

Second generation *N*-heterocyclic carbene–Pt(0) complexes as efficient catalysts for the hydrosilylation of alkenes†

Olivier Buisine,^c Guillaume Berthon-Gelloz,^a Jean-François Brière,^d Sébastien Stérin,^c Gérard Mignani,^c Paul Branlard,^c Bernard Tinant,^b Jean-Paul Declercq^b and István E. Markó^{*a}

Received (in Cambridge, UK) 6th May 2005, Accepted 27th May 2005

First published as an Advance Article on the web 21st June 2005

DOI: 10.1039/b506369h

A new class of benzimidazolylidene carbene–Pt(0) complexes was developed and used to efficiently catalyse the hydrosilylation of alkenes.

The hydrosilylation of alkenes, the second most important C–Si bond forming reaction after the Rochow process,¹ is of paramount importance for the silicon industry.² This transformation is efficiently catalysed by platinum complexes, such as the Speier catalyst (H₂PtCl₆–iPrOH)³ or the Karstedt catalyst (Pt₂{(η²-ViSiMe₂)₂O}₃, where Vi = vinyl).⁴ Although this reaction requires only ppm quantities of these platinum-containing species, it is plagued by numerous undesired side-reactions, such as isomerisation of the terminal alkene, hydrogenation of the C–C double bond and coloration of the reaction medium by formation of platinum colloids. It has therefore been a longstanding endeavour to minimize the formation of these unwanted by-products, and several efforts in this direction, employing modified platinum(0) complexes have been reported.^{5–7} We have previously described a new class of *N*-heterocyclic carbene platinum(0) complexes which catalyse efficiently the hydrosilylation of alkenes.⁸ These novel organometallic derivatives tolerate a wide range of functionalities and protecting groups, produce low amounts of isomerised olefins (<1%) and lead to no detectable formation of colloids.⁹

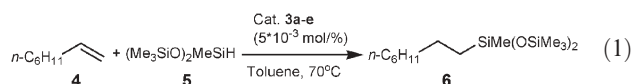
As part of an ongoing research effort aimed at exploring the vast potential offered by *N*-heterocyclic carbene-derived ligands in the hydrosilylation of alkenes, we investigated the use of the analogous benzimidazolylidene substituents in this transformation. Although a plethora of imidazolylidene ligands have been synthesised and used in homogeneous catalysis,¹⁰ the applications of their benzimidazolylidene¹¹ counterparts in metal-catalysed processes have remained relatively unexplored.^{12,13} These *N*-heterocyclic carbene derivatives display several interesting features. From an electronic point of view, they possess a σ-donating ability which is intermediate between that of imidazolylidene and imidazolinylidene carbenes. In addition,

benzimidazolylidene carbenes exhibit the topology of unsaturated *N*-heterocyclic carbenes but show structural properties and reactivity akin to those of carbenes containing a saturated *N*-heterocyclic ring system.¹⁴

Complexes **3a–d** were synthesised (Scheme 1, Table 1) in good to high yields, by *in situ* deprotonation of the corresponding benzimidazolium salts, in the presence of ^tBuOK, followed by reaction of the carbene with Karstedt's catalyst. Complex **3e** was prepared in a different manner. The benzimidazolylidene carbene was generated from the corresponding thiourea by reduction over Na–K amalgam, in toluene, for 20 days then reacted with Karstedt's catalyst.¹⁴

Crystals of complex **3e**† suitable for X-ray diffraction analysis were grown by slow evaporation of a dichloromethane solution. The molecular structure is shown in Fig. 1. Complex **3e** crystallises as a pair of enantiomers. The folding of the neopentyl arms around the benzimidazole core defines a C₂ symmetric environment. The divinyltetramethylsiloxane (dvtms) ligand and the carbene fragment adopt a trigonal planar geometry around the platinum(0) centre. The bidentate dvtms ligand exists in a pseudochair conformation which is a common coordination mode for this ligand.^{15–18} This complex owes its chirality to the fact that the C₂ symmetry of the carbene ligand is broken by the pseudochair conformation adopted by the dvtms ligand. The benzimidazole carbene is tilted by 68° (C20–Pt1–C1–N9 torsion angle) from the plane formed by the Pt centre and the alkene ligands. The strong σ-donating ability of the carbene substituent is evidenced by the amount of backbonding exerted on the dvtms ligand C20–C21 1.432(6) Å vs. 1.39(2) in the parent complex **1**.¹⁸ This strong backbonding, which is responsible for the remarkable activity of these complexes, renders them also inactive at room temperature.

