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Sulfonated Water-Soluble N-Heterocyclic Carbene Silver(I) Complexes: Behavior in Aqueous Medium and as NHC-Transfer Agents to Platinum(II)

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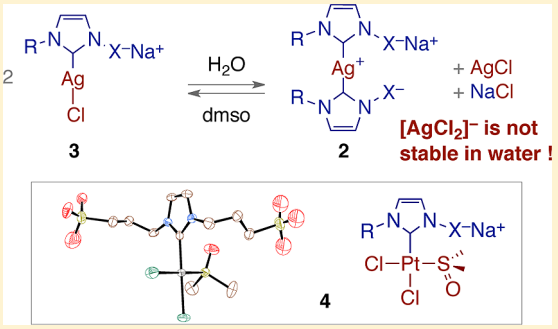
Supporting Information

ABSTRACT: This report describes the synthesis of water-soluble silver(I) and platinum(II) complexes bearing sulfonated mono- or dianionic N-heterocyclic carbene ligands. Thus, treatment of the corresponding zwitterionic imidazolium derivative with silver(I) oxide in water afforded the light-sensitive bis(carbene) complexes Ag[Ag(NHC)$_2$] (**2**$^{Ag+}$), which were transformed into the stable salts Na[Ag(NHC)$_2$] (**2**) by addition of sodium chloride. In contrast, the same reaction in dmso afforded mono(carbenes) of general formula Na[AgCl(NHC)] (**3**). The solvent-dependence of the reaction product can be rationalized on the basis of the equilibrium [AgCl$_2$]$^-$ ↔ AgCl + Cl$^-$. The precipitation of silver chloride is more favored in protic solvents than in aprotic solvents such as dmso, thus explaining the formation of bis(carbenes) in water. The formation of silver chloride may also promote the hydrolysis of silver NHC complexes under some conditions. The water-soluble platinum(II) complexes Na[PtCl$_2$(dmso)(NHC)] were synthesized by using either mono(carbene) silver complexes **3** as carbene-transfer agents or by direct metalation of the imidazolium salt with *cis*-[PtCl$_2$(dmso)$_2$] in the presence of NaHCO$_3$ as base. The (NHC)Pt(II) complexes were tested as catalysts for the hydration of alkynes in the aqueous phase and found to be active in neat water without the need for acidic cocatalysts.



INTRODUCTION

In terms of coordination versatility and stability, N-heterocyclic carbenes (NHCs) have proven to be a superb class of ancillary ligands in modern day organometallic chemistry.[1,2] In particular, those derived from imidazole are characterized by their very robust bonds to metals and their strong σ-donor capabilities,[3] forming excellent catalysts for a broad number of homogeneous processes.[4] Applications outside catalysis have led to recent developments in the fields of medicinal, luminescent, or functional materials.[5] The advantages of using water-soluble metal complexes for some of these applications are evident, and a convenient way to render metal NHC complexes water-soluble involves the attachment of hydrophilic substituents to the NHC ligand (sulfonates, carbonates, ammonium groups, sugar moieties, polyethers, etc.).[6] Herrmann and co-workers published the first examples of such water-soluble NHC complexes in a patent filed in 1995.[7] Several years later, Özdemir and co-workers reported the synthesis of 2,3-dimethylfuran catalyzed by a water-soluble NHC ruthenium catalyst.[8] In the past few years, new water-soluble NHC metal complexes have been reported as catalysts in aqueous-phase processes, including ruthenium complexes in olefin metathesis,[9] allylic alcohol isomerizations,[10] or acetophenone hydrogenations,[11] palladium complexes in cross-coupling reactions,[12,13] gold complexes in alkyne hydrations,[14−16] iridium complexes in transfer hydrogenations,[17] or copper complexes in click reactions.[18] Two recent reviews concerning the synthesis and applications of water-soluble NHC transition-metal complexes in catalysis have appeared in the last few months.[19]

Platinum(II) complexes containing conventional monodentate[20−23] or chelating[23,24] NHC ligands have proven to be useful in a variety of catalytic processes in organic solvents, such as for the diboration of unsaturated molecules,[25] tandem hydroboration−cross coupling,[26] or reductive cyclization of diines and enines,[27] and also as metal-based chemotherapeutic agents.[28] However, platinum complexes containing hydrophilic NHC ligands were unknown until recently, when we reported the synthesis of water-soluble (NHC)Pt(0) complexes that could be used as recoverable catalysts for the hydrosilylation of alkynes in water at room temperature.[29]

Although the applications of water-soluble NHC complexes are progressing rapidly, there is as yet little information available concerning basic aspects of the chemical reactivity of these complexes in water, including the limits of the hydrolytic stability of the metal−NHC bonds. However, water offers exceptional chemical reactivity due to its unique properties, such as its ability to solvate salts and polar compounds or its high dielectric constant. Our aim with this work was to undertake a study of water-soluble NHC platinum complexes and their aqueous-phase chemical reactivity. In this first report,

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we discuss the synthesis of water-soluble complexes of silver(I) and platinum(II) with the sulfonated NHC ligands **a**–**e** shown in Figure 1. The platinum(II) complexes have been tested in

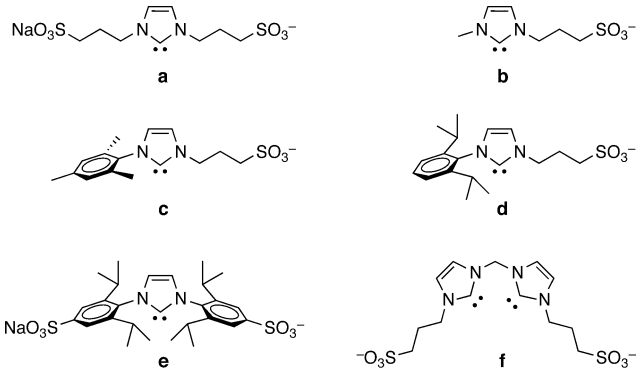


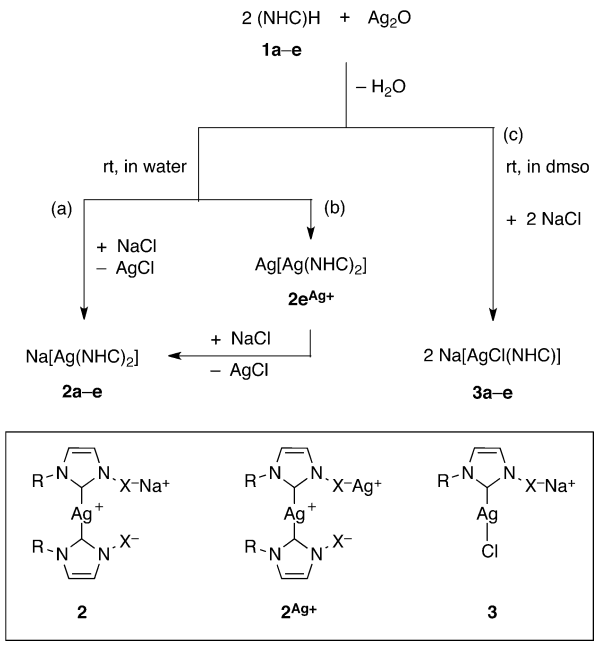
Figure 1. Sulfonate NHC ligands used in this work.

the catalytic hydration of alkynes in aqueous phase. Special emphasis has been paid to understanding the effects of water on the formation of silver(I) NHC complexes.

RESULTS AND DISCUSSION

Synthesis and Characterization of Mono- and Bis-(carbene) Silver(I) Complexes. The preparation of water-soluble NHC Pt(II) complexes was initially attempted by way of silver intermediates. Silver NHC complexes are excellent agents for the transfer of carbenes to a variety of other metals in straightforward reactions and, at the same time, are readily synthesized by treating imidazolium salts with silver(I) oxide.[30−33] To this end, complexes **2b**–**d** of general formula $Na[Ag(NHC)_2]$ (Scheme 1a) were prepared by the procedure reported in the literature based on the addition of sodium chloride to a mixture of silver(I) oxide and the corresponding imidazolium salt **1b**–**d** in water.[15,28] The new complex **2e** was

Scheme 1. Formation of Bis- (2) and Mono(carbene) (3) Complexes of Silver(I) with Sulfonated NHC Ligands

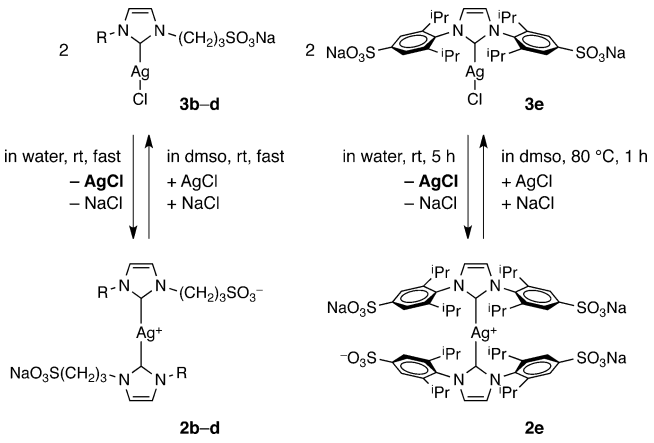


similarly obtained starting from the imidazolium **1e**.[13] As discussed below, transformation of imidazolium salt **1a** into complex **2a** invariably stopped when the molar ratio of both compounds reached a value of approximately 40−60%. The role played by the sodium halide is outlined in Scheme 1b. Imidazolium derivatives **1** are zwitterionic compounds, with the cationic charge internally balanced by one sulfonate. As such, their deprotonation with silver oxide results in compounds $\mathbf{2}^{Ag+}$, which contain an argentate anion $[Ag(NHC)_2]^-$ and a *naked* Ag^+ counterion. The latter is replaced by Na^+ upon addition of sodium chloride. This pathway has been demonstrated by the stepwise isolation of compounds $\mathbf{2e}^{Ag+}$ and **2e**, whose structures have been confirmed by X-ray diffraction studies (vide infra). The sensitivity of the resulting compound to light is significantly affected by the nature of the cation. Thus, the darkening of $\mathbf{2e}^{Ag+}$ in the presence of light is appreciable in the solid state as well as in solution, whereas the sodium salt **2e** is stable for an indeterminate period of time under both conditions.

Mono(carbene) complexes with sulfonated NHC ligands of general formula $[AgX(NHC)]^-$ were previously unknown. In the above procedure to synthesize bis(carbene) complexes **2**, NaCl was added after formation of the $Ag[Ag(NHC)_2]$ ($\mathbf{2}^{Ag+}$) intermediates. It might be reasonable to infer that the precipitation of silver chloride after the addition of NaCl could preclude the rearrangement required to afford mono-(carbene) complexes. However, the fact is that bis(carbene) complexes were likewise obtained when NaCl was added to the imidazolium salts **1** in water before silver oxide. Instead, the solvent was found to be fundamental in determining the final compound, with the mono(carbene) complexes **3a**–**e** being obtained in good yields (>80%) when the reactions were performed in dimethyl sulfoxide instead of water (Scheme 1c).

