# Highly Active and Selective Platinum(0)-Carbene Complexes. Efficient, Catalytic Hydrosilylation of Functionalised Olefins

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Received: February 17, 2004; Revised: August 20, 2004; Accepted: August 23, 2004

This article is dedicated fondly to Joe Richmond on the occasion of his 60th birthday.

**Abstract:** Readily available N-heterocyclic platinum-carbene complexes **1** are highly efficient catalysts for the regioselective hydrosilylation of alkenes. These novel organometallics tolerate a wide range of functional and protecting groups, can be stored for prolonged periods of time and are particularly active (TON $>10^6$).

**Keywords:** alkenes; N-heterocyclic carbenes; homogeneous catalysis; hydrosilylation; platinum

The hydrosilylation reaction, the addition of an Si–H unit onto a carbon-carbon double or triple bond to generate an alkyl- or a vinylsilane, is of paramount importance for the silicon industry.[1] This key transformation, which is highly atom-economical,[2] is at the heart of the production of silicon polymers, the basic materials for the manufacture of diverse commodities such as lubricating oils, resins, pressure-sensitive adhesives, liquid injection moulding products and paper release coatings.[3] The hydrosilylation of alkenes can be initiated in numerous ways.[4] Among these, the use of metal complexes has been the most successful, with platinum derivatives occupying a cardinal position.[5]

The Karstedt complex **8**[6] and the Speier system ($H_2PtCl_6$/*i*-PrOH)[7] are the most commonly employed industrial catalysts. However, over the years, Speier's catalyst has been gradually replaced by the more active and selective Karstedt derivative. Unfortunately, hydrosilylation of olefins catalysed by complex **8** leads, besides the desired adduct **3**, to a mixture of by-products among which the isomerised alkene **4**, the saturated derivative **5**, the secondary alkylsilane **6** and the vinylsilane **7** are the major components (Figure 1).

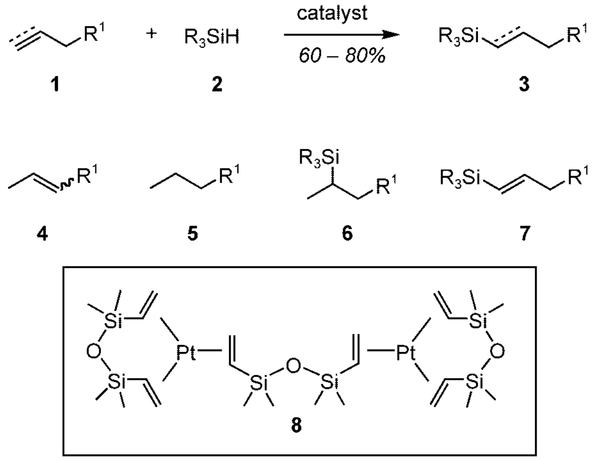


**Figure 1.** The hydrosilylation of alkenes and alkynes.

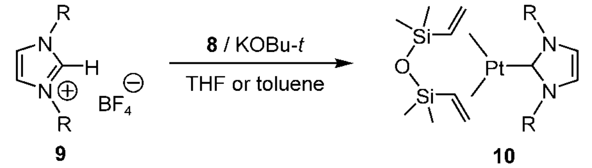
Furthermore, colloidal platinum species, allegedly responsible for some of the observed side-reactions, are always generated under these conditions.[8] Moreover, the extreme reactivity of **8** precludes its application in the case of substrates bearing sensitive functionalities, such as epoxides. To overcome some of these undesired side-reactions, recent research efforts have been aimed at the synthesis of new Pt(0) complexes.[9]

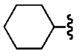
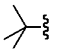
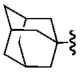
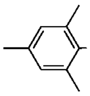
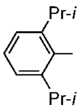
In a previous communication, we have reported that a novel class of platinum(0) carbene complexes **10** displayed good reactivity and excellent selectivity in the hydrosilylation of the model alkene, 1-octene.[10] In this article, we report the preparation of a variety of such platinum derivatives and the results of our study on the hydrosilylation of a range of functionalised alkenes catalysed by these organometallics. In addition, some insights into the mechanism of this transformation will be discussed.

