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Homogeneous Catalysis

User-Friendly Platinum Catalysts for the Highly Stereoselective Hydrosilylation of Alkynes and Alkenes

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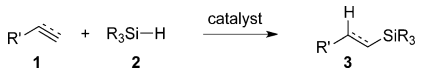
Abstract: With a view to addressing the shortcomings of traditional catalysts, a new generation of outstanding N-heterocyclic carbene platinum(0) complexes for the hydrosilylation of unsaturated carbon–carbon bonds is reported. Their discovery and application to the stereoselective addition of various silanes to silylated alkynes, terminal acetylenes, and olefins is presented. Insights into the catalytic cycle and the origin of the stereoselectivity are also discussed.

Introduction

The hydrosilylation of alkenes and alkynes, that is, the addition of silicon–hydrogen units across carbon–carbon double or triple bonds, represents the ideal pathway to produce organosilicon compounds (Scheme 1).[1] This reaction is usually



Scheme 1. General hydrosilylation process.

straightforward to perform and fully atom-economical. Moreover, the reagents are stable, cheap and readily available. Therefore, it is hardly surprising that this transformation constitutes the core of the organosilicon industry, together with the Rochow–Müller process.[2] Accordingly, it is used to produce various silicon derivatives, ranging from bulk commodities to fine chemicals, and specialty products such as lubricating oils, paper release coatings, or grafting agents. Besides, the organosilane products are valuable building blocks for organic synthesis that take advantage of the richness and versatility of organosilicon chemistry, beyond Tamao–Kumada oxidation and Hiyama–Denmark cross-coupling reactions.[3] Additionally, organosilicon compounds can undergo long synthetic sequences without decomposition.[3d]

Although this reaction is thermodynamically favored, it is not spontaneous and thus must be catalyzed. Platinum is the metal of choice for this purpose and nowadays the Karstedt complex **4** (Figure 1) is widely employed.[4] Despite its success, several drawbacks persist. Most noteworthy in the case of olefins, it is not completely selective and affords undesired side products, such as isomerized and reduced starting materials. Moreover, acetylenes usually afford mixtures of stereoisomeric vinyl silanes. At the same time, this catalyst is not stable under the reaction conditions and produces platinum colloids that can taint the final products and promote the formation of some of the byproducts. Interestingly, the addition of bulky phosphine ligands to this fragile complex improves its selectivity.[5] Unfortunately, these catalytic systems are sensitive towards air and moisture, and still form platinum colloids. Consequently, their use in large-scale hydrosilylations is severely hampered and the industry is still in need of improved catalysts.[6]

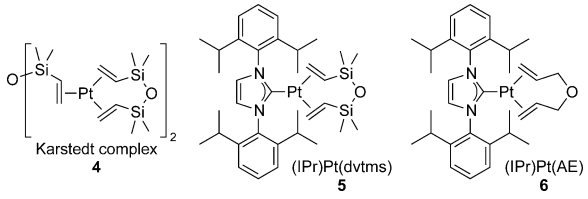


Figure 1. Hydrosilylation catalysts. AE = diallyl ether, dvtms = 1,3-divinyltetramethyldisiloxane, IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene.

Results and Discussion

In the course of our research program dedicated to the 2nd generation hydrosilylation precatalyst [(IPr)Pt(AE)] (**6**; Figure 1; IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene, AE = diallyl ether),[7] we recently discovered that silylated alkynes bind tightly to catalytically active platinum species, hence promoting deactivation pathways and leading to disappointing levels of selectivity (see below).[8] Intrigued by this unexpected reactivity, we decided to optimize the reaction parameters for this particular class of compounds (Table 1). In brief, the protocol was improved by (a) stirring the silane and precatalyst together

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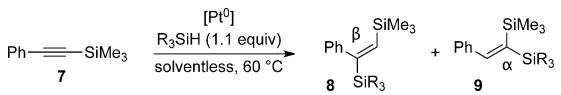
Table 1. Optimization of trimethylsilyl phenylacetylene (**7**) hydrosilylation.

