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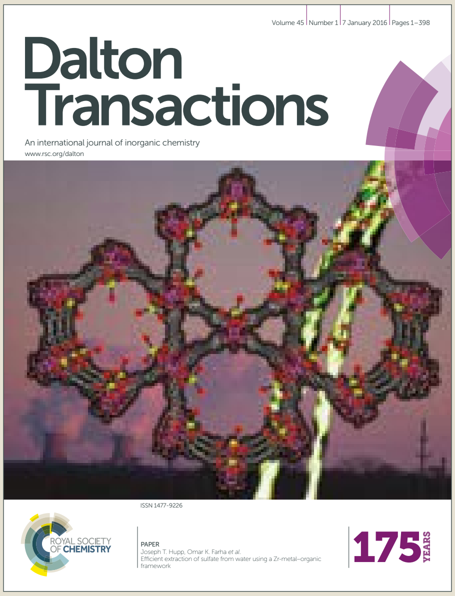

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ARTICLE

Highly selective hydrosilylation of olefins and acetylenes by platinum(0) complexes bearing bulky *N*-heterocyclic carbene ligands

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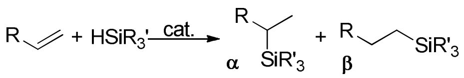
P. Żak, M. Bołt, M. Kubicki and C. Pietraszuk*

Platinum complexes bearing bulky *N*-heterocyclic carbene (NHC) ligands, i.e. [Pt(IPr*)(dvtms)] (where IPr*=1,3-bis{2,6-bis(diphenylmethyl)-4-methylphenyl}imidazol-2-ylidene) and [Pt(IPr*^{OMe})(dvtms)] (where IPr*^{OMe}=1,3-bis{2,6-bis(diphenylmethyl)-4-methoxyphenyl}imidazol-2-ylidene, dvtms = divinyltetramethyldisiloxane) catalyse nearly quantitatively and highly or completely selective hydrosilylation of terminal olefins as well as terminal or internal acetylenes.

This paper is dedicated to the memory of Professor Istvan E. Markó who pioneered the chemistry of [Pt(NHC)(dvtms)] complexes.

Introduction

Hydrosilylation of olefins and acetylenes is the most fundamental method for laboratory and industrial synthesis of organosilicon compounds,[1] widely used in both general organic synthesis[2] and special materials chemistry.[3] A significant disadvantage of the hydrosilylation of olefins as a synthetic method is the lack of selectivity. In the presence of many catalytic systems, the reaction leads to the formation of a mixture of regioisomers (Scheme 1). Moreover, the reaction is often accompanied by side-processes, such as dehydrogenative silylation, isomerization and hydrogenation of olefins.[1]

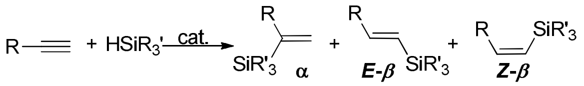


Scheme 1 Hydrosilylation of olefins with trisubstituted silanes

Although hydrosilylation of olefins has been investigated using various transition metal complexes as catalysts,[1,4-6] industry still relies largely on platinum-based systems such as the Speier[7] and Karstedt catalysts.[1,8-10] Despite the high activity, these catalytic systems have several drawbacks including low regioselectivity and instability under reaction condition causing the formation of colloidal platinum species which tend to promote formation of undesired side-products.

In 2002 Markó reported new structural type of platinum complexes of the general formula [Pt(NHC)(dvtms)] (where dvtms = 1,3-divinyl-1,1,3,3-tetramethyldisiloxane).[11] Compared with the Karstedt catalyst, these complexes used as catalysts in hydrosilylation of alkenes are characterized by slightly lower catalytic activity, higher chemo- and regioselectivity, and significantly improved stability. An important feature of these catalysts is no tendency towards decomposition to platinum colloids.[11] Main factors which affect the catalytic activity and regioselectivity of [Pt(NHC)(dvtms)] complexes are steric hindrance imparted by the N-aryl groups, the rate of formation of the monoligated platinum complex, and relative stability of Pt(NHC) species.[11] Development of the family of Markó complexes resulted in the synthesis of new catalysts permitting highly efficient and regioselective hydrosilylation of a range of functional olefins.[12]

Acetylenes are considered more demanding substrates for hydrosilylation than olefins because the reaction usually results in a mixture of regio- and stereoisomers (Scheme 2).



