

Rhodium(I) Complexes with Hemilabile N-Heterocyclic Carbenes: Efficient Alkyne Hydrosilylation Catalysts.

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Abstract

A series of alkylammonium-imidazolium chloride salts $[\text{RImH}(\text{CH}_2)_n\text{NMe}_2]\text{Cl}\cdot\text{HCl}$ ($\text{R} = \text{Me}, t\text{-Bu}, \text{Mes}, n = 2, 3$) have been prepared by alkylation of 1-substituted imidazole compounds with the corresponding chloro-alkyl-dimethylamine hydrochloride. These salts are precursors for the synthesis of a library of rhodium (I) complexes containing amino-alkyl functionalized N-heterocyclic carbene (NHC) ligands with hemilabile character by varying the substituent on the heterocyclic ring and the length of the linker with the dimethylamino moiety. The monodeprotonation of alkylammonium-imidazolium salts with NaH in the presence of $[\{\text{Rh}(\mu\text{-Cl})(\text{cod})\}_2]$ gave the amino-imidazolium salts $[\text{RImH}(\text{CH}_2)_n\text{NMe}_2][\text{RhCl}_2(\text{cod})]$. Further deprotonation with NaH under non anhydrous conditions gave the neutral complexes $[\text{RhCl}(\text{cod})(\text{RIm}(\text{CH}_2)_n\text{NMe}_2)]$ in good yields. The abstraction of the chloro ligand by silver salts rendered the cationic complexes $[\text{Rh}(\text{cod})(\kappa^2\text{C},\text{N-RIm}(\text{CH}_2)_3\text{NMe}_2)][\text{BF}_4]$ ($\text{R} = \text{Me}, \text{Mes}$) by coordination of the NMe_2 fragment of the sidearm of the functionalized NHC ligands. The catalytic activity of the rhodium complexes in the hydrosilylation of terminal alkynes using HSiMe_2Ph has been investigated with $\text{Ph-C}\equiv\text{CH}$, $t\text{-Bu-C}\equiv\text{CH}$, $n\text{-Bu-C}\equiv\text{CH}$, and $\text{Et}_3\text{Si-C}\equiv\text{CH}$ as substrates. Higher activities were achieved using neutral complexes having small substituents at the heterocyclic ring ($\text{R} = \text{Me}$). Excellent selectivities in the β -(*Z*)-vinylsilane isomer were found in the hydrosilylation of 1-hexyne and predominantly the β -(*E*) and α -bis(silyl)alkene isomers were obtained in the hydrosilylation of triethylsilylacetylene.

Introduction

N-Heterocyclic carbenes (NHC) have attracted considerable attention as a new class of ligands over the last few years.¹ Their bonding characteristics are comparable to the well studied tertiary phosphines, which are ubiquitous in their role as ligands in transition metal catalyzed processes. Nevertheless, it has become apparent that there are substantial differences between the two families of ligands: NHC are more electron donating and sterically more demanding than the most basic/bulky phosphane ligands.² NHC ligands have found widespread application in homogenous catalysis for processes as diverse as C-C coupling, olefin metathesis, hydrosilylation, or carbon monoxide/ethylene copolymerization.³

Ligand lability is a feature of many efficient catalysts, however this lability can also provide a route for the catalyst decomposition. In order to have easily accessible coordination sites and to protect the active catalytic site a number of hybrid hemilabile ligands, which can potentially provide a dynamic “on and off” chelating effect for the metal complex during catalysis, have been designed.⁴ Hybrid P,O-⁵ and P,N-based ligands⁶ have been the most intensively studied since P usually binds strongly to the metal center whereas the other donor atom (O or N) is generally only weakly bonded.

On the other hand, there is an increasing interest in the chemistry of functionalized NHC carbenes⁷ in which a donating group is attached to a strongly bonded imidazolyl ring. In this context, a variety of heteroatom-functionalized carbene ligands containing phosphine,⁸ pyridine,^{1a,9} amido,¹⁰ ester, keto or ether¹¹ and oxazoline¹² donor functions have been synthesized and, in some cases, used as catalysts for a number of catalytic transformations.¹³ The combination of a strongly bonded carbene moiety with the appropriate donor function should allow for potential hemilability. In fact, the hemilabile character of several alkenyl-,¹⁴ thioether-,¹⁵ alkoxide,¹⁶ and pyrazolylmethyl¹⁷ functionalized-imidazolylidene ligands, and of the terdentate 1,3-bis(2-pyridyl)imidazol-2-ylidene ligand¹⁸ have been demonstrated.

Hydrosilylation of carbon-carbon multiple bonds has been one of the most important laboratory and industrial methods of forming silicon-carbon bonds and to functionalize organic molecules.¹⁹ The hydrosilylation of alkynes represents the most straightforward and atom-economical access to

vinylsilanes which are useful intermediates for cross-linked silicones as well as reagents in organic synthesis and as nucleophilic partners in Pd-catalyzed cross-coupling reactions.²⁰ The hydrosilylation of alkynes can be promoted by a variety of catalysts including radical initiators, chloroplatinic acid and Wilkinson's type rhodium complexes.^{19,21} More recently some nickel,²² ruthenium,²³ platinum,²⁴ rhodium and iridium²⁵ complexes containing NHC carbenes have been used as hydrosilylation catalysts. Most of the recent efforts in the study of catalytic hydrosilylation concern the design of efficient catalysts which enable the stereodivergent preparation of both (*Z*)- and (*E*)-alkenylsilanes independently.

Our interest is focused in the synthesis of transition metal complexes containing heteroditopic ligands of hemilabile character that incorporate strong electron donors, such as tertiary phosphines and carbenes. The design of ligands that combine weak donor functions, as the -NMe₂ group, and a flexible backbone should allow for the potential of a dynamic interaction with the metal center and/or stabilization of polar intermediates in catalytic applications exerting some directing effect. In this work we describe the synthesis and characterization of a series of new rhodium(I) complexes with alkylamino-functionalized NHC ligands of the type 1-dimethylaminoalkyl-3-R-imidazol-2-ylidene that are efficient catalysts for the hydrosilylation of 1-alkynes.

Results and Discussion

Synthesis of Precursors for Hemilabile NHC Ligands. The imidazolium salts used as precursors for the new hemilabile N-heterocyclic carbene ligands were prepared by direct alkylation of several 1-substituted imidazole compounds. The reaction of chloro-alkyl-dimethylamine hydrochloride derivatives, Cl(CH₂)_nNMe₂·HCl (n = 2, 3), with the stoichiometric amounts of several 1-substituted imidazole compounds, RImH (R = Me, *t*-Bu, Mes), in refluxing acetonitrile for several days afforded the corresponding alkylammonium imidazolium chloride salts [RImH(CH₂)_nNMe₂]Cl·HCl (**1-5**) (Scheme 1). The salts were isolated as white hygroscopic solids in good yields, and characterized by elemental analysis, mass spectrometry (ES-MS) and ¹H and ¹³C{¹H} NMR spectroscopy. The ¹H NMR

spectra of **1–5** in CDCl_3 or CD_3OD showed a highly downfield shifted resonance in the range δ 12.0 - 9.0 ppm that is characteristic of the *NCHN* imidazolium proton. The methyl groups of the dimethylalkyl ammonium fragment were observed as a single resonance between δ 3.5-2.8 ppm and around 43 ppm in the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra, respectively. The NH was observed as a broad resonance only in compounds **1** (δ 4.02 ppm) and **2** (δ 3.55 ppm) although the methylenic groups of the side arms, triplet ($\text{N-CH}_2\text{-}$) or multiplet ($\text{-CH}_2\text{-}$), have been clearly identified in the ^1H NMR spectra of all alkylammonium imidazolium salts. The remaining resonances of the imidazolium fragment were observed at chemical shifts typical for imidazolium salts.²⁶

Synthesis of Rhodium(I) Salts Containing Dimethylalkylamino Imidazolium as Cations. The ammonium-imidazolium salts may be sequentially deprotonated to give different rhodium(I) compounds. The reaction of **1–5** with one molar-equiv of sodium hydride in tetrahydrofuran followed of half-equiv of $[\{\text{Rh}(\mu\text{-Cl})(\text{cod})\}_2]$ afforded cyclooctadienedichlororhodate(I) salts $[\text{RImH}(\text{CH}_2)_n\text{NMe}_2][\text{RhCl}_2(\text{cod})]$ that contain the amine-imidazolium cation ($\text{R} = \text{Me}$, $n = 2$, **6**, $n = 3$, **7**; $\text{R} = t\text{-Bu}$, $n = 2$, **8**, $n = 3$, **9**; $\text{R} = \text{Mes}$, $n = 3$, **10**) (Scheme 2). The salts containing the 3-methyl imidazolium, **6** and **7**, have been isolated in the solid state and fully characterized by analytical and spectroscopic means. In addition, the molecular structure of **6** has been determined by X-ray diffraction methods. The salts **8–10** have been characterized in solution as they are actually generated *in situ* and used as intermediates in the synthesis of rhodium(I) containing N-heterocyclic carbene ligands (see below).

The ^1H NMR spectra of compounds **6–10** showed a resonance around δ 10.5 ppm, diagnostic of the presence of a *NCHN* imidazolium proton, and the absence of any resonance attributable to NH in agreement with the deprotonation of the ammonium fragment. The amino-imidazolium cations were observed in the ES-MS+ of compounds **6** and **7** at m/z 154.1 $[\text{MeImH}(\text{CH}_2)_2\text{NMe}_2]^+$, and 168.3 $[\text{MeImH}(\text{CH}_2)_3\text{NMe}_2]^+$, respectively. Furthermore, the anion $[\text{RhCl}_2(\text{cod})]^-$ was identified in the ^1H

NMR spectra of the compounds as three resonances in a 1:1:1 ratio (4 protons each) corresponding to the =CH, and >CH₂ protons (*exo* and *endo* protons) of the 1,5-cyclooctadiene ligand. According to the C_{2v} symmetry of the anion, the ¹³C{¹H} NMR displayed two resonances at δ 77.70 (d, J_{C-Rh} = 11.1 Hz) and 31.09 ppm.

The molecular structure of compound [(MeImH(CH₂)₂NMe₂)] [RhCl₂(cod)] (**6**) is shown in Figure 1 and selected bond lengths and angles are listed in Table 1. The crystal structure shows the presence of both ions: the amino-imidazolium cation and the dichlorocyclooctadienerhodate(I) anion. The unique connection between both entities involves a clear hydrogen bond between the H(1) proton of the imidazolium cation and one of the chloro ligands of the metal complex (Cl(1)...C(1) 3.468(3), Cl(1)...H(1) 2.56(3) Å and C(1)-H(1)...Cl(1) 168(2) °). The internal bond distances and angles in the imidazolium ring lie within the range observed for other imidazolium salts.²⁷ In particular, the C-N distances at the C(1) atom are 1.374(3) and 1.378(3) Å, and the N-C-N angle is 108.3(2)°. On the other hand, the structural parameters of the [RhCl₂(cod)]⁻ anion are very similar to those reported in other ion-pair compounds including this specific anionic metal complex.²⁸

Synthesis of Neutral and Cationic Rhodium(I) Complexes Containing Hemilabile NHC Ligands.