As would be expected, mono(carbenes) **3b**–**e** evolved into the corresponding bis(carbenes) **2b**–**e** in water at room temperature (Scheme 2). At this point it is important to note

Scheme 2. Solvent-Dependent and Reversible Transformation of Mono- (3) into Bis(carbene) Silver(I) Complexes (2)



that the conversion of mono- into bis(carbenes) was accompanied by the precipitation of silver chloride instead of the usual formation of the ion $[AgCl_2]^-$ in solution. The conversion **3** → **2** was found to be reversible, with complexes **2b**–**e** affording mono(carbenes) **3b**–**e** in the presence of AgCl and NaCl when water was replaced by dmso. The trans-

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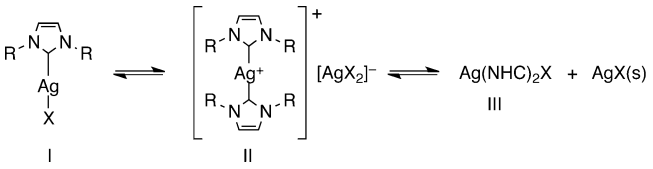
formations were fast in both directions at room temperature except for the complexes with the most sterically demanding NHC ligand (**2e** and **3e**). These results unequivocally show that the outcome of the reaction of imidazolium salts **1** with Ag_2O is governed by the (solvent-dependent) thermodynamic stability of the reaction products.

Imidazolium halides are known to afford NHC-silver complexes of stoichiometry AgX(NHC) (X = halide), which adopt neutral mono- (**I**) or ionic bis(carbene) (**II**) architectures[30] that are often in equilibrium in solution (Scheme 3).[34,35] The formation of bis(carbene) complexes of

Scheme 3. Equilibria Involving Different Structures Found for Silver(I) NHC Complexes



type **III**, where the counterion is X^- instead of AgX_2^-, is usually associated with imidazolium salts containing noncoordinating anions, although it has also been reported with imidazolium halides.[36] Note that the NHC ligands in the chemical formulas of **I**–**III** are considered neutral for generalization purposes. The fact that the silver complexes reported here are negatively charged is irrelevant for the following discussion.

It has been noted previously that the neutral mono(carbene) form **I** is, in general, favored with regard to the ionic bis(carbene) form **II** by bulkier NHCs and less polar solvents.[34] Despite this, our understanding of the formation of bis(carbenes) in protic solvents is incomplete without taking into account the equilibrium between **II** and **III**. The thermodynamics of this equilibrium is mainly determined by the stability of the dihalidoargentate(1−) anions with regard to the precipitation of silver halide. The constant K for the equilibrium $[AgX_2]^- \leftrightarrow AgX + X^-$ (X^- = halide) can be determined from the overall formation constant of the complex AgX_2^- (β_2) and the solubility constant of the silver halide (K_s).[37] A clear picture emerges from the values shown in Table 1. Complexes $[AgX_2]^-$ are quite stable in dimethyl sulfoxide, acetonitrile, or dimethylformamide ($K \approx 10^{-1}$–10^{-2}), whereas the precipitation of silver halides is strongly favored in water or methanol ($K \approx 10^{4}$–10^{5}). This is because the halides are less

Table 1. Constants for Equilibria Involving Silver(I) Ions and Halides at 25 °C

equilibrium	X	water	methanol	dmso	acetonitrile	dmf
$Ag^+ + 2\,X^- \rightleftharpoons [AgX_2]^-$, $p\beta_2$[a]	Cl	−5.4	−7.9	−11.7	−13.4	−16.3
	Br	−7.6	−10.6	−11.4	−13.7	−16.6
	I	−11.2	−14.8	−12.5		−17.8
$AgX \rightleftharpoons Ag^+ + X^-$, pK_s[a]	Cl	9.8	13.1	10.4	12.9	14.5
	Br	12.3	15.2	10.6	12.9	15.0
	I	16.0	18.3	11.4		15.8
$[AgX_2]^- \rightleftharpoons AgX + X^-$, pK[b]	Cl	−4.4	−5.2	1.3	0.5	1.8
	Br	−4.7	−4.6	0.8	0.8	1.6
	I	−4.8	−3.5	1.1		2.0

[a]Data from ref 37. [b]Determined as $pK = -(p\beta_2 + pK_s)$.

solvated in aprotic than in protic solvents, whereas the opposite occurs with the $[AgX_2]^-$ ions.[37] The equilibria in Scheme 3 are therefore expected to be shifted toward the formation of bis(carbenes) of type **III** in protic solvents due to the poor stability of the AgX_2^- anions in these solvents irrespective of the factors governing the mono(carbene)–bis(carbene) equilibrium **I** ↔ **II**.

To support the above hypothesis, a sample of the mono(carbene) complex **3e** was dissolved in methanol-d_4 and monitored by ^{1}H NMR spectroscopy. As expected, the transformation of **3e** into **2e** was accompanied by AgCl precipitation, although the process was quite slow, taking more than one day at 90 °C to go to completion. On the other hand, a look at the literature confirmed that water-soluble NHC silver complexes obtained by the reaction of imidazolium salts with silver oxide in the presence of halide anions have always been obtained in the form of bis(carbene) complexes in water.[14,38−41] It should be noted that Cazin and co-workers reported the preparation of mono(carbene) silver complexes of general formula [(NHC)AgCl] in water.[42] However, these reactions involved the formation of complexes containing hydrophobic NHC ligands (IPr, IMes, or ICy), whose insolubility in water is most likely responsible for displacing the equilibria in Scheme 3 toward the mono(carbene) form **I**.

The hydrolytic stability of the NHC silver complexes merits a comment. Bis(carbene) complexes **2b**–**e** were found to be indefinitely stable in air in the solid state, whereas mono(carbenes) **3a**–**e** were extensively hydrolyzed under the same conditions and had to be stored under an inert atmosphere. The stability in solution is, however, more complex to describe because it depends on numerous factors, some of which are discussed below. Bis(carbenes) **2b**–**e** again showed significant hydrolytic stability in pure water, and their aqueous solutions did not show any noticeable degradation (as evidenced by ^{1}H NMR spectroscopy) when heated for hours or even days at 90 °C. Complex **2e** was particularly stable in water and remained unaltered for at least 24 h at 100 °C, and two days at 130 °C, with only 3% hydrolysis. The behavior of complex **2a**, in contrast, is quite remarkable. This complex has previously been described to be unstable in water.[14] Indeed, we have discussed above that all attempts to synthesize this complex pure failed, as it was always obtained as an approximately 40–60% mixture with the corresponding imidazolium salt **1a**. In an attempt to understand this result, two NMR tubes containing a D_2O solution of the mixture of **2a** and **1a** (previously separated from the silver oxide/silver chloride precipitate) were prepared. One of these samples was heated for 24 h at 90 °C and showed no apparent changes in the composition of the **2a**/**1a** mixture. This result clearly indicates that **2a** is intrinsically stable toward hydrolysis. In a different experiment, in which sodium chloride (10 equiv with respect to silver) was added to the second sample, complex **2a** was completely hydrolyzed in less than one hour at room temperature. Acceleration of the hydrolysis upon addition of NaCl was also observed for other bis(carbene) complexes, although the effect was less marked with NHC ligands that are hydrolyzed more slowly.[43] The same effect was observed when bis(carbenes) were heated in dmso with a small amount of added water. For instance, the percentage of hydrolysis of **2c** after 15 h at 90 °C rose from 3% to approximately 30% in the presence of NaCl. Interestingly, the formation of small amounts of the mono(carbene) **3c** was observed in the last process.

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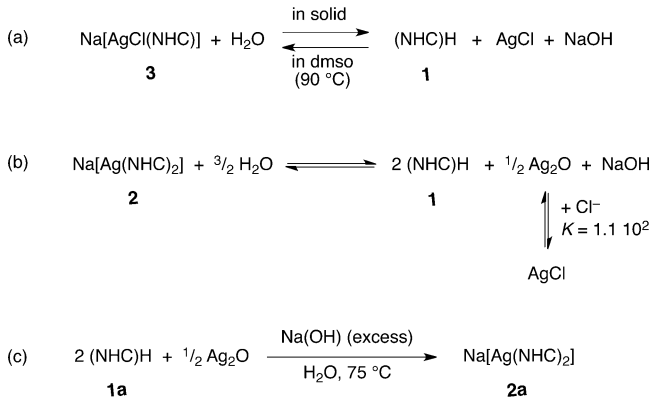
Any analysis of the hydrolytic stability of mono(carbene) complexes **3** is necessarily complicated by the fact discussed above, namely, that they evolve to the corresponding bis(carbenes) in water. Nevertheless, the behavior of complex **3a** was unique because it was completely hydrolyzed in water instead of evolving to the corresponding bis(carbene). This result does not necessarily mean that **3a** is intrinsically more reactive with water than the other mono(carbenes) but only that hydrolysis of the NHC−Ag bond occurs faster than the transfer of NHC ligands between Ag centers in this case. Another important point with respect to mono(carbenes) is the reversibility of the hydrolysis observed in the solid state (Scheme 4a). Thus, when a hydrolyzed solid sample of **3a**

Scheme 4. Hydrolysis of the Silver NHC Complexes



containing 24% of the NHC ligand in the form of the Ag complex (and 76% as imidazolium salt) was heated in dmso at 90 °C, the percentage of the mono(carbene) complex increased to 80% after 15 h. Similar transformations were observed for other complexes, although they were in general slower as the steric demand of the NHC ligand increased.

Although the hydrolysis of silver NHC complexes is a complex phenomenon in which both thermodynamics and kinetics play an important role, we can nevertheless extract several simple ideas. First, we should assume that solvation plays an important role in the thermodynamics of this hydrolysis to explain the differences found between mono-(carbenes) in the solid state and in solution. Second, hydrolysis of the complexes containing two sulfonatopropyl substituents (**2a** and **3a**) is quite interesting because forward (hydrolysis) and reverse processes are fast and therefore controlled by the thermodynamics. Third, the effect of the addition of sodium chloride on the hydrolysis of bis(carbenes) is likely thermodynamic in nature and might be motivated by displacement of the equilibrium shown in Scheme 4b from the bis(carbene) **2** to the imidazolium salt **1** due to the favorable formation of silver chloride from silver oxide ($K = 1.1 \times 10^2$ in water).[44] Indeed, the bis(carbene) complex **2a** was obtained spectroscopically pure by reaction of the imidazolium salt **1a** with silver oxide in the presence of an excess of sodium hydroxide (Scheme 4c).

The new NHC silver complexes **2e**, **2e**$^{Ag+}$, and **3a**−**e** were characterized by electrospray mass spectrometry and ^{1}H and ^{13}C NMR spectroscopy. These complexes were isolated as spectroscopically pure solids, which afforded inaccurate C, H, and N elemental analyses due to the presence of solvent molecules trapped within their structures (see X-ray structures below) and the likely contamination with inorganic salts. The narrow range in which carbenic C^2 resonances are found (176.8−182.7 ppm, Table 2) is characteristic of N-alkyl and N-aryl silver imidazolylidene complexes but cannot be used to differentiate between mono- and bis(carbene) structures.[33,45] The coupling constant of the C^2 resonance with ^{107,109}Ag is, in contrast, very informative when the intermolecular exchange of NHC ligands between silver centers is slow enough to observe splitting of the signal.[32,35] The $^1J(^{13}C-Ag)$ constants of neutral mono(carbenes) are, in general, 50−60 Hz larger than those of their corresponding ionic bis(carbenes) (values in the range 275−255 Hz for ^{109}Ag and 235−220 Hz for ^{107}Ag in mono(carbenes) versus 220−190 Hz for ^{109}Ag and 190−165 Hz for ^{107}Ag in bis(carbenes)).[31,33,35,45] The constants measured for complexes **2e** and **3e**, which bear the same NHC ligand, are within the expected ranges for their proposed structures (Table 2). In contrast, the C^2 resonances of the less encumbered complexes in Table 2 were observed as singlets (no $^1J(^{13}C-Ag)$ coupling), thereby suggesting that these complexes undergo intermolecular NHC ligand exchange that is fast on the NMR time scale. It is important to note that some of the bis(carbene) complexes listed in Table 2 undergo fast NHC exchange even in the absence of $[AgCl_2]^-$ counterions (or NaCl/AgCl).