Having obtained the desired carbene–platinum complexes, we next investigated their catalytic activity. As a model reaction, the hydrosilylation of 1-octene by silane **5** (a suitable polysiloxane backbone mimic) was selected [eqn (1)]. The reaction was performed at a concentration of 0.5 M and with a catalyst loading of 5 × 10^{−3} mol%.



Representative curves of the catalytic activity of selected complexes are displayed in Fig. 2. Examination of Fig. 2 reveals that, apart from **3e**, all the other benzimidazolylidene carbene complexes **3a–d** are more active than the parent

^aUnité de Chimie Organique et Médicinale Département de chimie, Université catholique de Louvain Place Louis Pasteur 1, 1348, Louvain-la-Neuve, Belgium. E-mail: marko@chim.ucl.ac.be; Fax: +32 1047 2788; Tel: +32 10478773

^bUnité d'Analyse Structurale, Université catholique de Louvain Place Louis Pasteur 1, 1348, Louvain-la-Neuve, Belgium

^cRhodia Centre de Recherche de Lyon, Av. des Frères Perret 85, F-69192, Saint-Fons Cedex, France

^dLaboratoire de Chimie Moléculaire et Thio-organique UMR CNRS 6507, ENSICAEN 6, Boulevard du Maréchal Juin, 14 050, Caen, France

† Electronic Supplementary Information (ESI) available: Experimental details. See <http://dx.doi.org/10.1039/b506369h>

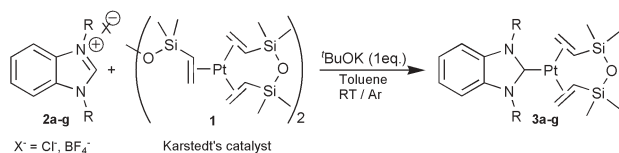


Table 1 Synthesis of benzimidazolylidene Pt(0) complexes^a

Entry	Complex	Yield (%)
1		80
2		60
3		78
4		77
5 ^b		50

^a Reaction conditions: benzimidazolium salt (1 mmol), **1** (1 mmol), ^tBuOK (2 mmol), THF (50 ml), RT. ^b The carbene was obtained by reduction of the corresponding thio benzimidazolidinone over Na-K in toluene for 20 days.¹⁴

Me-imidazolylidene-Pt(dvtms) catalyst. For example, after 100 min reaction, only 65% conversion is observed for the latter catalyst whilst 83% conversion is obtained in the case of **3b** and **3c**. The initial reaction rate is also faster for the benzimidazole-containing complexes **3a-d** as compared with their imidazole counterpart. Interestingly, the complex that displayed the highest activity contains the *n*-propyl substituted benzimidazolylidene ligand (**3b**). This is seemingly due to a good compromise between the steric and the electronic properties of the NHC substituent. In the second most active complex, **3d**, the remote ester function on the 6-position of the benzimidazole ring effectively reduces the electron density on the platinum centre, thus weakening the coordination of the dtvms ligand.

Of the complexes described above, both **3c** and **3e** display a slightly different catalytic behaviour, involving a prolonged induction period. For **3c**, this induction period can be attributed to the presence of the pendant alkene side-chains, which