These novel platinum(0) complexes **10** are readily prepared by the reaction of N-heterocyclic carbenes, generated from the corresponding imidazolium salts **9** and NaH or KOBu-*t*, with Karstedt catalyst **8**.[11] Exclusive displacement of the internal, more labile, bridging

**DOI: 10.1002/adsc.200404048**

**Table 1.** Preparation of the platinum(0) carbene catalysts.



| Entry | R | Product | Yield [%][a] |
|---|---|---|---|
| 1 | $CH_3$– | **10a** | 80[b] |
| 2 |  | **10b** | 85–90 |
| 3 |  | **10c** | 85–90 |
| 4 |  | **10d** | 70[b] |
| 5 |  | **10e** | 85–90 |
| 6 |  Pr-*i*<br>Pr-*i* | **10f** | 75–80 |

[a] All yields are for isolated, pure compounds.
[b] Performed only once.

divinyltetramethylsiloxane (DVTMS) ligand occurs, affording organometallics **10** in high yield and purity (Table 1).

These complexes are beautifully crystalline solids, insensitive to air and moisture. They can be stored for prolonged periods of time without noticeable loss in activity when protected from light. The Chem 3D views of the X-ray diffraction analyses of the cyclohexyl **10b** and *t*-butyl **10c** derivatives are displayed in Figure 2.

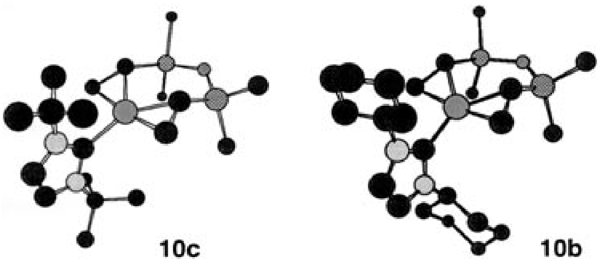


**Figure 2.** Chem 3D views of the X-ray diffraction analyses of **10c** and **10b**.

As depicted in Figure 2, the platinum occupies the centre of a trigonal planar arrangement and the carbene ligand is nearly perfectly orthogonal to the plane defined by the metal and its substituents. The DVTMS ligand folds around the platinum centre into a chair-like six-membered ring array. A selection of pertinent crystallographic data are displayed in Ref.[12]

These platinum(0) carbene complexes were initially tested in our model system using 1-octene as the substrate, 30 ppm of **10**, MD'M [$Me_3SiOSi(H)(Me)OSiMe_3$, **12**] as the silylating agent, in xylene, at 72 °C. The results of these experiments are collected in Figure 3.

As can be seen from Figure 3, the conversion of 1-octene **11** to 1-silyloctane **13** is excellent in all cases, reaching 80–90% after a few hours. Some catalysts – especially **10e** and **10f** – exhibit a significant induction period, which appears to depend upon the size of the carbene substituents. The cyclohexyl derivative **10b**, particularly easy to prepare and to handle, displays a good reaction profile with minimum induction period. It was thus selected for further studies with functionalised olefins. Some pertinent results of the hydrosilylation of repre-

