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# Water-Soluble N-Heterocyclic Carbene Platinum(0) Complexes: Recyclable Catalysts for the Hydrosilylation of Alkynes in Water at Room Temperature

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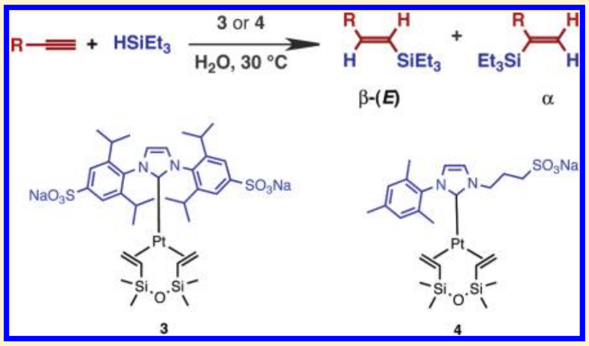
**ABSTRACT:** The synthesis and characterization of new water-soluble platinum(0) complexes bearing sulfonated N-heterocyclic carbene (NHC) and divinyltetramethylsiloxane (dvtms) ligands are described. These complexes, of the general formula (NHC)Pt(dvtms), are active and recyclable catalysts for the hydrosilylation of phenylacetylene and other alkynes at room temperature in water. Our findings indicate that the NHC−Pt(0) bonds are reasonably stable under these catalytic conditions, although hydrolysis is observed at temperatures above 80 °C in pure water.



## ■ INTRODUCTION

Catalytic reactions in water involving metal complexes and organic substrates have been growing in importance over the past few years.[1−4] Indeed, a large number of water-soluble ligands have been designed for this purpose by attaching neutral or, more often, ionic hydrophilic groups (sulfonate, carbonate, ammonium, etc.) to traditional hydrophobic ligands, such as phosphanes.[5] In the past decade, N-heterocyclic carbenes (NHCs) have contributed to significant advances in ruthenium-mediated olefin metathesis, palladium-promoted cross-coupling, and other transition-metal-catalyzed reactions.[6−8] The relative stability of NHC−metal bonds toward hydrolysis has promoted the use of NHC complexes in metal-catalyzed organic syntheses performed in water. Unmodified hydrophobic NHC ligands are often used for this purpose when ionic species are involved in the catalytic process or when water solubility is achieved by attaching another ligand to the metal center.[9−12] However, the attachment of hydrophilic substituents directly to the NHC ligands is more convenient to avoid leaching of the bond between the water-soluble ligand and the metal. Retention of the catalyst in the aqueous phase during and after the catalytic cycle by means of the hydrophilic groups is a key issue for catalyst recovery in biphasic processes.

Herrmann and co-workers published the first examples of complexes with water-soluble NHC ligands, in which a butyl-4-sulfonate group was bonded to one of the NHC nitrogen atoms, in a patent filed in 1995.[13] The same group subsequently reported the stability of rhodium(I) complexes with hydroxyalkyl- or carboxylate-functionalized NHC ligands in water.[14] Sulfonates, carbonates, ammonium groups, sugar moieties, or polyethers are among the most common solubilizing groups employed for this purpose. Applications in aqueous-phase catalysis have appeared more recently since the report of a ruthenium catalyst for the synthesis of 2,3-dimethylfuran by Özdemir and co-workers in 2001.[15] Subsequent papers have mainly dealt with ruthenium-catalyzed olefin metathesis,[16−22] palladium-catalyzed Suzuki−Miyaura cross-coupling reactions,[23−29] or, more recently, the hydration of terminal alkynes with gold complexes.[30,31] In addition to these metals, synthetic efforts have mainly been directed toward the synthesis of water-soluble NHC Ag complexes, especially for use as NHC transfer agents[23,32,33] or for medical applications,[34,35] although several examples have been reported containing other metals.[36−38]