Scheme 2 Hydrosilylation of acetylenes with trisubstituted silanes

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Adam Mickiewicz University in Poznań, Faculty of Chemistry, Umultowska 89b, 61-614 Poznań, Poland
E-mail: pietrasz@amu.edu.pl

† Footnotes relating to the title and/or authors should appear here.
Electronic Supplementary Information (ESI) available: Analytical data of isolated products and details of X-ray analyses. See DOI: 10.1039/x0xx00000x

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Literature provides reports on selective conversion of both terminal and internal acetylenes in the presence of a variety of transition metal complexes.[1] Commonly used Karstedt catalyst catalyzes cis addition of hydrosilane to acetylene, but with low regioselectivity.[1a,b] The use of complexes with bulky phosphine ligands has made significant improvement as far as regioselectivity is concerned. Platinum(0) complexes of the type [Pt(PR$_3$)(dvtms)], where PR$_3$ is a bulky phosphine ligand, e.g. P^{t}Bu$_3$, allow obtaining anti-Markovnikov product with relatively high *E* selectivity in hydrosilylation of terminal acetylenes.[14]

Markó has shown that [Pt(NHC)(dvtms)] complexes can be used as selective catalysts of hydrosilylation of acetylenes[15] and their selectivity depends strongly on the steric properties of carbene ligands. Development of application of Markó type complexes in acetylene hydrosilylation is a topic of several recent reports.[13f,16] The selectivity of hydrosilylation of 1-octyne expressed by molar ratio of isomers [β-*E*]/[α] was shown to increase with increasing steric parameter A$_H$.[15,17] The highest selectivity ([β-*E*]/[α] = 10.6) was obtained for a complex containing a bulky carbene ligand, i.e. 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr).[15] An analogous complex [Pt(IPr)(AE)] (where AE = diallyl ether) with similar steric parameters, but containing diallyl ether, a more labile throw-away ligand than dvtms, enabled selective hydrosilylation of terminal acetylenes with very high preference for the formation of *E*-*β*-adduct and different regioselectivity in hydrosilylation of unsymmetrical internal acetylenes.[16b] Relative, *N*-heterocyclic carbene platinum bis(silyl) complexes [Pt(IPr)(SiR$_3$)$_2$],[18] exhibit improved regioselectivity of hydrosilylation of unsymmetrical internal acetylenes giving the [β]/[α] ratio generally exceeding 20/1.[16a]

Recently, we have reported the synthesis of two Markó type platinum(0) complexes bearing bulky *N*-heterocyclic carbene ligands, e.i. [Pt(IPr*)(dvtms)] (**1**) (where IPr*=1,3-bis{2,6-bis(diphenylmethyl)-4-methylphenyl}imidazol-2-ylidene) and [Pt(IPr*^{OMe})(dvtms)] (**2**) (where IPr*^{OMe}=1,3-bis{2,6-bis(diphenylmethyl)-4-methoxyphenyl}imidazol-2-ylidene (Figure 1).[19] Because the values of A$_H$ angles in complexes **1** and **2** (equal to 201.6° and 213.4°, respectively) significantly surpass the corresponding values in the previously described complexes,[15] we decided to examine the complexes **1** and **2** in hydrosilylation of olefins and acetylenes and demonstrate the impact of bulky yet flexible NHC ligands on chemo- regio- and stereoselectivity. Herein, we report on the high productivity and striking selectivity of complexes **1** and **2** in hydrosilylation of terminal olefins as well as terminal and internal acetylenes.

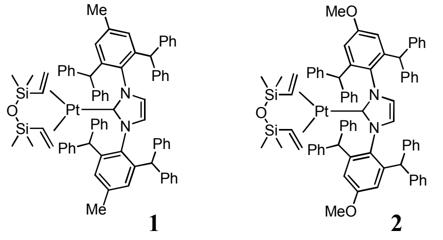
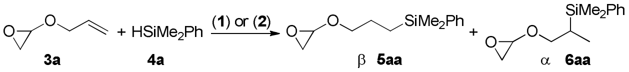


Figure 1 Platinum complexes with bulky NHC ligands used in the presented studies

Results and Discussion

Our examination started with the testing of catalytic properties of complexes **1** and **2** in olefin hydrosilylation. Allyl glycidyl ether was chosen as a test olefin, as it is commonly used in the studies of olefin hydrosilylation and it could undergo undesirable processes of isomerization. Both complexes **1** and **2** were tested as catalyst in hydrosilylation of allyl glycidyl ether with dimethylphenylsilane under a range of conditions in order to find the conditions for the efficient and selective course of the reaction (Scheme 3). The results are summarized in Table 1.



Scheme 3 Hydrosilylation of allyl glycidyl ether with dimethylphenylsilane catalyzed by **1** or **2**.

As shown in Table 1, the best results were achieved by conducting the reaction in toluene, at 80°C, under argon. Under optimized conditions the reaction in the presence of complexes **1** or **2** led to the exclusive formation of β-adduct.

