Anti-Markovnikov Terminal and Gem-Olefin Hydrosilylation Using a κ4-Diimine Nickel Catalyst: Selectivity for Alkene Hydrosilylation over Ether C-O Bond Cleavage

Journal:	*Dalton Transactions*
Manuscript ID	DT-ART-11-2018-004608
Article Type:	Paper
Date Submitted by the Author:	21-Nov-2018
Complete List of Authors:	Rock, Christopher; Arizona State University, School of Molecular Sciences Trovitch, Ryan; Arizona State University, School of Molecular Sciences

Journal Name

ARTICLE

Anti-Markovnikov Terminal and *Gem*-Olefin Hydrosilylation Using a κ^4-Diimine Nickel Catalyst: Selectivity for Alkene Hydrosilylation over Ether C-O Bond Cleavage

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Christopher L. Rock and Ryan J. Trovitch*

The phosphine-substituted α-diimine Ni precursor, **(^{Ph2PPr}DI)Ni**, has been found to catalyze alkene hydrosilylation in the presence of Ph_2SiH_2 with turnover frequencies of up to 124 h^{-1} at 25 °C (990 h^{-1} at 60 °C). Moreover, the selective hydrosilylation of allylic and vinylic ethers has been demonstrated, even though **(^{Ph2PPr}DI)Ni** is known to catalyze allyl ester C-O bond hydrosilylation. At 70 °C, this catalyst has been found to mediate the hydrosilylation of ten different *gem*-olefins, with turnover numbers of up to 740 under neat conditions. Prior and current mechanistic observations suggest that alkene hydrosilylation takes place though a Chalk-Harrod mechanism following phosphine donor dissociation.

Introduction

In addition to being valuable reagents in organic synthesis,[1] alkylsilane compounds form the backbone of the silicone, cosmetics, and coatings industries.[2] Alkylsilane monomers and polymers have long been synthesized using precious metal hydrosilylation catalysts, most notably Speier's[3] and Karstedt's[4] Pt-based precursors. While the efficiency of these catalysts promotes their continued utilization, the cost and toxicity concerns associated with precious metal reagents have provided motivation to develop more sustainable alternatives.[5] Owing to their natural abundance and low toxicity, recent efforts have focused on the development of alkene hydrosilylation catalysts that feature Mn,[6] Fe,[7] and Co[8] metal centres.

Being in the same group as Pt, Ni has long been considered a promising metal for this transformation.[9] Notable Ni catalysts for Markovnikov-selective alkene hydrosilylation include indenyl precatalysts having the general formula, (R-Ind)NiCl(PPh_3),[10] as well as [(allyl)Ni(NHC)][$BArF_4$], which has been found to catalyse alkene hydrosilylation with turnover frequencies (TOFs) of up to 25 h^{-1} at 60 °C.[11] Reports describing anti-Markovnikov product selectivity are somewhat more common. In 2012, Kuznetsov and Gevorgyan reported that $(PPh_3)_2NiBr_2$ catalyses the hydrosilylation of styrenes using Ph_2SiH_2 with modest TOF at 80 °C (up to 8 h^{-1}).[12] Lipschutz and Tilley employed $Ni[N(SiMe_3)(DIPP)]_2$ (Figure 1, **A**) to hydrosilylate 1-octene with Ph_2SiH_2 (TOFs of up to 24.7 h^{-1}),[13] while Shimada and co-workers utilized (salicylaldiminato)$NiCH_3$ complexes (Figure 1, **B**) and secondary silanes to convert internal and α-olefins to linear alkylsilanes at ambient temperature.[14] The Shimada group has also demonstrated efficient alkene hydrosilylation at room temperature using *in situ* activated $(acac)_2Ni$ compounds[15] and cationic Ni allyl catalysts (Figure 1, **C**).[16,17] To date, the most efficient Ni catalyst for alkene hydrosilylation is $(MeN_2N)Ni(OMe)$ (Figure 1, **D**), which has been found to convert 1-octene to Ph_2SiH(octyl) within 3 min at ambient temperature, allowing for TOFs of up to 83,000 h^{-1}.[18] The Hu group subsequently demonstrated that *in situ* generated Ni nanoparticles catalyse the ambient temperature hydrosilylation of alkenes in the presence of Ph_2SiH_2 or tertiary silanes.[19]

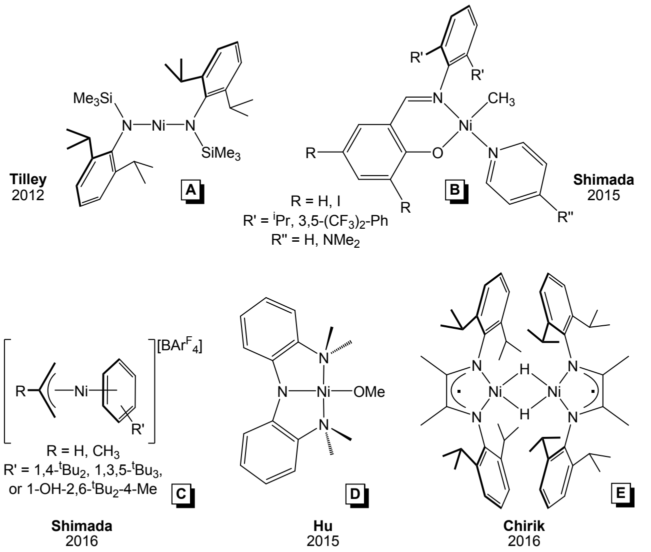


Figure 1. Leading Ni catalysts for anti-Markovnikov alkene hydrosilylation.