Alkenylsilanes are especially valuable intermediates in modern organic chemistry,[39,40] especially for palladium-catalyzed reactions,[41,42] such as the vinylation of aryl halides, recently adapted by our group and others to aqueous conditions.[43−45] Methods for the preparation of alkenylsilanes by hydrosilylation of alkynes in aqueous media would, therefore, be highly desirable.[46−50] In this respect, although the Pt Karstedt complex ($[\mathrm{Pt}_2(\mathrm{dvtms})_3]$, dvtms = 1,3-divinyl-1,1,3,3-tetramethyldisiloxane)[51,52] and the Speier system ($\mathrm{H_2PtCl_6}/{}^i\mathrm{PrOH}$)[53,54] are widely used in industry, they form colloidal Pt particles during the course of the reaction. Markó and co-workers have demonstrated that NHC platinum(0) complexes avoid the formation of platinum colloids[55] and catalyze the hydrosilylation of alkynes with remarkable efficiency and selectivity.[56,57] Moreover, the regioselectivity of these catalysts is proposed to be controlled by steric crowding when bulky aryl substituents are present at the nitrogen atoms of the NHC ligand.

Herein, we report the first examples of water-soluble NHC platinum(0) complexes and their use as catalysts for the hydrosilylation of terminal alkynes. These catalysts are active at room temperature and highly recyclable, a property that can be linked to the stability of the platinum−carbene bond in the aqueous reaction conditions.

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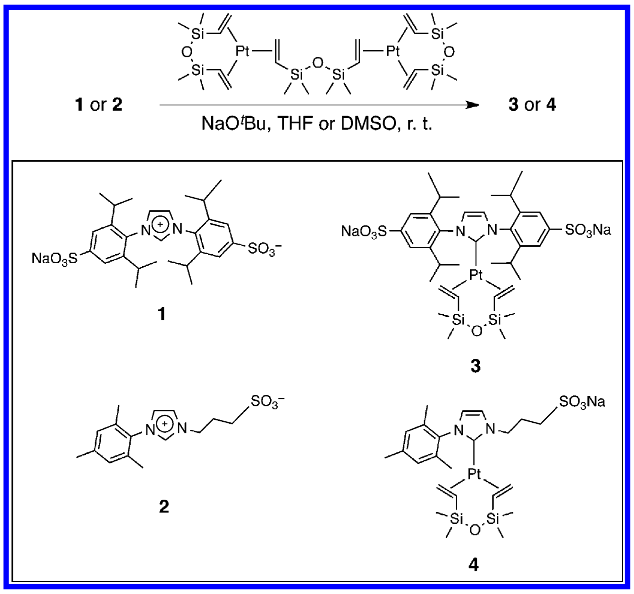
## RESULTS AND DISCUSSION

**Synthesis and Characterization.** The water-soluble platinum(0)−carbene complexes **3** and **4** were prepared in high yield in THF or DMSO from the commercial Karstedt complex and the corresponding imidazolium compounds **1**[23] and **2**[32,58] using sodium *tert*-butoxide as the deprotonating agent (Scheme 1). A similar procedure was previously used by Markó and co-workers to prepare related NHC platinum(0) complexes.[59,60] Purification of these products was straightforward due to their insolubility in acetone. They are very stable in air and can be stored for prolonged periods of time when protected from light. Complexes **3** and **4** can also be obtained by carbene transmetalation[61] from the appropriate NHC silver complex, prepared according to reported procedures,[32] to the Karstedt platinum(0) complex, although the solids thus obtained are contaminated by significant amounts of byproduct.

