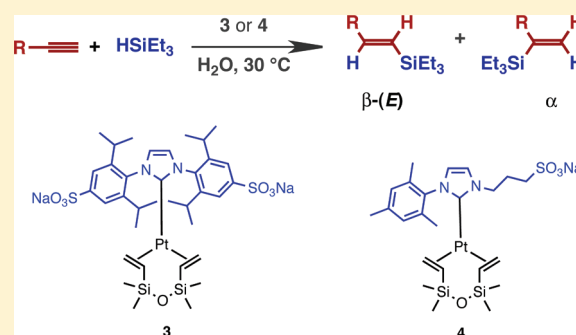


Water-Soluble N-Heterocyclic Carbene Platinum(0) Complexes: Recyclable Catalysts for the Hydrosilylation of Alkynes in Water at Room Temperature

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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 ($[\text{Pt}_2(\text{dvtms})_3]$, dvtms = 1,3-divinyl-1,1,3,3-tetramethylsiloxane)^{51,52} and the Speier system ($\text{H}_2\text{PtCl}_6/\text{PrOH}$)^{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 colloids⁵⁵ 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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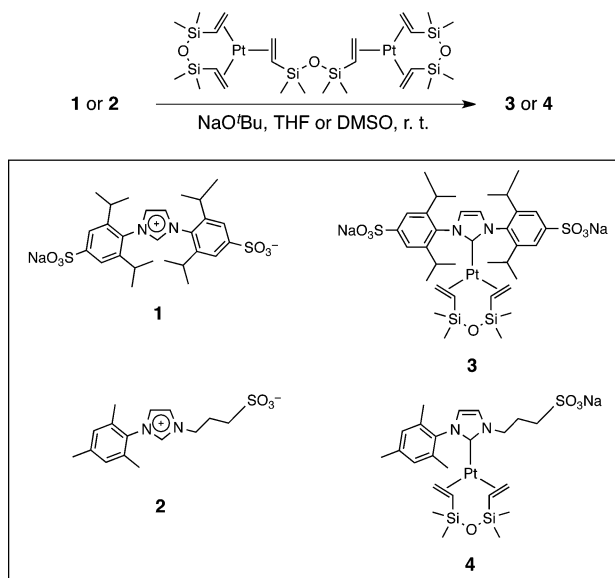
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RESULTS AND DISCUSSION

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

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



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 transmetalation⁶¹ 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.

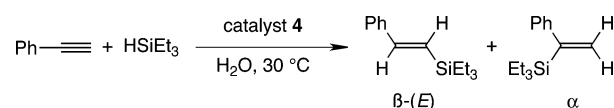
These complexes were fully characterized by ¹H, ¹³C, and ¹⁹⁵Pt NMR spectroscopy, elemental analysis, and mass spectrometry. ¹H NMR spectroscopy and elemental analyses showed their tendency to trap solvent molecules upon crystallization (see the Experimental Section for details). The electrospray ionization 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 ¹⁹⁵Pt satellites in the resonances assigned to the proton and carbon-13 nuclei at the 4- and 5-positions of the imidazole ring (⁴J(¹H-¹⁹⁵Pt) = 10 Hz, ³J(¹³C-¹⁹⁵Pt) = 40 Hz). The ¹⁹⁵Pt 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 ¹H 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 Phenylacetylene with Triethylsilane Catalyzed by Complex **4** in Water^a

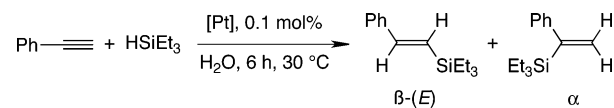


entry	Pt (mol %)	time (h)	$\beta(E)/\alpha^b$	conversion (%) ^b
1	0.5	1	93:7	91
2	0.5	3	92:8	100
4	0.25	6	91:9	100
5	0.1	6	90:10	100
6	0.05	6	87:13	100

^aIn 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. ^bDetermined by ¹H 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 α isomers) was determined by ¹H NMR spectroscopy and found to be comparable to that found with [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

Table 2. Comparison of Catalysts for the Hydrosilylation of Phenylacetylene 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	Pt ₂ (dvtms) ₃	85:15	>90	89
4	(NH ₄) ₂ [PtCl ₆]	74:26	64	60

^aSee Table 1 for general reaction conditions. Reaction time: 6 h. Pt loading: 0.1 mol %. ^bDetermined by ¹H NMR spectroscopy. ^cIsolated yield (mixture of isomers).

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).

