

Short communication

Selective hydrosilylation of styrene using an in situ formed platinum(1,3-dimesityl-dihydroimidazol-2-ylidene) catalyst

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Abstract

A highly active and selective in situ formed platinum(*N*-heterocyclic carbene) catalyst for the hydrosilylation of styrene with triethylsilane is described, which unlike all other known hydrosilylation catalysts, selectively yields hydrosilylation products, but (almost) no dehydrogenative silylation products.

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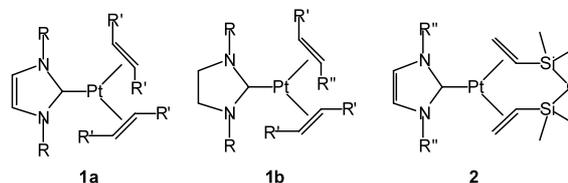
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1. Introduction

Platinum-catalyzed hydrosilylation is an important reaction in organosilicon chemistry, inter alia for the production of silicon polymers [1]. The Speier catalyst [2] (H₂PtCl₆/iPrOH) and Karstedt catalyst [3] (H₂PtCl₆/divinyltetramethyldisiloxane) show very high activities for this reaction, but exhibit low stabilities: rapid formation of inactive, colloidal platinum takes place. Development of new hydrosilylation catalysts is therefore a continuing challenge and indeed several other active platinum-complexes have been reported [1,4–6].

The use of *N*-heterocyclic carbenes (NHC) as ligands in homogeneous catalysis and organometallic chemistry is rapidly expanding at the moment [7]. Recently, we synthesized [Pt(IMes)(dimethylfumarate)₂] (**1a**) (IMes = 1,3-dimesityl-imidazol-2-ylidene) and [Pt(SIMes)(dimethyl fumarate)₂] (**1b**) (SIMes = 1,3-dimesityl-dihydroimidazol-2-ylidene) which are capable of activating the C–H bond of imidazolium salts at ambient temperature [8]. We reasoned that species like **1a** and **1b**

should readily dissociate one or two moles of alkene, thus forming a suitable species for activation of Si–H bonds and hence be active in catalytic hydrosilylation. A recent paper by Markó et al. [9], in which some platinum(0)-carbene complexes (**2**) have been reported for the efficient hydrosilylation of 1-octene and 1,1,1,3,5,5,5-heptamethyltrisiloxane, indeed shows that this reasoning is correct.

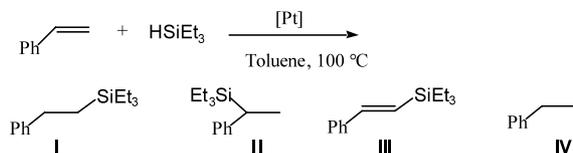


R = mesityl; R' = COOMe; R'' = methyl, cyclohexyl, *tert*-butyl

Here, we report the use of new platinum(0) complexes derived from bulky unsaturated and saturated carbenes in the hydrosilylation of styrene with triethylsilane, which proceeds with unprecedented high selectivity, yielding exclusively products **I** and **II**. The platinum-catalyzed hydrosilylation of styrene yielding the β- and α-silylated products **I** and **II** is normally accompanied by appreciable amounts of **III** and **IV** due to dehydrogenative silylation.

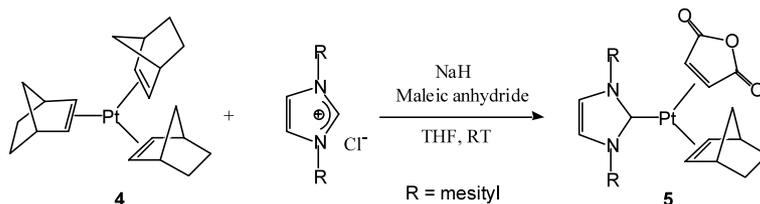
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2. Results and discussion

