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Platinum(II)-bis-(N-heterocyclic carbene) complexes: synthesis, structure and catalytic activity in the hydrosilylation of alkenes

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ABSTRACT

Chelating biscarbene ligands increase the stability of metal-organic catalyst systems. The catalytic activities of seven structurally different platinum(II)-bis-NHC-complexes in the hydrosilylation of alkenes have been investigated and compared with the catalytic activity of the Karstedt catalyst and of a highly active platinum(0)-NHC-complex. It is shown that a fine-tuning of the catalytic activity of the platinum(II)-bis-NHC-complexes is possible. The synthesis of a platinum(II)-bis-NHC-complex with similar activity, but additional advantages compared to the *Karstedt* catalyst, is reported. The solid state structure of 1,1-[Bis(3,3′-(4-methoxyphenyl)-1,1′-1*H*-imidazolium-2,2′-ylidene)methanediyl]platinum(II)-dichloride is presented.

1. Introduction

Several good reviews have been published on the hydrosilylation of alkenes, which is of particular importance for the silicon chemistry [1–14]. Alkyl-, alkenyl- and arylsilanes also find useful applications in organic syntheses, where they often replace the corresponding boron and tin compounds as they are in general less toxic, cheaper and more stable [15–17]. The hydrosilylation reaction can be initiated in numerous ways [18]. Among these, the transition metal catalyzed reaction, especially by platinum systems, is the most commonly used method.

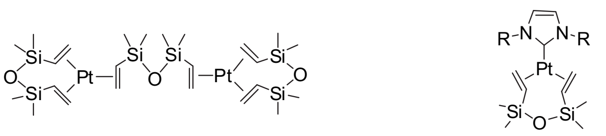
The two standard catalysts for industrial applications are the *Speier* catalyst [19] ($H_2PtCl_6 * 6\ H_2O$ in *i*-PrOH) and the *Karstedt* catalyst [20,21] (**1**, Chart 1). A few years ago, also platinum(0)-complexes with monodentate NHC-ligands (**2**, Chart 1) have been introduced and successfully employed in the hydrosilylation e.g. of 1-octene with bis(trimethylsiloxy)methylsilane [22,23].

Over the years, the *Speier* catalyst has been replaced by the more active and selective *Karstedt* catalyst. However, **1** not only catalyzes the formation of the desired hydrosilylation products **A** and **B**, but its use also results in several undesirable side reactions, in which vinylsilanes (**C**), saturated derivatives (**D**), disilanes (**E**) and isomerized alkenes (**F**) are produced (Chart 2) [23].

Another disadvantage of the *Karstedt* catalyst (**1**) is the formation of platinum black during the hydrosilylation reaction, which is responsible for some of the side products and leads to a contamination of the hydrosilylation product [24].

In addition to platinum [19–21,25–32] complexes, numerous other metal complexes [33–50] are used as catalysts in the hydrosilylation of alkenes and alkynes. In comparison to platinum complexes, these usually exhibit a lower activity and/or selectivity [51].

Due to their high stability towards heat, oxygen and moisture, metal complexes of *N*-heterocyclic carbenes (NHC's) are often



1 **2:** R = e.g. 4-Methoxyphenyl

Chart 1. *Karstedt* catalyst [20,21] (**1**) and *Markó's* NHC-catalysts [22,23] (**2**).

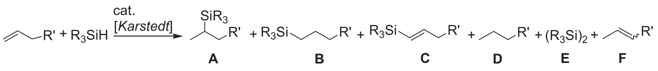


Chart 2. Hydrosilylation of alkenes with the Karstedt catalyst.

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[1] X-ray analysis.

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considered as valuable alternatives to phosphine ligands in homogeneous catalysis [52–57]. Especially chelated biscarbene complexes have been shown to be stable even under harsh reaction conditions and are expected to be more stable than monodentate NHC's, although only few examples of platinum complexes with chelating biscarbene ligands have been published [58–67].

2. Experimental

2.1. General procedure

Catalysis reactions were generally carried out under an atmosphere of dry argon [68–71], although there have been some reports in the literature that molecular oxygen can have an important effect in hydrosilylation catalysis, especially when colloids are involved [72–80].

1,4-Dioxane was dried over 4 Å molecular sieve prior to use. GC–MS spectra were measured on a Hewlett–Packard GC G1800A system. The conversion was measured against cyclooctadiene as internal standard. The turnover number (TON) is defined as (mol product)/(mol platinum), while the turnover frequency (TOF) is defined as (mol product)/[(mol platinum) * (reaction time in h)]. The amount of catalyst is given relative to the amount of the olefin. All catalytic experiments are repeated at least twice, most of them three times. The conversion, yield, TON and TOF given are the average values of the GC and NMR measurements, respectively.

^{1}H and ^{13}C NMR spectra were recorded with a Bruker AC 300 P spectrometer. The spectra were referenced internally to the resonances of the deuterated solvent (^{1}H, ^{13}C). Elemental analyses were performed by the microanalytical laboratory of our institute using an EuroVektor Euro EA-300 Elemental Analyzer. Melting and decomposition points of the complexes were determined by a melting point apparatus (Wagner and Munz PolyTherm A) and are uncorrected.

1-*N*-substituted imidazoles (substituent: 2,4,6-trimethylphenyl, 4-methoxyphenyl, 4-bromophenyl, isopropyl, cyclohexyl) [59,81], 1,1′-*N*-disubstituted-3,3′-methylene-bisimidazolium dichlorides (substituent: 2,4,6-trimethylphenyl, 4-methoxyphenyl, methyl) [82], 1,1′-*N*-disubstituted-3,3′-methylene-bisimidazolium dibromides (substituent: 2,4,6-trimethyl-phenyl, 4-bromophenyl, isopropyl, cyclohexyl) [59,83], 1,3-bis(4-methoxyphenyl)imidazolium chloride [84], 1,1-[Bis(3,3′-(*N*-disubstituted)-1,1′-1*H*-imidazolium-2,2′-ylidene)methanediyl]-platinum(II)-dichlorides (substituent: 2,4,6-trimethylphenyl (**3**), 4-methoxyphenyl (**5**), methyl (**7**)) [82] and 1,1-[Bis(3,3′-(*N*-disubstituted)-1,1′-1*H*-imidazolium-2,2′-ylidene)methanediyl]-platinum(II)-dibromides (substituent: 2,4,6-trimethylphenyl (**4**), 4-bromophenyl (**6**)) [59] were prepared according to the literature procedures. The *Karstedt* catalyst and N-Methylimidazol were purchased from ABCR and used as received.