**Scheme 1. Synthesis of Water-Soluble Pt(0) N-Heterocyclic Carbene Complexes 3 and 4**

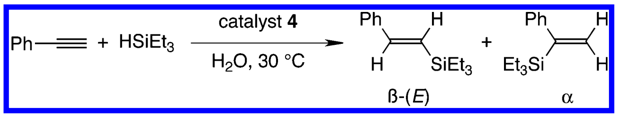


These complexes were fully characterized by $^{1}$H, $^{13}$C, and $^{195}$Pt NMR spectroscopy, elemental analysis, and mass spectrometry. $^{1}$H NMR spectroscopy and elemental analyses showed their tendency to trap solvent molecules upon crystallization (see the Experimental Section for details). The electrospray ionization mass spectra (ESI-TOF) obtained in methanol showed the molecular anion corresponding to the loss of a sodium(1+) ion for both complexes. The platinum-195 chemical shift at ca. −5340 ppm is similar to that found for related NHC platinum(0) complexes.[59] Coordination of the NHC ligand to the platinum atom was confirmed by the observation of $^{195}$Pt satellites in the resonances assigned to the proton and carbon-13 nuclei at the 4- and 5-positions of the imidazole ring ($^{4}J(^{1}\mathrm{H}-^{195}\mathrm{Pt}) = 10$ Hz, $^{3}J(^{13}\mathrm{C}-^{195}\mathrm{Pt}) = 40$ Hz). The $^{195}$Pt satellites for the carbene carbon at ca. 180 ppm could not be detected with accuracy due to the low intensity of the observed resonance.

The partition coefficients for the new platinum complexes in mixtures of water and common organic solvents could not be determined accurately due to the absence of characteristic absorptions in their UV−vis spectra. Qualitative information obtained by $^{1}$H NMR spectroscopy showed that both complexes are completely dissolved into the aqueous phase in mixtures of this solvent with diethyl ether or toluene.

**Hydrosilylation of Terminal Alkynes in Water.** The NHC complexes **3** and **4** were initially tested as catalysts in the hydrosilylation of phenylacetylene with triethylsilane in water. A first run of experiments showed that catalyst **4** was able to attain complete conversions at room temperature after 6 h of reaction even with Pt loadings as low as 0.05 mol % (Table 1).

**Table 1. Hydrosilylation of Phenyacetylene with Triethylsilane Catalyzed by Complex 4 in Water**[a]

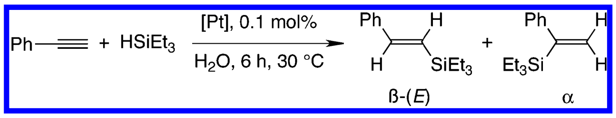


| entry | Pt (mol %) | time (h) | $\beta(E)/\alpha$[b] | conversion (%)[b] |
|---|---|---|---|---|
| 1 | 0.5 | 1 | 93:7 | 91 |
| 2 | 0.5 | 3 | 92:8 | 100 |
| 4 | 0.25 | 6 | 91:9 | 100 |
| 5 | 0.1 | 6 | 90:10 | 100 |
| 6 | 0.05 | 6 | 87:13 | 100 |

[a] In a typical experiment, 1 mmol of alkyne, 1.1 mmol of triethylsilane, and the Pt catalyst were stirred for the specified period of time at 30 °C in 3 mL of water. The reaction mixture was extracted with diethyl ether and the solvent removed in vacuo. [b] Determined by $^{1}$H NMR spectroscopy. Formation of the $\beta(Z)$ isomer was not observed.

The activity shown by this complex is comparable to that of the best Pt phosphane-based catalysts in hydrocarbon solvents for the same reaction.[62] The regioselectivity ($\beta$-($E$) with respect to $\alpha$ isomers) was determined by $^{1}$H NMR spectroscopy and found to be comparable to that found with $[\mathrm{Pt(PCy)_3}]$ for the same substrate, but lower than that reported for other phosphane or NHC complexes.[56,57,62] The more encumbered complex **3** was, as expected, less active (cf. entries 1 and 2 in Table 2) and showed poor selectivity. The efficiency of the commercial Karstedt catalyst in terms of activity or selectivity is intermediate between those shown by **3** and **4** (Table 2, entry 3), whereas the ammonium salt of the hexachloridoplatinate(IV) anion showed lower activity (Table 2, entry 4).