We envisaged that the double deprotonation of the ammonium-imidazolium salts [RImH(CH₂)_nNMe₂]Cl·HCl with a strong base should produce the free carbene ligands that could be trapped by [{Rh(μ-Cl)(cod)}₂] to give rhodium(I) complexes containing the hemilabile NHC ligands. However, the reaction of the ammonium-imidazolium salts with 2.2 mol-equiv of NaH in THF, followed of addition of half mol-equiv of [{Rh(μ-Cl)(cod)}₂], unexpectedly afforded the amino-imidazolium salts [RImH(CH₂)_nNMe₂][RhCl₂(cod)] (**6-10**). Interestingly, we have discovered that the reaction of these salts with NaH under non strictly anhydrous conditions resulted in the formation of the expected complexes. Thus, when water was deliberately added to yellow suspensions of compounds **6-10** and NaH in THF, darker suspensions were immediately formed and the neutral mononuclear

complexes $[\text{RhCl}(\text{cod})(\text{RIm}(\text{CH}_2)_n\text{NMe}_2)]$ (**11-15**) were isolated as yellow microcrystalline solids in 60-70% yield after the convenient work-up. It is evident that the NaOH formed in the reaction of NaH and water was responsible for the acid-base reaction resulting in the effective deprotonation of the imidazolium fragment. In agreement with this proposal, complexes **11-15** can be prepared directly from the ammonium-imidazolium salts in THF using a KOH aqueous solution (2 mol-equiv) as base; most probably, side-reactions account for the lower yields obtained following this synthetic path. The more efficient one-pot synthesis of complexes **11-15** from the ammonium-imidazolium salts $[\text{RImH}(\text{CH}_2)_n\text{NMe}_2]\text{Cl}\cdot\text{HCl}$ requires the *in situ* generation of the intermediate amino-imidazolium salts $[\text{RImH}(\text{CH}_2)_n\text{NMe}_2][\text{RhCl}_2(\text{cod})]$ and their deprotonation using NaH/H₂O.

The mononuclear neutral complexes containing the 1-(dimethylaminoalkyl)-3-R-imidazol-2-ylidene ligands $[\text{RhCl}(\text{cod})(\text{RIm}(\text{CH}_2)_n\text{NMe}_2)]$ (**11-15**, scheme 2) have been fully characterized by elemental analysis, mass spectrometry and multinuclear NMR spectroscopy. In particular, the full assignment of the resonances is based on the ¹H-¹H COSY NMR spectra of the complexes. Although the MALDI-TOF mass spectra showed peaks at *m/z* corresponding to the cations $[\text{Rh}(\text{cod})(\text{RIm}(\text{CH}_2)_n\text{NMe}_2)]^+$, the complexes are neutral as was evidenced by the conductivity measurements in acetone. The mononuclear complexes are moderately stable in solid state or in solution under an inert atmosphere. However, solutions of compounds **11** and **13** in chlorinated solvents (CH₂Cl₂ or CHCl₃) slowly decompose at room temperature to unidentified products as observed in related products.^{29,30}

The ¹H NMR spectra of compounds **11-15** showed no resonances attributable to the NCHN proton, that confirms the deprotonation of the imidazolium fragment. In addition, the coordination of the carbene to the rhodium center becomes evident as a doublet resonance in the range δ 182-180 ppm ($J_{\text{C-Rh}} \approx 50$ Hz) is observed in the ¹³C{¹H} NMR spectra. These chemical shifts and coupling constant values lie in the usual range for related Rh(I)-NHC complexes.²⁵ The olefinic carbons of the 1,5-cyclooctadiene ligand features four resonances ($J_{\text{C-Rh}} \approx 8$ and 15 Hz) in the ¹³C{¹H} NMR spectra of the complexes. This observation is indicative of the lack of an effective symmetry plane in the molecules probably as a result

of the hindered rotation³¹ about the carbene-rhodium bond due to the presence of the sidearm in the hemilabile NHC ligands. As a consequence, the methylenic protons of the 2-dimethylaminoethyl and 3-dimethylaminopropyl sidearms are diastereotopic.

Although no direct evidence of the coordination of the dimethylamino fragment to the rhodium center was obtained from the observed NMR chemical shifts, the ¹H NMR spectra showed sharp resonances at room temperature excluding a potential penta-coordinated structure. This fact has been further corroborated by the single-crystal X-ray diffraction analysis carried out on complex [RhCl(cod)(MeIm(CH₂)₂NMe₂)] (**11**). The molecular structure of compound **11** is shown in Figure 2 and the more significant bond distances and angles are collected in Table 1. The coordination geometry at the rhodium center is slightly-distorted square-planar formed by coordination to the metal of the two olefinic bonds of a 1,5-cyclooctadiene molecule, the carbene atom of the 1-(2-dimethylaminoethyl)-3-methyl-imidazol-2-ylidene group and the chloro ligand. The sum of the four *cis* intraligand angles at the metal environment is equal to 360° within experimental uncertainty, but the individual angles are distorted from ideal values due to the steric influence of the bulky 1,5-cyclooctadiene ligand. Thus, the largest bond angles, 92.25(7)° and 92.01(5)°, are M(1)-Rh-C(1) and M(2)-Rh-Cl (M(1) and M(2) represent the midpoints of the coordinated olefinic bonds). In contrast, the smallest angle, 88.15(5)°, is observed between the chloro (Cl(1)) and carbene (C(1)) ligands. A remarkable feature of molecular structure is the location of the NMe₂ fragment of the functionalized 1-N substituent (2-dimethylaminoethyl) oriented clearly away from the metal center.

The rhodium-carbene bond distance, 2.0292(17) Å, is within the range reported for Rh(I)-carbene complexes (mean 2.026 Å, CSD search on complexes of the type [RhCl(cod)(imidazol-2-ylidene)]). This carbene ligand exerts a high *trans* influence, producing a significant elongation of the Rh-C bonds situated in relative *trans* position (mean Rh-C 2.2031(12)Å) if compared to those *trans* to the chloride ligand (mean Rh-C 2.1058(13)Å). The imidazol-2-ylidene ring is placed almost perpendicular to the coordination plane of the rhodium center (dihedral angle 84.62(5)°). A comparison of the molecular

structures of the functionalized imidazolium cation **6** and the imidazol-2-ylidene complex **11** shows the typical increase in the C-N bond distances (1.328(3) and 1.326(3) Å in **6**, 1.356(2) and 1.355(2) Å in **11**) and the decrease in NCN angle (108.2(2) in **6** and 104.37(15)° in **11**) upon deprotonation and coordination to the rhodium center, reflecting the enhanced *s* character of the in-plane carbene lone pair σ -bonded to metal in the metal NHC complexes.³²

The coordination of the dimethylamino fragment of the hemilabile NHC's in the complexes **11-15** could be induced by abstraction of the chloro ligand. Thus, the reaction of complexes **12** and **15** with one molar-equiv of silver tetrafluoroborate in CH₃CN/acetone at 0° C resulted in the precipitation of AgCl and the formation of yellow solutions from which the cationic complexes [Rh(cod)(RIm(CH₂)₃NMe₂)] [BF₄] (R = Me, **16**; Mes, **17**) were isolated as microcrystalline yellow solids in good yield. The MALDI-TOF mass spectra gave a peak at *m/z* 378.1 (**16**) and 482.2 (**17**) that correspond to the cations [Rh(cod)(RIm(CH₂)₃NMe₂)]⁺. The IR spectra of the complexes showed the presence a broad band at 1071 cm⁻¹ corresponding to uncoordinated BF₄⁻ anions. In addition, the conductivity measurements in acetone solutions were in agreement with a formulation of the complexes as 1:1 electrolytes. Further support of the coordination of the dimethylamino group to the rhodium center comes from the ¹H NMR as no coordinated solvent was detected when the reaction was conducted in the presence of diverse coordinating solvents as acetone or acetonitrile. The ¹H and ¹³C{¹H} NMR spectra of both compounds are consistent with a chelating coordination mode (κ^2 C,N) of the NHC ligands that results in the formation of a seven-membered metallacycle (Scheme 3). The most relevant features of the NMR spectra are the significant reduction in the magnitude of the *J*_{C-Rh} of the carbenic atom, only observed for compound **16** at δ 179.63 ppm (*J*_{C-Rh} \approx 28 Hz), and the downfield shifting of *ca.* 1 ppm of the methylenic -CH₂-NMe₂ resonance relative to the related neutral complex, which is observed as a broad triplet and could be a diagnostic for the coordination of the -NMe₂ fragment.

Unfortunately, the chloro abstraction by silver salts in the neutral complexes containing the ligands

1-(2-dimethylaminoethyl)-3-R-imidazol-2-ylidene (R = Me, **11**; *t*-Bu, **13**) resulted in decomposition products even when the reaction was performed in coordinating solvents (acetone or acetonitrile) and/or in the presence of coordinating anions (triflate). Although the chelating coordination mode ($\kappa^2\text{C,N}$) of the 2-dimethylaminoethyl sidearm with a perpendicular disposition of the imidazol-2-ylidene fragment relative to the rhodium coordination plane produce a constrained six-membered metallacycle, the twist of the NHC diazole ring plane could relief strain and should allow the coordination of labile $-\text{NMe}_2$ fragment. In this context, it has been demonstrated that the dihedral angle between both planes in N-heterocyclic $(\text{CH}_2)_n$ -linked bis-NHC complexes is strongly dependent on the length of the linker.^{33b} Thus, several methylene-linked ($n = 1$) bis-NHC square planar rhodium (I) complexes with a six-membered metallacycle ring having a rather small dihedral angle have been structurally characterized.³³

For comparative purposes, the cationic bis-carbene rhodium(I) complex $[\text{Rh}(\text{cod})(\text{MeIm}(\text{CH}_2)_3\text{ImMe})][\text{BF}_4]$ (**18**) was prepared from the bis-imidazolium $[\text{MeImH}(\text{CH}_2)_3\text{ImHMe}]\text{Br}_2$ ³⁴ salt following a procedure similar to that used by Crabtree³³ in the synthesis of the related compound $[\text{Rh}(\text{cod})(n\text{-BuIm}(\text{CH}_2)_3\text{Im}n\text{-Bu})][\text{PF}_6]$. As expected, the spectroscopic properties of compound **18** matches with those reported for the related PF_6^- salt described independently by Peris³⁵ and Raubenheimer.³⁶

Hydrosilylation of 1-Alkynes. The neutral $[\text{RhCl}(\text{cod})(\text{RIm}(\text{CH}_2)_n\text{NMe}_2)]$ (**11-15**) and cationic $[\text{Rh}(\text{cod})(\text{RIm}(\text{CH}_2)_n\text{NMe}_2)][\text{BF}_4]$ (**16-18**) complexes were found to be active catalyst precursors for the hydrosilylation of terminal alkynes. The catalytic reactions were carried out in CDCl_3 at 60 °C using HSiMe_2Ph and were routinely monitored by ^1H NMR spectroscopy. The influence of the 1-alkyne has been studied using phenylacetylene, 3,3-dimethyl-but-1-yne, 1-hexyne, and triethylethynylsilane as substrates and the results are summarized in Table 2.

Transition metal-catalyzed hydrosilylation of 1-alkynes often gives a mixture of the three possible isomeric vinylsilane derivatives: (*Z*)- or (*E*)-1-silyl-1-alkenes, products from the anti-Markovnikov addition (β -(*Z*) and β -(*E*) isomers, respectively), and 2-silyl-1-alkene from the Markovnikov addition (α

isomer).^{19a,21,37} In addition, the formation of dehydrogenative silylation products, alkynylsilane and the corresponding alkene, have been sometimes observed in the case of sterically demanding substituents on the alkyne and/or the hydrosilane (Scheme 4).^{37,38}

When the hydrosilylation of phenylacetylene was performed in the presence of the catalyst precursors **11**, **13-14**, and **16** (entries 1, 3, 4, 6) the massive formation of poly-phenylacetylene was observed even at room temperature.^{39,21} However, the polymerization was considerably reduced for the cationic complexes **17** (entry 7) and **18** (entry 8), and was marginally observed for the neutral catalyst precursors **12** (entry 2) and **15** (entry 5). The major isomer formed was the β -(*E*) vinylsilane, particularly for **12**, **15** and **17**. In general, the dehydrogenative silylation product, styrene, was not detected or it is negligible when the polymerization process is operative. In these cases, considerable amounts of the α and β -(*Z*) vinylsilanes were also formed except for **17** that gave only the β -(*E*) and α isomers. The lack of selectivity in hydrosilylation of phenylacetylene has also been observed with cationic rhodium(I) precursors containing diphosphine as ancillary ligands.⁴⁰

The hydrosilylation of *tert*-butylacetylene at room temperature is quite slow and even at 60 °C long reaction times are generally required. Under these experimental conditions the reactions are unselective since although the β -(*E*) vinylsilane is the major product (50-75%), variable amounts of the β -(*Z*) (5-12%) and α (8-35%) isomers were also formed. In addition, the dehydrogenative silylation process is operative as significant percentages of 3,3-dimethyl-but-1-ene (5-20%) were observed and *t*-Bu-C \equiv C-SiMe₂Ph was detected by GC-MS. Interestingly, the less active catalyst precursors were **15** and **17**, which have the bulky mesityl substituent in imidazol-2-ylidene ligand, probably as a consequence of the steric interference with the bulky substrate. As expected, complexes containing the less sterically demanding methyl-substituted NHC ligands (**12**, **16** and **18**) were the most active in the series although the regio- and stereoselectivities attained with the bis-carbene complex **18** were lower.

