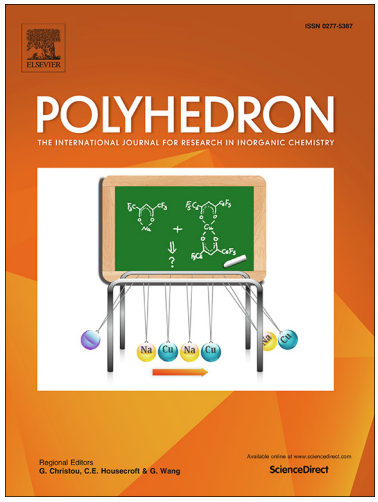


A Rh(I) Complex with an Annulated N-Heterocyclic Carbene Ligand for *E*-Selective Alkyne Hydrosilylation

Akshi Tyagi, Suman Yadav, Prosenjit Daw, Chitrakar Ravi, Jitendra K. Bera

PII: S0277-5387(19)30274-8
DOI: https://doi.org/10.1016/j.poly.2019.04.027
Reference: POLY 13887

To appear in: *Polyhedron*

Received Date: 19 February 2019
Accepted Date: 19 April 2019

Please cite this article as: A. Tyagi, S. Yadav, P. Daw, C. Ravi, J.K. Bera, A Rh(I) Complex with an Annulated N-Heterocyclic Carbene Ligand for *E*-Selective Alkyne Hydrosilylation, *Polyhedron* (2019), doi: https://doi.org/10.1016/j.poly.2019.04.027

A Rh(I) Complex with an Annulated N-Heterocyclic Carbene Ligand for *E*-Selective Alkyne Hydrosilylation[$]

Akshi Tyagi, Suman Yadav, Prosenjit Daw, Chitrakar Ravi and Jitendra K Bera*

Department of Chemistry and Center for Environmental Sciences and Engineering,

Indian Institute of Technology Kanpur, Kanpur 208016 India.

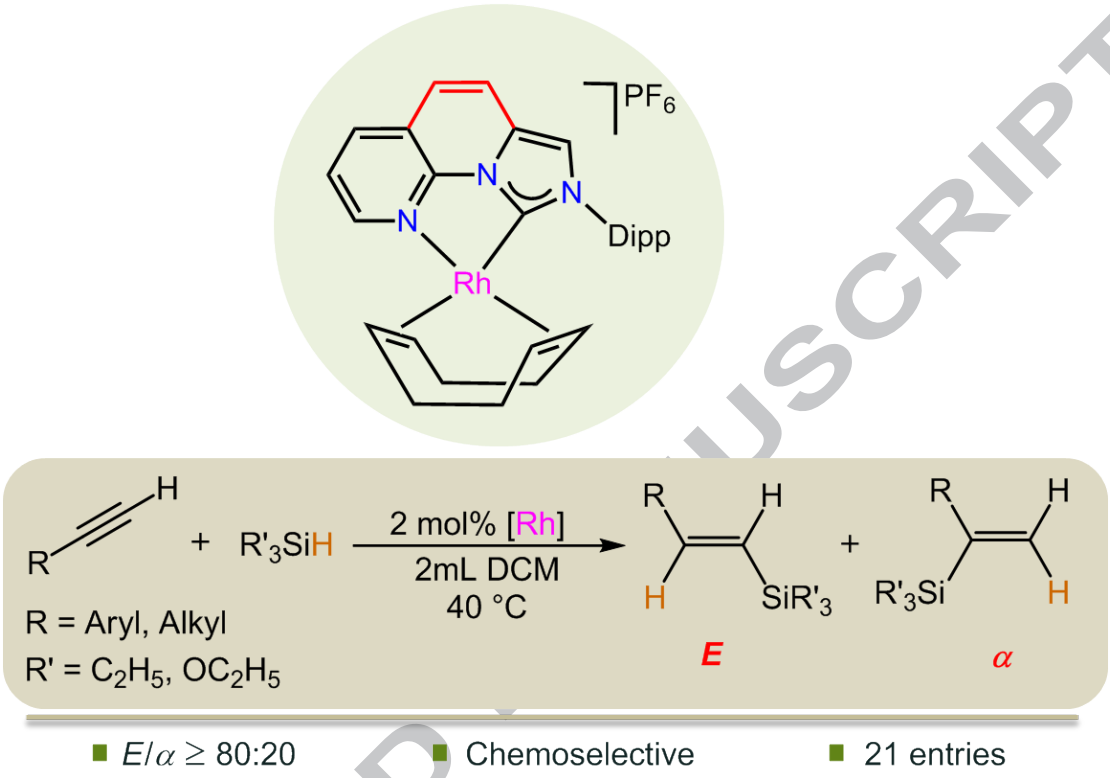
Fax: +91–512–2596806; Tel: +91–512–2597336

E–mail: jbera@iitk.ac.in

* To whom correspondence should be addressed.

$ Special issue on “Bio-inspired Inorganic Chemistry” dedicated to Prof. Akhil R. Chakravarty on the occasion of his 65th birthday

TOC



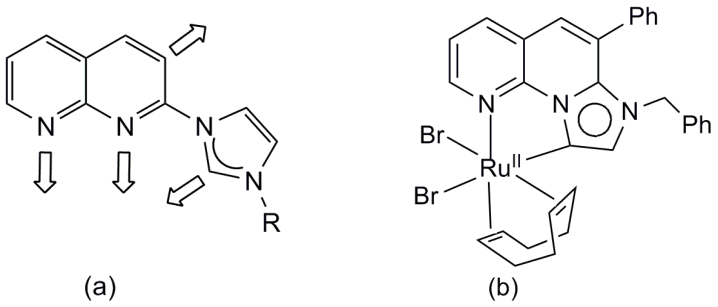
Abstract

A Rh(I) complex supported by a fused π-conjugated imidazo[1,2-*a*][1,8]naphthyridine-based N-heterocyclic carbene ligand with a Dipp attachment on the imidazole nitrogen has been synthesized and structurally characterized. The title complex is found to be an excellent catalyst for accessing *E*-vinylsilanes. The scope of the chemoselective hydrosilylation is examined for a range of terminal alkynes with silanes Et_3SiH and $(EtO)_3SiH$.

Keywords: NHC, Rhodium, Catalysis, Hydrosilylation, Vinylsilanes

1. Introduction

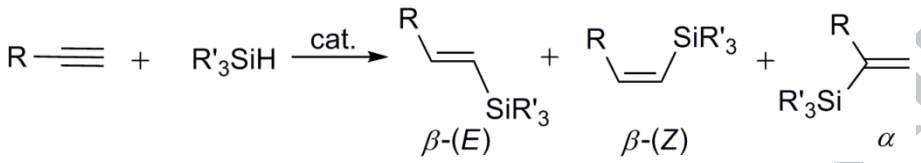
N-heterocyclic carbenes (NHCs) constitute an important class of ligands because of their easy accessibility, structural varieties, steric and electronic tunability, ability to bind an array of metal ions, and for the remarkable applications of metal-NHC complexes for a broad range of catalytic transformations.[1,2] Although the metal-NHC complexes are well suited for oxidation chemistry,[3] the prospect of ligand dissociation from a putative (NHC)metal-hydride intermediate *via* reductive elimination restricts the use of the NHC ligands in direct hydrogenation reactions.[4] Introduction of a donor functionality on the NHC scaffold favors the formation of the chelate complex and thus suppresses ligand dissociation during the catalytic cycles. Several donor groups are attached to the imidazole nitrogen either directly or through the linkers which offer wide structural diversity and improve the stability of the metal-NHC complexes.[5-7] We reported naphthyridine-functionalized NHC ligands which show multifaceted coordination to different metal ions (Scheme 1a).[6] The rotational flexibility could be circumvented by synthetic fusion of the carbene ring and the donor moiety. Suitable annulation has resulted in a series of NHC ligands where extended π-delocalization affords the higher conjugational stability and the enhanced σ-donor ability compared to their non-annulated analogues.[8] An annulated π-conjugated C_4/C_5-bound mesoionic carbene (MIC)[9] ligand forms a stable complex [Ru(MIC)(COD)Br_2] which endures oxidative conditions and selectively cleaves olefins to the corresponding aldehydes (Scheme 1b).[3d]



Scheme 1. (a) Multifaceted coordination of naphthyridine-functionalized NHC ligand, (b) an annulated MIC complex of Ru.