2.2. Synthesis of 1,3-Bis(4-methoxyphenyl)imidazoline-2-ylidene platinum(0) divinyltetramethyl-siloxane (*2*)

The synthesis follows a modified literature protocol [85]. Under an argon atmosphere a dry Schlenk tube was loaded with 1,3-Bis(4-methoxyphenyl)imidazolium chloride (567 mg, 1.97 mmol), a solution of the *Karstedt* catalyst (2.01 g, 1.63 mmol of platinum) in 5 mL dry toluene and ^{t}BuOK (336 mg, 3 mmol). The reaction mixture was stirred for 2 h at room temperature. The heterogeneous mixture was filtered over Celite and the filtrate was obtained as a clear, orange solution. The solvent was removed in vacuo and the resulting beige solid was washed three times with ice-cold isopropanol (5 mL) and dried in vacuo (yield: 584 mg, 54%). ^{1}H NMR (300.13 MHz, $CDCl_3$): $\delta = 7.38$ (m, 6H, *o*-C*H* of Ar and N–C*H* of Im), 6.79 (d, $J = 8.9$ Hz, 4H, *m*-C*H* of Ar), 3.77 (s, 6H, O-CH_3), 1.91 (dd, $^{3}J = 9.3$ Hz, $^{2}J = 1.9$ Hz, 2H, CH = C$H_{2\ \mathrm{eq}}$), 1.53–1.60 (m, 4H, Si–C*H* = and = C$H_{2\ \mathrm{ax}}$), 0.20 (s, 6H, Si-C$H_{3\ \mathrm{eq}}$), −0.60 (s, 6H, Si-C$H_{3\ \mathrm{ax}}$) ppm. ^{13}C NMR (75.475 MHz, $CDCl_3$): $\delta = 180.7$ (N–*C*–N), 158.4 (*p*-*C* of Ar), 133.5 (*i*-*C* of Ar), 125.6 (*o*-*C*H of Ar), 123.4 (*m*-*C*H of Ar), 113.6 (N–*C*H), 55.4 (O–CH_3), 40.3 (CH_2 = CH–Si), 32.3 (CH_2 = *C*H–Si), 1.6 (Si–$CH_{3\ \mathrm{eq}}$), −2.9 (Si–$CH_{3\ \mathrm{ax}}$) ppm.

2.3. Synthesis of 1,1-[Bis(3,3′-(isopropyl)-1,1′-1H-imidazolium-2,2′-ylidene)methanediyl]-platinum(II)-dibromide (*8*)

The synthesis follows a modified literature procedure [86]. 1,1′-Diisopropyl-3,3′-methylene-bisimidazolium dibromide (394 mg, 1 mmol) and platinum(II)acetylacetonate (393 mg, 1 mmol) are dissolved in 6 mL dimethylsulfoxide. The reaction mixture was stirred for 3 h at 60 °C, for 3 h at 80 °C and for 3 h at 110 °C. After removal of the solvent, the light brown residue was washed three times with ethanol (5 mL) and three times with tetrahydrofurane (5 mL). The product was obtained as a colorless solid (yield: 410 mg, 70%), m. p.: 326 °C (decomp.). ^{1}H NMR (300.13 MHz, DMSO-d_6): $\delta = 7.61$ (s, 2H, NC*H*), 7.60 (s, 2H, NC*H*), 6.12 (d, $J = 13.1$ Hz, 1H, NCH_2N), 6.03 (d, $J = 13.1$ Hz, 1H, NCH_2N), 5.61 (sept, $J = 6.6$ Hz, 2H, NC*H*(CH_3)$_2$), 1.51 (d, $J = 6.7$ Hz, 6 H, NCH(CH_3)$_2$), 1.26 (d, $J = 6.8$ Hz, 6 H, NCH(CH_3)$_2$) ppm. ^{13}C NMR (75.475 MHz, DMSO-d_6): $\delta = 144.8$ (N*C*N), 121.2 (N*C*H), 117.5 (N*C*H), 61.9 (N*C*H_2N), 51.4 (N*C*H(CH_3)$_2$), 23.3 (NCH(*C*H_3)$_2$), 21.5 (NCH(*C*H_3)$_2$) ppm. Anal. Calc. for $C_{13}H_{20}N_4PtBr_2$: C, 26.57; H, 3.43; N, 9.54. Found: C, 26.43; H, 3.46; N, 9.37.