Table 2. Chemical Shifts and Coupling Constants for the Carbenic C^2 Carbon in Silver NHC Complexes 2 and 3

complex	δ (C^2, ppm)	$^1J(^{109}Ag-^{13}C)$, $^1J(^{107}Ag-^{13}C)$ in Hz
	Bis(carbene) Complexes, Na[Ag(NHC)$_2$] in D$_2$O	
2a	178.4 (singlet)	
2b[a]	179.7 (singlet)	
2c[b]	180.6 (two doublets)	208, 180
2d[b]	182.7 (broad doublet)	193.9
2e	181.2 (two doublets)	217, 188
	Mono(carbene) Complexes, Na[AgX(NHC)] in dmso-d_6	
3a	176.8 (broad singlet)	
3b	177.8 (singlet)	
3c	not observed	
3d	not observed	
3e	181.4	268, 232

[a]From ref 14. [b]From ref 38.

The ESI mass spectra of the silver complexes, recorded in methanol, further supported the proposed structures. Thus, in the case of the bis(carbene) complexes **2e** and **2e**$^{Ag+}$, the most intense peaks correspond to the whole molecular fragment ionized by the loss of one or more cations (Na^+ or Ag^+) in negative mode or by addition of a hydrogen ion, probably from the solvent, in positive mode. The same anion $[M - Na]^-$ was also observed in the case of the monocarbene complexes **3a**−**e**, although the most intense peaks were those corresponding to bis(carbene) fragments, probably due to the rearrangement of these complexes in protic solvents (Scheme 2). Conversely, the ESI mass spectra of **3c** recorded in acetonitrile showed intense peaks for the mono(carbene) ions $[M - Na]^-$ and $[M - Na - Cl + CN]^-$. Acetonitrile appears to be the most likely source of CN^- in the latter fragment.[46]

X-ray Crystal Structures of the Silver(I) Complexes 2e, 2e^{Ag+}, and 3a. The crystal structures of the NHC silver complexes **2e**, **2e**$^{Ag+}$, and **3a** have been determined by X-ray diffraction methods. In the case of complex **2e**, X-ray determinations were performed on two different crystalline samples, one obtained from dichloromethane/methanol solvent

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mixtures (**2e**·6MeOH) and the other from acetone/dmso (**2e**·5dmso·H_2O). The structures of **2e**·6MeOH, **2e**·5dmso·H_2O, and $\mathbf{2e}^{Ag+}$ contain similar $[Ag(NHC)_2]^{3-}$ moieties packed in different arrangements together with counterions and solvent molecules.

Figure 2 shows the molecular structure of the $[Ag(NHC)_2]^{3-}$ unit in **2e**·6MeOH together with a selection of distances and

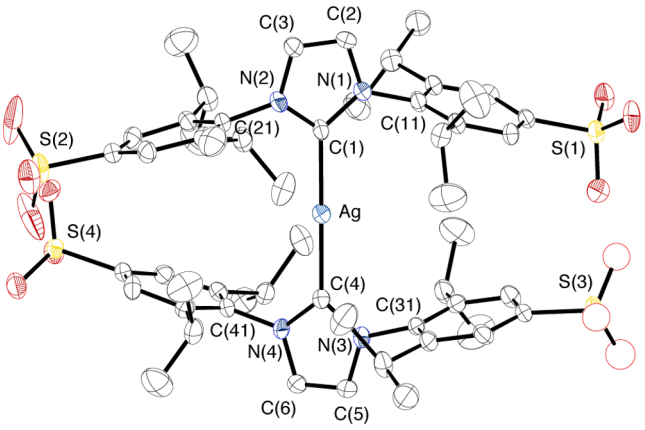

Figure 2. ORTEP diagram (50% probability ellipsoids) of the organometallic moiety of **2e**·6MeOH (H and Na atoms omitted for clarity). Essentially identical $[Ag(NHC)_2]^{3-}$ moieties are present in the crystal structures of **2e**·5Me_2SO·H_2O and $\mathbf{2e}^{Ag+}$. Selected bond lengths (Å) and angles (deg) for **2e**·6MeOH: Ag−C(1), 2.115(5); Ag−C(4), 2.108(5); C(1)−Ag−C(4), 178.4(2); N(1)−C(1)−N(2), 103.2(4); N(3)−C(4)−N(4), 103.4(4). Selected bond lengths (Å) and angles (deg) for **2e**·5Me_2SO·H_2O: Ag−C(1), 2.092(11); Ag−C(28), 2.099(11); C(1)−Ag−C(28), 178.3(4); N(1)−C(1)−N(2), 102.9(9); N(3)−C(28)−N(4), 103.5(10). Selected bond lengths (Å) and angles (deg) for $\mathbf{2e}^{Ag+}$: Ag(1)−C(1), 2.111(7); C(1)−Ag(1)−C(1′), 179.8(4); N(1)−C(1)−N(2), 103.8(6) [both NHCs are related by a crystallographic 2-fold axis].

angles found in the three structures that contain this unit. The two carbene ligands are almost linearly coordinated to Ag in all three structures, with C_{NHC}−Ag-C_{NHC} angles ranging from 178.3(4)° to 179.8(4)°. The NHC rings are twisted with respect to each other by between 40.2° and 45.5°, thereby avoiding the steric hindrance that would otherwise arise between the bulky 2,6-diisopropylphenyl groups. The Ag−C_{NHC} distances are in the narrow range 2.092(11)−2.111(5) Å. These parameters can be compared with those found in $[Ag(IPr)_2][SbF_6]$ [180° for the C_{NHC}−Ag−C_{NHC} angle, 37.8° for the angle between the NHC rings, and 2.13(2) Å for the Ag−C_{NHC} distances].[47]

The extended structure of $\mathbf{2e}^{Ag+}$ consists of one-dimensional chains assembled by bridging Ag^+ counterions lying in a pseudotetrahedral environment between the sulfonate groups of two adjacent $[Ag(NHC)_2]^{3-}$ moieties, with mean short $Ag^+\cdots{}^-OSO_2R$ contacts of 2.59 Å (Figure 3). These negatively charged chains are aligned along the crystallographic *b* axis and stacked along the *a* axis via the sodium cations, which complete their coordination spheres with two water molecules (mean $Na^+\cdots O$ distance of 2.33 Å for sulfonate and 2.40 Å for water). The $[Ag(NHC)_2]^{3-}$ moieties in **2e**·6MeOH are distributed along the crystallographic *a* and *b* axes in a similar manner to that described for $\mathbf{2e}^{Ag+}$, although they are packed together exclusively by sodium cations bridging two or three sulfonate groups (mean $Na^+\cdots{}^-OSO_2R$ distance of 2.45 Å). The coordination sphere of these Na^+ ions is completed with

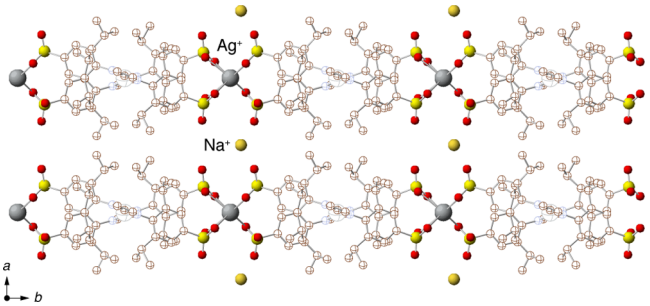

Figure 3. View of the crystal structure of $\mathbf{2e}^{Ag+}$ along the crystallographic *c* axis highlighting the enchainment of $[Ag(NHC)_2]^{3-}$ moieties by interaction of the sulfonate groups with the Ag^+ counterions, and the position of the Na^+ counterions between the chains.

methanol molecules (mean $Na^+\cdots O(H)Me$ distance of 2.34 Å). The crystal packing is markedly different in the case of **2e**·5Me_2SO·H_2O. In this case, the biscarbene moieties are organized centrosymmetrically around a cluster of six sodium ions arranged in a chair-type disposition with intermetallic distances in the range 3.42−3.93 Å (Figure 4a). This hexanuclear cluster of sodium ions is supported by coordination of the oxygen atoms from the eight sulfonate groups, four molecules of dmso, and two molecules of water, most of which bridge the edges and the triangular or square-planar faces of the cluster (Figure 4b).

Figure 5a shows a view of the crystal structure of **3e**, whereas Figure 5b shows the molecular structure of an isolated moiety, $[AgCl(NHC)]^{2-}$. The organometallic silver anions and the sodium counterions are arranged in layers. The coordination spheres of the Na^+ ions are composed by the oxygen atoms of two (Na(2)) or three (Na(1)) sulfonates from different silver moieties and one or two dmso molecules in tetrahedral environments (mean distances $Na^+\cdots{}^-OSO_2R$ = 2.27 Å, $Na^+\cdots OSMe_2$ = 2.31 Å). The C(1)−Ag−Cl angle (176.6(2)°) and the Ag−C(1) ((2.063(7) Å) and Ag−Cl (2.298(3) Å) distances are very similar to those found in the nonsulfonated analogue [AgCl(IPr)] (175.2°, 2.056 Å, and 2.316 Å, respectively).[34]

Synthesis of Platinum(II) NHC Complexes. No reaction was observed between the silver bis(carbenes) **2b−e** and the precursor *cis*-$[PtCl_2(dmso)_2]$ when a mixture of both was heated in water at 90 °C for 12−14 h (Scheme 5a). Although the platinum precursor is poorly soluble in water, the same lack of reactivity was found in mixtures of water and dimethyl sulfoxide (50%−50%), in which the platinum precursor is soluble. In contrast, the reaction of one equivalent of the mono(carbene) silver complexes **3a−d** with the above Pt precursor in dimethyl sulfoxide led to complexes of general formula $Na[PtCl_2(dmso)(NHC)]$ (**4a−d**) after heating at 80 °C for several hours (Scheme 5b). No transmetalation was observed with the most sterically hindered silver complex **3e** under the same conditions. These reactions took place with formation of the *cis* isomers of **4a−d** as the only Pt complexes. However, hydrolysis of the silver mono(carbenes) with traces of water, which are difficult to remove from the dmso solvent, resulted in concomitant formation of variable amounts of the corresponding imidazolium salt. The lack of an efficient method for separation of the platinum complexes and the imidazolium salts prompted us to search for an alternative approach to the synthesis of complexes **4**.

