$(Br{\cdot}H_3O)^+$. The calculated IP of this species is ~10.3 eV, which is lower than the IP of the molecular complex by 0.7 eV. Such a dramatic change in the energetics with solvent rearrangement implies that the ability to detach the electron from the fully solvated complex (solvent-separated ion pair) should increase.

In agreement with this expectation, the data in Fig. 1 show that as the degree of solvation increases, so does the rise time of the pump-probe response. Because the rise in the pump-probe response is sensitive to the solvent reorganization about the contact ion pair, the amount of time it will take for the molecules to reorganize to form the solvent-separated ion pair will increase with the number of solvent molecules surrounding the ion pair core. Similar results were observed for protonated HBr clusters, which indicate that self-solvation can induce ion pair formation in the excited state by a mechanism analogous to solvation by water molecules (*12*).

According to theoretical predictions (*1–3*), ion pair formation should begin in mixed clusters $[HBr(H_2O)_n$ with $n = 3]$; and in clusters with $n = 4$ or higher, complete dissolution should occur. If the ion pair forms in these species as suggested, upon sufficient hydration it should become observable in the ground state without being photon-mediated. Formation of the ion pair should also alter the potential energy surface so that photon absorption should not occur in the same way as it does in the case of the hydrated complex, in which the molecular nature of HBr is retained. The ion intensity at the zero delay time decreases with increasing cluster size. This decrease in intensity is attributed to the formation of the ion pair in the ground state. An increase in the H-Br internuclear separation accompanies the formation of the ion pair and is expected to result in a decrease in the absorption cross sections for photons of the same frequency. The observed rise in the signal of the $H^+(H_2O)_4$ cluster shows that a substantial population rearranges on the picosecond time scale to form the fully solvated ion pair $H^+(H_2O)_4{\cdot}Br^-$ in the excited state. Thus, complete ion pair formation could not have occurred in the ground state at $n = 4$, and a portion of the species in the molecular beam exists in the molecular $HBr(H_2O)_4$ form rather than the ion pair form.

In the mass spectra, we observed $H^+(H_2O)_n$ with $n = 1$ to 4, whereas HBr clusters were readily observed with sizes ranging up to 10. We found that water replacement in the acid clusters was facile at all cluster sizes; therefore, failure to observe the $n = 5$ cluster was not due to intensity issues. From the large change in the cross section at $n = 4$, and particularly from the lack of observation of an $n = 5$ protonated water cluster (despite observing the larger clustered HBr species), we conclude that this represents evidence that the cluster size for complete dissolution is five water molecules. In clusters smaller than this, ion pair formation can be induced by electronic excitation. The theoretical predictions (*1–3*) of HBr dissolution were determined for equilibrium structures, whereas the experiments were performed at a finite temperature, though accurate knowledge of the molecular beam temperature was not known. Therefore, our experimental findings of complete dissolution of HBr by water at the $n = 5$ cluster size can be considered to be in reasonably good agreement with the theoretical predictions.

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20. Financial support by the Atmospheric Sciences Division and the Experimental Physical Chemistry Division of NSF, grant NSF-089233, is gratefully acknowledged. Computational support was provided by the Materials Simulation Center, a facility of the Materials Research Institute at the Pennsylvania State University.

20 June 2002; accepted 28 August 2002

Selective and Efficient Platinum(0)-Carbene Complexes As Hydrosilylation Catalysts

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The hydrosilylation reaction enables the production of silicon polymers. Platinum-carbene complexes are reported that catalyze the hydrosilylation reaction of alkenes with remarkable efficiency and exquisite selectivity and avoid the formation of platinum colloids. By-products, typically encountered with previous catalytic systems, are suppressed with these platinum derivatives.

The hydrosilylation reaction, the addition of a Si-H unit to a C-C double bond to form an alkylsilane (Fig. 1A) (*1–3*), enables the production of silicon polymers used in silicon rubbers, liquid injection molding products, paper release coatings, and pressure-sensitive adhesives (*4*). The hydrosilylation reaction can be initiated or catalyzed in numerous ways (*5*). Among these, the use of metal salts, supported metals, and transition metal complexes are the most common, with platinum derivatives being overwhelmingly preferred (*6*). Two Pt-based systems, the Speier (*7*) catalyst ($H_2PtCl_6/{}^iPrOH$) and the Karstedt catalyst **8** (Fig. 1C), have found widespread use in the silicone industry (*8*).