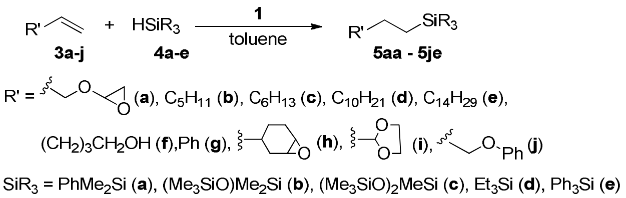
Table 1 Hydrosilylation of allyl glycidyl ether with dimethylphenylsilane. Optimization of the reaction conditions

Entry	Cat. (% mol)	Time [h]	Temp. [°C]	Conv.[a] [%]	β:α [b]
1	**1** (1×10^{-3})	5	100	90	94:6
2	**1** (1×10^{-4})	2	100	99	95:5
3	**1** (1×10^{-4})	6	80	99	β[c]
4	**2** (1×10^{-4})	6	80	98	β[c]
5	**1** (1×10^{-4})	24	60	92	β[c]
6	**2** (1×10^{-4})	24	60	90	β[c]
7	**1** (1×10^{-3})	24	25	75	β[c]

Reaction condition: Toluene, argon; [**3a**]:[**4a**] = 1:1; [a] Determined by GC analysis; [b] Determined by GC analysis and confirmed by ^{1}H NMR spectroscopy of the crude reaction mixture; [c] no α addition product was detected

Both catalysts showed similar catalytic properties. Therefore, in the following part of the publication, only the results obtained for catalyst **1** were reported. The results obtained using catalyst **2** are included in Supporting Information. The tests performed have shown that the process can be carried out in solvent-free conditions, but due to the fact that many of the potential substrates are solids, toluene is suggested as the reaction medium.

Having an active and selective catalyst in hand, the range of substrates was extended to determine the versatility of the method (Scheme 4). The results were collected in Table 2.



Scheme 4 Hydrosilylation of terminal olefins catalyzed by **1**

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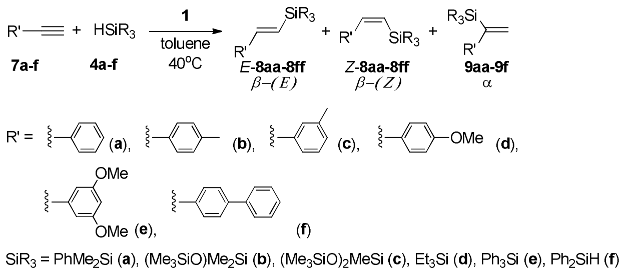
Table 2 Hydrosilylation of terminal alkenes in the presence of complex **1**

Entry	Olefin	$HSiR_3$	**1** [mol%]	Time [h]	Yield[a] [%] (isolated)
1	**3a**	**4b**	5×10^{-3}	2	98[b]
2		**4c**	5×10^{-3}	6	98
3		**4d**	5×10^{-3}	9	97[b]
4		**4a**	1×10^{-4}	6	99
5		**4e**	1×10^{-1}	24	99
6	**3b**	**4b**	1×10^{-4}	8	99[b]
7		**4c**	5×10^{-3}	24	99 (95)
8		**4d**	1×10^{-3}	24	98[b]
9		**4a**	1×10^{-5}	18	99
10		**4e**	1×10^{-1}	24	92
11	**3c**	**4b**	1×10^{-3}	5	99[b]
12		**4c**	5×10^{-3}	2	98
13		**4d**	1×10^{-4}	7	99[b]
14		**4a**	1×10^{-5}	3	99
15		**4e**	1×10^{-1}	24	94
16	**3d**	**4b**	1×10^{-4}	8	99[b]
17		**4c**	5×10^{-3}	24	99
18		**4d**	1×10^{-3}	24	97[b]
19		**4a**	1×10^{-5}	24	99
20		**4e**	1×10^{-1}	24	95
21	**3e**	**4b**	5×10^{-4}	2	99[b]
22		**4c**	5×10^{-3}	24	91
23		**4d**	1×10^{-4}	24	89[b]
24		**4a**	1×10^{-5}	4	99
25		**4e**	1×10^{-1}	24	95
26	**3f**	**4b**	5×10^{-3}	9	97[b]
27		**4c**	5×10^{-3}	9	96
28		**4d**	5×10^{-3}	24	99[b]
29		**4a**	5×10^{-4}	5	99
30		**4e**	1×10^{-1}	24	80
31	**3g**	**4a**	1×10^{-3}	24	100
32		**4e**	1×10^{0}	24	85
33	**3h**	**4b**	5×10^{-4}	6	99[b]
34		**4c**	5×10^{-4}	9	99 (95)
35		**4d**	5×10^{-4}	9	97[b]
36		**4a**	1×10^{-5}	8	99
37		**4e**	1×10^{-1}	24	99 (91)
38	**3i**	**4b**	5×10^{-4}	2	99[b]
39		**4c**	5×10^{-4}	3	99
40		**4d**	5×10^{-4}	9	99[b]
41		**4a**	1×10^{-5}	9	98
42		**4e**	1×10^{-1}	24	96
43	**3j**	**4b**	1×10^{-3}	4	97[b]
44		**4c**	1×10^{-3}	4	99
45		**4d**	1×10^{-3}	6	93[b]
46		**4a**	2×10^{-4}	8	98
45		**4e**	1×10^{-1}	24	99