2.4. Synthesis of 1,1-[Bis(3,3′-(cyclohexyl)-1,1′-1H-imidazolium-2,2′-ylidene)methanediyl]-platinum(II)-dibromide (*9*)

The synthesis follows a modified literature procedure [86]. 1,1′-Dicyclohexyl-3,3′-methylene-bisimidazolium dibromide (237 mg, 0.5 mmol) and platinum(II)acetylacetonate (197 mg, 0.5 mmol) were dissolved in 6 mL dimethylsulfoxide. The reaction mixture was stirred for 3 h at 60 °C, for 3 h at 80 °C and for 3 h at 110 °C. After removal of the solvent, the light brown residue was washed three times with ethanol (5 mL) and three times with tetrahydrofurane (5 mL). The product was obtained as a colorless solid (yield: 143 mg, 43%), m. p.: 366 °C (decomp.). ^{1}H NMR (300.13 MHz, DMSO-d_6): $\delta = 7.61$ (s, 2H, NC*H*), 7.58 (s, 2H, NC*H*), 6.13 (d, $J = 13.1$ Hz, 1H, NCH_2N), 6.04 (d, $J = 13.0$ Hz, 1H, NCH_2N), 5.21 (m, 2H, N–C*H* of Cy), 1.88-1.17 (m, 20 H, CH_2 of Cy) ppm. ^{13}C NMR (75.475 MHz, DMSO-d_6): $\delta = 144.6$ (N*C*N), 121.0 (N*C*H), 118.2 (N*C*H), 61.7 (N*C*H_2N), 58.3 (N*C*H of Cy), 33.3 (*C*H_2 of Cy), 31.9 (*C*H_2 of Cy), 25.3 (*C*H_2 of Cy), 24.6 (*C*H_2 of Cy), 24.5 (*C*H_2 of Cy) ppm. Anal. Calc. for $C_{19}H_{28}N_4PtBr_2$ * 0.5 DMSO: C, 34.01; H, 4.42; N, 7.93; S, 2.27. Found: C, 34.19; H, 4.40; N, 7.84; S, 2.18.

2.5. General procedure for the hydrosilylation of styrene with bis(trimethylsiloxy)methylsilane

A degassed 10 mL Schlenk flask equipped with a reflux condenser was first charged with the noted amount of the catalyst, bis(trimethylsiloxy)methylsilane (4.4 mmol) and styrene (4 mmol) under an atmosphere of argon before it immediately afterwards was put in a preheated oil bath. Temperatures given in the tables correspond to the temperature of the oil bath. For analysis, aliquots (0.2 mL) were removed from the reaction mixture after a defined period of time, put in an NMR tube, diluted by 0.5 mL deuterated chloroform and analyzed by NMR

Table 1
Crystal data and crystallographic details for compound **5**.

	5
Formula	$C_{21}H_{20}Cl_2N_4O_2Pt$ *C_2H_6OS
Formula weight (g/mol)	704.53
Color/shape	Colorless/block
Crystal system	Triclinic
Space group	$P\overline{1}$ (No. 2)
a (Å)	9.7010(4)
b (Å)	9.9370(8)
c (Å)	14.1590(8)
α (°)	102.755(6)
β (°)	106.255(5)
γ (°)	94.455(5)
V (Å^3)	1263.75(15)
Z	2
ρ_{calc} (g/cm^3)	1.852
μ (mm^{-1})	5.878
Temperature (K)	198
λ (Å)	0.71073
$\theta_{min/max}$ (°)	4.054/21.835
Reflections integrated	33084
Independent reflections (all data)	5169
Observed reflections [I > 2σ(I)]	4798
Parameter refined	315
R_1 (observed/all data)	0.0147/0.0180
wR_2 (observed/all data)	0.0313/0.0320
Goodness-of-fit (observed/all data)	1.025/1.025
Residual electron density (e/Å^3)	−0.501/0.538

spectroscopy. The estimated error of this method is ±5%, the average standard deviation is 3.6.

2.6. General procedure for the hydrosilylation of styrene with dimethylphenylsilane

A degassed 10 mL Schlenk flask equipped with a reflux condenser was charged with the noted amount of catalyst, 2 mmol cyclododecane, 2 mL dioxane, 2.2 mmol dimethylphenylsilane and 2 mmol styrene under an atmosphere of argon. Immediately afterwards the flask was put in a preheated oil bath. Temperatures given in the tables correspond to the temperature of the oil bath. For analysis, aliquots (0.2 mL) were removed from the reaction mixture after a defined period of time and diluted by dichloromethane (15 mL). The solution was analyzed by gas chromatography. The estimated error of this method is ±2%, the average standard deviation is 3.5.

Table 2
Selected bond length (Å) and angles (°) of compound **5**.

	5
Pt1–C1	1.956(2)
Pt1–C11	1.957(2)
Pt1–Cl1	2.3653(6)
Pt1–Cl2	2.3561(6)
C1–N1	1.352(3)
C1–N2	1.351(3)
C11–N3	1.353(3)
C11–N4	1.353(3)
C1–Pt1–C11	84.62(9)
C1–Pt1–Cl1	92.43(7)
C1–Pt1–Cl2	174.55(7)
C11–Pt1–Cl1	175.09(7)
C11–Pt1–Cl2	92.33(7)
Cl1–Pt1–Cl2	90.30(2)
N1–C1–N2	104.70(19)
N3–C11–N4	104.9(2)
C1–N1–C4–C19	57.9(3)
C11–N4–C9–C15	−45.2(4)
C1–N1–C4–C23	−124.4(3)
C11–N4–C9–C10	134.7(3)

2.7. General procedure for testing the reusability

A 10 mL Schlenk flask equipped with a reflux condenser was degassed and put under an atmosphere of argon. It was charged with the denoted amount of the catalyst, bis(trimethylsiloxy)methylsilane (4.4 mmol) and styrene (4 mmol) and put in a preheated oil bath. Aliquots (0.2 mL) were removed from the reaction mixture after a defined period of time, poured into an NMR tube, diluted by 0.5 mL deuterated chloroform and analyzed by NMR spectroscopy. After complete conversion of the starting materials the reaction mixture was cooled to room temperature. Then, the Schlenk flask was again charged with bis(trimethylsiloxy)methylsilane (4.4 mmol) and styrene (4 mmol) and put back in the preheated oil bath. Aliquots (0.2 mL) were again removed from the reaction mixture after a defined period of time and analyzed as described above.

