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Synthesis and behavior of novel sulfonated water-soluble N-heterocyclic carbene (η^4-diene) platinum(0) complexes

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A series of water-soluble (NHC)Pt(0)(dvtms) and (NHC)Pt(0)(AE) complexes containing different sulfonated NHC ligands (dvtms = divinyltetramethyldisiloxane and AE = diallyl ether) are reported. The dvtms compounds have been found to be quite robust and to display some conformational rigidity, whereas their AE counterparts are less stable and more flexible. The catalytic evaluation of these complexes in the hydrosilylation of alkynes in water revealed no benefits in favor of the complexes containing the more labile spectator diene (AE), and a fairly regular catalytic behavior for all complexes that restricts the location of the sulfonate group in the proximity of the metal site.

Introduction

The chemistry of N-heterocyclic carbenes (NHCs) has flourished over the past few decades, mainly due to their outstanding properties as ancillary ligands.[1] As NHCs offer a unique combination of properties, such as thermal and oxidative stability, strong σ-donating character, and electronic and steric tunability due to their versatile substitution, they usually provide steric protection and bind strongly to metal centers,[2] thus resulting in complexes that are very often stable to air and moisture. Such compounds are of great utility for a large number of homogenous catalytic processes[1,3] and for a broad range of other applications.[1a,4]

Simultaneously with these advances, the use of water as a reaction medium has attracted growing attention, initially based on environmental considerations but subsequently also because, in many instances, the distinctive characteristics of this solvent provide different benefits, such as exceptional chemical reactivity and selectivity, milder reaction conditions, easier work-up procedures and catalyst recovery.[5] Coordination and organometallic chemistry have contributed to the subject with the development of a large number of hydrophilic ligands and complexes that have been designed mostly for use as aqueous-phase metal catalysts,[6] as well as for timely applications related with the environment, drugs, luminescent agents, or the stabilization of metal nanoparticles, to cite just a few.[7]

In the majority of examples, the common approach to constraining metal complexes in aqueous media is the attachment of ligands substituted with hydrophilic groups. Such ligands have traditionally been based on phosphanes or N-donor derivatives.[6] Nevertheless, as the rapid development of carbenes in general has revealed a set of features that makes them potentially suitable for applications in water, NHCs have also attracted attention in this area and, indeed, research in this field has intensified over the last few years, as documented in three comprehensive and recent reviews[8] and in numerous papers published in the last couple of years.[9] Amongst several ionic or nonionic tags introduced into NHC ligands to render metal complexes hydrophilic (*e.g.*, carboxylate, ammonium, hydroxyl, PEGs, etc.), sulfonate derivatives are probably the most popular functionality due to their poor coordinating character.[8b] In fact, the first examples of water-soluble NHC ligands and metal complexes, which were claimed in patent literature filed by Herrmann and co-workers in 1995, contained sulfonated moieties as hydrophilic groups.[10] Despite this, water-soluble NHC complexes of platinum were unknown until recently, when we reported the synthesis of a few examples of Pt(0)[11] and Pt(II)[12] compounds containing sulfonated NHC ligands, which were found to be recoverable catalysts for the hydrosilylation of alkynes in water in the former case or for their hydration in water in the latter. In a subsequent paper we focused on basic aspects of the chemical reactivity of related alkyl complexes in the aqueous-phase and found the Pt–NHC bond to be hydrolytically quite inert.[13] Furthermore, our findings in the course of that study suggested the possible utility of these complexes for the synthesis and stabilization of water-soluble Pt(0) nanoparticles, as was subsequently confirmed.[14]

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Since the chemical behavior of a complex is largely dictated by the nature and substitution pattern of the coordinated ligands, we have turned our attention to the influence of the NHC and diolefinic moieties employed on the synthesis, stability and reactivity of this type of platinum complexes. Herein, we report the preparation of a series of sulfonated water-soluble NHC-Pt(η^4-1,6-diene) complexes containing several carbene ligands (Chart 1) and divinyltetramethyldisiloxane or diallyl ether as the diene. Contrary to what could be expected, most of the platinum complexes gave quite similar catalytic outcomes in the hydrosilylation reaction of alkynes in water.

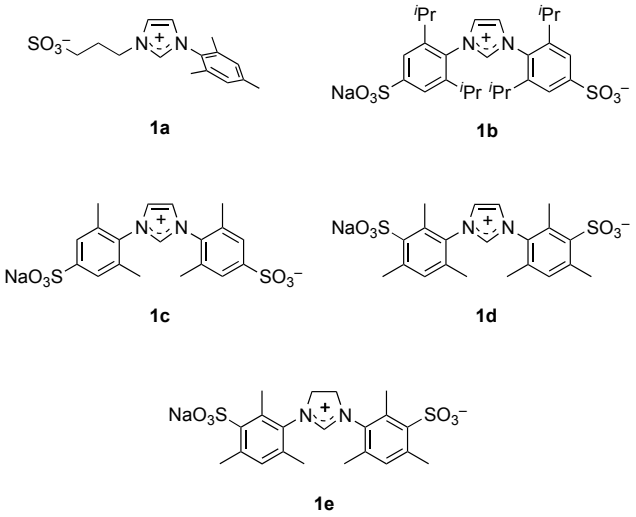


Chart 1. Sulfonated NHC ligand precursors used in this work.

Results and discussion

It has been well established that 16 e$^-$ complexes of general formula (*TP*-3)-[Pt(0)L(η^4-1,6-diene)] (L = two electron-donor) are stabilized by chelation of the diene with little strain and that their reactivity changes with the stereo-electronic effects imparted by the L ligand and with the acceptor strength of the diolefin. Thus, for instance, certain inertia is observed for coordinated divinyltetramethyldisiloxane (dvtms), whereas diallyl ether (AE) appears to render complexes with a more convenient stability/reactivity balance.[15,16] Taking into account these observations, and considering our previous results with water-soluble NHC complexes of this type (Chart 2),[11] we performed a comparative study of the synthesis and behavior of novel sulfonated-NHC platinum(0) complexes containing either dvtms or AE as the diene.

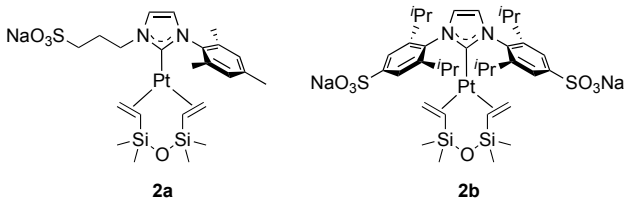
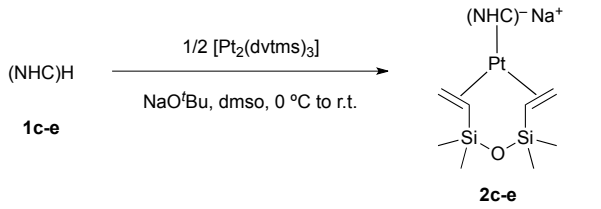
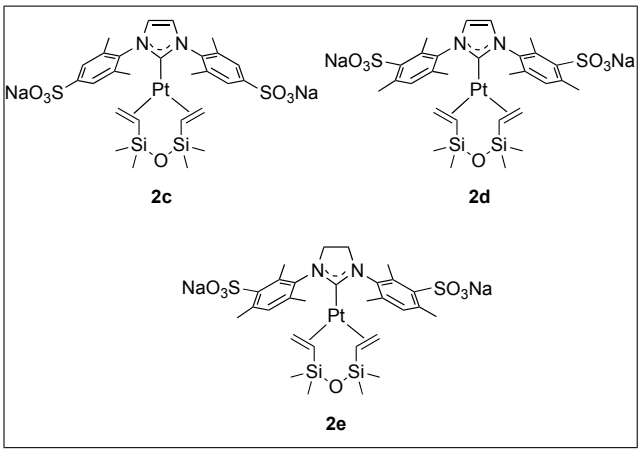


Chart 2. First examples of water-soluble NHC-Pt(0) complexes[11]

Platinum(0) complexes **2c-e** were prepared according to modified literature procedures,[17] and on the basis of those used for the synthesis of **2a** and **2b**,[11] which involves deprotonation of the corresponding imidazoli(ni)um salts **1c-e**[18,19] with sodium *tert*-butoxide in dmso in the presence of Karstedt's complex (Scheme 1). Work-up for the isolation of complexes **2c-e** involved their precipitation by slow addition of the reaction mixture (previously concentrated under vacuum) to a large volume of THF, with vigorous stirring, to afford these complexes in yields estimated to be almost quantitative, although containing residual dmso and THF that persisted after heating the solids under vacuum at 60 ºC (6-12 h, partial decomposition observed for **2e**; *vide infra*). Purification of this kind of compound is often challenging due to their hygroscopic nature, general tendency to trap polar solvents that tightly solvate the ionic moieties, and their inherent solubility, which makes it difficult to separate them from contaminating hydrophilic salts (*e.g.*, alkali-metal halides often involved in their preparation). However, hydrates of the imidazol-2-ylidenes **2c** and **2d** free from other trapped solvents (*i.e.*, dmso and THF) were obtained as orange and yellow solids by subsequent dialysis of the precipitated solids dissolved in water with moderate overall yield (50–70%, see Experimental Section).