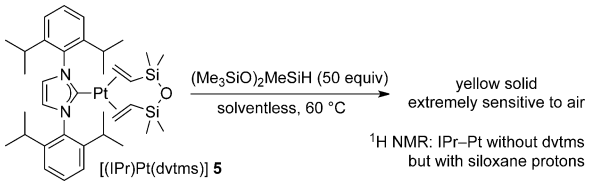


	[Pt^0] (mol%)	R_3SiH	Activation time[a] [h]	Reaction time [h]	β/α[b]	Yield[c] [%]
1	**6** (0.1)	$(Me_3SiO)_2MeSiH$	0	36	6:1	n.d.
2	**6** (0.1)	$(Me_3SiO)_2MeSiH$	1	18	10:1	87
3	**6** (0.1)	$PhMe_2SiH$	1	3	12:1	90
4	**6** (1)	$(Me_3SiO)_2MeSiH$	1	3	10:1	84
5	**5** (1)	$(Me_3SiO)_2MeSiH$	1	3	10:1	88

Performed on 3 mmol scale. [a] Time of activation of the precatalyst by the silane, before addition of the substrate **7**; [b] determined by ^1H NMR spectroscopy on the crude reaction mixture; [c] yield of product isolated by filtration through a plug of silica gel/celite/$MgSO_4$, GC purity >95%.

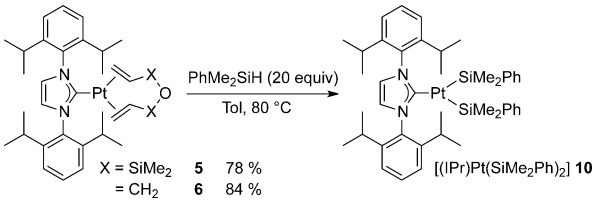
for 1 h before adding the substrate (Table 1, entry 2 vs. 1), (b) replacing bis(trimethylsilyloxy)methylsilane with the more reactive phenyldimethylsilane (entry 3 vs. 1), and (c) increasing the catalyst loading to 1 mol% (entry 4 vs. 1). At this point, serendipity came into play as we ran out of the 2nd generation precatalysts **6**. As a result, the 1st generation precatalyst [(IPr)Pt(dvtms)] (**5**; Figure 1; dvtms = 1,3-divinyltetramethyldisiloxane) was employed instead and, under otherwise identical conditions, the two complexes unexpectedly performed similarly (Table 1, entry 5 vs. 4).[9]

The activation effect of the silane on the precatalyst might have been challenging to rationalize if the two generations of precatalysts had not afforded the same result. Undoubtedly, this observation suggested that, upon activation, both **5** and **6** lead to a common intermediate, which is the real catalyst (or precatalyst) of the transformation. To confirm this hypothesis, we undertook the isolation of this putative species. For that purpose, **5** was treated with bis(trimethylsilyloxy)methylsilane for 2 h at 60 °C and the excess silane was removed under reduced pressure (Scheme 2). Disappointingly, the resulting



Scheme 2. Reaction between [(IPr)Pt(dvtms)] **5** and bis(trimethylsilyloxy)-methylsilane.

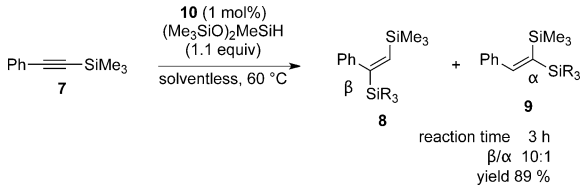
crude yellow solid was not stable enough to be isolated in pure form by classical purification techniques. Nevertheless, a crude ^1H NMR spectrum suggested that the carbene IPr was still coordinated to platinum. Furthermore, there were siloxane proton signals but no trace of a double bond. According to these data, it could be postulated that the new compound was an [(IPr)–Pt] complex bearing several silyl ligands.[10]



Scheme 3. Preparation of [(IPr)$Pt(SiMe_2Ph)_2$] **10**.