Higher regio- and stereoselectivities were obtained in the hydrosilylation of 1-hexyne (entries 17-24,

Table 2). In general, an opposite stereoselectivity towards the β -(*Z*) vinylsilane was observed in all cases, in clear contrast to the catalytic processes involving the precedent substrates. The activities and selectivities are comparable or slightly higher than the previously reported for other rhodium-catalyzed 1-hexyne hydrosilylation reactions.^{19a,25h} Outstandingly, the catalyst precursor [RhCl(cod)(MeIm(CH₂)₂N(CH₃)₂)] (**11**) gave a 96% of conversion in 1.5h with complete selectivity in β vinylsilanes, a *Z/E* ratio of 49, and a TOF of 64 turnover/h (entry 17, Table 2). The reaction profile, conversion *vs* time, for the hydrosilylation of 1-hexyne catalyzed by complexes **11-18** is shown in Figure 3. The neutral complexes [RhCl(cod)(RIm(CH₂)_nN(CH₃)₂)], (**11-13**) are, in general, far more active and selective than the cationic counterparts or complexes containing the bulky mesityl-substituted NHC ligand. Interestingly, the hydrosilylation reaction can be carried out on a preparative scale as has been demonstrated for the synthesis of β -hexen-1-enyl-methyl-diphenyl-silane using compound **12** as catalyst precursor (see Experimental Section).

Compound [Rh(cod)(MeIm(CH₂)₃N(CH₃)₂)] [BF₄] (**16**) is the most active and selective in the cationic series (**16-18**). Interestingly, complexes **16** and **17** are more selective than the biscarbene catalyst **18** (entries 22-24). The effect of the length of the linker become important in complexes [RhCl(cod)(RIm(CH₂)_nN(CH₃)₂)] (R = *t*-Bu, **13**, **14**) being compound **13** (n = 2) considerably more active and selective than compound **14** (n = 3). However, this effect is not so significant in complexes **11** and **12** (R = Me) (entries 17 and 18). The influence of the size of the R substituent on the heterocyclic ring became evident along the series [RhCl(cod)(RIm(CH₂)₃N(CH₃)₂)] (R = Me, **12**; *t*-Bu, **14**; Mes, **15**). Thus, the excellent activity observed for complex **12** contrasts with that of the catalyst precursors **14** and **15** (Figure 3). As far as the selectivity is concerned, the regioselectivity remains constant but bulky substituents drops off the stereoselectivity as was evidenced by a significant reduction of the *Z/E* ratio (19, R = Me; 12.6, R = *t*-Bu and 9.4, R = Mes) (entries 18, 20 and 21) that is more pronounced in the Mes complex.

We have checked the *E/Z* ratio dependence *versus* time in the hydrosilylation of 1-hexyne

using the catalyst precursor $[\text{RhCl}(\text{cod})(t\text{-BuIm}(\text{CH}_2)_3\text{N}(\text{CH}_3)_2)]$ (**13**). As it can be seen in Figure 4, the *E/Z* ratio remained approximately constant (0.05) during the catalytic process, however, after the complete consumption of 1-hexyne ($t = 120$ min), the *E/Z* ratio increases owing to the isomerization of the β -(*Z*)-vinylsilane into the thermodynamically favored β -(*E*)-vinylsilane isomer. Thus, the stability of the *E/Z* ratio during the catalysis suggests the kinetic control of the product distribution. The isomerization activity has been observed in all the catalytic systems under investigation (Table 3) and is particularly important for compounds $[\text{RhCl}(\text{cod})(t\text{-BuIm}(\text{CH}_2)_n\text{N}(\text{CH}_3)_2)]$ (**13**, **14**) (entries 6 and 8, Table 3). Taken into account that the catalytic reactions were conducted with 10% excess of hydrosilane in order to avoid the polymerization process, the responsible species for the isomerization should be generated by mediation of hydrosilane. In fact, the isomerization of (*Z*)-alkenylsilanes to (*E*)-alkenylsilanes catalyzed by rhodium(I) complexes in the presence of hydrosilanes has already been observed.^{37a} Also in some systems the heating of the catalytic solutions resulted in the formation of minor amounts of *n*-hexenes. More important, in the catalytic systems based on precursors **13**, **14** and **16** significant amounts of hex-2-enyl-dimethyl-phenyl-silane were formed (entries 6, 8 and 12, Table 3). The slow rearrangement of vinylsilanes to allylsilane has been reported by Crabtree *et al* in the hydrosilylation of 1-hexyne with HSiMePh_2 catalyzed by $[\text{RhCl}(\text{PPh}_3)_3]$.^{37a} Interestingly, Doyle *et al* have also found that dinuclear rhodium(II) perfluorobutyrate-bridged complexes catalyze the hydrosilylation of 1-octyne to allylsilanes by precise adjustment of the reaction conditions.⁴¹

The hydrosilylation of alkenylsilanes has been scarcely studied.⁴² In order to evaluate the electronic effects introduced by the silyl group on the selectivity, the hydrosilylation of $\text{Et}_3\text{SiC}\equiv\text{CH}$ has also been investigated (Table 2). Surprisingly, in almost all cases the reaction gave exclusively the β -(*Z*) and α bis(silyl)alkenes but not β -(*E*)-vinylsilane. Again the less active catalyst precursors were **15** and **17**, which have the bulky mesityl substituent on the imidazol-2-ylidene ligand. Interestingly, the cationic compounds **16** and the neutral **11** are the more selective catalyst precursors in α -vinylsilane with α/β

ratios of 1.60 and 1.15, respectively. Nevertheless, it is difficult to establish a clear correlation with neither the length of the linker nor the steric effect of the substituents.

It has been reported that cationic rhodium(I) complexes catalyze the hydrosilylation of 1-alkynes to give preferentially the β -(*E*)-vinylsilane isomer while neutral analogs show the opposite stereoselectivity, as they are highly selective for the β -(*Z*)-vinylsilane.^{37b,39,43} In contrast, the above described results indicate that this trend should not be considered a general rule as it is not applicable to NHC carbene containing complexes^{25b,44} since in these cases the selectivity is essentially determined by the alkyne substitution.

Mechanistic considerations. The strong influence of the 1-alkyne structure on the selectivity can be rationalized in the frame of the widely accepted mechanism for the metal-catalyzed hydrosilylation, that is, the modified Chalk-Harrod mechanism that accounts for the unusual β -(*Z*)-vinylsilane isomer resulting from a formal *trans* addition. The mechanism starts with Si-H oxidative addition to the metal and invoke the insertion of a coordinated alkyne into the Rh-Si bond to form the alkenyl-Rh intermediate (**A**), instead of the insertion into the Rh-H bond. Direct reductive elimination from **A** would give the β -(*E*)-vinylsilane isomer. Alternatively, this intermediate could undergo a metal assisted isomerization to alkenyl-Rh (**B**) via a zwitterionic carbene-like intermediate (**i**)^{19a}, or a η^2 -vinyl complex (**ii**)^{19b} (Scheme 5). The driving force for this isomerization, which leads to the thermodynamically less stable β -(*Z*)-vinylsilane, is the relief of steric strain between the metal and the adjacent silane. However, the direct *trans* addition, without *cis-trans* isomerization, resulting in the formation of the Markovnikov product has been observed in cationic ruthenium complexes⁴⁵ and sustained by DFT calculations.⁴⁶ In the same way, we have proposed that the involvement of dinuclear ruthenium complexes could also explain the formal *trans* addition.⁴⁷ Additionally, an alternative reaction mechanism that accounts for the observed *trans* addition in the intramolecular alkyne hydrosilylation catalyzed by ruthenium complexes have been also described.^{48,49}

When the R group in R-C≡C-H is not sterically demanding, as is the case of 1-hexyne (R = *n*-C₄H₉), the β-(*Z*)-vinylsilane isomer is selectively formed because the position of the equilibrium is shifted towards **B**. However, when the R group is very bulky, as is the case of *tert*-butylacetylene (R = *t*-C₄H₉), the reactions used to be unselective.³⁷ Probably the introduction of additional steric congestion results in an equilibration between **A** and **B** that is expected to be translated to a mixture of β-(*E*)-vinylsilane and β-(*Z*)-vinylsilane isomers after reductive elimination.^{19b} Besides, the bulkiness of R produces an additional steric repulsion with the metal center that makes the alkenyl-Rh intermediate **C** less sterically demanding resulting in the formation of the α-vinylsilane isomer.⁵⁰ However, an alternative pathway for the formation of the α regioisomer could be the 1,2-silyl shift in the η²-vinyl intermediate (**ii**).^{49,51,52} In addition, the dehydrogenative silylation products, that also are frequently formed in catalytic systems using alkynes and/or hydrosilane with sterically demanding substituents, can be formed by β-reductive elimination from **B**.³⁷

In the particular case of Et₃SiC≡CH, the no formation of the β-(*Z*)-vinylsilane isomer strongly suggest that the isomerization of the alkenylrhodium intermediate **A** does not take place and, in consequence, only the β-(*E*) and the α-vinylsilane isomers are formed from **A** and **C**. Although the steric influence of the -SiEt₃ moiety could completely inhibit the **A**⇌**B** equilibrium, probably the electronic effects are even more important. Although the silyl group at the β carbon stabilizes the adjacent carbanion through a ππ-dπ interaction in the zwitterionic intermediate **i**,^{19a} the silyl group at the α carbon should destabilizes the carbenic fragment in both intermediates (**i** and **ii**). In addition, the (*Z*)-silylalkenyl catalytic intermediate **A** should be stabilized by the hyperconjugative interaction between low-lying silicon-substituent-based unoccupied molecular orbitals and occupied π-type orbitals.⁵³ This effect is further reinforced by the presence of two silyl groups in *trans* position in **A**. Thus, the interplay between steric and electronic effects, based on the stabilization of the silylalkenyl catalytic intermediate **A** and the destabilization of the probable intermediates **i** or **ii**, could give full account of the experimental

observations.

It is worth to mention that some methods for the regioselective production of 1,1-disubstituted vinylsilanes (α isomer) by direct *trans* addition have been recently described.^{45,46} Interestingly, 1,1-bis(silyl)alkenes have been obtained by *cis* addition of hydrosilanes to alkyl-silyl acetylenes.⁴²

Conclusions

We have described the synthesis of several ammonium-imidazolium chloride salts that are precursor for the synthesis of a range of rhodium (I) complexes containing amino-alkyl functionalized NHC ligands with hemilabile character of the type 1-dimethyl-amino-alkyl-3-R-imidazol-2-ylidene. The sequential deprotonation of the ammonium-imidazolium salts allowed the preparation of amine-imidazolium cyclooctadienedichlororhodate(I) salts and neutral mononuclear complexes $[\text{RhCl}(\text{cod})(\text{RIm}(\text{CH}_2)_n\text{NMe}_2)]$. When the length of the linker is appropriate ($n = 3$) chloride abstraction by silver salts resulted in the formation of cationic mononuclear complexes by coordination of the dimethylamino fragment to the rhodium center.