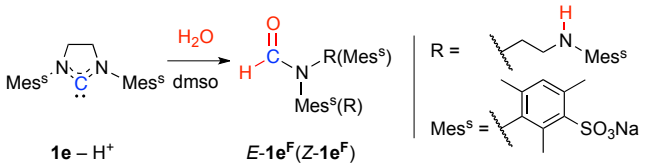




Scheme 1. Synthesis of sulfonated NHC-Pt(0) divinyltetramethyldisiloxane complexes **2c-e.**

The synthesis and purification of the imidazolin-2-ylidene **2e** was more troublesome due to the thermal instability shown by this compound and the facile hydrolysis of the corresponding free carbene. Thus, upon heating under vacuum in the solid state (60 ºC, 3-6 h) in an attempt to remove solvating molecules, **2e** partially decomposed with formation of Pt-black. In addition, after formation, this complex

precipitated from dmso/THF mixtures with significant amounts of formamide **1e**^{F} (≥ 50 mol% of the initial **1e**) generated by hydrolysis of the non-coordinated NHC generated *in situ* (Scheme 2). Since dialysis in water failed to permeate the byproduct **1e**^{F} from the target compound, complex **2e** was purified by gel permeation chromatography using Sephadex® G10 as the stationary phase and water as the only eluent (see Experimental Section) to give a hydrate of the compound as an analytically pure yellow solid, but in low yield (18%).

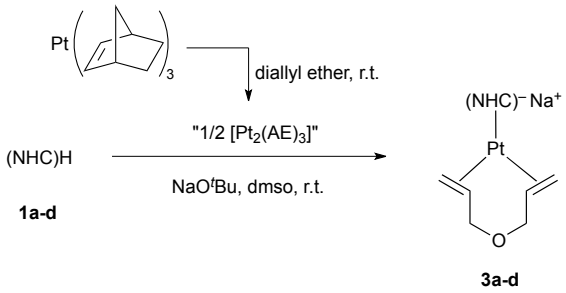


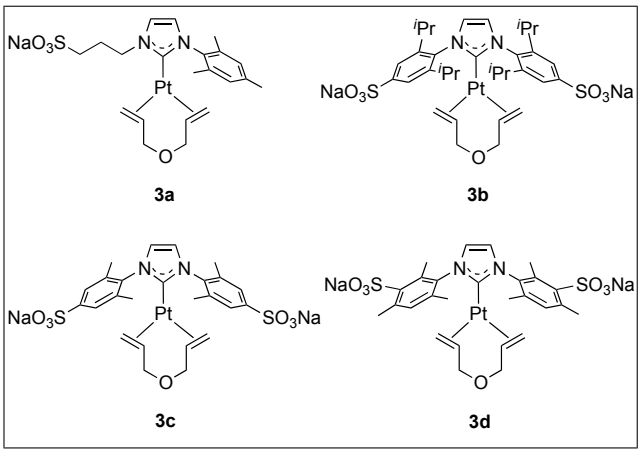
Scheme 2. Formation of formamide **1e**^{F} by ring-opening hydrolysis of the carbene derived from **1e**.

In contrast to aromatically stabilized imidazol-2-ylidenes, ring-opening hydrolysis of saturated imidazolic NHCs has been found to occur almost instantaneously in aprotic polar solvents containing traces of moisture.[20] Moreover, it has been elegantly demonstrated that this hydrolysis is favored in the presence of smaller amounts of water because the basicity of the hydroxide anion increases with poorer solvation.[21] We tried to obtain thoroughly dry dmso, and thus prevent the formation of **1e**^{F}, but all our efforts failed, probably because of the highly hygroscopic nature of this solvent and the counterproductive effect of a lower concentration of water. In fact, in a control experiment performed in the absence of [Pt_2(dvtms)$_3$], we confirmed the straightforward and total conversion of the imidazolin-2-ylidene to **1e**^{F} by stirring the imidazolium salt **1e** with NaO^{t}Bu in dmso (freshly distilled over CaH_2) for 30 min at room temperature and under argon (see Experimental Section for details and characterization data). As a result of the rotation barrier at the N–CHO bond, the formamide was obtained as a mixture of *E*- and *Z*-isomers with a 60/40% composition, similar to that observed when formed as by-product in the synthesis of **2e** (65/35%), thus indicating that the steric repulsion between the bulkiest substituents around that bond slightly favors the *E*-conformation of **1e**^{F}.

Compounds **2c-e** were found to be soluble in water (>50 g/L), methanol, and dmso and insoluble in THF, acetone, or diethyl ether. In the solid state they were found to be hygroscopic, air-stable at room temperature and could be stored for a prolonged time when protected from light. Their solutions in dmso-d_6 or D_2O remained unaltered at room temperature for an indefinite time period (for at least five months in D_2O) in the presence of air — a remarkable finding in the case of **2e** considering the above-mentioned lack of hydrolytic stability of the corresponding free carbene. The complexes were also found to be stable in dmso-d_6 upon heating at 100 ºC under argon (*e.g.*, **2c** unchanged after 5 days), but decomposed slowly (completion in *ca.* one week for **2c** and **2d**) or more quickly (noticeable in 4 h and complete within 48 h for **2e**) in D_2O at that temperature, although **2c** and **2d** were fairly stable in this solvent at 80 ºC (no apparent changes to the naked eye and unaltered ^{1}H NMR spectra after 5 days).

The allyl ether complexes **3a-d** were prepared by modifying the procedure reported by Markó's group for the one-pot synthesis of LPt(0)(η^4-AE) complexes in THF, which involves [Pt_2(AE)$_3$] generated *in situ* because the dynamic properties in solution and the unstable nature of the isolated species complicate the direct characterization and isolation of this type of complex.[16] Although we tested the use of solutions of [Pt_2(AE)$_3$] in ^{i}PrOH/AE, prepared as described from H_2PtCl_6 (or from K_2PtCl_4), in the solvent required to solubilize our ligands (*i.e.*, dmso) the formation reaction of the NHC complexes worked better (*e.g.*, 54% *vs*. 99% yield for **3b**) when the source of the Pt(η^4-AE) synthon was prepared by dissolving [Pt(η^2-nbe)$_3$] (nbe = norbornene)[22] in neat AE (Scheme 3, see Experimental Section).





Scheme 3. Synthesis of sulfonated NHC-Pt(0) diallyl ether complexes **3a-d**.

Compounds **3a-d** were isolated by precipitation from THF as described above. Complexes **3a** and **3b** thus obtained required no further purification (≥98% yield), whereas subsequent work-up in order to isolate samples with accurate elemental analyses succeeded for **3c** (31% yield, purified by GPC in Sephadex® G10); all attempts for **3d** failed. At this point it is worth mentioning that compounds **3** were less stable in solution than their analogs **2** containing dvtms as the diene. For instance, all of them decomposed relatively fast in dmso-d_6 or D_2O at just 80 ºC in the absence of air (<24 h, decomposition is also evident at room temperature after a week) and, except for **3b**, some degree of decomposition (^{1}H NMR evidence) was observed in their solids after storage for several weeks (4-8) at room temperature. This reduced

stability, combined with the proclivity of saturated carbenes to hydrolyse (*vide supra*), hampered the preparation of the corresponding complex **3e** from **1e**, which always led to mixtures in which **3e** could be detected by NMR and MS, but no purification method was practicable (see Experimental Section and Electronic Supplementary Information).

Complexes **3a-d** were found to be soluble in water (>50 g/L) and dmso, and insoluble in THF, diethyl ether, or acetone. They were obtained as beige (**3b**), orange (**3c**) or red (**3a** and **3d**) solids and were stored at low temperature under argon.