Unfortunately, hydrosilylation by Karstedt catalyst **8** suffers from a number of drawbacks, including the formation of significant amounts (20 to 40%) of the isomeric olefins **4** and **5**, the reduced alkene **6**, and the dehydrocondensation adduct **7** (Fig. 1A) (*9*). If these impurities are not removed in a subsequent postreaction treatment, they lead to deleterious effects on the quality or properties of the final materials. In addition, the formation of colloidal Pt species during the course of the hydrosilylation reaction often results in undesired side reactions and coloration of the final product (*10, 11*). We now report that readily available platinum(0)-carbene complexes catalyze the hydrosilylation reaction with remarkable efficiency and exquisite selectivity and, in many cases, produce almost exclusively adduct **3** (*12*).

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Initial experiments with the commercial monomer silane **9**, the model alkene **10**, and Karstedt catalyst (Fig. 1B) showed that, although catalyst **8** was highly active (30 ppm, 72°C, 30 min, 80% yield), the products **4** through **7** ($R^1 = C_4H_9$) were also generated in significant quantity (up to 20% overall). The appearance of by-products **4** through **7** is concomitant with the formation of adduct **11** and coincides with the generation of colloidal Pt species (*10, 11*). The divinyltetramethylsiloxane (dvtms) ligand appears to be too labile and dissociates rapidly, leading to colloidal Pt species and undesired side products. To stabilize the catalyst, we appended more strongly binding, electron-rich ligands onto the Pt and prepared the corresponding monophosphine complexes (*13, 14*).

Addition of several phosphines to Karstedt catalyst in toluene led to the quantitative formation of the corresponding monophosphine-dvtms complexes **12a** to **12e** (Table 1). These highly soluble catalysts could be purified by crystallization in moderate to good yields (*15*). The ORTEP (Oak Ridge thermal ellipsoid plot) x-ray structure of the *tris*-furyl phosphine adduct **12c** is shown in Fig. 1C.

Organoplatinum derivatives **12a** to **12e** were next tested in the model hydrosilylation reaction. Some selected results are summarized in Fig. 2A, which also includes a control experiment using Karstedt catalyst. The amount of isomerized alkenes formed during these experiments is shown in Fig. 2B.

The Karstedt catalyst is superior to complexes **12** in terms of rate of reaction (Fig. 2A). However, the amount of by-products is higher with **8** than with any of the derivatives **12a** to **12e** (*16*). Unfortunately, and depending upon the nature of the phosphine ligand, colloidal platinum species are still produced, indicating that the phosphorus substituent is displaced to some extent during the course of the reaction (*17*).

In order to circumvent this problem, we decided to use more robust σ-donor ligands and selected the corresponding imidazolyl carbenes (*18*). The desired Pt-carbene complexes were readily prepared by treatment of Karstedt catalyst with the imidazolyl carbenes, generated by deprotonation of the corresponding imidazolium salts (Table 1) (*19*). Complexes **14a** to **14c** proved to be highly crystalline solids that were readily stored for extended periods of time without particular precautions (*20*).