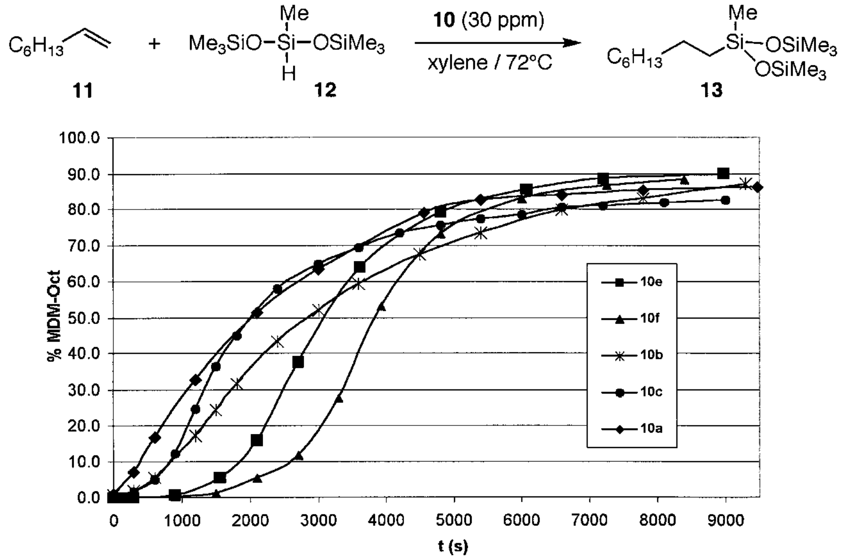
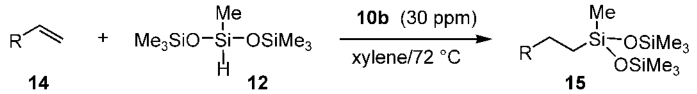
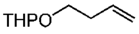
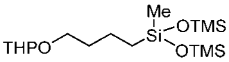
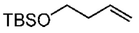
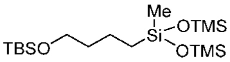
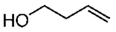
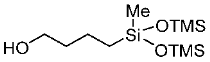
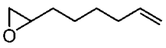
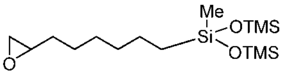
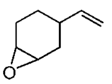
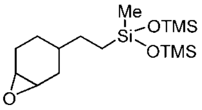
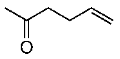
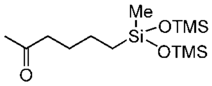
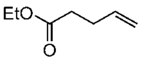
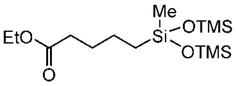
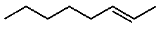


**Figure 3.** Model hydrosilylation with various platinum(0) carbene catalysts.

**Table 2.** Hydrosilylation of functionalised alkenes catalysed by **10b**.



| Entry | R | Product | Yield [%][a, b] |
|---|---|---|---|
| 1 |  |  | 92 |
| 2 |  |  | 81 |
| 3 |  |  | 96 |
| 4 |  |  | 90 |
| 5 |  |  | 92 |
| 6 |  |  | 78[c] |
| 7 |  |  | 80 |
| 8 |  | – | – [d] |

[a] All yields are for isolated, pure compounds. Unless otherwise mentioned, all the conversions are quantitative.

[b] In all cases, the use of Karstedt catalyst **8** leads to a mixture of products and to the formation of colloidal platinum species.

[c] The reaction was stopped after 80% conversion.

[d] No reaction was observed and the starting materials were recovered unchanged.

sentative alkenes, catalysed by **10b** are collected in Table 2.

As illustrated in Table 2, catalytic hydrosilylation of all the terminal olefins proceeds smoothly and leads in excellent yields to the desired addition products (Entries 1–7). In all cases, complete regiocontrol is observed and only the *anti*-Markovnikov adduct is obtained. Internal alkenes are totally inert under these conditions and the starting material is recovered quantitatively (Entry 8). The reaction tolerates a variety of functionalities and protecting groups. Thus, hydrosilylation of olefins containing a tetrahydropyranyl ether (Entry 1) or a *t*-butyl dimethylsilyl ether (Entry 2) affords the desired adducts in high yields. It is noteworthy that free alcohol functions are unaffected under these conditions (Entry 3). No trace of the corresponding silyl ether could be detected in the crude reaction mixture.[13] In stark contrast to Karstedt catalyst **8**, which leads to significant decomposition of epoxide-containing substrates, the carbene complex **10b** tolerates the presence of this sensitive functionality (Entries 4 and 5) and the hydrosilylated adducts are obtained in excellent yields.[14] Finally, complete chemoselectivity in favour of the hydrosilylation of the terminal alkene is observed in the presence of a ketone or an ester function (Entries 6 and 7).