Hydrosilylation of carbon-carbon multiple bonds is one of the important methods for the construction of Si-C bond. Transition-metal catalyzed hydrosilylation of alkynes gives the straightforward and atom-economical access to vinylsilanes,[10] which are useful intermediates in organic synthesis,[11] coupling partners in Hiyama cross coupling reactions[10c,12,13] and industrial reagents to synthesize cross-linked silicone polymers.[14] Three possible stereo-isomeric products, namely, β-(*Z*), β-(*E*) and branched *α*-isomers are formed in the hydrosilylation of terminal alkynes (Scheme 2). Despite the major advances in recent years, the selectivity has remained a challenging issue. The nature of the catalysts, the substrates and reagents (alkynes and silanes) and the reaction conditions influence the product selectivity. While the Pt catalysts gave selectively β-(*E*) vinylsilane,[15,16] the Ru catalysts afforded β-(*Z*) or *α*-isomers.[17-19] Several Rh catalysts have been reported that allowed to make a few general observations.[5c,7,19-33] Neutral Rh complexes tend to show selectivity for β-(*Z*) vinylsilanes whereas cationic complexes provide β-(*E*) vinylsilanes.[19,32,33] Metal-assisted isomerization of β-(*Z*) to β-(*E*) vinylsilane is reported with Rh complexes.[16,27,29,30,33] Selectivity also depends on the nature of the silanes– electron-rich silanes give β-(*Z*) vinylsilanes whereas β-(*E*) isomers are obtained from electron-poor silanes.[20] Further, oligomerisation,[23]

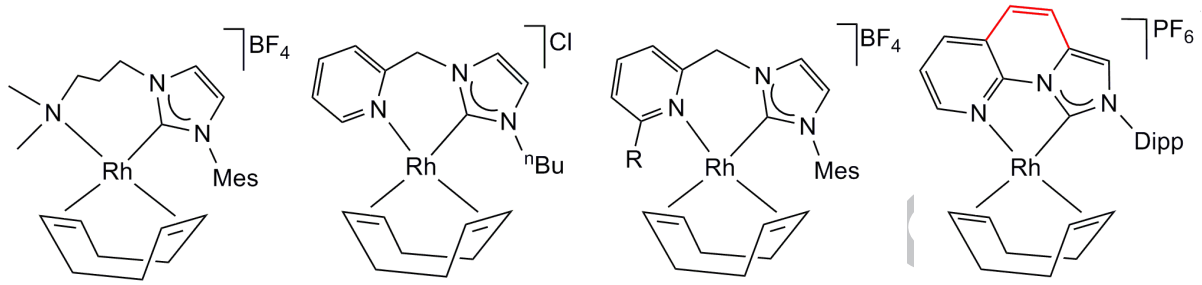
polymerization of arylalkynes[24,26,32] and the formation of alkynyl-silanes from the dehydrogenative silylation products[25,30,31] are the side reactions that complicate the Rh catalyzed hydrosilylation reactions.



Scheme 2. Hydrosilylation of terminal alkynes.

Jimenez, Oro and coworkers employed both neutral and cationic Rh complexes with amino-alkyl functionalized NHC ligands (Scheme 3a).[26] High β-(*Z*)-selectivity was reported for 1-hexyne whereas sterically hindered alkynes gave *E*-selective products. In addition, *Z* to *E* isomerization was observed over a prolonged time, along with extensive polymerization of the phenylacetylene. Similar *Z* to *E* isomerization of the resulting vinylsilanes was also reported by Cassani and Mazzoni for a neutral Rh(I) complex containing BOC-protected amino functionalized NHC ligand, although alkyne polymerization was not observed.[27] Peris and coworkers introduced a pyridine functionalized Rh-NHC complex for $HSiMe_2Ph$ addition to phenylacetylene (Scheme 3b).[7] A mixture of *E*/*Z*/*α* isomers was obtained at higher temperature (60 °C), but β-(*Z*)-selectivity could be improved by carrying out the reaction at room temperature. Recently, Salazar, Suarez and coworkers reported Rh(I) complexes containing sterically controlled picolyl-NHC ligands which offered excellent β-(*E*)-selectivity for hydrosilylation of a variety of alkynes with both electron-rich and electron-poor silanes (Scheme 3c).[22] It is apparent from literature reports that the ligand flexibility and the steric congestion at the metal center influence the product selectivity. To recognize the

effect of ligand rigidity, herein we report a Rh(I) complex containing an annulated π-conjugated chelate ligand bearing bulky diisopropylphenyl (Dipp) substituent on the imidazole ring for the selective addition of silanes to the terminal alkynes (Scheme 3d).



(a) Jimenez and Oro, 2008

(b) Peris, 2005

(c) Salazar and Suarez, 2017

(d) This work

Scheme 3. Rh(I) complexes containing N-donor functionalized ligand scaffolds employed in hydrosilylation of alkynes.

2. Results and Discussion

*2.1 Synthesis and characterization of [Rh(L)(COD)]PF_6 (**1**)*

The NHC ligand precursor 1,8-naphthyrido[1,2-*a*]-(2',6'-diisopropylphenyl)imidazolium hexaflurophosphate [LH]PF_6 and its silver complex [AgL_2]PF_6 were synthesized using literature procedures.[34] Transmetalation reaction of [AgL_2]PF_6 with [Rh(μ-Cl)(COD)]$_2$ followed by the addition of $AgPF_6$ in dichloromethane (DCM) at room temperature resulted in the complex [Rh(COD)(L)]PF_6 (**1**) in high yield (85%). The molecular structure of **1** reveals the chelate binding of the ligand to the metal through the carbene carbon (C2) and the naphthyridine nitrogen (N3) (Figure 1). The Rh1−C2 and Rh1−N3 bond distances are 2.032(4) and 2.137(3) Å respectively. The ligand bite angle (∠C2–Rh1–N3 = 79.6°) is similar to the analogous bis-carbene (∠C–Rh–C = 80.7°)[8d] and 1,10-phenanthroline (∠N–Rh–N 79.8°) complexes,[35] but slightly shorter than that

observed in Suarez's complexes (84.0°, 84.6° for R=H and 2,6-$(OMe)_2$-C_6H_3, respectively).[22] One COD molecule completes the distorted square planer geometry around the metal. The Rh-C (COD) distances (Rh1–C26/C27 = 2.186(4)/2.218(4) Å) trans to the carbene carbon are slightly longer than the corresponding distances (Rh1–C23/C30 = 2.148(4)/2.131(4) Å) that are opposed to the pyridyl nitrogen, reflecting the trans influence of the carbene carbon. The ^{1}H NMR spectrum of **1** in chloroform-d shows sets of multiplets for the COD protons (δ 1.96−5.24 ppm). A singlet resonance at δ 8.06 ppm is observed for the imidazole proton. The naphthyridine protons appear as four different signals in the range δ 7.45−8.42 ppm. Two doublets are observed at δ 1.31 ppm and 1.08 ppm for the chemically non-equivalent isopropyl methyl protons –*CHMe*$_2$. In addition, multiplets at δ 3.40–3.47ppm are assigned to two non-equivalent isopropyl-*CH* protons. The carbene carbon appears at δ 162.3 ppm as doublet ($J_{C\text{-}Rh}$ = 52 Hz) in the ^{13}C NMR spectrum (Figure S1). ESI-MS shows a signal at *m/z* = 540.1867 (*z* = 1) which is assigned for [**1** – PF_6]$^+$ (Figure S2).