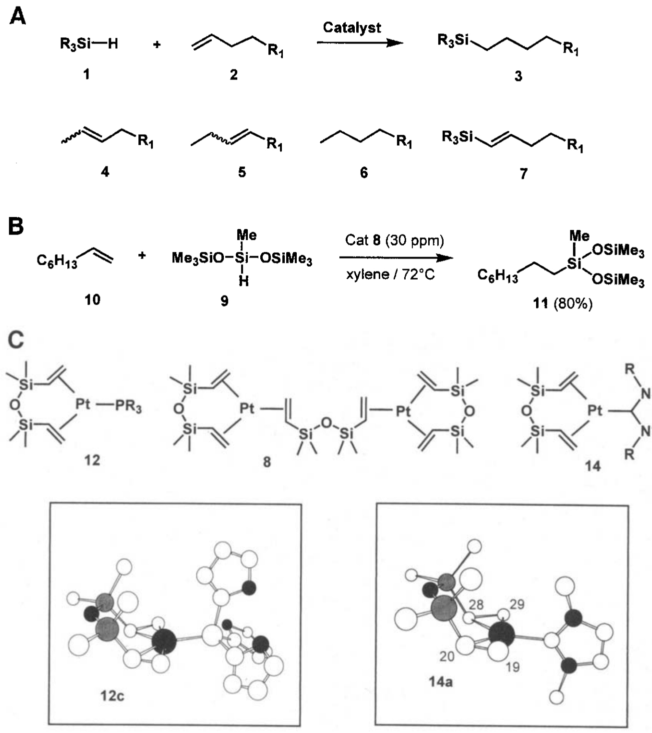

Fig. 1. (**A**) The hydrosilylation reaction along with by-products. (**B**) The model hydrosilylation reaction. (**C**) Schematics and x-ray structures for catalysts **8**, **12c**, and **14a**.

Table 1. Synthesis of phosphine-bound Pt complexes **12** and Pt-carbene complexes **14**. R indicates functional group. All yields are for pure, isolated products.

Product	R	Yield (%)
12a	Phenyl	54
12b	Cyclohexyl	49
12c	Furyl	90
12d	*tert*-Butyl	60
12e	ortho-Tolyl	55
14a	Methyl	54
14b	Cyclohexyl	60
14c	*tert*-Butyl	90

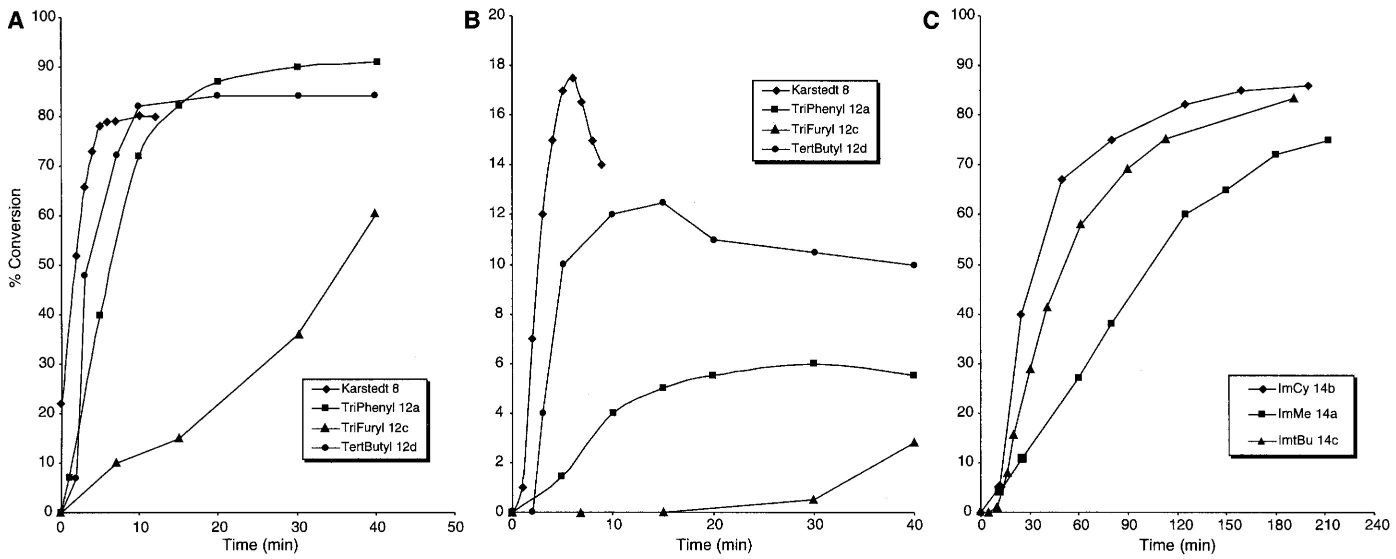

Fig. 2. (**A**) Hydrosilylation with Pt-phosphine complexes. (**B**) Isomerization with Pt-phosphine complexes. (**C**) Hydrosilylation with Pt-carbene complexes.