2.8. Structure determination of compound *5*

Crystal data and details on the structure determination are presented in Table 1. Table 2 summarizes selected bond lengths and bond angles. Suitable single crystals for the X-ray diffraction study were grown by cooling a saturated, hot solution of **5** in DMSO (see

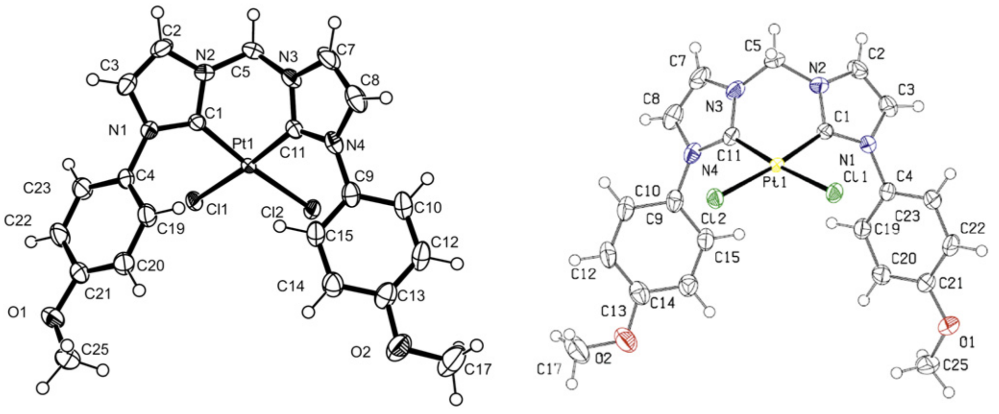


Fig. 1. ORTEP plot of **5** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are plotted as spheres of arbitrary radius. The DMSO molecule is omitted for clarity.

Fig. 1). A clear colorless block ($0.27 \times 0.19 \times 0.09$ mm) was stored under perfluorinated ether, transferred on a glass capillary and fixed. Preliminary examination and data collection were carried out on an area detecting system (kappa-CCD; Nonius) at the window of a sealed X-ray tube (Nonius, FR590) and graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The unit cell parameters were obtained by full-matrix least-squares refinement of 153 reflections. Data collection was performed at 198 K within a θ-range of $4.10 < \theta < 26.40^\circ$. A total number of 33084 intensities were integrated. Raw data were corrected for Lorentz, polarization, decay and absorption effects. After merging ($R_{\text{int}} = 0.035$) a sum of 5169 independent reflections remained and were used for all calculations. The structure was solved by a combination of direct methods and difference Fourier synthesis. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were calculated in ideal positions riding on the parent carbon atoms. Full-matrix least-square refinements with 315 parameters were carried out by minimizing $\sum w(F_0^2 - F_c^2)^2$ with SHELXL-97 weighting scheme and stopped at shift/err < 0.001. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from the *International Tables for Crystallography* [87]. All calculations were performed with the SHELXL-97 [88] package and the programs COLLECT [89], DIRAX [90], EVALCCD [91], SIR92 [92], SADABS [93], PLATON [94] and ORTEP III [95].

3. Results and discussion

3.1. Preparation and structural properties of selected platinum-NHC-complexes

We have investigated the catalytic activity of selected platinum-NHC-complexes (Chart 3) in the hydrosilylation reaction and compared their activity to that of the *Karstedt* catalyst (**1**) and the *Markó* catalyst (**2**). Of special interest was the catalytic activity of *N*-aryl substituted platinum(II)-bis-NHC-complexes in comparison to the catalytic activity of different *N*-alkyl substituted NHC-complexes. It should be possible to systematically fine-tune the catalytic activity of the *N*-aryl NHC complexes by changing the nature of the substituents on the aromatic ring from electron-donating to electron-withdrawing!

Platinum(II)-NHC-complexes have been previously used as catalysts for this reaction [32]. We therefore investigated the use of chelating bis-NHC-complexes with a variety of aromatic and aliphatic substituents. Mesityl (2,4,6-trimethylphenyl) (**3**,**4**), 4-methoxyphenyl (**5**) and 4-bromophenyl (**6**) as well as the aliphatic substituents methyl- (**7**), isopropyl- (**8**) and cyclohexyl- (**9**) were used in combination with chloride and bromide counterions since we had previously observed significant counterion effects in other catalytic reactions (Chart 3).

Complex **2** was synthesized by a modified literature procedure described in the experimental section. Complexes **3**–**7** were synthesized as previously published [59,82].

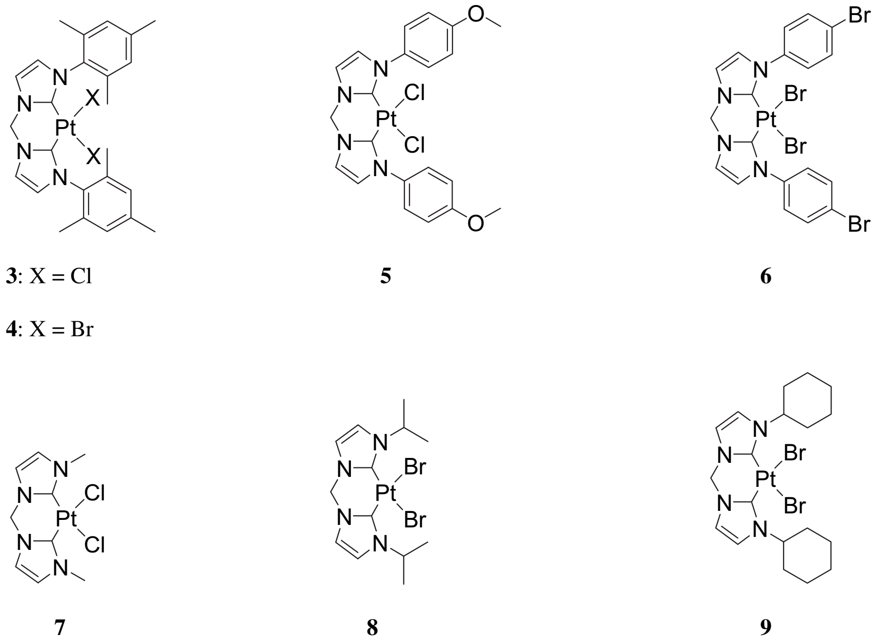
3.2. Solid state structure of **5**

Crystals of **5** suitable for X-ray diffraction were obtained by cooling of a hot DMSO solution. Complex **5** crystallizes as a DMSO solvate with one DMSO molecule per platinum (Fig. 1). The structure of complex **5** is similar to the corresponding platinum-bis-NHC-complex with bromide counterions (**10**) [82] and the palladium-bis-NHC-complex **11** [65]. All three complexes contain a bowl-shaped NHC-ligand. The platinum-carbene-C distances are the same within the margin of the error. Only the torsional angles of the plane of the imidazole rings towards the plane of the aromatic rings represented by the torsional angle C11-N4-C9-C10 in Fig. 1 (**5**: 134.7°, **10**: 128.0°, **11**: 128.2°) differ slightly.