It is interesting to note that most of these substrates (Entries 1–3, 6 and 7) are excellent chelating ligands, binding strongly to a variety of metals and impeding their catalytic activity. Such an inhibition was usually not observed in the hydrosilylations catalysed by the carbene complex **10b**. One exception is allylacetone (Entry 6), which slows down the rate of the reaction though it never completely represses it.[15]

It is worth mentioning that hydrosilylations catalysed by **10b** afford crude products that are typically $>95\%$ pure. Only traces ($<2\%$) of internal alkenes can be detected in the unpurified reaction mixtures and no colloidal platinum species are formed. Even more important is the observation that the catalytically active species is still competent at the end of the reaction. Indeed, addition of a second and third portion of alkene **14** and silane **12** leads, with equal efficiency, to the desired adduct **15**. It is noteworthy that, after several days at ambient temperature, the platinum-

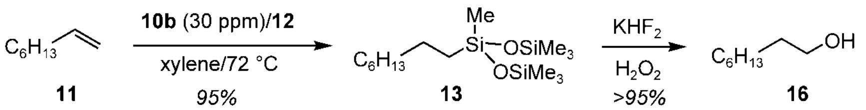


**Figure 4.** An efficient Tamao–Kumada–Fleming oxidation.

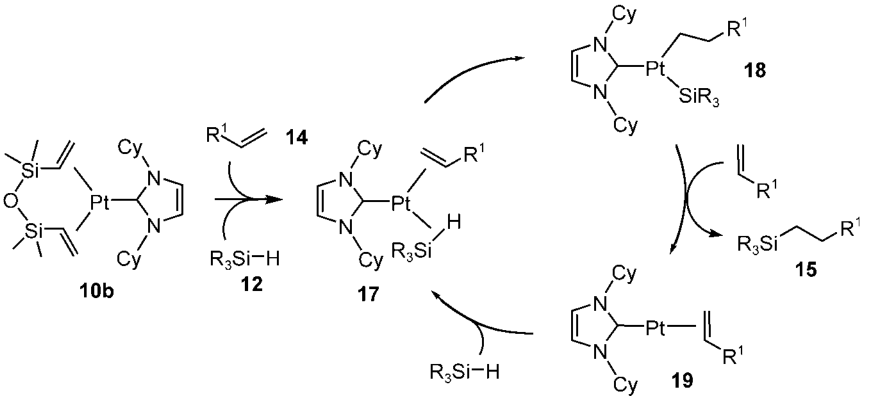


**Figure 5.** Proposed mechanism for the platinum-carbene catalysed hydrosilylation

carbene catalyst is still active and turnover numbers beyond $10^6$ have been obtained. In sharp contrast, the use of Karstedt catalyst **8** leads, in all cases, to numerous side-products and to the generation of colloidal platinum, with concomitant loss of activity.[16]

In order to broaden the scope of this hydrosilylation protocol, adduct **13** was treated with $KHF_2/H_2O_2$ under the usual Tamao–Kumada–Fleming conditions.[17] Gratifyingly, a smooth reaction occurred, leading to 1-octanol **16** in essentially quantitative yields (Figure 4).

Thus, the platinum-carbene-catalysed hydrosilylation of terminal alkenes, coupled with a Tamao–Fleming oxidative protocol, offers an efficient, cheap and highly regio- and chemo-selective alternative to the more classical hydroboration of olefins.[18]

Although the mechanism of the hydrosilylation reaction catalysed by the platinum-carbene complex **10b** is not yet fully elucidated, preliminary kinetic studies have already revealed some interesting facets of the reactivity of these novel organometallic derivatives (Figure 5).