The rhodium complexes are efficient catalyst precursors for the hydrosilylation of terminal alkynes. It has been found that the stereo- and regioselectivity of the reactions is mainly determined by the substitution of the 1-alkyne whereas the charge of the complexes, the length of the side arm and the 3-R substituents on the heterocyclic ring strongly influence the activity and, in some extent, the selectivity. Neutral complexes having amino-functionalized NHC ligands with a small substituent at the heterocycle are generally the most active and selective catalysts. Good selectivities in the β -(*Z*)-vinylsilane isomer were found in the hydrosilylation of 1-hexyne. However, moderate selectivities in the opposite β -(*E*)-vinylsilane stereoisomer were obtained in the hydrosilylation of *tert*-butyl-acetylene. Unexpectedly, only the β -(*E*) and α bis(silyl)alkenes isomers were observed in the hydrosilylation of triethylsilylacetylene.

Experimental Section

Scientific Equipment. C, H and N analyses were carried out in a Perkin-Elmer 2400 CHNS/O analyzer. Infrared spectra were recorded on a FT-Perkin-Elmer Spectrum One spectrophotometer using Nujol mulls between polyethylene sheets. NMR spectra were recorded on a Bruker Avance 300 MHz, and a Bruker Avance 400 MHz spectrometers. ^1H (300.1276 MHz, 400.1625 MHz) and ^{13}C (75.4792 MHz, 100.6127 MHz) NMR chemical shifts are reported in ppm relative to tetramethylsilane and referenced to partially deuterated solvent resonances. Coupling constants (J) are given in Hertz. Spectral assignments were achieved by combination of ^1H - ^1H COSY, NOESY, ^{13}C DEPT and ^1H - ^{13}C HMQC experiments. MALDI-TOF mass spectra were obtained on a Bruker MICROFLEX spectrometer using DCTB (*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile) as matrix.⁵⁴ Electrospray mass spectra (ESI-MS) were recorded on a Bruker MicroTof-Q using sodium formate as reference. Conductivities were measured in *ca.* $5 \cdot 10^{-4}$ M acetone solutions of the complexes using a Philips PW 9501/01 conductimeter.

Synthesis. All experiments were carried out under an atmosphere of argon using Schlenk techniques, and the solvents were distilled immediately prior to use from the appropriate drying agents. Oxygen-free solvents were employed throughout. CDCl_3 was dried using activated molecular sieves, methanol- d_4 (<0.02% D_2O) was purchased from Euriso-top and used as received. The compounds *t*-BuImH,⁵⁵ MesImH,⁵⁶ MeImH(CH₂)₃ImHMe³³ were prepared by the reported methods. MeImH was obtained from Sigma-Aldrich and distilled prior to use. The alkynes, HSiMe₂Ph and chloro-alkyl-dimethylamine hydrochloride compounds were obtained from common commercial sources and, unless otherwise stated, were used as received. [$\{\text{Rh}(\mu\text{-Cl})(\text{cod})\}_2$] was prepared following the published method.⁵⁷

General Procedure for the Preparation of [RImH(CH₂)_nNMe₂]Cl·HCl (1-5). The alkylammonium imidazolium chloride salts were synthesized through the following procedure. A mixture of 2-chloro-N,N-dimethylalkylamine hydrochloride, Cl(CH₂)_nNMe₂·HCl, and imidazole, RImH, in deoxygenated

CH₃CN (10 mL) was refluxed for several days until reaction was completed. The white solid formed was filtered, washed with a CH₃CN/diethyl ether mixture, and vacuum dried.

[MeImH(CH₂)₂NMe₂]Cl·HCl (1). Cl(CH₂)₂NMe₂·HCl (3.16 g, 21.93 mol) and MeImH (1.75 mL, 21.93 mmol), reflux for 5 days, yield: 82%. Anal. Calcd for C₈H₁₇Cl₂N₃: C, 42.49; H, 7.58; N, 18.58. Found: C, 42.72; H, 7.45; N, 18.68. ¹H NMR (298 K, CDCl₃): δ 9.15 (s, CH_{NCHN}), 7.8 (s, 1H, CH), 7.65 (s, 1H, CH), 4.75 (t, *J*_{H-H} = 6.5 Hz, 2H, NCH₂), 4.02 (br s, 1H, NH), 3.97 (s, 3H, NMe), 3.76 (t, *J*_{H-H} = 6.5 Hz, 1H, NCH₂), 2.99 (s, NMe₂). ¹³C{¹H} NMR (298 K, CD₃OD): δ 124.25, 122.35 (CH), 55.62, 55.30 (NCH₂), 42.91 (NMe), 35.43 (s, NMe₂). ESI-MS (CH₃OH) *m/z* = 154.1 [M-2Cl-H]⁺.

[MeImH(CH₂)₃NMe₂]Cl·HCl (2). Cl(CH₂)₃NMe₂·HCl (0.79 g, 5.01 mol) and MeImH (0.40 mL, 5.01 mol), reflux for 5 days, yield: 75 %. Anal. Calcd for C₉H₁₉Cl₂N₃: C, 45.01; H, 7.97; N, 17.49. Found: C, 44.92; H, 7.54; N, 16.99. ¹H NMR (298 K, CD₃OD): δ 9.03 (s, 1H, CH_{NCHN}), 7.70 (s, 1H, CH), 7.61 (s, 1H, CH), 4.36 (t, *J*_{H-H} = 7.2 Hz, 2H, NCH₂), 3.94 (s, 3H, NMe), 3.55 (br s, 1H, NH), 3.19 (m, 2H, NCH₂), 2.89 (s, 6H, NMe₂), 2.34 (m, 2H, CH₂). ¹³C{¹H} NMR (298 K, CD₃OD): δ 125.43, 123.86 (CH), 55.57, 47.81 (NCH₂), 43.77 (NMe), 36.82 (NMe₂), 26.52 (CH₂). ESI-MS (CH₃OH) *m/z* = 168.1 [M-2Cl-H]⁺.

[*t*-BuImH(CH₂)₂NMe₂]Cl·HCl (3). Cl(CH₂)₂NMe₂·HCl (1.48 g, 10.28 mol) and *t*-BuImH (1.28 g, 10.28 mol), reflux for 4 days, yield: 82 %. Anal. Calcd for C₁₁H₂₃Cl₂N₃: C, 49.26; H, 8.64; N, 15.66. Found: C, 49.20; H, 8.40; N, 15.90. ¹H NMR (298 K, CD₃OD): δ 9.35 (s, 1H, CH_{NCHN}), 7.95 (s, 1H, CH), 7.81 (s, 1H, CH), 4.73 (t, *J*_{H-H} = 6.3, 2H, NCH₂), 3.78 (t, *J*_{H-H} = 6.6, 2H, NCH₂), 3.42 (s, 6H, NMe₂), 1.71 (s, 9H, *t*-Bu). ¹³C{¹H} NMR (298 K, CD₃OD): δ 141.35 (C_{NCHN}), 124.15, 122.37 (CH), 57.18 (C, *t*-Bu), 56.87, 45.39 (NCH₂), 44.18 (NMe₂), 29.87 (CH₃, *t*-Bu). ESI-MS (CH₃OH) *m/z* = 196.6 [M-2Cl-H]⁺.

[*t*-BuImH(CH₂)₃NMe₂]Cl·HCl (4). Cl(CH₂)₃NMe₂·HCl (1.28 g, 8.08 mol) and *t*-BuImH (1.00 g, 8.08 mol), reflux for 4 days, yield: 73 %. Anal. Calcd for C₁₂H₂₅Cl₂N₃: C, 51.06; H, 8.93; N, 14.81. Found: C, 51.22; H, 8.33; N, 14.72. ¹H NMR (298 K, CD₃OD): δ 10.47 (s, 1H, CH_{NCHN}), 8.04 (s, 1H,

CH), 7.40 (s, 1H, CH), 4.69 (t, $J_{\text{H-H}} = 12.3$, 2H, NCH₂), 3.32 (t, $J_{\text{H-H}} = 6.9$, 2H, NCH₂), 2.87 (s, 6H, NMe₂), 2.67 (m, 2H, CH₂), 1.66 (s, 9H, CH₃, *t*-Bu). ¹³C{¹H} NMR (298 K, CDCl₃): δ 123.56, 119.03 (CH), 60.45 (C, *t*-Bu), 54.12, 46.83 (NCH₂), 43.07 (NMe₂), 30.06 (CH₃, *t*-Bu), 25.63 (CH₂). ESI-MS (CH₃OH) $m/z = 210.2$ [M-2Cl-H]⁺.

[MesImH(CH₂)₃NMe₂]Cl·HCl (5). Cl(CH₂)₃NMe₂·HCl (0.85 g, 5.37 mol) and MesImH (1.00 g, 5.37 mmol), reflux for 7 days, yield: 78 %. Anal. Calcd for C₁₇H₂₇Cl₂N₃: C, 59.30; H, 7.90; N, 12.20. Found: C, 59.28; H, 7.41; N, 12.63. ¹H NMR (298 K, CDCl₃): δ 11.84 (br s, 1H, NH), 10.31 (s, 1H, CH_{NCHN}), 8.57 (s, 1H, CH), 7.15 (s, 1H, CH), 7.89 (s, 2H, CH Mes), 4.98 (t, $J_{\text{H-H}} = 10.0$, 2H, NCH₂), 3.45 (t, $J_{\text{H-H}} = 10.0$, 2H, NCH₂), 2.93 (s, 6H, NMe₂), 2.83 (m, 2H, CH₂), 2.32 (s, 3H, CH₃ Mes), 2.05 (s, 6H, CH₃ Mes). ¹³C{¹H}NMR (298 K, CDCl₃): δ 141.37 (s, C_{NCHN}), 134.08, 130.67 (Mes), 129.87 (CH Mes), 124.26, 123.04 (CH Im), 54.10, 47.17 (NCH₂), 43.07 (NMe₂), 25.92 (CH₂), 21.03, 17.57 (CH₃ Mes). ESI-MS (CH₃OH) $m/z = 272.1$ [M-2Cl-H]⁺.

General Procedure for the Preparation of Dichlorocyclooctadienerhodate(I) Salts [RImH(CH₂)_nNMe₂][RhCl₂(cod)] (6-10). [RImH(CH₂)_nNMe₂]Cl·HCl (2.21 mmol) (1-5) and NaH (55.7 mg, 2.32 mmol) were reacted in THF (10 mL) for 30 min. Then [{Rh(μ-Cl)(cod)}₂] (1.11 mmol) was added and the suspension was stirred overnight at room temperature. The pale yellow solids formed were separated by filtration, washed with diethyl ether and dried in vacuo.

[MeImH(CH₂)₂NMe₂][RhCl₂(cod)] (6). Yield: 84%. Anal. Calcd for C₁₆H₂₈Cl₂N₃Rh: C, 44.05; H, 6.47; N, 9.63. Found: C, 44.09; H, 6.34; N, 9.60. ¹H NMR (298 K, CDCl₃): δ 10.41 (s, 1H, CH_{NCHN}), 7.38 (s, 1H, CH), 7.13 (s, 1H, CH), 4.45 (t, $J_{\text{H-H}} = 5.4$, 2H, NCH₂), 4.21 (m, 4H, CH cod), 4.05 (s, 3H, NMe), 2.73 (t, $J_{\text{H-H}} = 5.4$, 2H, NCH₂), 2.39 (m, 4H, CH₂ cod), 2.26 (s, 6H, NMe₂), 1.65 (m, 4H, CH₂ cod). ¹³C{¹H} NMR (298 K, CDCl₃): δ 122.27, 121.78 (CH), 77.70 (d, $J_{\text{C-Rh}} = 11.1$, CH cod), 58.60, 47.29 (NCH₂), 45.27 (NMe), 36.62 (NMe₂), 31.09 (CH₂ cod). ESI-MS (CH₃CN) $m/z = 154.1$ [MeImH(CH₂)₂NMe₂]⁺, 211.0 [Rh(cod)]⁺.