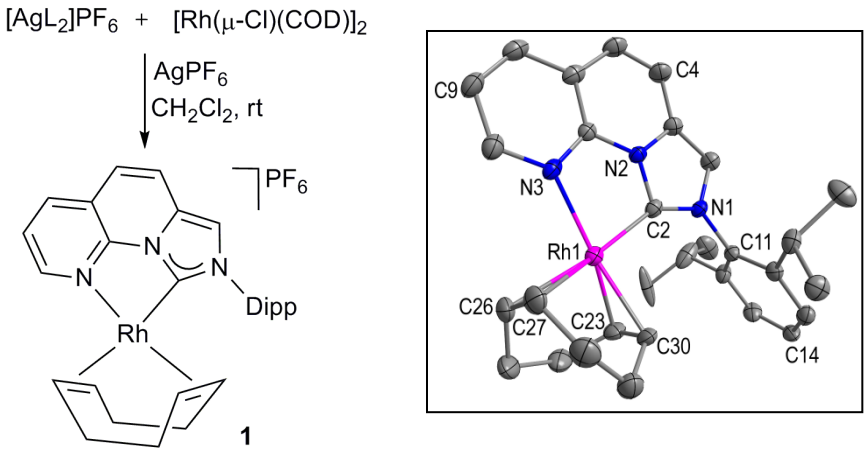
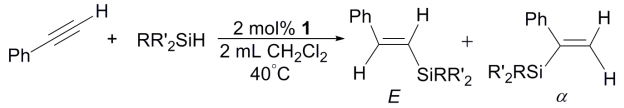


Figure 1. Synthesis of **1** (left) and the molecular structure of the cationic unit in **1** with selected atoms labeled (right). All hydrogen atoms are omitted for the sake of clarity. Thermal ellipsoids are drawn at the 40% probability level.

2.2 Catalytic studies

The catalytic utility of **1** was evaluated for the hydrosilylation of terminal alkynes. Initial reaction of phenylacetylene (1 mmol), Et_3SiH (1.2 mmol) and 2 mol% catalyst **1** in DCM at 40 °C afforded 97% conversion of the alkyne to the corresponding vinylsilane (85:15, *E*:*α*) after 6 h (Table 1). Possible side products arising out of the dehydrogenative silylation and the alkyne polymerization were not observed. Performing the same reaction at room temperature gave only 70% of the desired product (entry 1, Table S2). A range of solvents including $CHCl_3$, THF, CH_3CN, 1,4-dioxane, toluene and 1,1,2,2-tetrachloroethane were screened and the best conversion (95%) could be achieved in 1,4-dioxane with good selectivity (80:20, *E*:*α*) at 80 °C. The optimization studies revealed that the DCM was the best choice among the solvents studied. Increasing the catalyst loading from 2 to 3 mol% did not affect the yield and the selectivity. Further, reducing the catalyst loading from 2 to 1 mol% diminished the yield of the reaction. Hydrosilylation of phenylacetylene was performed with other silanes, $PhSiH_3$, Me_2PhSiH and $(EtO)_3SiH$ (Table 1). The primary silane $PhSiH_3$ gave a mixture of β-(*E*) and *α*-vinylsilane along with divinylsilane ($(PhCH{=}CH)_2SiPhH$) in 54:40:6 ratio (entry 2). Dimethylphenylsilane gave excellent yield with moderate *E*-selectivity (78:22, *E*:*α*) (entry 3). Addition of $(EtO)_3SiH$ to phenylacetylene afforded the corresponding vinylalkoxysilane with higher *E*-selectivity (86:14, *E*:*α*) (entry 4).

Table 1: Complex **1** catalyzed hydrosilylation of phenylacetylene.[a]



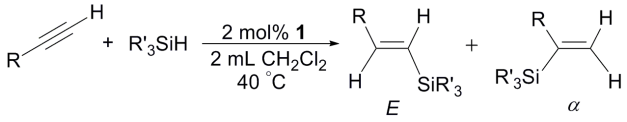
Entry	Silane	Yield %[b]	Ratio *E*/*α*[b]
1.	Et_3SiH	97	85/15
2.	$PhSiH_3$	93	54/40/6[c]
3.	$(CH_3)_2PhSiH$	98	78/22
4.	$(EtO)_3SiH$	98	86/14

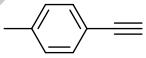
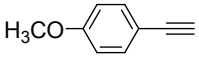
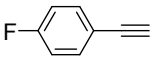
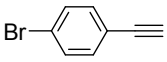
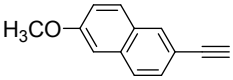
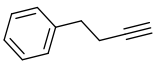
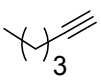
[a]Reaction conditions: alkyne:silane:**1** = 1:1.2:0.02 mmol, in CH_2Cl_2, 40 °C, 6 h. [b]Yields and *E*/*α* ratio are determined by GC-MS using mesitylene as an internal standard. [c]divinylsilane.

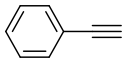
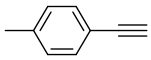
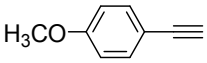
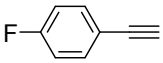
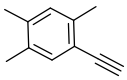
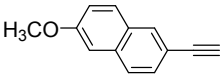
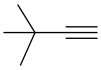
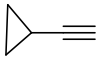
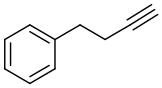
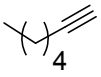
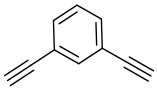
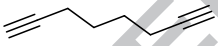
With an optimized catalytic condition in hand, substrate scope of **1** for alkyne hydrosilylation was explored with two different silanes, Et_3SiH and $(EtO)_3SiH$ (Table 2). Electron-rich alkynes 4-methylphenylacetylene and 4-methoxyphenylacetylene on reactions with Et_3SiH afforded high yields (>95%) to the corresponding vinylsilanes with good *E*-selectivity (86:14, *E*:*α*; entries 2,3). Electron-deficient alkynes (4-fluoro and 4-bromophenylacetylene) afforded relatively lower yield (89% and 87% respectively, with 80:20, *E*:*α* selectivity; entries 4, 5). An excellent result was obtained for the bulky alkyne (2-ethynyl-6-methoxynaphthalene) which showed 99% *E*-selectivity (entry 6). Aliphatic alkynes 4-phenyl-1-butyne and 1-hexyne gave 86:14 and 83:17 ratio of *E*- and *α*-vinylsilane with 85% and 89% conversions respectively (entries 7, 8). Isomerization of vinyl silanes to allyl silanes are reported for the silylation of the aliphatic alkynes,[26,27] but no such isomerized products are observed for catalyst **1**. Hydrosilylation of trimethylsilylacetylene gave excellent yield 97% (94:6, *E*:*α*) of the vinyldisilane (entry 9), a useful substrate for chemoselective derivatization reactions in organic synthesis.[36]

Further, the scope of **1** was extended to $(EtO)_3SiH$ with a wide variety of aryl and alkyl alkynes (entries 10 - 21). A list of vinylalkoxysilanes were obtained which are important substrates in organic synthesis.[13] Electron-rich aromatic alkynes offered excellent yields (99 and 96%) of the corresponding vinylsilanes (83:17, *E*:*α*) (entries 11, 12). 4-fluorophenylacetylene gave 92% yield with 81:19 ratio of *E*:*α* isomers (entry 13). Similar to Et_3SiH, the $(EtO)_3SiH$ also resulted in high selectivity (>94%) and excellent yields (>96%) with bulky substrates (entries 14 - 16). Aliphatic alkynes ethynylcyclopropane, 4-phenyl-1-butyne and 1-heptyne gave more than 87% yields with good *E*-selectivity (82 - 87%) (entries 17 - 19). In addition, diynes 1,3-diethynylbenzene and 1,7-dioctyne were also employed with 2 equivalents of $(EtO)_3SiH$ which showed 80% (80:20, *E*:*α*) and 78% (82:18, *E*:*α*) yields of the corresponding *bis*-vinylsilanes, respectively (entries 20, 21).

