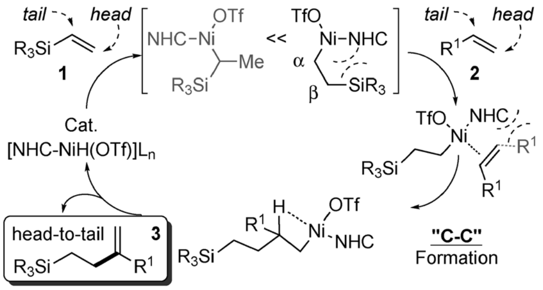
***Via* a cooperation of NHC, Si substituents and a M center, β-Si elimination was attenuated, revealing a new way to attain a high Ni-β-SiR$_3$: Ni-σ-SiR$_3$ ratio. The scope is illustrated by a head-to-tail vinylsilane-α-olefin hydroalkenylation.**

Catalytic cross-hydroalkenylation (H.A.) of vinylarenes or dienes with simple olefins is recognized as one of the most efficient methods for producing olefins of a higher complexity.[1] Expanding this process to other widely available and structurally diverse olefin acceptors is highly desirable, yet remains a daunting challenge due to potential complications. In particular, vinylsilanes should be able to undergo cross-H.A. using various very efficient P based Pd/NiH catalysts, but we are unaware of any protocols that can overcome the competitive β-Si elimination (S.E.) followed by intermolecular insertion of an unactivated olefin.[1g,h] Only certain activated π-systems, which have a close-by stabilizing olefin tether, can be used, possibly because the competition can be strong even when bidentate ligand is used.[2] Large differences in various SiR$_3$ groups' reactivity and size may also present inherent complications that need special attention to obtain better results.[3] Thus a new general approach that can shuffle off β-S.E. is imperative before the full potential of vinylsilanes for preparing organosilanes by C–C formation can be realized.

Continuing our studies aimed at discovering new applications of NHC in Ni catalysis,[4] and with the key precedents for efficient hydrometallated vinylsilane β-S.E.[5–7] and H.A.[1] in mind, we envision a new approach that can shuffle off the facile β-S.E., with its scope illustrated by vinylsilane–α-olefin cross-H.A. The strategy involves a bulky NHC-NiH.[8] This combination may concurrently suppress the anticipated β-S.E. and accommodate the chemo- and regioselectivity problems associated with the variability in size and polarizability of vinylsilanes. Under the remarkable influence of NHC steric bulk, a 1,2- over a 2,1-hydronickelated vinylsilane species is generated preferentially and the overlap of the Ni–Si orbitals is positively attenuated (*i.e.*, β-S.E. becomes difficult). This species may then undergo a chemo- and regioselective alkene insertion guided by both the NHC and the size of the alkene substituents (H, R^1 and SiR$_3$). The cycle closes with a β-H elimination to form the H.A. products. A hypothetical scenario with high selectivity for (1) H.A. to β-S.E., (2) head-to-tail (h–t) to h–h or t–t or t–h, and (3) cross- to homo-product, is outlined in Scheme 1.



Scheme 1 Hypothetical scenario for a cross-H.A. of **1** and **2** to **3**.

As SiMe$_2$Ph is a medium-sized Si group that is frequently employed as a masked OH in organic syntheses,[9] and an expedient pilot test can be conducted using an easily accessible *in situ* generated [IPr-NiH(OTf)],[4a] (vinyl)SiMe$_2$Ph **1a** was first tested in the presence of the above NHC-NiH with 1-octene **2a**. Our results show that the homoallylsilane **3a** can be obtained catalytically for the first time under optimized conditions.[10] This process is scalable and can be done in THF, with a low level of **1a** homo-dimerization and **3a** iso-/oligo-/polymerization (Table 1, entries 1, 2). This is also the first Ni-catalyzed, intermolecular α-olefin cross-H.A. that does not use vinylarenes/dienes as the basis for high chemo- and regioselectivity (*i.e.* it is not a benzylic/π-stabilization directed event). Although the 1,2-hydrometallated **1a** offers no such stabilization and is less sterically hindered, the competitive events *versus* the desired C–C formation, (*e.g.* NHC-alkyl reductive or adverse β-H elimination[4,11]) are both positively attenuated. Equally significant for the above H.A. aspects is that this study reveals the potential of IPr-Ni as a general organosilane preparation tool, complementing the outcomes of those featuring a β-S.E. key step from the same set of substrates (Scheme 2).[5–7]