**Table 2. Comparison of Catalysts for the Hydrosilylation of Phenyacetylene with Triethylsilane in Water**[a]

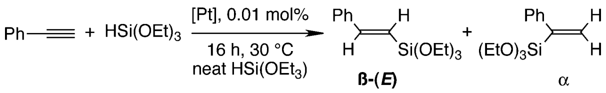


| entry | Pt catalyst | $\beta(E)/\alpha$[b] | conversion (%)[b] | yield (%)[c] |
|---|---|---|---|---|
| 1 | **4** | 90:10 | 100 | 97 |
| 2 | **3** | 60:40 | 71 | 67 |
| 3 | $\mathrm{Pt_2(dvtms)_3}$ | 85:15 | >90 | 89 |
| 4 | $\mathrm{(NH_4)_2[PtCl_6]}$ | 74:26 | 64 | 60 |

[a] See Table 1 for general reaction conditions. Reaction time: 6 h. Pt loading: 0.1 mol %. [b] Determined by $^{1}$H NMR spectroscopy. [c] Isolated yield (mixture of isomers).

All our attempts to use tris(ethoxy)silane instead of triethylsilane failed to attain observable conversions. It is well known that the silicon−hydrogen bonds in alkoxysilanes are generally less reactive than those in alkylsilanes. However, in this case, the complete failure of the tris(ethoxy)silane to react is due to hydrolysis of the silicon−alkoxide bonds, which gives rise to the formation of polysiloxane species that are scarcely soluble in water. In fact, the platinum(0) catalysts reported here are quite active when the same reaction is performed in neat tris(ethoxy)silane as the solvent (Table 3).

Table 3. Hydrosilylation of Phenylacetylene in Neat Tris(ethoxy)silane[a]



| entry | Pt catalyst | $\beta(E)/\alpha$[b] | conversion (%)[b] |
|---|---|---|---|
| 1 | 4 | 73:27 | 80 |
| 2 | 3 | 70:30 | 77 |

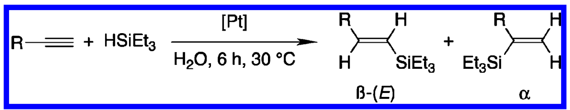
[a] See Table 1 for general reaction conditions. Reaction time: 16 h. Pt loading: 0.01 mol %. [b] Determined by $^1$H NMR spectroscopy.

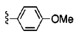
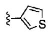
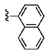
The scope of these reaction conditions was subsequently studied with a selection of terminal alkynes (Table 4). An interesting observation is that the reactivity differences between **3** and **4** are especially noticeable with alkynes bearing aryl substituents (entries 7−12). Both catalysts were inactive in the hydrosilylation of propargyl alcohol and propiolic acid under these conditions. The selectivities were found to depend on both the catalyst and the substrate, with both catalysts affording similar regioselectivities in most cases. Interestingly, the regioselectivity was drastically modified upon replacing a phenyl by a naphthyl group (cf. Table 2, entry 1, and Table 4, entry 12).

The tremendous popularity of N-heterocyclic carbenes (NHCs) as ligands for transition metals is based on the enhanced stability imparted by their strong $\sigma$-donating properties, which is associated with high steric hindrance. Here, we raise the question of the stability of the metal−carbene bonds in aqueous solution during the catalytic process. The studies reported to date, and summarized above, have shown that metal−NHC complexes are stable when dissolved in water and even that the formation of such bonds is sometimes possible in this solvent.[30,63] However, the literature gives scarce information on the long-term hydrolytic durability of metal−carbene bonds, especially at high temperatures or under catalytic conditions. Catalysts **3** and **4** are stable in $D_2O$ at room temperature for at least 1 month and at 70 °C for at least 3 days. However, partial hydrolysis (ca. 50%) was observed when the solutions were heated at 80 °C for 24 h. A similar decomposition temperature in $D_2O$ was reported for the complex [RuCl(*p*-cymene)(PTA)(NHC)]$^+$, which bears a hydrophobic 1-butyl-3-methylimidazol-2-ylidene NHC ligand.[64] Although the stability of these complexes during the catalytic experiments at room temperature is debatable, two findings support their durability under these conditions. First, the formation of colloidal Pt particles was never observed by TEM microscopy when samples of the aqueous solutions were analyzed at the end of the reaction under the conditions specified in entries 1 and 2 of Table 2. Second, catalysts **3** and **4**, which differ only in terms of the carbene moiety, afforded very different regioselectivities with substrates such as phenylacetylene, and these regioselectivities were maintained in recycling experiments, as described below.