Reaction conditions: toluene, 80°C, argon, [olefin]:[$HSiR_3$] = 1:1; [a] Determined by GC analysis; [b] Reaction performed in closed system

Catalytic hydrosilylation of a range of terminal olefins bearing a variety of functionalities studied in the presence of low loading of catalyst **1** (down to 10^{-5} mol% = 0.1 ppm) proceeds with complete regioselectivity and gives excellent yields of anti-Markovnikov products (Scheme 3). Hydrosilylation of olefins catalyzed by **1** is fully chemoselective. Only when 1-alkenes were used as olefins (Entry 6-25) trace amounts (< 3%) of the alkene isomerization products were observed. The results contribute to expansion of current knowledge on the reaction[12-13] by providing data on the reactivity of a wide range of olefins and trisubstituted silanes. In each case, nearly quantitative and fully selective hydrosilylation have been achieved in the presence of extremely low concentration of catalysts. Significant values of turnover numbers reaching TON = 10^7 were obtained with average values of TON = ca 10^5.

Catalytic properties of complex **1** were also evaluated in the hydrosilylation of a series of terminal arylacetylenes with a variety of trisubstituted silanes and with the disubstituted one (Scheme 5).



Scheme 5 Hydrosilylation of terminal acetylenes catalyzed by complex **1**

Hydrosilylation was found to proceed easily in the presence of 0.1 – 0.05 mol% of complex **1**, in toluene at 40 °C by using equimolar ratio of reacting partners. Such conditions permit quantitative or nearly quantitative conversion of reagents. The results obtained are collected in Table 3. In each case complete or excellent selectivity towards the formation of product β-(*E*) was achieved. For triphenylsilane as a reagent, irrespectively of the acetylene used, the process was fully regioselective. Similarly, fully selective hydrosilylation was observed when diphenylsilane was used as reacting partner. (Table 3, entries 4, 8, 12). Small amounts of β-(*Z*) and α isomers were observed when using $HSiEt_3$ (4d) and even smaller when using $HSiMe_2Ph$ (**4a**). Interestingly, the hydrosilylation of 4-ethynylbiphenyl (**7f**) irrespective of the silane used, led to the exclusive formation of β-(*E*). To increase the diversity of silanes tested, hydrosilylation of selected acetylenes (**7a-c**) were performed with diphenylsilane (**4f**). Reactions result in the chemo- regio- and stereoselective formation of single β-(*E*) products bearing $SiPh_2H$ group with one Si-H bond untouched (Table 3, entries 4,8 and 12). Compared to earlier proposals,[10,13f] the presented procedure permits highly selective hydrosilylation of a series of terminal arylacetylenes with several substituted silanes under mild conditions and low catalyst loadings. The obtained values of turnover numbers were in the range of TON = 1×10^3 and 2×10^4. In order evaluate the possibility to reach even higher TON values a reaction between (dimethylphenylsilyl)acetylene (**7j**) and dimethylphenylsilane (**4a**) in the presence of 0.01 mol% of catalyst **1** were performed until complete conversion was obtained and then repeated without addition of the catalyst. Each time the reaction was carried out to obtain a

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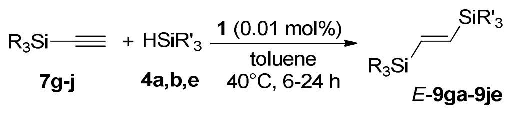
complete conversion. This procedure was repeated four times, without the decrease in the conversion. Only during the fifth repetition, significant drop in the conversion down to 56% was observed. No decrease in selectivity was observed. This experiment indicates that the actual productivity of the catalyst **1** can significantly exceed the values reported above.