3.3. Catalysis

We studied the hydrosilylation of styrene with bis(trimethylsiloxy) methylsilane in a more detailed investigation, and the slightly less reactive dimethylphenylsilane using two different catalytic systems (Chart 4) [96].

We observed the formation of the branched hydrosilylation product **A**, the linear hydrosilylation product **B** and the dehydrosilylation product **C**. No other side products could be identified.



3: X = Cl

4: X = Br

5

6

7

8

9

Chart 3. Platinum(II)-bis-NHC-complexes tested in the hydrosilylation of alkenes.

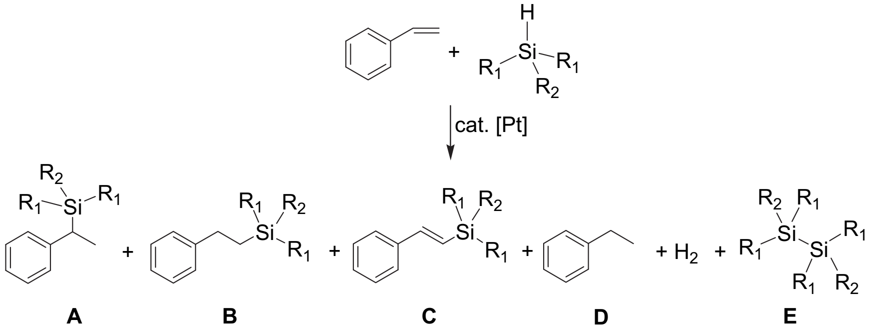


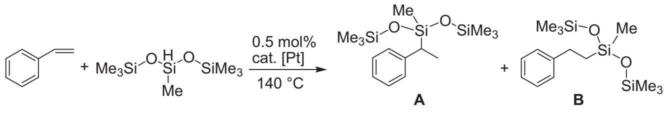
Chart 4. Hydrosilylation of styrene with bis(trimethylsiloxy)methylsilane (R_1 = OSiMe$_3$, R_2 = Me) and dimethylphenylsilane (R_1 = Me, R_2 = Ph).

3.4. *Hydrosilylation of styrene with bis(trimethylsiloxy) methylsilane*

The results for a series of hydrosilylation reactions are shown in Table 3. To compare the catalytic activity of the platinum(II)-bis-NHC-complexes **3**–**9** with that of the *Karstedt* catalyst (**1**) in the hydrosilylation of styrene with bis(trimethylsiloxy)methylsilane (Table 3), we carried out the reactions at 140 °C with 0.5 mol% catalyst.

There is a significant influence of steric and electronic effects on the catalytic activity of the platinum(II)-bis-NHC-complexes. The 4-methoxyphenyl-substituted complex (**5**) turned out to be the most reactive of the platinum(II)-bis-NHC-complexes investigated. With **5** a yield of 69% of the hydrosilylation products **A** and **B** was obtained after a reaction time of only 30 s (Table 3, entry 5), while all other platinum(II) complexes did not show any conversion after 30 s. The activity of **5** is comparable to the activity of the *Karstedt* catalyst (**1**). One obtains 86% of the hydrosilylation products after a reaction time of only 10 min with complex **5** (Table 3, entry 6) and 83% after the same reaction time with **1** (Table 3, entry 1). Complete conversion is probably achieved at a different time for each catalyst, but for comparison both reactions were run for a time of 6 h (Table 3, entries 7 and 2). In comparison to **1**, complex **5** has some important advantages. The formation of platinum black is not observed for complex **5** during the reaction, while it is generated from **1** immediately after the addition of the silane.

Table 3
Hydrosilylation of styrene with bis(trimethylsiloxy)methylsilane.



Entry	Cat.	Time [min]	Conversion (siloxane) [%][a]	Conversion (styrene) [%][a]	Yield (hydrosilylation products) [%][a]	Ratio A:B
1	**1**	10	97	96	83	16:84
2	**1**	360	100	100	91	15:85
3	**3**	360	85	96	82	13:87
4	**4**	360	69	78	67	13:87
5	**5**	½	69	69	69	22:78
6	**5**	10	88	82	82	14:86
7	**5**	360	99	99	97	15:85
8	**6**	360	94	95	94	17:83
9	**7**	360	94	96	89	16:84
10	**8**	360	84	79	79	17:83
11	**9**	360	29	21	21	19:81

[a] Determined by NMR analysis (error: ± 5%).

Nearly complete conversion is also obtained with the 4-bromophenyl-substituted complex (**6**) and the methyl-substituted complex (**7**) after a reaction time of 6 h (Table 3, entries 8/9), but the reaction starts slower. The catalytically active species is proposed to be a platinum(0) species [74] and the formation of the platinum(0) species seems to be promoted by the electron-donating effect of the methoxy-substituents in the *para*-positions of the phenyl rings. We believe that the silane reduces the complex, which is supported by the observation that the reaction starts more quickly if the silane is added to the solution before the addition of the olefin.