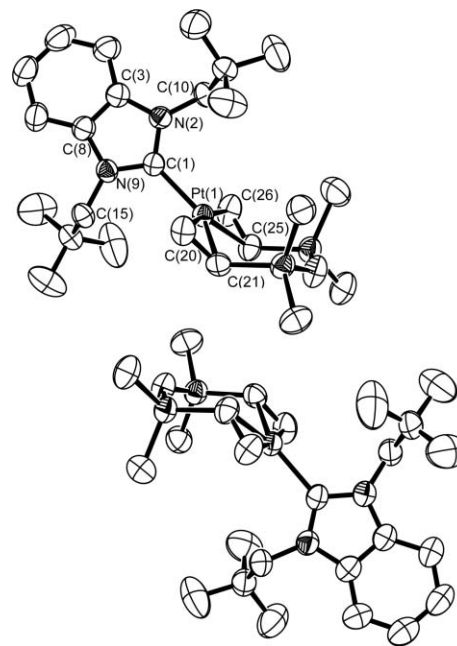


Fig. 1 Solid-state molecular structure of complex **3e**. Hydrogen atoms are omitted for clarity, thermal ellipsoids at 40% probability. Selected bond lengths (Å) and angles (°): C(1)–Pt(1) 2.059(4), C(20)–Pt(1) 2.143(4), C(21)–Pt(1) 2.147(4), C(22)–Pt(1) 2.150(4), C(23)–Pt(1) 2.144(4), C(26)–C(25) 1.432(6), C(22)–C(23) 1.415(7), C(1)–N(2) 1.365(5), C(1)–N(9) 1.361(5), N(2)–C(1)–N(9) 106.0(3), C(26)–Pt(1)–C(1)–N(9) 110.0(3), C(22)–Pt(1)–C(20)–C(21) 0.0(4), C(21)–Pt(1)–C(23)–C(22) 1.4(4).

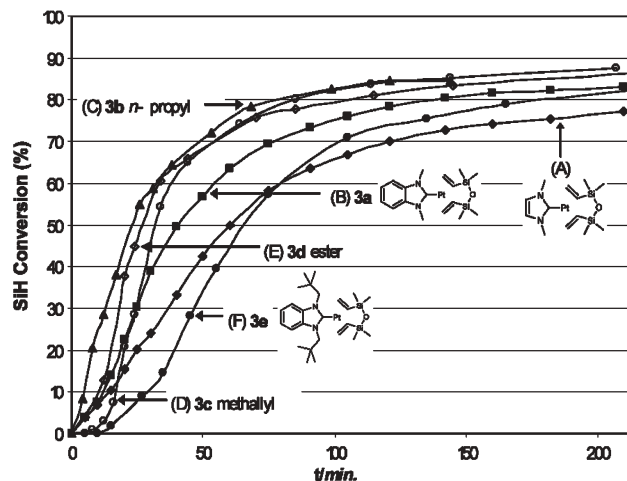


Fig. 2 Kinetic curves for the hydrosilylation of 1-octene with silane **5** catalysed by complexes **3a-e**. Reaction conditions: [Pt] = 5×10^{-3} mol%, [1-octene] = [5] = 0.5 mol L⁻¹, *o*-xylene, *T* = 70 °C. (A) Me-NHC-Pt(dvtms). (B) **3a**. (C) **3b**. (D) **3c**. (E) **3d**. (F) **3e**.

coordinate to the platinum centre after the loss of the dtvms ligand, efficiently inhibiting the approach of the reactants. Hydrosilylation of these substituents is thus required before the catalyst could exert its full activity. The catalytic behaviour of **3e** can be understood in part by its solid-state structure. The bulky neopentyl groups wrap around the platinum, effectively blocking both sides and significantly increasing the induction period. Even after the departure of the dtvms ligand, the neopentyl substituents

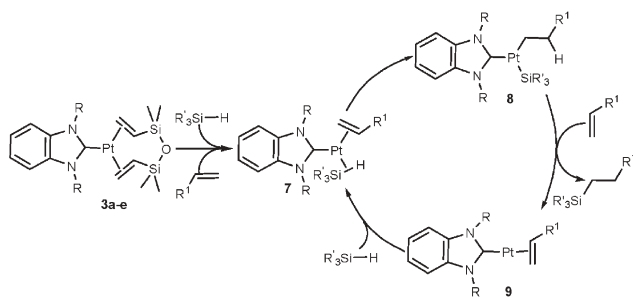


Fig. 3 Proposed catalytic cycle.

are sufficiently bulky to reduce significantly the rate of the hydrosilylation of 1-octene. These experiments also indicate that the loss of the dtvms ligand, probably by hydrosilylation, might be the rate determining step of these reactions. Finally, it is important to note that, in all cases, colloidal platinum species were never detected.

