



# Platina- $\beta$ -diketones as catalysts for hydrosilylation and their reactivity towards hydrosilanes

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## ABSTRACT

The platina- $\beta$ -diketones [Pt<sub>2</sub>{(COMe)<sub>2</sub>H<sub>2</sub>( $\mu$ -Cl)<sub>2</sub>}] (**1**), [PPh<sub>4</sub>][Pt{(COMe)<sub>2</sub>H}Cl<sub>2</sub>] (**2**) and [Pt{(COMe)<sub>2</sub>H}-(acac)] (**3**) were found to catalyze the hydrosilylation of alkynes (hex-1-yne, hex-2-yne, hex-3-yne) and alkenes (hex-1-ene, styrene, trimethylvinylsilane) with methylphenylsilane ( $n_{\text{silane}}:n_{\text{substrate}}:n_{\text{Pt}} = 3000:3000:1$ ,  $T = 27^\circ\text{C}$ , in C<sub>6</sub>D<sub>6</sub>). The comparison with the well-established catalysts from Speier (**4**) and Karstedt (**5**) exhibited up to twice as high activities for catalyst **1** and comparable regioselectivities. To get insight into the mechanism of the hydrosilylation, Si-H oxidative addition reactions towards the dinuclear platina- $\beta$ -diketone **1** have been explored. Reactions of **1** with 2-picolyl substituted hydrosilanes of the type N $\widehat{\text{C}}\text{SiMe}_2\text{H}$  and N $\widehat{\text{C}}\text{SiMeH}\widehat{\text{N}}$  resulted in decomposition with the formation of platinum black, only. On the other hand, the analogous reaction with the 8-quinolyl substituted silane of the type N $\widehat{\text{C}}\text{SiMeH}\widehat{\text{N}}$  was found to proceed under loss of H<sub>2</sub> with the formation of a diacetyl(silyl)platinum(IV) complex [Pt(COMe)<sub>2</sub>Cl(N $\widehat{\text{C}}\text{SiMe}\widehat{\text{N}}\text{-}\kappa^2\text{N,N',}\kappa\text{Si}$ )] (**23**). DFT calculations gave insight into the reason for this different reactivity and into the course of reaction. For comparison, the reaction of **1** with bis(2-picolyl)amine was performed resulting under proton shift in the sense of an oxidative addition reaction in the formation of the diacetyl(hydrido)platinum(IV) complex [Pt(COMe)<sub>2</sub>Cl(N $\widehat{\text{C}}\text{NH}\widehat{\text{N}}\text{-}\kappa^3\text{N,N',N''}$ )] (**25**). The complexes **23** and **25** were fully characterized spectroscopically (<sup>1</sup>H, <sup>13</sup>C, <sup>195</sup>Pt, <sup>29</sup>Si NMR, IR) and by single-crystal X-ray structure determinations.

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## 1. Introduction

For decades catalytic hydrosilylation reactions have played an important role in synthetic organic chemistry by facilitating the introduction of silicon functionalities to a broad variety of unsaturated compounds [1]. In polymer chemistry hydrosilylations are broadly used, above all, for cross coupling reactions of silicones [1a,2]. With the help of a wide range of catalytic systems it is possible to perform these reactions under mild reaction conditions. Most widely used are homogeneous platinum containing catalytic systems such as Speier's catalyst (hexachloroplatinic acid in isopropanol, **4**) [3] and Karstedt's catalyst ([Pt<sub>2</sub>{(CH<sub>2</sub>=CHSiMe<sub>2</sub>)<sub>2</sub>O<sub>3</sub>}]<sub>3</sub>, **5**) [4]. Furthermore, a wide range of other platinum complexes in all typical oxidation states (0, II, IV) can be used as precatalysts. Catalytic intermediates in most cases are organometallic Pt(0)/Pt(II) complexes, whereas in selected cases the catalytic cycle has been described via Pt(II)/Pt(IV) intermediates [5]. Although convincing, no direct proof of the Pt(IV) intermediates has been provided.

We have previously prepared platinum(II) complexes that contain hydroxycarbene and acetyl ligands, stabilized through an

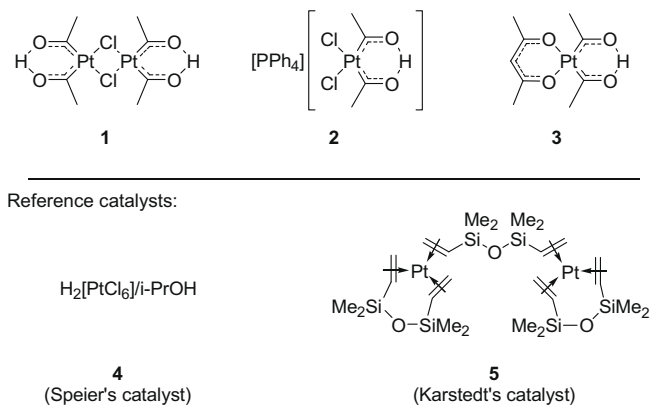
intramolecular hydrogen bond (**1–3**, Scheme 1). Because these type of complexes can be formally derived from organic  $\beta$ -diketones in their enolic form by replacing the central methine moiety with a metal fragment, they are called metalla- $\beta$ -diketones [6]. Among the metalla- $\beta$ -diketones known, the platina- $\beta$ -diketones in Scheme 1 possess unique properties. Due to their 16 valence electrons, they easily undergo oxidative addition and reductive elimination reactions [7]. Because of this, it can be expected that these complexes are capable of catalyzing hydrosilylation reactions. Here we report on the catalytic potential of the platina- $\beta$ -diketones shown in Scheme 1 in hydrosilylations of non-activated alkynes and alkenes. Furthermore, we have investigated the reactivity of the platina- $\beta$ -diketone **1** towards hydrosilanes as the oxidative addition of hydrosilanes to the platinum center is expected to be the first step in the catalytic cycle [8].

## 2. Experimental

### 2.1. General procedure

All reactions and manipulations were carried out under an argon atmosphere using standard Schlenk techniques. Benzene, hexadeuterobenzene, toluene, *n*-pentane and thf were dried over Na/benzophenone, dichloromethane was dried over CaH<sub>2</sub>,

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Scheme 1.

isopropanol with Na, and all solvents were freshly distilled prior use. Hexachloroplatinic acid was available from m&k GmbH (47.4% Pt). The platina- $\beta$ -diketones [Pt<sub>2</sub>{(COMe)<sub>2</sub>H}<sub>2</sub>( $\mu$ -Cl)<sub>2</sub>] (**1**) [9], [PPh<sub>4</sub>][Pt<sub>2</sub>{(COMe)<sub>2</sub>H}<sub>2</sub>( $\mu$ -Cl)<sub>2</sub>] (**2**) and [Pt<sub>2</sub>{(COMe)<sub>2</sub>(acac)}<sub>2</sub>] (**3**) [10] as well as 8-bromoquinoline [11] and bis(8-quinolyl)methylsilane (**22**) [12] were prepared according to known procedures. All other substrates were commercially available and used as received. <sup>1</sup>H, <sup>13</sup>C, <sup>29</sup>Si and <sup>195</sup>Pt NMR spectra were recorded on Varian Gemini 200 and Unity 500 spectrometers. Chemical shifts are relative to solvent signals (CDCl<sub>3</sub>,  $\delta_{\text{H}}$  7.24,  $\delta_{\text{C}}$  77.0; CD<sub>2</sub>Cl<sub>2</sub>,  $\delta_{\text{H}}$  5.32,  $\delta_{\text{C}}$  53.8; C<sub>6</sub>D<sub>6</sub>,  $\delta_{\text{H}}$  7.15,  $\delta_{\text{C}}$  128.0) as internal references;  $\delta(^{29}\text{Si})$  and  $\delta(^{195}\text{Pt})$  are relative to external SiMe<sub>4</sub> ( $\delta_{\text{Si}}$  0.0) and H<sub>2</sub>[PtCl<sub>6</sub>] in D<sub>2</sub>O ( $\delta_{\text{Pt}}$  0.0), respectively. Assignments of NMR signals, if necessary, were revealed by means of NMR correlation experiments. Microanalyses were performed in the Microanalytical Laboratory of the University of Halle using a CHNS-932 (LECO) as well as a VARIO EL (Elementaranalysensysteme) elemental analyzer. IR spectra were recorded on a Mattson 5000 Galaxy FT-IR spectrometer using CsBr or KBr pellets and a Tensor 27 FT-IR spectrometer using an ATR sampler, respectively.

## 2.2. Preparations

### 2.2.1. General procedure for the synthesis of 2-picolyl silanes

The synthesis was adapted from previously published procedures [13]. At  $-78^\circ\text{C}$  *n*-butyllithium in *n*-hexane (1.6 M, 64 ml, 102 mmol) was added dropwise to 2-picoline (10 ml, 102 mmol) in thf (200 ml). The resulting red suspension was stirred at room temperature for 1 h. Afterwards, the corresponding chlorosilanes (102 mmol) and dichlorosilanes (51 mmol), respectively, in thf (50 ml) were added dropwise within 2 h. The volumes of the resulting reaction mixtures were reduced in vacuo (20 ml) and toluene (20 ml) was added. Then, the lithium chloride was filtered and washed with toluene (3  $\times$  5 ml). From the combined solutions the solvents were evaporated under reduced pressure and the residue was distilled in vacuo.

### 2.2.2. (2-Picolyl)dimethylsilane (**18**)

Yield: 3.5 g (23%). *Kp.*: 47–50  $^\circ\text{C}$  (6 Torr). <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta$  0.05 (d, <sup>3</sup>J<sub>H,H</sub> = 3.6 Hz, 6H, CH<sub>3</sub>), 2.37 (d, <sup>3</sup>J<sub>H,H</sub> = 3.3 Hz, 2H, CH<sub>2</sub>), 3.98 (m, 1H, SiH), 6.94 (m, 2H, 3,5-pyH), 7.31–7.60 (m, 1H, 4-pyH), 8.40 (m, 1H, 6-pyH). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>):  $\delta$  –4.5 (s, CH<sub>3</sub>), 27.5 (s, CH<sub>2</sub>), 119.3 (s, 5-pyC), 122.2 (s, 3-pyC), 135.9 (s, 4-pyC), 149.1 (s, 6-pyC), 160.8 (s, 2-pyC).

### 2.2.3. (2-Picolyl)trimethylsilane (**19**)

Yield: 4.2 g (25%). *Kp.*: 41–44  $^\circ\text{C}$  (5 Torr). <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta$  0.00 (s + d, <sup>2</sup>J<sub>Si,H</sub> = 6.5 Hz, 9H, SiCH<sub>3</sub>), 2.32 (s + d,

<sup>2</sup>J<sub>Si,H</sub> = 8.1 Hz, 2H, SiCH<sub>2</sub>), 6.94 (t, <sup>3</sup>J<sub>H,H</sub> = 6.3 Hz, 2H, 3,5-py), 7.47 (td, <sup>3</sup>J<sub>H,H</sub> = 7.6 Hz, <sup>4</sup>J<sub>H,H</sub> = 1.9 Hz, 1H, 4-py), 8.40 (d, <sup>3</sup>J<sub>H,H</sub> = 4.8 Hz, 1H, 6-py). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>):  $\delta$  –2.0 (s + d, <sup>1</sup>J<sub>Si,C</sub> = 51.6 Hz, SiCH<sub>3</sub>), 30.0 (s + d, <sup>1</sup>J<sub>Si,C</sub> = 44.0 Hz, SiCH<sub>2</sub>), 118.8 (s, 5-py), 121.8 (s, 3-py), 135.4 (s, 4-py), 148.7 (s, 6-py), 161.0 (s, 2-py). <sup>29</sup>Si NMR (99 MHz, CDCl<sub>3</sub>):  $\delta$  2.3 (s). GC-MS: *m/z* 165, 150, 120, 106, 93, 73, 65, 43, 29, 15.