Table 3 Hydrosilylation of terminal arylacetylenes in the presence of complex **1**

Entry	R’C≡CH	HSiR$_3$	**1** [mol%]	Time [h]	Yield[a] (isol.)[%]	Selectivity [b] β-*(E)*:β-*(Z)*:α
1	7a	4a	5×10^{-2}	3	100	99:1:0
2		4d	5×10^{-2}	8	99	97:2:1[c]
3		4e	1×10^{-1}	24	88	100:0:0
4		4f	1×10^{-1}	24	95 (90)	100:0:0
5	7b	4a	5×10^{-2}	7	99	100:0:0
6		4d	5×10^{-2}	10	98	97:3:0[c]
7		4e	1×10^{-1}	24	99	100:0:0
8		4f	1×10^{-1}	24	96	100:0:0
9	7c	4a	5×10^{-2}	7	99	98:1:1
10		4d	5×10^{-2}	8	99	96:3:1[c]
11		4e	1×10^{-1}	24	99	100:0:0
12		4f	1×10^{-1}	24	97	100:0:0
13	7d	4a	5×10^{-2}	7	99	99:1:0
14		4d	5×10^{-2}	24	90	95:3:2[c]
15		4e	1×10^{-1}	24	98	100:0:0
16	7e	4a	5×10^{-2}	8	99	98:1:1
17		4d	1×10^{-2}	10	96	96:2:2[c]
18		4e	1×10^{-1}	24	96	100:0:0
19	7f	4a	5×10^{-2}	10	100	100:0:0
20		4b	5×10^{-2}	12	97	100:0:0[c]
21		4c	1×10^{-2}	12	95	100:0:0
22		4d	5×10^{-2}	10	94[c]	100:0:0[c]
23		4e	5×10^{-2}	24	53	100:0:0
24		4e	1×10^{-1}	24	99	100:0:0

Reaction conditions: toluene, 40°C, [silane]:[acetylene] = 1:1; [a] Determined by GC analysis; [b] β-*(E)*:β-*(Z)*:α determined by GC analysis and confirmed by ^{1}H NMR spectroscopy of the crude reaction mixture; [c] Reaction performed in closed system

To increase the applicability of the reaction we tested hydrosilylation of selected silylacetylenes (Scheme 6). In each case, near quantitative conversion and complete regio- and stereoselectivity were observed (Table 4). High conversions were observed upon preserving the equimolar ratio of the reagents.



SiR$_3$ = SiMe$_3$ (**g**), SiEt$_3$ (**h**), SiPr$_3$ (**i**), SiMe$_2$Ph (**j**)
SiR'$_3$ = PhMe$_2$Si (**a**), (Me$_3$SiO)Me$_2$Si (**b**), (Ph$_3$Si) (**e**)

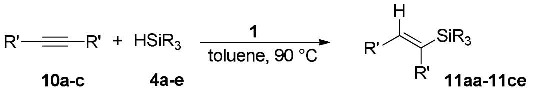
Scheme 6 Hydrosilylation of silylacetylenes catalyzed by **1**

Table 4 Hydrosilylation of terminal silylacetylenes in the presence of complex **1**

Entry	R$_3$SiC≡CH	HSiR’$_3$	Isolated yield [%]
1	7g	4a	90
2	7g	4e	96
3	7h	4a	95
4	7h	4b	92
5	7i	4a	93
6	7i	4b	95
7	7j	4a	94

Reaction conditions: toluene, 40°C, [silane]:[acetylene] = 1:1, cat. **1** (10^{-2} mol%), 6-24 h

To investigate the scope of this reaction with respect to the reagent type, internal acetylenes were used to afford the corresponding unsaturated products. Hydrosilylation of symmetrically substituted internal acetylenes in the presence of catalyst **1** proceeds quantitatively or nearly quantitatively. Only in the hydrosilylation of diphenylacetylene with triphenylsilane, a reduced conversion of the reactants was observed. Important advantage of the process is its complete selectivity (Scheme 7). Characteristic of platinum complexes selective cis-addition resulted in exclusive formation of single stereoisomer irrespective of the nature of the substituents in reacting partners. The results obtained are collected in Table 5.



R' = Ph (**a**), C$_3$H$_7$ (**b**), CH$_2$O(CO)CH$_3$ (**c**)
SiR$_3$ = PhMe$_2$Si (**a**), (Me$_3$SiO)Me$_2$Si (**b**), (Me$_3$SiO)$_2$MeSi (**c**), Et$_3$Si (**d**), Ph$_3$Si (**e**)

Scheme 7 Hydrosilylation of symmetrically substituted internal acetylenes catalyzed by complex **1**

Table 5 Hydrosilylation of symmetrically substituted internal acetylenes in the presence of complex **1**