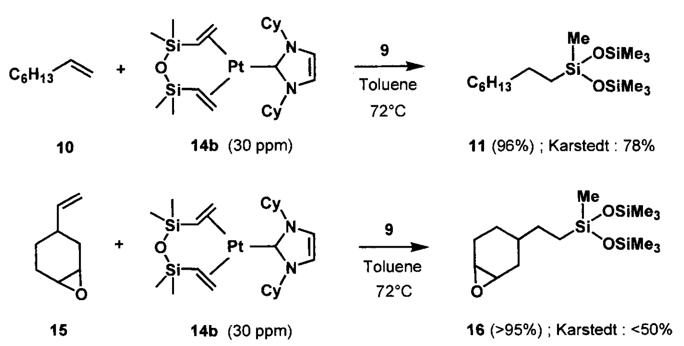

Fig. 3. Regio- and chemoselectivity of the Pt-carbene catalyzed hydrosilylation.

The ortep x-ray structure of **14a** (Fig. 1C) shows the trigonal planar environment of the Pt atom with the carbene ligand bisecting the plane of the dvtms substituent. This siloxane ligand wraps around the Pt center and exists in an almost perfect chair conformation. The C_{19}-C_{20} and C_{28}-C_{29} bond lengths are indicative of a π-backdonation from Pt to each of the siloxane double bonds. The ^{195}Pt nuclear magnetic resonance (NMR) spectrum of all these complexes reveals that the oxidation state of platinum is zero (*21*) in these monocarbene complexes (*22*).

Having obtained the desired organometallic catalysts **14a** to **14c**, we engaged them in the model hydrosilylation reaction. In all cases, hydrosilylation took place to afford the desired adduct **11** in good to excellent yields (Fig. 2C).

Although these complexes are slightly less reactive than the Karstedt catalyst, good reaction rates were still obtained at a loading of 30 ppm or less. More remarkably, the amount of undesired by-products was greatly reduced with **14a** to **14c**, and no colloidal Pt species were formed during the reaction. The reactivity and selectivity of these catalysts also appeared to depend upon the steric hindrance provided around the Pt center by the carbene substituents; an optimum was reached with the cyclohexyl moiety. It is noteworthy that the hydrosilylation of alkenes, catalyzed by **14b**, is completely regioselective; only the primary alkylsilane is obtained.

In order to further optimize the process, we performed the coupling by using an inverse addition (*23*) of **9** to a mixture of olefin **10** and catalyst **14b** (Fig. 3). From this, we isolated the desired adduct **11** in 96% yield. Less than 1% impurity was detected in the crude reaction mixture. Under similar conditions, Karstedt catalyst provided **11** in only 78% yield, accompanied by 13 to 15% of isomerized products and 5 to 7% of reduced material.

The usefulness of these Pt-carbene catalysts is further exemplified by their chemoselectivity and tolerance toward reactive functionalities, such as free alcohols, protected alcohols, silyl ethers, ketones, esters, and epoxides. For example, hydrosilylation of epoxide **15** with Karstedt catalyst generated, besides adduct **16** (<50%), large amounts of decomposition material (>35%) resulting from the opening/polymerization of the sensitive epoxide function. However, hydrosilylation of **15**, using Pt-carbene **14b**, afforded the desired product **16** in >95% isolated yield. No decomposition of the epoxide is detected under these conditions (*24*), which were easily applied to the preparation of an industrially relevant polyepoxy silicone oil (*25*) from alkene **15** and Me_3SiO-$(Me_2SiO)_{80}$-$(MeHSiO)_7$-$SiMe_3$.