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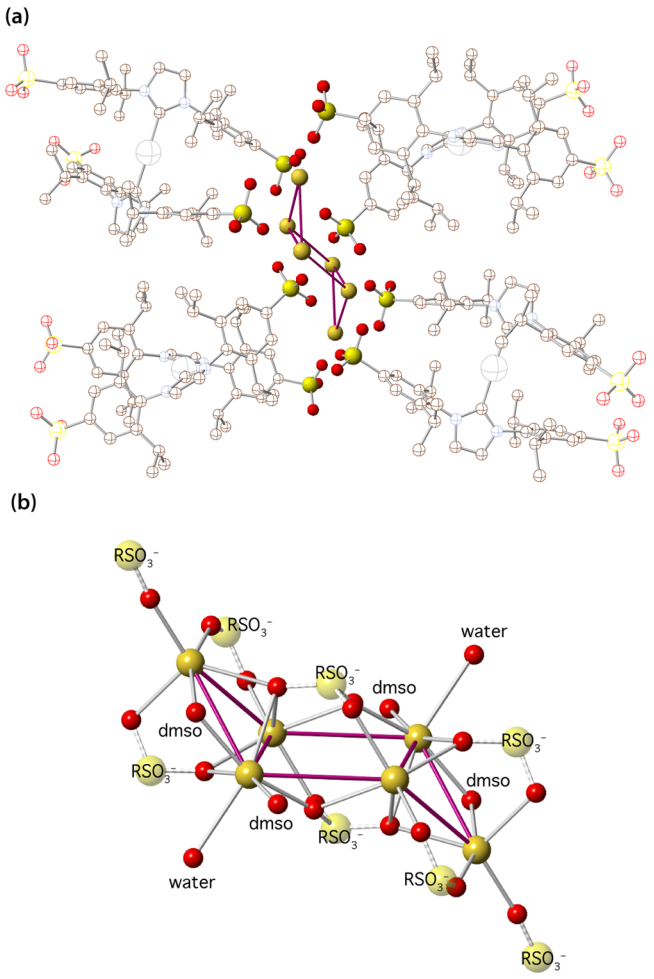
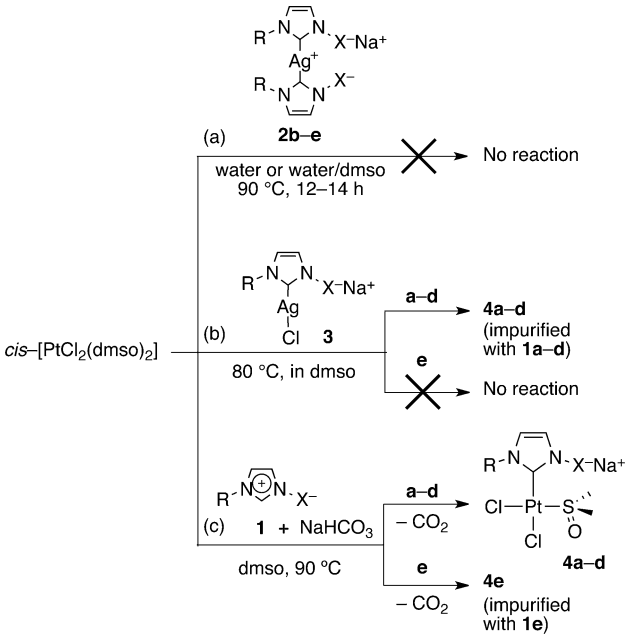


Figure 4. (a) Packing diagram showing the arrangement of $[Ag(NHC)_2]^{3-}$ moieties in **2e**·$5Me_2SO·H_2O$ around a chairlike hexanuclear cluster of sodium ions. Solvent molecules have been omitted for clarity. (b) Detail of the hexanuclear cluster of sodium ions and its coordination sphere formed by oxygen atoms from sulfonate groups, dmso, and water.

Scheme 5. Synthesis of the NHC Platinum(II) Complexes $Na[PtCl_2(dmso)(NHC)]$ (4)



An improved procedure for the synthesis of complexes **4** consisted in the direct reaction of *cis*-$[PtCl_2(dmso)_2]$ with imidazolium compounds **1** in dimethyl sulfoxide at 90 °C in the presence of sodium hydrogencarbonate as the deprotonating agent (Scheme 5c). This procedure afforded complexes **4a–d** as analytically pure solids in good to high yields (60–90%), with carbon dioxide being generated as the only byproduct. Reaction times ranged from 17 to 25 h, with longer times being required for the more sterically demanding NHC ligands. Indeed, pure samples of the complex with the IPr-like NHC ligand **4e** could not be isolated due to the low conversion (65% after 10 days at 90 °C). A similar result was obtained when replacing sodium hydrogencarbonate with sodium *tert*-butoxide as the base. Despite this, complex **4e** could still be characterized by ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry. A

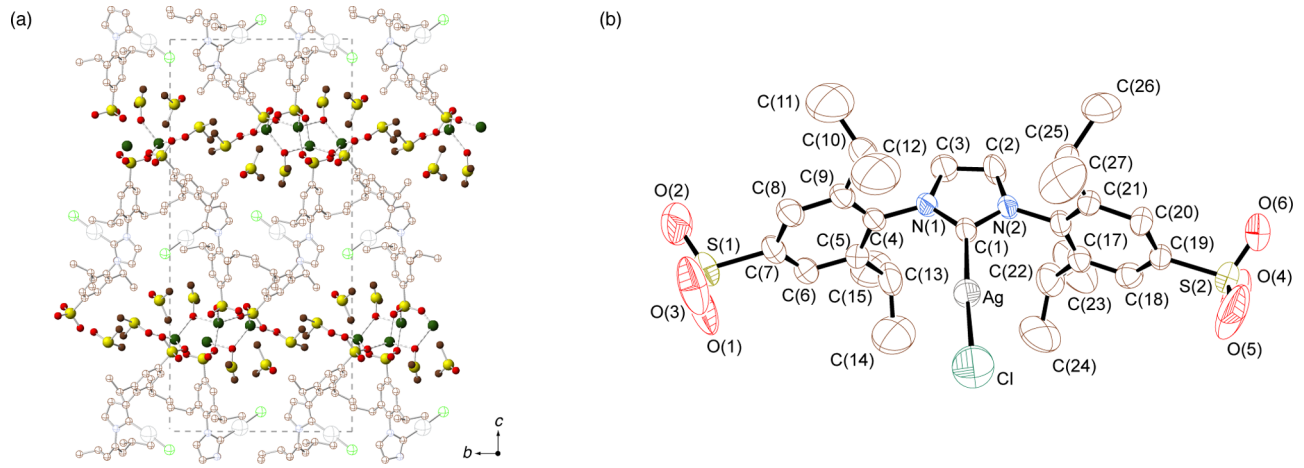


Figure 5. (a) View of the crystal structure of **3e** along the crystallographic *a* axis highlighting the interactions of Na^+ ions with the sulfonate groups of the $[AgCl(NHC)]^{2-}$ moieties and with the dmso molecules. (b) ORTEP diagram (50% probability ellipsoids) of the organometallic moiety of **3e** (H and Na atoms omitted for clarity). Selected bond lengths (Å) and angles (deg): Ag–C(1), 2.063(7); Ag–Cl, 2.298(3); C(1)–N(2), 1.354(8); C(1)–N(1), 1.344(8); C(2)–N(2), 1.359(9); C(3)–N(1), 1.377(9); C(2)–C(3), 1.351(10); C(1)–Ag–Cl, 176.6(2); N(1)–C(1)–N(2), 104.3(5).

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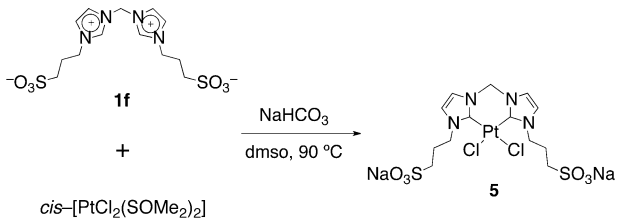
similar procedure was used to synthesize the chelate complex **5**, which was isolated analytically pure in 76% yield from the zwitterionic bisimidazolium salt **1f** (Scheme 6).

Scheme 6. Synthesis of the Bis(NHC) Platinum(II) Complex 5



The new water-soluble (NHC)Pt(II) complexes were characterized by ^{1}H, ^{13}C, and ^{195}Pt NMR spectroscopy, mass spectrometry, and elemental analysis. The ESI-TOF mass spectra of platinum complexes **4a–e** and **5** were recorded in methanol in negative mode and showed intense peaks corresponding to the fragments $[M - Na]^-$, with isotopic distributions matching the calculated patterns. The only clearly observed ^{195}Pt satellites in their $^{13}C\{^1H\}$ NMR spectra, recorded in dmso-d_6, were those of the carbenic carbon of complex **4b** ($^1J(^{13}C_{NHC}-^{195}Pt)$ = 1378 Hz). Solvents of relatively high viscosity, such as dimethyl sulfoxide, increase the contribution of chemical shift anisotropy to the ^{195}Pt relaxation, thereby often resulting in the broadening or disappearance of ^{195}Pt satellites.[48] Nevertheless, coordination of the NHC ligands to platinum was supported by the chemical shifts of the carbenic carbons (144.1–140.8 ppm). The ^{195}Pt chemical shifts ranged from −3474 to −3529 ppm in mono(carbenes) **4a–d**, whereas the resonance of the bis(carbene) **5** was shifted slightly to higher field (−3572 ppm). The above ^{13}C and ^{195}Pt chemical shifts are in agreement with those previously reported for *cis*-$[PtCl_2(dmso)(NHC)]$ complexes.[21,22,49] The ^{1}H and $^{13}C\{^1H\}$ NMR spectra recorded in dimethyl sulfoxide revealed the existence of some asymmetry in mono(carbenes) **4a–d**, as seen by the lack of equivalence between (a) the two methylene protons α to the imidazole nitrogen in the sulfonatepropyl chains of **4a–d**; (b) the proton and carbon-13 nuclei in the *ortho* and *meta* positions of the mesityl or 2,6-bis(isopropyl)phenyl groups in **4c–e**; and (c) the two methyl groups of the dmso molecule coordinated to Pt in the case of complexes with asymmetrically substituted NHCs. These observations can only be explained by assuming a *cis* stereochemistry of the square-planar metal environment, with a chloride *trans* to the carbene ligand and with the NHC ring arranged perpendicularly to the coordination plane rotating slowly around the Pt–NHC bond on the NMR time scale.[22] The fact that this rotation is faster in water means that the α-methylene protons of the sulfonatepropyl chains and the coordinated dmso of **4a,b** appear as single resonances in this solvent. On the other hand, the chelate coordination in complex **5** is confirmed by the chemical nonequivalence of the two protons of the methylene bridge in the ^{1}H NMR spectrum, as would be expected for a boat conformation of the six-membered metallacycle with a slow boat-to-boat exchange of conformers on the NMR time scale.