Table 2: Scope of complex **1** catalyzed hydrosilylation of terminal alkynes.[a]

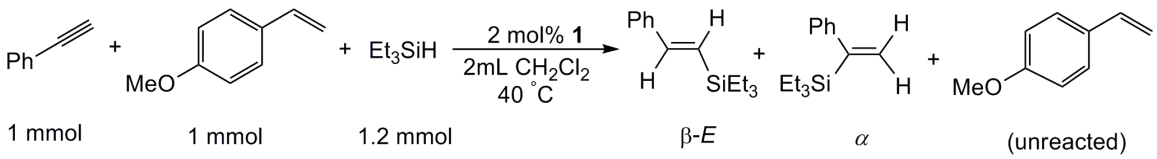


Entry	Substrate	Silane	Yield (%)[b]	*E*/*α* ratio[b]
1		Et_3SiH	97	85/15
2		Et_3SiH	95	86/14
3		Et_3SiH	96	86/14
4		Et_3SiH	89	80/20
5		Et_3SiH	87	80/20
6		Et_3SiH	97	99/1
7		Et_3SiH	85	86/14
8		Et_3SiH	89	83/17

9		Et_3SiH	97	94/6
10		$(EtO)_3SiH$	98	86/14
11		$(EtO)_3SiH$	99	83/17
12		$(EtO)_3SiH$	96	83/17
13		$(EtO)_3SiH$	92	81/19
14[d]		$(EtO)_3SiH$	97	94/6
15		$(EtO)_3SiH$	98	97/3
16		$(EtO)_3SiH$	96	95/5
17		$(EtO)_3SiH$	92	87/13
18		$(EtO)_3SiH$	87	82/18
19		$(EtO)_3SiH$	89	83/17
20		$(EtO)_3SiH$	80	80/20
21		$(EtO)_3SiH$	78	82/18

[a]Reaction conditions: alkyne:silane:**1** = 1:1.2:0.02 mmol, in CH_2Cl_2, 40 °C, 6 h. [b]Yields and *E/α* ratio are determined by GC–MS using mesitylene as an internal standard. [c]Reaction time 10 h. [d]2 mmol silane.

To evaluate the chemoselectivity of the catalyst, a competitive experiment was performed with equimolar mixture of phenylacetylene and *p*-methoxystyrene under the optimized reaction conditions (Scheme 4). The silane addition product styryltriethylsilane was obtained as expected, but the styrene remains unreacted. This experiment confirms that the hydrosilylation of alkynes is chemoselectively achieved in the presence of alkenes.



Scheme 4. Chemoselectivity experiment.

2.3 Proposed Mechanism

The progress of the reaction involving phenylacetylene and Et_3SiH was monitored by GC-MS (Figure 2). The substrate is gradually consumed with the appearance of the *E*-vinylsilane. A small amount of *α*-vinylsilane was also observed but the *Z*-isomer was not identified in the reaction. Therefore, the possibility of a *Z* to *E* isomerization could be ruled out.

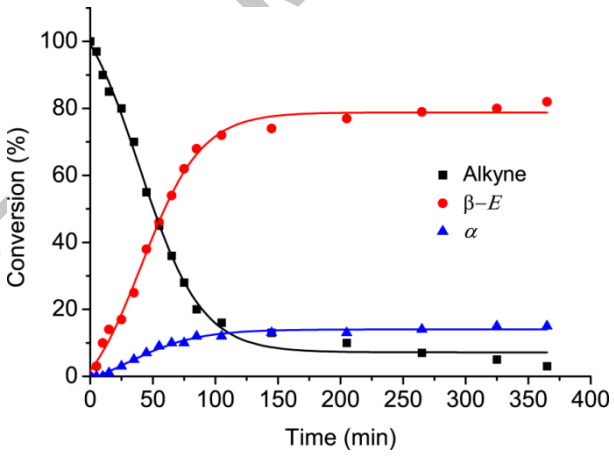
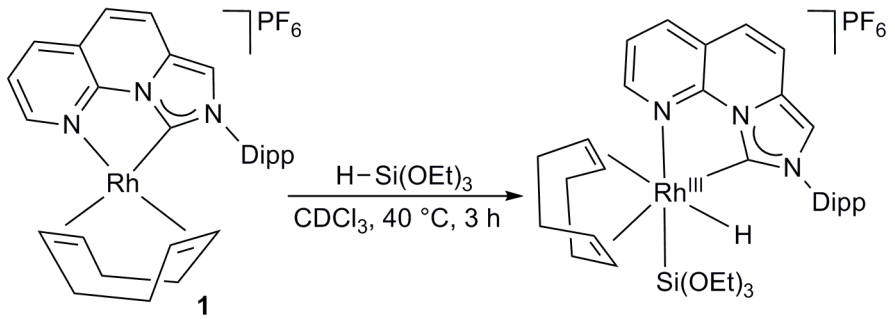


Figure 2. Time-conversion profile of hydrosilylation of phenylacetylene.

To garner further insight into the reaction mechanism, a 4:1 mixture of phenylacetylene and **1** in $CDCl_3$ was heated inside a screw-cap NMR tube for 3 h. The ^1H NMR signals corresponding to **1** and phenylacetylene remained unchanged,

indicating a Chalk-Harrod mechanism that is initiated by silane reaction with the catalyst.[28,37] Next, a $CDCl_3$ solution of **1** and $HSi(OEt)_3$ (1:4 molar ratio) was treated at 40 °C for 3 h and the reaction was followed by ^1H NMR spectroscopy (Scheme 5). At room temperature, a broad signal for Rh-H appeared at δ –17.71 ppm. However, a clear doublet was observed with *J* = 30.9 Hz at lower temperature (–30 °C) (Figure S4). This supports the plausible intermediacy of a mononuclear Rh-H species **A** in the catalytic cycle (Scheme 6).[22,38] The ^1H NMR spectrum further reveals one set of protons for COD and NHC ligand in 1:1 ratio (Figure S4). Six signals corresponding to nine aromatic ligand protons appear in the range of 7.25 – 8.42 ppm. Two doublets are observed at δ 1.33 ppm (*J* = 6.9 Hz) and 1.10 ppm (*J* = 6.9 Hz) for the chemically non-equivalent isopropyl methyl protons (–*CHMe*$_2$) of the Dipp unit. In addition, multiplets in the range δ 2.41–2.49 ppm are assigned for two non-equivalent isopropyl -*CH* protons. The methylene and methyl protons of the metal-coordinated silyl group appear at δ 3.70 ppm (*J* = 6.9 Hz) and δ 1.22 ppm (*J* = 6.9 Hz) respectively. Eight COD methylene protons appear as four multiplets in the range 1.93 – 2.37 ppm whereas vinylic protons resonate at δ 4.27 and 5.24 ppm. ESI-MS analysis of the same mixture in methanol showed a signal at *m/z* = 628.2420 (*z* = 1) which is assigned for $[Rh(L)H(Si(OEt)_3)(CH_3OH)]^+$ (Figure S5).