### 2.2.4. Bis(2-picolyl)methylsilane (**20**)

Yield: 5.1 g (30%). *Kp.*: 110–114  $^\circ\text{C}$  (0.08 Torr). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  0.04 (d, <sup>3</sup>J<sub>H,H</sub> = 3.66 Hz, 3H, CH<sub>3</sub>), 2.42 (m, 4H, CH<sub>2</sub>), 4.09 (m, 1H, SiH), 6.95 (m, 2H, 5-py), 6.97 (m, 2H, 3-py), 7.46 (m, 2H, 4-py), 8.41 (m, 2H, 6-py). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  –6.4 (s, CH<sub>3</sub>), 25.8 (s, CH<sub>2</sub>), 119.6 (s, 5-py), 122.5 (s, 3-py), 136.0 (s, 4-py), 149.2 (s, 6-py), 160.3 (s, 2-py). <sup>29</sup>Si NMR (99 MHz, CDCl<sub>3</sub>):  $\delta$  –8.4 (s).

### 2.2.5. Bis(2-picolyl)dimethylsilane (**21**)

Yield: 4.7 g (38%). *Kp.*: 85–88  $^\circ\text{C}$  (0.04 Torr). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  –0.07 (s, 6H, SiCH<sub>3</sub>), 2.32 (s, 4H, CH<sub>2</sub>), 6.87–6.91 (m, 4H, 3,5-py), 7.38–7.41 (m, 2H, 4-py), 8.35–8.36 (m, 2H, 6-py). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  –3.5 (s, CH<sub>3</sub>), 28.4 (s, CH<sub>2</sub>), 119.2 (s, 5-py), 122.3 (3-py), 135.7 (s, 4-py), 148.9 (s, 6-py), 160.6 (s, 2-py). <sup>29</sup>Si NMR (99 MHz, CDCl<sub>3</sub>):  $\delta$  3.5 (s).

### 2.2.6. [Pt(COMe)<sub>2</sub>Cl]{(C<sub>9</sub>H<sub>6</sub>N)<sub>2</sub>SiMe- $\kappa^2$ N,N', $\kappa$ Si} (**23**)

At  $-60^\circ\text{C}$  a solution of bis(8-quinolyl)methylsilane (**22**, 98 mg, 0.33 mmol) in thf (5 ml) was added dropwise to a solution of the platina- $\beta$ -diketone [Pt<sub>2</sub>{(COMe)<sub>2</sub>H}<sub>2</sub>( $\mu$ -Cl)<sub>2</sub>] (**1**, 108 mg, 0.17 mmol) in thf (5 ml). The solution was warmed to room temperature with stirring within 30 min and stirred at that temperature for further 30 min. Then the volume of the resulting reaction mixture was reduced in vacuo (1 ml) and diethyl ether (16 ml) was added. The precipitate was filtered, washed with diethyl ether (3  $\times$  5 ml) and dried in vacuo. Yield: 80 mg (40%). *T*<sub>dec</sub>: 107–108  $^\circ\text{C}$ . Anal. Calc. for C<sub>23</sub>H<sub>21</sub>ClN<sub>2</sub>O<sub>2</sub>PtSi (616.04): C, 44.84; H, 3.44. Found: C, 44.86; H, 3.78%. <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  1.14 (s + d, <sup>3</sup>J<sub>Pt,H</sub> = 22.7 Hz, 3H, SiCH<sub>3</sub>), 2.25 (s (br), 6H, COCH<sub>3</sub>), 7.49 (dd, <sup>3</sup>J<sub>H,H</sub> = 5.1 Hz, <sup>3</sup>J<sub>H,H</sub> = 8.1 Hz, 2H, 3-QuinH), 7.55 (dd, <sup>3</sup>J<sub>H,H</sub> = 7.4 Hz, <sup>3</sup>J<sub>H,H</sub> = 7.4 Hz, 2H, 6-QuinH), 7.75 (d, <sup>3</sup>J<sub>H,H</sub> = 8.0 Hz, 2H, 5-QuinH), 8.11 (d, <sup>3</sup>J<sub>H,H</sub> = 6.7 Hz, 2H, 4-QuinH), 8.21 (d, <sup>3</sup>J<sub>H,H</sub> = 8.0 Hz, 2H, 7-QuinH), 10.33 (d (br), <sup>3</sup>J<sub>H,H</sub> = 3.8 Hz, 2H, 2-QuinH). <sup>13</sup>C NMR (125 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  –7.8 (s, SiCH<sub>3</sub>), 41.0 (s + d, <sup>2</sup>J<sub>Pt,C</sub> = 194.9 Hz, COCH<sub>3</sub>), 122.7 (s, 3-QuinC), 128.0 (s, 6-QuinC), 129.7 (s, 4a-QuinC), 129.9 (s, 4-QuinC), 136.6 (s + d, *J*<sub>Pt,C</sub> = 24.2 Hz, 7-QuinC), 140.0 (s, 5-QuinC), 142.0 (s + d, <sup>2</sup>J<sub>Pt,C</sub> = 43.5 Hz, 8a-QuinC), 151.5 (s + d, *J*<sub>Pt,C</sub> = 33.3 Hz, 8-QuinC), 152.7 (s, 2-QuinC) 200.9 (s + d, <sup>1</sup>J<sub>Pt,C</sub> = 991.8 Hz, PtC). <sup>29</sup>Si NMR (99 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  13.7 (s + d, <sup>1</sup>J<sub>Pt,Si</sub> = 1233 Hz). <sup>195</sup>Pt NMR (107 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  –2078 (s + d, <sup>1</sup>J<sub>Pt,Si</sub> = 1245 Hz). IR (ATR):  $\nu$  3049 (w), 2960 (w), 2905 (w), 2055 (w), 1643 (s), 1588 (m), 1567 (m), 1495 (m), 1416 (m), 1373 (m), 1333 (m), 1301 (m), 1244 (m), 1229 (m), 1103 (s), 1082 (s), 1024 (m), 996 (m), 931 (m), 844 (s), 787 (s), 766 (s), 730 (s), 589 (s), 550 (m), 446 (s), 414 (s), 388 (s), 227 (s), 208 (s) cm<sup>-1</sup>.

### 2.2.7. Reaction of [Pt<sub>2</sub>{(COMe)<sub>2</sub>H}<sub>2</sub>( $\mu$ -Cl)<sub>2</sub>] (**1**) with [(2-C<sub>5</sub>H<sub>4</sub>N)CH<sub>2</sub>]<sub>2</sub>NH

At  $-75^\circ\text{C}$  bis(2-picolyl)amine (139 mg, 0.700 mmol) was added by means of a syringe to a solution of the platina- $\beta$ -diketone **1** (222 mg, 0.350 mmol) in dichloromethane (2 ml). Then the reaction mixture is warmed to room temperature within 30 min while stirring. Afterwards, *n*-pentane (10 ml) is carefully added on top of the reaction mixture by condensation. Colorless crystals could be obtained from this mixture at  $-40^\circ\text{C}$  after 12 h that were filtered and washed with *n*-pentane (2  $\times$  10 ml) and dried in vacuo. The

product was recrystallized from dichloromethane/*n*-pentane (2 ml/10 ml). Yield: 265 mg (73%). Two products with an approx. ratio of 9:1 are formed. *Main product*:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  -17.74 (s + d,  $^1J_{\text{Pt,H}} = 1579.3$  Hz, 1H, PtH), 2.62 (s + d,  $^3J_{\text{Pt,H}} = 33.4$  Hz, 3H,  $\text{COCH}_3$  *trans* to NHR<sub>2</sub>), 3.07 (s + d,  $^3J_{\text{Pt,H}} = 26.8$  Hz, 3H,  $\text{COCH}_3$  *trans* to py), 4.44 (d,  $^1J_{\text{H,H}} = 17.9$  Hz, 1H, CHH<sub>endo</sub>), 4.74 (d,  $^1J_{\text{H,H}} = 17.3$  Hz, 1H, C'HH<sub>endo</sub>), 4.94 (dd,  $^1J_{\text{H,H}} = 17.9$  Hz,  $^3J_{\text{H,H}} = 7.3$  Hz, 1H, CHH<sub>exo</sub>), 5.13 (dd,  $^1J_{\text{H,H}} = 17.3$  Hz,  $^3J_{\text{H,H}} = 6.3$  Hz, 1H, C'HH<sub>exo</sub>), 7.24–7.26 (m, 1H, 5'-pyH), 7.35–7.38 (m, 1H, 5-pyH), 7.47 (d,  $^3J_{\text{H,H}} = 7.8$  Hz, 3-pyH), 7.62 (d,  $^3J_{\text{H,H}} = 3'$ -pyH), 7.76–7.81 (m, 2H, 4-pyH/4'-pyH), 8.46 (d,  $^3J_{\text{H,H}} = 5.2$  Hz, 1H, 6'-pyH), 8.62 (dd,  $^3J_{\text{H,H}} = 7.3$  Hz,  $^3J_{\text{H,H}} = 6.3$  Hz, 1H, NH), 8.99 (d,  $^3J_{\text{H,H}} = 5.5$  Hz, 1H, 6-pyH).  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ ):  $\delta$  46.6 (s + d,  $^2J_{\text{Pt,C}} = 250.9$  Hz,  $\text{COCH}_3$  *trans* to NHR<sub>2</sub>), 47.1 (s + d,  $^2J_{\text{Pt,C}} = 249.1$  Hz,  $\text{COCH}_3$  *trans* to py), 59.8 (s, CH<sub>2</sub>), 61.2 (s, C'H<sub>2</sub>), 122.8 (s, 3-pyC), 123.7 (s, 3'-pyC), 124.3/124.4 (s/s, 5-pyC/5'-pyC), 139.4/139.6 (s/s, 4-pyC/4'-pyC), 148.3/148.6 (s/s, 6-pyC/6'-pyC), 160.4/160.6 (s/s, 2-pyC/2'-pyC), 193.5 (s + d,  $^1J_{\text{Pt,C}} = 836.1$  Hz, COMe), 200.9 (s + d,  $^1J_{\text{Pt,C}} = 840.5$  Hz, COMe). *Side product*:  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  -19.28 (s + d,  $^1J_{\text{Pt,H}} = 1529.6$  Hz, 1H), 2.17 (s + d,  $^3J_{\text{Pt,H}} = 31.3$  Hz, 3H,  $\text{COCH}_3$ ), 2.87 (s + d,  $^3J_{\text{Pt,H}} = 26.9$  Hz, 3H,  $\text{COCH}_3$ ). 2-Picolyl groups *trans* to the acetyl ligand are marked by a dash.

