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Water-soluble gold(I)–NHC complexes of sulfonated IMes and SIMes and their catalytic activity in hydration of alkynes

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ABSTRACT

The water-soluble carbene ligand precursors sIMesH$^+$Cl$^-$ and sSIMesH$^+$Cl$^-$ were synthesized in high yields by direct sulfonation of IMesH$^+$Cl$^-$ (1,3-bis(2,4,6-trimethylphenyl) imidazolium chloride) and SIMesH$^+$Cl$^-$ (1,3-bis(2,4,6-trimethylphenyl)imidazolinium chloride). Gold(I)-N-heterocyclic carbene complexes [AuCl(sIMes)] and [AuCl(sSIMes)] were prepared by carbene transfer from the zwitterionic [Ag(sIMes)$_2$] and [Ag(sSIMes)$_2$] to [AuCl(tht)] (tht = tetrahydrothiophene). In methanol–water mixtures or in neat water, the new gold(I)–NHC complexes showed high catalytic activity in Markovnikov type hydration of terminal alkynes (up to a turnover frequency 1990 h^{-1}; ethynyltoluene, 0.1 mol% catalyst) but were markedly less active in case of internal alkynes (TOF = 3.6 h^{-1}; diphenylethyne, 1 mol% catalyst). These new Au(I)-NHC catalysts do not require acid co-catalysts or activation by Ag(I)-additives.

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1. Introduction

Aqueous organometallic catalysis allows substantial advances towards making chemical processes greener not only by leading to increased reaction rates and selectivities but also by replacing organic solvents by an environmentally benign one [1–4]. Water has many excellent solvent properties (amply discussed in the literature), however, less attention is focussed on H$_2$O as a reagent. Transition-metal catalyzed reactions such as the telomerization of dienes with water [5], hydration of alkynes [6,7], alkenes [7] and nitriles [8] afford valuable products. All these processes require water-soluble or at least water-tolerant catalysts. These can be simple salts, such as RhCl$_3$ [9] in hydration of acetylene or more elaborate catalysts, in most cases with tertiary phosphine ligands carrying sulfonate [10] or other hydrophilic solubilizing groups. A recent example is the use of a Ru(II)–arene complex with Ph$_2$PC$_6$H$_4$-2 or 3-CH$_2$NHR (R = Pr^i or Bu^t) ligand for the very efficient hydration of nitriles [8] under mild conditions. In most cases, hydration of alkynes proceeds according to Markovnikov's rule and yields methyl ketones. This reaction was traditionally carried out using strongly acidic solutions of Hg(II)-salts, however, this is a noxious procedure and more efficient transition metal complex-

catalyzed reactions have been developed. By now hydration of alkynes became a valuable tool in organic synthesis [6,7].

An important development in homogeneous catalysis is the use of well-defined, stable N-heterocyclic carbene (NHC) complexes of transition metals for a wide variety of chemical transformations [11–13] owing to the relative ease of their synthesis, to the large flexibility of ligand structure modifications and to the high stabilities of their metal complexes. Taking into account the very successful use of water-soluble phosphine complexes in organometallic catalysis [1–4], it is reasonable to expect, that the catalytic chemistry by water-soluble N-heterocyclic carbene complexes might be similarly transferred to purely aqueous or biphasic systems by using suitable ligands.

Convenient precursors to carbene ligands are the corresponding imidazolium salts from which the NHC-s can be obtained by deprotonation [14]. A fairly large number of properly 1,3-disubstituted imidazolium salts are known (incorporating sulfonate, carboxylate or ammonium groups) which – in principle – allow the synthesis of water soluble transition metal–NHC complexes [15–17]. However, free N-heterocyclic carbenes are highly basic [18], so much that their synthesis in water is not possible. Nevertheless, Taube and co-workers observed the spontaneous formation in aqueous solution of several C-2-bound imidazole species [19] in the reaction of N-protonated 4,5-dimethylimidazole and [Ru(NH$_3$)$_5$(H$_2$O)]$^{2+}$. High thermodynamic stability of late transition metal–NHC complexes is also shown by the findings that such complexes can be prepared in partly or fully aqueous

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solutions at elevated temperatures. A case in point is the reaction of 1,3-dibenzylimidazolium bromide and [{RhCl(cod)}$_2$] (cod = 1,5-cyclooctadiene) in aqueous K$_2$CO$_3$ solution affording [RhCl(dbim)(cod)] (dbim = 1,3-dibenzylimidazol-2-ylidene) in quantitative yield [20]. Similarly, the simplest synthesis of Ag(I)- and Cu(I)–NHC complexes involves refluxing of suspensions of Ag$_2$O [21] or Cu$_2$O [22] together with an equivalent amount of the appropriate imidazolium salt in water. Several cationic NHC-complexes showed appreciable water-solubility and stability in aqueous solutions [23–26].