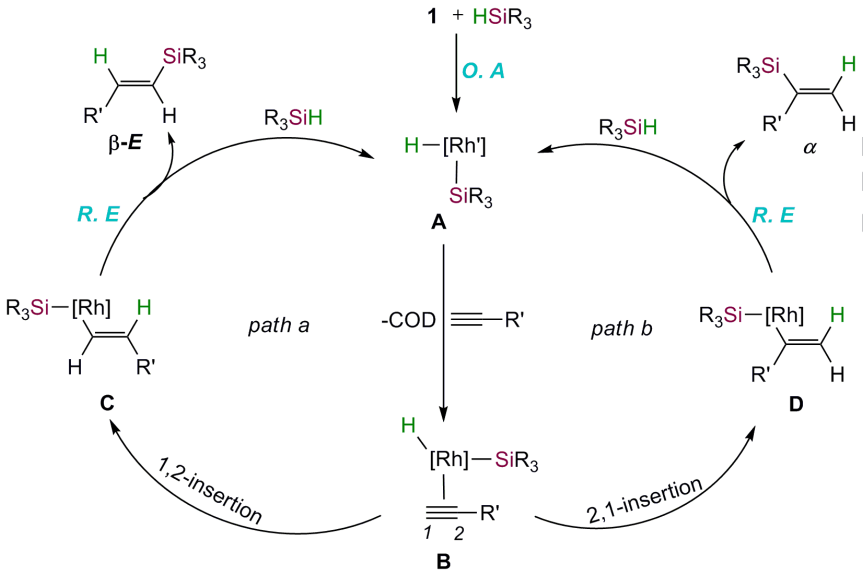
Scheme 5. Oxidative addition of $HSi(OEt)_3$ to **1**.

On close examination, the intensity of the Rh-H signal was found to be low relative to the ligand protons in both $CDCl_3$ and CD_2Cl_2. Literature reports reveal that the hydrido-rhodium(III) complexes exhibit low stability in the chlorinated solvents and the hydride is exchanged by the chloride.[39] We attribute the loss of Rh-H signal intensity to the hydride-chloride exchange in chlorinated solvents. To circumvent this problem, we performed the same reaction in non-chlorinated solvent CD_3CN,[40] however, no Rh-H signal was observed. Different silanes were used and the reaction conditions were varied, but catalyst **1** failed to produce the Rh-H intermediate in CD_3CN.

A GC-MS analysis of the reaction mixture of catalyst **1** and silane did not reveal free COD or its hydrogenated product. ^{1}H NMR spectrum of the silyl-rhodium(III)-hydride intermediate indicated COD coordination to the metal. The weak coordination of COD to the high-valent Rh(III) is evident from the ESI-MS which shows loss of COD in methanol. It is conceivable that COD would be readily replaced by coordinating solvents such as acetonitriles.[22] In the absence of a coordinating solvent, the COD molecule remains bound to the metal in **A**. An immediate product formation was detected by ^{1}H NMR on addition of phenylacetylene to **A**, suggesting the viability of the catalytic cycle shown in Scheme 6.

The first step is the oxidative addition of the silane to the Rh center to generate the hydrido-silyl-Rh species **A**. The COD is then extruded from the metal centre to pave the way for alkyne coordination. The resulting intermediate **B** follows two pathways of alkyne migratory insertion into the Rh-H bond. An 1,2-insertion followed by reductive elimination directs *E*-vinylsilanes (*path a)*, while in *path b*, *α*-isomer is formed through reductive elimination following a 2,1-insertion of alkyne into the Rh-H bond. In the case

of bulky substrates, the formation of *α*-isomer is decreased due to steric hindrance between the substituents on the alkyne and the silyl group.



Scheme 6. Proposed pathways for Chalk-Harrod mechanism of **1**-catalyzed alkyne hydrosilylation. [Rh'] = $[Rh(L)(COD)]PF_6$, [Rh] = $[Rh(L)]PF_6$.

An alternate alkyne insertion into the Rh-Si bond[29,30] could give rise to β-(*Z*) along with β-(*E*) and *α*-isomers (Figure S6). However, β-(*Z*) isomer was not observed in the reaction. Furthermore, the bulky alkynes afforded *E*-isomers as the major products with very little to no *α*-isomers. These are inconsistent with a pathway that involves alkyne insertion into the Rh-Si bond and thus discarded.

3. Concluding Remarks

This work examines the effect of ligand rigidity for the Rh(I) catalyzed hydrosilylation of terminal alkynes. A Rh(I) complex bearing an annulated π-conjugated chelate ligand affords vinylsilane derivatives for a variety of terminal alkynes with good to excellent yields and high β-(*E*) selectivity. Although the *α*-isomers are invariably obtained up to

20% of the overall products, polymerization and dehydrosilylation reactions were avoided. The β-(*E*) selectivity is excellent for bulky alkynes. Further, chemoselective hydrosilylation of alkyne was achieved in the presence of alkene. The ligand rigidity appears to play a crucial role for the β-(*E*) selectivity.

4. Experimental

4.1 Instrumentation

All reactions with the metal complex were carried out under an atmosphere of purified nitrogen using standard Schlenk–vessel and vacuum line techniques. Glasswares were flame–dried under vacuum prior to use. ^{1}H and ^{13}C NMR spectra were obtained on JEOL JNM–LA 400 MHz and JEOL JNM–LA 500 MHz spectrometers. ^{1}H NMR chemical shifts were referenced to the residual hydrogen signal of the deuterated solvents. The chemical shift is given as dimensionless δ value and frequency referenced relative to TMS for ^{1}H and ^{13}C NMR spectroscopy. Elemental analyses were performed on a Thermoquest EA1110 CHNS/O analyzer. The crystallized compound was powdered, washed several times with dry petroleum ether, and dried in vacuum for at least 48 h prior to elemental analyses. ESI–MS were recorded on a Waters Micromass Quattro Micro triple–quadrupole mass spectrometer. The GC-MS experiments were performed by using an Agilent 7890A GC and 5975C MS system.

4.2 Materials

All solvents were purified and dried by conventional methods prior to use. $RhCl_3.xH_2O$ was purchased from Arora Matthey, India. All other chemicals were purchased from Sigma–Aldrich. The ligand precursor $[LH]PF_6$,[34] $[AgL_2]PF_6$[34] and $[Rh(COD)(\mu\text{-}Cl)]_2$[41] were prepared according to the literature procedures.

*4.3 Synthesis of **1***

In a flame dried schlenk flask, $[Rh(COD)(\mu\text{-}Cl)]_2$ (0.032 g, 0.06 mmol) was added to a DCM solution of $[AgL_2]PF_6$ (0.060 g, 0.06 mmol). An immediate color change from yellow to red was observed. $AgPF_6$ (0.016 g, 0.06 mmol) was added to the reaction mixture and stirred for 2 h under the exclusion of light in N_2 atmosphere. The resulting suspension was filtered through a small pad of celite to remove the precipitated silver halide. The filtrate was concentrated under reduced pressure followed by the addition of 15 mL of petroleum ether with stirring to induce precipitation. Repeated washing followed by prolonged drying in vacuum provided **1** as an orange solid. Crystals suitable for X-ray diffraction were grown by layering diethyl ether over a concentrated DCM solution of the compound inside an 8 mm o.d. vacuum sealed glass tube. Yield: 85%; ESI–MS, *m/z*=540.1867 (*z* = 1) for $[\mathbf{1} - PF_6]^+$; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.42 (d, *J* = 7.1 Hz, 1H, NP), 8.06 (s, 1H, Im), 7.77 (dd, *J* = 7.9 Hz, 5.4 Hz, 1H, NP), 7.56 - 7.52 (m, 2H, NP), 7.45 (d, *J* = 9.6 Hz, 1H, NP), 7.32 - 7.29 (m, 3H, Ar), 5.24 (br, 2H, CH═ COD), 4.01 (br, 2H, CH═ COD), 2.48-2.40 (m, 2H, $CH_{isopropyl}$), 2.37-2.30 (m, 2H, CHH COD), 2.25-2.18 (m, 2H, COD), 2.07 - 2.02 (m, 2H, COD), 1.99 - 1.93 (m, 2H, COD), 1.31 (d, *J* = 6.8 Hz, 6H, $Me_{isopropyl}$), 1.08 (d, *J* = 6.8 Hz, 6H, $Me_{isopropyl}$); ^{13}C NMR (125 MHz, $CDCl_3$): 162.3 (d, C-2, NHC), 147.7 (NCN, NP), 144.9 (CH, NP), 140.7 (NC_{Ar}), 133.4 (CH, NP), 131.6 (CH, NP), 128.6 (C, Im), 124.8 (CH, NP), 124.5 (CH, Ar), 124.2 (CH, Ar), 120.6 (CH, Ar), 118.4 (CH, Im), 118.1(C,NP), 95.8 (d, CH═ COD), 77.8 (d, CH═ COD), 32.1 (CH_2, COD), 28.4 ($CH_{isopropyl}$), 22.9 (CH_2, COD), 22.5 (Me); Anal. Calcd for $RhC_{30}H_{35}N_3PF_6$: C, 66.64; H, 6.52; N, 7.77. Found: C, 66.43; H, 6.28; N, 7.45.