Entry	R’C≡CHR’	HSiR$_3$	**1** [mol%]	Time [h]	Yield[a] (isol.) [%]
1	10a	4a	5×10^{-2}	7	100 (93)
2		4b	5×10^{-2}	10	98[b]
3		4c	5×10^{-2}	8	100 (95)
4		4d	5×10^{-2}	9	100[b]
5		4e	1×10^{-1}	24	65
6		4e	1	24	100
7	10b	4a	5×10^{-2}	12	99
8		4b	5×10^{-2}	18	99[b]
9		4c	5×10^{-2}	7	99
10		4d	5×10^{-2}	8	99 (95)[b]
11		4e	1×10^{-1}	24	99
12	10c	4a	5×10^{-2}	8	100
13		4b	5×10^{-2}	6	99 (95)[b]
14		4c	5×10^{-2}	5	99 (94)
15		4d	5×10^{-2}	8	95 (90)[b]
16		4e	1×10^{-1}	24	92

Reaction conditions: toluene, 90°C, [silane]:[acetylene] = 1:1; [a] Determined by GC analysis; [b] Reaction performed in closed system

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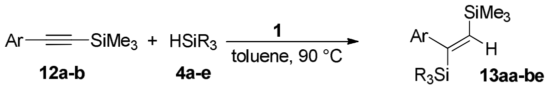
The structures of the obtained products were proposed on the basis of the NMR spectroscopic characterization of selected products.

much more challenging unsymmetrically substituted internal acetylenes. For this purpose, acetylenes (**12a**) and (**12b**) having substituents at carbon-carbon triple bond differing in steric hindrance were subjected to reactions with a series of trisubstituted silanes. In each case complete or nearly complete conversion of reacting partners was achieved under conditions optimized for hydrosilylation of the internal acetylenes. Regardless of silane used, formation of a single isomer was observed (Table 6). The structure of the hydrosilylation product of **12a** with triphenylsilane was determined by X-ray structure analysis methods (Figure 2). The use of acetylenes containing a strongly electron-withdrawing trifluoromethyl group in the phenyl ring at para position (**12b**), did not affect the reaction selectivity but permitted a two-fold reduction in the catalyst concentration.



Ar = C_6H_5 (**a**), $C_6H_4(CF_3)$-4 (**b**);
SiR_3 = $PhMe_2Si$ (**a**), $(Me_3SiO)Me_2Si$ (**b**), $(Me_3SiO)_2MeSi$ (**c**), Et_3Si (**d**), Ph_3Si (**e**)

Scheme 8 Hydrosilylation of unsymmetrically substituted internal acetylenes catalyzed by **1**

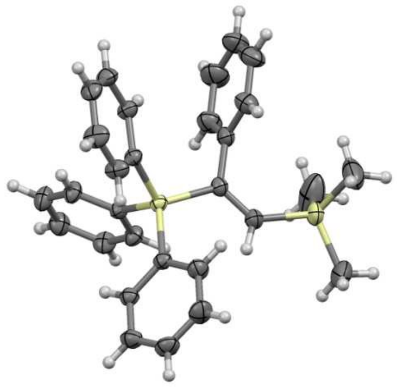


Figure 2. A perspective view of the molecule **13ae**. Ellipsoids are drawn at the 30% probability level, hydrogen atoms are represented by spheres of arbitrary radii.

Table 6 Hydrosilylation of 1-aryl-2-trimethylsilylacetylene with trisubstituted silanes in the presence of complex **1**

Entry	$ArC{\equiv}CSiMe_3$	$HSiR_3$	**1** [mol%]	Time [h]	Yield[a] (isol.) [%]
1	12a	4a	$1{\times}10^{-1}$	24	99[b]
2		4b	$1{\times}10^{-1}$	24	99 (91)
3		4c	$1{\times}10^{-1}$	24	95[b]
4		4d	$1{\times}10^{-1}$	18	99 (92)
5		4e	$1{\times}10^{-1}$	24	97
6	12b	4a	$5{\times}10^{-2}$	20	99[b]
7		4b	$5{\times}10^{-2}$	18	99
8		4c	$5{\times}10^{-2}$	12	98[b]
9		4d	$5{\times}10^{-2}$	18	100 (92)
10		4e	$5{\times}10^{-2}$	24	98

Reaction conditions: toluene, 90°C, [silane]:[acetylene] = 1:1; [a] Determined by GC analysis; [b] Reaction performed in closed system

The results of the reported catalytic tests demonstrate the ability of all tertiary silanes (**4a-e**) to undergo efficient and selective hydrosilylation with olefins and acetylenes. Under optimized reaction conditions, the effect of substituents at silicon atoms can be observed. In the hydrosilylation of olefins, the highest efficiency was observed for dimethylphenylsilane (**4a**). Hydrosilylation this reagent, irrespective of the olefin used, required catalyst loading of ca. 10^{-4}-10^{-5} mol%, i.e. ten times less than the one required for the other silanes (Table 2). The lowest process efficiency was observed for the reactions involving triphenylsilane (4e), where it was necessary to use the catalyst in an amount of 10^{-1} mol% and to extend the reaction time up to 24 hours in order to reach quantitative conversion. A similar effect of substituents at silicon on the reaction efficiency was observed in hydrosilylation of terminal acetylenes (Table 3).