The catalytic activity is influenced not only by the reduction of the platinum center, but also from the steric demand of the substituents, which leads to a significantly lower activity of complexes **4** and **9**. The cyclohexyl-substituted complex **9** shows the lowest activity of all investigated complexes (Table 3, entry 11), which is especially obvious during the early stage of the reaction (Fig. 2). The steric effect reduces the activity and leads to a slightly prolonged initiation time for complex **4** in comparison to complex **6** (Fig. 2). The formation of platinum black is only observed for the methyl substituted complex **7** after a reaction time of 3 h, all other complexes are stable under the reaction conditions. The selectivity of all investigated complexes is similar, we observe about 20% formation of the branched product **A** and about 80% of the linear product **B**.

3.5. *Reusability*

An important factor for an industrial application of a catalyst is the number of catalytic cycles it allows the reaction to be run before it looses its activity. Therefore we tested the loss of activity in several runs for the most active catalyst **5** and the *Karstedt* catalyst **1** under the same reaction conditions (Table 4). Additional results for the measurements after 2 and 4 h are given in the supplementary material.

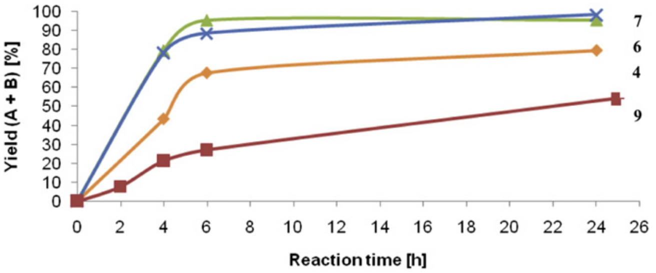
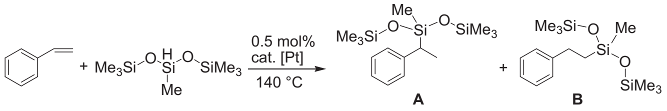


Fig. 2. Yields of the hydrosilylation products **A** and **B** in dependence of the reaction time for catalysts **4**, **6**, **7** and **9**.

Table 4
Reusability of complex **5** in comparison to the *Karstedt* catalyst **1**.



Cycle	Cat.	Conversion (siloxane) [%][a]	Conversion (styrene) [%][a]	Yield (hydrosilylation products) [%][a,b]	Ratio A:B	TON	TOF [h^{-1}]
1.	**1**	100	100	91	15:85	182	30
1.	**5**	99	99	97	15:85	194	32
2.	**1**	97	96	87	16:84	174	29
2.	**5**	94	94	85	15:85	170	28
3.	**1**	90	89	86	16:84	172	29
3.	**5**	96	95	95	17:83	190	32
4.	**1**	99	95	85	16:84	170	28
4.	**5**	88	92	78	17:83	156	26
5.	**1**	99	98	93	17:83	186	31
5.	**5**	89	99	84	14:86	168	28
6.	**1**	99	94	94	15:85	188	31
6.	**5**	86	97	74	16:84	148	25

[a] Determined by NMR analysis (error: ± 5%).
[b] Reaction time 6 h.

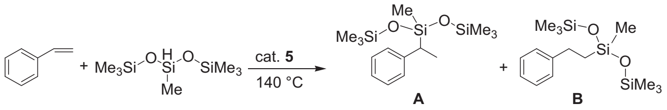
During the first catalytic cycle, the yields of the hydrosilylation products **A** and **B** are comparable for both catalysts (Table 4), but the *Karstedt* catalyst **1** obviously produces more side reactions. Keeping in mind that the catalyst concentration is reduced with every sample drawn from the reaction mixture, somewhat lower yields observed during the following catalytic cycle can be explained. The yields of the hydrosilylation products are comparable for both catalysts with somewhat higher yields for the Karstedt catalyst. But complex **5** has two important advantages in comparison with the industrially used *Karstedt* catalyst **1**. On one hand, no decomposition of complex **5** to platinum black can be observed even after several catalytic cycles. On the other hand, complex **5** is at room temperature less soluble in starting materials and hydrosilylation products which makes it easier to separate it after the reaction.

3.6. *Concentration dependency*

We also looked at the catalyst concentration (between 1 mol% and 0.01 mol%) for the 4-methoxyphenyl-substituted complex **5** (Table 5).

As can be seen from Table 5 the catalyst is highly active with yields of 90% even at a low catalyst loading of 0.01% (entry 12), but the lowest amount of side-products is formed at a catalyst concentration of 0.5 mol% (entry 6). Increasing the amount of catalyst to 1 mol% does not lead to a better conversion, only to more side products (entry 3). At 0.01 mol% concentration a significantly reduced reactivity at the beginning of the reaction (Table 5, entry 10) is observed. The reaction seems to start slower, which might also explain the good selectivity. Complex **5** shows a remarkably high TON of 9000 and a TOF of 1500 h^{-1}.

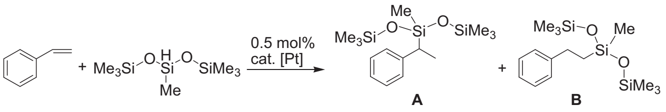
Table 5
Concentration dependence of the conversion with catalyst **5**.



Entry	mol% cat.	t [min]	Conver-sion (siloxane) [%][a]	Conver-sion (styrene) [%][a]	Yield (hydrosilylation products) [%][a]	Ratio A:B	TON	TOF [h^{-1}]
1	1	½	89	86	78	21:79	78	–
2	1	240	98	97	90	17:83	90	23
3	1	360	99	99	90	17:83	90	15
4	0.5	½	69	69	69	22:78	137	–
5	0.5	240	99	99	97	15:85	194	49
6	0.5	360	99	99	97	15:85	194	32
7	0.1	½	61	56	51	22:78	510	–
8	0.1	240	82	85	70	17:83	700	175
9	0.1	360	94	95	75	15:85	750	125
10	0.01	½	0	0	0	–	–	–
11	0.01	240	89	93	82	16:84	8200	2050
12	0.01	360	93	97	90	17:83	9000	1500

[a] Determined by NMR analysis (error: ± 5%).

Table 6
Temperature dependence.