The crystal structure of **4a** has been determined by X-ray diffraction methods. The asymmetric unit contains the organometallic dianion $[PtCl_2(dmso)(NHC)]^{2-}$ (Figure 6), together with two (disordered) sodium counterions and water molecules (not shown in Figure 6). Each sodium ion is adjacent to one sulfonate, with $RS(O_2)O^-\cdots Na^+$ distances in the range of 2.8 to 2.9 Å, whereas the nearest oxygen atoms of the other surrounding sulfonates are at 3.8–4.2 Å. The square-planar environment of the Pt atom is almost regular, with the metal lying 0.01 Å out the coordination plane defined by atoms S(3), C(1), Cl(1), and Cl(2), and the angles between *cis* bonds ranging from 88.3° to 91.0°. The dmso is coordinated to the metal center via the sulfur atom with the sulfur–oxygen moiety lying parallel to the Pt–C bond and pointing toward the NHC ligand. This arrangement presumably reduces any steric interactions between the methyl groups of the dmso and the heterocyclic ligand. The imidazolium ring is tilted 75.2(4)° relative to the platinum coordination plane. The Pt–C(1) distance of 1.97(2) Å is in the range of those reported for neutral *cis*-$[PtCl_2(dmso)(NHC)]$ complexes (1.88–1.99 Å).[21,22,49] The chlorine atoms are mutually arranged in a *cis* position, with the Pt–Cl distance of the chloride *trans* to the NHC ligand being significantly larger (2.359(5) versus 2.309(5) Å), as expected in light of the high sensitivity of Pt–Cl distances to the different influences of their *trans* ligands.[50]

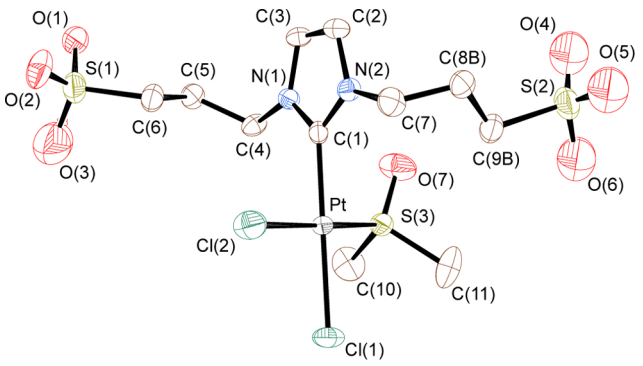


Figure 6. Molecular structure of the organometallic moiety of **4a** (50% probability ellipsoids). Selected bond lengths (Å) and angles (deg): Pt–C(1), 1.97(2); Pt–Cl(1), 2.359(5); Pt–Cl(2), 2.309(5); Pt–S(3), 2.208(4); C(1)–Pt–Cl(1), 177.6(5); S(3)–Pt–Cl(2), 177.4(2); C(1)–Pt–S(3), 91.0(5); C(1)–Pt–Cl(2), 88.3(5); Cl(1)–Pt–Cl(2), 90.4(2); S(3)–Pt–Cl(1), 90.4(2).

Hydration of Terminal Alkynes in Water. The hydration of alkynes is an important reaction for the synthesis of aldehydes or ketones. As such, major efforts have been made over the last few decades to develop new transition-metal catalysts for this reaction to replace traditional and highly toxic mercury-based catalysts.[51] Important developments in this area have included the discovery of the first anti-Markovnikov addition that yielded aldehydes from terminal alkynes, which is catalyzed by ruthenium(II) complexes,[52] or the publication of gold complexes that are highly active in acidic media.[53] In addition to gold(I) and gold(III), platinum(II) complexes are among the best metal catalysts for Markovnikov-selective alkyne hydration. Chatt and Duncanson reported the first platinum(II)-catalyzed hydration of alkynes using $Na_2PtCl_4\cdot H_2O$ in ethanolic solution.[54] Subsequently, Jennings and co-workers showed that Zeise's dimer and Pt(II) halides were efficient catalysts for the addition of water to inactivated (electron-rich) terminal and internal alkynes in THF. These authors noted that the addition of acid was neither necessary nor advantageous in this case.[55] More recently, Atwood and co-workers used platinum(II) complexes with water-soluble

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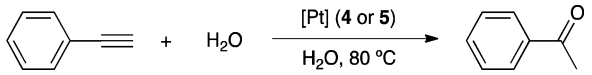
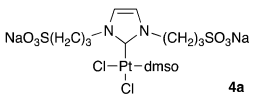
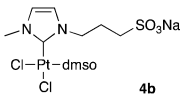
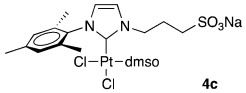
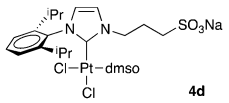
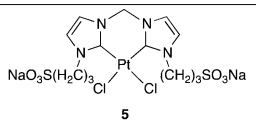
Table 3. Hydration of Phenylacetylene Catalyzed by Complexes 4a−d and 5 in Water[a−c]



entry	catalyst	[Pt] (mol %)	time (h)	conversion (%)[b]
1	 4a	2	1	91
2		2	2	93
3		2	4	100
4	 4b	2	1	20
5		2	2	32
6		2	3	48
7		2	9	100
8	 4c	2	1	90
9		2	2	98
10		2	3	100
11		2	8 (rt)[c]	44
12		2	24 (rt)[c]	100
13		1	3	47
14		0.5	3	30
15	 4d	2	1	91
16		2	2	95
17		2	4	100
18	 5	2	3	97
19		2	4	100

[a]Standard reaction conditions: 0.455 mmol of phenylacetylene; 2 mL of H_2O. [b]Conversions determined by ^1H NMR spectroscopy. [c]Reaction at room temperature.

sulfonated phosphines to hydrate alkynols in this solvent.[56] To the best of our knowledge, although NHC-Pt complexes have not been studied in this reaction, notable decreases in catalyst loadings were achieved when NHC ligands were involved with gold complexes.[57] More recently, Joó and co-workers have reported the hydration of alkynes with water-soluble sulfonated NHC gold(I) complexes in methanol/water mixtures.[14,15]

The NHC complexes **4a−d** and **5** were found to be active catalysts for the hydration of alkynes in water in the absence of an acid cocatalyst. The hydration of phenylacetylene was initially used as a benchmark reaction to compare the different Pt catalysts and to optimize the reaction conditions (Table 3). The activity of mono(carbene) complexes **4** was rather similar, reaching conversions of phenylacetylene to benzophenone of around 90% at 80 °C in 1 h (Table 3, entries 1, 8, and 15) and 100% in 3−4 h (Table 3, entries 3, 10, and 17) using Pt loadings of 2.0 mol %. The only exception was complex **4b**, which required 9 h for complete conversion (Table 3, entry 7). The bis(carbene) complex **5** also showed a similar activity to that observed for **4a**,**c**,**d**, completing the reaction in 4 h under the same conditions (Table 3, entry 19). The reaction also progressed at room temperature with catalyst **4d**, although the reaction time had to be prolonged to 24 h for completion (Table 3, entry 12).

We subsequently studied the hydration of selected terminal and internal alkynes catalyzed by **4c** in neat water at 80 °C (Table 4). The activity of **4c** in the addition of water to *para*-substituted phenylacetylenes decreased in the order −H > −OMe > $-CF_3$ > NO_2 (Table 3, entry 10, and Table 4, entries 1−3), thus correlating with the trend of electron-richness of the alkynes. The heterogeneous nature of the catalytic reaction cannot, however, be ignored when interpreting these results. Indeed, the limited reactivity of 3-nitrophenylacetylene may well be linked to the insolubility of this solid compound in the reaction medium (all the other phenylacetylenes tested are liquids under the same conditions). This may well also explain the lack of reactivity observed for diphenylacetylene.

Taking the hydration of phenylacetylene as a reference, the conversions obtained with **4c** can be compared with those reported for water-soluble NHC gold(I) complexes using the

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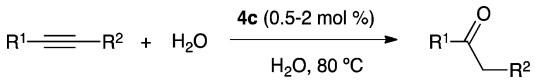
Table 4. Hydration of Selected Alkynes in Water Catalyzed by Complex 4c[a]



entry	R^1	R^2	[Pt] mol %	time (h)	conversion (%)[b]
1	4-MeO-Ph	H	2	5	100
2	4-CF_3-Ph	H	2	24	100
3	3-NO_2-Ph	H	2	24	2
4	$HO(CH_2)_3$–	H	0.5	0.3	100
5	$HO(CH_2)_2$–	CH_3	0.5	0.3	100
6	$HOCH_2$–	H	0.5	24	100 (43[c])
7	$HOCH_2CH_2$–	H	0.5	24	80 (23[c])

[a]Standard reaction conditions: 1 mmol of alkyne; 2 mL of H_2O. [b]Conversions determined by ^1H NMR spectroscopy. [c]Ketone yield measured by ^1H NMR spectroscopy using NEt_4I as internal standard.

same metal loadings (2.0 mol %). Although a sulfoalkyl-substituted NHC-Au complex provided conversions of only 17% after 3 h in refluxing water (compared with 100% for **4c** in the same time period at 80 °C, entry 10, Table 3),[14] the reported activities are similar to those observed with **4c** with the use of a bulky IMes-like NHC ligand (90% in 1 h at reflux; cf. entry 8, Table 3).[15] Another reference reaction for **4c** is Atwood's hydration of water-soluble alkynols with Pt(II) complexes of sulfonated phosphines.[56] Thus, in agreement with Atwood's findings, complex **4c** directs the hydration of either 3- or 4-pentynol exclusively to the formation of 5-hydroxy-2-pentanone, irrespective of the starting alkynol (Table 4, entries 4 and 5). For these reactions, Atwood and co-workers proposed an anchimeric assistance of the unsaturated bond by the hydroxyl group of the substrate once the alkyne coordinates to the Pt center.[56] All reactions involving **4c** were complete in only 18 min at 80 °C with Pt loadings as low as 0.5 mol % (compared with 1 h for the sulfonated phosphine complexes). In agreement with the mechanism proposed above, the disfavored participation of the neighboring hydroxyl group explains the much slower kinetics found for the hydration of propargyl alcohol and 3-butyn-1-ol under the same conditions (Table 4, entries 6 and 7). As a consequence, extensive competitive polymerization was found with the latter alkynes.

CONCLUSIONS

Despite their increasing interest in catalytic or biomedical applications, the chemistry of water-soluble NHC complexes in water has barely been studied. One of the aspects considered in this report is the influence of an aqueous medium on the preparation and stability of sulfonated NHC silver complexes. In this respect, we have shown that precipitation of silver halides makes the difference between protic (such as water and alcohols) and aprotic solvents. In simple thermodynamic terms, the sequence of equilibria 2 [AgCl(NHC)] ↔ [Ag(NHC)$_2$][AgCl$_2$] ↔ [Ag(NHC)$_2$]Cl + AgCl is shifted to the right in protic solvents, partly because hydrogen bonds are involved in solvation of the chloride anion. This explains why the literature (and this work) reports the exclusive formation of bis(carbene) species when water-soluble Ag-NHC complexes are prepared in this solvent. In addition, we have shown that the sulfonated mono(carbenes) Na[AgCl(NHC)] (**3**), which can be prepared in aprotic solvents such as dmso, evolve reversibly to their bis(carbene) analogues Na[Ag(NHC)$_2$] (**2**) when dissolved in water. The NHC–Ag bonds in these bis(carbene) complexes are very resistant to hydrolysis, even in refluxing water. However, hydrolysis is favored under some conditions, and we can especially highlight the fact that the promotion of hydrolysis by chlorides might explain the problems found in the literature as regards the synthesis of various NHC silver complexes in water. Although water is the most natural solvent for the preparation of water-soluble NHC complexes, the use of silver complexes for this purpose can prove problematic, as shown in the synthesis of the water-soluble platinum(II) NHC complexes **4**. Thus, the most suitable procedure for the synthesis of these complexes was direct metalation of the corresponding imidazolium salts in dmso, as silver(I) NHC intermediates failed to transfer their NHC ligands to the Pt centers in water (but not in dmso). Nevertheless, the transfer of NHC ligands from Ag to Au, Ru, or Os centers has been reported to happen in water,[14,41,58] and NHC exchange between Ag centers also occurs rapidly in water on the NMR time scale in the case of **2a,b**. However, steric hindrance probably makes bis(carbene) complexes kinetically worse transfer agents and water makes them thermodynamically more stable. Finally, we have shown that *cis*-[PtCl$_2$(dmso)(NHC)] complexes are active catalysts for the hydration of alkynes in aqueous media, although their activity is currently comparable to that reported with platinum(II) complexes of sulfonated phosphines.