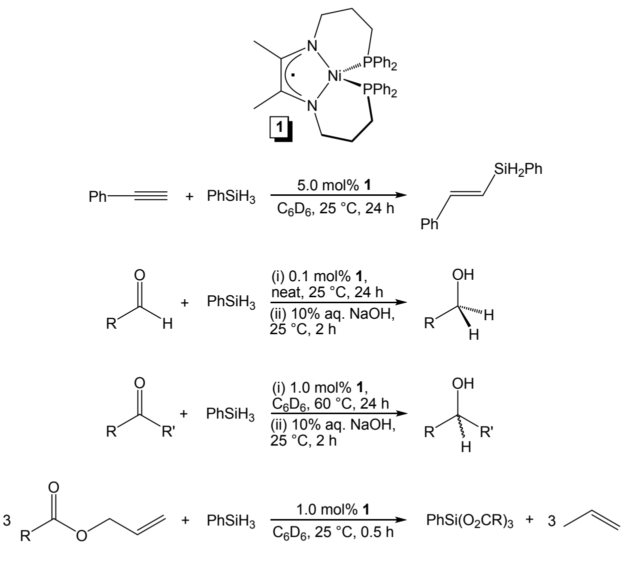
The utilization of redox active supporting ligands has also aided Ni hydrosilylation catalysis. In 2013, we described the synthesis and characterization of an α-diimine (DI) Ni compound, **(^{Ph2PPr}DI)Ni** (Scheme 1, **1**),[20] which features a Ni(I) center that is antiferromagnetically coupled to a chelate radical monoanion. At that time, we found that 5.0 mol% **1** catalyses the hydrosilylation of phenylacetylene, cyclohexanone, and diisopropyl ketone using $PhSiH_3$ over the course of 24 h at ambient temperature. Earlier this year, we reported an expanded aldehyde and ketone hydrosilylation scope for **1** that includes substrates featuring halogen, ether, and nitrile substitution.[21] Interestingly, when attempts were made to hydrosilylate allylic esters using $PhSiH_3$ and **1**, we identified an

---

[a] *School of Molecular Sciences, Arizona State University, Tempe, AZ 85287, USA. E-mail: ryan.trovitch@asu.edu; Tel: +480-727-8930*

†Electronic Supplementary Information (ESI) available: Experimental procedures and spectroscopic characterization of products. See DOI: 10.1039/x0xx00000x

efficient ester C-O bond cleavage pathway that produces propylene and the corresponding tricarboxysilane with TOFs of up to 990 h^{-1} at 25 °C.[21] Following our 2013 report, redox active ligands were used by other research groups for Ni-mediated alkene hydrosilylation. In 2015, Steiman and Uyeda described a dimetallic Ni catalyst featuring a redox active naphthyridene-based ligand that is active for 1-octene and styrene hydrosilylation using Ph_2SiH_2.[22] Chirik and co-workers subsequently found that the *in situ* generated compound, $[(^{2,6\text{-}iPr2Ph}DI)NiH]_2$ (Figure 1, **E**), hydrosilylates 1-octene with TOFs of up to 166 h^{-1} at 40 °C (up to 33 h^{-1} at 23 °C).[23] Earlier this year, the groups of Adhikari and Mandal reported that the bis(phenalenyl) complex, $(PLY)_2Ni(THF)_2$, undergoes successive ligand-based reduction events to generate a dianionic species that is believed to mediate alkene hydrosilylation through a radical pathway.[24] In this contribution, we expand upon these results by utilizing **1** for the selective hydrosilylation of α-olefins over ether C-O bonds and the hydrosilylation of *gem*-olefins at extended reaction times.

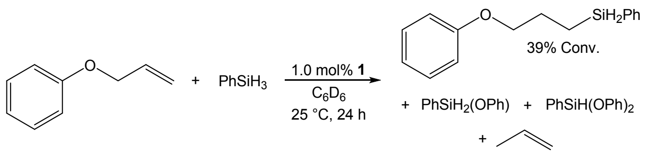


Scheme 1. Hydrosilylation of phenylacetylene,[20] aldehydes,[21] ketones,[21] and allyl esters[21] using **1**.

Results and discussion

Alkene Hydrosilylation

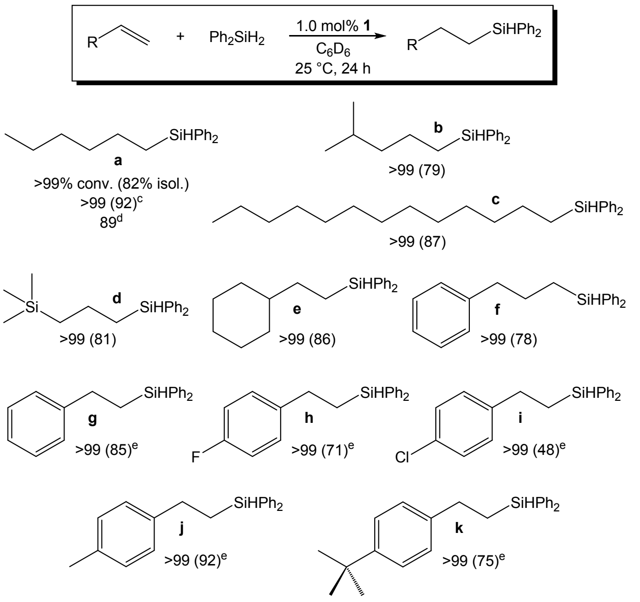
To commence this study, allyl phenyl ether was combined with a stoichiometric quantity of $PhSiH_3$ and 1.0 mol% **1** in benzene-d_6 for 24 h. The evolution of propylene was observed along with the formation of $PhSiH_2(OPh)$ and $PhSiH(OPh)_2$ by ^1H NMR spectroscopy (Scheme 2), indicating that partial C-O bond hydrosilylation had occurred. However, in contrast to our previous work with allyl esters,[21] an additional product identified as $PhSiH_2(PrOPh)$ was observed, indicating that **1** can catalyze the anti-Markovnikov hydrosilylation of terminal alkenes.



Scheme 2. Products of allyl phenyl ether hydrosilylation due to competing alkene hydrosilylation and deallylation.