This interpretation suggested the yellow solid to be an analog of the bis-silyl platinum complex [(IPr)$Pt(SiMe_2Ph)_2$] (**10**), which was previously isolated by our group (Scheme 3).[11] Both generations of platinum precatalysts **5** and **6** afford, under similar conditions, the same bis-silyl complex **10**.

Consequently, complex **10** was synthesized again and employed in the hydrosilylation of trimethylsilyl phenylacetylene (**7**). At the onset, **10** was stirred with $(Me_3SiO)_2MeSiH$ for 1 min before addition of the substrate **7** (Scheme 4). Gratifyingly, the

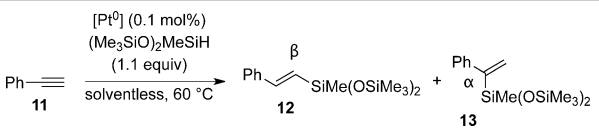


Scheme 4. Hydrosilylation of trimethylsilyl phenylacetylene catalyzed by [(IPr)$Pt(SiMe_2Ph)_2$] **10**.

same outcome was observed as when either **6** or **5** was used under optimized conditions (Table 1, entries 4 and 5). These observations strongly suggest that a bis-silyl platinum complex is a plausible intermediate.

Realizing that we had potentially in hand a 3rd generation of hydrosilylation platinum precatalysts, we decided to compare the three generations under the same conditions, that is, by adding all of the reagents at the same time, and using a fairly simple substrate; phenylacetylene (**11**; Table 2). It rapidly transpired from these experiments that bis-silyl platinum complex **10** is truly a potent hydrosilylation precatalyst. It is more efficient than the previous precatalysts **5** and **6**, not only in the difficult hydrosilylation of silylated alkynes, but also for terminal alkynes.

Table 2. Comparison of the three generations of platinum precatalysts.



	[Pt^0]	Reaction time [h]	β/α[a]	Yield[b] [%]
1	**5**	7	12:1	95
2	**6**	4	16:1	95
3	**10**	1	>20:1	96

Performed on 3 mmol scale. [a] Determined by ^1H NMR spectroscopy on the crude reaction mixture; [b] yield of product isolated by filtration through a plug of silica gel/celite/$MgSO_4$, GC purity >95%.

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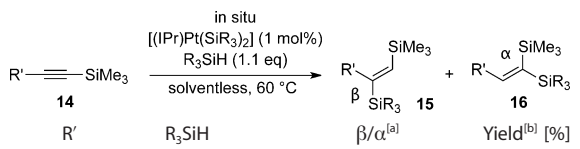
Recognizing that the complexes of the type [(IPr)Pt(SiR_3)$_2$] are exceptional hydrosilylation precatalysts, we endeavored to explore their potential.[12] However, the single isolated member of this family, [(IPr)Pt($SiMe_2Ph$)$_2$] **10**, cannot be stored for more than two days. Longer storage requires it to be kept away from light and under high vacuum in a sealed ampoule.[13] For this practical reason, we resolved to use the more convenient activation pathway of the robust [(IPr)Pt(dvtms)] **5** by the silanes, generating the 3rd generation precatalyst in situ for all following hydrosilylation reactions.

The results of the hydrosilylation of silylated alkynes by our new precatalysts are presented in Table 3. For every substrate, the selectivities and yields were excellent. Interestingly, where-

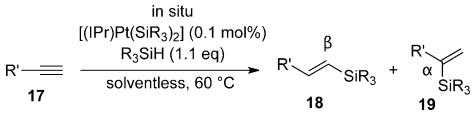
Table 3. Hydrosilylation of silylated alkynes.