Initially, we applied $[\text{Pt}(\text{IMes})_2]$ (**3**) [10] as a catalyst, but a very low activity was observed even in refluxing toluene. Apparently, two carbenes coordinated to the platinum center results in a complex that is too stable for effective catalytic hydrosilylation. We reasoned that a platinum(mono-carbene) complex containing two labile ligands, such as alkenes, should be a suitable precursor to a platinum(carbene) species exhibiting good catalytic performance. Therefore attempts were made to synthesize $[\text{Pt}(\text{IMes})(\text{norbornene})_2]$ by stirring $[\text{Pt}(\text{norbornene})_3]$ (**4**) with one equivalent of IMesHCl ($\text{IMesHCl} = 1,3\text{-dimesityl-imidazolium chloride}$) and 1.5 equivalents of NaH in THF at room temperature for 16 h. A stable white solid was obtained, $^1\text{H-NMR}$ and $^{195}\text{Pt-NMR}$ revealed that it was a mixture of two complexes, which could not be separated. Two platinum resonances, at -3821 and -3940 ppm, were observed and the $^1\text{H-NMR}$ spectrum showed a carbene/norbornene ratio of 1. Addition of one equivalent of maleic anhydride to this solid gave the white pure complex $[\text{Pt}(\text{IMes})(\text{maleic anhydride})(2\text{-norbornene})]$ (**5**) in 74% yield. The synthesis of the analogous complex with the saturated carbene ligand, starting from SIMesHCl , was also attempted, but was not successful.



Since the activity of platinum(0)-complexes strongly depends on the nature of the coordinated alkenes, [4] catalysis by in situ formed catalysts derived from $[\text{Pt}(\text{norbornene})_3]$ (**4**) and NHC is interesting. Thus, the $\text{Pt}(\text{NHC})$ catalyst was prepared by stirring an imidazolium-salt with two equivalents of KO^tBu and one equivalent of **4**, after which catalysis was started by addition of styrene and triethylsilane. The isolated platinum-compounds **1a**, **1b**, **3** and **5** were also evaluated

Table 1
Hydrosilylation of styrene with triethylsilane

Entry	Catalyst	Yield ^a (%)	TOF ^b (h^{-1})	Selectivity (%) I:II:III
1	4 + ImesHCl ^{c,d}	18.9	8.1	85.2:3.2:11.0
2	4 + IMesHCl ^{c,e}	26.7	9.8	76.6:19.9:2.8
3	4 + IMesHCl ^{c,f}	31.2	12.7	78.3:15.9:5.8
4	4 + I^tBuHCl ^{c,f}	7.2	2.1	69.7:3.5:26.8
5	4 + SIMesHCl ^{c,f}	> 99	53.4	82.5:17.2:0.3
6	4 + SI-MesHCl ^{c,f,g}	> 99	80.2	83.2:16.6:0.2
7	4 + SI^tBuHCl ^{c,f}	4.5	2.3	92.2:0.7:7.1
8	4 + SI-DippHCl ^{c,f}	0	0	–
9	1a	18.0	11.1	64.7:14.9:20.4
10	1b	76.2	41.6	83.1:16.8:0.1
11	3	< 2	2	35.3:11.6:53.1
12	5 ^h	4.9	5.2	78.1:20.1:1.7
13	5	24.6	9.1	79.6:19.9:0.5
14	5 ^g	34.6	12.4	79.5:19.7:0.8

Triethylsilane/styrene ratio 1.0, 1 mol% of catalyst, toluene, 100 °C.

^a Total GC-Yield after 3 h using *n*-decane as internal standard.

^b Turn-over frequency, determined at 25% conversion, defined as moles of styrene converted per mole of catalyst per hour.

^c Complex **4** stirred with one equivalent of the imidazolium-salt and two equivalents of KO^tBu for a period of time.

^d No complex formation time.

^e Complex formation time of 30 min.

^f Complex formation time of 60 min.

^g Triethylsilane/styrene ratio 3.0.

^h Triethylsilane/styrene ratio 0.33.

as catalysts. Results of the hydrosilylation of styrene with triethylsilane in toluene at 100 °C using these catalysts have been compiled in Table 1.