Given the complicated product mixture obtained following allyl phenyl ether reduction, we initially sought to optimize the conditions for simple α-olefin hydrosilylation. Combining an equimolar solution of 1-hexene and $PhSiH_3$ in benzene-d_6 with 1.0 mol% **1** resulted in minimal conversion (11%) at ambient temperature within 24 h. Seeking to identify a more efficient silane reductant, we screened a variety of secondary [$(TMSO)_2SiH_2$, $(Et_2N)_2SiH_2$, Et_2SiH_2, $^iPr_2SiH_2$, $^tBu_2SiH_2$, Ph_2SiH_2] and tertiary silanes [$(EtO)_3SiH$, $Ph(EtO)_2SiH$, $Me(EtO)_2SiH$, $Me_2(EtO)SiH$, $Me_2(Ph)SiH$, $Me(Ph)_2SiH$, Ph_3SiH, Et_3SiH, $^iPr_3SiH$], finding that $(TMSO)_2SiH_2$ and Et_2SiH_2 allowed for 56% and 21% 1-hexene hydrosilylation, respectively, under these conditions. Although the tertiary silanes were not effective, the use of Ph_2SiH_2 resulted in greater than 99% conversion of 1-hexene to Ph_2SiH(hexyl) (Table 1, **a**, TOF = 4.1 h^{-1}). Alternatively, heating to 60 °C allowed for complete 1-hexene hydrosilylation within 1 h (TOF = 99 h^{-1}) and no side product formation was observed. To determine the limit of **1**-catalyzed α-olefin hydrosilylation activity, the catalyst loading was first lowered to 0.1 mol%, which afforded complete conversion after either 24 h at 25 °C (TOF = 41 h^{-1}) or 1 h at 60 °C (TOF = 990 h^{-1}). Lowering the loading of **1** to 0.01 mol% allowed for 89% 1-hexene hydrosilylation after 72 h at 25 °C (TOF = 124 h^{-1}, TON = 8,900) and 58% conversion after 6 h at 60 °C (TOF = 967 h^{-1}).

Table 1. Hydrosilylation of terminal alkenes using Ph_2SiH_2 and 1.0 mol% **1** at 25 °C.[a,b]

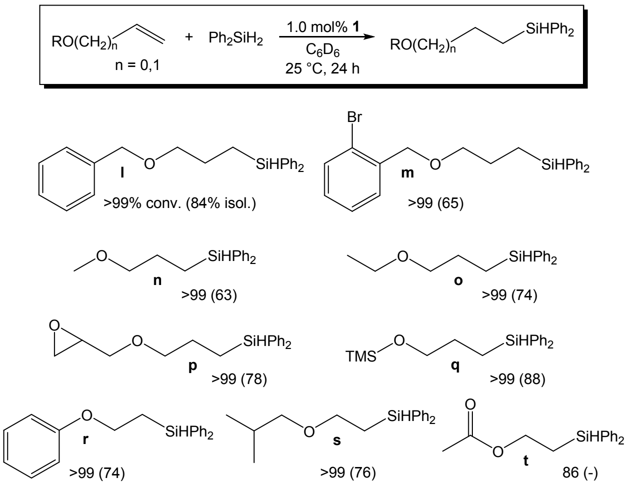


[a]Percent conversion determined by ^1H NMR spectroscopy. [b]Isolated yields in parentheses (spectroscopic analysis provided in the ESI). [c]Neat conditions using 0.1 mol% **1**. [d]Neat conditions using 0.01 mol% **1** after 72 h. [e]Trial completed in 3 h at 60 °C.

With optimized conditions in hand, we sought to broaden the scope of terminal alkene hydrosilylation (Table 1). Sterically unencumbered alkenes including 4-methyl-1-pentene, 1-tridecene, allyltrimethylsilane, and allylbenzene were fully hydrosilylated within 24 h using 1.0 mol% **1** (**b-d, f**). At this loading, the same substrates were hydrosilylated upon heating to 60 °C for 1 h. Although complete conversion was also noted for vinylcyclohexane (**e**), the sterically bulky vinyltrimethylsilane was left untouched after 24 h at 25 °C or 1 h at 60 °C. Moreover, halogen functionalized alkenes including 3,3,4,4,5,5,6,6,6-nonafluoro-1-hexene, 6-chloro-1-hexene, and 6-bromo-1-hexene were not hydrosilylated, possibly due to catalyst deactivation. Styrenes were not efficiently hydrosilylated by **1** at ambient temperature; however, heating to 60 °C for 3 h afforded the linear tertiary silane product in modest to good yield (**g**-**k**).

Armed with a better understanding of the alkene hydrosilylation activity of **1**, we returned to investigating the reduction of unsaturated ethers. Mixing allyl phenyl ether with Ph_2SiH_2 and 1.0 mol% **1** in benzene-d_6 yielded a mixture of $Ph_2SiH(PrOPh)$ and $Ph_2Si(OPh)_2$ after 24 h at ambient temperature. However, alkyl-substituted allyl and vinyl ethers were smoothly converted to alkyl silane products after 24 h at 25 °C (Table 2, **l**-**s**) or 1 h at 60 °C. Notably, the epoxide functionality of allyl glycidyl ether remained intact following hydrosilylation, even at 60 °C. The formation of **p** is noteworthy since the epoxide moiety can allow for further functionalization. The ability of **1** to hydrosilylate vinyl phenyl ether, vinyl isobutyl ether, and vinyl acetate was also investigated. No C-O bond hydrosilylation was noted for the ethers (**r**-**s**), while minimal C-O cleavage was observed during vinyl acetate hydrosilylation (**t** is the major product).