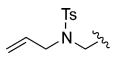


	R′	R_3SiH	β/α[a]	Yield[b] [%]
1[c]	*n*Hex	$(Me_3SiO)_2MeSiH$	13:1	97
2	*t*Bu	$(Me_3SiO)_2MeSiH$	1:14	82
3	Ph	$(Me_3SiO)_2MeSiH$	13:1	97
4	Ph	$PhMe_2SiH$	19:1	88
5	Ph	Ph_2MeSiH	>20:1	90

Performed on 3 mmol scale. [a] Determined by ^{1}H NMR spectroscopy on the crude reaction mixture; [b] yield of product isolated by filtration through a plug of silica gel/celite/$MgSO_4$, GC purity >95%; [c] 0.1 mol% of precatalyst was used.

Table 4. Hydrosilylation of terminal alkynes.



	R′	R_3SiH	β/α[a]	Yield[b] [%]
1	*n*Hex	Et_3SiH	7:1	93
2	*n*Hex	$(Me_3SiO)Me_2SiH$	>20:1	94
3	*n*Hex	$(Me_3SiO)_2MeSiH$	96:1[c]	98
4[d]	*n*Hex	$(Me_3SiO)_2MeSiH$	41:1[c]	98
5[e]	*n*Hex	$(Me_3SiO)_2MeSiH$	13:1[c]	92
6	*n*Hex	$(Me_3SiO)_3SiH$	>20:1	96
7[f]	*n*Hex	$PhMe_2SiH$	>20:1	86
8	*n*Hex	Ph_2MeSiH	>20:1	96
9[g]	*n*Hex	Ph_2ClSiH	>20:1	87
10[d]	*n*Hex	$(EtO)_2MeSiH$	>20:1	98
11[h]	Ph	$(Me_3SiO)_2MeSiH$	>20:1	91
12		$(Me_3SiO)_2MeSiH$	>20:1	95
13		$(Me_3SiO)_2MeSiH$	>20:1	98
14		$PhMe_2SiH$	>20:1	97
15[h]		$PhMe_2SiH$	14:1	82[i]

Performed on 3 mmol scale, with the exception of entry 4, which was performed on 65 mmol scale. [a] Determined by ^{1}H NMR spectroscopy on the crude reaction mixture; [b] yield of product isolated by filtration through a plug of silica gel/celite/$MgSO_4$, GC purity >95%; [c] determined by GC/MS on the crude reaction mixture; [d] 0.03 mol% precatalyst; [e] 0.01 mol% precatalyst; [f] 0.05 mol% precatalyst; [g] quenched with ethanol/triethylamine and isolated as ethoxy(hexenyl)diphenylsilane; [h] 1 mol% precatalyst; [i] yield of product isolated by column chromatography on silica gel, GC purity >95%. Ts = *para*-toluenesulfonyl.

as an *n*-hexyl or a phenyl substituent directed the incoming silyl group at the β position and afforded the expected (*E*)-bis-silylvinyl products (Table 3, entries 1, 3–5),[7b] a bulky *tert*-butyl group led to the opposite regioisomer (entry 2). This is in agreement with a regioselectivity model governed by steric effects (see below). Pleasingly, arylsilanes were perfectly tolerated, leading to improved regioselectivities (Table 3, entries 4 and 5).

The 3rd generation platinum precatalysts proved to be exceptional promoters for the hydrosilylation of terminal acetylenes, affording exquisite selectivities for almost every substrate examined (Table 4). Surprisingly, triethylsilane provided relatively low regioselectivity levels, although the yields were excellent (Table 4, entry 1). Notwithstanding this specific case, every other silane scrutinized, including silyloxy-, aryl-, chloro-, and alkoxysilanes, achieved high yields and outstanding selectivities (Table 4, entries 2–10). It should be noted that the catalyst loading could be reduced to 0.01 mol% while still maintaining excellent selectivities (Table 4, entries 3–5). Moreover, the procedure was scaled up to 65 mmol without any difficulties (Table 4, entry 4)[14] and phenylacetylene was also successfully hydrosilylated (entry 11). Under these conditions, free alcohols were not silylated (Table 4, entries 12–14) and increased steric hindrance proved not to be detrimental to the selectivity (entry 13). It is important to point out that the reaction of the tosylamine derivative (Table 4, entry 15) represents three challenges: a) both unsaturated groups can be hydrosilylated; b) the 1,6-enyne system might poison the catalyst by chelation; c) the double bond could direct the reversible 1,2-migratory insertion toward the α isomer (see below). Therefore, this substrate was introduced in one portion (see below) and the catalyst loading was increased to 1 mol%. We were pleased to note that there was no trace of hydrosilylation of the double bond and that the vinylsilane could be obtained with excellent regioselectivity. The perfect discrimination between both unsaturations is attributed to the higher coordinating ability of the alkyne (stronger π-acidity).[15]