No induction period was observed for any of the catalytic hydrosilylation reactions and plots of conver-

sion against time gave straight lines, indicating that all catalysts were stable under the reaction conditions. Firstly, an in situ formed catalyst from IMesHCl and **4** was investigated. Using pre-set complex-formation times of 0, 30 and 60 min (entries 1–3) it became clear that the yields and turn-over frequencies (TOFs) steadily increase with longer complex formation periods. Apparently, a certain time is required for the formation of the catalytically active complex. Therefore, for all

further catalytic experiments involving in situ formation of the catalyst from these and comparable precursors, a complex-formation time of 60 min was used. If the formation time for the complex was omitted when the catalyst was formed from IMesHCl and **4**, the selectivity observed was similar to that observed using **4** alone. By applying pre-set periods of 30 (entry 2) and 60 min (entry 3), indeed less dehydrogenative silylation was observed: 2.8 and 5.8%, respectively. However, these experiments yielded an increased amount of the branched hydrosilylation product (**II**), 19.9 and 15.9%, respectively. When the imidazolium salt I^tBuHCl (entry 4) was used, which yields a carbene ligand that was also used by Markó et al. [9], a very low activity (TOF = 2.1 h⁻¹) and an increased amount of dehydrogenative silylation (26.8%) was obtained.

Interestingly, when the saturated imidazolium chloride, SIMesHCl, (SIMesHCl = 1,3-dimesityl-4,5-dihydro-imidazolium chloride) was employed (entry 5) instead of the unsaturated analogues used so far, a very high activity (TOF = 53.4 h⁻¹) was observed. Significantly, but completely unexpectedly, dehydrogenative silylation was virtually absent (only 0.3%) in this case, whereas it is known to occur in all reported cases [11–13]. Furthermore, this side-reaction is strongly influenced by the ratio triethylsilane/styrene with those catalysts. However, no change in selectivity was observed with our catalyst when using a triethylsilane/styrene ratio of 3 (entry 6), but the TOF (80.2 h⁻¹) significantly increased. Similar to what is observed with IMesHCl, a relatively large amount (about 17%) of the regioisomer **II** is formed.

Using SI^tBuHCl (entry 7) yielded a slow catalyst however the selectivity of the reaction changed: a considerable amount **III** was formed, 7.1%, but product **II** was virtually absent. When employing SIDippHCl, (SIDippHCl = 1,3-(2,6-diisopropylphenyl)-4,5-dihydro-imidazolium chloride) no catalytic activity was observed (entry 8). It would appear that the isopropyl-substituents are too sterically demanding and therefore interfere with either the addition of the hydrosilane or the addition of styrene to the platinum center.

The high activity and selectivity of the platinum compounds derived from SIMesHCl was confirmed by testing the pre-formed platinum(0) complexes **1a** (entry 9) and **1b** (entry 10). Indeed, complex **1b**, with the saturated carbene ligand, was more active and selective than **1a**. However, overall lower yields were obtained when compared to the in situ prepared catalysts. The selectivity obtained with complex **1b** is the same as the in situ generated catalyst (entry 5). This is not the case for complex **1a**, where more dehydrogenative silylation (20%) was observed for the pre-formed compound. These complexes give rise to quite effective catalysts when compared to [Pt(IMes)₂] (entry 11). As mentioned, the known complex [Pt(IMes)₂] is very inefficient: a

TOF of only 2 h⁻¹ was obtained together with a high degree of dehydrogenative silylation (53.1%).

The higher reactivity of platinum complexes derived from SIMesHCl relative to its unsaturated analogue can be explained by the difference in σ -donor strength between these two ligands. Although all NHC are almost pure σ -donors, saturated carbene ligands exert an even larger σ -donor strength. Presumably, the oxidative addition of triethylsilane to the platinum(0) is rate-determining, which step is favored by a higher electron density on the platinum center. Studying complex **5** using different triethylsilane/styrene ratios demonstrated this once more. A higher activity was obtained by using a larger triethylsilane/styrene ratio (increasing from 0.33 to 3; entries 12–14), indicating a positive order on the rate in triethylsilane. Probably, styrene acts as an inhibitor, thereby blocking the oxidative addition of triethylsilane.