### 2.3. X-ray crystal structure determinations

Suitable crystals for X-ray diffraction analyses of complexes **23**·CH<sub>2</sub>Cl<sub>2</sub> and **25**·CH<sub>2</sub>Cl<sub>2</sub> have been obtained from dichloromethane solutions after addition of diethyl ether. Intensity data were collected on a STOE-IPDS diffractometer using graphite-monochromatized Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at 220(2) K. A summary of the crystallographic data, the data collection parameters and the refinement parameters is given in Table 1. Absorption corrections were applied semiempirically ( $T_{\text{min.}}/T_{\text{max.}}$ : 0.23/0.48, **23**; 0.13/0.40, **25**). The structures were solved by direct methods with SHELXS-97 and refined using full-matrix least-squares routines against  $F^2$  with SHELXL-97. [14] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms

**Table 1**  
Crystallographic and data collection parameters for complexes **23** and **25**.

	<b>23</b> ·CH <sub>2</sub> Cl <sub>2</sub>	<b>25</b> ·CH <sub>2</sub> Cl <sub>2</sub>
Empirical formula	C <sub>23</sub> H <sub>21</sub> ClN <sub>2</sub> O <sub>2</sub> PtSi·CH <sub>2</sub> Cl <sub>2</sub>	C <sub>16</sub> H <sub>19</sub> ClN <sub>3</sub> O <sub>2</sub> Pt·CH <sub>2</sub> Cl <sub>2</sub>
$M_r$	700.97	600.81
Crystal system	Orthorhombic	Triclinic
Space group	$P2_12_12_1$	$P\bar{1}$
$a$ (Å)	11.1963(9)	8.4675(8)
$b$ (Å)	10.4562(7)	10.1020(9)
$c$ (Å)	22.353(2)	14.270(1)
$\alpha$ (°)	90	107.38(1)
$\beta$ (°)	90	94.06(1)
$\gamma$ (°)	90	110.24(1)
$V$ (Å <sup>3</sup> )	2616.9(4)	1072.1(2)
$Z$	4	2
$D_{\text{calc}}$ (g cm <sup>-3</sup> )	1.779	1.861
$\mu$ (Mo K $\alpha$ ) (mm <sup>-1</sup> )	5.738	6.933
$F(0\ 0\ 0)$	1360	578
$\theta$ range (°)	2.03–25.98	2.27–25.00
No. of reflections collected	17 708	7616
No. of independent reflections ( $R_{\text{int}}$ )	5065 (0.054)	3464 (0.069)
No. of reflections observed [ $I > 2\sigma(I)$ ]	4788	3074
No. of data/restraints/parameters	5065/0/298	3464/2/247
Goodness-of-fit (GOF) $F^2$	1.013	1.028
$R_1/wR_2$ ( $I > 2\sigma(I)$ )	0.0226, 0.0493	0.0294, 0.0652
$R_1/wR_2$ ( $\Sigma$ )	0.0249, 0.0502	0.0366, 0.0678
Largest difference peak and hole (e Å <sup>-3</sup> )	-1.153 and 0.672	-2.002 and 1.422

were refined isotropically and their positions were included in the models in calculated positions using the riding model.

### 2.4. Computational details

DFT calculations of compounds were carried out by the GAUSSIAN 03 program package [15] using the hybrid functional B3LYP [16]. The 6-311G(d,p) basis sets as implemented in GAUSSIAN 03 were employed for main group atoms. The valence shell of platinum has been approximated by a split valence basis set too; for its core orbitals an effective core potential in combination with consideration of relativistic effects has been used [17]. The appropriateness of the functional in combination with the basis sets and effective core potential used for reliable interpretation of structural and energetic aspects of related platinum complexes has been demonstrated [18,19]. All systems were fully optimized without any symmetry restrictions if not stated otherwise explicitly. The resulting geometries were characterized as equilibrium structures by the analysis of the force constants of normal vibrations. Solvent effects were considered according to the polarized continuum model as implemented in GAUSSIAN 03 [20]. The AIM analyses were performed using the program package AIMPACK as provided by Bader et al. [21].

### 2.5. Catalytic experiments

All hydrosilylation reactions were carried out in C<sub>6</sub>D<sub>6</sub> under argon atmosphere in NMR tubes that were sealed by melting. At -78 °C the NMR tube was loaded by means of syringes with the solvent (C<sub>6</sub>D<sub>6</sub>, 250  $\mu$ l), the two substrates (methylidiphenylsilane and alkyne/olefin), the catalyst solution and, finally, an additional amount of the solvent (250  $\mu$ l). If the catalyst was added in the solid state, it was added to the NMR tube first, followed by the addition of all solutions. The course of the reactions was monitored by  $^1\text{H}$  NMR spectroscopic measurements at 15 min intervals during the first 4 h and every 60 min for the following 6 h. Additional measurements have been undertaken if the reaction was not complete after this time. The product signals were assigned using  $^1\text{H}$ ,  $^{13}\text{C}$  and correlated NMR spectroscopic methods. For kinetic analyses, the sum of the integrals over all aromatic  $^1\text{H}$  NMR signals were used as internal standard.

Stock solutions of the catalysts were prepared under an argon atmosphere and stored at -40 °C. The dinuclear platinum- $\beta$ -diketone [Pt<sub>2</sub>{(COMe)<sub>2</sub>H}<sub>2</sub>( $\mu$ -Cl)<sub>2</sub>] (**1**,  $1.7 \times 10^{-5}$  mol, 11 mg) was dissolved in C<sub>6</sub>D<sub>6</sub> (500  $\mu$ l). Speier's catalyst (**4**) was prepared by dissolving hexachloroplatinic acid ( $50.7 \times 10^{-5}$  mol, 217 mg) in isopropanol (4 ml). Karstedt's catalyst (**5**) was obtained from Aldrich as a solution of platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex in xylene (Pt 2%). The monomeric platinum- $\beta$ -diketones [PPh<sub>4</sub>][Pt{(COMe)<sub>2</sub>H}] (**2**) and [Pt{(COMe)<sub>2</sub>H}(acac)] (**3**) have been added as solids due to low solubility in common solvents and/or decomposition reactions in suitable solvents.

In a typical experiment a molar ratio of unsaturated substrate:methylidiphenylsilane:platinum of 3000:3000:1 has been employed using 0.88 mmol of hexynes and 0.81 mmol of olefins, respectively, and the requisite amounts of methylidiphenylsilane and catalyst.

### 2.6. NMR data of products

#### 2.6.1. (*E*)-1-(Methylidiphenylsilyl)hex-1-ene (**6**)

$^1\text{H}$  NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  0.56 (s, 3H, SiCH<sub>3</sub>), 0.79 (t,  $^3J_{\text{H,H}} = 7.3$  Hz, 3H, CH<sub>2</sub>CH<sub>3</sub>), 1.17–1.26 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 2.05 (m, 2H, =CCH<sub>2</sub>), 5.98 (dt,  $^3J_{\text{H,H}} = 18.5$  Hz,  $^4J_{\text{H,H}} = 1.5$  Hz, 1H, =CHSi), 6.17 (dt,  $^3J_{\text{H,H}} = 18.5$  Hz,  $^3J_{\text{H,H}} = 6.2$  Hz, 1H, =CHCH<sub>2</sub>), 7.14–7.17 (m, 6H, CH<sub>Ar</sub>), 7.55–7.57 (m, 4H, CH<sub>Ar</sub>).  $^{13}\text{C}$  NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  -3.3 (s, SiCH<sub>3</sub>), 14.2 (s, CH<sub>2</sub>CH<sub>3</sub>), 22.6 (s, CH<sub>2</sub>CH<sub>3</sub>), 31.0 (s,



CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 37.0 (s, =CHCH<sub>2</sub>), 125.9 (s, =CHSi), 128.1/129.4/135.2 (s/s/s, C<sub>Ar</sub>), 151.7 (s, =CHCH<sub>2</sub>). <sup>29</sup>Si NMR (99 MHz, C<sub>6</sub>D<sub>6</sub>): δ -15.3 (s).

### 2.6.2. 2-(Methyldiphenylsilyl)hex-1-ene (7)

<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>): δ 0.59 (s, 3H, SiCH<sub>3</sub>), 0.73 (t, <sup>3</sup>J<sub>H,H</sub> = 7.3 Hz, 3H, CH<sub>2</sub>CH<sub>3</sub>), 1.27–1.33 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 2.17–2.20 (m, 2H, =CCH<sub>2</sub>), 5.48–5.49/5.82 (m/m, 1H/1H, =CHH/=CHH), 7.14–7.17 (m, 6H, CH<sub>Ar</sub>), 7.55–7.57 (m, 4H, CH<sub>Ar</sub>). <sup>13</sup>C NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>): δ -3.6 (s, SiCH<sub>3</sub>), 14.1 (s, CH<sub>2</sub>CH<sub>3</sub>), 23.3 (s, CH<sub>2</sub>CH<sub>3</sub>), 31.4 (s, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 36.2 (s, =CHCH<sub>2</sub>), 128.6 (s, =CH<sub>2</sub>), 128.1/129.4/135.2 (s/s/s, C<sub>Ar</sub>), 148.8 (s, =CSi).

### 2.6.3. (E)-1-(Methyldiphenylsilyl)hex-2-ene (8)

<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>): δ 0.47 (s, 3H, SiCH<sub>3</sub>), 0.77 (t, <sup>3</sup>J<sub>H,H</sub> = 7.3 Hz, 3H, CH<sub>2</sub>CH<sub>3</sub>), 1.10–1.14 (m, 2H, CH<sub>2</sub>CH<sub>3</sub>), 1.85 (m, 2H, =CHCH<sub>2</sub>CH<sub>2</sub>), 1.94 (dq, <sup>3</sup>J<sub>H,H</sub> = 7.7 Hz, <sup>4</sup>J<sub>H,H</sub> = 1.0 Hz, 2H, =CCH<sub>2</sub>Si), 5.24–5.30 (m, <sup>3</sup>J<sub>H,H</sub> = 15.1 Hz [22], 1H, =CHCH<sub>2</sub>CH<sub>2</sub>), 5.38–5.45 (m, <sup>3</sup>J<sub>H,H</sub> = 15.1 Hz [22], 1H, =CHCH<sub>2</sub>Si), 7.14–7.17 (m, 6H, CH<sub>Ar</sub>), 7.55–7.57 (m, 4H, CH<sub>Ar</sub>). <sup>13</sup>C NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>): δ -4.7 (s, SiCH<sub>3</sub>), 13.8 (s, CH<sub>2</sub>CH<sub>3</sub>), 22.8 (s, CH<sub>2</sub>CH<sub>3</sub>), 20.6 (s, CH<sub>2</sub>Si), 35.3 (s, =CHCH<sub>2</sub>CH<sub>2</sub>), 125.4 (s, =CHCH<sub>2</sub>Si), 128.1/129.4/135.2 (s/s, C<sub>Ar</sub>), 130.6 (s, =CHCH<sub>2</sub>CH<sub>2</sub>).