**Catalyst Recycling.** In an ideal situation, a hydrophilic catalyst can be recovered from the organic product stream by simple phase separation at the end of the reaction. We, therefore, reasoned that high recyclability, in addition to practical advantages, should serve as experimental support for the proposed stability of the metal−carbene bonds in these platinum(0) complexes during the catalytic cycle. Recovery experiments were performed using trimethylsilylacetylene as the substrate and 0.01 or 0.5 mol % loadings of the NHC−Pt complex (**3** or **4**) or the Karstedt catalyst. Each recycling experiment was repeated until the conversion dropped below 95%; the number of cycles that attained this conversion can be found in Table 5, together with the reaction conditions. The Karstedt and hexachloridoplatinate(IV) complexes suffered from significant activity losses after the initial cycles, whereas the NHC catalysts attained high levels of recyclability. The percentage of platinum retained in the aqueous solution at the end of the recycling experiments was

Table 4. Hydrosilylation of Terminal Alkynes in Water[a,b,c,d]



| entry | R | catalyst (mol%) | β(E)/α[b] | conv (%)[b] | yield (%)[c] |
|---|---|---|---|---|---|
| 1 | $-(CH_2)_5CH_3$ | **3** (0.5) | 88:12 | 80 | 75 |
| 2 | | **4** (0.5) | 93:07 | 100 | 94 |
| 3 | $-SiMe_3$ | **3** (0.1) | 60:40 | 100 | 92 |
| 4 | | **4** (0.1) | 64:36 | 100 | 90 |
| 5 | $-CH_2Br$ | **3** (0.1) | 49:51 | 100 | 85 |
| 6 | | **4** (0.1) | 50:50 | 100 | 83 |
| 7[d] |  | **3** (0.5) | 80:20 | 60 | 62 |
| 8[d] | | **4** (0.1) | 88:12 | 65 | 58 |
| 9[d] |  | **3** (0.5) | 71:29 | 23 | 18 |
| 10[d] | | **4** (0.5) | 72:28 | 48 | 42 |
| 11 |  | **3** (0.5) | 72:28 | 13 | 10 |
| 12 | | **4** (0.5) | 48:52 | 28 | 20 |

[a] See Table 1 for general conditions. Reaction time: 6 h. [b] Determined by $^1$H NMR spectroscopy. [c] Isolated yield (mixture of isomers). [d] Reaction time: 24 h.

### Table 5. Recycling Experiments Using Trimethylsilylacetylene as Substrate[a]

| catalyst | Pt (mol %) | no. of cycles[b] | $\beta(E)/\alpha$[c] |
|---|---|---|---|
| **3** | 0.5 | >8[d] | 55:45 to 60:40 |
| **4** | 0.5 | >9[d] | 56:44 to 65:35 |
| Karstedt | 0.5 | 2 | 57:43 to 59:41 |
| **3** | 0.01 | 4 | 56:44 to 60:40 |
| **4** | 0.01 | 4 | 58:42 to 59:41 |
| Karstedt | 0.01 | 1 | 56:44 |
| $(NH_4)_2[PtCl_6]$ | 0.01 | 1 | 56:44 |

[a] See Table 1 for general conditions. Substrate: trimethylsilylacetylene. Reaction time: 6 h. After every cycle, the products were extracted with diethyl ether and a new load of substrate was added to the aqueous solution. [b] Number of cycles in which conversions of >95% are attained. Isolated yields were always >87%. [c] Determined by $^1$H NMR spectroscopy. [d] 100% conversions were obtained in all the cycles performed.

high (TRXF analysis showed that the final Pt concentrations were 60−86% of the initial concentrations), thus showing the efficiency of the NHC ligands in trapping the platinum(0) species in this phase.