Though the mechanism of the hydrosilylation reaction catalysed by platinum carbene complexes **3a–e** has not yet been investigated in detail, the similarity in kinetic behaviour between these complexes and the parent imidazolylidene complexes prompted us to draw a parallel. A thorough kinetic study on the parent imidazolylidene platinum(0) complexes has revealed a unique mode of action of these organometallic derivatives (Fig. 3).

Carbene complexes **3a–e** are precatalysts that initially undergo hydrosilylation–dissociation of the dtvms substituent. The departure of this ligand, the slowest step of the whole process, requires the presence of the alkene **4** and the silane **5** and generates the transient intermediate—or transition state—**7**.¹⁹ Insertion of the Si–H bond into the olefinic linkage leads to the platinum(II) derivative **8** which, after reductive elimination of **6**, affords the platinum(0) species **9**, probably stabilised by coordination to one or two alkenes.²⁰ Addition of the silane then regenerates the active complex **7** and a new catalytic cycle ensues.²¹ The variation in the induction period observed with different precatalysts **3a–e** reflects the respective difficulty in hydrosilylating the chelating dtvms ligand and correlates with the steric encumbrance provided by the *N*-heterocyclic carbene substituents.

In summary, a new family of benzimidazolylidene platinum(0) complexes has been synthesized and characterised. These novel species display interesting catalytic activity in the hydrosilylation of alkenes. Their activity, which is superior to that of the parent imidazolylidene carbenes, can be finely tuned by the judicious modulation of their steric and electronic properties.‡

Financial support by the Université catholique de Louvain, Rhodia Silicones and Rhodia Corporate is gratefully acknowledged. I.E.M. is thankful to Rhodia for receiving the 2002 Rhodia Outstanding Award.

Notes and references

‡ *Crystallographic details for 3e*: C₂₅H₄₄N₂O₂Si₂, *M* = 639.89, colourless parallelepiped, triclinic, *a* = 12.915(4), *b* = 13.155(4), *c* = 18.436(7) Å, α = 96.35(2)°, β = 93.73(2)°, γ = 111.56(2)°, *U* = 2876(2) Å³, *T* = 293(2) K, space group *P*1̄ (no. 2), *Z* = 4, μ (Mo–K α) = 4.98 mm^{−1}, 61207 reflections measured, 12925 unique (*R*_{int} = 0.063) which were used in all calculations. The final *R*₁(*F*²) and *wR*(*F*²) were 0.046 and 0.12 respectively. CCDC