### 2.6.4. (E)-2-(Methyldiphenylsilyl)hex-2-ene (9)

<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>): δ 0.58 (s, 3H, SiCH<sub>3</sub>), 0.80 (t, <sup>3</sup>J<sub>H,H</sub> = 7.4 Hz, 3H, CH<sub>2</sub>CH<sub>3</sub>), 1.20–1.30 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.71–1.72 (m, 3H, CH<sub>3</sub>C=), 2.03 (q, <sup>3</sup>J<sub>H,H</sub> = 7.1 Hz, 2H, =CCH<sub>2</sub>), 5.93 (qt, <sup>4</sup>J<sub>H,H</sub> = 1.7 Hz, <sup>3</sup>J<sub>H,H</sub> = 6.9 Hz, 1H, =CH), 7.15–7.17/7.53–7.56 (m/m, 6H/4H, CH<sub>Ar</sub>). <sup>13</sup>C NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>): δ -4.0 (s, SiCH<sub>3</sub>), 14.1 (s, CH<sub>2</sub>CH<sub>3</sub>), 15.5 (s, CH<sub>3</sub>C=), 22.2 (s, CH<sub>2</sub>CH<sub>3</sub>), 31.0 (s, =CCH<sub>2</sub>), 128.1/129.4/135.5 (s/s/s, C<sub>Ar</sub>), 136.7 (s, C<sub>i</sub>), 137.2 (s, =CSi), 144.8 (s, =CH). <sup>13</sup>C NMR (gated decoupling, 125 MHz, C<sub>6</sub>D<sub>6</sub>): δ 15.5 (qd, <sup>1</sup>J<sub>C,H</sub> = 126 Hz, <sup>3</sup>J<sub>C,H</sub> = 11 Hz, CH<sub>3</sub>C=).

### 2.6.5. (E)-3-(Methyldiphenylsilyl)hex-2-ene (10)

<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>): δ 0.59 (s, 3H, SiCH<sub>3</sub>), 0.73 (t, <sup>3</sup>J<sub>H,H</sub> = 7.3 Hz, 3H, CH<sub>2</sub>CH<sub>3</sub>), 1.20–1.30 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.57 (d, <sup>3</sup>J<sub>H,H</sub> = 6.6 Hz, 3H, CH<sub>3</sub>C=), 2.19 (m, 2H, =CCH<sub>2</sub>), 5.99 (q, <sup>3</sup>J<sub>H,H</sub> = 6.6 Hz, 1H, =CH), 7.15–7.17/7.53–7.56 (m/m, 6H/4H, CH<sub>Ar</sub>). <sup>13</sup>C NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>): δ -3.3 (s, SiCH<sub>3</sub>), 14.6 (s, CH<sub>2</sub>CH<sub>3</sub>), 14.7 (s, CH<sub>3</sub>C=), 23.4 (s, CH<sub>2</sub>CH<sub>3</sub>), 32.4 (s, =CCH<sub>2</sub>), 128.1/129.4/135.5 (s/s/s, C<sub>Ar</sub>), 132.8 (s, C<sub>i</sub>), 138.7 (s, =CSi), 139.7 (s, =CH).

### 2.6.6. (E)-3-(Methyldiphenylsilyl)hex-3-ene (11)

<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>): δ 0.60 (s, 3H, SiCH<sub>3</sub>), 0.82 (t, <sup>3</sup>J<sub>H,H</sub> = 7.6 Hz, 3H, =CSiCH<sub>2</sub>CH<sub>3</sub>), 0.83 (t, <sup>3</sup>J<sub>H,H</sub> = 7.5 Hz, 3H, =CHCH<sub>2</sub>CH<sub>3</sub>), 2.04 (m, 2H, =CHCH<sub>2</sub>), 2.91 (q, <sup>3</sup>J<sub>H,H</sub> = 7.6 Hz, 2H, =CSiCH<sub>2</sub>), 5.89 (t, <sup>3</sup>J<sub>H,H</sub> = 7.0 Hz, 1H, =CH), 7.14–7.17/7.54–7.57 (m/m, 6H/4H, CH<sub>Ar</sub>). <sup>13</sup>C NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>): δ -3.3 (s, SiCH<sub>3</sub>), 14.2 (s, =CHCH<sub>2</sub>CH<sub>3</sub>), 15.2 (s, =CSiCH<sub>2</sub>CH<sub>3</sub>), 22.2 (s, =CHCH<sub>2</sub>), 23.3 (s, =CSiCH<sub>2</sub>), 128.1/129.4/135.6 (s/s/s, C<sub>Ar</sub>), 137.2 (s, C<sub>i</sub>), 138.4 (s, =CSi), 146.9 (s, =CH). <sup>29</sup>Si NMR (99 MHz, C<sub>6</sub>D<sub>6</sub>): δ -10.3 (s).

### 2.6.7. Hexyl(methyl)diphenylsilane (12)

<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>): δ 0.46 (s, 3H, SiCH<sub>3</sub>), 0.82 (t, <sup>3</sup>J<sub>H,H</sub> = 7 Hz, 3H, CH<sub>2</sub>CH<sub>3</sub>), 0.99–1.02 (m, 2H, SiCH<sub>2</sub>), 1.12–1.29 (m, 6H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.33–1.39 (m, 2H, SiCH<sub>2</sub>CH<sub>2</sub>), 7.09–7.16/7.44–7.48 (m/m, 6H/4H, CH<sub>Ar</sub>). <sup>13</sup>C NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>): δ -4.2 (s, SiCH<sub>3</sub>), 14.3 (s, CH<sub>2</sub>CH<sub>3</sub>), 14.6 (s, SiCH<sub>2</sub>), 23.0 (s, CH<sub>2</sub>), 24.2 (s, SiCH<sub>2</sub>CH<sub>2</sub>), 31.4 (s, CH<sub>2</sub>), 33.7 (s, CH<sub>2</sub>), 128.1/129.4/134.8 (s/s/s, C<sub>Ar</sub>), 137.7 (s, C<sub>i</sub>). <sup>29</sup>Si NMR (99 MHz, C<sub>6</sub>D<sub>6</sub>): δ -7.4 (s).

### 2.6.8. Methyl(diphenyl)(2-phenylethyl)silane (15)

<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>): δ 0.45 (s, 3H, SiCH<sub>3</sub>), 1.34–1.38 (m, 2H, SiCH<sub>2</sub>), 2.62–2.66 (m, 2H, SiCH<sub>2</sub>CH<sub>2</sub>), 7.07–7.12/7.15–7.16/

7.45–7.48 (m/m/m, 1H/8H/6H, CH<sub>Ar</sub>). <sup>13</sup>C NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>): δ -4.3 (s, SiCH<sub>3</sub>), 16.7 (s, SiCH<sub>2</sub>), 30.3 (s, SiCH<sub>2</sub>CH<sub>2</sub>), 125.9/128.2/128.6/129.5/134.8/135.2/137.2/145.0 (s/s/s/s/s/s/s, C<sub>Ar</sub>). <sup>29</sup>Si NMR (99 MHz, C<sub>6</sub>D<sub>6</sub>): δ -7.4 (s).

### 2.6.9. Dimethyl(phenyl)[2-(trimethylsilyl)ethyl]silane (17)

<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>): δ -0.06 (s + d, 9H, Si(CH<sub>3</sub>)<sub>3</sub>), 0.48 (s, 3H SiPh<sub>2</sub>CH<sub>3</sub>), 0.47–0.51 (m, 2H, CH<sub>2</sub>SiMe<sub>3</sub>), 0.96–0.99 (m, 2H, CH<sub>2</sub>SiMePh<sub>2</sub>), 7.14–7.18/7.49–7.51 (m/m, 6H/4H, CH<sub>Ar</sub>). <sup>13</sup>C NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>): δ -4.7 (s, SiPh<sub>2</sub>CH<sub>3</sub>), -2.1 (s, Si(CH<sub>3</sub>)<sub>3</sub>), 6.8 (s, CH<sub>2</sub>SiPh<sub>2</sub>Me), 9.1 (s, CH<sub>2</sub>SiMe<sub>3</sub>), 128.2/134.9 (s/s, C<sub>o</sub>/C<sub>m</sub>), 129.4 (s, C<sub>p</sub>), 137.5 (s, i-C).

## 3. Results and discussion

### 3.1. Catalysis

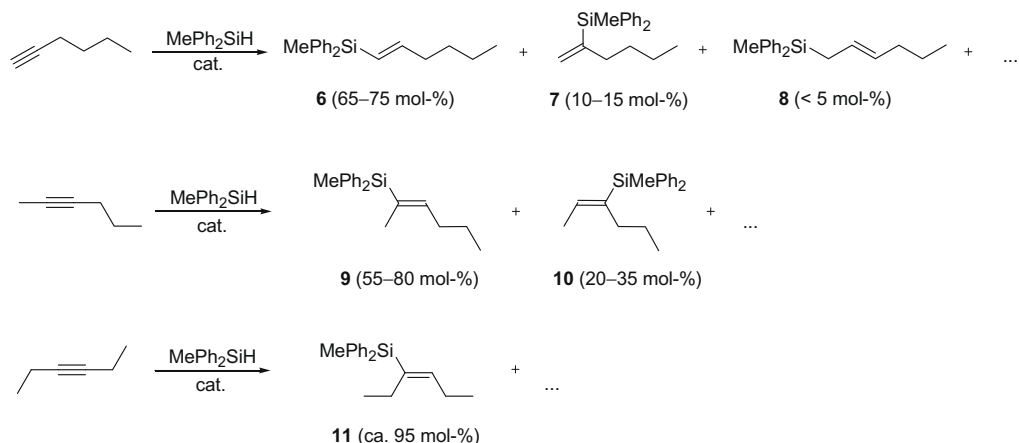
#### 3.1.1. Hydrosilylation of Hexynes

The hydrosilylation reactions were carried out at 27 °C with a molar ratio of *n*<sub>alkyne/olefin</sub>:*n*<sub>silane</sub>:*n*<sub>Pt</sub> = 3000:3000:1. Because of the dinuclear structure of the platina-β-diketone **1** (Scheme 1) the resulting molar ratio was *n*<sub>silane</sub>:*n*<sub>1</sub> = 6000:1. Methyldiphenylsilane was chosen as the hydrosilane because the <sup>1</sup>H NMR signal of the methyl group was well separated from other signals and thus the course of reaction could be followed easily using <sup>1</sup>H NMR spectroscopy.

Reactions of hex-1-yne with equimolar amounts of methyldiphenylsilane in the presence of 0.33 mol% Pt catalyst (**1**, **4** and **5**) yielded the hydrosilylation product (E)-1-(methyldiphenylsilyl)hex-1-ene (**6**) together with smaller amounts of 2-(methyldiphenylsilyl)hex-1-ene (**7**) and (E)-1-(methyldiphenylsilyl)hex-2-ene (**8**) (Scheme 2). Most likely, compound **8** was formed from **6** by double bond isomerization. The Markovnikov product **7** is only obtained to the extent of 10–15 mol%. The exclusive formation of the (E) isomers was proved by the magnitude of the vicinal H,H coupling constants (<sup>3</sup>J<sub>H,H</sub> = 18.5 Hz, **6**; <sup>3</sup>J<sub>H,H</sub> = 15.1 Hz, **8**). This is, as expected, in accord with a *syn* addition of the hydrosilane to the triple bond [23].

The periods after which the hydrosilane was consumed by 50% (*t*<sub>50</sub>) and 95% (*t*<sub>95</sub>) are given in Table 2 showing the following order of activity: platina-β-diketone (**1**) > Speier's catalyst (**4**) > Karstedt's catalyst (**5**). The formation of the main product **6** for the three different catalysts used versus the reaction time is shown in Fig. 1. The decrease in the yield of product **6** at longer reaction times using the catalysts **1** and **5** is in accord with an increase in the yield of the double bond isomer **8**.