When phenylacetylene was used as the substrate, only two cycles attained conversions above 95%, even when Pt loadings of 0.5 mol % were employed. Recycling of the catalyst can alternatively be performed using a temperature-dependent or thermomorphic multicomponent solvent (TMS) system, which consists of a mixture of a polar and a nonpolar solvent together with a third component of intermediate polarity. The mixture forms two phases at low temperature but becomes homogeneous at high temperature.[65,66] The catalytic reaction is then run homogeneously at high temperature, with phase separation being performed at low temperature. The hydrosilylation of phenylacetylene with thiethylsilane was performed in a water/toluene/DMF TMS system at 80 °C in the presence of 0.1 mol % of catalyst **3** and monitored by gas chromatography (see the Experimental Section for details). The reaction was complete in 9 h and afforded a mixture of $\beta(E)$ (86%), $\beta(Z)$ (4%), and $\alpha$ (10%) isomers. The catalyst could be reused in four cycles, during which the catalytic activity and selectivity remained practically constant, thus meaning that recyclability was enhanced in comparison with experiments performed in pure water.

## ■ CONCLUSIONS

In summary, we have shown that water-soluble platinum(0) complexes containing sulfonated N-heterocyclic carbene ligands are active and recyclable catalysts that can activate the hydrosilylation of some terminal alkynes at room temperature in water. Our results support the proposal that NHC−Pt(0) bonds have a reasonable stability under these catalytic conditions, although they are hydrolyzed at high temperatures in pure water. Further work underway in our laboratories is focused on the reactivity of these water-soluble NHC platinum(0) complexes.

## ■ EXPERIMENTAL SECTION

**General Procedures.** All operations were performed under an argon atmosphere using standard Schlenk techniques. Deionized water (type II quality) was obtained using a Millipore Elix 10 UV Water Purification System. Organic solvents were dried and distilled under argon and degassed prior to use. Unless otherwise stated, reagents were obtained from commercial sources and used as received. $^1$H, $^{13}$C, and $^{195}$Pt NMR spectra were recorded with a Varian Unity 300 or 500 Plus spectrometer. Chemical shifts ($\delta$, parts per million) are quoted relative to $SiMe_4$ ($^1$H, $^{13}$C) and $H_2PtCl_6$ ($^{195}$Pt) and were measured by internal referencing to the $^{13}$C or residual $^1$H resonances of the deuterated solvents, or by the substitution method in the $^{195}$Pt case. Coupling constants ($J$) are given in hertz. The Analytical Services of the Universidad de Alcalá performed the C, H, S, and N analyses using a Heraeus CHN-O-Rapid microanalyzer, and the ESI mass spectra using an Automass Multi, ThermoQuest spectrometer. The SIDI laboratories of the Universidad Autónoma de Madrid performed TXRF analysis using an 8030 C spectrometer (FEI Company, Munich, Germany), equipped with two X-ray fine focus lines, Mo and W anodes, and a Si(Li) detector with an active area of 80 mm$^2$ and a resolution of 148 eV at 5.895 keV (Mn KR). STEM images were obtained by the Microscopy Centre "Luis Bru" of the Universidad Complutense de Madrid using a JEOL 2000FX microscope operating at an accelerating voltage of 200 kV. Samples were prepared by placing two drops of the aqueous solutions on a holey-carbon-coated grid and allowing the solvent to evaporate in air.

**Synthesis of the Imidazolium Salts.** Compounds **1**[23] and **2**[32,58] were prepared according to reported procedures. The yield in the preparation of **1** was increased from the previously reported 70% to 98% by replacing the final chromatographic purification by precipitation of the product from DMSO solution with acetone. Water solubility at 25 °C: 160 (**1**) and 72.5 g/L (**2**).