4.4 Procedure for the generation of metal hydride intermediate

A screw-cap NMR tube was charged with a solution of complex **1** (0.020 g, 0.03 mmol) and $(EtO)_3SiH$ (21 µL, 0.12 mmol) in $CDCl_3$ (0.5 mL). The reaction mixture was heated to 40 °C for 3 h. A plausible metal-hydride intermediate was identified by ^1H-NMR spectroscopy.

4.5 General procedure for catalytic alkyne hydrosilylation

An oven-dried reaction vessel was charged with **1** (0.02 mmol), alkyne (1 mmol), silane (1.2 mmol) and mesitylene (1 mmol) in 2 mL of DCM and heated at 40 °C for 6 h. The reaction mixture was cooled, diluted with ethyl acetate and passed through a short column of silica for GC–MS analysis to determine the yield and the *E*/*α* ratio. For NMR characterization of the product, the solvent was evaporated under vacuum and the residue was purified by column chromatography on silica gel (by petroleum ether/ethyl acetate).

Acknowledgment

We thank the anonymous reviewers for valuable insights. Financial supports from the Department of Atomic Energy and Indo-French Centre for the Promotion of Advanced Research are gratefully appreciated. J.K.B. thanks the SERB, DST for the J C Bose fellowship. A.T. and S.Y. thank the UGC India for fellowship. C.R. thanks IITK for a post-doctoral fellowship.

References

[1] For Selected reviews on N-heterocyclic carbenes, see: (a) M. N. Hopkinson, C. Richter, M. Schedler, F. Glorius, Nature, 510 (2014) 485-496; (b) S. P. Nolan, N-Heterocyclic Carbenes in Synthesis, Wiley-VCH, Weimheim, Germany, 2006; (c) F. E. Hahn, M. C. Jahnke, Angew. Chem. Int. Ed., 47 (2008) 3122-3172; (d) R. H. Crabtree, J. Organomet. Chem., 690 (2005) 5451-5471; (e) H. Jacobsen, A. Correa, A. Poater, C. Costabile, L. Cavallo, Coord. Chem. Rev., 253 (2009) 687-703; (f) D. Bourissou, O. Guerret, F. P. Gabbai, G. Bertrand, Chem. Rev., 100 (2000) 39-92; (g) K. Y. Wan, F. Roelfes, A. J. Lough, F. E.

Hahn, R. H. Morris, Organometallics, 37 (2018) 491-504; (h) M. C. Jahnke, F. E. Hahn, Coord. Chem. Rev., 293 (2015) 95-115; (i) H. V. Huynh, Chem. Rev., 118 (2018) 9457-9492.

[2] For selected reviews on metal-NHC catalyzed organic transformations, see: (a) S. D. González, N. Marion, S. P. Nolan, Chem. Rev., 109 (2009) 3612-3676; (b) E. Peris, Chem. Rev., 118 (2018) 9988-10031; (c) F. Glorius, N-Heterocyclic Carbenes in Transition Metal Catalysis, in: Topics in Organometallic Chemistry, Ed. Springer, Verlag Berlin, 2007; (d) V. Dragutan, I. Dragutan, L. Delaude, A. Demonceau, Coord. Chem. Rev., 251 (2007) 765-794; (e) S. Gaillard, C. S. J. Cazin, S. P. Nolan, Acc. Chem. Res., 45 (2012) 778-787; (f) Á. Vivancos, C. Segarra, M. Albrecht, Chem. Rev., 118 (2018) 9493-9586; (g) L. Mercs, M. Albrecht, Chem. Soc. Rev., 39 (2010) 1903-1912; (h) H. V. Huynh, The Organometallic Chemistry of N-heterocyclic Carbenes. John Willey & Sons Ltd., The Atrium, Southern Gate, Chichester, West Sussex, PO19 8SQ, United Kingdom, 2017; (i) W. A. Herrmann, Angew. Chem. Int. Ed., 41 (2002) 1290-1309.

[3] For metal-NHC catalyzed oxidation reactions, see: (a) M. M. Konnick, I. A. Guzei, S. S. Stahl, J. Am. Chem. Soc., 126 (2004) 10212-10213; (b) M. J. Schultz, S. S. Hamilton, D. R. Jensen, M. S. Sigman, J. Org. Chem., 70, (2005) 3343-3352; (c) M. Poyatos, J. A. Mata, E. Falomir, R. H. Crabtree, E. Peris, Organometallics, 22 (2003) 1110-1114; (d) P. Daw, R. Petakamsetty, A. Sarbajna, S. Laha, R. Ramapanicker, J. K. Bera, J. Am. Chem. Soc., 136 (2014) 13987-13990.

[4] (a) W. S. Knowles, Angew. Chem. Int. Ed., 41 (2002) 1998-2007; (b) R. Noyori, Angew. Chem. Int. Ed., 41 (2002) 2008-2022; (c) M. T. Powell, D. R. Hou, M. C. Perry, X. Cui, K. Burgess, J. Am. Chem. Soc., 123 (2001) 8878-8879; (d) J. W. Sprenger, J. Wassenaaar, N. D. Clement, K. J. Cavell, C. J. Elsevier, Angew. Chem. Int. Ed., 44 (2005) 2026-2029; (e) D. Baskakov, W. A. Herrmann, E. Herdtweck, S. D. Hoffmann, Organometallics, 26 (2007) 626-632; (f) D. Chen, V. Banphavichit, J. Reibenspies, K. Burgess, Organometallics, 26 (2007) 855-859; (g) K. D. Camm, N. M. Castro, Y. Liu, P. Czechura, J. L. Snelgrove, D. E. Fogg, J. Am. Chem. Soc., 129 (2007) 4168-4169.

[5] For chelated metal-NHC complexes, see: (a) J. A. Mata, M. Poyatos, E. Peris, Coord. Chem. Rev., 251 (2007) 841-859; (b) M. Bierenstiel, E. D. Cross, Coord. Chem. Rev., 255 (2011) 574-590; (c) A. R. Naziruddin, C.-S. Zhuang, W.-J. Lin, W.-S. Hwang, Dalton Trans., 43 (2014) 5335-5342; (d) Z. Xi, X. Zhang, W. Chen, S. Fu, D. Wang, Organometallics, 26 (2007) 6636-6642; (e) V. Diachenko, M. J. Page, M. R. D. Gatus, M. Bhadbhade, B. Messerle, Organometallics, 34 (2015) 4543-4552; (f) A. A. Danopoulos, N. Tsoureas, S. A. Macgregor, C. Smith, Organometallics 26 (2007) 253-263; (g) E. Mas-Marzá, M. Sanaú, E. Peris, J. Organomet. Chem., 690 (2005) 5576-5580; (h) S. Winston, N. Stylianides, A. A. D. Tulloch, J. A. Wright, A. A. Danopoulos,. Polyhedron, 23 (2004) 2813-2820; (i) M. C. Cassani, M. A. Brucka, C. Femoni, M. Mancinelli, A. Mazzanti, R. Mazzoni, G. Solinas, New J. Chem., 38 (2014) 1768-1779; (j) G. Mancano, M. J. Page, M. Bhadbhade, B. A. Messerle, Inorg. Chem., 53 (2014) 10159-10170.