Table 2. Hydrosilylation of allyl ethers, vinyl ethers, and vinyl acetate using Ph_2SiH_2 and 1.0 mol% **1** at 25 °C.[a,b]



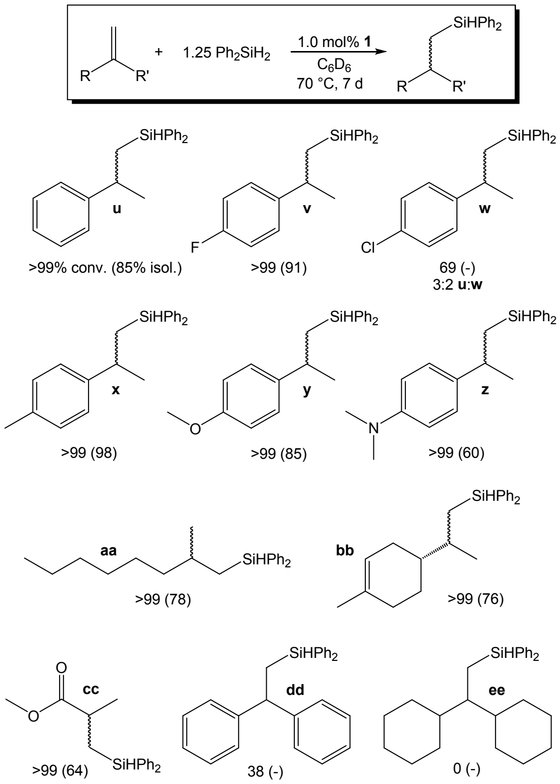
[a]Percent conversion determined by ^1H NMR spectroscopy. [b]Isolated yields in parentheses (spectroscopic analysis provided in the SI).

It should be emphasized that it is notoriously difficult to selectively hydrosilylate the alkene functionality of allylic ethers using common Pt hydrosilylation catalysts, as competing C-O cleavage and alkene isomerization are observed.[25] This tendency to undergo both alkene hydrosilylation and C-O hydrosilylation has limited the overall utility of allyl ethers for the preparation of γ-substituted propylsilanes, which are used on an industrial scale to prepare silicone polymers, oils, and resins.[5a] The results in Table 2 are impactful since they suggest that Ni catalysts hold promise for the preparation of high-performance silicones that require the hydrosilylation of non-carboxylate allylic substrates.

After elucidating the scope of terminal olefin hydrosilylation, we turned our attention to disubstituted alkenes. Although **1** was incapable of mediating cyclohexene hydrosilylation, 23% α-methylstyrene conversion to $Ph_2SiH(CH_2CH(CH_3)Ph)$ was observed after 24 h at 60 °C using a 1.0 mol% catalyst loading. Heating for an additional 4 d allowed for 60% conversion but coupled silane products were also observed.[26] Repeating this trial at 90 °C resulted in 87% conversion after 24 h; however, extending the time frame did not result in additional substrate consumption, despite unreacted Ph_2SiH_2 remaining. Moreover, this elevated temperature also increased the formation of coupled silanes and afforded small amounts of the quaternary silane and Markovnikov addition products. There was minimal evidence for coupled silane formation during the terminal olefin trials in Table 1; however, this competing reaction pathway was anticipated since it was observed during prior ketone hydrosilylation trials.[21]

Fortunately, complete α-methylstyrene hydrosilylation was achieved in the presence of 1.25 equivalents of Ph_2SiH_2 and 1.0 mol% **1** after 7 d at 70 °C (Table 3, **u**). To determine the limit of **1**-catalyzed *gem*-olefin hydrosilylation activity, a neat mixture of α-methylstyrene and Ph_2SiH_2 containing 0.1 mol% **1** was heated to 70 °C for 7 d, after which time 74% conversion was observed (TOF = 4.4 h^{-1}, TON = 740). Five additional α-methylstyrenes were hydrosilylated using **1** and the racemic anti-Markovnikov silane products were isolated in good yield (Table 3, **v**-**z**). Primary alkylsilane products derived from 2-methyl-1-octene (**aa**), D-limonene (**bb**), and methyl methacrylate (**cc**) were also obtained, demonstrating selectivity for *gem*-olefin hydrosilylation over cyclic olefin and ester reduction. In contrast, the sterically hindered substrate 1,1-diphenyl ethene was only 38% hydrosilylated after 7 d at 70 °C (**dd**), while 1,1-dicylohexyl ethene proved unreactive (**ee**). The hydrosilylation of 4-chloro-α-methylstyrene is also of interest. While the intended alkylsilane was observed (**w**), dechlorinated alkylsilane was found to be the primary product (a 3:2 ratio of dechlorinated:chlorinated alkylsilanes was obtained, see Figure S71). To confirm that **1** is active for arene hydrosilylation, the dehalogenation of chlorobenzene was performed and 67% conversion to benzene and Ph_2SiHCl[27] was observed after 7 d at 70 °C in toluene-d_8.

Table 3. Hydrosilylation of *gem*-olefins using Ph_2SiH_2 and 1.0 mol% **1** at 70 °C.[a,b]



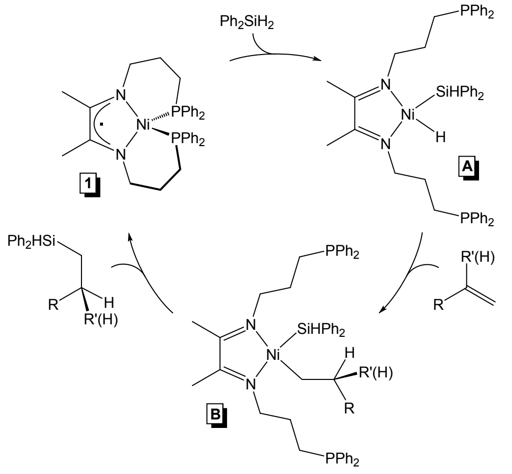
[a]Percent conversion determined by ^1H NMR spectroscopy. [b]Isolated yields in parentheses (spectroscopic analysis provided in the SI).