The first attempts to use water-soluble transition metal–NHC complexes for organometallic catalysis were made by Herrmann et al. who synthesized the 1-methyl-3(butyl-4-sulfonate) betain and applied its in situ formed Rh(I)-complex for hydroformylation of various olefins [27]. Çetinkaya and co-workers obtained Ru(II)- and Rh(I)–NHC complexes with –NMe$_2$ functionalized imidazolin-2-ylidene ligands, protonation of which resulted in stable, water-soluble complexes. The latter were found active catalysts for the synthesis of 2,3-dimethylfuran by cyclization of (Z)-3-methylpent-2-en-4-yn-1-ol in aqueous-organic biphasic systems [28]. Hydroformylation of 1-octene under aqueous biphasic conditions was studied by Weberkirsch et al. using a Rh(I)–NHC complex covalently attached to an amphiphilic block copolymer [29]. We have reported that redox isomerization of allylic alcohols in neat water was catalyzed by [RuCl$_2$L(η^6-p-cymene)] (L = 1-butyl-3-methylimidazol-2-ylidene, p-cymene = p-isopropyltoluene) [24,25]. For the same reaction Peris and co-workers used cationic Cp-functionalized NHC complexes of Ru(II) [30], as well as an arene–Ru(II) catalyst [31] having a 1-methyl-3(propyl-3-sulfonate)imidazol-2-ylidene ligand. Ru–NHC complexes play an extremely important role in catalysis of olefin metathesis; this reaction can also be run in aqueous systems with various water-soluble NHC complexes as catalysts [32–35].

Palladium(II)–NHC complex-catalyzed C–C coupling reactions (Heck-, Suzuki-Miyaura-, Sonogashira-couplings) have been actively investigated [36–40] using water-soluble Pd-complexes with various N-heterocyclic carbene ligands. Plenio and co-workers studied Suzuki-Miyaura- and Sonogashira-couplings in aqueous solvents applying in situ formed catalysts obtained from Na$_2$PdCl$_4$ and disulfonated 1,3-diarylimidazolium or 1,3-diarylimidazolinium salts [41,42]. In particular, the NHC ligands included disulfonated IMes, SIMes and IPr (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene). These compounds were prepared starting from the appropriate 3-sulfonated alkylaniline via the respective diimine or diamine followed by ring-closure. Alternatively, the same products could be obtained by direct sulfonation of the 1,3-diarylimidazolium or –imidazolinium salts with chlorosulfonic acid followed by hydrolysis with aqueous NaOH.

For a long period, complexes of gold did not attract much interest in homogeneous organometallic catalysis due to their generally conceived inactivity in such processes. However, this situation has drastically changed in the last two decades and now gold has a prominent place among the most valued homogeneous catalysts [12,43–45]. It is illustrative to mention, that although the complex formation of gold(I) with a sulfonated tertiary phosphine, mtppms (diphenylphosphinobenzene-m-sulfonate) were studied in aqueous solution as early as 1970 [46], the first paper on the catalytic activity of a water-soluble gold(I)–tertiary phosphine complex was published not before 2007 [47]. Since gold shows high affinity for alkynes, its use for catalytic hydration has been studied by several groups [48–57]. For effective catalysis, in most cases a strong acid co-catalyst is needed. Laguna et al. studied the water soluble [AuCl(PR$_3$)] complexes with PR$_3$ = mtppms, mtppds and mtppts, i.e. mono-, di- and trisulfonated triphenylphoshines and established, that in the presence of sulfuric acid they all showed high catalytic

activity in hydration of a series of alkynes [46,55,56]. Recently Leyva and Corma reported [58] that cationic [Au(PR$_3$)]NTf$_2$ (PR$_3$ = tertiary phosphine, NTf$_2$ = bis(trifluoromethanesulfonate)imidate) catalysts exhibited high activity without the need for acid co-catalysts. Also recently, Nolan et al. disclosed, that [AuCl(IPr)] was an extremely active catalyst for alkyne hydration (ppm catalyst loadings) in combination with AgSbF$_6$ in the absence of acids [59]. Interestingly, under the same conditions [AuCl(IMes)] was completely inactive. Protonation of [Au(OH)(IPr)] with a Brønsted acid yielded an active, silver-free catalyst for alkyne hydration [60].