[MeImH(CH₂)₃NMe₂][RhCl₂(cod)] (7). Yield: 84%. Anal. Calcd for C₁₇H₃₀Cl₂N₃Rh: C, 45.35; H,

6.71; N, 9.33. Found: C, 44.84; H, 6.34; N, 9.60. ^1H NMR (298 K, CDCl_3): δ 10.64 (s, 1H, CH_{NCHN}), 7.24 (s, 1H, CH), 7.10 (s, 1H, CH), 4.47 (t, $J_{\text{H-H}} = 6.8$, 2H, NCH_2), 4.26 (m, 4H, CH cod), 4.13 (s, 3H, NMe), 2.47 (m, 4H, CH_2 cod), 2.35 (t, $J_{\text{H-H}} = 6.5$, 2H, NCH_2), 2.25 (s, 6H, NMe_2), 2.15 (m, 2H, CH_2), 1.71 (m, 4H, CH_2 cod). $^{13}\text{C}\{^1\text{H}\}$ NMR (298 K, CDCl_3): δ 122.14, 121.96, 120.99 (CH), 77.70 (d, $J_{\text{C-Rh}} = 11.1$, CH cod), 54.97, 47.57 (NCH_2), 44.92 (NMe), 36.78 (NMe_2), 31.09 (CH_2 cod), 27.61 (CH_2). ESI-MS (CH_3CN) $m/z = 168.3$ [$\text{MeImH}(\text{CH}_2)_3\text{NMe}_2$] $^+$, 211.0 [$\text{Rh}(\text{cod})$] $^+$.

[*t*-BuImH(CH_2) $_2$ NMe $_2$][RhCl $_2$ (cod)] (8). NMR data. ^1H NMR (298 K, CDCl_3): δ 10.20 (s, 1H, CH_{NCHN}), 7.97 (s, 1H, CH), 7.23 (s, 1H, CH), 5.16 (t, $J_{\text{HH}} = 7.5$, 2H, NCH_2), 4.22 (m, 4H, CH cod), 4.10 (t, $J_{\text{HH}} = 7.5$, 2H, NCH_2), 3.06 (s, 6H, NMe_2), 2.42 (m, 4H, CH_2 cod), 1.80 (s, 9H, CH_3 , *t*-Bu), 1.68 (m, 4H, CH_2 cod).

[*t*-BuImH(CH_2) $_3$ NMe $_2$][RhCl $_2$ (cod)] (9). NMR data. ^1H NMR (298 K, CDCl_3): δ 10.38 (s, 1H, CH_{NCHN}), 7.63 (s, 1H, CH), 7.27 (s, 1H, CH), 4.68 (t, $J_{\text{HH}} = 7.8$, 2H, NCH_2), 4.22 (m, 4H, CH cod), 2.99 (t, $J_{\text{HH}} = 7.5$, 2H, NCH_2), 2.66 (s, 6H, NMe_2), 2.52 (m, 2H, CH_2), 2.40 (m, 4H, CH_2 cod), 1.77 (s, 9H, CH_3 , *t*-Bu), 1.68 (m, 4H, CH_2 cod).

[MesImH(CH_2) $_3$ NMe $_2$][RhCl $_2$ (cod)] (10). NMR data. ^1H NMR (298 K, CDCl_3): δ 10.20 (s, 1H, CH_{NCHN}), 7.80 (s, 1H, CH), 7.20 (s, CH Mes), 7.03 (s, 1H, CH), 6.96 (s, 2H, CH Mes), 4.79 (t, $J_{\text{H-H}} = 7.1$, 2H, NCH_2), 4.09 (m, 4H, CH cod), 3.68 (m, 2H, NCH_2), 2.85 (m, 2H, CH_2 cod), 2.51 (s, 3H, CH_3 Mes), 2.45 (m, 2H, CH_2 cod), 2.29 (s, 6H, NMe_2), 2.04 (s, 6H, CH_3 Mes), 1.78 (m, 2H, CH_2), 1.58 (m, 4H, CH_2 cod).

General Procedure for the Preparation of the Complexes [RhCl(cod)(RIm(CH_2) $_n$ NMe $_2$)] (11-15).

Method A. A suspension of the compounds [RImH(CH_2) $_n$ NMe $_2$][RhCl $_2$ (cod)] (6-10) (1 mmol) in THF (10 mL) was treated with NaH (27.85 mg, 1.16 mmol) and H $_2$ O (0.3 mL) to give an orange suspension. The solid was removed by filtration and the resulting orange solution evaporated to dryness. Recrystallization from diethyl ether/pentane rendered the products as yellow solids which were filtered, washed with pentane, and dried in vacuo. *Method B.* The corresponding [RImH(CH_2) $_n$ NMe $_2$]Cl·HCl (1

mmol), NaH (1.16 mmol) and $[\{\text{Rh}(\mu\text{-Cl})(\text{cod})\}_2]$ (0.5 mmol) were reacted in THF (10 mL) for 16 h to give suspensions of the compounds $[\text{RImH}(\text{CH}_2)_n\text{NMe}_2][\text{RhCl}_2(\text{cod})]$ (**6-10**). Further reaction with NaH (27.85 mg, 1.16 mmol) and H₂O (0.3 mL) afforded orange suspensions from which the compounds were isolated following the procedure described above.

[RhCl(cod)(MeIm(CH₂)₂NMe₂)] (11). Yield: 55 % (Method A). Anal. Calcd for C₁₆H₂₇ClN₃Rh: C, 48.07; H, 6.81; N, 10.51. Found: C, 46.95; H, 6.59; N, 9.47. ¹H NMR (298 K, CDCl₃): δ 6.99 (d, $J_{\text{H4-H5}} = 1.8$, 1H, CH), 6.78 (d, $J_{\text{H4-H5}} = 1.8$, 1H, CH), 5.02 (m, 2H, CH cod), 4.73 (m, 1H, NCH₂), 4.50 (m, 1H, NCH₂), 4.07 (s, 3H, NCH₃), 3.34 (m, 1H, CH cod), 3.26 (m, 1H, CH cod), 2.84 (m, 1H, NCH₂), 2.74 (m, 1H, NCH₂), 2.40 (m, 4H, CH₂ cod), 2.35 (s, 6H, NMe₂), 1.99 (m, 4H, CH₂ cod). ¹³C{¹H} NMR (298 K, CDCl₃): δ 182.37 (d, $J_{\text{C-Rh}} = 50.9$, C_{N₃}), 121.72, 121.16 (CH), 98.46 (m, CH cod), 68.13 (d, $J_{\text{C-Rh}} = 14.4$, CH cod), 67.39 (d, $J_{\text{C-Rh}} = 15.1$, CH cod), 59.89 (NCH₂), 48.39 (s, NCH₂), 45.64 (NCH₃), 37.65 (NMe₂), 33.32, 32.59, 29.22, 28.52 (CH₂ cod). MS (MALDI-TOF, DCTB matrix, CH₂Cl₂) $m/z = 364.2$ [M-Cl]⁺, 154.1 [MeImH(CH₂)₂NMe₂]⁺. Λ_{M} (acetone) = 1.42 Ω⁻¹cm²mol⁻¹.

[RhCl(cod)(MeIm(CH₂)₃NMe₂)] (12). Yield: 63 % (Method A). Anal. Calcd for C₁₇H₂₉ClN₃Rh: C, 49.34; H, 7.06; N, 10.15. Found: C, 49.06; H, 6.69; N, 9.75. ¹H NMR (298 K, CDCl₃): δ 6.86 (d, $J_{\text{H4-H5}} = 1.8$ Hz, 1H, CH), 6.80 (d, $J_{\text{H4-H5}} = 1.8$ Hz, 1H, CH), 5.02 (m, 2H, CH cod), 4.66 (m, 1H, NCH₂), 4.39 (m, 1H, NCH₂), 4.09 (s, 3H, NMe), 3.36 (m, 1H, CH cod), 3.26 (m, 1H, CH cod), 2.41 (m, 6H, CH₂ cod and NCH₂), 2.30 (s, 6H, NMe₂), 1.95 (m, 6H, CH₂ cod and CH₂). ¹³C{¹H} NMR (298 K, CDCl₃): δ 121.79, 120.75 (CH), 98.39 (d, $J_{\text{C-Rh}} = 7.1$, CH cod), 98.24 (d, $J_{\text{C-Rh}} = 6.8$, CH cod), 68.23 (d, $J_{\text{C-Rh}} = 14.7$, CH cod), 67.41 (d, $J_{\text{C-Rh}} = 14.6$, CH cod), 56.46, 48.71 (NCH₂), 45.45 (NMe), 37.75 (NMe₂), 33.36, 32.55, 29.23 (CH₂ cod), 29.11 (CH₂), 28.53 (CH₂ cod). ESI-MS (CH₃CN) $m/z = 378.1$ [M-Cl]⁺. Λ_{M} (acetone) = 3.60 Ω⁻¹cm²mol⁻¹.

[RhCl(cod)(*t*-BuIm(CH₂)₂NMe₂)] (13). Yield: 63 % (Method B). Anal. Calcd for C₁₉H₃₃ClN₃Rh: C, 51.65; H, 7.53; N, 9.59. Found: C, 51.15; H, 7.44; N, 9.57. ¹H NMR (298 K, CDCl₃): δ 7.09 (d, $J_{\text{H4-H5}} =$

1.8, 1H, CH), 7.00 (d, $J_{\text{H5-H4}} = 1.8$, 1H, CH), 5.43 (m, 1H, NCH₂), 4.96 (m, 2H, CH cod), 4.67 (m, 1H, NCH₂), 3.27 (m, 2H, CH cod), 2.93 (m, 1H, NCH₂), 2.78 (m, 1H, NCH₂), 2.45 (m, 4H, CH₂ cod), 2.39 (s, 6H, NMe₂), 1.96 (s, 9H, *t*-Bu), 1.80 (m, 4H, CH₂ cod). ¹³C{¹H} NMR (298 K, CDCl₃): δ 180.15 (d, $J_{\text{C-Rh}} = 49.8$, C_{N₃}), 120.55, 119.55 (CH), 96.27 (d, $J_{\text{C-Rh}} = 7.5$, CH cod), 94.01 (d, $J_{\text{C-Rh}} = 7.5$, CH cod), 69.84 (d, $J_{\text{C-Rh}} = 15.1$, CH cod), 66.95 (d, $J_{\text{C-Rh}} = 14.3$, CH cod), 59.72 (NCH₂), 58.22 (*t*-Bu), 50.22 (NCH₂), 45.66 (NMe), 33.25 (CH₂ cod), 32.27 (CH₃, *t*-Bu), 31.85, 29.15, 28.50 (CH₂ cod). MS (MALDI-TOF, DCTB matrix, CH₂Cl₂) $m/z = 406.2$ [M-Cl]⁺, 196.1 [*t*-BuImH(CH₂)₂NMe₂]⁺. Λ_{M} (acetone) = 1.14 Ω⁻¹cm²mol⁻¹.

[RhCl(cod)(*t*-BuIm(CH₂)₃NMe₂)] (14). Yield: 72 % (Method B). Anal. Calcd for C₂₀H₃₅ClN₃Rh: C, 52.69; H, 7.74; N, 9.22. Found: C, 52.48; H, 7.44; N, 9.35. ¹H NMR (298 K, CDCl₃): δ 7.03 (d, $J_{\text{H4-H5}} = 2.0$, 1H, CH), 6.94 (d, $J_{\text{H5-H4}} = 2.0$, 1H, CH), 5.25 (m, 1H, NCH₂), 4.95 (m, 3H, CH cod and NCH₂), 4.61 (m, 1H, NCH₂), 3.29 (m, 3H, CH cod and NCH₂), 2.38 (m, 5H, CH₂ cod and CH₂), 2.31 (s, 6H, NMe₂), 1.98 (s, 9H, *t*-Bu), 1.93 (m, 5H, CH₂ cod, CH₂). ¹³C{¹H} NMR (298 K, CDCl₃): δ 180.35 (d, $J_{\text{C-Rh}} = 51.4$, C_{N₃}), 119.00, 119.60 (s, CH), 96.27 (d, $J_{\text{C-Rh}} = 7.7$, CH cod), 93.99 (d, $J_{\text{C-Rh}} = 7.5$, CH cod), 69.78 (d, $J_{\text{C-Rh}} = 15.5$, CH cod), 67.07 (d, $J_{\text{C-Rh}} = 14.4$, CH cod), 58.29 (*t*-Bu), 56.86, 50.80 (NCH₂), 45.53 (NCH₃), 33.15 (CH₂ cod), 32.30 (CH₃, *t*-Bu), 31.98 (CH₂ cod), 29.12 (CH₂ cod and CH₂), 28.59 (CH₂ cod). MS (MALDI-TOF, DCTB matrix, CH₂Cl₂) $m/z = 420.1$ [M-Cl]⁺, 210.1 [*t*-BuImH(CH₂)₃NMe₂]⁺. Λ_{M} (acetone) = 0.38 Ω⁻¹cm²mol⁻¹.