Finally, [(IPr)Pt(SiR_3)$_2$] precatalysts were evaluated in the hydrosilylation of olefins (Table 5). 1-Octene and (+)-β-citronellene were straightforwardly hydrosilylated with complete regiocontrol (Table 5, entries 1 and 2). Epoxides (readily opened with Karstedt catalyst **4**) as well as alcohols were tolerated (Table 5, entries 3 and 4). The hydrosilylation of allyl ethers and esters was carried out in good yields without degradation through π-allyl platinum intermediates (Table 5, entries 3–7), enabling us to easily assemble γ-functionalized propylsilanes, which are highly desired building blocks for industrial applications.[6] Although allyl methacrylate was easily polymerized, introducing a radical inhibitor minimized this side reaction and the hydrosilylated adduct could be obtained in good yields (Table 5, entry 7). Furthermore, the hydrosilylation of a 1,1-disubstitued alkene was also successfully

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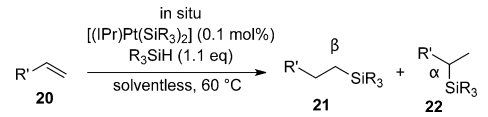
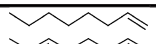
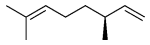
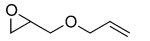
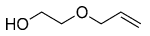
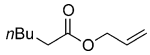
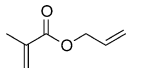
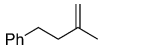
Table 5. Hydrosilylation of alkenes.



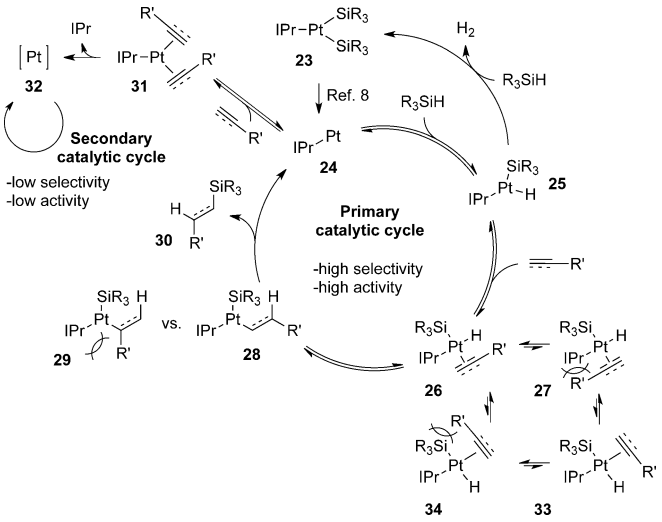
	Alkene	R_3SiH	β/α[a]	Yield[b] [%]
1		$(Me_3SiO)_2MeSiH$	>20:1	91
2		$(Me_3SiO)_2MeSiH$	>20:1	99
3		$(Me_3SiO)_2MeSiH$	>20:1	78[c]
4		$(Me_3SiO)_2MeSiH$	>20:1	95[d]
5[e]		$(EtO)_3SiH$	>20:1	96
6[f]		$(EtO)_2MeSiH$	>20:1	86
7[g]		$(Me_3SiO)_2MeSiH$	>20:1	54[d]
8[h]		$(Me_3SiO)_2MeSiH$	>20:1	86
9[i]		Ph_2MeSiH	–	n.c.