The NMR spectra for complexes **2c-e** and **3a-e** display the features reported by Markó and coworkers for non-sulfonated analogous containing dvtms[17,23] and AE[16] as the diene, thus corroborating the η^4-coordination mode of the chelating ligand. For instance, its pseudo-chair conformation in solution results in two distinct resonances for the protons of the $SiMe_2$ or OCH_2 moieties, corresponding to those at pseudo-equatorial (*ca*. δ 0.0 and 3.8 for $SiMe_{eq}$ and OCH_{eq}, respectively) and at pseudo-axial positions pointing towards the NHC substituents (*ca*. δ –0.8 and 1.5 for $SiMe_{ax}$ and OCH_{ax}, respectively), thus indicating the absence of a fast chair-to-chair conformational exchange on the NMR timescale. Coordination of the alkene to the metal is also confirmed by the observation, in many instances, of ^{195}Pt satellites on the resonances for the nuclei of the $CH{=}CH_2$ ($^2J_{Pt\text{-}H}$ ~ 50-60 Hz for complexes **2** and **3**, $^1J_{Pt\text{-}C}$ ~ 140 and 190 Hz observed for complexes **3**) and OCH_2 groups ($^3J_{Pt\text{-}H}$ ~ 45, $^2J_{Pt\text{-}C}$ ~ 30 Hz). The carbenic carbon resonates at δ 180-184 for the unsaturated NHC complexes, and at δ 210 for the imidazolin-2-ylidene compound **2e** (not observed for **3e**), in consonance with the literature values disclosed by Markó's group for related compounds, and pointing to stronger electron donating properties of the saturated ligand. Likewise, in some cases (*i.e.*, **3b-d**), the coupling constant between ^{195}Pt and the other imidazolic carbons (Imz-C[4,5]) could be observed ($^3J_{Pt\text{-}C}$ ~ 40 Hz).

Markó has utilized the ^{195}Pt NMR spectra of this type of complex as a diagnostic probe of the electronic environment of the platinum center, and observed a correlation, in series in which the nature of one of the ligands remains constant, between the thermodynamic stability of the diene complex and its $\delta(^{195}\text{Pt})$ value.[16a,17a] The relationship establishes that a higher π-back donation to the alkene results in more stable NHC-Pt(η^4-1,6-diene) complexes and the shift of the platinum resonance to lower field. The ^{195}Pt NMR signal for complexes **2** appears at around –5350 ppm, whereas for complexes **3** it is found at –5580 ppm (average $\Delta\delta$ ~ 230 for pairs of complexes with the same NHC ligand), thereby suggesting a higher stability of the complexes containing the dvtms ligand than those with the weaker π-acceptor AE as the diene. Likewise, the comparison of the ^{195}Pt NMR data for **2d** (–5343 ppm) and **2e** (–5373 ppm) also agrees with a somewhat superior σ-donating character for the saturated NHC ligand.[17a]

The characteristic trigonal-planar geometry around the platinum center found for non-sulfonated NHC-Pt(diene) complexes in the solid state locates the olefinic moieties coplanar to the coordination plane of the metal to maximize the overlap between the orbitals involved in the π bonding contribution, thus resulting in the mentioned pseudo-chair conformation, whilst the carbene ligand tends to be orthogonal to that metal coordination plane, adopting a less hindered arrangement.[16a,17,23] Whereas rigidity in the metallacycle is observed in solution (*vide supra*), the absence of a rotation barrier around the NHC–Pt bond is evidenced by the presence of a single set of NMR signals for the NHC ligand in all complexes, including unsymmetrically N,N'-substituted **2a**[11] or **3a**. In this regard, a salient feature arises for complexes containing the sulfonated mesityl ring **2d,e** when compared with the behavior observed in solution for **3d,e**. The longitudinal asymmetry of this substituent enables the presence of *anti* and *syn* conformers depending on the relative position of the two aryl rings of the carbene (Figure 1). The presence of these two conformers is clearly corroborated by NMR for the dvtms complexes **2d,e** in solution (*ca.* 1:1) with the observation of two sets of signals in the ^{1}H, ^{13}C, and ^{195}Pt spectra. The ^{1}H, ^{13}C assignments for each one were possible by performing two-dimensional NMR experiments such as ^{1}H-^{13}C-HSQC, ^{1}H-^{13}C-HMBC and 2D-ROESY, in D_2O. The data collected also provided conformational information confirming the rapid rotation around the NCH–Pt bond (*e.g.*, magnetic equivalences for analogous nuclei in both mesityl rings of each rotamer, or ROE correlation between the protons of those rings with the corresponding $SiMe_{ax}$ protons) and hindered one around the NHC–mesityl bond (*e.g.*, absence of cross-peaks due to intramolecular chemical exchange between the $SiMe_{ax}$ groups of the two rotamers). The spectra for the *anti*-conformers for **2d,e** is characterized by magnetically non equivalent halves of the dvtms ligand (*i.e.*, $-SiMe_2CH{=}CH_2$ moieties) showing, for instance, two equatorial and two axial SiMe groups, whereas the two halves are observed to be equivalent for the *syn*-conformers, as would be expected as the fast rotation around the NCH–Pt bond interconverts one part of the dialkene ligand into the other. Interestingly, the rotamers are barely detected for complexes **3d,e** (some indications only for **3e** with very close sets of resonances recorded in a 500 MHz spectrometer for the *ortho*-Me groups and for the olefinic carbons), in agreement with a higher conformational flexibility in complexes with the less bulky diene (*i.e.*, AE).

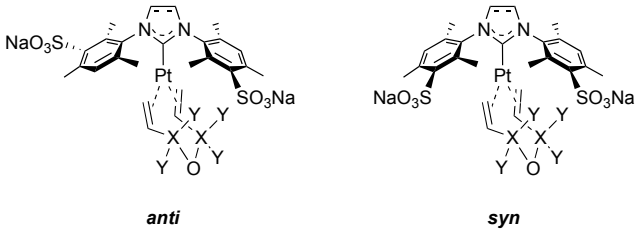


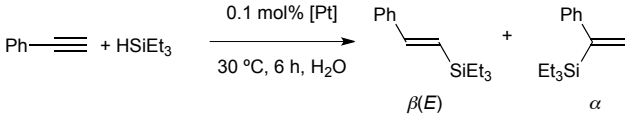
Figure 1. *Anti*- and *syn*-conformers for complexes **2d,e** and **3d,e** containing sulfonated mesityl groups.

The ESI(–) mass spectra of the complexes show the peak arising from the loss of one Na^+ (**3a**) or that corresponding to the dianion $[M - 2Na]^{2-}$ (**2c-e** and **3b-e**) as the most intense

signal, in some cases together with the protonated daughter species $[M - 2Na + H]^-$.

The complexes isolated as species with accurate elemental analysis (*i.e.*, **2c-e** and **3a-c**) were tested as catalysts in some model hydrosilylation reactions of acetylenes studied in our previous work in water.[11] Under the conditions optimized for **2a,b** with phenylacetylene and triethylsilane, none of the new platinum catalysts was superior in activity than **2a** or **2b**, and displayed regioselectivities towards the $\beta(E)$ product (77-81%) between those reported previously (90% and 60% for **2a** and **2b**, respectively; see Table 1). The results with triethylsilylacetylene as the alkyne, maintaining the rest of the reaction conditions, were also similar (*e.g.*, 100% conversions after 6 h leading to 60% of the $\beta(E)$ isomer for **2d** and **3a** *vs.* total conversion with a 64% or 60% to that isomer for **2a** and **2b**,[11] respectively). Besides, the water solution of these new catalysts could be recovered and reutilized, at least one time, without loss of their catalytic performance.