**Synthesis of [1,3-Bis(2,6-diisopropyl-4-sodiumsulfonatophenyl)imidazol-2-ylidene](1,1,3,3-tetramethyl-1,3-divinyldisiloxane)platinum(0) (3).** A commercial solution of Karstedt's catalyst (0.1 M in poly(dimethylsiloxane), 1.5 mL, 0.15 mmol) and the imidazolium salt **1** (0.085 g, 0.15 mmol) were dissolved in DMSO (3 mL) under argon at 0 °C. Sodium *tert*-butoxide (0.020 g, 0.21 mmol) was then added to the above solution and the reaction mixture stirred for 24 h at room temperature. The mixture was filtered through a pad of kieselguhr, acetone (6 mL) was added to the resulting solution, and the mixture was stirred overnight. Subsequent filtration of the reaction mixture afforded complex **3** as a pale yellow solid (0.142 g, 96%), which was washed with acetone (3 × 5 mL) and dried under vacuum. Complex **3** is soluble in water, methanol, *tert*-butanol, and DMSO; partially soluble in isopropanol; and insoluble in tetrahydrofuran, diethyl ether, and acetone. $^1$H NMR (500 MHz, DMSO-$d_6$): $\delta$ 7.73 (s with $^{195}$Pt satellites, $^4J_{Pt-H}$ = 10, 1H, $H_{Im}$), 7.41 (s, 2H, Ar), 2.88 (h, $^3J_{H-H}$ = 7.0, 2H, −C*H*Me$_2$), 1.63 (d with $^{195}$Pt satellites, $^3J_{H-H}$ = 12.0, $^2J_{Pt-H}$ = 50, 1H, vinyl), 1.42 (d, $^3J_{H-H}$ = 13.5, 1H, vinyl), 1.21 (dd, 1H, vinyl), 1.16 (d, $^3J_{H-H}$ = 7.0, 6H, CH*Me*$_2$), 1.09 (d, $^3J_{HH}$ = 7.0, 6H, CH*Me*$_2$), 0.00 (s, 3H, SiMe$_2$), −0.84 (s, 3H, SiMe$_2$). $^1$H NMR (500 MHz, D$_2$O): $\delta$ 7.57 (s, 1H, $H_{Im}$), 7.55 (s, 2H, Ar), 2.87 (h, $^3J_{H-H}$ = 7.0, 2H, −C*H*Me$_2$), 1.70 (d, $^3J_{H-H}$ = 11.5, 1H, vinyl), 1.49 (d, $^3J_{H-H}$ = 13.5, 1H, vinyl), 1.29 (dd, 1H, vinyl), 1.17 (d, $^3J_{H-H}$ = 7.0, 6H, CH*Me*$_2$), 1.05 (d, $^3J_{HH}$ = 7.0, 6H, CH*Me*$_2$), 0.00 (s, 3H, SiMe$_2$), −0.84 (s, 3H, SiMe$_2$). $^{13}$C NMR (75 MHz, DMSO-$d_6$): $\delta$ 181.8 (Pt−C$^2$ im), 148.4 (C Ar), 144.0 (CH Ar), 135.9 (C Ar), 124.7 ($^3J_{Pt-C}$ = 41.4, C$^1$ Ar), 120.1 ($^3J_{Pt-C}$ = 39.6, C$^{4,5}$ im), 40.7 (SiCH═CH$_2$), 33.9 ($^1J_{Pt-C}$= 121.3, SiCH═CH$_2$), 27.5 (CHMe$_2$), 24.9 (CH*Me*$_2$), 21.6 (CH*Me*$_2$), 1.2 (SiMe$_2$), −2.6 (SiMe$_2$). $^{195}$Pt NMR (107 MHz, DMSO-$d_6$): $\delta$ −5332. ESI-MS (negative ion, MeOH) *m*/*z*: 950.23 $[M - Na]^-$, 928.25 $[MH - 2Na]^-$, 463.6 $[M - 2Na]^{2-}$. Anal. Calcd for $C_{39}H_{64}N_2Na_2O_9S_4Si_2Pt$ (**3**·2DMSO): C, 41.44; H, 5.71; N, 2.48. Found: C, 40.98; H, 5.68; N, 2.60.