Outside of Table 3, literature examples of nickel catalyzed *gem*-olefin hydrosilylation are limited. In 1976, Kumada and co-workers reported low yields and optical purity for asymmetric α-methylstyrene, 2,3-dimethyl-1-butene, and 2-methyl-1-butene hydrosilylation using $[(R)\text{-}(PhCH_2)MePhP]_2NiCl_2$.[28] Hu and co-workers found that 1.0 mol% $(^{Me}N_2N)Ni(OMe)$ (Figure 1, **D**) mediates 2-methyl-1-heptene and α-methylstyrene hydrosilylation using Ph_2SiH_2 after 6 h at ambient temperature (TOF = 16.5 h^{-1}).[18] This group also reported that Ni nanoparticles allow for 60% α-methylstyrene hydrosilylation after 4 h at ambient temperature.[19] Two of Puerta and Valerga's (NHC)Ni(allyl) catalysts were found to mediate α-methylstyrene hydrosilylation at 60 °C; however, yields below 35% were obtained in both cases.[11] Although **1** exhibits lower alkene hydrosilylation TOFs than $(^{Me}N_2N)Ni(OMe)$, this report demonstrates for the first time a substantive scope for Ni-catalyzed *gem*-olefin hydrosilylation. Additionally, the α-methylstyrene hydrosilylation TON of 740 determined for **1** is believed to be the highest reported for Ni catalyzed *gem*-olefin hydrosilylation.

Past and Current Mechanistic Insight

Earlier this year, we determined that **1** catalyzes carbonyl hydrosilylation through a modified Ojima mechanism, whereby $PhSiH_3$ oxidative addition is followed by carbonyl insertion and Si-O reductive elimination.[21] Experiments showing that exogenous PMe_3 inhibits carbonyl hydrosilylation were also consistent with phosphine donor arm dissociation during catalysis. Importantly, it was also found that adding 100 equiv. of $PhSiH_3$ to **1** in the absence of substrate resulted in partial silane coupling, even at ambient temperature (35% conversion after 24 h).[21]

As part of this contribution, we sought to identify the active Ni species, initially by monitoring dehydrogenative $PhSiH_3$ coupling in the absence of alkene by ^{31}P NMR spectroscopy. After 24 h at 25 °C, **1** remained along with several minor resonances that in aggregate account for ~5% of the Ni compounds present (Figure S92). Similarly, adding 100 equiv. of Ph_2SiH_2 to **1** in the absence of alkene produced two very minor resonances at 20.64 and 16.68 ppm after 24 h at 25 °C (Figure S93), which are believed to be intermediates of silane coupling. Interestingly, following 1-hexene hydrosilylation using Ph_2SiH_2 and 1.0 mol% **1** by ^{31}P NMR spectroscopy revealed that only **1** is present after 1 or 5 h. However, following the completion of 1-hexene hydrosilylation, a small peak was again observed at 20.64 ppm (Figure S94). No reaction was observed between **1** and 1-hexene after 24 h at 25 °C.



Scheme 3. Chalk-Harrod mechanism for **1**-mediated alkene hydrosilylation.

Given these experiments and our prior evaluation of **1**-catalyzed carbonyl hydrosilylation,[21] we propose that Si-H oxidative addition results in the formation of intermediate **A** (Scheme 3). Once formed, an incoming alkene can coordinate to **A** and insert into the Ni-H bond to generate **B** (Scheme 3). We have found that the insertion of sterically demanding olefins such as 1,1-diphenylethene (**dd**) is slow, leading to increased formation of coupled silane (via σ-bond metathesis between the Ni-H of **A** and an additional Si-H equivalent). Slow alkene insertion to generate **B** also accounts for the observed dechlorination of 4-chloro-α-methylstyrene (**w**), since σ-bond metathesis between the Ni-H of **A** and C-Cl becomes competitive. Substrates that undergo fast insertion into the Ni-H bond of **A**, including 4-chlorostyrene (**i**), 4-chlorobenzaldehyde,[21] and 4-chloroacetophenone,[21] are not dechlorinated in the presence of silane reductant. Once insertion takes place and intermediate **B** is formed, reductive elimination leads to product formation and regeneration of the catalyst resting state, **1** (catalyst **1** is always observed by ^{31}P NMR spectroscopy throughout the course of catalysis – intermediates **A** and **B** cannot be observed). The two electron pathway in Scheme 3 is largely consistent with the alkene hydrosilylation mechanism popularized by Chalk and Harrod;[29] however, the redox activity and phosphine co-donors of $^{\mathbf{Ph2PPr}}$**DI** serve to stabilize **1**, allowing it to remain active for up to 7 d at 70 °C.

Conclusions

In summary, we have determined that **1** is an efficient catalyst for the hydrosilylation of primary and *gem*-olefins using Ph_2SiH_2. For primary olefins, TOFs of up to 124 h^{-1} have been achieved at 25 °C, while heating to 60 °C allowed for maximal TOFs of up to 990 h^{-1}. Furthermore, selectivity for alkene hydrosilylation over ether C-O bond cleavage was demonstrated, which differs from our prior report of **1**-catalyzed allyl ester C-O bond cleavage. The observation of a broad *gem*-olefin hydrosilylation scope indicates that it should be possible to develop effective Ni catalysts for the asymmetric hydrosilylation of prochiral olefins. Furthermore, by employing a redox-active ligand that takes advantage of the chelate effect to stabilize catalyst resting state **1**, TONs of up to 8,900 and 740 have been demonstrated for α-olefin and *gem*-olefin hydrosilylation, respectively.