Table 1: Comparison of catalysts for the hydrosilylation of phenylacetylene with triethylsilane in water.[a]



$\beta(E)$ α

entry	catalyst	conv (%)[b]	$\beta(E)/\alpha$[b]	TON/TOF(h^{-1})[c]
1[d]	**2a**	100	90:10	1000/167
2[d]	**2b**	71	60:40	710/118
3	**2c**	31	80:20	310/52
4	**2d**	47	77:23	470/78
5	**2e**	42	81:19	420/70
6	**3a**	67	77:23	670/112
7	**3b**	43	78:22	430/72
8	**3c**	44	80:20	440/73

[a] 1 mmol alkyne, 1.1 mmol triethylsilane, Pt loading: 0.1 mol%, 3 mL of water, 6 h, 30 ºC. [b] Determined by GC-MS. Formation of the $\beta(Z)$ isomer was ≤0.3% when detected. [c] Based on mol of substrate converted. [d] Results reported in the literature.[11]

Several structure-reactivity correlations have been proposed for related nonhydrophilic NHC-Pt(dvtms) complexes, showing enhanced activities and selectivities with saturated instead of unsaturated NHC ligands, or with increasing bulkiness of *ortho*-groups on aryl substituted carbenes, or with the latter type of substitution rather than NHCs bearing alkyl groups.[17a,23a] In addition, better outcomes in hydrosilylation reactions have also been described for complex (IPr)Pt(AE) compared to (IPr)Pt(dvtms) (nonsulfonated analogs of **3b** and **2b**, respectively), which were ascribed to easier removal of the less tightly bound spectator diene (*i.e.*, AE) to form catalytically active [(IPr)Pt] fragments.[16b] All these facts and relationships appear to be masked in water for the platinum compounds described here. Thus, in general, no significant improvements are observed on going from dvtms to AE complexes (Table 1, entries 1-3 *vs.* 6-8), which could be associated with the reduced stability shown by the latter. Interestingly, within the **2a-e** and **3a-c** series, the most productive catalysts contain an alkylsulfonate substituent and a nonsulfonated aryl ring (**2a** and **3a**), whereas all complexes N,N'-substituted with sulfonated aryl rings display a quite similar catalytic behavior. A possible interpretation of these findings is that hydration of the anionic moieties must play a major role. For complexes **2a** and **3a** the solvated sulfonate group can be located further away from the metal center, at the same time as the aryl group maintains some degree of lipophilicity and the required steric protection around it, whereas the positioning of the hydration sphere of both ionic groups in the diaryl compounds must provide a hydrophilic environment around the metal site, thus interfering with the catalytic reaction and somehow buffering the structural effects caused by the NHC ligands in nonsulfonated complexes.

Conclusions

In this work, we have extended the family of water-soluble (NHC)Pt(dvtms) complexes available and introduced (NHC)Pt(AE) analogs for the first time. Their synthesis and characterization revealed the latter type of compounds to be significantly less stable, whereas the former could be more straightforwardly prepared and purified (precipitation, or dialysis and GPC in water). Additional difficulties have been encountered for the preparation of complexes with saturated NHC ligands due to the propensity of the free carbene to undergo ring-opening hydrolysis in the solvent for these syntheses, namely dmso. The platinum compounds with dvtms demonstrated higher rigidity in solution, with restricted rotation of the aryl substituents, than those with AE (a less bulky and weaker π-acceptor diene) in which more conformational flexibility is observed. Contrary to what has been observed with nonsulfonated compounds, the catalytic evaluation of the complexes in the hydrosilylation of alkynes indicates that replacement of dvtms by AE as the spectator diene has no catalytic benefits in water. The location of the hydrophilic groups in the complex appears to be a relevant issue, since better performances are observed when the sulfonate moiety is located far away from the platinum site. Further work is currently underway to investigate the chemistry, redesign, and applications of these complexes.

Experimental section

General Procedures. All reactions were performed under an argon atmosphere using standard Schlenk techniques. The complex $[Pt(\eta^2\text{-nbe})_3]$ (*i.e.* (tris(bicyclo[2.2.1]heptene)platinum(0); nbe = norbornene),[22] and the imidazoli(ni)um salts **1a**,[24] **1b-c**,[18] and **1d-e**,[19] were

prepared according to reported methods, although **1c** was isolated by precipitation with acetone from the preparation reaction mixture in dmso. Unless otherwise stated, other reagents and solvents were obtained from commercial sources and used as received. Karstedt's catalyst solution in propan-2-ol/divinyltetramethyldisiloxane (3.83% Pt) was purchased from Johnson-Matthey. Deionized water (type II quality) was obtained using a Millipore Elix 10 UV Water Purification System. Dimethyl sulfoxide was purified and dried through chromatography with activated neutral alumina and/or warmed over the drying agent overnight calcium hydride before trap to trap distillation. Diethyl ether and THF were dried using an MBraun-Solvent Purification System and deoxygenated prior to use. ^{1}H, ^{13}C and ^{195}Pt NMR spectra were recorded using a Varian Gemini 200, Mercury 300, Unity 300, or Unity 500 Plus spectrometer. When required, two-dimensional ^{1}H–^{13}C HMBC, ^{1}H–^{13}C HSQC, 2D ROESY or NOESY experiments were carried out for the unequivocal assignment of ^{1}H and ^{13}C resonances, or to discern the stereochemistry of the complexes. Chemical shifts (δ, parts per million) are quoted relative to $SiMe_4$ (^{1}H, ^{13}C) and K_2PtCl_6 in water (^{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 case of ^{195}Pt. Coupling constants (J) are given in Hertz. The Analytical Services of the Universidad de Alcalá performed the C, H, and N analyses using a LECO CHNS-932 microanalyzer, and recorded the mass spectra using an Agilent 6210 LC/MS TOF (Multimode source MM ESI/APCI) spectrometer in electrospray ionization mode. The outcomes of the hydrosilylation reactions were determined by GC chromatography in an Agilent GC-MS turbo system (5975-7820A model) equipped with an autoinjector. Purification by dialysis was carried out in water using a Float-A-Lyzer® G2 device (1 mL, Biotech Grade Cellulose Ester membrane with MWCO = 0.1-0.5 kDa) by repeated bathing of the samples in 500 mL of deionized water, at room temperature, and under constant stirring for 1.5 h. Chromatographic purifications were carried out using a GE Healthcare Column XK 16 (40 cm × 16 mm) packed with cross-linked dextran-epichlorohydrin polymer (Sephadex® G-10 purchased from Sigma-Aldrich) as the stationary phase and water as the only eluent.[25] The column was connected to a Shimadzu Liquid Chromatograph LC-9A pump in-line with a Rheodyne Manual Sample Injector 7725(i) equipped with a 5 mL loop. The injected samples were eluted with a set flow of 0.25 mL/min, measured at the outlet of the column, at room temperature and under a constant pressure of argon (0.25 bar).

Synthesis of [{1,3-bis(2,6-dimethyl-4-sodium sulfonatophenyl)imidazol-2-ylidene}(1,1,3,3-tetramethyl-1,3-divinyldisiloxane)platinum(0)] (2c): A commercial solution of Karstedt's catalyst (5.43 g, 3.83% in Pt, 1.07 mmol Pt) and imidazolium salt **1c** (486 mg, 1.06 mmol) were dissolved in dmso (15 mL) under argon at 0 ºC, sodium *tert*-butoxide (127 mg, 1.33 mmol) was then added, and the dark orange reaction mixture stirred for 2.5 h at room temperature in the absence of light. The mixture was filtered under argon through a pad of celite 545, concentrated at 60 ºC to half its initial volume under vacuum, and the resulting solution was then slowly added to a large stirring volume of THF (300 mL). The suspension formed was allowed to stir for 10-20 min at room temperature before filtration. After removal of the volatiles by warming the precipitate under vacuum (60 ºC, 6 h), **2c** was obtained in virtually quantitative yield, although the elemental analysis and NMR spectra indicated the presence of persistent dmso and THF. The trapped solvents were removed by dialysis in water to obtain complex **2c** as an orange solid, which was found to be soluble in water, methanol and dmso and insoluble in THF and diethyl ether. Yield: 0.63 g (70%). ^{1}H NMR (300 MHz, D_2O): δ 7.43 (s, 4H, *m*-Ar), 7.38 (s, 2H, Imz-H^{4,5}), 2.12 (s, 12H, *o*-*Me*Ar), 1.88 (d with ^{195}Pt satellites, $^{3}J_{H\text{-}H}$ = 11.5, $^{2}J_{Pt\text{-}H}$ = 51, 2H, C=CH_2), 1.68 (d with ^{195}Pt satellites, $^{3}J_{H\text{-}H}$ = 13.5, $^{2}J_{Pt\text{-}H}$ = 51, 2H, C=CH_2), 1.34 (t with ^{195}Pt satellites, $^{3}J_{H\text{-}H}$ = 12.0, $^{2}J_{Pt\text{-}H}$ = 61, 2H, Si-C*H*=C), 0.01 (s, 6H, SiMe_{eq}), –0.88 (s, 6H, SiMe_{ax}). ^{13}C NMR (75 MHz, D_2O): δ 180.3 (Imz-C^{2}), 142.6, 141.0, 137.0 and 125.4 (Ar), 124.0 (Imz-C^{4,5}), 41.7 (C=*C*H$_2$), 34.7 (Si-*C*H=C), 17.6 (*o*-*Me*Ar), 0.6 (SiMe_{eq}), –3.1 (SiMe_{ax}). ^{195}Pt NMR (64 MHz, D_2O): –5336. ESI-MS (negative ion, H_2O): *m/z* (%) 408.0549 (100%) $[M - 2Na]^{2-}$ (calcd 408.0581). Anal. Calc. for $C_{27}H_{41}N_2Na_2O_{9.5}PtS_2Si_2$ (**2c**·2.5H_2O): C, 35.76; H, 4.56; N, 3.09%. Found: C, 35.67; H, 4.62; N, 3.43%.