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 alkoxy silanes are generally less reactive than those in alkylsilanes. However, in this case, the complete failure of the tris(ethoxy)silane to react

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

^aSee 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. ^bNumber of cycles in which conversions of >95% are attained. Isolated yields were always >87%. ^cDetermined by ¹H NMR spectroscopy. ^d100% 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 α (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. ¹H, ¹³C, and ¹⁹⁵Pt NMR spectra were recorded with a Varian Unity 300 or 500

Plus spectrometer. Chemical shifts (δ , parts per million) are quoted relative to SiMe₄ (¹H, ¹³C) and H₂PtCl₆ (¹⁹⁵Pt) and were measured by internal referencing to the ¹³C or residual ¹H resonances of the deuterated solvents, or by the substitution method in the ¹⁹⁵Pt 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 mm² 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-divinylidisiloxane)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. ¹H NMR (500 MHz, DMSO-*d*₆): δ 7.73 (s with ¹⁹⁵Pt satellites, ⁴*J*_{Pt-H} = 10, 1H, H_{im}), 7.41 (s, 2H, Ar), 2.88 (h, ³*J*_{H-H} = 7.0, 2H, -CHMe₂), 1.63 (d with ¹⁹⁵Pt satellites, ³*J*_{H-H} = 12.0, ²*J*_{Pt-H} = 50, 1H, vinyl), 1.42 (d, ³*J*_{H-H} = 13.5, 1H, vinyl), 1.21 (dd, 1H, vinyl), 1.16 (d, ³*J*_{H-H} = 7.0, 6H, CHMe₂), 1.09 (d, ³*J*_{H-H} = 7.0, 6H, CHMe₂), 0.00 (s, 3H, SiMe₂), -0.84 (s, 3H, SiMe₂). ¹H NMR (500 MHz, D₂O): δ 7.57 (s, 1H, H_{im}), 7.55 (s, 2H, Ar), 2.87 (h, ³*J*_{H-H} = 7.0, 2H, -CHMe₂), 1.70 (d, ³*J*_{H-H} = 11.5, 1H, vinyl), 1.49 (d, ³*J*_{H-H} = 13.5, 1H, vinyl), 1.29 (dd, 1H, vinyl), 1.17 (d, ³*J*_{H-H} = 7.0, 6H, CHMe₂), 1.05 (d, ³*J*_{H-H} = 7.0, 6H, CHMe₂), 0.00 (s, 3H, SiMe₂), -0.84 (s, 3H, SiMe₂). ¹³C NMR (75 MHz, DMSO-*d*₆): δ 181.8 (Pt–C² im), 148.4 (C Ar), 144.0 (CH Ar), 135.9 (C Ar), 124.7 (³*J*_{Pt-C} = 41.4, C¹ Ar), 120.1 (³*J*_{Pt-C} = 39.6, C^{4,5} im), 40.7 (SiCH=CH₂), 33.9 (¹*J*_{Pt-C} = 121.3, SiCH=CH₂), 27.5 (CHMe₂), 24.9 (CHMe₂), 21.6 (CHMe₂), 1.2 (SiMe₂), -2.6 (SiMe₂). ¹⁹⁵Pt NMR (107 MHz, DMSO-*d*₆): δ -5332. ESI-MS (negative ion, MeOH) *m/z*: 950.23 [M – Na][–], 928.25 [MH – 2Na][–], 463.6 [M – 2Na]^{2–}. Anal. Calcd for C₃₉H₆₄N₂Na₂O₉S₄Si₂Pt (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-divinylidisiloxane)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. ¹H NMR (500 MHz, DMSO-*d*₆): δ 7.69 (d, ³*J*_{H-H} = 2.0, ⁴*J*_{Pt-H} = 10, 1H, H_{im}), 7.35 (d, ⁴*J*_{Pt-H} = 10, 1H, H_{im}), 6.84 (s, 2H, Ar), 4.02 (t, ³*J*_{H-H} = 7.0, 2H, NCH₂), 2.30 (t, ³*J*_{H-H} = 7.5, 2H, CH₂S), 2.16 (s, 3H, *p*-MeAr), 1.97 (q, 2H, CH₂CH₂CH₂), 1.96 (s, 6H, *o*-MeAr), 2.05 (m, 2H, vinyl), 1.63 (d, ³*J*_{H-H} = 11.5, 2H, vinyl), 1.48 (t with ¹⁹⁵Pt

satellites, $^3J_{\text{H-H}} = 12.5$, $^2J_{\text{Pt-H}} = 42.1$, 2H, vinyl), 0.09 (s, 6H, SiMe₂), -0.26 (s, 6H, SiMe₂). ^{13}C NMR (75 MHz, DMSO-*d*₆): δ 179.8 (Pt-C² im), 137.1 (C Ar), 136.1 ($^4J_{\text{C-Pt}} = 12.3$, C¹ Ar), 134.1 (C Ar), 127.8 (CH Ar), 123.0 ($^3J_{\text{Pt-C}} = 40.1$, CH im), 121.5 ($^3J_{\text{Pt-C}} = 40.1$, CH im), 47.9 (NCH₂), 47.7 (SCH₂), 32.7 ($^1J_{\text{Pt-C}} = 117.9$, SiCH=CH₂), 30.2 (SiCH=CH₂), 26.0 (CH₂), 20.0 (*p*-MeAr), 17.1 (*o*-MeAr), 1.1 (SiMe₂), -2.9 (SiMe₂). ^{195}Pt NMR (107 MHz, DMSO-*d*₆): δ -5352. ESI-MS (negative ion, MeOH) *m/z*: 688.21 [M - Na]⁻. Anal. Calcd for C₂₅H₄₃N₂O₅NaSi₂Pt (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 ^1H 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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