EXPERIMENTAL SECTION

General Procedures. All reactions were performed under an argon atmosphere using standard Schlenk techniques. Unless otherwise stated, reagents and solvents were used as received from commercial sources. The complex *cis*-dichlorobis(dimethyl sulfoxide)-platinum(II)[59] and the imidazolium salts **1a**,[14] **1b**,[60] **1c,d**,[38] **1e**,[13] and **1f**[39] were prepared as described in the literature. All solvents were deoxygenated prior to use. Dimethyl sulfoxide was distilled under argon over calcium hydride. Deionized water (type II quality) was obtained using a Millipore Elix 10 UV water purification system. ^1H, ^{13}C, ^{15}N, and ^{195}Pt NMR spectra were recorded with a Varian Mercury 300, Unity 300, or Unity 500 Plus spectrometer. Chemical shifts (δ, parts per million) are quoted relative to $SiMe_4$ (^1H, ^{13}C), CH_3NO_2 (^{15}N), and K_2PtCl_6 in water (^{195}Pt). They were measured by internal referencing to the ^{13}C or residual ^1H resonances of the deuterated solvents or by the substitution method in the case of ^{15}N and ^{195}Pt. Coupling constants (J) are given in hertz. When required, two-dimensional ^1H–^{13}C HSQC and HMBC experiments were carried out for the unequivocal assignment of ^1H and ^{13}C resonances. The Analytical Services of the Universidad de Alcalá performed the C, H, and N analyses using a Heraeus CHN-O-Rapid microanalyzer, and the mass spectra were obtained using an Agilent G3250AA LC/MSD TOF Multi (MALDI and ESI) mass spectrometer.

Synthesis of the Biscarbene Silver Complexes (2). The silver NHCs **2b**[14] and **2c,d**[38] were prepared according to published procedures and characterized by comparison of their NMR spectra with those previously described for all complexes.

*Trisodium [1,3-Bis(3-sulfonatepropyl)imidazol-2-ylidene]-argentate(3–) (**2a**).* A spectroscopically pure sample of **2a** was prepared by heating a mixture of the imidazolium salt **1a** (0.1632 g, 0.483 mmol), silver oxide (0.0684 mg, 0.295 mmol), and an excess of sodium hydroxide (0.0911 g, 2.28 mmol) in water (3 mL) for 36 h at 75 °C. ^1H NMR (300 MHz, D_2O): δ 7.19 (s, 1H, Imz), 4.12 (t, $^3J_{HH}$ = 6.3, 2H, NCH_2), 2.71 (t, $^3J_{HH}$ = 7.2, 2H, CH_2S), 2.13 (m, 2H, $CH_2CH_2CH_2$). $^{13}C\{^1H\}$ NMR (125 MHz, D_2O): δ 178.4 (s, Imz C^2), 121.3 (s, Imz $C^{4,5}$), 49.7 (s, NCH_2), 47.2 (s, CH_2S), 26.4 (s, $CH_2CH_2CH_2$). ESI-MS (negative ion, MeOH) m/z: 772.9449 [M – Na]$^-$ (calcd 772.9438) 87%; 750.9629 [M + H – 2Na]$^-$ (calcd 750.9619) 85%; 728.9821 [M + 2H – 3Na]$^-$ (calcd 728.9799) 100%.

*Silver Disodium Bis[1,3-bis(2,6-diisopropyl-4-sulfonatophenyl)-imidazol-2-ylidene]argentate(3–) (**2e^{Ag+}**).* An excess of silver oxide

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(0.072 g, 0.31 mmol) was added to a solution of the imidazolium salt **1e** (0.191 g, 0.335 mmol) in water (7 mL). The mixture was stirred for 4 h at room temperature, then centrifuged and filtered through a plug of kieselguhr. The resulting solution was evaporated to dryness under vacuum (4 h, 80 °C, 4 mbar). Compound $\mathbf{2e}^{Ag+}$ was isolated as a light-sensitive white solid (0.415 g, 90%). ^{1}H NMR (300 MHz, D_2O): δ 7.44 (s, 2H, Ar), 7.25 (s, 1H, Imz), 2.13 (m, 2H, C*H*Me$_2$), 0.86 (d, $^3J_{HH}$ = 6.8, 6H, CH*Me*$_2$), 0.58 (d, $^3J_{HH}$ = 6.8, 6H, CH*Me*$_2$). ^{1}H NMR (300 MHz, dmso-d_6): δ 7.75 (s, 1H, Imz), 7.54 (s, 2H, Ar), 2.14 (m, 2H, C*H*Me$_2$), 0.99 (d, $^3J_{HH}$ = 6.8, 6H, CH*Me*$_2$), 0.69 (d, $^3J_{HH}$ = 6.8, 6H, CH*Me*$_2$). ^{13}C{^{1}H} NMR (75 MHz, D_2O): δ 181.2 (two d with $^1J(^{13}C-^{109}Ag)$ = 217 and $^1J(^{13}C-^{107}Ag)$ = 188, respectively, Imz C^2), 146.8 (s, Ar C^3), 144.8 (s, Ar C^1), 136.7 (s, Ar C^4), 125.1 (d, Imz C^{4,5}, $^3J(Ag-^{13}C)$ = 5.6), 121.7 (s, Ar C^2), 28.6 (s, *C*HMe$_2$), 23.6 (s, CH*Me*$_2$), 22.5 (s, CH*Me*$_2$). ESI-MS (negative ion, MeOH) *m*/*z*: 1245.2563 [M − Ag]$^-$ (calcd 1245.2563) 36%; 1201.2919 [M − Ag − 2Na + 2H]$^-$ (calcd 1201.2929) 100%; 600.1414 [M − Ag − 2Na + H]$^{2-}$ (calcd 600.1428) 52%.

*Trisodium Bis[1,3-bis(2,6-diisopropyl-4-sulfonatephenyl)-imidazol-2-ylidene]argentate(3−) (**2e**).* A solution of sodium chloride (0.0099 g, 0.170 mmol) in water (1 mL) was added dropwise to a solution of $\mathbf{2e}^{Ag+}$ (0.230 g, 0.170 mmol) in the same solvent (2 mL) in the dark. Formation of a silver chloride precipitate was observed immediately. Stirring was continued for 30 min at room temperature; then the solution was centrifuged and filtered through a plug of kieselguhr. The resulting solution was evaporated to dryness under vacuum (4 h, 80 °C, 4 mbar). Compound **2e** was obtained as a white solid (0.230 g, 98%). The ^{1}H and ^{13}C NMR data for this compound are identical to those given above for $\mathbf{2e}^{Ag+}$. ESI-MS (positive ion, MeOH) *m*/*z*: 1269.2538 [M + H]$^+$ (calcd 1269.2539) 10%; 1247.2715 [M − Na + 2H]$^+$ (calcd 1247.2714) 46%; 1225.2858 [M − 2Na + 3H]$^+$ (calcd 1225.2894) 88%; 1203.3044 [M − 3Na + 4H]$^+$ (calcd 1203.3075) 100%. The negative ion ESI mass spectrum is similar to that found for $\mathbf{2e}^{Ag+}$.

General Procedure for the Synthesis of Monocarbene Silver(I) Complexes (3). An excess of silver oxide (0.333 g, 1.44 mmol) was added to a solution of the corresponding imidazolium salt (1.19 mmol) and sodium chloride (0.070 g, 1.20 mmol) in dimethyl sulfoxide (5 mL). The mixture was stirred for the time and at the temperature indicated below for each complex. The precipitate was then separated by centrifugation and filtration through a plug of kieselguhr, and the resulting solution evaporated to dryness under vacuum (6 h, 90 °C, 4 mbar) to give the corresponding NHC silver(I) complex.

*Chlorido[1,3-bis(3-sodiumsulfonatepropyl)imidazol-2-ylidene]-silver(I) (**3a**).* Complex **3a** was obtained from **1a** (0.398 g, 1.19 mmol) as an off-white solid (0.547 g, 92%) after 17 h of reaction at 60 °C. ^{1}H NMR (300 MHz, dmso-d_6): δ 7.46 (s, 1H, Imz), 4.15 (t, $^3J_{HH}$ = 6.7, 2H, NCH$_2$), 2.38 (t, $^3J_{HH}$ = 7.0, 2H, CH$_2$S), 2.03 (m, 2H, CH$_2$C*H*$_2$CH$_2$). ^{13}C{^{1}H} NMR (75 MHz, dmso-d_6): δ 176.8 (br, Imz C^2), 121.4 (s, Imz C^{4,5}), 49.6 (s, NCH$_2$), 47.6 (s, CH$_2$S), 27.1 (s, CH$_2$CH$_2$CH$_2$). ESI-MS (negative ion, MeOH) *m*/*z*: 474.8939 [M − Na]$^-$ (calcd 474.8930) 35%; 750.9629 [M − Na − Cl + NHC + H]$^-$ (calcd 750.9619) 100%.

*Chlorido[1-methyl-3-(3-sodiumsulfonatepropyl)imidazol-2-ylidene]silver(I) (**3b**).* Complex **3b** was obtained from **1b** (0.243 g, 1.19 mmol) as an off-white solid (0.422 g, 96%) after 17 h of reaction at 60 °C. ^{1}H NMR (300 MHz, dmso-d_6): δ 7.46 (d, $^3J_{HH}$ = 2.0, 1H, Imz), 7.41 (d, $^3J_{HH}$ = 1.7, 1H, Imz), 4.16 (t, $^3J_{HH}$ = 6.9, 2H, NCH$_2$), 3.76 (s, 3H, NMe), 2.41 (t, $^3J_{HH}$ = 7.6, 2H, CH$_2$S), 2.03 (m, 2H, CH$_2$C*H*$_2$CH$_2$). ^{13}C{^{1}H} NMR (75 MHz, dmso-d_6): δ 177.8 (s, Imz C^2), 122.4 (s, Imz C^5), 121.4 (s, Imz C^4), 49.4 (s, NCH$_2$), 47.6 (s, CH$_2$S), 37.7 (s, NMe), 27.1 (s, CH$_2$CH$_2$CH$_2$). ESI-MS (negative ion, MeOH) *m*/*z*: 344.9243 [M − Na]$^-$ (calcd 344.9230) 29%; 513.0041 [M − Na − Cl + NHC$^-$]$^-$ (calcd 513.0037) 100%.

*Chlorido[1-(3-sodiumsulfonatepropyl)-3-(2,4,6-trimethylphenyl)-imidazol-2-ylidene]silver(I) (**3c**).* Complex **3c** was obtained from **1c** (0.367g, 1.19 mmol) as a brown solid (0.552 g, 98%) after 20 h of reaction at 60 °C. ^{1}H NMR (300 MHz, dmso-d_6): δ 7.74 (s, 1H, Imz), 7.46 (s, 1H, Imz), 7.05 (s, 2H, Ar), 4.26 (t, $^3J_{HH}$ = 2.0, 2H, NCH$_2$), 2.43 (t, $^3J_{HH}$ = 7.9, 2H, CH$_2$S), 2.30 (s, 3H, Ar *p*-*Me*), 2.11 (m, 2H, CH$_2$C*H*$_2$CH$_2$), 1.90 (s, 6H, Ar *o*-*Me*). ^{13}C{^{1}H} NMR (75 MHz, dmso-d_6): δ Imz C^2 not observed, 138.1 (s, Ar C^4), 135.3 (s, Ar C^2), 134.0 (s, Ar C^1), 128.5 (s, Ar C^3), 122.7 (s, Imz C^4), 121.9 (s, Imz C^5), 49.6 (s, NCH$_2$), 47.5 (s, CH$_2$S), 27.2 (s, CH$_2$CH$_2$CH$_2$), 20.2 (s, Ar *p*-*Me*), 16.7 (s, Ar *o*-*Me*). ESI-MS (negative ion, MeOH) *m*/*z*: 448.9832 [M − Na]$^-$ (calcd 448.9856) 10%; 721.1278 [M − Na − Cl + NHC]$^-$ (calcd 721.1289) 100%. ESI-MS (negative ion, acetonitrile) *m*/*z*: 440.0205 [M − Na − Cl + CN]$^-$ (calcd 440.0204) 29%; 448.9862 [M − Na]$^-$ (calcd 448.9856) 20%; 721.1293 [M − Na − Cl + NHC]$^-$ (calcd 721.1289) 100%.