Performed on 3 mmol scale. [a] Determined by ^1H NMR spectroscopy on the crude reaction mixture; [b] yield of product isolated by filtration through a plug of silica gel/celite/$MgSO_4$, GC purity >95%; [c] yield of product isolated by distillation, GC purity >95%; [d] yield of product isolated by column chromatography on silica gel, GC purity >95%; [e] 0.05 mol% precatalyst; [f] 0.025 mol% precatalyst; [g] 1 mol% 2,6-di-*tert*-butyl-*p*-cresol introduced as radical inhibitor; [h] 1 mol% precatalyst; [i] 5 mol% precatalyst, 85 °C.

carried out (Table 5, entry 8). In stark contrast, internal double bonds, as in cyclohexene, did not react, even when increased catalyst loadings and temperatures were used (Table 5, entry 9).

Although our platinum(0) complexes mediate hydrosilylation with various silanes, bis(trimethylsilyloxy)methylsilane is our preferred reagent. Indeed, it is cheap, stable, and mimics the backbone of siloxane polymers. Rewardingly, its stability does not preclude its hydrosilylation adducts from undergoing Tamao–Kumada oxidation,[9b,16] Hiyama–Denmark cross-coupling,[7b,16,17] and other transformations.[16]

Based upon the experimental results reported herein and in earlier studies,[7–11,18] a general mechanism for the hydrosilylation of carbon–carbon multiple bonds catalyzed by [(IPr)Pt(SiR_3)$_2$] **23** can be proposed (Scheme 5). We have previously demonstrated that, upon coordination of a π-ligand, the bis-silyl complex **23** releases its silyl ligands.[11] Two pathways are concomitantly operating: a) the direct reductive elimination of a disilane molecule (R_3Si–SiR_3) and b) the bis-silylation of the incoming π-ligand to produce a 1,2-bis-silane. The resulting active catalyst **24** subsequently undergoes an oxidative addition to the silane, yielding the platinum(II) complex **25**. After coordination of the substrate, a 1,2-migratory insertion leads to the alkyl/alkenyl platinum compound **28**. Finally, a reductive elimination yields the hydrosilylated product **30**, closing the catalytic cycle and regenerating the active species **24**. Remarkably, in the case of some olefins, the oxidative addition and the 1,2-migratory insertion steps might be concerted. Indeed, extensive kinetic studies of the hydrosilylation of



Scheme 5. Proposed general mechanism for the hydrosilylation of alkynes and alkenes catalyzed by [(IPr)Pt(SiR_3)$_2$] **23**.

1-hexene with bis(trimethylsilyloxy)methylsilane catalyzed by [(IPr)Pt(dvtms)] revealed the reaction to be first order in the alkene, the silane, and the catalyst.[18]

Details of the origin of the selectivity in favor of the β regioisomers remain unclear.[18] It is assumed that, following coordination of the substrate, the two isomers **26** and **27** can be formed and are most probably in equilibrium.[19] In complex **27**, the larger substituent of the unsaturated group is facing the bulky carbene IPr moiety, generating repulsive steric interactions and shifting the equilibrium towards its counterpart **26**. Alternatively, equilibration can take place between species **26** and **27** with the silyl *cis*-complexes **33** and **34**.[20] Due to steric repulsion between the R′ substituent and the silicon moiety, **33** should be favored over **34**. Subsequent hydride insertion into either **33** or **26** produces almost exclusively intermediate **28**. Moreover, this adduct is thermodynamically favored over its regioisomer **29** due to reduced steric repulsion between IPr and the alkyl/alkenyl substituent.