271531. See <http://dx.doi.org/10.1039/b506369h> for crystallographic data in CIF or other electronic format.

- 1 E. G. Rochow, *J. Am. Chem. Soc.*, 1945, **67**, 963–965.
- 2 B. Marciniak, J. Gulinski, W. Urbaniak and Z. W. Kornetka, *Comprehensive Handbook on Hydrosilylation*, Pergamon, Oxford, UK, 1992.
- 3 J. L. Speier, J. A. Webster and G. H. Barnes, *J. Am. Chem. Soc.*, 1956, **79**, 974.
- 4 B. D. Karstedt, General Electric, *US Pat.* 3,715,334, 1973.
- 5 J. W. Sprengers, M. J. Agerbeek and C. J. Elsevier, *Organometallics*, 2004, **23**, 3117–3125.
- 6 J. W. Sprengers, M. J. Mars, M. A. Duin, K. J. Cavell and C. J. Elsevier, *J. Organomet. Chem.*, 2003, **679**, 149–152.
- 7 J. W. Sprengers, M. D. Greef, M. A. Duin and C. J. Elsevier, *Eur. J. Inorg. Chem.*, 2003, 3811–3819.
- 8 I. E. Markó, S. Stérin, O. Buisine, G. Mignani, P. Branlard, B. Tinant and J.-P. Declercq, *Science*, 2002, **298**, 204–207.
- 9 I. E. Markó, G. Michaud, G. Berthon-Gelloz, O. Buisine and S. Stérin, *Adv. Synth. Catal.*, 2004, **346**, 1429–1434.
- 10 W. A. Herrmann, *Angew. Chem., Int. Ed.*, 2002, **41**, 1290–1309.
- 11 (a) K. Öfele, W. A. Herrmann, D. Mihalios, M. Elison, E. Herdtweck, T. Priermeier and P. Kiprof, *J. Organomet. Chem.*, 1995, **498**, 1–14; (b) B. Bildstein, M. Malaun, H. Kopacka, K.-H. Ongania and K. Wurst, *J. Organomet. Chem.*, 1998, **552**, 45–61; (c) F. E. Hahn and M. Foth, *J. Organomet. Chem.*, 1999, 585; (d) F. M. Rivas, U. Riaz, A. Giessert, J. A. Smulik and S. T. Diver, *Org. Lett.*, 2001, **3**, 2673–2676; (e) F. E. Hahn, C. G. Plumed, M. Munder and T. Lugger, *Chem. Eur. J.*, 2004, **10**, 6285–6293; (f) H. Sakurai, K. Sugitani, T. Moriuchi and T. Hirao, *J. Organomet. Chem.*, 2005, **690**, 1750–1755.
- 12 H. Kückükbay, B. Cetinkaya, S. Guesmi and P. H. Dixneuf, *Organometallics*, 1996, **15**, 2434–2439.
- 13 Recent examples: (a) E. Mas-Marza, M. Poyatos, M. Sanau and E. Peris, *Inorg. Chem.*, 2004, 2213–2219; (b) F. E. Hahn, C. Holtgrewe, T. Pape, M. Martin, E. Sola and L. A. Oro, *Organometallics*, 2005, **24**, 2203–2209.
- 14 F. E. Hahn, L. Wittenbecher, R. Boese and D. Bläser, *Chem. Eur. J.*, 1999, **5**, 1931–1935.
- 15 A. R. Bassindale, S. S. D. Brown and P. Lo, *Organometallics*, 1994, **13**, 738–740.
- 16 P. B. Hitchcock, M. F. Lappert, C. MacBeath, F. P. E. Scott and N. J. W. Warhurst, *J. Organomet. Chem.*, 1997, **528**, 185–190.
- 17 G. Chandra, P. Y. Lo, P. B. Hitchcock and M. F. Lappert, *Organometallics*, 1986, **6**, 191.
- 18 P. B. Hitchcock, M. F. Lappert and N. J. W. Warhurst, *Angew. Chem., Int. Ed.*, 1991, **30**, 438–440.
- 19 The rate of the hydrosilylation reaction appears to be first order in the alkene **4** and in the silane **5**, implying that both partners are involved at the same time in the “rate determining step” of the catalytic cycle. Interestingly, incubation of the Cy-NHC-Pt(dtvms) complex with excess alkene does not promote the exchange between the dtvms ligand and the olefin. In contrast, treatment of the same complex with excess silane generates the corresponding *N*-heterocyclic platinum(II) silyl hydride dimer. This dimer is, however, a less efficient catalyst than the parent complex. For the preparation and structure determination of the analogous phosphine-containing dimers, see: M. Ciriano, M. Green, J. A. K. Howard, J. Proud, J. L. Spencer, G. A. F. Stone and C. A. Tsipis, *J. Chem. Soc., Dalton Trans.*, 1978, 801–808. For the hydrosilylation of alkenes using these dimers, see: M. Green, J. L. Spencer, G. A. F. Stone and C. A. Tsipis, *J. Chem. Soc., Dalton Trans.*, 1977, 1519.
- 20 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 **9**.
- 21 The addition of a second portion of silane and alkene, at the end of the first hydrosilylation reaction, leads to a second complete hydrosilylation. Therefore the catalyst is not deactivated at the end of the reaction but remains in a stable resting-state. This is in contrast to Karstedt’s catalyst which remains inactive upon addition of fresh reactants.