Synthesis of [{1,3-bis(2,4,6-trimethyl-3-sodium sulfonatophenyl)imidazol-2-ylidene}(1,1,3,3-tetramethyl-1,3-divinyldisiloxane)platinum(0)] (2d): Complex **2d** was obtained as described above for complex **2c**, starting from the commercial solution of Karstedt's catalyst (5.17 g, 3.83% in Pt, 1.02 mmol Pt), the imidazolium salt **1d** (491 mg, 1.01 mmol) and sodium *tert*-butoxide (121 mg, 1.26 mmol). Complex **2d** was isolated as an orange solid (870 mg, 97%), which was found to be soluble in water, methanol and dmso and insoluble in THF and diethyl ether, and was characterized as a mixture of two conformers in solution (***anti-*** and ***syn*-2d**, 50/50%). Residual dmso and THF in the solid could be removed by dialysis. Yield: 440 mg (49%). Conformer ***anti*-2d**: ^{1}H NMR (500 MHz, D_2O): δ 7.36 (s, 2H, Imz-H^{4,5}), 7.02 (s, 2H, *m*-Ar), 2.45 (s, 6H, *p*-*Me*Ar), 2.34 (s, 6H, *o*-*Me*Ar adjacent to SO_3^-), 2.02 (s, 6H, *o*-*Me*Ar), 2.00 (d, $^{3}J_{H\text{-}H}$ = 11.5, 1H, C=CH_2), 1.78 (d, $^{3}J_{H\text{-}H}$ = 11.5, 2H, C=CH_2), 1.59 (d, $^{3}J_{H\text{-}H}$ = 13.5, 1H, C=CH_2), 1.39-1.27 (m, 2H, Si-C*H*=C), 0.04 (s, 3H, SiMe_{eq}), 0.03 (s, 3H, SiMe_{eq}), –0.74 (s, 3H, SiMe_{ax}), –0.98 (s, 3H, SiMe_{ax}). ^{13}C NMR (75 MHz, D_2O): δ 182.0 (Imz-C^{2}), 139.2, 138.1, 138.0, 137.8, 134.8 and 132.2 (Ar), 124.2 (Imz-C^{4,5}), 42.0 (C=*C*H$_2$), 41.6 (C=*C*H$_2$), 34.4 (Si-*C*H=C), 34.3 (Si-*C*H=C), 22.4 (*p*-*Me*Ar), 17.6 (*o*-*Me*Ar), 16.7 (*o*-*Me*Ar adjacent to SO_3^-), 0.6 (SiMe_{eq}), –3.0 (SiMe_{ax}), –3.4 (SiMe_{ax}). Conformer ***syn*-2d**: ^{1}H NMR (500 MHz, D_2O): δ 7.35 (s, 2H, Imz-H^{4,5}), 7.00 (s, 2H, *m*-Ar), 2.44 (s, 6H, *p*-*Me*Ar), 2.31 (s, 6H, *o*-CH_3 adjacent to SO_3^-), 2.05 (s, 6H, *o*-*Me*Ar), 1.88 (d, $^{3}J_{H\text{-}H}$ = 11.5, 2H, C=CH_2), 1.68 (d, $^{3}J_{H\text{-}H}$ = 13.5, 2H, C=CH_2), 1.39-1.27 (m, 2H, Si-C*H*=C), 0.03 (s, 6H, SiMe_{eq}), –0.86 (s, 6H, SiMe_{ax}). ^{13}C NMR (75 MHz, D_2O): δ 181.9 (Imz-C^{2}), 139.3, 138.1, 138.0, 137.5, 135.0 and 132.0 (Ar), 124.2 (Imz-C^{4,5}), 41.7 (C=*C*H$_2$), 34.5 (Si-*C*H=C), 22.5 (*p*-*Me*Ar), 17.9 (*o*-*Me*Ar), 16.5 (*o*-*Me*Ar adjacent to SO_3^-), 0.5 (SiMe_{eq}), –3.0 (SiMe_{ax}). ^{195}Pt NMR (64 MHz, D_2O) for conformers ***anti-*** and ***syn*-2d**: δ –5342 and –5344. ESI-MS (negative ion, H_2O): *m/z* (%) 845.1548 (1%) [M –

2Na + H]$^-$ (calcd 845.1551), 422.0742 (100%) [M – 2Na]$^{2-}$ (calcd 422.0740). Anal. Calc. for $C_{29}H_{48}N_2Na_2O_{11}PtS_2Si_2$ (**2d**·4H_2O): C, 36.21; H, 5.03; N, 2.91%. Found: C, 36.02; H, 4.87; N, 3.30%.

Synthesis of [{1,3-bis(2,4,6-trimethyl-3-sodium sulfonatophenyl)imidazolin-2-ylidene}(1,1,3,3-tetramethyl-1,3-divinyldisiloxane)platinum(0)] (2e): Complex **2e** was obtained as described above for **2c**, starting from a commercial solution of Karstedt's catalyst (4.69 g, 3.83% in Pt, 0.921 mmol Pt), the imidazolinium salt **1e** (445 mg, 0.91 mmol) and sodium *tert*-butoxide (129 mg, 1.34 mmol). After precipitation in THF, the crude (550 mg) contained a 49/51% mixture of the desired complex **2e** and formamide **1e^F** (in turns, as a 65/35% mixture of *E*- and *Z*-isomers), which could not be separated by dialysis. Removal of the formamide was accomplished by GPC in Sephadex® G10 using deionized water as the eluent. Complex **2e** was obtained as a light yellow solid, which was found to be soluble in water, methanol and dmso and insoluble in THF and diethyl ether, and was characterized as a mixture of *two* conformers in solution (***anti-*** and ***syn*-2e**, 47/53%). Yield: 150 mg (18%). Conformer ***anti*-2e**: ^{1}H NMR (300 MHz, D_2O): δ 6.87 (s, 2H, *m*-Ar), 3.97 (s, 4H, Imz-H^{4,5}), 2.63 (s, 6H, *o*-*Me*Ar adjacent to SO_3^-), 2.37 (s, 6H, *p*-*Me*Ar), 2.19 (s, 6H, *o*-*Me*Ar), 2.06 (d, $^3J_{H\text{-}H}$ = 11.7, 1H, C=CH_2), 1.78 (apparent t, $^3J_{H\text{-}H}$ = 12.0, 2H, C=CH_2), 1.57 (d, $^3J_{H\text{-}H}$ = 12.0, 1H, C=CH_2), 1.26 (apparent t, $^3J_{H\text{-}H}$ = 12.0, 2H, Si-C*H*=C), –0.01 (s, 3H, SiMe_{eq}), –0.02 (s, 3H, SiMe_{eq}), –0.76 (s, 3H, SiMe_{ax}), –1.08 (s, 3H, SiMe_{ax}). ^{13}C NMR (75 MHz, D_2O): δ 211.1 (Imz-C^2), 139.4, 139.2, 139.1, 138.6, 138.5, 136.8, 135.8, 135.7 and 132.4 (Ar for ***anti-*** and ***syn*-2e**), 51.1 (Imz-C^{4,5}), 42.7 (C=*C*H_2), 41.8 (C=*C*H_2), 34.8 (Si-*C*H=C), 22.2 (*p*-*Me*Ar), 17.6 (*o*-*Me*Ar), 16.5 (*o*-*Me*Ar adjacent to SO_3^-), 0.5 (SiMe_{eq}), 0.4 (SiMe_{eq}), –3.0 (SiMe_{ax}), –3.6 (SiMe_{ax}). Conformer ***syn*-2e**: ^{1}H NMR (300 MHz, D_2O): δ 6.80 (s, 2H, *m*-Ar), 3.97 (s, 2H, Imz-H^{4,5}), 3.84 (s, 2H, Imz-H^{4,5}), 2.54 (s, 6H, *o*-*Me*Ar adjacent to SO_3^-), 2.34 (s, 6H, *p*-*Me*Ar), 2.20 (s, 6H, *o*-*Me*Ar), 1.89 (d, $^3J_{H\text{-}H}$ = 12.0, 2H, C=CH_2), 1.66 (d, $^3J_{H\text{-}H}$ = 13.5, 2H, C=CH_2), 1.26 (apparent t, $^3J_{H\text{-}H}$ = 12.0, 2H, Si-*C*H=C), –0.03 (s, 6H, SiMe_{eq}), –0.92 (s, 6H, SiMe_{ax}). ^{13}C NMR (75 MHz, D_2O): δ 211.0 (Imz-C^2), 139.4, 139.2, 139.1, 138.6, 138.5, 136.8, 135.8, 135.7 and 132.4 (Ar for ***anti-*** and ***syn*-2e**), 51.1 (Imz-C^{4,5}), 42.2 (C=*C*H_2), 34.8 (Si-*C*H=C), 22.4 (*p*-*Me*Ar), 18.0 (*o*-*Me*Ar), 16.3 (*o*-*Me*Ar adjacent to SO_3^-), 0.6 (SiMe_{eq}), –3.1 (SiMe_{ax}). ^{195}Pt NMR (64 MHz, D_2O) for conformers ***anti-*** and ***syn*-2e**: δ –5372 and –5373. ESI-MS (negative ion, H_2O): *m/z* (%) 423.0809 (100%) [M – 2Na]$^{2-}$ (calcd 423.0818). Anal. Calc. for $C_{29}H_{48}N_2Na_2O_{10}PtS_2Si_2$ (**2e**·3H_2O): C, 36.82; H, 5.11; N, 2.96%. Found: C, 36.52; H, 5.03; N, 3.27 %.