Postulated dependence of reaction selectivity on the stereoelectronic environment of Pt site[15] was checked by performing hydrosilylation of phenylacetylene (**7a**) with dimethylphenylsilane (**4a**) in the presence of a series of complexes of the type [Pt(NHC)(dvtms)] differing in steric properties, characterized by A_H and $\%V_{bur}$ values[17]. The obtained results are collected in Table 7. Under optimized conditions higher selectivities from those described in the literature [16a] were observed for catalysts containing IMes (IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene), IPr and SIPr (SIPr = 1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-ylidene) ligands. In the presence of catalysts **1** and **2** characterized by higher values of the A_H and $\%V_{bur}$ parameters slightly higher selectivities were observed.

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Table 7 Hydrosilylation of phenylacetylene with dimethylphenylsilane in the presence of [Pt(IMes)(dvtms)] (**14**), [Pt(IPr)(dvtms)] (**15**), [Pt(SIPr)(dvtms)] (**16**), [Pt(IPr*)(dvtms)] (**1**) and [Pt(IPr*^{OMe})(dvtms)] (**2**)

Cat	A_H	$\%V_{bur}$	Reaction time [h]	Conv.	Selectivity [b] β-*(E)*:β-*(Z)*:α
14	71	40.8	6	100	97:3:0
15	97	-	5	99	97:3:0
16	99	46.6	7	99	97:3:0
1	201.6	50.9	3	100	99:1:0
2	213.4	52.8	3	100	98:2:0

Reaction conditions: toluene, 40 °C, [silane]:[acetylene] = 1:1; cat. 0.05 mol%; [a] Determined by GC analysis; [b] β-*(E)*:β-*(Z)*:α determined by GC analysis

Moreover, catalytic tests carried out under the conditions described in ref. 13f for exemplary hydrosilylation of terminal and internal acetylene in the presence of complexes **1**, **2** and **15** indicate similar dependence of selectivity on steric properties of the catalysts (Tables S6 and S7).

In all the tests performed, under the reaction conditions used, no generation of platinum nanoparticles was observed. The heterogeneity problems of the hydrosilylation conducted in the presence of N-heterocyclic carbene platinum complexes has not been studied. Therefore, the mercury poisoning experiment [20] has been performed for the hydrosilylation of phenyl propargyl ether (**3j**) with dimethylphenylsilane (**4a**) occurring in the presence of complex **1**. The obtained result unexpectedly indicates a partial inhibition of the reaction by mercury excess (Figure S1). Hot filtration test [21] performed for the same reaction indicates retaining the catalytic activity of the filtrate and lack of any catalytic activity of the residue (Figure S2). Due to the known limitations of methods used for resolving the heterogeneity problems in homogeneous catalysis [22] any unambiguous conclusion cannot be drawn on the basis of performed tests. Results do not exclude the possibility of formation of soluble oligonuclear platinum(0) species and their contribution to catalysis. However, our attempts to confirm formation of such species by mass spectrometry have failed.

From the point of view of the utility in organic and organometallic synthesis, the results show a number of advantages. The simple and convenient protocols presented permit nearly quantitative conversions and highly or fully selective syntheses of the desired products using low loadings of catalyst **1** or **2**. These catalysts are highly productive (TON reaches 10^7 for olefins and 10^4 for terminal and internal acetylenes). No generation of platinum colloids was observed under the reaction conditions used, which helps avoiding the undesired side reactions. Precatalysts **1** and **2** are insensitive towards air and moisture and can be stored as solids for extended periods of time without loss of activity. In contrast to the less bulky structural analogues, for catalyst **1** and **2** there is no need to substitute the dvtms ligand by the more labile diallyl ether to achieve high activity.[16a] In contrast to the catalysts described by Marko,[13f] complexes **1** and **2** do not need preliminary generation of active species. For each of the reactions tested, i.e. for hydrosilylation of terminal olefin, terminal and internal acetylenes, the proposed procedures were scaled up to gram-scale without a decrease in conversions and selectivities (See Supporting Information).