Entry	Cat.	T [°C]	Conversion (siloxane) [%][a]	Conversion (styrene) [%][a]	Yield (hydrosilylation products) [%][a,b]	Ratio A:B	TON	TOF [h^{-1}]
1	**1**	50	100	97	89	17:83	178	30
2	**2**	50	95	94	85	20:80	170	28
3	**5**	50	99	99	99	19:81	200	33
4	**1**	70	100	99	95	17:83	190	32
5	**2**	70	85	100	85	17:83	200	33
6	**5**	70	97	98	97	15:85	194	32
7	**1**	80	100	96	90	17:83	180	30
8	**5**	80	100	100	94	18:82	188	31
9	**1**	100	100	99	86	15:85	172	29
10	**5**	100	98	98	97	18:82	194	32
11	**1**	120	100	83	63	16:84	126	21
12	**5**	120	99	95	91	17:83	182	30
13	**1**	140	100	100	91	15:85	182	30
14	**5**	140	99	99	97	15:85	194	32

[a] Determined by NMR analysis (error: ± 5%).
[b] Reaction time 6 h.

3.7. *Reaction temperature*

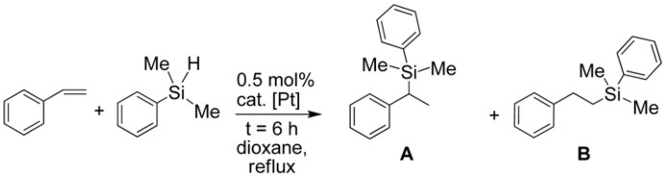
Another parameter with an important effect on the catalytic activity is the reaction temperature, which was varied between 50 °C and 140 °C for catalysts **1** and **5**. Additionally **2** was tested at 50 °C and 70 °C. We could not run the reaction lower than 50 °C due to the poor solubility of **5** at lower temperatures.

Table 6 shows only selected data points, the full Table 6 is given in the Supplementary Material. Catalyst **5** performs very well over the full temperature range, the yields have always been higher than 90%, while the *Karstedt* catalyst **1** has significant limitations between 80 °C and 120 °C, where the yields were as low as 63% (Table 6, entry 11). Catalyst **2** on the other hand performs significantly better at 70 °C. **5** was superior to both other catalysts at 50 °C with the added benefit that less by-products are formed at a reaction temperature of 50 °C, as e.g. the thermal polymerization of styrene does not proceed below a reaction temperature of 90 °C in a noteworthy amount. With catalyst **5** full conversion of the starting materials to the hydrosilylation products is observed at 50 °C after a reaction time of 6 h (Table 6, entry 3). Hence, the catalytically active species, which is formed from complex **5**, is highly reactive and very selective in the hydrosilylation reaction of alkenes. The *Karstedt* catalyst **1** on the other hand produces 10% side products already at 50 °C (Table 6, entry 1).

3.8. *Hydrosilylation of styrene with dimethylphenylsilane*

As described in Chart 4 different products are formed under the reaction conditions of the hydrosilylation of styrene with dimethyl-

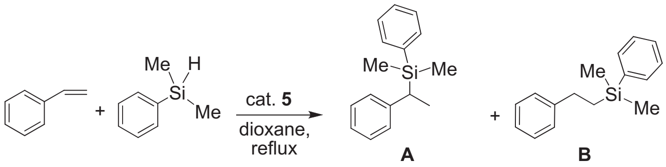
Table 7
Hydrosilylation of styrene with dimethylphenylsilane.



Entry	Cat.	Conversion (silane) [%][a]	Conversion (styrene) [%][a]	Yield (hydrosilylation products) [%][a]	Ratio A:B	TON	TOF [h^{-1}]
1	**1**	100	60	52 + 2[b]	4:96	108	18
2	**3**	17	24	15 + 1[b]	2:98	31	5
3	**4**	60	41	8 + 42[b]	2:98	16	3
4	**5**	58	59	48 + 8[b]	19:81	96	16
5	**6**	29	33	14 + 5[b]	7:93	28	5
6[c]	**7**	49	68	33 + 3[b]	6:94	66	11
7	**8**	13	8	0	–	–	–
8	**9**	26	43	0.4	0:100	0.8	0.1

[a] Determined by GC–MS analysis (internal standard: cyclododecane).
[b] Dehydrosilylation product.
[c] Reaction time 24 h.

Table 8
Influence of the concentration of **5** on the conversion of the hydrosilylation reaction.



Entry	mol% Cat. [mol%]	t [h]	Conversion (silane) [%][a]	Conversion (styrene) [%][a]	Yield(products) [%][a]	Ratio A:B	TON	TOF [h^{-1}]
1	1	4	72	77	45 + 8[b]	4:96	45	11
2	1	6	92	91	50 + 12[b]	4:96	50	8
3	0.5	4	48	50	41 + 5[b]	15:85	82	21
4	0.5	6	58	59	48+ 8[b]	19:81	96	16
5	0.1	4	28	24	26 + 3[b]	2:98	260	65
6	0.1	6	43	36	36 + 5[b]	3:97	360	60
7	0.01	4	35	22	15	3:97	1500	375
8	0.01	6	41	29	24	8:92	2400	400
9	0.001	4	42	13	10	5:95	10000	3250
10	0.001	6	51	28	26	3:97	26000	4333

[a] Determined by GC–MS analysis (internal standard: cyclododecane).
[b] Dehydrosilylation product.

phenylsilane: the branched hydrosilylation product (Chart 4, **A**), the linear hydrosilylation product (Fig. 6, **B**), the dehydrosilylation product (Chart 4, **C**) and the 1,1,2,2-tetramethyl-1,2-diphenyldisilane (Chart 4, **E**). The hydrogen, which is a byproduct of the disilane formation, partially reacts with styrene in a platinum catalyzed hydrogenation to 1-ethylbenzene (Chart 4, **D**).