Carbene complexes **10** are precatalysts that initially undergo hydrosilylation/dissociation of the DVTMS substituent. The departure of this ligand, the slowest step of the whole process, requires the presence of the alkene **14** and the silane **12** and generates the transient intermediate – or transition state – **17**. The rate of the hydrosilylation reaction appears to be first order in the alkene **14** *and* in the silane **12**, implying that both partners are involved at the same time in the "rate-determining step" of the catalytic cycle. Interestingly, incubation of complex **10b** with excess alkene does not promote the exchange between the DVTMS ligand and the olefin. In contrast, treatment of **10b** with excess silane generates the corresponding N-heterocyclic platinum(II) silyl hydride dimer. This dimer is, however, a less efficient catalyst than **10b**.[19]

Insertion of the Si–H bond into the olefinic linkage leads to the platinum(II) derivative **18** which, after reductive elimination of **15**, affords the platinum(0) species **19**, probably stabilised by coordination to one or two alkenes. Interestingly, the reaction displays saturation kinetics. Whilst increasing the concentration of the alkene leads initially to an enhanced reaction rate, the presence of a large excess of olefin eventually results in a partial inhibition of the hydrosilylation reaction, probably arising from the saturation of the coordination sphere of the platinum complex **19**. Addition of the silane then regenerates the active complex **17** and a new catalytic cycle ensues. The variation in the induction period observed with different precatalysts **10**, reflects the respective difficulty in hydrosilylating the chelating DVTMS ligand and correlates with the steric encumbrance provided by the N-heterocyclic carbene substituents.

In summary, we have shown that readily prepared platinum(0)-carbene complexes **10** efficiently catalyse the regio- and chemoselective hydrosilylation of a range of functionalised terminal alkenes. These novel precatalysts are stable towards air and moisture and can be stored for extended periods of time without loss of activity. Coupled with a Tamao–Fleming oxidation, this hydrosilylation procedure provides an efficient and somewhat more ecologically friendly alternative to the hydroboration of olefins. The synthetic utility of this reaction and its intimate mechanism are currently being actively investigated.

## Experimental Section

### General Considerations

All reactions were conducted under argon unless otherwise stated. All solvents were freshly distilled. All chemicals were used as received without prior purification. Divinyltetramethyldisiloxane (DVTMS) and Karstedt's catalyst (15% weight in Pt) were generously donated by Rhodia Silicones S. A. Imidazolium salts were prepared according to literature procedures.[11] $^1$H and $^{13}$C NMR spectra were recorded using a Varian Gemini 200 MHz. $^{195}$Pt NMR spectra were recorded on Bruker 500 MHz and externally referenced to $H_2PtCl_6$.

### General Procedure for the Synthesis of the Pt(0)-Carbene Complexes (Table 1, Entries 1–6)

***Synthesis of platinum-carbene complex 10b (Table 1, Entry 2):*** In an oven-dried 3-necked round-bottomed flask (50 mL), the dicyclohexylimidazolium tetrafluoroborate salt **9b** (573 mg, 1.79 mmol) and Karstedt's catalyst **8** (15.8% weight of Pt, 2.01 g, 1.63 mmol in Pt) were suspended in 5 mL of distilled toluene. To this suspension, *t*-BuOK (274 mg, 2.45 mmol) was added all at once. The formation of a fine $KBF_4$ suspension was observed immediately. The reaction was stirred for 2 hours. The reaction mixture was filtered on a pad of celite that was rinsed with toluene. A clear, light orange solution was obtained. The solvents were removed under vacuum. At this point, the complex begins to precipitate in the remaining DVTMS, as a white microcrystalline solid. The solid was filtered and washed with cold isopropanol to afford a fine white powder; typical yields of **10b**: 85–90%. $^1$H NMR ($CDCl_3$): $\delta = -0.25$ (s, 6H, $SiCH_3^{eq}$), 0.34 (s, 6H, $SiCH_3^{ax}$), 1.14–2.20 [m, 6H + 16H, $CH_2$ (cyclohexyl) + $SiCH{=}CH_2$], 4,25 (m, 2H, NCH), 7.02 (t, $^4J_{Pt\text{-}H} = 8.75$ Hz, 2H, im-$H^{4,5}$); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta = -1.9$ ($SiCH_3^{eq}$), 1.4 ($SiCH_3^{ax}$), 25.3 ($CH_2$), 33.5 ($Si\underline{C}H{=}CH_2$), 33.9 ($NCH\underline{C}H_2$), 40.3 ($SiCH{=}\underline{C}H_2$), 58.4 ($N\underline{C}H$), 117.2 (im-$C^{4,5}$), 180.0 (im-$C^2$); $^{195}$Pt NMR ($CDCl_3$): $\delta = -5338$; IR (film): $\nu = 2933$ (w), 2856 (m), 1450 (m), 1423 (m), 1410 (m), 1296 (m), 1237 (m), 1195 (m), 1170, 993 (w), 896 (m), 860 (m), 837 (m), 779 (m) cm$^{-1}$; MS (APCI): *m/z* (%) = 585 (88), 586.1 (100), 587 (93), 588 (30), 589 (30) $[M{-}C_2H_3]^+$, 453 (100), 454 (97) $[CyNHC{-}Pt{-}C_2H_3]^+$, 233 (100), 234 (20) $[CyNHC]^+$.