Experimental Section

General methods and reagents

Unless otherwise indicated, all operations were carried out under dry argon, using standard Schlenk techniques. All syntheses and catalytic tests were performed in an open system. Closed system was used only for carrying out the reaction at temperatures exceeding the boiling point of substrates. Reagents were purchased from commercial sources and, unless otherwise indicated, were used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Varian 400 operating at 402.6 and 101.2 MHz, respectively. GC analyses were carried out on a Bruker Scion 436-GC (column: DB-5 30 m I.D. 0.53mm) equipped with a TCD. The GC/MS analyses were performed on a Varian Saturn 2100T equipped with DB-5, 30m capillary column and Ion Trap detector. Thin layer chromatography (TLC) was recorded on plates coated with 250 mm thick silica gel and column chromatography was performed on silica gel 60 (70–230 mesh) using hexane/dichloromethane. Synthesis and characterization of complexes [Pt(IPr*)(dvtms)] (**1**) and [Pt(IPr*^{OMe})(dvtms)] (**2**) was reported in Supporting Information. All solvents used for the synthesis of the complexes were dried prior to use over CaH_2 and stored under argon. DCM was additionally passed through a column with alumina, and after that it was degassed by repeated freeze−pump−thaw cycles.

General procedure for hydrosilylation

A 5 mL glass reactor (open system) or 10 mL high-pressure Schlenk vessel (closed system) was filled successively with toluene (1 mL), appropriate olefin (0.19 mmol) or acetylene (0.19 mmol), silane (0.19 mmol) and internal standard (decane or dodecane, 20 µL). Then, catalyst **1** was added to solution (10^{-5}–10^0 mol%) of Pt (detailed amounts were indicated in the footnotes below the tables). The reaction mixture was heated and stirred at 40 °C (hydrosil. of terminal acetylenes), 80 °C (hydrosil. of olefin) or 90 °C (hydrosil. of internal acetylenes) until full conversion of Si–H was detected. Conversion of the substrates and yield of hydrosilylated products was determined by gas chromatography (GC). Reaction selectivities were calculated on the basis of the ^{1}H NMR spectra of the reaction mixture.

General procedure for the synthesis of hydrosilylation products

A 25 mL glass reactor equipped with a reflux condenser (open system) or 10 mL high-pressure Schlenk vessel (closed system) was charged with toluene (4 mL), silane (2 mmol) and appropriate alkene (2 mmol) or alkyne (2 mmol). Then platinum catalyst **1** was added in the amount of 10^{-5}–10^0 mol% of platinum complex, depending on the experiment. The

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reaction mixture was heated to appropriate temperature (40°C, 80°C or 90°C) and stirred until full conversion of Si–H was detected. Then, the solvent was evaporated under vacuum. The crude product was dissolved in petroleum ether or dichloromethane (depending on product polarity) and filtered through silica gel. After evaporation of solvents the product was characterized by spectroscopic methods.

Synthesis of (E)-9ia in a preparative scale

A 10 mL high-pressure Schlenk vessel was charged with toluene (2 mL), (triisopropylsilyl)acetylene (0.43 ml, 1.92×10^{-3} mol) and dimethylphenylsilane (0.29 ml, 1.92×10^{-3} mol). The reaction mixture was warmed up to 40 °C in an oil bath and platinum complex **1** (0.25 mg, 1.92×10^{-7} mol) was added. The reaction was carried out for 24 h. Then the solvent was evaporated under vacuum and the residue was purified using column chromatography (silica gel 60/petroleum ether : DCM = 5 : 1). Evaporation of the solvent gave the analytically pure product (oil, 0.553 g, 90 %).

Conclusions

By using platinum(0) complexes [Pt(IPr*)(dvtms)] (**1**) and [Pt(IPr*^{OMe})(dvtms)] (**2**) as catalysts of hydrosilylation of olefins and acetylenes it was demonstrated that postulated dependence of selectivities of hydrosilylation processes on steric bulk of NHC ligand remains true for complexes containing *N*-heterocyclic carbene ligands significantly bulkier (Nolan height parameter A_H > 200 °) than the previously described complexes. Complexes efficiently catalyze the highly regio- and chemoselective hydrosilylation of a wide range of functionalized terminal olefins, as well as terminal and internal acetylenes. Moreover, the complexes tested are characterized by particularly high values of TON reaching 10^7 for hydrosilylation of olefins and 10^4 for hydrosilylation of acetylenes.

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SiR_3 = $SiMe_2Ph$, $SiMe_2(OSiMe_3)$, $SiMe(OSiMe_3)_2$, $SiEt_3$, $SiPh_3$
R^1 = Alkyl, Aryl; R^2 = Aryl, SiR'_3; R^3 = R^4 = Alkyl, Aryl
$R^3 \neq R^4$ R^3 = Aryl, R^4 = $SiMe_3$

Platinum(0) complexes bearing bulky *N*-heterocyclic carbene ligands, catalyse selective hydrosilylation of terminal olefins as well as terminal and internal acetylenes.