Under those classic conditions with less steric hindrance (*e.g.* ^SL = P or small NHC, ^LM = Ru, Rh, Co, Fe, Pd), the reactions along H.A. pathways cease as a result of C$_2$H$_4$ loss due to more effective β-S.E. Balancing the sizes of SiR$_3$, R^1 and

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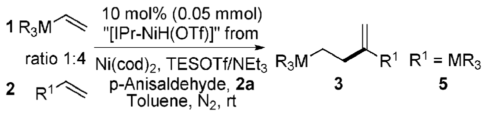
Table 1 Group 14 vinylmetalloid–α-olefin h–t cross-hydroalkenylation[a]

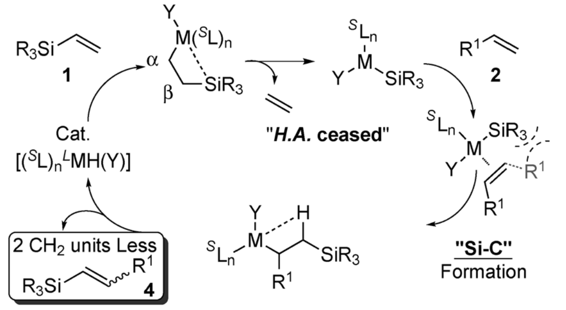


Entry	**1**, R$_3$M =		**2**, R^1 =		**3**	Yield (%) (**3**:**5**)
1	Me$_2$PhSi	**1a**	*n*-Hexyl	**2a**	**3a**	95; 95^b; 84^c; 11^d; 6^e
2^f		**1a**	—			< 5; 10^g
3	Me$_3$Si	**1b**		**2a**	**3b**	70
	Et$_3$Si	**1c**			**3c**	86; 93^h
4	(MeO)$_3$Si	**1d**		**2a**	**3d**	90 (71 : 29) 95^i (77 : 23)
	(EtO)$_3$Si	**1e**			**3e**	95^i (80 : 20)
	(*i*-PrO)$_3$Si	**1f**			**3f**	85^i (85 : 15)
5	Me(MeO)$_2$Si	**1g**		**2a**	**3g**	95^i (80 : 20)
	Me(TMSO)$_2$Si	**1h**			**3h**	86
6	Me$_2$(EtO)Si	**1i**		**2a**	**3i**	81^i (84 : 16)
	Bu$_2$(BuO)Si	**1j**			**3j**	70
	Ph$_2$(EtO)Si	**1k**			**3k**	56^h (83 : 17)
	Me$_2$Si(OSiMe$_2$vinyl)	**1l**			**3l**	70^j
7	Et$_3$Ge	**1m**		**2a**	**3m**	30^{k,l}
8	*cis*-TES-styrene	**1n**	*iso*-Butyl	**2n**	**3n**	24^{l,m}
9		**1a**	CH$_2$Ph	**2o**	**3o**	95
10			CH$_2$CH$_2$Ph	**2p**	**3p**	88^l
11			*p*-CH$_2$(veratrole)	**2q**	**3q**	95
12			(CH$_2$)$_9$OMe	**2r**	**3r**	72
13			CH$_2$OCH$_2$Ph	**2s**	**3s**	95^n
14			(CH$_2$)$_8$COOMe	**2t**	**3t**	80
15		**1b**		**2s**	**3u**	75^n
16		**1e**		**2o**	**3v**	95^i (75 : 25)
17		**1k**			**3w**	95^h (85 : 15)
18		**1m**			**3x**	63^k
19		**1a**	*t*-Butyl; Cy; Ph		—	< 5