### General Procedure for the Hydrosilylation of Functionalized Alkenes (Table 2, Entries 1–8)

***Hydrosilylation of 1,2-epoxy-7-octene (Table 2, Entry 4):*** To a solution of 1,2-epoxy-7-octene (504 mg, 4 mmol) and silane **12** (896 mg, 4 mmol) in 5.5 mL of xylene, at 72 °C, was added 90 μL (0.0002 mmol) of a xylene solution of carbene complex **10b** (prepared by dissolving 27.5 mg of **10b** in 20 mL of xylene). The reaction mixture was heated at 72 °C for 210 min (the reaction was monitored by GC). The cold, colourless solution was filtered through a short pad of charcoal and the solvent was removed under vacuum. The crude product was purified by chromatography on silica gel (eluent: petroleum ether/5% $Et_3N$), affording the pure adduct; yield: 1.25 g (90%); $^1$H NMR ($CDCl_3$, 300 MHz): $\delta = 0.01$ (s, 3H), 0.09 (s, 18H), 0.43–0.48 (m, 2H), 1.32–1.58 (m, 10H), 2.48 (dd, $J_1 = 3$ Hz, $J_2 = 5.4$ Hz, 1H), 2.76 (brt, 1H), 2.89–2.95 (m, 1H); $^{13}$C NMR ($CDCl_3$, 50 MHz): $\delta = -0.2$, 2.0, 17.6, 23.0, 26.0, 29.2, 32.6, 33.2, 47.2, 52.4; MS (CI): *m/z* = 349 ($M^{+\cdot} + 1$), 333 ($M^+ {-} CH_3$), 221 $[SiMe(OSiMe_3)_2^{\ +}]$.

## Acknowledgements

*Financial support of this work by Rhodia Silicone, Rhodia CST and the Université catholique de Louvain is gratefully acknowledged. I. E. M. is also indebted to Rhodia for receiving the 2002 Rhodia Outstanding Award.*

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[13] Hydrosilylation of alcohol-containing substrates using the Karstedt catalyst results in significant formation of the corresponding silyl ethers (up to 40%).

[14] The high reactivity of the Karstedt catalyst precludes its use in the case of epoxide-bearing substrates. For example, more than 50% of vinyl cyclohexyl epoxide (Table 2, Entry 5) is decomposed in the presence of this complex.

[15] While most hydrosilylations are complete within 2–4 h, the reaction of allylacetone with **10b**, under identical conditions, requires up to 24 h to reach 80% conversion. In the case of the platinum-carbene complex **10b**, the catalyst is still active and prolonged reaction time leads to full conversion.

[16] All the hydrosilylations performed using the carbene complex **10b** afford crude products which are at least 95% pure and which typically contain less than 2% of isomerised alkene. With Karstedt catalyst **8**, yellow solutions, including colloidal platinum species, are generated. The purity of the crude reaction mixture varies between 72–92% and the amount of isomerised alkene oscillates between 5–11%. In the case of epoxide-containing substrates, extensive decomposition is observed.

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