The hydrosilylation of hex-2-yne with methyldiphenylsilane was investigated with the dinuclear (**1**) and the mononuclear platina-β-diketones (**2**, **3**) and with Speier's (**4**) and Karstedt's catalysts (**5**) for comparison (Table 2). In the hydrosilylation reactions the two regioisomers **9** and **10** were formed. In the main product (**9**) the silicon group is attached to the carbon atom possessing the sterically less demanding group (Me versus *n*-Pr) (Scheme 2). The highest regioselectivity (*n*<sub>9</sub>:*n*<sub>10</sub> = 80:20) was achieved with complex **2**. The <sup>3</sup>J<sub>C,H</sub> coupling constant of 11 Hz indicated the formation of the (E) isomer of **9** being in accord with a *syn* addition to the triple bond. The hydrosilylation reactions with the platina-β-diketones **1** and **3** proceeded noticeably faster than those with the reference catalysts **4** and **5**. Due to its symmetry, the hydrosilylation of hex-3-yne yielded one main product only (**11**, Scheme 2). The <sup>3</sup>J<sub>C,H</sub> coupling constant of 10.5 Hz gave proof for the formation of the (E) isomer manifesting a *syn* addition of the hydrosilane. In all these reactions the platina-β-diketone **1** showed a substantially higher activity compared to the reference catalysts (Table 2). Even using half the catalyst concentration of



Scheme 2.

**Table 2**

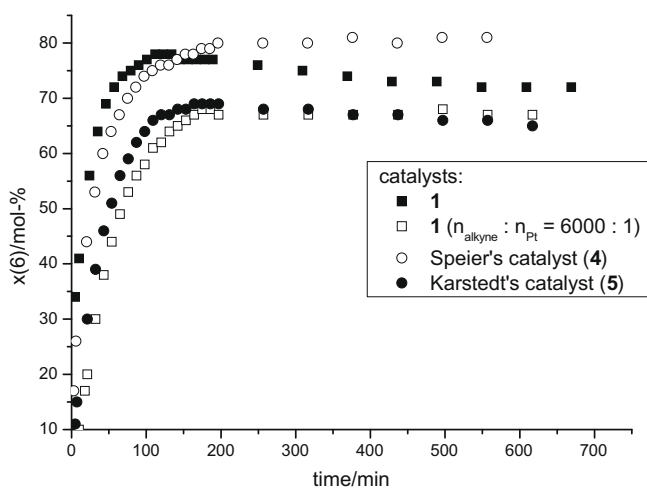
Times at 50/95% degree of conversion of methyl-diphenylsilane ( $t_{50}/t_{95}$  in min) in hydrosilylation reactions of hexynes using the platinum- $\beta$ -diketone  $[\text{Pt}_2\{(\text{COMe})_2\text{H}\}_2(\mu\text{-Cl})_2]$  (**1**) as well as Speier's (**4**) and Karstedt's (**5**) catalysts ( $n_{\text{alkyne}}:n_{\text{Pt}} = 3000:1$ , in  $\text{C}_6\text{D}_6$ , 27 °C). Additionally, in the case of hex-2-yne  $[\text{PPh}_4][\text{Pt}\{(\text{COMe})_2\text{H}\}\text{Cl}_2]$  (**2**) and  $[\text{Pt}\{(\text{COMe})_2\text{H}\}(\text{acac})]$  (**3**) have been used as catalysts.

Catalyst	Hex-1-yne		Hex-2-yne		Hex-3-yne	
	$t_{50}$	$t_{95}$	$t_{50}$	$t_{95}$	$t_{50}$	$t_{95}$
<b>1</b>	5–10	90	45–50	470–510	15–30	50–70
<b>1<sup>a</sup></b>	40–45	200 <sup>b</sup>	130–180	530–660	55–70	170–200
<b>2</b>			125–130	475–510		
<b>3</b>			65–70	700–930		
<b>4</b>	15–20	120–130	110–115	1070–1300	100–110	420–570
<b>5</b>	25–30	250 <sup>c</sup>	115–120	1050–1400 <sup>c</sup>	100–105	430–510

<sup>a</sup>  $n_{\text{alkyne}}:n_{\text{Pt}} = 6000:1$ .

<sup>b</sup>  $t_{85}$ .

<sup>c</sup>  $t_{90}$ .



**Fig. 1.** Degree of formation of (E)-1-(methyl-diphenylsilyl)hex-1-ene (**6**) vs. time for the catalysts **1**, **4** and **5**.

**1** resulted in lower reaction times compared to the reference catalysts.

### 3.1.2. Hydrosilylation of olefins

The results of the reactions of hex-1-ene with methyl-diphenylsilane in the presence of the platinum catalysts **1**, **3**, **4** and **5** are shown in Scheme 3 and Table 3. The hydrosilylation product

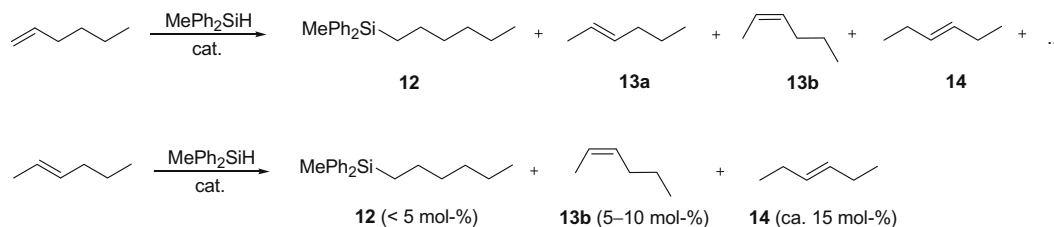
hexyl(methyl)diphenylsilane (**12**) could be identified as the main product, but in all cases considerable amounts of double bond isomerization products (**13a**, **13b** and **14**) were also formed. All platinum complexes exhibited roughly the same initial activity (see Supporting Information). Karstedt's catalyst (**5**) showed the lowest productivity, a degree of conversion of hex-1-ene of only about 50% was reached after 1 h. The anionic complex **2** showed a very low activity, after 6 h the degree of conversion amounted to 15% only.

Under the same reaction conditions, treatment of hexenes with internal double bonds (*cis*- and *trans*-hex-2-ene, *cis*- and *trans*-hex-3-ene) with methyl-diphenylsilane mainly resulted in double bond isomerizations (see Scheme 3 for *trans*-hex-2-ene and the Supporting Information for the others). The only hydrosilylation product found (**12**) is identical with that of hex-1-ene, but it is only formed to an extent of <5 mol%. Thus, prior to the hydrosilylation a double bond shift into the terminal position took place.

The hydrosilylation of styrene with methyl-diphenylsilane proceeded comparatively slow with a yield of approximately 80% after five days at room temperature (catalysts **1** and **5**). Catalyst **4** showed the lowest productivity giving a yield of only 40% after four days. The reactions proved to be highly regioselective, only the anti-Markovnikov product **15** was found (Scheme 4 and Table 4). Additionally, minor amounts (<5 mol%) of ethylbenzene (**16**) were formed, possibly as the product of a dehydrogenative silylation [24]. Trimethylvinylsilane reacted with methyl-diphenylsilane in the presence of platinum complexes as catalysts giving the expected hydrosilylation product **17** (Scheme 4). The reaction was relatively fast with  $t_{50}$  values ranging from 5 to 40 min (Table 4). Minor amounts of side products were obtained (<10 mol%), but not identified.

### 3.2. Reactions of the platinum- $\beta$ -diketone **1** with hydrosilanes

Reactions of the dinuclear platinum- $\beta$ -diketone **1** with simple hydrosilanes ( $\text{Et}_2\text{MeSiH}$ ,  $\text{Et}_3\text{SiH}$ ,  $\text{MePh}_2\text{SiH}$ ) resulted in all cases in decomposition of the platinum species yielding platinum black, only. Subsequently, we applied the concept of the chelate-assisted hydrosilylation [25] to our reaction system in order to facilitate the oxidative addition reaction on the one hand and to reduce the possibility of subsequent Si-X reductive eliminations ( $\text{X} = \text{Cl}$ , Me, COMe, etc.) on the other hand. For this purpose 2-picolyl substituted hydrosilanes of the type N-SiMe<sub>2</sub>H (**18**) and N-SiMeH-N (**20**) (Scheme 5) have been prepared by deprotonation of the methyl group of 2-picoline with *n*-BuLi followed by treatment with the corresponding chlorosilanes (see Section 2). Additionally, the



Scheme 3.

Table 3

Times at 50/80% degree of conversion of hex-1-ene ( $t_{50}/t_{80}$  in min) and product ratios at  $t_{80}$  (in mol%) in the hydrosilylation reaction of hex-1-ene with methylphenylsilane ( $n_{\text{alkene}}:n_{\text{Pt}} = 3000:1$ , in  $\text{C}_6\text{D}_6$ , 27 °C).

Catalyst	$t_{50}$	$t_{80}$	$\chi(\mathbf{12})$	$\chi(\mathbf{13a})$	$\chi(\Sigma(\mathbf{14} + \mathbf{13b} + \text{SP}))^a$
<b>1</b>	15–20	110–150	55	15	5–10
<b>3</b>	45–55	110–135	55	15	10
<b>4</b>	15–20	140–180	60	10	<5
<b>5</b>	150–270	–	50 <sup>b</sup>	<5 <sup>b</sup>	<5 <sup>b</sup>

<sup>a</sup> SP – unidentified side products.

<sup>b</sup> Ratio at  $t_{50}$ .

analogous methyl derivatives  $\text{N}-\text{SiMe}_3$  (**19**) and  $\text{N}-\text{SiMe}_2-\text{N}$  (**21**) have also been prepared in order to test the general reactivity of silylated pyridines towards the platina- $\beta$ -diketone **1**. But all these reactions resulted also in its decomposition forming platinum black, only. Several attempts have been made to isolate products even at temperatures as low as  $-78$  °C but due to the high instability of the products formed, this was also not successful. Interestingly, a decomposition took place regardless of which hydrosilanes (**18/20**) or their methylated congeners (**19/21**) were used as substrates. Thus, these results must not be interpreted in terms of the instability of a hydrido-silyl-platinum(IV) intermediate complex, which might be formed by an oxidative addition starting from **18/20** and **1**.

A quinoline based bidentate (being potentially tridentate after deprotonation)  $\text{N}-\text{SiMeH}-\text{N}$  hydrosilane (**22**, Scheme 6) that is very similar to the silane **20** has been successfully used by Tilley and co-workers in oxidative addition reactions to Rh(I), Ir(I) and Pt(II) [12,26]. The reaction of this hydrosilane with the platina- $\beta$ -diketone **1** resulted in the Pt(IV) complex **23** bearing the tridentate  $[\text{N}-\text{SiMe}-\text{N}]^-$  ligand, two acetyl groups and a chloro ligand (Scheme 6). The constitution of complex **23** could be unambiguously proved by NMR spectroscopy and an X-ray crystal structure determination (Fig. 2). The release of dihydrogen during the reaction was proved by GC-MS. The bonding of Si to Pt(IV) gives rise to a large Pt–Si coupling constant ( $J_{\text{Pt,Si}} = 1239$  Hz) that was observed both in  $^{195}\text{Pt}$  and  $^{29}\text{Si}$  NMR spectra. The existence of only one set of the acetyl and quinolyl signals in  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra clearly indicates the equivalence of these ligands thus proving the OC-6-24 configuration.