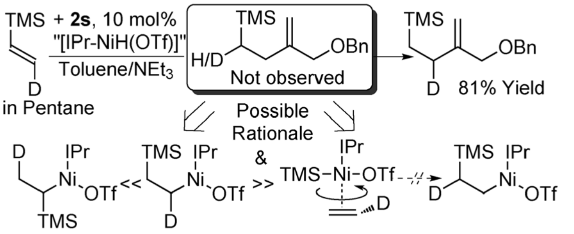
[a] See ESI for a detailed procedure. Yields are an average of at least two runs based on **1**; **3** were determined by ^{1}H NMR and isolation; **5** and **3**:**5** were determined only by ^{1}H NMR because of its limited stability on isolation. Several entries were analyzed also by GC, see ESI. [b] In THF. [c] 2.5 fold scale. [d] IMes as ligand. [e] PCy$_3$ as ligand. [f] 1.0 mmol **1a**. [g] 45 °C. [h] 40 h. [i] 0 °C. [j] **3l** refers to both ends being h–t reacted cross-product, see ESI for other products observed. [k] 30 mol% catalyst. [l] Not fully separated, NMR yield only. [m] 3 mmol **2n**, 48 h, **3n** = (3-^{i}Bu-2-Ph)-homoallylTES. [n] 1 mmol **2s**.

L allows a regioselective 2,1-insertion which forms a Si–C bond and produces internal olefin **4**. In our case, a high Ni-β-SiR$_3$ to σ-SiR$_3$ ratio is achieved instead, as implied by the < 5% β-Si transferred product **4** that was observed in the crude NMR spectrum. The detrimental effect of the combination of either a smaller L (IMes) with Ni, or IPr with a larger M (Pd) on the yield, or **3**:**4** ratio, demonstrates that the choice of L–M combination is strikingly critical (see ESI‡).

Next, several samples of **1** with different SiR$_3$ properties were examined to evaluate the scope of the IPr-Ni-directed β-S.E. suppression *via* H.A. (entries 3–6). They all reacted smoothly with **2a** with high H.A. to β-S.E. ratio and chemo- and regioselectivity. This consistency is notable because the electronic properties of the Si center can be perturbed strongly by its substituents, resulting in the reverse polarization of the proximate vinyl,[3] suggesting it is an IPr catalyst-directed process. If the 1,2-hydronickelation step was hampered by the choice of **1**, (*e.g.* a small vinylSi(OR)$_3$), then a limited amount of h–t dimer **5** was also observed. This is presumably due to more significant **2** consumption and a lower second insertion energy barrier. The preference for **3** can be retained by enlarging the SiR$_3$ or lowering the temperature. When we used vinylGeEt$_3$[5d] or β-substituted **1**, modest yields of **3** were observed and notably no **4** or **5** resulted (entries 7, 8, 18).



Scheme 2 Classic vinylsilane–olefin coupling with β-S.E. key step.

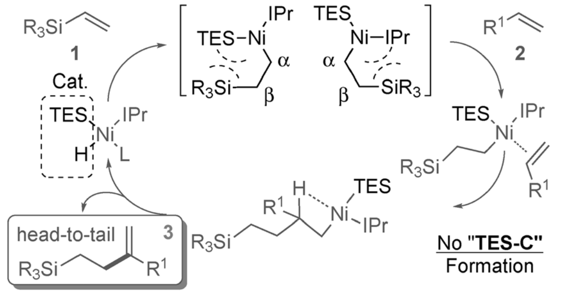


Scheme 3 Vinylsilane labelling experiment.

The cross-H.A. scope and chemo- and regioselectivity are also fine. α-Olefins with alkyl/allyl/aryl/benzyl ethers and the enolizable ester (**2q–t**) are all compatible. Attempts to employ **1a** with α-olefins commonly used in vinylsilane couplings failed (entry 19, < 5% **1a** conversion),[5] possibly due to the anticipated unfavorable steric effect in both pathways.