As dimethylphenylsilane is a less reactive substrate than bis(trimethylsiloxy)methylsilane, we were curious whether we would also find a significant substituent effect on the catalytic activity of the platinum-bis-NHC-complexes for the hydrosilylation of styrene (Table 7).

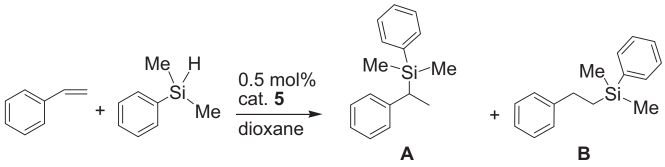
The yields of the hydrosilylation reaction of styrene with dimethylphenylsilane are significantly lower compared to the reaction with bis(trimethylsiloxy)methylsilane (Tables 3 and 7), due to the lower reactivity of dimethylphenylsilane and to the dilution of the reaction mixture as the reaction is run in dioxane. It is therefore an excellent reaction to study the substituent influence on the catalytic activity of the platinum-bis-NHC-complexes.

The difference between the substituents, especially between the aliphatic and aromatic substituents is obvious from Table 7. For the aliphatic substituents (**8** and **9**), nearly no hydrosilylation product is formed after a reaction time of 6 or 24 h, respectively (Table 7, entries 7/8). The methyl-substituted complex **7** shows a surprisingly high reactivity in this reaction (Table 7, entry 6), but decomposes to platinum black after a reaction time of only 3 h.

Also in this case, the most active catalyst for the hydrosilylation reaction of styrene with dimethylphenylsilane is the 4-methoxyphenyl-substituted complex **5** (Table 7, entry 4). Complex **5** shows a comparable catalytic activity as the *Karstedt* catalyst **1** (Table 7, entry 1), again with the least amount of side-products. In the case of **1** the silane is completely consumed for 52% product, while **5** produces almost the same yield of product from a lot less starting material.

Comparing entries 2 and 3 of Table 7 one could also discuss a counterion effect as the mesityl system leads to significantly different results depending on the counterion. The mesityl-substituted complex with bromide counterions **4** additionally is the most active catalyst for the dehydrosilylation reaction (Table 7, entry 3). It is well known that platinum complexes catalyze the dehydrosilylation reaction of substrates like styrene [30,97,98] and that the formation of the dehydrosilylation product depends not

Table 9
Influence of the reaction temperature on the conversion of the hydrosilylation reaction with catalyst **5**.



Entry	T [°C]	t [h]	Conversion (silane) [%][a]	Conversion (styrene) [%][a]	Yield (hydrosilylation products) [%][a]	Ratio A:B	TON	TOF [h^{-1}]
1	50	6	72	67	67	1:99	144	24
2	70	6	50	46	46	3:97	104	17
3	80	6	55	57	55	5:95	112	19
4	100	6	49	48	48	3:97	98	16
5	reflux	6	64	61	61	3:97	126	21

[a] Determined by GC–MS analysis (internal standard: cyclododecane).

only on the nature of the catalyst, but also on the substrates, the ratio of the substrates, the solvent and the reaction temperature. It is therefore not surprising that all investigated complexes with the exception of the very unreactive complexes **8** and **9** catalyze the hydrosilylation as well as the dehydrosilylation reaction. Still, these effects need further investigation, which will be the subject of future studies. For the in general most active complex **5** we also looked at the concentration- and temperature effects for the dimethylphenylsilane (Tables 8 and 9). For all concentrations no reaction was observed after 30 s.

3.9. Concentration dependence

The results are in line with those given in Table 5. Increasing the amount of catalyst from 0.5 to 1.0 mol% does not lead to higher yields of hydrosilylation product. Reducing the catalyst amount from 0.5 to 0.1 mol% leads to a lower conversion, but even with only 0.001 mol% **5**, a yield of 26% is obtained after a reaction time of only 6 h. The highest selectivity for the formation of the linear hydrosilylation product (Table 8, entries 2, 6, 7 and 10) was found for 0.1 mol%. Dehydrosilylation was only observed for the higher catalyst concentrations 0.1–1 mol% (Table 8, entries 2, 4 and 6).

In the course of this study we had learned that in the case of the bis(trimethylsiloxy)methyl-silane the reaction could be run at lower temperatures (Table 6) and we therefore also looked at the influence of the reaction temperature on the conversion of the reaction of styrene with dimethylphenylsilane (Table 9).

3.10. Temperature dependence

Also in this case the reaction works best at low temperatures. It can be run as low as 50 °C, with perfect selectivity and 67% yield (Table 7, entry 1). Higher temperatures reduce the yields as well as the selectivity. The dimethylphenylsilane is less reactive compared to the bis(trimethylsiloxy)methylsilane and we observed in general lower yields.

4. Conclusion

We could show that platinum(II)-bis-NHC-complexes are highly active and very stable catalysts for the hydrosilylation of alkenes. A fine-tuning of the catalytic activity of the platinum(II)-bis-NHC-complexes is possible by variation of the substituents on the imidazole ring. The most active catalyst of all investigated platinum(II)-bis-NHC-complexes is 1,1-[Bis(3,3′-(4-methoxyphenyl)-1,1′-1*H*-imidazolium-2,2′-ylidene)methanediyl] platinum(II)-di-chloride (**5**). The catalytic activity of complex **5** is comparable to the catalytic activity of the *Karstedt* catalyst (**1**) and higher than that of the corresponding platinum(0)-NHC-complex **2**. Complex **5** does not decompose to platinum black during the reaction and therefore less by-products are formed, which is an important advantage of catalyst **5** in comparison to the *Karstedt* catalyst **1**. The optimum conditions are 0.5 mol % catalyst **5** at a reaction temperature of 50 °C.

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Appendix A. Supplementary material

CCDC 822864 contains the supplementary crystallographic data for **5**, which can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

Appendix. Supplementary material

Supplementary data associated with this article can be found, in the online version, at: doi:10.1016/j.jorganchem.2011.04.030.

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