The substrate can also trigger a deactivation pathway by binding to the platinum(0) catalyst **24**, generating the complex **31**. Although inactive, this intermediate can lose its N-heterocyclic carbene (NHC) ligand to give the unidentified platinum species **32**.[7b,21] These complexes enter a secondary catalytic cycle that displays lower activity and selectivity, presumably due to the lack of a bulky controlling ligand. Thus, maintaining a low substrate concentration throughout the transformation should limit the access to the deactivation pathway. Hence, in almost all hydrosilylation reactions summarized in Tables 3–5, the acetylenes and olefins were introduced slowly using a syringe pump, leading to a noticeable increase in stereoselectivity.[7b,22]

Conclusion

The unexpected behavior of silylated alkynes in our previously reported catalytic system led to the discovery and development of a new generation of N-heterocyclic carbene platinum

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catalysts for the hydrosilylation of alkenes and alkynes. Outstanding yields and stereoselectivities, high functional group and silane compatibilities, and very low catalyst loadings are the hallmark of this new hydrosilylation protocol. Fortunately, the precatalyst precursor **5** is insensitive towards air and moisture, bench-stable for extended periods of time, readily synthesized, and commercially available.[23] In general, all of the reagents were mixed directly from their bottles and stirred in air without any precaution. Moreover, the use of solventless conditions, coupled with a fully atom-economical transformation, leads to a green process that is attractive for industry.

Experimental Section

Typical hydrosilylation procedure: [(IPr)Pt(dvtms)] (**5**; 0.1 mol%) and the silane (1.1 equiv) were stirred in a round-bottomed flask at 60 °C for 1 h. To the resulting yellow solution, the substrate (1 equiv) was introduced slowly with a syringe pump (0.5–3 mmol h^{-1}). After confirming the completion of the reaction by GC, the reaction mixture was cooled to room temperature and filtered through a pad of silica gel/Celite/$MgSO_4$ (1:1:1 v/v/v), eluting with petroleum ether or diethyl ether (depending on product polarity). The filtrate was concentrated under reduced pressure and the last traces of volatiles were removed under high vacuum to afford the product as a colorless or light-yellow liquid. If necessary, analytically pure samples can usually be obtained by Kugelrhor distillation or column chromatography on silica gel.

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Keywords: carbenes · homogeneous catalysis · hydrosilylation · platinum · silanes

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[10] The conversion of **5** into **10** could be partially followed by ^{1}H NMR spectroscopy. As the signals of the dvtms ligand gradually disappeared, those belonging to the bis-silyl platinum species **10** rose. When this crude NMR solution was evaporated carefully under vacuum and the resulting orange oil was treated with 1-octyne and $HSiMe_2Ph$, silylated alkene **18** (R′ = ^{n}Hex) was formed in good yield and selectivity (F. Chellé, I. E. Markó, *unpublished results*). It must be emphasized however that this crude NMR solution contains several other impurities and precise kinetic measurements have not been performed on such an impure sample.

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[13] IPr)Pt$(SiMe_2Ph)_2$ **10** can be prepared and stored in a glovebox for extended periods of time.

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[19] In the lowest energy isomer, the π-ligand is most probably perpendicular to the coordination plane of the complex. However, it must rotate into the plane for the 1,2-migratory insertion to occur.

[20] Coordination of the alkene or the alkyne *cis* to the silyl substituent might explain the observed variation in selectivity according to the size

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of the silyl group. We are grateful to a referee for providing us with this suggestion.

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[22] We reported in reference [7b] that strongly coordinating alkynes had a deleterious effect on both the rate and the selectivity of the hydrosilylation reaction. This is especially true for silylated alkynes that bind rather tightly to platinum(0) complexes. Solutions to this problem involve greater catalyst loading, higher temperature or slow addition of the alkyne, which has been our preferred solution. For example, hydrosilylation of **14** (R′ = Ph) by adding the alkyne all at once leads to a reduced selectivity of 8:1 in favor of **15** (compare with Table 3, entry 4).

[23] Available from Umicore AG. Catalog number HS425, CAS number 849830-54-2. Visit chemistry.umicore.com.

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