Experimental

General Considerations

All reactions were carried out inside an MBraun glovebox under an atmosphere of purified nitrogen. 1-Hexene, α-methylstyrene, 4-methylstyrene, D-limonene, phenylsilane, diphenylsilane, methyltriphenylphosphonium bromide, potassium *tert*-butoxide, 4-fluoroacetophenone, 4-methylacetophenone, allyl trimethylsilane, vinyl trimethylsilane, allyl phenyl ether, 2-octanone, 6-chloro-1-hexene, 6-bromo-1-hexene, and trimethylsilylchloride were purchased from Oakwood. Diethylsilane, 1,1,1,5,5,5-hexamethyltrisiloxane, and all other silanes were obtained from Gelest. Allyl benzene, 1-tridecene, cyclohexene, 4-chloroacetophenone, benzophenone, allyl methyl ether, allyl ethyl ether, 4-fluorostyrene, 4-chlorostyrene, vinyl phenyl ether, chlorobenzene, and diethyl ether were purchased from Sigma Aldrich. Allyl glycidyl ether, 4-methoxyacetophenone, *N*,*N*-dimethylaminoacetophenone, dicyclohexylketone, vinyl acetate, methyl methacrylate, styrene, 4-*tert*-butylstyrene, vinyl isobutyl ether, 3,3,4,4,5,5,6,6,6-nonafluoro-1-hexene, and 4-methyl-1-pentene were purchased from TCI. Allyl benzyl ether, allyl (2-bromophenyl)methyl ether, and vinyl cyclohexane were purchased from Santa Cruz. Allyl alcohol was obtained from Alfa Aesar. Benzene-d_6 was purchased from Oakwood and dried over 4 Å molecular sieves and potassium prior to use. **(^{Ph2PPr}DI)Ni** (**1**),[20] allyl trimethylsilyl ether,[30] 4-fluoro-α-methylstyrene, 4-chloro-α-methylstyrene, 4,α-dimethylstyrene, 4-methoxy-α-methylstyrene, 4-(*N*,*N*-dimethylamino)-α-methylstyrene, 1,1-diphenylethene, 2-methyloctene, and 1,1-dicyclohexylethene were synthesized using literature methods.[31] Liquid substrates were dried over 4 Å molecular sieves, solid substrates were recrystallized from diethyl ether, and all were stored at -35 °C prior to use.

Solution ^{1}H nuclear magnetic resonance (NMR) spectra were recorded at room temperature on a Bruker 400, Varian 400, or Varian 500 MHz NMR spectrometer. All ^{1}H and ^{13}C NMR chemical shifts (ppm) are reported relative to $Si(CH_3)_4$ using ^{1}H (residual) and ^{13}C chemical shifts of the solvent as secondary standards. ^{29}Si NMR chemical shifts are reported relative to $Si(CH_3)_4$ as an external reference. DEPT135 ^{29}Si NMR data was collected using a one bond coupling constant of 260 Hz.

General Procedure for Primary Alkene Hydrosilylation at 25 °C. Under an inert atmosphere, the primary alkene (approx. 0.42 mmol) and Ph_2SiH_2 (approx. 0.42 mmol) were added to a vial containing **1** (approx. 0.0042 mmol) dissolved in 0.6 mL of benzene-d_6. The resulting red solution was then transferred into J. Young NMR tube. After 24 h, greater than 99% conversion was observed via ^{1}H NMR spectroscopy. The reaction was then exposed to air to deactivate the catalyst, filtered through Celite, and volatile compounds were removed under reduced pressure. Diphenyl alkyl silanes were isolated and characterized via ^{1}H and ^{13}C NMR spectroscopy.

General Procedure for Primary Alkene Hydrosilylation at 60 °C. Under an inert atmosphere, the primary alkene (approx. 0.42 mmol) and Ph_2SiH_2 (approx. 0.42 mmol) were added to a vial containing **1** (approx. 0.0042 mmol) dissolved in 0.6 mL of benzene-d_6. The resulting red solution was then transferred into a J. Young NMR tube and heated to 60 °C. After 1 h, greater than 99% conversion was observed via ^{1}H NMR spectroscopy. The reaction was then exposed to air to deactivate the catalyst, filtered through Celite, and volatile compounds were removed under reduced pressure. Diphenyl alkyl silanes were isolated and characterized via ^{1}H and ^{13}C NMR spectroscopy.

General Procedure for Styrene Hydrosilylation at 60 °C. Under an inert atmosphere, the styrene (approx. 0.45 mmol) and Ph_2SiH_2 (approx. 0.045 mmol) were added to a vial containing **1** (approx. 0.0045 mmol) dissolved in 0.6 mL of benzene-d_6. The resulting red solution was then transferred into a J. Young NMR tube and heated to 60 °C. After 3 h, greater than 99% conversion was observed via ^{1}H NMR spectroscopy. The reaction was then exposed to air to deactivate the catalyst, filtered through Celite, and volatile compounds were removed under reduced pressure. Diphenyl alkyl silanes were isolated and characterized via ^{1}H and ^{13}C NMR spectroscopy.

General Procedure for *Gem*-Alkene Hydrosilylation at 70 °C. Under an inert atmosphere, the *gem*-alkene (approx. 0.54 mmol) and Ph_2SiH_2 (approx. 0.67 mmol) were added to a vial containing **1** (approx. 0.0054 mmol) dissolved in 0.6 mL of benzene-d_6. The resulting red solution was then transferred into a J. Young NMR tube and heated to 70 °C. After 7 d, greater than 99% conversion was observed via ^{1}H NMR spectroscopy. The reaction was then exposed to air to deactivate the catalyst, filtered through Celite, and volatile compounds were removed under reduced pressure. Diphenyl alkyl silanes were isolated and characterized via ^{1}H and ^{13}C NMR spectroscopy.

Conflicts of interest

The authors declare the following competing financial interest(s): R. J. T. retains rights to **1** through US20160176908 and WO2014201082. This catalyst has been commercialized by Sigma-Aldrich Corporation (a subsidiary of Merck KGaA).

Acknowledgements

This material is based upon work supported by the National Science Foundation under Grant No. 1651686. Tyler M. Porter is acknowledged for preliminary NMR experiments that demonstrated the reductive C-O cleavage of allyl phenyl ether.