The immediate formation of platinum black in reactions of the platina- $\beta$ -diketone **1** with pyridine functionalized silanes **20** and

Table 4

Times at 50% degree of conversion of methylphenylsilane ( $t_{50}$  in min) in the hydrosilylation reaction of methylphenylsilane with styrene and trimethylvinylsilane ( $n_{\text{alkene}}:n_{\text{Pt}} = 3000:1$ , in  $\text{C}_6\text{D}_6$ , 27 °C).

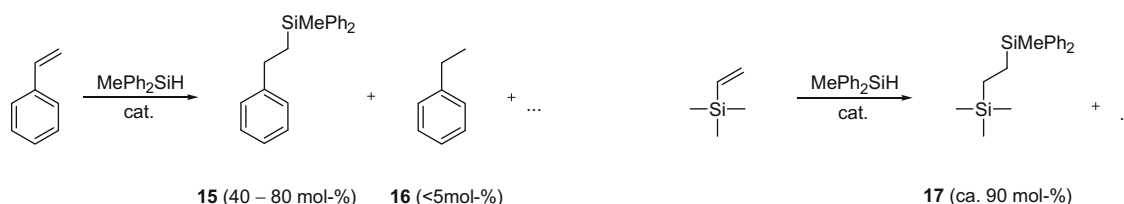
Catalyst	Styrene $t_{50}$	Trimethylvinylsilane $t_{50}$
<b>1</b>	525–560	5–10
<b>4</b>	550–750 <sup>a</sup>	35–40
<b>5</b>	875–1010	10–15

<sup>a</sup>  $t_{35}$ .

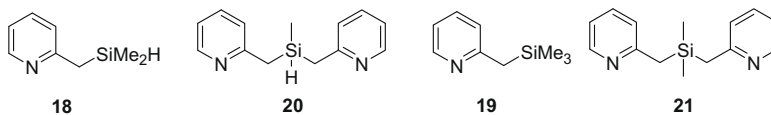
**21** (Scheme 5) prompted us to investigate the analogous reaction using the bis(2-picoly)amine  $\text{N}-\text{NH}-\text{N}$  (**24**, Scheme 7). The reaction resulted in facial coordination of the tridentate ligand and a proton shift from the  $\text{O}-\text{H}\cdots\text{O}$  bridge of the platina- $\beta$ -diketone to the metal center in the sense of an oxidative addition reaction forming the octahedral hydridoplatin(IV) complex **25** as the main product. This complex could be fully characterized by NMR spectroscopy and an X-ray crystal structure determination. Furthermore, the formation of a side product (ca. 10%) was detected NMR spectroscopically. Although its constitution could not be fully revealed, it was made clear that it is a platinum(IV) complex bearing a hydrido ligand and two chemically nonequivalent acetyl ligands.

### 3.2.1. Structures of complexes **23** and **25**

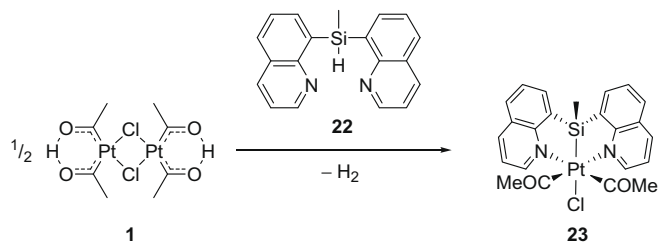
Crystals of the NSiN-coordinated complex **23** could be obtained from dichloromethane solutions by adding a layer of diethyl ether. The complex crystallized as a dichloromethane adduct **23**· $\text{CH}_2\text{Cl}_2$  in the chiral space group  $P2_12_12_1$ . The molecular structure of complex **23** is shown in Fig. 2, selected geometrical parameters are given in the figure caption. The platinum atom is coordinated in an octahedral geometry by the facial binding NSiN ligand, two acetyl groups and one chloro ligand in *trans* position to the Si atom. The  $\text{N}-\text{Pt}-\text{Si}$  ( $83.61(9)/83.63(9)^\circ$ ) angles are clearly below  $90^\circ$  due to the rigidity of the NSiN ligand. The Pt–Cl1 bond is remarkably long ( $2.536(1)$  Å) in comparison with known Pt(IV)–Cl bonds (median:  $2.318$  Å, lower/upper quartile:  $2.308/2.330$  Å, number of observations  $n = 1232$ ), obviously due to the high *trans* influence of the silyl ligand and the hydrogen bonds in which the chloro ligand is involved (see below). Interestingly, the Pt–X ( $\text{X} = \text{Cl1}, \text{Si}, \text{N1/N2}$ ) bonds in the octahedral Pt(IV) complex **23** are longer than the cor-



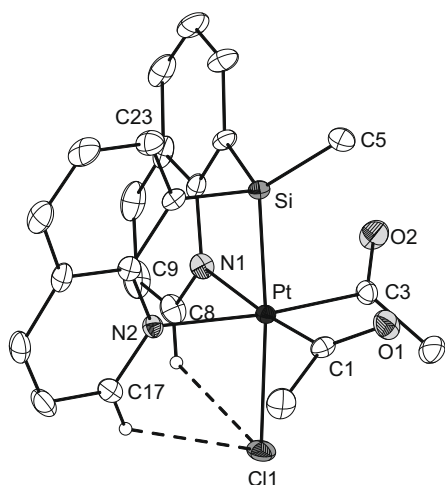
Scheme 4.



Scheme 5.



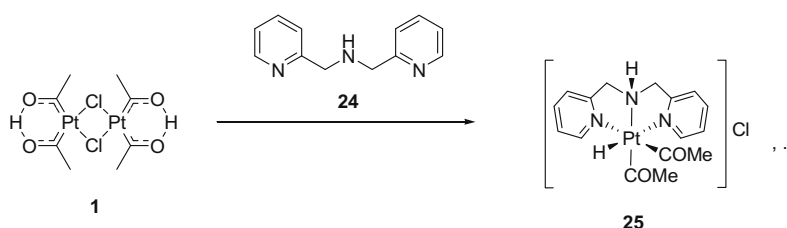
Scheme 6.



**Fig. 2.** Structure of the octahedral complex **23** in crystals of **23**·CH<sub>2</sub>Cl<sub>2</sub>. Thermal ellipsoids are shown at the 30% probability level. H atoms are omitted for clarity except those involved in hydrogen bonds. Selected bond lengths (Å) and angles (°): Pt–C1 2.032(5), Pt–C2 2.031(3), Pt–N1 2.216(4), Pt–N2 2.217(3), Pt–Si 2.294(1), Pt–Cl1 2.536(1); N1–Pt–N2 87.6(1), N1–Pt–C3 89.5(2), Si–Pt–Cl1 175.18(4), Si–Pt–N1 83.6(1), Si–Pt–N2 83.63(9), N1–Pt–C1 174.0(2), N2–Pt–C3 174.8(2).

responding bonds in the square planar Pt(II) complex [Pt(NSiN)Cl] (X = Cl: 2.536(1) versus 2.528(2) Å; X = Si: 2.294(1) versus 2.225(2) Å, X = N: 2.216(4)/2.217(3) versus 2.031(5)/2.040(5) Å [26a,27]).

In crystals of **23**·CH<sub>2</sub>Cl<sub>2</sub> several hydrogen bonds were found (Table 5). On the one hand, the chloro ligand acts as hydrogen acceptor in intramolecular C–H···Cl1 hydrogen bonds (Fig. 2). On the other hand intermolecular hydrogen bonds between **23** and the solvate molecule (C24–H···Cl1', C24–H···O1) and between two neighbored molecules **23** (C9–H···Cl1'', C23–H···O2') were found.



Scheme 7.

Crystals of the bis(2-picolyl)amine-coordinated complex **25** could be obtained by crystallisation from dichloromethane/diethyl ether as a dichloromethane solvate (**25**·CH<sub>2</sub>Cl<sub>2</sub>). The complex crystallizes in the space group *P* $\bar{1}$ . In the crystals there were found complex cations, chloride anions and solvate molecules that are connected through a network of hydrogen bonds, see the asymmetric unit shown in Fig. 3. Selected bond lengths and angles are given in the figure caption. As observed elsewhere [28], the hydrido ligand was not found in the electron density map but its existence was unambiguously proved by <sup>1</sup>H NMR spectroscopy. The atoms of one of the two acetyl ligands were found to be disordered over two positions (67/33%).

In the complex cation the platinum atom is coordinated in an octahedral fashion by the facially binding bis(2-picolyl)amine, two acetyl ligands and the hydrido ligand. Due to the rigid backbone of the tridentate NNN-ligand the angles around the complex center are substantially different from 90° ranging from 77.8(2)° (N2–Pt–N1) to 102(1)° (N1–Pt–C3b). The Pt–N bond lengths (2.176(4)–2.205(4) Å) are noticeably longer than other typical Pt(IV)–N bond lengths (median: 2.064 Å, upper/lower quartile: 2.148/2.033 Å, *n* = 2465 [29]), most likely due to the high *trans* influences of the ligands in *trans* position (acetyl and hydrido ligands). In the cations of complex **25** were found C–H···O hydrogen bonds where the O atom of an acetyl ligand acts as a hydrogen acceptor (C9–H···O2b, C15–H···O2b, C15–H···O2a, see Table 5). Furthermore, the chloride anions act as hydrogen acceptors both for the N–H group (N–H···Cl1) and for a C–H group of the dichloromethane molecule (C17–H···Cl1), see Fig. 3 and Table 5.

### 3.3. Quantum chemical calculations

To get insight into the different reactivities of the N–SiMeH–N hydrosilanes having quinoline (**22**) and pyridine (**20**) backbones, respectively, quantum chemical calculations on the DFT level of theory using the hybrid functional B3LYP and high-quality 6-311G(d,p) basis sets for all main group atoms as well as a double- $\zeta$  basis set for Pt along with a pseudopotential considering relativistic effects for its core electrons (see Section 2) were performed.

The calculations exhibited that the diacetylchloroplatinum(IV) complexes bearing the quinoline and the pyridine based anionic N–SiMe–N– $\kappa^2$ N,N', $\kappa$ Si ligands (**23**<sub>calc</sub> versus **26**), respectively, are very similar in their structures, see Fig. 4 and Table 6. Furthermore, the calculated structure **23**<sub>calc</sub>, representing the structure in the gas phase, was found to be very close to the experimentally observed structure in crystals of **23**·CH<sub>2</sub>Cl<sub>2</sub>.

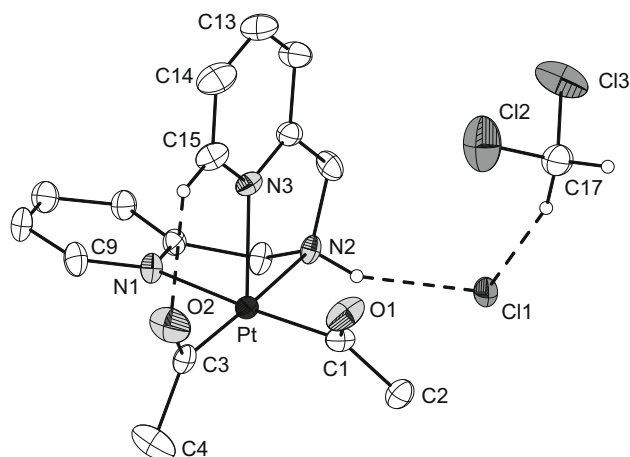


**Table 5**

Selected parameters (distances in Å, angles in °) of hydrogen bonds in the crystals **23**·CH<sub>2</sub>Cl<sub>2</sub> and **25**·CH<sub>2</sub>Cl<sub>2</sub>.