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9. The isomerized olefins **4** are the major by-products, and alkane **6** is usually formed in smaller amounts. Compounds **5** and **7** are typically minor contaminants. It is noteworthy that the internal alkenes **4** and **5** do not undergo hydrosilylation under these conditions. Isomerization of **2** to **4** and/or **5** is believed to be catalyzed by multinuclear platinum species, which are inactive in the hydrosilylation reaction.
10. The presence of colloidal Pt species is easily detected by ultraviolet-visible spectroscopy and is commonly associated with the appearance of a yellow color in the reaction medium.
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15. These monophosphine complexes are formed rapidly and quantitatively by the exchange reaction between **8** and the corresponding phosphine. However, their high solubility, and sometimes sensitivity, leads to significant losses during the purification step.
16. In all cases, the amount of isomerized alkenes **4** and **5** increases initially, then decreases. The disappearance of **4** and **5** results from their hydrogenation into alkane **6**, probably by the in situ–generated colloidal Pt species.
17. The amount of by-products is related to the rate of the reaction and the leaving group ability of the phosphine ligands. The formation of multinuclear Pt species appears to correlate with the weakness of the Pt-P bond.
18. For an excellent review on metal-carbene complexes, see D. Bourissou, O. Gueret, F. P. Gabbaï, G. Bertrand, *Chem. Rev.* **100**, 39 (2000).
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20. Samples of these Pt-carbene complexes have been stored for several months without noticeable loss of activity. Although they are insensitive toward air and moisture, it is advisable to protect them from light.
21. Selected NMR data for **14b**: ^{195}Pt: $\delta = -5343$ ppm. ^{29}Si NMR: $\delta = -2.55$ ($J_{Pt\text{-}Si} = 42$ Hz). ^{13}C NMR: $\delta = -1.9$; 1.4; 25.3; 33.5; 40.3; 58.5; 117; and 180 ppm. ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = -0.27$ (s, 6H); 0.31 (s, 6H); 1.0-2.3 (m, 26H); 4.25 (m, 2H); 7.0 (s + d, $J = 12$ Hz, 2H).
22. Several Pt(II) complexes have been described [D. S. McGuinness, K. J. Cavell, B. F. Yates, *J. Chem. Soc. Chem. Commun.* **2001**, 355 (2001), and references cited therein].
23. Under "normal" conditions, the Pt complexes **14a** to **14c** are added to a mixture of silane **9** and olefin **10**. The "inverse" protocol implies the addition of the silane **9** to a mixture of alkene **10** and Pt catalysts **14a** to **14c**. No colloidal Pt is formed upon increasing the amount of Pt-carbene catalysts from 30 ppm up to 300 ppm. The rate increases concomitantly with the amount of catalyst, and the reaction can become highly exothermic.
24. The high selectivity observed with this "inverse" procedure stems from the kinetics of the hydrosilylation reaction using our Pt-carbene complexes, which differs significantly from the Karstedt-catalyzed system. To obtain a fair comparison between the two catalysts, both reactions have been performed under identical, nonoptimized conditions.
25. Full experimental and analytical data will be published in a forthcoming full paper. The experimental procedure and comparison data in the case of the industrially interesting polyepoxy silicone oil is described in (*26*).
26. Typical experimental procedure: (a) Using Karstedt catalyst **8**. A 1-liter reactor containing 4-vinyl cyclohexene oxide 15 (65 g, 0.52 mol) is warmed to 70°C. Under stirring, 51 μl (10 ppm Pt as compared to the substrate) of a Karstedt solution (10% in Pt) is added, followed by the slow addition of Me_3SiO-$(Me_2SiO)_{80}$-$(MeHSiO)_7$-$SiMe_3$ (450 g, 0.476 mol) over a period of 3 hours. After 5 hours at 70°C, the crude mixture is cooled to 25°C and 22 mg (600 ppm) of thiodiethanol is added. The resulting oil is warmed at 120°C, under vacuum (<5 mbar) for 7 hours to eliminate the remaining volatile material. A thick oil is obtained, which possesses a viscosity at 25°C of 1700 mPa/s, indicating that a significant proportion of epoxide opening/polymerization has occurred during the hydrosilylation reaction. (b) Using carbene complex **14b**. A 1-liter reactor containing 4-vinyl cyclohexene oxide 15 (65 g, 0.52 mol) is warmed to 70°C. Under stirring, 152 μl (10 ppm Pt as compared to the substrate) of a Pt-carbene **14b** solution (2.68% in toluene) is added, followed by the slow addition of Me_3SiO-$(Me_2SiO)_{80}$-$(MeHSiO)_7$-$SiMe_3$ (450 g, 0.476 mol) over a period of 3 hours. After 5 hours at 70°C, the crude mixture is cooled to 25°C and 22 mg (600 ppm) of thiodiethanol is added. The resulting oil is warmed at 120°C under vacuum (<5 mbar) for 7 hours to eliminate the remaining volatile material. A light oil is obtained, which possesses a viscosity at 25°C of 325 mPa/s, indicating that essentially no epoxide opening/polymerization has occurred during the hydrosilylation reaction.

27. Financial support for this work by Rhodia Silicones and the Université Catholique de Louvain is gratefully acknowledged. I.E.M. is grateful to Rhodia for receiving the 2001 Rhodia Outstanding Award and to J.-P. Delarche for performing some of the reported experiments.

26 April 2002; accepted 29 August 2002