[RhCl(cod)(MesIm(CH₂)₃NMe₂)] (15). Yield: 63 % (Method B). Anal. Calcd for C₂₅H₃₇ClN₃Rh: C, 57.97; H, 7.20; N, 8.11. Found: C, 56.94; H, 7.34; N, 7.97. ¹H NMR (298 K, CDCl₃): δ 7.03 (s, 1H, CH Mes), 7.00 (d, $J_{\text{H4-H5}} = 1.8$, 1H, CH), 6.85 (s, 1H, CH Mes), 6.67 (d, $J_{\text{H4-H5}} = 1.8$, 1H, CH), 5.11 (m, 1H, NCH₂), 4.79 (m, 1H, CH cod), 4.71 (m, 1H, CH cod), 4.36 (m, 1H, NCH₂), 3.35 (m, 1H, CH cod), 2.92 (m, 1H, CH cod), 2.37 (s, 3H, CH₃ Mes), 2.35 (m, 1H, CH₂), 2.32 (s, 3H, CH₃ Mes), 2.31 (m, 1H, CH₂), 2.22 (s, 7H, CH₂ and NMe₂), 2.13 (m, 1H, CH₂), 2.09 (m, 2H, CH₂ cod), 1.91 (m, 2H, CH₂ cod), 1.65

(m, 2H, CH₂ cod), 1.76 (s, 3H, CH₃ Mes), 1.42 (m, 2H, CH₂ cod). ¹³C{¹H} NMR (298 K, CDCl₃): δ 181.88 (d, $J_{C-Rh} = 51.1$, C_{N₃}), 138.59, 137.22, 136.27, 134.31 (Mes), 129.56, 128.02 (CH), 126.48 (CH Mes), 96.80, 96.75 (m, CH cod), 68.03 (d, $J_{C-Rh} = 14.3$, CH cod), 67.40 (d, $J_{C-Rh} = 14.3$, CH cod), 56.46, 49.38 (NCH₂), 45.09 (NMe₂), 33.75, 31.41 (CH₂ cod), 28.80 (s, CH₂ and CH₂ cod), 27.86 (CH₂ cod), 20.83, 19.50, 17.45 (CH₃). MS (MALDI-TOF, DCTB matrix, CH₂Cl₂) m/z = 482.3 [M-Cl]⁺, 272.2 [MesImH(CH₂)₃NMe₂]⁺. Λ_M (acetone) = 0.82 Ω⁻¹cm²mol⁻¹.

Preparation of [Rh(cod)(MeIm(CH₂)₃NMe₂)] [BF₄] (16). AgBF₄ (47 mg, 0.24 mmol) was added to a solution of complex **12** (100 mg, 0.24 mmol) in CH₃CN/acetone. After 6h of stirring at 0 °C the solid formed was separated by filtration. The resulting yellow solution was concentrated to ca. 1mL and treated with diethyl ether to give a yellow solid. The solid was separated by decantation, washed with diethyl ether, and dried in vacuo. Yield: 62 %. Anal. Calcd for C₁₇H₂₉BF₄N₃Rh: C, 43.90; H, 6.28; N, 9.03. Found: C, 44.10; H, 6.17; N, 9.09. ¹H NMR (298 K, CDCl₃): δ 7.06 (d, $J_{H4-H5} = 2.0$, 1H, CH), 7.01 (d, $J_{H4-H5} = 2.0$, 1H, CH), 5.65 (m, 1H, NCH₂), 4.63 (m, 2H, CH cod), 4.32 (m, 1H, NCH₂), 3.96 (s, 3H, NMe), 3.66 (m, 2H, CH cod), 2.68 (m, 3H, CH₂ and CH₂ cod), 2.54 (m, 2H, CH₂ cod), 2.41 (m, 6H, NMe₂), 2.24 (m, 3H, CH₂ and CH₂ cod), 2.17 (m, 1H, CH₂), 1.89 (s, 3H, CH₂ and CH₂ cod). ¹³C{¹H} NMR (298 K, CDCl₃): δ 179.63 (d, $J_{C-Rh} = 28.8$, C_{N₃}), 125.86, 123.99 (CH), 100.40 (d, $J_{C-Rh} = 8.4$, CH cod), 100.21 (d, $J_{C-Rh} = 7.8$, CH cod), 77.33 (d, $J_{C-Rh} = 13.5$, CH cod), 72.45 (m, CH cod), 65.13 (NCH₂), 51.51 (NMe), 49.35 (NCH₂), 39.21 (NMe₂), 35.79 (CH₂), 32.14, 31.60, 29.67, 27.86 (CH₂ cod). MS (MALDI-TOF, DCTB matrix, CH₂Cl₂) m/z = 378.1 [M]⁺. Λ_M (acetone) = 74 Ω⁻¹cm²mol⁻¹.

[Rh(cod)(MesIm(CH₂)₃NMe₂)] [BF₄] (17). AgBF₄ (37.6 mg, 0.19 mmol) and **15** (100 mg, 0.19 mmol) were reacted in CH₃CN/acetone at 0 °C for 6 h. Work-up as described above gave the compound as a yellow solid. Yield: 71 %. Anal. Calcd for C₂₅H₃₇BF₄N₃Rh: C, 52.74; H, 6.55; N, 7.38. Found: C, 52.79; H, 6.31; N, 7.39. ¹H NMR (298 K, CDCl₃): δ 7.45 (d, $J_{H4-H5} = 1.7$, 1H, CH), 7.09 (s, 1H, CH Mes), 6.93 (s, 1H, CH Mes), 6.79 (d, $J_{H4-H5} = 1.7$, 1H, CH), 5.90 (m, 1H, NCH₂), 4.79 (m, 1H, CH cod),

4.61 (m, 1H, NCH₂), 4.06 (m, 1H, CH cod), 3.50 (m, 1H, CH cod), 3.13 (m, 1H, CH cod), 2.39 (m, 2H, CH₂ cod), 2.29 (s, 9H, NMe₂ and CH₃ Mes), 2.22 (m, 3H, CH₂ and CH₂ cod), 2.18 (s, 3H, CH₃ Mes), 1.85 (m, 3H, CH₂ and CH₂ cod), 1.73 (s, 3H, CH Mes), 1.65 (m, 3H, CH₂ and CH₂ cod), 1.55 (m, 1H, CH₂). ¹³C{¹H} NMR (298 K, CDCl₃): δ 139.47 (CN Mes), 135.33, 134.85, 134.24 (Mes), 129.32 (CH Mes), 125.32, 122.24 (CH), 98.97 (d, *J*_{CRh} = 8.7, CH cod), 94.97 (m, CH cod), 72.64 (d, *J*_{CRh} = 11.8, CH cod), 71.38 (m, CH cod), 62.58, 47.14 (s, NCH₂), 32.99, 30.84, 28.79, 28.30, 25.25 (s, CH₂ cod and CH₂), 20.99, 18.99, 17.78 (s, CH₃). MS (MALDI-TOF, DCTB matrix, CH₂Cl₂) *m/z* = 482.2 [M]⁺. Λ_M (acetone) = 77 Ω⁻¹cm²mol⁻¹.

Preparation of [Rh(cod)(MeIm(CH₂)₃ImMe)][BF₄] (18). A mixture MeIm(CH₂)₃ImMe (0.138 g, 0.5 mmol) and Ag₂O (0.462 g, 2.0 mmol) was stirred in water (10 mL) at 0 °C for 30 min. The excess of Ag₂O was removed by filtration and a saturated solution of NaBF₄ (0.137 g, 1.25 mmol) in water was added to the resulting solution. The white solid formed was filtered and dried under vacuum. The solid was dissolved in CH₂Cl₂ at reflux temperature and [{Rh(μ-Cl)(cod)}₂] (0.25 mmol, 123.3 mg) was added and the mixture heated for further 30 min. The AgCl formed was removed by filtration, and the solvent was pumped off from the resulting yellow solution. The yellow residue was washed and treated with pentane until a yellow solid was formed, which was isolated by filtration, washed with pentane and dried in vacuum. The compound was recrystallized from THF/pentane. Yield: 63 %. Anal. Calcd for C₁₉H₂₈BF₄N₄Rh: C, 45.44; H, 5.62; N, 11.16. Found: C, 45.30; H, 5.60; N, 10.72. ¹H NMR (298 K, CDCl₃): δ 6.96 (d, *J*_{H4-H5} = 1.8 Hz, 1H, CH), 6.88 (d, *J*_{H4-H5} = 1.8 Hz, 1H, CH), 4.93 (m, 2H, NCH₂), 4.50 (m, 4H, CH cod), 4.35 (m, 2H, NCH₂), 3.96 (s, 6H, NMe), 2.47 (m, 4H, CH₂ cod), 2.25 (m, 4H, CH₂ cod), 1.75 (m, 2H, CH₂). ¹³C{¹H} NMR (298 K, CDCl₃): δ 181.8 (d, *J*_{C-Rh} = 47.3, C_{NCN}), 122.86, 122.64 (CH), 89.71 (d, *J*_{C-Rh} = 7.8, CH cod), 88.52 (d, *J*_{C-Rh} = 7.7, CH cod), 78.86, 78.67 (s, CH cod), 52.55 (NCH₂), 37.81 (NMe), 32.76 (CH₂), 30.83, 30.69, 30.49 (s, CH₂ cod). ESI-MS (CH₃CN) *m/z* = 415.1 [M]⁺, 307.0 [M-cod]⁺.

General Procedure for the Hydrosilylation of 1-Alkynes with HSiMe₂Ph. A 5 mm

NMR tube was charged with the catalyst precursors (**11-18**) (7.7×10^{-4} mmol), CDCl_3 (0.5 mL), the corresponding alkyne ($\text{PhC}\equiv\text{CH}$, *t*-Bu-C $\equiv\text{CH}$, 1-hexyne or $\text{Et}_3\text{C}\equiv\text{CH}$) (0.077 mmol), and a light excess of HSiMe_2Ph (0.085 mmol). The solution was kept in a thermostatic bath at 60 °C and the progress of the reactions monitored by ^1H NMR spectroscopy. The reaction products were identified by NMR by comparison with literature reported data. The catalytic solutions obtained from $\text{Et}_3\text{C}\equiv\text{CH}$ were filtered through a pad of Celite and the volatiles removed under reduced pressure. The new compounds were characterized by ^1H NMR and GC-MS.

1-(Dimethylphenylsilyl)-1-(triethylsilyl)ethene: ^1H NMR (CDCl_3): $\delta = 7.35, 7.19$ (m, 5H, Ph), AB system ($\delta_{\text{A}} = 6.22, \delta_{\text{B}} = 6.21, J_{\text{AB}} = 5.2, 2\text{H, CH}$), 0.64 (t, $J_{\text{HH}} = 7.8, 6\text{H, CH}_2$), 0.32 (q, $J_{\text{HH}} = 7.8, 9\text{H, CH}_3$), 0.19 (s, 6H, CH_3).