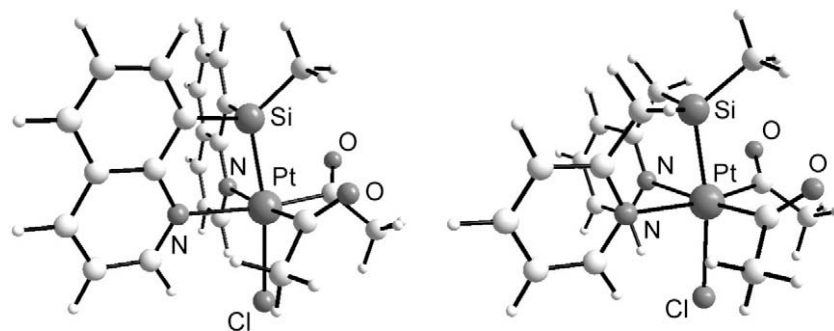
<b>23</b> ·CH <sub>2</sub> Cl <sub>2</sub>		<b>25</b> ·CH <sub>2</sub> Cl <sub>2</sub>	
D–H···A	d(D···A)/∠(D–H···A)	D–H···A	d(D···A)/∠(D–H···A)
<i>Intramolecular</i>			
C8–H···Cl1	3.385(5)/131	C15–H···O2a	3.15(3)/133
C17–H···Cl1	3.371(5)/131	C15–H···O2b	3.04(2)/137
		C9–H···O2b	3.09(4)/136
<i>Intermolecular</i>			
C24–H···O1 <sup>a</sup>	3.220(8)/164	N2–H···Cl1	3.14(1)/157
C24–H···Cl1'	3.666(7)/162	C17–H···Cl1	3.592(7)/155
C9–H···Cl1''	3.575(5)/157	C17–H···Cl1'	3.602(8)/170
C23–H···O2'	3.402(6)/162	C9'–H···O2b	3.11(3)/147
		C14–H···O1'	3.259(9)/131

<sup>a</sup> C24 is the C atom of the solvate molecule (CH<sub>2</sub>Cl<sub>2</sub>).



**Fig. 3.** Solid-state structure of the octahedral complex **25**·CH<sub>2</sub>Cl<sub>2</sub>. Thermal ellipsoids are shown at the 30% probability level. The sixth “free” coordination site is occupied by an hydrido ligand that could not be located in the electron density map. The atoms of the acetyl group C3/C4/O2 are disordered over two positions (67:33), only the major occupied positions are shown. H atoms are omitted for clarity except those involved in hydrogen bonds. Selected bond lengths (Å) and angles (°): Pt–C1 2.037(5), Pt–C3 2.02(1)/2.02(2) (the values for the major occupied positions are given first), Pt–N1 2.176(4), Pt–N2 2.182(5), Pt–N3 2.205(4); N1–Pt–N2 77.8(2), N2–Pt–N3 78.2(2), N1–Pt–N3 84.5(2), N3–Pt–C3 101.1(5)/102(1), N1–Pt–C1 176.6(2), N2–Pt–C3 178.0(3)/167.0(8).

Furthermore, analogous to reactions with other bidentate chelate ligands (NN, PP, NO, NS donors) [7,30], the first step of the reaction of **1** with **22/20** can be assumed to be the cleavage of the Pt–Cl–Pt bridges forming mononuclear cationic platina-β-diketones having bidentately *N,N'* coordinated hydrosilane ligands



**Fig. 4.** Calculated structures of [Pt(COME)<sub>2</sub>Cl(SiMe(quin)<sub>2</sub>-κ<sup>2</sup>N,N',κSi)] (**23**<sub>calc</sub>, left) and [Pt(COME)<sub>2</sub>Cl(SiMe(CH<sub>2</sub>py)<sub>2</sub>-κ<sup>2</sup>N,N',κSi)] (**26**, right).

**Table 6**

Calculated structural parameters (lengths in Å, angles in °) of [Pt(COME)<sub>2</sub>Cl(SiMe(quin)<sub>2</sub>-κ<sup>2</sup>N,N',κSi)] (**23**<sub>calc</sub>) and [Pt(COME)<sub>2</sub>Cl(SiMe(CH<sub>2</sub>py)<sub>2</sub>-κ<sup>2</sup>N,N',κSi)] (**26**). For comparison the requisite values in crystals of **23**·CH<sub>2</sub>Cl<sub>2</sub> are given.

	<b>23</b> <sub>calc</sub>	<b>23</b>	<b>26</b>
Pt–C	2.059/2.062	2.031(3)/2.032(5)	2.054/2.057
Pt–N	2.316/2.350	2.216(4)/2.217(3)	2.329/2.366
Pt–Si	2.331	2.294(1)	2.338
Pt–Cl	2.574	2.536(1)	2.575
Si–Pt–Cl	169.6	175.18(4)	170.3
Si–Pt–N	80.7/81.9	83.6(1)/83.63(9)	80.8/81.4
Pt–Si–C <sub>Me</sub>	123.9	123.2(2)	122.4

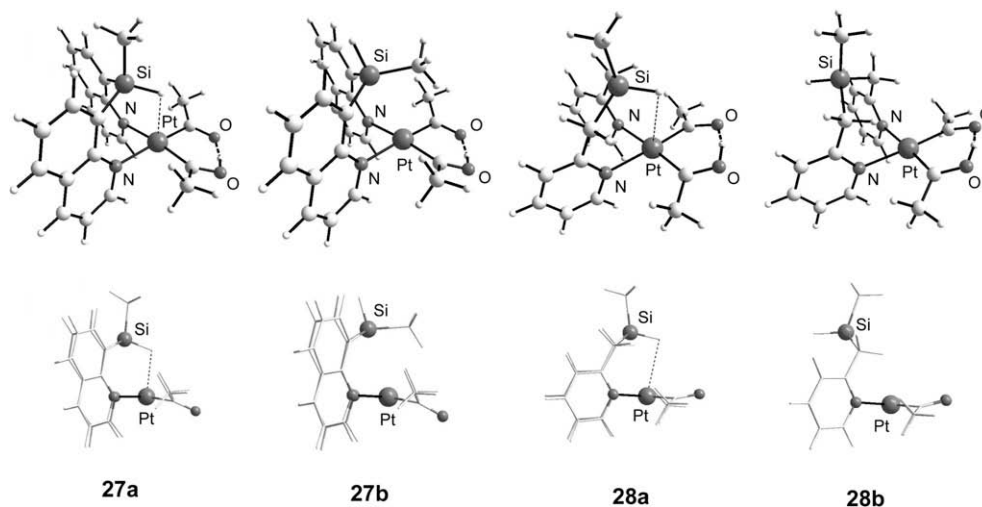
(Scheme 8). These complexes have been calculated both with the quinoline and the pyridine based ligands whereas two isomers have been considered each, namely those having the Si–H group directed towards the platinum (**27a/28a**) and those having the Si–Me group directed towards the platinum (**27b/28b**). The structures are shown in Fig. 5, selected structural parameters and the relative energies are given in Table 7.

Comparison of the Si–H distances (**27a** versus **27b** and **28a** versus **28b**) shows that the complexes in which the Si–H group is directed towards the Pt do not have prolonged Si–H bonds, although the Pt···H distance of 2.410 Å in **27a** and, likely also of 2.939 Å in **28a**, points to a Pt···H interaction via the doubly occupied 6d<sub>z<sup>2</sup></sub> orbital of Pt. This is also supported by the existence of bond critical points ( $\rho_{\text{bcip}}$ ) within the framework of the AIM theory [31], see Supplemental material. Thus, the Si–H···Pt interactions can be understood in terms of 3-center–4-electron bonds [32]. Compared with the non-coordinated ligands, the Si–C<sub>8-quin</sub>–C<sub>8a-quin</sub> (**27a/27b**) and Si–CH<sub>2</sub>–C<sub>2-py</sub> (**28a/28b**) angles are widened up by 7/11° (**27a/27b**) and 12/3° (**28a/28b**), respectively, exhibiting (apart from **28b**) a remarkable coordination induced angle strain.

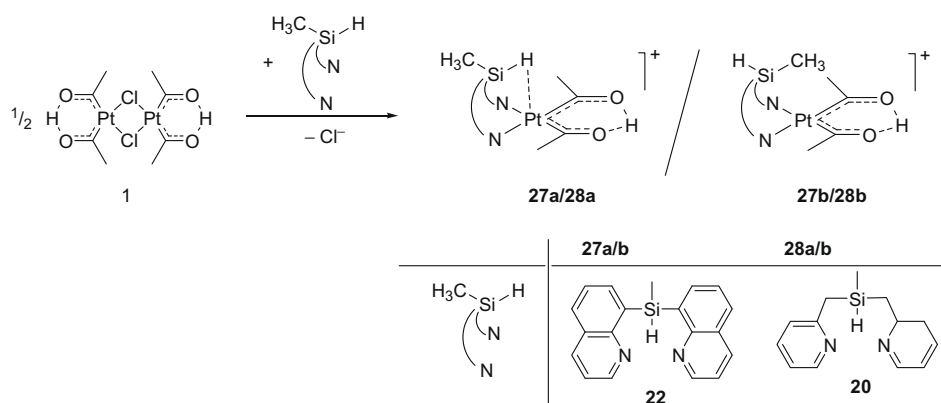
Remarkably, in the case of the quinoline based ligand, the complex with the Si–H group directed towards platinum (**27a**) is more stable by 3.24 kcal/mol than **27b**, whereas in the case of the pyridine based ligand the complex with the Si–Me group directed towards platinum (**28b**) is by 8.57 kcal/mol more stable than **28a**. As clearly seen in the side view pictures of the complexes (Fig. 5) this is due to the flexibility of the Si–CH<sub>2</sub>–py units allowing that the whole SiMeH group is bent away from platinum. It should be mentioned that we failed to localize other equilibrium structures (analogous **28a** and **28b** but with exchanged H and Me groups each) on the energy hypersurface.

In all four complexes, the platina-β-diketone units show the expected features [19]. The O–H···O hydrogen bonds are unsymmetrical. This gives rise to shorter Pt–C and longer C–O bonds in the hydroxycarbene-like moieties compared with the requisite values in the acetyl-like moieties ( $\Delta(\text{Pt–C}) = 0.021\text{--}0.024$  Å,  $\Delta(\text{C–O}) = 0.024\text{--}0.028$  Å). The O···O distances indicate very strong





**Fig. 5.** Calculated structures of  $[\text{Pt}((\text{COMe})_2\text{H})\{\text{SiMeH}(\text{quin})_2-\kappa^2\text{N},\text{N}'\}]^+$  (**27a/27b**) and  $[\text{Pt}((\text{COMe})_2\text{H})\{\text{SiMeH}(\text{CH}_2\text{py})_2-\kappa^2\text{N},\text{N}'\}]^+$  (**28a/28b**) and the side views as wire models (lower row).