**Synthesis of [1-Mesityl-3-(3-sodiumsulfonatopropyl)-imidazol-2-ylidene](1,1,3,3-tetramethyl-1,3-divinyldisiloxane)-platinum(0) (4).** Complex **4** was obtained as a pale yellow solid (0.095 g, 98%) by a similar procedure to that described for complex **3**, starting from a commercial solution of Karstedt's catalyst (0.1 M in poly(dimethylsiloxane), 1.5 mL, 0.15 mmol), the imidazolium salt **2** (0.046 g, 0.15 mmol), and sodium *tert*-butoxide (0.020 g, 0.21 mmol). Complex **4** is soluble in water, methanol, *tert*-butanol, isopropanol, and DMSO and insoluble in tetrahydrofuran, diethyl ether, and acetone. $^1$H NMR (500 MHz, DMSO-$d_6$): $\delta$ 7.69 (d, $^3J_{H-H}$ = 2.0, $^4J_{Pt-H}$ = 10, 1H, $H_{Im}$), 7.35 (d, $^4J_{Pt-H}$ = 10, 1H, $H_{Im}$), 6.84 (s, 2H, Ar), 4.02 (t, $^3J_{H-H}$ = 7.0, 2H, NCH$_2$), 2.30 (t, $^3J_{H-H}$ = 7.5, 2H, CH$_2$S), 2.16 (s, 3H, *p*-*Me*Ar), 1.97 (q, 2H, CH$_2$C*H*$_2$CH$_2$), 1.96 (s, 6H, *o*-*Me*Ar), 2.05 (m, 2H, vinyl), 1.63 (d, $^3J_{H-H}$ = 11.5, 2H, vinyl), 1.48 (t with $^{195}$Pt satellites, $^3J_{H-H}$ = 12.5, $^2J_{Pt-H}$ = 42.1, 2H, vinyl), 0.09 (s, 6H, $SiMe_2$), −0.26 (s, 6H, $SiMe_2$). $^{13}$C NMR (75 MHz, DMSO-$d_6$): δ 179.8 (Pt−$C^2$ im), 137.1 (C Ar), 136.1 ($^4J_{C-Pt}$ = 12.3, $C^1$ Ar), 134.1 (C Ar), 127.8 (CH Ar), 123.0 ($^3J_{Pt-C}$ = 40.1, CH im), 121.5 ($^3J_{Pt-C}$ = 40.1, CH im), 47.9 ($NCH_2$), 47.7 ($SCH_2$), 32.7 ($^1J_{Pt-C}$ = 117.9, $SiCH{=}CH_2$), 30.2 ($SiCH{=}CH_2$), 26.0 ($CH_2$), 20.0 (*p*-MeAr), 17.1 (*o*-MeAr), 1.1 ($SiMe_2$), −2.9 ($SiMe_2$). $^{195}$Pt NMR (107 MHz, DMSO-$d_6$): δ −5352. ESI-MS (negative ion, MeOH) *m*/*z*: 688.21 [M − Na]$^-$. Anal. Calcd for $C_{25}H_{43}N_2S_2O_5NaSi_2Pt$ (4·DMSO): C, 38.01; H, 5.49; N, 3.55. Found: C, 38.49; H, 5.63; N, 3.47.

**General Procedure for the Hydrosilylation of Alkynes in Water.** The alkyne (1.0 mmol) and a slight excess of triethylsilane (1.1 mmol) were added to a solution of the corresponding Pt catalyst (0.1−5 μmol; see Tables 1−3 for mol % Pt) in 3 mL of water previously warmed to 30 °C. The mixture was stirred magnetically for 3 h, then extracted with diethyl ether, and the solvent removed under vacuum. Yields and selectivities were obtained by analysis of the diethyl ether solutions by GC chromatography (naphthalene internal standard) and complemented by analysis of the final crude product by $^1$H NMR spectroscopy. The aqueous phase was reused for several cycles as specified in the Results and Discussion section.

**Hydrosilylation in a Thermomorphic System.** The alkyne (1.0 mmol), a slight excess of triethylsilane (1.1 mmol), and the [(NHC)Pt(dvtms)] catalyst **3** (1 μmol) were dissolved in 4 mL of a thermomorphic solvent mixture of water/toluene/dimethylformamide (0.5/2.1/1.4, respectively). The biphasic reaction mixture was saturated with argon and stirred magnetically for 9 h at 80 °C, the temperature at which it became homogeneous. After this time, the reaction was rapidly cooled to 0 °C and the organic phase separated and analyzed as specified above.

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### Notes

The authors declare no competing financial interest.

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