Notes and references

1 Y. Hatanaka and T. Hiyama, *J. Org. Chem.* 1988, **53**, 918–920.
2 B. Marciniec, *Comprehensive Handbook on Hydrosilylation*, 1st Ed., Pergamon Press, New York, USA, 1992.
3 J. L. Speier, J. A. Webster, G. H. Barnes, *J. Am. Chem. Soc*. 1957, **79**, 974–979.
4 B. D. Karstedt, General Electric Company. U.S. Patent No. 3775452A, 1973.
5 (a) D. Troegel and J. Stohrer, *Coord. Chem. Rev.* 2011, **255**, 1440–1459. (b) X. Du and Z. Huang, *ACS Catal.* 2017, **7**, 1227–1243. (d) J. V. Obligacion and P. J. Chirik, *Nat. Rev. Chem.* 2018, **2**, 15–34.
6 (a) J. R. Carney, B. R. Dillon, L. Campbell and S. P. Thomas, *Angew. Chem. Int. Ed.* 2018, **57**, 10620–10624. (b) T. K. Mukhopadhyay, M. Flores, T. L. Groy and R. J. Trovitch, *Chem. Sci.* 2018, **9**, 7673-7680. (c) X. Yang and C. Wang, *Chin. J. Chem.* 2018, **36**, 1047-1051.
7 (a) A. M. Tondreau, C. C. H. Atienza, K. J. Weller, S. A. Nye, K. M. Lewis, J. G. P. Delis and P. J. Chirik, *Science* 2012, **335**, 567–570. (b) K. Kamata, A. Suzuki, Y. Nakai and H. Nakazawa, *Organometallics* 2012, **31**, 3825–3828. (c) A. M. Tondreau, C. C. H. Atienza, J. M. Darmon, C. Milsmann, H. M. Hoyt, K. J. Weller, S. A. Nye, K. M. Lewis, J. Boyer, J. G. P. Delis, E. Lobkovsky and P. J. Chirik, *Organometallics* 2012, **31**, 4886–4893. (d) D. Peng, Y. Zhang, X. Du, L. Zhang, X. Leng, M. D. Walter and Z. Huang, *J. Am. Chem. Soc.* 2013, **135**, 19154–19166. (e) M. D. Greenhalgh, D. J. Frank and S. P. Thomas, *Adv. Synth. Catal.,* 2014, **356**, 584–590. (f) J. Chen, B. Cheng, M. Cao and Z. Lu, *Angew. Chem. Int. Ed.* 2015, **54**, 4661–4664. (g) R. Gilbert-Wilson, W.-Y. Chu and T. B. Rauchfuss, *Inorg. Chem.* 2015, **54**, 5596–5603. (h) B. Marciniec, A. Kownacka, I. Kownacki, M. Hoffmann, R. Taylor, *J. Organomet. Chem.* 2015, **791**, 58–65. (i) Y. Sunada, D. Noda, H. Soejima, H. Tsutsumi, H. Nagashima, *Organometallics* 2015, **34**, 2896–2906. (j) G. I. Nikonov, *ChemCatChem* 2015, **7**, 1918–1919. (k) X. Jia and Z. Huang, *Nature Chem.* 2016, **8**, 157–161. (l) D. Noda, A. Tahara, Y. Sunada, H. Nagashima, *J. Am. Chem. Soc.* 2016, **138**, 2480–2483. (m) X. Du, Y. Zhang, D. Peng, Z. Huang, *Angew. Chem. Int. Ed.* 2016, **55**, 6671–6675. (n) A. J. Challinor, M. Calin, G. S. Nichol, N. B. Carter and S. P. Thomas, *Adv. Synth. Catal.* 2016, **358**, 2404–2409. (o) K. Hayasaka, K. Kamata and H. Nakazawa, *Bull. Chem. Soc. Japan* 2016, **89**, 394–404. (p) Y. Toya, K.

Hayasaka and H. Nakazawa, *Organometallics* 2017, **36**, 1727–1735. (q) M.-Y. Hu, Q. He, S.-J. Fan, Z.-C. Wang, L.-Y. Liu, Y.-J. Mu, Q. Peng and S.-F. Zhu, *Nature Commun.* 2018, **9**, 221. (r) B. Cheng, W. Liu and Z. Lu, *J. Am. Chem. Soc.* 2018, **140**, 5014–5017.

8 (a) C. C. H. Atienza, T. Diao, K. J. Weller, S. A. Nye, K. M. Lewis, J. G. P. Delis, J. L. Boyer, A. K. Roy and P. J. Chirik, *J. Am. Chem. Soc.* 2014, **136**, 12108–12118. (b) C. Chen, M. B. Hecht, A. Kavara, W. W. Brennessel, B. Q. Mercado, D. J. Weix and P. L. Holland, *J. Am. Chem. Soc.* 2015, **137**, 13244–13247. (c) J. Sun and L. Deng, *ACS Catal.* **2016**, *6*, 290–300. (d) A. Gorczyński, M. Zaranek, S. Witomska, A. Bocian, A. R. Stefankiewicz, M. Kubicki, V. Patroniak and P. Pawluć, *Catal. Commun.* 2016, **78**, 71–74. (e) C. H. Schuster, T. Diao, I. Pappas and P. J. Chirik, *ACS Catal.* 2016, **6**, 2632–2636. (f) A. D. Ibrahim, S. W. Entsminger, L. Zhu and A. R. Fout, *ACS Catal.* 2016, **6**, 3589–3593. (g) B. Raya, S. Biswas and T. V. RajanBabu, *ACS Catal.* 2016, **6**, 6318–6323. (h) W.-Y. Chu, R. Gilbert-Wilson and T. B. Rauchfuss, *Organometallics* 2016, **35**, 2900–2914. (i) C. Wang, W. J. Teo and S. Ge, *ACS Catal.* 2017, **7**, 855–863. (j) B. Raya, S. Jing, V. Balasanthiran and T. V. RajanBabu, *ACS Catal.* 2017, **7**, 2275–2283. (k) Y. Liu and L. Deng, *J. Am. Chem. Soc.* 2017, **139**, 1798–1801. (l) C. Wang, W. J. Teo and S. Ge, *Nature Commun.* 2017, **8**, 2258. (m) B. Cheng, P. Lu, H. Zhang, X. Cheng and Z. Lu, *J. Am. Chem. Soc.* 2017, **139**, 9439–9442.