(E)-2-(Dimethylphenylsilyl)-1-(triethylsilyl)ethene: ^1H NMR (CDCl_3): $\delta = 7.32, 7.15$ (m, 5H, Ph), AB system ($\delta_{\text{A}} = 6.55, \delta_{\text{B}} = 6.47, J_{\text{AB}} = 22.8, 2\text{H, CH}$), 0.76 (t, $J_{\text{HH}} = 8.0, 6\text{H, CH}_2$), 0.41 (q, $J_{\text{HH}} = 8.0, 9\text{H, CH}_3$), 0.15 (s, 6H, CH_3).

Synthesis of β -hexen-1-enyl-methyl-diphenyl-silane. A schlenk tube with a screw tap was charged with the catalyst precursors **12** (38.5×10^{-3} mmol, 16 mg), CHCl_3 (5 mL), 1-hexyne (3.85 mmol, 456 μL), and HSiMe_2Ph (4.25 mmol, 675 μL). The solution was stirred at 60 °C for 30 min and then transferred to a round-bottom flask under Argon. Distillation in a Kugelrohr oven 160 °C (ca. 0.1 Torr) gave β -hexen-1-enyl-methyl-diphenyl-silane as a colourless liquid (Z:E = 94:6, 817 mg, 97%). The α isomer was observed only in traces amounts.

X-ray Structural Determination of Compounds $[\text{MeImH}(\text{CH}_2)_2\text{NMe}_2][\text{RhCl}_2(\text{cod})]$ (6**) and $[\text{RhCl}(\text{cod})(\text{MeIm}(\text{CH}_2)_2\text{NMe}_2)]$ (**11**).** Suitable yellow crystals for X-ray diffraction experiments were obtained by slow diffusion of diethyl ether (**6**) or pentane (**11**) into concentrated THF solutions of the complexes. Intensity data were collected at low temperature (100(2)K) on a Bruker SMART CCD area detector diffractometer equipped with graphite-monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) using

narrow frames (0.3° in ω). Cell parameters were refined from the observed setting angles and detector positions of strong reflections (9406 refl., $2\theta < 56.3^\circ$, **6**; 9743 refl., $2\theta < 56.6^\circ$, **11**). Data were corrected for Lorentz and polarisation effects, and multi-scan absorption corrections were applied with SADABS program.⁵⁸ The structures were solved by Patterson method and completed by successive difference Fourier syntheses (SHELXS-86).⁵⁹ Refinement, by full-matrix least-squares on F^2 with SHELXL97,⁵⁹ was similar for both structures, including isotropic and subsequent anisotropic displacement parameters for all non-hydrogen atoms. Most of the hydrogen atoms were included from observed positions and refined as free isotropic atoms; details are included below. All the highest electronic residuals (smaller than $1.0 \text{ e}/\text{\AA}^3$) were observed in close proximity of the Rh metal and have no chemical sense. Atomic scattering factors, corrected for anomalous dispersion, were used as implemented in the refinement program.⁵⁹

Crystal data for compound 6: $\text{C}_{16}\text{H}_{28}\text{Cl}_2\text{N}_3\text{Rh}$, $M = 436.22$; yellow needle, $0.198 \times 0.055 \times 0.052 \text{ mm}^3$; trigonal, $R\bar{3}$; $a = 36.9644(10)$, $c = 7.2845(4) \text{ \AA}$; $Z = 18$; $V = 8619.8(6) \text{ \AA}^3$; $D_c = 1.513 \text{ g/cm}^3$; $\mu = 1.171 \text{ mm}^{-1}$, min. and max. transmission factors 0.801 and 0.942; $2\theta_{\text{max}} = 56.70^\circ$; 30250 reflections collected, 4698 unique [$R_{\text{int}} = 0.0396$]; number of data/restrains/parameters 4698/0/287; final GoF 1.020, $R1 = 0.0289$ [4066 reflections, $I > 2\sigma(I)$], $wR2 = 0.0684$ for all data. Only hydrogens of three methylenic $-\text{CH}_2-$ groups of the cod molecule required a restrained refinement (calculated positions and positional and displacement riding refinement), all the rest were refined as free isotropic atoms.

Crystal data for compound 11: $\text{C}_{16}\text{H}_{27}\text{ClN}_3\text{Rh}$, $M = 399.77$; yellow irregular block, $0.167 \times 0.125 \times 0.079 \text{ mm}^3$; monoclinic, $P2_1/c$; $a = 10.3428(7)$, $b = 13.0938(9)$, $c = 12.7756(9) \text{ \AA}$, $\beta = 97.2510(10)^\circ$; $Z = 4$; $V = 1716.3(2) \text{ \AA}^3$; $D_c = 1.547 \text{ g/cm}^3$; $\mu = 1.148 \text{ mm}^{-1}$, min. and max. transmission factors 0.831 and 0.915; $2\theta_{\text{max}} = 56.60^\circ$; 20970 reflections collected, 4181 unique [$R_{\text{int}} = 0.0310$]; number of data/restrains/parameters 4181/0/298; final GoF 1.106, $R1 = 0.0233$ [3921 reflections, $I > 2\sigma(I)$], $wR2 = 0.0522$ for all data. All hydrogens were refined as free isotropic atoms.

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Supporting Information Available: X-ray crystallographic information files containing full details of the structural analysis of complexes **6** and **11** (CIF format). This material is available free of charge via Internet at <http://pubs.acs.org>.

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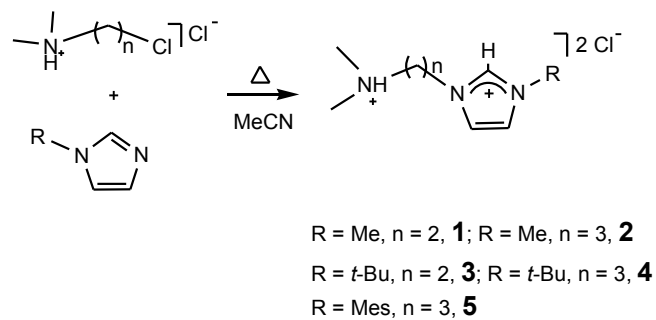
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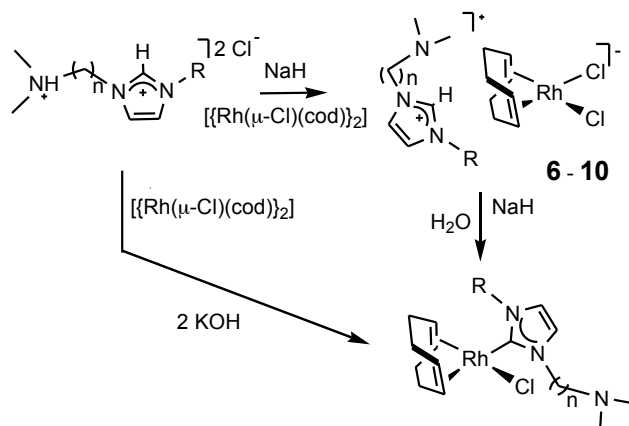
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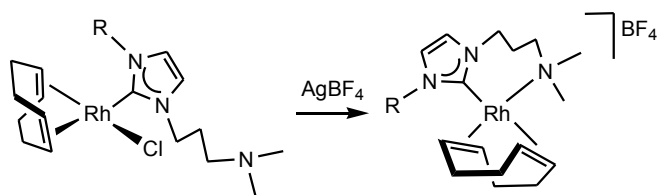


Scheme 1



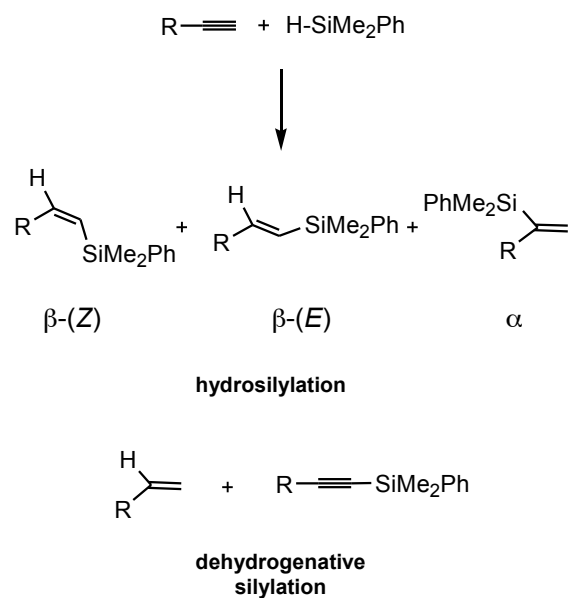
R = Me, n = 2, **11**; R = Me, n = 3, **12**
 R = *t*-Bu, n = 2, **13**; R = *t*-Bu, n = 3, **14**
 R = Mes, n = 3, **15**

Scheme 2

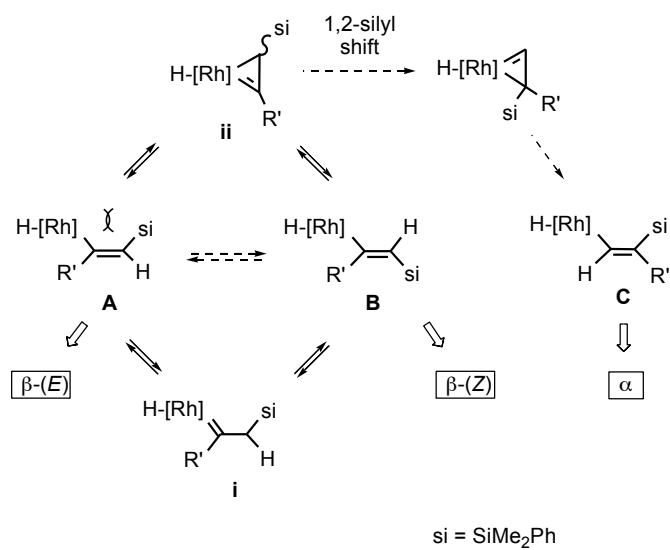


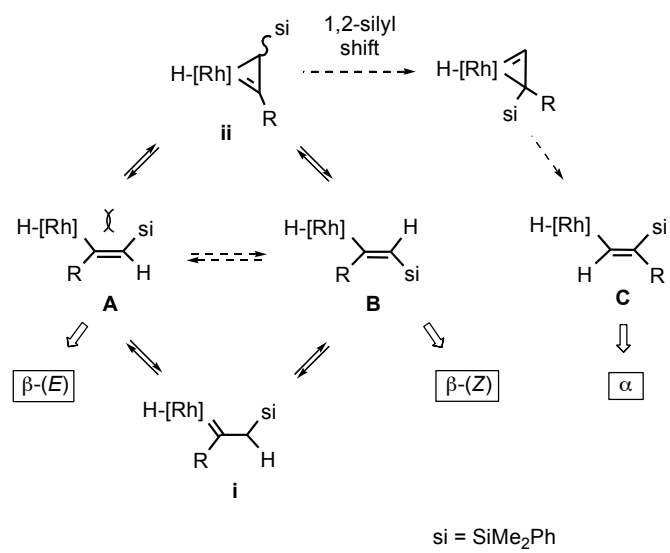
R = Me, **16**; R = Mes, **17**

Scheme 3



Scheme 4





Scheme 5

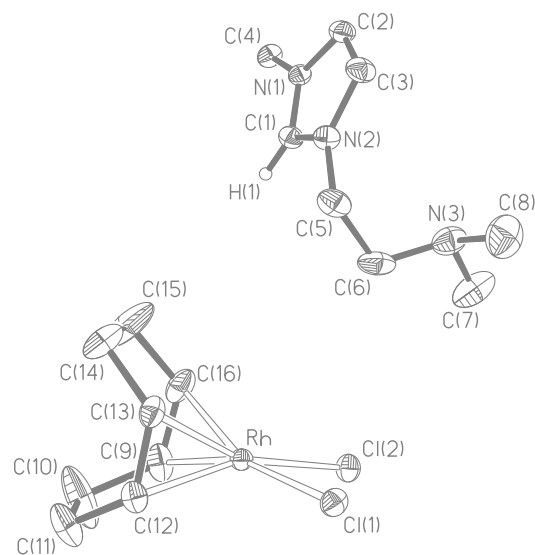


Figure 1: Molecular structure of compound $[(\text{MeImH}(\text{CH}_2)_2\text{NMe}_2)[\text{RhCl}_2(\text{cod})]$ (**6**). (Most hydrogen atoms have been omitted for clarity).