The following experiments were carried out to gain insight into the proposed β-S.E. suppression mechanism, and to provide more information on the hydrometallation regioselectivity achieved by this system. Firstly, sterically fair TMS(2-D-ethenyl) and allylic cleavage viable **2s** were tested as substrates in this context (Scheme 3, see ESI for details‡). These yielded the h–t **3** with < 5% D/H scrambling according to the NMR spectrum. This is notable given that β-D/H eliminations can be competitive if a 2,1-hydronickelation occurs, and ethylene Si-metallation reversibility is high even at low temperatures.[2] Since the oxidative cyclization/addition or vinylic CD/H activation based on Ni(0),[12] or Ir/Ru vinylsilane–styrene/carbonyl coupling mechanisms[10,13] may not be generally compatible with allyl ethers **2s**, working hypotheses based on these processes may not be fully accountable.

Secondly, the use of TESOTf means that there are other mechanistic paradigms that can plausibly explain the results if the competitive Si–C bond formation is not efficient, such as one based on a Chalk–Harrod type of silylation.[14] We thus studied the effect of this additive (Scheme 4, *i.e.* selectivities are obtained by the action of both TES and IPr rather than Scheme 1 as shown). A IPr(σ-TES)NiH catalyst could arise from unintended TESH generation and addition to IPr-Ni, so we attempted to mimic Scheme 4 by adding TESH directly to IPr-Ni(0). However, this did not result in the formation of any **3a** or corresponding hydrogenative dimers under these mild conditions. We also found that the cross-H.A. is insensitive to



Scheme 4 Alternative mechanism directed by an IPr(σ-TES)NiH.

the size of the silyl triflate. Yet, the most convincing evidence for excluding (σ-TES)Ni species participation is that the desired H.A. can be performed in silyl triflate free catalyst generation conditions, such as a AgOTf accelerated anion exchange with [IPrNi(allyl)Cl][15] (see ESI‡).

Thirdly, on the basis that treating the catalyst mixture with the selected **1** can provide high Si recovery without dehydrosilylation even in the equimolar reactions and in the absence of **2**, and the insertion of competitive π-systems into Ni-SiR$_3$/H/β-SiR$_3$ could be sensitive to the σ-SiR$_3$ properties,[6,14] describing the results in terms of a σ-SiR$_3$Ni catalyst may be less important. Overall, these results are consistent with Scheme 1, yet efforts to further support the hypothesized intermediates using crystals or *in situ* NMR failed, thus the precise mechanism awaits further study.

Synthetically, when comparing with the products obtained by silylation of corresponding alkynes and 2-substituted dienes, olefin cross-metathesis, or the classic M–H catalyzed vinylsilane–olefin coupling (vinyl/allylsilanes),[5–7,13,14] this work represents the first general catalytic non-reductive tool to access homoallylsilanes featuring a less readily available *gem*-olefin. Simply starting with two off-the-shelf chemical feedstocks directly, this approach lowers the hurdles caused by using **3** as a primary material in both organosilicon/organic syntheses or in studying their reactivity. The value of **3** is underscored by its many synthetic applications, such as in Fleming–Tamao oxidations[9] and formal alkene functionalizations (*e.g.* γ-Si alcohols/halides, β-Si carbonyls), and also the utilization of the Si-activating/directing α-/β-/γ-effect. See ESI for a pendent Si promoted regioselective Riley oxidation and related examples.

In summary, the NHC-Ni combination was first recognized as a potential tool that may attenuate β-S.E.-alkene evolution activity by a series of highly selective vinylsilane–α-olefin h–t cross-H.A. examples. Based on the generality and selectivity of this β-S.E. suppression approach, along with the strategic advantages it enables, we anticipate that it will find even broader prospects in other Ni-catalyses involving a β-Si, such as in general C–C forming reactions or insertions other than those using α-olefins as partners.

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