[6] (a) A. Sinha, S. M. W. Rahaman, M. Sarkar, B. Saha, P. Daw, J. K. Bera, Inorg. Chem., 48 (2009) 11114-11122; (b) P. Daw, A. Sinha, S. W. M. Rahaman, S. Dinda, J. K. Bera, Organometallics, 31 (2012) 3790-3797.

[7] E. Mas-Marzá, M. Sanaú, E. Peris, Inorg. Chem., 44 (2005) 9961-9967.

[8] Selected examples: (a) D. J. Nelson, S. P. Nolan, Chem. Soc. Rev., 42 (2013) 6723-6753; (b) M. Alcarazo, S. J. Roseblade, A. R. Cowley, R. Fernandez, J. M. Brown, J. M. Lassaletta, J. Am. Chem. Soc., 127 (2005) 3290-3291; (c) G. Song, Y. Zhang, X. Li, Organometallics, 27 (2008) 1936-1943; (d) V. Gierz, C. M. Mössmer, D. Künz, Organometallics, 31 (2012) 739-747; (e) A. K. Phukan, A. K. Guha, S. Sarmah, R. D. Dewhurst, J. Org. Chem.,78 (2013) 11032-11039; (f) M. D. Sanderson, J. W. Kamplain, C. W. Bielawski, J. Am. Chem. Soc., 128 (2006) 16514-16515; (g) C. H. Suresh, M. J. Ajitha, J. Org. Chem., 78 (2013) 3918-3924; (h) S. R. Yetra, T. Kaicharla, S. S. Kunte, R. G. Gonnade, A. T. Biju, Org. Lett., 15 (2014) 5202-5205; (i) A. J. Arduengo, L. I. Iconaru, Dalton Trans., (2009), 6903-6914.

[9] (a) O. Schuster, L. Yang, H. G. Raubenheimer, M. Albrecht, Chem. Rev., 109 (2009) 3445-3478; (b) P. L. Arnold, S. Pearson, Coord. Chem. Rev., 251 (2007) 596–609; (c) R. H. Crabtree, Coord. Chem. Rev., 257 (2013) 755–766.

[10] (a) K. Tamao, N. Ishida, T. Tanaka, M. Kumada, Organometallics, 2 (1983) 1694-1696; (b) I. Fleming, R. Henning and H. Plaut, J. Chem. Soc., Chem. Commun., (1984) 29-31; (c) S. E. Denmark, C. S. Regens, Acc. Chem. Res., 41 (2008) 1486-1499; (d) A. K. Roy, A Review of Recent Progress in Catalyzed Homogeneous Hydrosilation (Hydrosilylation), in: Adv. Organomet. Chem.; Robert West, A. F. H., Mark, J. F., Eds.; Academic Press: New York, 2007, 55, 1-59; (e) C. Yann, W. Christophe, B. K. Lydia, D. J. Pierre, A. N. Francine, M. Christophe, Journal of Molecular Catalysis A: Chemical, 423, (2016) 256-263.

[11] a) P. Somfai, B seashore-ludlow, Organosilicon reagent: Vinyl-, Alkynyl-, and arylsilanes, in: Comprehensive Organic Synthesis Ed. Springer, Amsterdam, Netherlands, 2014; (b) B. Marciniec, M. Majchrzak, W. Prukała, M. Kubicki, D. Chadyniak, J. org. Chem., 70, (2005) 8550-8555; (c) T. Bunlaksananusorn, A. L. Rodriguez, P. Knochel, Chem. Commun. (2001), 745-746.

[12] For selected examples of cross coupling reactions, see: (a) T. Hiyama, in: F. Diederich, P. J. Stang (Eds.), Metal-Catalyzed Crosscoupling Reaction, Wiley-VCH, New York, 1998, pp. 421-453; (b) C. J. Handy, A. S. Manoso, W. T. McElroy, W. M. Seganish, P. DeShong, Tetrahedron, 61 (2005) 12201-12225; (c) T. Hiyama, E. Shirakawa, Top. Curr. Chem., 219 (2002) 61-85; (d) T. Komiyama, Y. Minami, T. Hiyama, ACS. Catal., 7 (2017) 631-651.

[13] (a) S. E. Denmark, M. H. Ober, Aldrichimica Acta, 36 (2003) 75-85; (b) S. E. Denmark, R. F. Sweis, Acc. Chem. Res. 35 (2002) 835-846.

[14] E. Pouget, J. Tonnar, P. Lucas, P. L. Desmazes, F. Ganachaud, B. Boutevin, Chem. Rev., 110 (2010) 1233-1277.

[15] For selected examples, see: (a) L. N. Lewis, K. G. Sy, G. L. Bryant, P. E. Donahue, Organometallics 10 (1991) 3750-3759; (b) J. P. Murphy, J. L. Spencer, G. Procter, Tetrahedron Lett., 31 (1990) 1051-

1054; (c) T. Kyoko, Tetrahedron Lett., 34 (1993) 8263-8266; (d) S. E. Denmark, Z. Wang, Org. Lett., 3 (2001) 1073-1076; (e) K. Itami, K. Mitsudo, A. Nishino, J. Yoshida, J. Org. Chem., 67 (2002) 2645-2652; (f) M. Blug, X. -F.Le Goff, N. Mezailles, P. Le Floch, Organometallics, 28 (2009) 2360-2362; (g) W. Wu, C. -J. Li, Chem. Commun., (2003) 1668-1669; (h) H. Aneetha, W. Wu, J. G. Verkade, Organometallics, 24 (2005) 2590-2596; (i) G. De Bo, G. Berthon-Gelloz, B. Tinant, I. É. Markó, Organometallics, 25 (2006) 1881-1890; (j) G. Berthon-Gelloz, J. -M. Schumers, G. De Bo, I. É. Markó, J. Org. Chem., 73 (2008) 4190-4197; (j) G. F. Silbestri, J. C. Flores, E. de Jesús, Organometallics, 31 (2012) 3355-3360; (k) L. Ortega-Moreno, R. Peloso, C. Maya, A. Suarez, É. Carmona, Chem. Commun., 51 (2015) 17008-17011; (l) S. Dierick, E. Vercruysse, G. BerthonGelloz, I. É. Markó, Chem. Eur. J., 21 (2015) 17073-17078.

[16] M. P. Doyle, K. G. High, C. L. Nesloney, T. W. Clayton, J. Lin, Organometallics, 10 (1991) 1225−1226.

[17] For selective synthesis of β-(*Z*)-vinylsilane with Ru catalysts, see; (a) M. A. Esteruelas, J. Herrero, L. A. Oro, Organometallics, 12 (1993) 2377-2379; (b) Y. Na, S. Chang, Org. Lett., 2 (2000) 1887-1889; (c) M. Nagao, K. Asano, K. Umeda, H. Katayama, F. Ozawa, J. Org. Chem. 70 (2005) 10511-10514; (d) S. V. Maifeld, M. N. Tran, D. Lee, Tetrahedron Lett., 46 (2005) 105-108; (e) R. Gao, D. R. Pahls, T. R. Cundari, C. S. Yi, Organometallics, 33 (2014) 6937-6944; (f) C. Conifer, C. Gunanathan, T. Rinesch, M. Hölscher, W. Leitner, Eur. J. Inorg. Chem., 2015, (2015) 333-339.

[18] For selective synthesis of *α*-vinylsilane with Ru catalysts, see: (a) B. M. Trost, Z. T. Ball, J. Am. Chem. Soc., 123 (2001) 12726-12727; (b) Y. Kawanami, Y. Sonoda, T. Mori, K. Yamamoto, Org. Lett., 4 (2002) 2825-2827; (c) B. M. Trost, Z. T. Ball, J. Am. Chem. Soc., 127 (2005) 17644-17655.

[19] H. Katayama, K. Taniguchi, M. Kobayashi, T. Sagawa, T. Minami, F. Ozawa, J. Organomet. Chem., 645 (2002) 192-200.