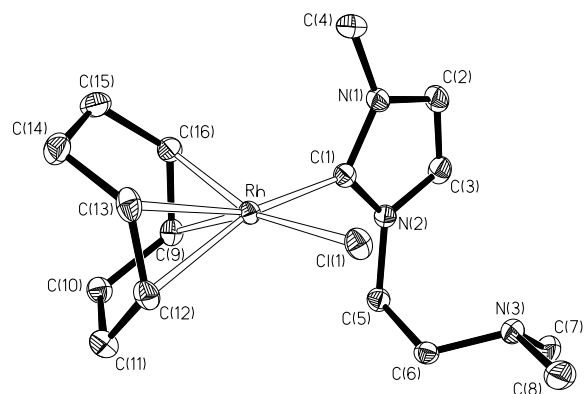


Figure 2: Molecular diagram of complex $[\text{RhCl}(\text{cod})(\text{MeIm}(\text{CH}_2)_2\text{NMe}_2)]$ (**11**).

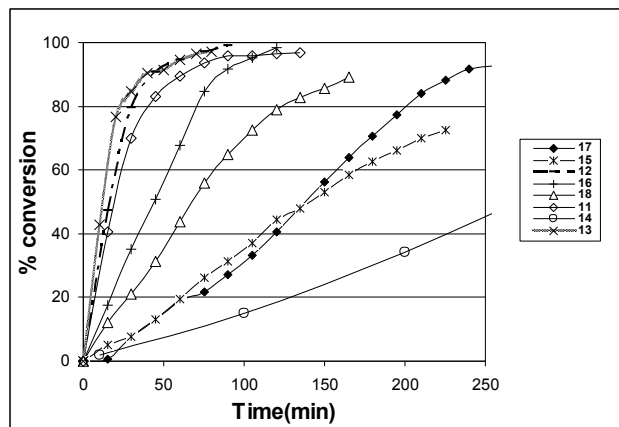


Figure 3: Reaction profile of conversion vs time for the hydrosilylation of $n\text{-BuC}\equiv\text{CH}$ with different precursors.

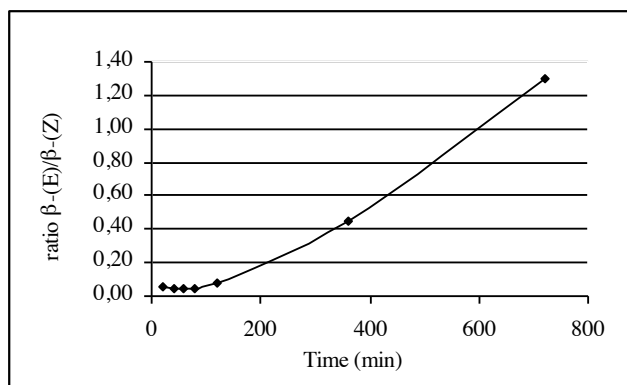


Figure 4: $\beta\text{-(E)}/\beta\text{-(Z)}$ ratio for the hydrosilylation of $n\text{-BuC}\equiv\text{CH}$ catalyzed by $[\text{RhCl}(\text{cod})(t\text{-BuIm}(\text{CH}_2)_2\text{N}(\text{CH}_3)_2)]$ (**13**) at $60\text{ }^\circ\text{C}$. Total consumption of 1-hexyne at $t = 120$ min.

Table 1. Selected Bond Distances (\AA) and Angles (deg) for Compounds **6** and **11**.^a

Compound	6	11	6	11
				40

Rh-Cl(1)	2.3766(5)	2.3868(4)	Rh-M(1) ^a	1.981(3)	1.9843(19)
Rh-Cl(2)/C(1)	2.3878(5)	2.0292(17)	Rh-M(2) ^a	1.994(2)	2.0927(17)
Rh-C(9)	2.102(2)	2.1101(17)	Rh-C(12)	2.109(2)	2.1985(17)
Rh-C(16)	2.095(2)	2.1016(18)	Rh-C(13)	2.115(5)	2.2078(17)
N(1)-C(1)	1.328(3)	1.356(2)	N(2)-C(1)	1.326(3)	1.355(2)
N(1)-C(2)	1.375(3)	1.389(2)	N(2)-C(3)	1.378(3)	1.387(2)
N(1)-C(4)	1.467(3)	1.460(2)	N(2)-C(5)	1.470(3)	1.466(2)
N(3)-C(6)	1.448(4)	1.458(2)	C(2)-C(3)	1.344(4)	1.341(3)
N(3)-C(7)	1.457(4)	1.457(3)	C(5)-C(6)	1.516(4)	1.517(2)
N(3)-C(8)	1.451(4)	1.462(2)			
Cl(1)-Rh-Cl(2)/C(1)	89.752(19)	88.15(5)	C(3)-N(2)-C(5)	126.1(2)	123.71(15)
Cl(1)-Rh-M(1) ^a	177.87(7)	179.44(5)	C(6)-N(3)-C(7)	109.4(3)	112.54(15)
Cl(1)-Rh-M(2) ^a	90.16(7)	92.01(5)	C(6)-N(3)-C(8)	112.5(3)	109.63(15)
Cl(2)/C(1)-Rh-M(1) ^a	91.80(8)	92.25(7)	C(7)-N(3)-C(8)	110.3(3)	110.34(17)
Cl(2)/C(1)-Rh-M(2) ^a	178.69(8)	177.61(7)	Rh-C(1)-N(1)	-	124.88(13)
M(1)-Rh-M(2) ^a	88.32(10)	87.60(7)	Rh-C(1)-N(2)	-	130.72(13)
C(1)-N(1)-C(2)	108.94(19)	111.18(16)	N(1)-C(1)-N(2)	108.2(2)	104.37(15)
C(1)-N(1)-C(4)	125.1(2)	124.21(15)	N(1)-C(2)-C(3)	106.9(2)	106.44(16)
C(2)-N(1)-C(4)	126.0(2)	124.61(16)	N(2)-C(3)-C(2)	107.2(2)	107.09(16)
C(1)-N(2)-C(3)	108.73(19)	110.91(15)	N(2)-C(5)-C(6)	111.4(2)	112.24(14)
C(1)-N(2)-C(5)	125.0(2)	124.66(15)	N(3)-C(6)-C(5)	113.0(2)	113.05(15)

^a M(1) and M(2) represent the midpoints of the olefinic double bonds C(9)-C(16) and C(12)-C(13), respectively.

Table 2. Hydrosilylation of Terminal Alkynes with Aminoalkyl-functionalized NHC Carbene

Rhodium(I) Complexes ^{a, b}

entry	alkyne	catalyst	time, h	conv %	% β -(E)	% β -(Z)	% α	% alkene	% polym.
1 ^c	PhC \equiv CH	11	2.00	97	20	13	0	0	67
2	"	12	2.00	99	58	16	19	6	1
3 ^c	"	13	0.50	97	41	0	10	0	49
4 ^c	"	14	0.50	99	14	10	1	0	75
5	"	15	12.00	98	67	13	8	4	8
6 ^c	"	16	0.25	97	32	0	6	0	62
7	"	17	12.00	98	67	0	15	0	18
8	"	18	4.00	95	47	17	15	3	18
9	<i>t</i> -BuC \equiv CH	11	12.00	99	79	9	9	3	
10	"	12	12.00	97	76	6	8	10	
11	"	13	12.00	95	77	9	10	4	
12	"	14	12.00	99	74	9	11	7	
13	"	15	24.00	87	58	13	15	14	
14	"	16	7.00	90	65	12	13	10	
15	"	17	24.00	72	73	6	11	9	
16	"	18	5.35	93	57	5	28	10	
17	<i>n</i> -BuC \equiv CH	11	1.50	96	2	98	0	0	
18	"	12	1.25	97	5	95	0	0	
19	"	13	1.00	95	5	95	0	0	
20	"	14	8.00	87	7	88	4	0	
21	"	15	5.00	82	9	85	3	3	
22	"	16	2.00	98	14	79	6	0	
23	"	17	4.50	92	10	88	2	0	
24	"	18	4.25	94	22	64	8	6	
25	Et ₃ SiC \equiv CH	11	5.00	93	56	0	42	2	
26	"	12	12.00	98	74	4	21	0	
27	"	13	1.00	98	45	0	55	0	
28	"	14	9.00	94	51	0	49	0	
29	"	15	24.00	81	67	0	33	0	
30	"	16	1.75	98	38	1	61	0	
31	"	17	24.00	78	55	1	43	0	
32	"	18	5.35	90	81	2	17	0	

a) Reactions were monitored by ¹H NMR. b) Experiments were carried out using a HSiMe₂Ph/RC \equiv CH/catalyst ratio of 110/100/1, [catalyst]₀ = 1.54 x 10⁻³ M in CDCl₃, temperature 60°C. c) Room temperature.

Table 3. Distribution of products after prolonged heating at 60 °C for the hydrosilylation of *n*-BuC \equiv CH

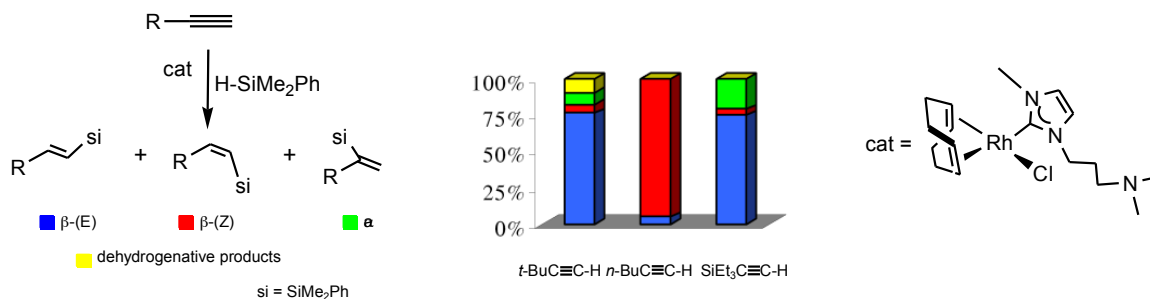
in CDCl₃.

entry	catalyst	time, h	conv %	β -(<i>E</i>)/ β -(<i>Z</i>)	% α	% allyl	% alkene
1	11	1.50	96	0.02	0	0	0
2		10.00	100	0.13	5	0	0
3	12	1.25	97	0.05	0	0	0
4		12.00	100	0.27	7	0	5
5	13	1.00	95	0.05	0	0	0
6		12.00	100	1.29	3	18	0
7	14	5.00	57	0.32	6	0	0
8		15.00	100	4.09	3	41	0
9	15	3.50	70	0.10	3	0	2
10		10.00	100	0.24	7	0	4
11	16	2.00	98	0.18	6	0	0
12		9.00	100	0.64	0	23	0
13	17	4.50	92	0.11	2	0	0
14		12.00	100	0.35	12	0	0

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Rhodium(I) Complexes with Hemilabile N-Heterocyclic Carbenes: Efficient Alkyne Hydrosilylation Catalysts.

M. Victoria Jiménez,* Jesús J. Pérez-Torrente, M. Isabel Bartolomé, Verena Gierz, Fernando J. Lahoz, and Luis A. Oro



A series of neutral and cationic rhodium (I) complexes containing hemilabile amino-alkyl functionalized NHC ligands have been prepared from the appropriate ammonium-imidazolium chloride salts. These complexes are efficient catalyst precursors for the hydrosilylation of terminal alkynes. Excellent selectivities in the β -(Z)-vinylsilane isomer have been found in the hydrosilylation of 1-hexyne. Noteworthy, the hydrosilylation of triethylsilylacetylene gave mainly β -(E) and α bis(silyl)alkenes.