*Chlorido[1-(2,6-diisopropylphenyl)-3-(3-sodiumsulfonatepropyl)-imidazol-2-ylidene]silver(I) (**3d**).* Complex **3d** was obtained from **1d** (0.417 g, 1.19 mmol) as a brown solid (0.602 g, 98%) after 20 h of reaction at 60 °C. ^{1}H NMR (300 MHz, dmso-d_6): δ 7.78 (s, 1H, Imz), 7.63 (s, 1H, Imz), 7.50 (t, $^3J_{HH}$ = 7.6, 1H, Ar H^4), 7.34 (d, $^3J_{HH}$ = 7.6, 2H, Ar H^3), 4.28 (t, $^3J_{HH}$ = 6.4, 2H, NCH$_2$), 2.43 (t, $^3J_{HH}$ = 7.0, 2H, CH$_2$S), 2.28 (m, 2H, C*H*Me$_2$), 2.12 (m, 2H, CH$_2$C*H*$_2$CH$_2$), 1.14 (d, $^3J_{HH}$ = 6.7, 6H, CH*Me*$_2$), 1.09 (d, $^3J_{HH}$ = 6.7, 6H, CH*Me*$_2$). ^{13}C{^{1}H} NMR (75 MHz, dmso-d_6): δ Imz C^2 not observed, 144.9 (s, Ar C^2), 134.6 (s, Ar C^1), 129.6 (s, Ar C^4), 124.1 (s, Imz C^5), 123.4 (s, Ar C^3), 121.8 (s, Imz C^4), 49.6 (s, NCH$_2$), 47.5 (s, CH$_2$), 27.3 (s, CH$_2$CH$_2$CH$_2$), 27.2 (s, C*H*Me$_2$), 23.7 (s, CH*Me*$_2$), 23.3 (s, CH*Me*$_2$). ESI-MS (negative ion, MeOH) *m*/*z*: 491.0338 [M − Na]$^-$ (calcd 491.0325) 7.9%; 805.2223 [M − Na − Cl + NHC]$^-$ (calcd 805.2228) 100%.

*Chlorido[1,3-bis(2,6-diisopropyl-4-sodiumsulfonate)-phenylimidazol-2-ylidene]silver(I) (**3e**).* Complex **3e** was obtained from **1e** (0.682 g, 1.19 mmol) as a white solid (0.701 g, 80%) after 48 h of reaction at room temperature. ^{1}H NMR (300 MHz, dmso-d_6): δ 8.01 (s, 1H, Imz), 7.59 (s, 2H, Ar), 2.45 (m, 2H, C*H*Me$_2$), 1.18 (t, *J* = 5.7, 12H, CH*Me*$_2$). ^{13}C{^{1}H} NMR (75 MHz, dmso-d_6): δ 181.4 (two d with $^1J(^{13}C-^{109}Ag)$ = 268 and $^1J(^{13}C-^{107}Ag)$ = 232, respectively, Imz C^2) 149.3 (s, Ar C^1), 144.3 (s, Ar C^3), 134.1 (s, Ar C^4), 124.5 (d, $^3J(^{13}C-Ag)$ = 6.8, Imz C^{4,5}), 120.6 (s, Ar C^2), 27.8 (s, *C*HMe$_2$), 23.7 (s, CH*Me*$_2$), 22.9 (s, CH*Me*$_2$). ESI-MS (negative ion, MeOH) *m*/*z*: 711.0483 [M − Na]$^-$ (calcd 711.0495) 1.5%; 653.0820 [M − 2Na − Cl]$^-$ (calcd 653.0915) 6%; 1201.2871 [M − 2Na + NHC + 2H]$^-$ (calcd 1201.2929) 100%.

General Procedure for the Synthesis of Platinum(II) Complexes 4 and 5. Sodium hydrogencarbonate (0.160 g, 1.91 mmol) was added to a solution of *cis*-[PtCl$_2$(dmso)$_2$] (0.322 g, 0.764 mmol) and the corresponding imidazolium salt (0.764 mmol) in dimethyl sulfoxide (5 mL). The mixture was stirred at 90 °C for the time indicated below, then filtered through a plug of kieselguhr, and the solvent was partially removed under vacuum to a remaining volume of 2−3 mL. The platinum complex was then precipitated with acetone (60 mL), separated by filtration, washed with acetone (3 × 20 mL), and dried under vacuum (2 h, 90 °C, 4 mbar).

*cis-Dichlorido[1,3-bis(3-sodiumsulfonatepropyl)imidazol-2-ylidene](dimethyl sulfoxide)platinum(II) (**4a**).* Complex **4a** was obtained from **1a** (0.255 g, 0.764 mmol) as a white solid (0.401 g, 75%) after 17 h of reaction at 90 °C. ^{1}H NMR (300 MHz, dmso-d_6): δ 7.39 (s, 1H, Imz), 4.51 (m, 1H, NCH$_2$), 4.21 (m, 1H, NCH$_2$), 3.49 (s, 3H, Me$_2$SO), 2.49 (m, 2H, CH$_2$S), 2.20 (m, 2H, CH$_2$C*H*$_2$CH$_2$). ^{1}H NMR (300 MHz, D_2O): δ 7.18 (s, 1H, Imz), 4.37 (t, $^3J_{HH}$ = 7.3, 2H, NCH$_2$), 3.42 (s, 3H, Me$_2$SO), 2.84 (m, 2H, CH$_2$S), 2.24 (m, 2H, CH$_2$C*H*$_2$CH$_2$). ^{13}C{^{1}H} NMR (75 MHz, dmso-d_6): δ 140.4 (s, Imz C^2), 120.9 (s, Imz C^{4,5}), 48.6 (s, NCH$_2$), 47.7 (s, CH$_2$S), 25.6 (s, CH$_2$CH$_2$CH$_2$). ^{195}Pt NMR (107 MHz, dmso-d_6): δ −3518. ESI-MS (negative ion, MeOH) *m*/*z*: 675.9366 [M − Na]$^-$ (calcd 675.9355) 73%. Anal. Calcd (%) for $C_{11}H_{20}Cl_2N_2Na_2O_7PtS_3$: C, 18.86; H, 2.88; N, 4.00. Found (%): C, 18.90; H, 3.66; N, 3.84.

*cis-Dichlorido(dimethyl sulfoxide)[1-methyl-3-(3-sodiumsulfonatepropyl)imidazol-2-ylidene]platinum(II) (**4b**).* Complex **4b** was obtained from **1b** (0.156 g, 0.764 mmol) as a white solid (0.261 g, 60%) after 17 h of reaction at 90 °C. ^{1}H NMR (500 MHz, dmso-d_6): δ 7.39 (d, $^3J_{HH}$ = 2.0, 1H, Imz), 7.35 (d, $^3J_{HH}$ = 2.0, 1H, Imz), 4.50 (m, 1H, NCH$_2$), 4.20 (m, 1H, NCH$_2$), 3.85 (s, 3H, NMe), 2.50 (m, 2H, CH$_2$S), 2.20 (m, 2H, CH$_2$C*H*$_2$CH$_2$). ^{1}H NMR (300

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MHz, D_2O): δ 7.11 (d, $^3J_{HH}$ = 1.3, 1H, Imz), 7.05 (d, $^3J_{HH}$ = 1.6, 1H, Imz), 4.32 (t, $^3J_{HH}$ = 7.2, 2H, NCH_2), 3.78 (s, 3H, NMe), 3.38 (s with ^{195}Pt satellites, $^3J(^1H-^{195}Pt)$ = 26.4, 6H, Me_2SO), 2.79 (m, 2H, CH_2S), 2.20 (m, 2H, $CH_2CH_2CH_2$). $^{13}C\{^1H\}$ NMR (75 MHz, dmso-d_6): δ 140.8 (s with ^{195}Pt satellites, $^1J(^{13}C-^{195}Pt)$ = 1378, Imz C^2), 122.1 (s, Imz C^5), 120.9 (s, Imz C^4), 48.3 (s, NCH_2), 47.6 (s, CH_2S), 36.6 (s, NMe), 25.7 (s, $CH_2CH_2CH_2$). $^{13}C\{^1H\}$ NMR (75 MHz, D_2O): δ 138.0 (s, Imz C^2), 123.6 (s, Imz C^5), 121.8 (s, Imz C^4), 48.8 (s, NCH_2), 47.8 (s, CH_2S), 45.4 (s, Me_2SO), 44.9 (s, Me_2SO), 37.1 (s, NMe), 25.2 (s, $CH_2CH_2CH_2$). ^{15}N NMR (50 MHz, dmso-d_6): δ −194.0 (s, NCH_2), −206.3 (s, NMe). ^{195}Pt NMR (107 MHz, dmso-d_6): δ −3529. ESI-MS (negative ion, MeOH) m/z: 545.9673 $[M - Na]^-$ (calcd 545.9655) 19%. Anal. Calcd (%) for $C_9H_{17}Cl_2N_2NaO_4PtS_2$: C, 18.95; H, 3.00; N, 4.91. Found (%): C, 18.53; H, 3.64; N, 4.76.

*cis-Dichlorido[1-(3-sodiumsulfonatepropyl)-3-(2,4,6-trimethylphenyl)imidazol-2-ylidene](dimethyl sulfoxide)platinum(II) (**4c**).* Complex **4c** was obtained from **1c** (0.236 g, 0.764 mmol) as a pale yellow solid (0.479 g 93%) after 23 h of reaction at 90 °C. The solid was isolated by evaporation of the dimethyl sulfoxide solution to dryness and drying the resulting solid for 24 h at 90 °C and 4 mbar. ^{1}H NMR (500 MHz, dmso-d_6): δ 7.66 (d, $^3J_{HH}$ = 2.0, 1H, Imz), 7.42 (d, $^3J_{HH}$ = 2.0, 1H, Imz), 7.07 (s, 1H, Ar), 7.04 (s, 1H, Ar), 4.71 (m, 1H, NCH_2), 4.30 (m, 1H, NCH_2), 3.47 (s, 3H, Me_2SO), 2.86 (m, 2H, CH_2S), 2.81 (s, 3H, Me_2SO), 2.33 (m, 2H, $CH_2CH_2CH_2$), 2.31 (s, 3H, Ar *p*-Me), 2.18 (s, 3H, Ar *o*-Me), 2.03 (s, 3H, Ar *o*-Me). $^{13}C\{^1H\}$ NMR (125 MHz, dmso-d_6): δ 141.7 (s, Imz C^2), 138.2 (s, Ar C^4), 135.5 (s, Ar C^2), 135.2 (s, Ar C^2), 134.1 (s, Ar C^1), 128.7 (s, Ar C^3), 128.3 (s, Ar C^3), 123.3 (s, Imz C^4), 121.4 (s, Imz C^5), 49.0 (s, NCH_2), 47.9 (s, CH_2S), 45.0 (s, Me_2SO), 44.0 (s, Me_2SO), 25.7 (s, $CH_2CH_2CH_2$), 20.1 (s, Ar *p*-Me), 18.7 (s, Ar *o*-Me), 17.7 (s, Ar *o*-Me). ^{15}N NMR (50 MHz, dmso-d_6): δ −190.9 (s, NCH_2), −192.0 (s, NAr). ^{195}Pt NMR (107 MHz, dmso-d_6): δ −3478. ESI-MS (negative ion, MeOH) m/z: 650.0301 $[M - Na]^-$ (calcd 650.0281) 100%. Anal. Calcd (%) for $C_{17}H_{25}Cl_2N_2NaO_4PtS_2$: C, 30.27; H, 3.74; N, 4.15. Found (%): C, 30.00; H, 3.92; N, 3.62.