Summarizing, we have shown that the in situ generated platinum(1,3-dimesityl-dihydroimidazol-2-ylidene) catalyst is by far the most efficient Pt(carbene) catalyst for the hydrosilylation of styrene with triethylsilane. High yields of product and almost 100% selectivity towards hydrosilane addition products, and the virtual absence of dehydrogenative silylation make it a very effective catalytic system. Further studies aimed at elucidating details of this hydrosilylation reaction and the platinum compounds involved are in progress.

3. Experimental

3.1. Synthesis of [Pt(IMes)(maleic anhydride) (2-norbornene)]

NaH (31 mg, 0.78 mmol) and 1,3-dimesityl-imidazolium chloride (171 mg, 0.50 mmol) were suspended in tetrahydrofuran (10 ml). Then **4** (240 mg, 0.50 mmol) was added to the mixture which was stirred at room temperature for 18 h. The solution was filtered and maleic anhydride (46.5 mg, 0.47 mmol) was added and the solvent was evaporated after 10 min of stirring at room temperature. The solid compound was washed with ether (3 × 2 ml) and dried in vacuo. A light yellow powder was obtained. Yield: 249 mg, 0.36 mmol, 74%; ¹H-NMR (499.8 MHz, benzene-*d*₆, δ (ppm)): 6.69 (s, 2H), 6.47 (s, 2H), 6.14 (s, ⁴J_{PtH} 9.4 Hz, 2H), 3.34 (d, ³J_{HH} 4.4 Hz, ²J_{PtH} = 49.6 Hz, 1H), 3.17 (d, ³J_{HH} 5.4 Hz, ²J_{PtH} 66.9 Hz, 1H), 2.87 (d, ³J_{HH} 4.4 Hz, ²J_{PtH} = 49.3 Hz, 1H), 2.76 (d, ³J_{HH} 5.4 Hz, ²J_{PtH} 65.5 Hz, 1H), 2.70 (s, 1H), 2.23 (s, 1H), 1.93 (s, 18H), 1.39 (m, 1H), 1.23 (m, 1H), 0.93 (m, 1H), 0.84 (m, 1H), 0.39 (d, ³J_{HH} 8.6 Hz, 1H), 0.05 (d, ³J_{HH} 8.8 Hz, 1H). ¹³C-NMR (125.7 MHz, benzene-*d*₆, δ (ppm)): 175.9 (NCN, ¹J_{PtC} 1425.7 Hz), 175.3 (C=O, ²J_{PtC} 32.9 Hz), 171.2 (C=O, ²J_{PtC} 41.0 Hz), 139.2, 128.3, 71.9 (CH=CH, ¹J_{PtC} 191.7 Hz), 67.1 (CH=

CH, $^1J_{\text{PtC}}$ 199.8 Hz), 43.7, 43.2, 41.9 (CH=CH, $^1J_{\text{PtC}}$ 207.5 Hz), 41.2 ($^3J_{\text{PtC}}$ 45.6 Hz), 40.5 (CH=CH, $^1J_{\text{PtC}}$ 148.6 Hz), 28.4 ($^3J_{\text{PtC}}$ 45.3 Hz), 28.2 ($^3J_{\text{PtC}}$ 44.5 Hz), 20.9, 17.8. ^{195}Pt -NMR (85.6 MHz, benzene- d_6 , δ (ppm)): –5291. Anal. Found: C 55.48, H 5.21, N 4.02. Calc.: C 55.56, H 5.25, N 4.05%.

3.2. Catalytic hydrosilylation of styrene

A Schlenk tube equipped with septum, condenser cooler and stirring bar was charged with 0.05 mmol of the relevant complex (Table 1) with or without one equivalent of an imidazolium-salt and two equivalents of KO- t Bu. The Schlenk tube was evacuated and filled with nitrogen three times and 20 ml toluene. Then, 5.0 or 15.0 mmol of styrene, 3.0 mmol of n -decane and 5.0 or 15.0 mmol of triethylsilane were added in quick succession via syringes. The reactor was immediately immersed in an oil bath, which was kept at 100 °C. Samples were taken periodically for GC analysis.

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