[20] I. Ojima, N. Clos, R. J. Donovan, P. Ingallina, Organometallics, 9 (1990) 3127-3133.

[21] (a) G. T. S. Andavan, E. B. Bauer, C. S. Letko, T. K. Hollis, F. S. Tham, J. Organomet. Chem., 690 (2005) 5938-5947; (b) G. Rivera, O. Elizalde, G. Roa, I. Montiel, S. Berne's, J. Organomet. Chem., 699 (2012) 82-86; (c) A. J. Huckaba, T. K. Hollis, T. O. Howell, H. U. Valle, Y. Wu, Organometallics, 32 (2013) 63-69; (d) M. F. Lappert, R. K. Maskell, J. Organomet. Chem., 264 (1984) 217-228; (e) J. Y. Zeng, M. –H. Hsieh, H. M. Lee, J. Organomet. Chem., 690 (2005) 5662-5671; (f) M. Poyatos, E. Mas-Marzá, J. A. Mata, M. Sanaú, E. Peris, Eur. J. Inorg. Chem., 2003 (2003) 1215-1221; (g) J. E. Hill, T. A. Nile, J. Organomet. Chem., 137 (1977) 293-300; (h) E. Mas-Marzá, M. Poyatos, M. Sanaú, E. Peris, Inorg. Chem., 43 (2004) 2213-2219; (i) M. Poyatos, A. Maisse-Francois, S. B. Laponnaz, L. H. Gade, Organometallics, 25 (2006) 2634-2641; (j) M. Iglesias, M. A. Lavrijsen, P. J. S. Miguel, F. J. Fernandez-Álvarez, J. J. P. Torrente, L. A. Oro, Adv. Synth. Catal., 357 (2015) 350-354.

[22] J. P. Morales-Ceron, P. Lara, J. Lopez-Serrano, L. L. Santos, V. Salazaŕ, E. Álvarez, A. Suárez, Organometallics, 36 (2017) 2460-2469.

[23] D. Field, A. J. Ward, J. Organomet. Chem., 681 (2003) 91-97.

[24] R. Takeuchi, S. Nitta, D. Watanabe, J. Org. Chem., 60 (1995) 3045-3051.

[25] (a) M. A. Esteruelas, M. Olivan, L. A. Oro, Organometallics, 15 (1996) 814-822; (b) C. Vicent, M. Viciano, E. Mas-Marza, M. Sanau, E. Peris, Organometallics, 25 (2006) 3713-3720.

[26] M. V. Jiménez, J. J. P. Torrente, M. I. Bartolomé, V. Gierz, F. J. Lahoz, L. A. Oro, Organometallics, 27 (2008), 224-234.

[27] L. Busetto, M. C. Cassani, C. Femoni, M. Mancinelli, A. Mazzanti, R. Mazzoni, G. Solinas, Organometallics, 30 (2011) 5258-5272.

[28] B. M. Trost, Z. T. Ball, Synthesis, 2005 (2005) 853-887.

[29] R. S. Tanke, R. H. Crabtree, J. Am. Chem. Soc., 112 (1990) 7984-7989.

[30] C. H. Jun, R. H. Crabtree, J. Organomet. Chem., 447 (1993) 177-187.

[31] M. Viciano, E. Mas-Marzá, M. Sanaú, E. Peris, Organometallics, 25 (2006) 3063−3069.

[32] (a) A. Sato, H. Kinoshita, H. Shinokubo, K. Oshima, Org. Lett., 6 (2004) 2217-2220; (b) A. Mori, E. Takahisa, Y. Yamamura, T. Kato, A. P. Mudalige, H. Kajiro, K. Hirabayashi, Y. Nishihara, T. Hiyama, Organometallics, 23 (2004) 1755-1765.

[33] J. W. Faller, D. G. Alliesi, Organometallics, 21 (2002) 1743-1746.

[34] M. Kriechbaum, M. List, R. J. F. Berger, M. Patzschke, U. Monkowius, Chem. Eur. J., 18 (2012) 5506-5509.

[35] C. Pettinari, F. Marchetti, A. Cingolani, G. Bianchini, A. Drozdov, V. Vertlib, S. Troyanov, J. Organomet. Chem., 651 (2002) 5-14.

[36] S. Ding, Li-J. Song, L. Wa Chung, X. Zhang, J. Sun, Y.-Dong Wu, J. Am. Chem. Soc., 135 (2013) 13835-13842.

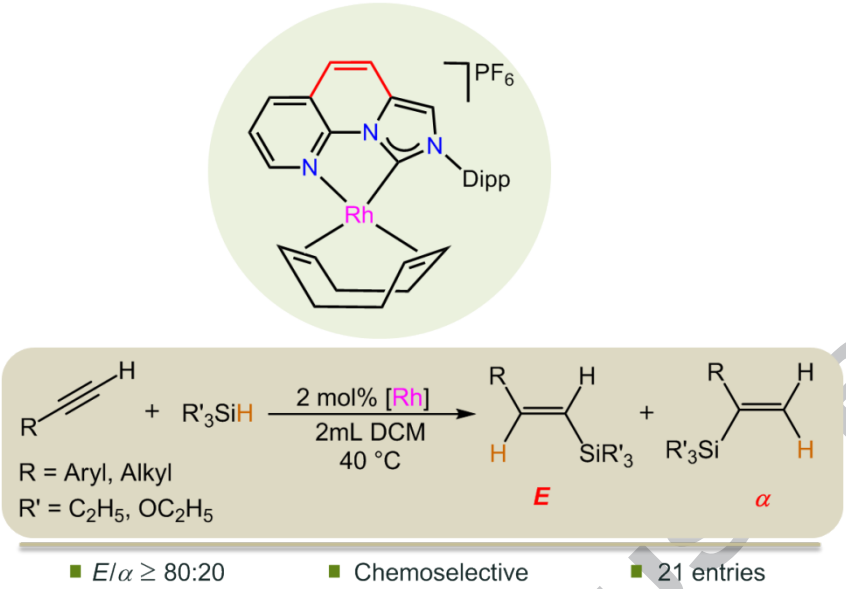
[37] A. J. Chalk, J. F. Harrod, J. Am. Chem. Soc., 87 (1965) 16-21.

[38] A. Bakac, L. N. Thomas, Inorg. Chem., 35 (1996) 5880-5884.

[39] (a) S. Azpeitia, M. Barquín, C. Mendicute-Fierro, M. A. Huertos, A. Rodríguez-Diéguez, J. M. Seco, E. S. Sebastian, L. Ibarluceaa, M. A. Garralda, Dalton trans., 48 (2019) 3300-3313; (b) V. S. Nacianceno, S. Azpeitia, L. Ibarlucea, C. Mendicute-Fierro, A. Rodríguez-Diéguez, J. M. Seco, E. S. Sebastiana, M. A. Garralda, Dalton trans., 44 (2015) 13141-13155; (c) M. A. Garralda, R. Hernández, L. Ibarlucea, E. Pinilla, M. R. Torres, M. Zarandona, Organometallics, 26 (2007) 1031-1038; (d) M. J. Ingleson, S. K. Brayshaw, M. F. Mahon, G. D. Ruggiero, A. S. Weller, Inorg. Chem., 44 (2005) 3162-3171; (e) C. Tejel, M. A. Ciriano, M. Millaruelo, J. A. López, F. J. Lahoz, L. A. Oro, Inorg. Chem., 42 (2003) 4750-4758.

[40] Suarez's catalyst showed full-intensity signal for the corresponding Rh-H complex in CD_3CN. See, reference 22.

[41] G. Giordano, R. H. Crabtree, Inorg. Synth., 28 (1990) 90.



A Rh(I) complex supported by an annulated π-conjugated imidazo-naphthyridine based N-heterocyclic carbene ligand featuring a Dipp attachment is an excellent catalyst for *E*-selective hydrosilylation of a range of terminal alkynes.