Synthesis of [{1-(3-sodium sulfonatepropyl)-3-(2,4,6-trimethylphenyl)imidazol-2-ylidene} (diallylether)platinum(0)] (3a): Complex [Pt(η^2-nbe)$_3$] (240 mg, 0.502 mmol) was dissolved in AE (diallyl ether, 0.48 g, 4.9 mmol) in a Schlenk tube, and allowed to stir at room temperature for 20 min in the absence of light. In another Schlenk flask, the free carbene was generated by reaction of the imidazolium salt **1a** (150 mg, 0.486 mmol) with sodium *tert*-butoxide (58 mg, 0.60 mmol) in dmso (6 mL) for 5 min at room temperature. The free carbene was then slowly added to the platinum precursor solution via a cannula, and the reaction mixture was allowed to stir for 3 h at room temperature in the absence of light. The resulting solution was filtered through a pad of celite 545, and then concentrated to half its initial volume under vacuum. Addition of the solution over to a large stirring volume of THF (100 mL) resulted in precipitation of complex **3a**, which was filtered, washed with THF (2 × 25 mL), and dried under vacuum. Compound **3a** was obtained as a red solid, which was found to be soluble in dmso and water, and insoluble in THF and acetone. Yield: 298 mg (98%). ^{1}H-NMR (300 MHz, dmso-d_6): δ 7.64 and 7.31 (2 × d, $^3J_{H\text{-}H}$ = 1.8, 2H, Imz-H^{4,5}), 6.86 (s, 2H, *m*-Ar), 4.02 (t, $^3J_{H\text{-}H}$ = 6.9, 2H, NCH_2), 3.92 (dd with ^{195}Pt satellites, $^3J_{H\text{-}H}$ = 12.4, $^2J_{H\text{-}H}$ = 3.2, $^3J_{Pt\text{-}H}$ = 43, 2H, OCH_{eq}), 2.48 (m, 2H, CH_2S), 2.31–2.27 (m, 2H, C-C*H*=C), 2.19 (s, 3H, *p*-*Me*Ar), 2.00–1.94 (m, 2H, $CH_2CH_2CH_2$), 1.94 (s, 6H, *o*-*Me*Ar), 1.62 (dd with ^{195}Pt satellites, $^3J_{H\text{-}H}$ = 8.2, $^2J_{H\text{-}H}$ = 1.8, $^2J_{Pt\text{-}H}$ = 50, 2H, C=CH_2), 1.62 (t, $^3J_{H\text{-}H}$ = 11.9, 2H, OCH_{ax}), 1.18 (dd with ^{195}Pt satellites, $^3J_{H\text{-}H}$ = 9.6, $^2J_{H\text{-}H}$ = 1.8, $^2J_{Pt\text{-}H}$ = 60, 2H, C=CH_2). ^{1}H-NMR (300 MHz, D_2O): δ 7.33 and 6.79 (2 × d, $^3J_{H\text{-}H}$ = 1.8, 2H, Imz-H^{4,5}), 6.59 (s, 2H, *m*-Ar), 3.99 (t, $^3J_{H\text{-}H}$ = 6.3, 2H, NCH_2), 3.86 (broad d with ^{195}Pt satellites, $^3J_{H\text{-}H}$= 9.2, 2H, $^3J_{Pt\text{-}H}$ = 44, OCH_{eq}), 2.70–2.64 (m, 2H, CH_2S), 2.53–2.36 (m, 2H, C-C*H*=C), 2.04 (apparent q, $^3J_{H\text{-}H}$ = 7.5, 2H, $CH_2CH_2CH_2$), 1.91 (s, 3H, *p*-*Me*Ar), 1.76 (s, 6H, *o*-*Me*Ar), 1.67 (d, $^3J_{H\text{-}H}$ = 9.3, 2H, C=CH_2), 1.65 (t, $^3J_{H\text{-}H}$= 13.2, 2H, OCH_{ax}), 1.21 (broad d with ^{195}Pt satellites, $^3J_{H\text{-}H}$= 9.7, $^2J_{Pt\text{-}H}$= 52, 2H, C=CH_2). ^{13}C NMR (50 MHz, D_2O): δ 181.3 (Imz-C^2), 136.9 (*p*-Ar), 135.8 (*ipso*-Ar), 134.4 (*o*-Ar), 127.2 (*m*-Ar), 121.7 and 120.3 (Imz-C^{4,5}), 68.2 (OCH_2), 47.7 (NCH_2), 47.1 (*C*H_2S), 46.3 (C=*C*H_2), 31.5 (C-*C*H=C), 24.4 ($CH_2CH_2CH_2$), 19.4 (*p*-*Me*Ar), 16.4 (*o*-*Me*Ar). ^{195}Pt NMR (64 MHz, dmso-d_6): δ –5597. ESI-MS (negative ion, H_2O): *m/z* (%) 600.1312 (100%) [M – Na]$^-$ (calcd 600.1501), 502.0583 (2%) [M – Na – AE]$^-$ (calcd 502.0771). Anal. Calcd for $C_{21}H_{34}N_2NaO_{6.5}PtS$ (**3a**·2.5H_2O): C, 37.72; H, 5.13; N, 4.19%. Found: C, 37.57; H, 5.09; N, 4.02%.

Synthesis of [{1,3-bis(2,6-diisopropyl-4-sodium sulfonate-phenyl)imidazol-2-ylidene} (diallylether)platinum(0)] (3b): Complex **3b** was obtained as described above for **3a**, starting from [Pt(η^2-nbe)$_3$] (239 mg, 0.500 mmol), AE (0.48 mL, 4.9 mmol), the imidazolium salt **1b** (281 mg, 0.492 mmol), sodium *tert*-butoxide (55 mg, 0.57 mmol), and dmso (6 mL). After filtration of the mixture through a pad of celite 545 at the end of the reaction, the solvent was partially removed under vacuum up to a remaining volume of 2–3 mL, and the complex was then precipitated with THF (60 mL), separated by filtration, washed with THF (3 × 20 mL), and dried under vacuum. Complex **3b** was isolated as a beige solid, and was found to be soluble in dmso and water, and insoluble in THF and acetone. Yield: 432 mg (99%). ^{1}H NMR (500 MHz, dmso-d_6): δ 7.73 (s, 2H, Imz-H^{4,5}), 7.41 (s, 4H, *m*-Ar), 3.77 (dd with ^{195}Pt satellites, $^3J_{H\text{-}H}$ = 12.0, $^2J_{H\text{-}H}$ = 3.1, $^3J_{Pt\text{-}H}$ = 44, 2H, OCH_{eq}), 2.89 (hept, $^3J_{H\text{-}H}$ = 6.8, 4H, C$H(CH_3)_2$), 2.30–2.23 (m, 2H, C-C*H*=C), 1.40 (t, $^3J_{H\text{-}H}$ = 11.3, 2H, OCH_{ax}), 1.26 (dd with ^{195}Pt satellites, $^3J_{H\text{-}H}$ = 8.3, $^2J_{H\text{-}H}$ = 3.1, $^2J_{Pt\text{-}H}$ = 59, 2H, C=CH_2), 1.09 (d, $^3J_{H\text{-}H}$ = 6.9, 12H, CH(CH_3)$_2$), 1.06 (d, $^3J_{H\text{-}H}$ = 7.1, 12H, CH(CH_3)$_2$), 0.76 (dd with ^{195}Pt satellites, $^3J_{H\text{-}H}$ = 10.4, $^2J_{H\text{-}H}$ = 0.8, $^2J_{Pt\text{-}H}$ = 58, 2H, C=CH_2). ^{1}H NMR (500 MHz, D_2O): δ 7.55 (s, 4H, *m*-Ar), 7.54