*cis-Dichlorido[1-(2,6-diisopropylphenyl)-3-(3-sodiumsulfonatepropyl)imidazol-2-ylidene](dimethyl sulfoxide)-platinum(II) (**4d**).* Complex **4d** was obtained from **1d** (0.268 g, 0.764 mmol) as a pale yellow solid (0.492 g, 90%) after 25 h of reaction at 90 °C. The solid was isolated by evaporation of the dmso solution to dryness and drying the resulting solid for 24 h at 90 °C and 4 mbar. ^{1}H NMR (500 MHz, dmso-d_6): δ 7.67 (d, $^3J_{HH}$ = 2.0, 1H, Imz), 7.545 (d, $^3J_{HH}$ = 2.0, 1H, Imz), 7.541 (t, $^3J_{HH}$ = 7.8, 1H, Ar H^4), 7.40 (d, $^3J_{HH}$ = 7.9, 1H, Ar H^3), 7.35 (d, $^3J_{HH}$ = 7.9, 1H, Ar H^3), 4.83 (m, 1H, NCH_2), 4.28 (m, 1H, NCH_2), 3.43 (s, 3H, Me_2SO), 3.14 (m, 1H, C*H*Me_2), 2.64 (s, 3H, Me_2SO), 2.59 (m, 2H, CH_2S), 2.53 (m, 1H, C*H*Me_2), 2.33 (m, 2H, $CH_2CH_2CH_2$), 1.29 (d, J = 6.6, 3H, CHMe_2), 1.20 (d, J = 6.6, 3H, CHMe_2), 1.04 (d, J = 6.6, 3H, CHMe_2), 0.88 (d, J = 6.6, 3H, CHMe_2). $^{13}C\{^1H\}$ NMR (125 MHz, dmso-d_6): δ 146.6 (s, Ar C^2), 145.9 (s, Ar C^2), 142.7 (s, Imz C^2), 133.7 (s, Ar C^1), 129.7 (s, Ar C^4), 124.6 (s, Imz C^5), 123.6 (s, Ar C^3), 123.3 (s, Ar C^3), 120.9 (s, Imz C^4), 49.2 (s, NCH_2), 47.7 (s, CH_2S), 27.4 (s, *C*HMe_2), 27.3 (s, *C*HMe_2), 26.4 (s, $CH_2CH_2CH_2$), 25.9 (s, CHMe_2), 25.7 (s, CHMe_2), 22.2 (s, CHMe_2), 22.0 (s, CHMe_2). ^{15}N NMR (50 MHz, dmso-d_6): δ −190.5 (s, NCH_2), −193.7 (s, NAr). ^{195}Pt NMR (107 MHz, dmso-d_6): δ −3474. ESI-MS (negative ion, MeOH) m/z: 692.0782 $[M - Na]^-$ (calcd 692.0750) 100%. Anal. Calcd (%) for $C_{20}H_{31}Cl_2N_2NaO_4PtS_2$: C, 33.52; H, 4.36; N, 3.91. Found (%): C, 32.45; H, 4.69; N, 3.80.

*cis-Dichlorido[1,3-bis(2,6-diisopropyl-4-sodiumsulfonatephenyl)-imidazol-2-ylidene](dimethyl sulfoxide)platinum(II) (**4e**).* Using the above procedure, only 65% of the imidazolium salt **1e** was converted into **4e** after 10 days of reaction at 90 °C (^{1}H NMR analysis). All attempts to isolate pure samples of complex **4e** failed. The characterization data are nevertheless given. ^{1}H NMR (300 MHz, dmso-d_6): δ 7.81 (s, 1H, Imz), 7.62 (d, $^3J_{HH}$ = 1.6, 1H, Ar), 7.59 (d, $^3J_{HH}$ = 1.6, 1H, Ar), 3.14 (hept, $^3J_{HH}$ = 6.6, 1H, C*H*Me_2), 2.97 (hept, $^3J_{HH}$ = 6.6, 1H, C*H*Me_2), 1.33 (d, $^3J_{HH}$ = 6.6, 3H, CHMe_2), 1.30 (d, $^3J_{HH}$ = 6.6, 3H, CHMe_2), 1.05 (d, J = 6.6, 3H, CHMe_2), 1.01 (d, $^3J_{HH}$ = 6.6, 3H, CHMe_2). $^{13}C\{^1H\}$ NMR (75 MHz, dmso-d_6): δ 149.0 (s, Ar C^4), 146.0 (s, Ar C^2), 144.9 (s, Ar C^2), 144.1 (s, Imz C^2), 134.2 (s, Ar C^1), 124.8 (s, Imz $C^{4,5}$), 120.8 (s, Ar C^3), 120.3 (s, Ar C^3), 28.1 (s, *C*HMe_2), 27.6 (s, *C*HMe_2), 25.6 (s, two CHMe_2 overlapping), 22.5 (s, CHMe_2), 22.0 (s, CHMe_2). ESI-MS (negative ion, MeOH) m/z: 912.0954 $[M - Na]^-$ (calcd 912.0920) 1.6%; 444.5531 $[M - 2Na]^{2-}$ (calcd 444.5516) 100%.

*cis-Dichlorido{bis[3-(3-sodiumsulfonatepropyl)imidazol-2-ylidene]methane}platinum(II) (**5**).* Complex **5** was obtained from **1f** (0.300 g, 0.764 mmol) as a white solid (0.408 g, 76%) after 34 h of reaction at 90 °C. ^{1}H NMR (500 MHz, dmso-d_6): δ 7.51 (d, J = 1.9, 2H, Imz), 7.34 (d, $^3J_{HH}$ = 1.9, 1H, Imz), 6.13 (d, $^2J_{HH}$ = 13.2, 1H, NCH_2N), 5.91 (d, $^2J_{HH}$ = 12.9, 1H, NCH_2N), 4.75 (m, 2H, NCH_2), 4.18 (m, 2H, NCH_2), 2.46 (m, 2H, CH_2S), 2.27 (m, 2H, CH_2S), 2.06 (m, 4H, $CH_2CH_2CH_2$). $^{13}C\{^1H\}$ NMR (75 MHz, dmso-d_6): δ 143.6 (s, Imz C^2), 121.9 (s, Imz C^5), 121.0 (s, Imz C^4), 62.3 (s, NCH_2N), 48.5 (s, CH_2S), 48.5 (s, NCH_2), 27.2 (s, $CH_2CH_2CH_2$). ^{15}N NMR (50 MHz, dmso-d_6): δ −190.0 (s, NCH_2), −200.0 (s, NCH_2N). ^{195}Pt NMR (107 MHz, dmso-d_6): δ −3572. ESI-MS (negative ion, MeOH) m/z: 677.9590 $[M - Na]^-$ (calcd 677.9590) 7.3%; 620.0033 $[M - 2Na - Cl]^-$ (calcd 620.0010) 24%. Anal. Calcd (%) for $C_{13}H_{18}Cl_2N_4Na_2O_6PtS_2$: C, 22.23; H, 2.58; N, 7.98. Found (%): C, 22.39; H, 3.09; N, 7.46.

General Method for the Hydration of Alkynes in Water. The reaction of phenylacetylene and water is given as an example. Phenylacetylene (0.05 mL g, 0.455 mmol), the corresponding platinum complex (9.1 μmol, 2 mol %), and water (2 mL) were introduced into an ampule tube equipped with a PTFE valve. The mixture was vigorously stirred at the temperature and for the time specified in Tables 3 and 4. After cooling to room temperature, sodium chloride (1 g) was added to the resulting emulsion to facilitate the separation of layers, and the organics were extracted with diethyl ether (3 × 15 mL). The combined ethereal layers were dried over $MgSO_4$, and the solvent was removed under vacuum (25 °C and 500 mbar). Conversions were determined by integration of the ^{1}H NMR spectra.

X-ray Crystallographic Studies. Suitable single crystals were obtained by slow diffusion of diethyl ether into a dmso solution (**2e**$^{Ag+}$), dichloromethane into a methanol solution (**2e**·6MeOH), acetone into a dmso solution (**2e**·5Me_2SO·H_2O and **3e**), or acetone into an aqueous solution (**4a**). A summary of crystal data, data collection, and refinement parameters for the structural analyses is given in Table S1 (Supporting Information). Crystals were glued to a glass fiber using an inert polyfluorinated oil and mounted in the low-temperature N_2 stream (200 K) of a Bruker-Nonius Kappa-CCD diffractometer equipped with an area detector and an Oxford Cryostream 700 unit (**2e**·6MeOH and **2e**$^{Ag+}$) or at 100 K (**2e**·5Me_2SO·H_2O) or 296 K (**3e** and **4a**) in a Bruker Kappa Apex II diffractometer.

Intensities were collected using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Data were measured with exposure times of 19 s per frame for **2e**·6MeOH (13 sets; 599 frames; phi/omega scans; 1.9° scan-width), 120 s per frame for **2e**·5Me_2SO·H_2O (3 sets; 592 frames; phi/omega scans; 0.5° scan-width), 171 s per frame (4 sets; 288 frames; phi/omega scans; 1.9° scan-width) for **2e**$^{Ag+}$, 10 s per frame for **3e** (5 sets; 1662 frames; phi/omega scans; 0.5° scan-width), and 5 s per frame for **4a** (10 sets; 3812 frames; phi/omega scans; 0.5° scan-width). Raw data were corrected for Lorenz and polarization effects. The structures were solved by direct methods, completed by subsequent difference Fourier techniques, and refined by full-matrix least-squares on F^2 (SHELXL-97).[61] Anisotropic thermal parameters were used in the last cycles of refinement for the non-hydrogen atoms. Absorption correction procedures were carried out using the multiscan SORTAV (semiempirical from equivalent, **2e**·6MeOH and **2e**$^{Ag+}$)[62] or SADABS programs (**2e**·5dmso·H_2O, **3e**, and **4a**).[63] Hydrogen atoms were included in the last cycle of refinement from geometrical calculations and refined using a riding model. All the calculations were made using the WINGX system.[64] In the case of **2e**·6MeOH, the disorder observed for O(21), O(22), and O(23), and for O(56) was modeled in two positional sets with occupancy factors of 0.54 and 0.46, and 0.81 and 0.19, respectively. In the case of **2e**$^{Ag+}$, the disorder

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observed for O(1), O(2), and O(3) was modeled in two sets with occupancy factors of 0.85 and 0.15. In this compound, it was not possible to model some remaining electronic density found in the difference Fourier map and due to disordered solvent molecules. The Squeeze procedure[65] was used to remove this contribution to the structure factors.

■ ASSOCIATED CONTENT

Supporting Information

Crystallographic data and CIF files for compounds **2e**·6MeOH, **2e**·5Me_2SO·H_2O, **2e**$^{Ag+}$, **3e**, and **4a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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