**Scheme 8.**

**Table 7**  
Calculated structural parameters (lengths in Å, angles in °) and relative energies (in kcal/mol) of cationic platina-β-diketones  $[\text{Pt}((\text{COMe})_2\text{H})\{\text{SiMe}(\text{quin})_2-\kappa^2\text{N},\text{N}'\}]^+$  (**27a/27b**) and  $[\text{Pt}((\text{COMe})_2\text{H})\{\text{SiMe}(\text{CH}_2\text{py})_2-\kappa^2\text{N},\text{N}'\}]^+$  (**28a/28b**).

	<b>27a</b> (Si-H towards Pt)	<b>27b</b> (Si-Me towards Pt)	<b>28a</b> (Si-H towards Pt)	<b>28b</b> (Si-Me towards Pt)
Pt-C <sub>carb</sub> /Pt-C <sub>acyl</sub>	1.994/2.017	1.999/2.023	1.997/2.018	1.994/2.017
C-O <sub>carb</sub> /C-O <sub>acyl</sub>	1.264/1.237	1.265/1.237	1.261/1.237	1.263/1.238
O...O	2.398	2.403	2.394	2.396
Si-H	1.486	1.486	1.483	1.487
Si-C-C <sup>a</sup>	127.2/128.0	130.5/131.3	124.9/126.0	116.9/117.0
Pt...H	2.410		2.939	
Pt...Si	3.142	3.216	3.294	4.042
Relative energy	0	+3.24 (+3.42/+1.96) <sup>b</sup>	0	-8.57 (-6.56/-6.02) <sup>b</sup>

<sup>a</sup> **27a/27b**: Si-C<sub>8-quin</sub>-C<sub>8a-quin</sub>. **28a/28b**: Si-CH<sub>2</sub>-C<sub>2-py</sub>. In the non-coordinated ligands these angles were calculated to be 119.7/120.9° and 113.6/114.2°, respectively.

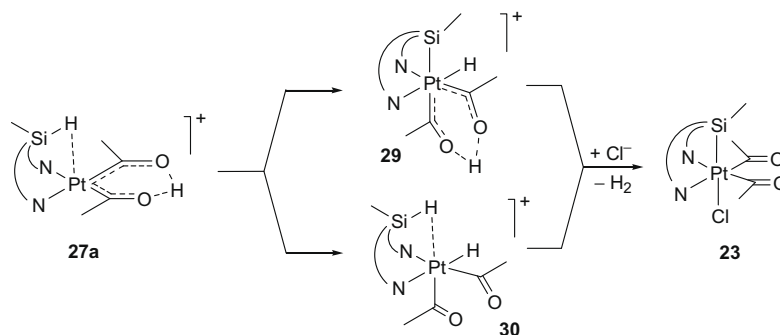
<sup>b</sup> In parentheses Gibbs free enthalpy at 298 K for the reaction in the gas phase and in the solvent thf, respectively, is given.

hydrogen bonds. On the basis of the linear relationship between the O...O distances and the strength of the hydrogen bonds found in a series of metalla-β-diketones [10,19] a strength of the hydrogen bonds in **27/28** of about 27 kcal/mol can be estimated.

If we assume that complex **27a** is an intermediate in the reaction of **1** with **22** yielding the diacetylchloroplatinum(IV) complex **23** having the quinoline based ligand tridentately coordinated (N-SiMe-N-κ<sup>2</sup>N,N',κSi), there can only be speculated on the precursor complex for the dihydrogen elimination. Among others, the formation of a hydridoplatinum(IV) intermediate complex

seems to be feasible which could be obtained by an oxidative addition either of the Si-H group (**29**) or by a shift of the O-H...O proton of the platina-β-diketone unit (**30**, Scheme 9). The calculated molecular structures of complexes **29** and **30** are given in Supplemental material. They are only higher in energy by 6.51 kcal/mol (**29**, ΔG = 8.08 kcal/mol, ΔG<sub>thf</sub> = 8.80 kcal/mol)<sup>1</sup> and

<sup>1</sup> Gibbs free enthalpy at 298 K for the reaction in the gas phase and in the solvent thf, respectively.



Scheme 9.

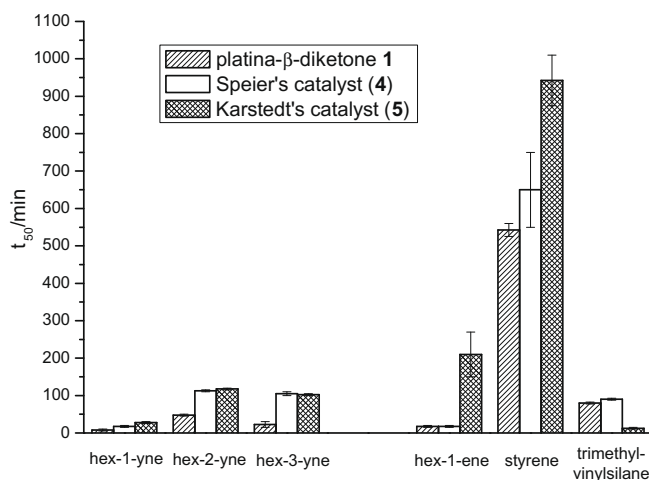


Fig. 6. Times at 50% degree of conversion of methylphenylsilane in the hydrosilylation reactions reported in this paper for the catalysts used. In the case of hex-1-ene the  $t_{50}$  values are based on the conversion of hex-1-ene instead of the silane.

by 5.80 kcal/mol (**30**,  $\Delta G = 4.51$  kcal/mol,  $\Delta G_{thf} = 6.48$  kcal/mol), respectively, than complex **27a**. Thus, from the thermodynamic point of view, either of these two complexes could be an intermediate in the reaction **27a**  $\rightarrow$  **23**.

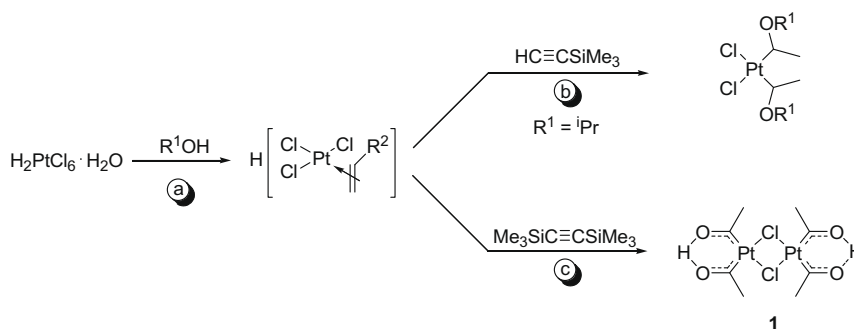
#### 4. Conclusions

In this work, catalytic properties of the platina-β-diketones **1–3** (Scheme 1) in the hydrosilylation of non-activated alkynes and alkenes have been investigated and compared with the well-established hydrosilylation catalysts from Speier (**4**) and Karstedt (**5**). The results are summarized in Fig. 6 and show that the activity of the dinuclear platina-β-diketone **1** in the hydrosilyla-

tion of hexynes is superior to Speier's and Karstedt's catalysts. In the case of the alkenes (hex-1-ene, styrene, trimethylvinylsilane) complex **1** and Speier's catalyst exhibited comparable activities. On the other hand, there are no remarkable differences in the regioselectivities in the investigated hydrosilylation reactions between the platina-β-diketones **1–3** and the reference catalysts **4** and **5**.

A solution of hexachloroplatinic acid ( $H_2PtCl_6 \cdot 6H_2O$ ) in isopropanol (Speier's catalyst **4**) undergoes a reduction of Pt(IV) at elevated temperatures (or after adequate time even at room temperature) yielding a  $\pi$ -propene platinum(II) complex  $H[PtCl_3(\eta^2-C_3H_6)]$  (Scheme 10, reaction a,  $R^1 = iPr$ ,  $R^2 = Me$ ) [33] analogous to Zeise's acid ( $H[PtCl_3(\eta^2-C_2H_4)]$ ) that is obtained in the requisite reaction with ethanol [34]. The subsequent reaction with  $Me_3SiC\equiv CH$  was found to result under cleavage of the Si–C bond in the formation of the carbene platinum(II) complex  $cis-[PtCl_2(C(O^iPr)Me)_2]$  (Scheme 10, reaction b) [35]. Analogously, the platina-β-diketone **1** is formed in the reaction of hexachloroplatinic acid in *n*-butanol with silylated alkynes (preferably  $Me_3SiC\equiv CSiMe_3$ ) again with cleavage of the Si–C bond via a  $\pi$ -butene platinum(II) complex as intermediate (Scheme 10, reaction a/c,  $R^1 = nBu$ ,  $R^2 = Et$ ). Interestingly, also good catalytic activity of the carbene platinum(II) complex  $cis-[PtCl_2(C(O^iPr)Me)_2]$  for hydrosilylation of alkynes has been acknowledged without giving any further details [35].

It has been shown, that reactions of the platina-β-diketone **1** with hydrosilanes, even with hydrosilanes containing *N*-donor sites in the molecule, do not lead to stable hydridosilylplatinum(IV) complexes. In most cases, reduction to platinum black occurred. Only in one case – using a hydrosilane with a very rigid quinoline based backbone – a silylplatinum(IV) complex (**23**) could be isolated. From the quantum chemical calculations there is no obvious reason why reactions of the platina-β-diketone **1** with **22** and **20** result in the formation of the stable complex **23** (see



Scheme 10.

Scheme 6) and in immediate decomposition yielding platinum black even at lower temperatures, respectively. The facial coordination mode of the deprotonated pyridine based ligand **20** in platinum(IV) complexes should be generally possible as has been shown both in the calculations and with the synthesis of complex **25** having bound the corresponding bis(2-picoly)amine ligand **24**. Particularly with regard to the analogous decomposition in the reaction of the platina- $\beta$ -diketone **1** with the pyridine based permethylated silane N-SiMe<sub>2</sub>-N (**21**), the unexpected difference in reactivity of the pyridine based compared to the quinoline based silanes (**20/21** versus **22**) towards **1** might be reasoned by a relatively high acidity of the CH<sub>2</sub> group [13] in **20/21**.

Obviously due to a facile reductive Si-H elimination, till now, only few hydridosilylplatinum(IV) complexes could be prepared [28a,37]. Even silylplatinum(IV) complexes easily undergo reductive elimination reactions if halogeno or organo ligands are present [28a,37a,38]. It could not be determined whether in the reaction of **1** with the quinoline based hydrosilane **22** yielding the stable Pt(IV) complex **23** (Scheme 6) prior to the elimination of H<sub>2</sub> a hydridosilylplatinum(IV) complex is formed as an intermediate or not. The results of the DFT calculations showed, that – from the thermodynamic point of view – such intermediates formed either from an oxidative Si-H addition reaction or a proton shift of the hydroxycarbene moiety onto the platinum atom in the sense of an intramolecular oxidative addition (Scheme 9) could be taken into consideration.

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## Appendix A. Supplementary material

CCDC 721482 and 721483 contains the supplementary crystallographic data for **23**·CH<sub>2</sub>Cl<sub>2</sub> and **25**·CH<sub>2</sub>Cl<sub>2</sub>. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.07.020.

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