(s, 2H, Imz-H^{4,5}), 3.78 (dd with ^{195}Pt satellites, $^{3}J_{H\text{-}H}$ = 12.2, $^{2}J_{H\text{-}H}$ = 3.6, $^{3}J_{Pt\text{-}H}$= 48, 2H, OCH_{eq}), 2.85 (hept, $^{3}J_{H\text{-}H}$ = 7.7, 4H, CH(CH$_3$)$_2$), 2.36–2.28 (m, 2H, C-CH=C), 1.51 (t, $^{3}J_{H\text{-}H}$ = 11.4, 2H, OCH_{ax}), 1.41 (d, $^{3}J_{H\text{-}H}$= 6.9, 2H, C=CH_2), 1.13 (d, $^{3}J_{H\text{-}H}$= 6.9, 12H, CH(CH_3)$_2$), 1.04 (d, $^{3}J_{H\text{-}H}$= 6.9, 12H, CH(CH_3)$_2$), 0.89 (dd with ^{195}Pt satellites, $^{3}J_{H\text{-}H}$= 10.8, $^{2}J_{H\text{-}H}$= 0.9, $^{2}J_{Pt\text{-}H}$= 52, 2H, C=CH_2). ^{13}C NMR (75 MHz, dmso-d_6): δ 184.4 (Imz-C^2), 148.1 (*p*-Ar), 144.3 (*o*-Ar), 136.1 (*ipso*-Ar), 124.2 (with ^{195}Pt satellites, $^{3}J_{Pt\text{-}C}$ = 41, Imz-C^{4,5}), 120.0 (*m*-Ar), 67.9 (with ^{195}Pt satellites, $^{2}J_{Pt\text{-}C}$ = 32, OCH$_2$), 46.3 (with ^{195}Pt satellites, $^{1}J_{Pt\text{-}C}$= 142, C=CH$_2$), 31.2 (with ^{195}Pt satellites, $^{1}J_{Pt\text{-}C}$ = 195, C-CH=C), 27.5 (*C*H(CH$_3$)$_2$), 24.7 (CH(*C*H$_3$)$_2$), 21.7 (CH(*C*H$_3$)$_2$). ^{195}Pt NMR (64 MHz, dmso-d_6): δ –5572. ESI-MS (negative ion, H_2O): *m/z* (%) 840.2319 (3%) [M – 2Na + H]$^-$ (calcd 840.2321), 419.6122 (100%) [M – 2Na]$^{2-}$ (calcd 419.6124). Anal. Calcd for $C_{33}H_{53}N_2Na_2O_{11.5}PtS_2$ (**3b**·4.5H_2O): C, 40.99; H, 5.52; N, 2.90%. Found: C, 41.07; H, 5.33; N, 2.76%.

Synthesis of [{1,3-bis(2,6-dimethyl-4-sodium sulfonatophenyl)imidazol-2-ylidene}(diallylether) platinum(0)] (3c): The platinum carbene **3c** was obtained as described above for **3a**, starting from [Pt(η^2-nbe)$_3$] (190 mg, 0.398 mmol), AE (0.43 g, 4.4 mmol), imidazolium salt **1c** (180 mg, 0.393 mmol), sodium *tert*-butoxide (39 mg, 0.406 mmol), and dmso (5 mL). In this case the reaction mixture was stirred 15 min before the standard work up. Complex **3c** was isolated as an orange solid, and was found to be soluble in dmso, methanol and water, and insoluble in THF and diethyl ether. The solid obtained after precipitation with THF was spectroscopically pure (267 mg, 88%), but it was chromatographed (GPC in Sephadex® G10, with deionized water as eluent) in order to isolate samples with accurate elemental analyses. Although analytically pure samples were obtained using this purification procedure, partial decomposition of the complex occurred on the column. Yield: 94 mg (31%). ^{1}H NMR (300 MHz, D_2O): δ 7.44 (s, 4H, *m*-Ar), 7.40 (s, 2H, Imz-H^{4,5}), 3.80 (dd with ^{195}Pt satellites, $^{3}J_{H\text{-}H}$ = 12.3, $^{2}J_{H\text{-}H}$ = 3.3, $^{3}J_{Pt\text{-}H}$ = 45, 2H, OCH_{eq}), 2.49-2.32 (m, 2H, C-CH=C), 2.11 (s, 12H, *o*-*Me*Ar), 1.52 (dd with ^{195}Pt satellites, $^{3}J_{H\text{-}H}$ = 8.4, $^{2}J_{H\text{-}H}$ = 2.1, $^{2}J_{Pt\text{-}H}$ = 55, 2H, C=CH_2), 1.39 (t, $^{3}J_{H\text{-}H}$ = 11.7, 2H, OCH_{ax}), 1.03 (dd with ^{195}Pt satellites, $^{3}J_{H\text{-}H}$ = 10.5, $^{2}J_{H\text{-}H}$ = 2.1, $^{2}J_{Pt\text{-}H}$ = 62, 2H, C=CH_2). ^{13}C NMR (75 MHz, D_2O): δ 182.1 (Imz-C^2), 142.3, 141.2, 137.2 and 124.8 (Ar), 123.0 (with ^{195}Pt satellites, $^{3}J_{Pt\text{-}C}$ = 38, Imz-C^{4,5}), 69.0 (with ^{195}Pt satellites, $^{2}J_{Pt\text{-}C}$= 32, OCH$_2$), 47.3 (with ^{195}Pt satellites, $^{1}J_{Pt\text{-}C}$ = 139, C=CH$_2$), 33.1 (with ^{195}Pt satellites, $^{1}J_{Pt\text{-}C}$ = 186, C-CH=C), 17.5 (*o*-*Me*Ar). ^{195}Pt NMR (64 MHz, dmso-d_6): δ –5562. ESI-MS (negative ion, H_2O): *m/z* (%) 363.5502 (100%) [M – 2Na]$^{2-}$ (calcd 363.5500). Anal. Calc. for $C_{25}H_{36}N_2Na_2O_{11}PtS_2$ (**3c**·4H_2O): C, 35.50; H, 4.29; N, 3.31%. Found: C, 35.13; H, 4.11; N, 3.71%.

Synthesis of [{1,3-bis(2,4,6-trimethyl-3-sodium sulfonatophenyl)imidazol-2-ylidene} (diallylether)platinum(0)] (3d). Complex **3d** was obtained as described above for **3a**, starting from [Pt(η^2-nbe)$_3$] (335 mg, 0.701 mmol), imidazolium salt **1d** (340 mg, 0.700 mmol), AE (0.29 g, 3.0 mmol), sodium *tert*-butoxide (81 mg, 0.84 mmol), and dmso (6 mL). Compound **3d** was obtained as a red solid, and was found to be soluble in water, methanol and dmso, and insoluble in THF, diethyl ether and acetone. After precipitation of the complex in THF (570 mg), minor impurities (NMR and e.a. evidence) could not be removed, and all attempt to purify it resulted in deterioration and a higher content of impurities (see Electronic Supplementary Information). ^{1}H NMR (300 MHz, D_2O): δ 7.34 (s, 2H, *m*-Ar), 7.01 (s, 2H, Imz-H^{4,5}), 3.78 (broad d with ^{195}Pt satellites, $^{3}J_{H\text{-}H}$ = 12.3, $^{3}J_{Pt\text{-}H}$ = 43, 2H, OCH_{eq}), 2.42 (s, 6H, *p*-*Me*Ar), 2.24 (s and m, 8H, *o*-*Me*Ar adjacent to SO_3^- and C-CH=C overlapping), 2.00 (s, 6H, *o*-*Me*Ar), 1.49-1.40 (m, 4H, C=CH_2 and OCH_{ax} overlapping), 1.00 (broad d with ^{195}Pt satellites, $^{3}J_{H\text{-}H}$ = 10.2, $^{2}J_{Pt\text{-}H}$ = 59, 2H, C=CH_2). ^{1}H NMR (300 MHz, dmso-d_6): $\underline{\delta}$ 7.49 (s, 2H, Imz-H^{4,5}), 6.86 (s, 2H, *m*-Ar), 3.71 (broad d,$^{3}J_{H\text{-}H}$ = 12.0, 2H, OCH_{eq}), 2.53-2.49 (*p*-*Me*Ar and residual dmso overlapping), 2.31 (s and broad s, 8H, *o*-*Me*Ar adjacent to SO_3^- and C-CH=C overlapping), 2.00 (s, 6H, *o*-*Me*Ar), 1.40-1.30 (m, 4H, C=CH_2 and OCH_{ax} overlapping), 0.93 (broad d, $^{3}J_{H\text{-}H}$ = 8.1, 2H, C=CH_2). ^{13}C NMR (50 MHz, dmso-d_6): δ 184.3 (Imz-C^2), 143.9, 137.8, 135.9, 134.4, 134.0 and 130.4 (Ar), 123.4 (with ^{195}Pt satellites, $^{3}J_{Pt\text{-}C}$ = 39, Imz-C^{4,5}), 68.8 (with ^{195}Pt satellites, $^{2}J_{Pt\text{-}C}$= 32, OCH$_2$), 46.8 (with ^{195}Pt satellites, $^{1}J_{Pt\text{-}C}$ = 142, C=CH$_2$), 31.6 (with ^{195}Pt satellites, $^{1}J_{Pt\text{-}C}$ = 191, C-CH=C), 23.1 (*p*-*Me*Ar), 17.7 (*o*-*Me*Ar), 16.5 (*o*-*Me*Ar adjacent to SO_3^-). ESI-MS (negative ion, CH_3OH): *m/z* (%) 377.5666 (100%) [M – 2Na]$^{2-}$ (calcd 377.5657), 756.1395 (5%) [M – 2Na + H]$^-$ (calcd 756.1385). Anal. Calcd for $C_{27}H_{43}N_2Na_2O_{12.5}PtS_2$ (**3d**·5.5H_2O): C, 36.00; H, 4.81; N, 3.11%. Found: C, 35.36; H, 4.10; N, 3.40%.