9 For early examples see: (a) A. D. Petrov, V. F. Mironov, V. M. Vdovin and S. I. Sakykh-Zade, *Russ. Chem. Bull.* 1956, **5**, 247−248. (b) S. Nozakura and S. Konotsune, *Bull. Chem. Soc. Jpn.* 1956, **29**, 326−331. (c) E. T. Chukovskaya and R. K. Freidlina, *Russ. Chem. Bull.* 1963, **12**, 685−686. (d) M. Kumada, Y. Kiso and M. Umeno, *J. Chem. Soc. D, Chem. Commun.* 1970, 611. (e) Y. Kiso, M. Kumada, K. Tamao and M. Umeno, *J. Organomet. Chem.* 1973, **50**, 297−310. (f) Y. Kiso, M. Kumada, K. Maeda, K. Sumitani and K. Tamao, *J. Organomet. Chem.* 1973, **50**, 311−318.

10 F.-G. Fontaine, R.-V. Nguyen and D. Zargarian, *Can. J. Chem.* 2003, **81**, 1299−1306. (b) F.-G. Fontaine and D. Zargarian, *J. Am. Chem. Soc.* 2004, **126**, 8786−8794. (c) Y. Chen, C. Sui-Seng, S. Boucher and D. Zargarian, *Organometallics* 2005, **24**, 149−155. (d) Y. Chen and D. Zargarian, *Can. J. Chem.* 2009, **87**, 280−287.

11 L. Benítez Junquera, M. C. Puerta and P. Valerga, *Organometallics* 2012, **31**, 2175−2183.

12 A. Kuznetsov and V. Gevorgyan, *Org. Lett.* 2012, **14**, 914−917.

13 M. I. Lipschutz and D. T. Tilly, *Chem. Commun.* 2012, **48**, 7146-7148.

14 V. Srinivas, Y. Nakajima, W. Ando, K. Sato and S. Shimada, *Catal. Sci. Technol.* 2015, **5**, 2081−2084.

15 V. Srinivas, Y. Nakajima, W. Ando, K. Sato and S. Shimada, *J. Organomet. Chem.* 2016, **809**, 57−62.

16 J. Mathew, Y. Nakajima, Y.-K. Choe, Y. Urabe, W. Ando, K. Sato and S. Shimada, *Chem. Commun.* 2016, **52**, 6723−6726.

17 For a personal account see: Y. Nakajima, K. Sato and S. Shimada, *Chem. Rec.* 2016, **16**, 2379−2387.

18 I. Buslov, J. Becouse, S. Mazza, M. Montandon-Clerc and X. Hu, *Angew. Chem. Int. Ed.* 2015, **54**, 14523−14526.

19 I. Buslov, F. Song and X. Hu, *Angew. Chem. Int. Ed.* 2016, **55**, 12295-12299.

20 T. M. Porter, G. B. Hall, T. L. Groy and R. J. Trovitch, *Dalton Trans*. 2013, **42**, 14689−14692.

21 C. L. Rock, T. L. Groy and R. J. Trovitch, *Dalton Trans.* 2018, **47**, 8807−8816.

22 T. J. Steiman and C. Uyeda, *J. Am. Chem. Soc.* 2015, **137**, 6104-6110.

23 I. Pappas, S. Treacy and P. J. Chirik, *ACS Catal*. 2016, **6**, 4105−4109.

24 G. Vijaykumar, A. Pariyar, J. Ahmed, B. K. Shaw, D. Adhikari and S. K. Mandal, *Chem. Sci.* 2018, **9**, 2817-2825.

25 (a) Z. V. Belyakova, M. G. Pomerantseva, L. A. Efimova, E. A. Chernyshev and P. A. Storozhenko, *Russ. J. Gen. Chem.* 2010, **80**, 728-733. (b) M. Igarashi, T. Kobayashi, K. Sato, W. Ando, T. Matsumoto, S. Shimada, M. Hara and H. Uchida, *J. Organomet. Chem.* 2013, **725**, 54-59. (c) M. Igarashi, T. Matsumoto, T. Kobayashi, K. Sato, W. Ando, S. Shimada, M. Hara and H. Uchida, *J. Organomet. Chem.*, 2014, **749**, 421-427.

26 D. Schmidt, T. Zell, T. Schaub and U. Radius, *Dalton Trans.* 2014, **43**, 10816−10827.

27 Y. Kawakami, Y. Sakuma, T. Wakuda, T. Nakai, M. Shirasaka and Y. Kabe, *Organometallics*, 2010, **29**, 3281−3288.

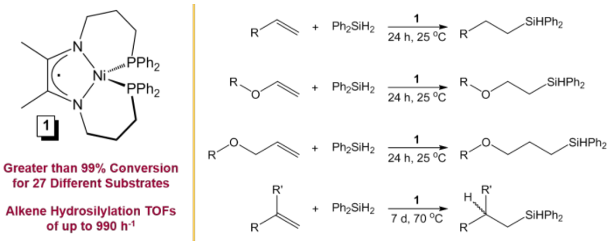
28 K. Yamamoto, T. Hayashi, Y. Uramoto, R. Ito and M. Kumada, *J. Organomet. Chem.* 1976, **118**, 331-348.

29 (a) A. J. Chalk and J. F. Harrod, *J. Am. Chem. Soc.* 1965, **87**, 16−21. (b) A. K. Roy and R. B. Taylor, *J. Am. Chem. Soc.* 2002, **124**, 9510−9524. (c) T. K. Meister, K. Riener, P. Gigler, J. Stohrer, W. A. Herrmann and F. E. Kühn, *ACS Catal.* 2016, **6**, 1274−1284.

30 A. J. Cresswell and G. C. Lloyd-Jones, *Chem. Eur. J.* 2016, **22**, 12641−12645.

31 L. Jiang, B. Hu, X. Xie and Z. Zhang, *Tetrahedron*, 2017, **73**, 6901−6905.

TOC Graphic



The hydrosilylation of terminal alkenes, allyl ethers, and *gem*-olefins has been demonstrated using **(^{Ph2PPr}DI)Ni** between 25 and 70 °C.