Formation and identification of [{1,3-bis(2,4,6-trimethyl-3-sodium sulfonatophenyl)imidazolin-2-ylidene} (diallylether)platinum(0)] (3e): The formation reaction of complex **3e** was performed as described above for **3a**, starting from [Pt(η^2-nbe)$_3$] (71 mg, 0.15 mmol), imidazolinium salt **1e** (51 mg, 0.10 mmol), AE (86 mg, 0.88 mmol), sodium *tert*-butoxide (15 mg, 0.16 mmol), and dmso (2 mL). Compound **3e** was obtained as a dark orange solid (63 mg) together with impurities, including formamide **1e^F**, which could not be removed as all purification attempts resulted in marked decomposition of the platinum complex. Nevertheless, complex **3e** was identified in the crude reaction mixture by NMR and MS (see Electronic Supplementary Information). ^{1}H NMR (500 MHz, D_2O): δ 6.97 (s, 2H, *m*-Ar), 4.03 (s, 4H, Imz-H^{4,5}), 3.78 (dd, $^{3}J_{H\text{-}H}$ = 12.5, $^{2}J_{H\text{-}H}$ = 3.5 Hz, 2H, OCH_{eq}), 2.56 and 2.53 (2 × s, 6H, *o*-*Me*Ar adjacent to SO_3^-), 2.42 (s, 6H, *p*-*Me*Ar), 2.39-2.36 (m, 2H, C-CH=C), 2.27 and 2.25 (2 × s, 6H, *o*-*Me*Ar), 1.55 (dd, $^{3}J_{H\text{-}H}$ =8.5, $^{2}J_{H\text{-}H}$ = 2.0, 2H, C=CH_2), 1.34-1.28 (m, 2H, OCH_{ax}), 1.16-1.08 (m, 2H, C=CH_2). ^{13}C NMR (125 MHz, D_2O): δ 139.5, 139.0, 138.9, 138.6, 136.5, 135.99, 135.96 and 132.1 (Ar), 68.85 and 68.79 (OCH$_2$), 50.8 (Imz-C^{4,5}), 47.86, 47.80 and 47.76 (C=CH_2), 33.8 and 33.7 (C-CH=C), 22.2 (*p*-*Me*Ar), 17.59 and 17.55 (*o*-*Me*Ar), 16.44 and 16.39 (*o*-*Me*Ar adjacent to SO_3^-), Imz-C^2 not observed. ESI-MS (negative ion, H_2O): *m/z* (%) 378.5739 (100%) [M – 2Na]$^{2-}$ (calcd 378.5735).

Synthesis of the formamide N,N'-bis(2,4,6-trimethyl-3-sodium sulfonatephenyl)-N-formylethylenediamine 1e^F: In a 10 mL Schlenk flask, the imidazolinium salt **1e** (150 mg, 0.31 mmol) and sodium *tert*-butoxide (30 mg, 0.31 mmol) were dissolved in dmso (2 mL) under argon at room temperature,

and the yellow reaction mixture was stirred for 30 min. The mixture was then evaporated to dryness under vacuum. According to its NMR data and elemental analysis, the resulting solid (200 mg) retained dmso and water molecules, and the ^{1}H NMR spectrum showed the presence of the formamide in the *E*- and *Z*-conformations in a 60/40% ratio. ^{1}H NMR (500 MHz, D_2O) for the *E*- and *Z*-conformers: δ 8.23 and 7.87 (2 × s, 1H, C*H*O), 7.044, 7.038, 6.83 and 6.82 (4 × s, 2H, *m*-Ar), 3.84-3.49 and 3.06-2.92 (2 × m, 4H, CH_2CH_2), 2.470, 2.467 and 2.35 (3 × s, 6H, *p*-*Me*Ar), 2.34, 2.33 and 2.29 (3 × s, 6H, *o*-*Me*Ar adjacent to SO_3^-), 2.02, 1.96 and 1.95 (3 × s, 6H, *o*-*Me*Ar). ^{13}C NMR (125 MHz, D_2O) for the *E*- and *Z*-conformers: δ 166.6 and 165.3 (*C*HO), 143.3, 143.0, 139.49, 139.46, 139.20, 139.19, 139.0, 138.2, 137.8, 137.7, 136.6, 135.7, 134.5, 134.4, 132.81, 132.79, 132.75, 132.73, 132.4, 132.35, 132.28, 131.2, 129.2 and 129.1 (Ar), 49.6, 46.0, 45.6 and 45.0 (*C*H_2*C*H_2), 22.20, 22.18 and 21.8 (*p*-*Me*Ar), 17.5, 17.4, 17.33 and 17.28 (*o*-*Me*Ar), 16.3, 16.06, 16.05 and 15.97 (*o*-*Me*Ar adjacent to SO_3^-). ESI-MS (negative ion, H_2O): *m/z* (%) 505.1094 (13%) $[M - Na]^-$ (calcd 505.1085), 483.1272 (9%) $[M - 2Na + H]^-$ (calcd 483.1265), 241.0609 (100%) $[M - 2Na]^{2-}$ (calcd 241.0596). Anal. Calc. for $C_{22}H_{39}N_2Na_2O_{12.5}S_{2.5}$ (**1e**^{F}·0.5dmso·5H_2O): C, 40.18; H, 5.98; N, 4.26%. Found: C, 39.56; H, 5.37; N, 4.33%.

General Procedure for the Hydrosilylation of Alkynes in Water. In a typical experiment, the alkyne (1.0 mmol), triethylsilane (1.1 mmol), and the platinum precatalyst (0.1 mol% [Pt], 1 μmol) were combined under argon in an ampoule equipped with a PTFE plug valve, together with water (V_{Total} = 3.0 mL). The tube was sealed and the mixture stirred at 30 °C for 6 h. The reaction mixture was extracted with dichloromethane (for PhC≡CH) or diethyl ether (for Me_3SiC≡CH). Conversions and selectivities were determined by analysis of the organic extracts by GC-MS (injection volume of 1 μL; naphthalene as internal standard), using an HP-5MS capillary column (30 m × 0.25 mm i.d.; 0.25 μm df; 95% dimethylpolysiloxane) under the following conditions: time delay: 1.80 min; injector and detector temperatures: 250 °C and 230 °C, respectively; oven temperature program: 34 or 50 ˚C for 5 or 0 min, 10˚C/min ramp, 220 ºC or 230˚C for 0 or 2 min for Me_3SiC≡CH or PhC≡CH, respectively. The catalytic reactions were performed at least in triplicate, and the reproducibility of the conversions measured is estimated at ±5%. The absence of Pt nanoparticles formed during the catalysis was confirmed by TEM using samples of the aqueous solutions inspected at the end of the reactions performed with **3b**.

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Novel water-soluble (NHC)Pt(0)(1,6-diene) complexes are presented, along with details of their preparation, stability, and use as catalysts for the hydrosilylation of acetylenes in water.