In the course of our studies on catalysis by transition metal-NHC complexes in water, we synthesized several ω-sulfoalkylimidazolium salts and used them for the synthesis of water-soluble Ag(I)–NHC and Au(I)–NHC complexes. Such Au(I)–NHC complexes were successfully applied for hydration of terminal alkynes [61]. In continuation of these studies we developed an independent procedure for the synthesis of disulfonated 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride (sIMesH$^+$Cl$^-$, **1a**) and 1,3-bis(2,4,6-trimethylphenyl)imidazolinium chloride (sSIMesH$^+$Cl$^-$, **1b**). This procedure is reported here together with the syntheses of the respective Ag(I)–NHC and Au(I)–NHC complexes. Hydration of various alkynes in aqueous solvents with [AuCl(sIMes)] (**3a**) and [AuCl(sSIMes)] (**3b**) as catalysts was studied in detail and the results are also given below.

2. Experimental

All experiments were carried out in deaerated solvents under an oxygen-free atmosphere (Ar or N$_2$) using standard Schlenk techniques. The chemicals used in this work were purchased from Sigma–Aldrich, Fluka, Molar Chemicals and Spektrum 3D and were used without further purification. Fuming sulfuric acid was obtained from Merck. Ag$_2$O was prepared by the reaction of AgNO$_3$ and NaOH. [AuCl(tht)] was prepared by the method described in the literature [62]. Doubly distilled water was used throughout.

Reaction mixtures were analyzed by gas chromatography (HP5890 Series II; Chrompack WCOT Fused Silica 30 m × 32 mm CP WAX52CB; FID; carrier gas: argon). The products were identified by comparison to known compounds. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 360 MHz spectrometer and referenced to 3-(trimethylsilyl)propanesulfonic acid Na-salt (TSPSA). ESI mass data were collected on a BRUKER BioTOF II ESI-TOF spectrometer. IR spectra were recorded on a Perkin Elmer Instruments Spectrum One FT-IR spectrometer equipped with a Universal ATR Sampling Accessory.

2.1. Sulfonation of 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride

To a mixture of 4 mL 30% fuming sulfuric acid (oleum) and 1 mL cc. H$_2$SO$_4$ cooled to 0 °C in an ice bath was added 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride (1.00 g, 2.93 mmol) in small portions. Addition of the total amount of the imidazolium salt took at least 20 min. The mixture was then allowed to warm to room temperature and the content of the flask was carefully added to a 100 mL flask containing crushed ice (36 g). The reaction mixture was again cooled in ice bath and neutralized to pH 7 with 50% NaOH. The water was removed in vacuum. The white solid residue was extracted at room temperature with dry methanol (40 mL), filtered and the remaining Na$_2$SO$_4$ was treated again with 2 × 40 mL methanol at room temperature. The combined extracts were evaporated to dryness to give sIMesH$^+$Cl$^-$ (**1a**) as white solid. Yield: 1.16 g, 72%.

^{1}H NMR (360 MHz, H$_2$O saturated with NaCl, D$_2$O capillary), δ [ppm]: 8.91 (s, 1H, CH$_{im}$); 7.56 (s, 2H, CH); 6.97(s, 2H, ArH); 2.26 (s, 6H, CH$_3$); 1.98 (s, 3H, CH$_3$) 1.99 (s, 3H, CH$_3$); 1.77 (s, 3H,

CH_3); 1.78 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (90 MHz, D_2O), all singlets, δ [ppm]: 140.3 (HC_{im}-N); 139. 8 (C_{aryl}-N); 137.9 (C_{aryl}-SO_3Na); 137.1 (C_{aryl}-Me); 133.9 (C_{aryl}-Me); 132.9 (C_{aryl}-H); 132.4 (C_{aryl}-Me); 125.1 (CH_{im}); 22.5 (CH_3); 16.8 (CH_3); 15.8 (CH_3). ESI-MS: m/z observed 509.079, calcd. for $C_{21}H_{23}N_2Na_2O_6S_2$ [M–Cl]$^+$ 509.078 (see Fig. S1 in Supplementary Material). IR (ATR) $\nu(SO_3)$ = 1183, 1049 cm^{-1}.

Caution: Fuming sulfuric acid is strongly corrosive and reacts violently with water. Protective clothing, glasses and suitable gloves should be worn and all manipulations should be done in a well ventilated fume-hood.

2.2. Sulfonation of 1,3-bis(2,4,6-trimethylphenyl)imidazolinium chloride

sSIMesH$^+$Cl$^-$ (**1b**) was prepared from SIMesH$^+$Cl$^-$ (1.00 g, 2.93 mmol) using the same procedure as for the preparation of sIMesH$^+$Cl$^-$ (**1a**). White powder, yield 1.30 g, 81%.

^1H NMR: (360 MHz, H_2O saturated with NaCl, D_2O capillary), δ [ppm]: 8.88 (s, 1H, CH_{im}); 7.33 (s, 2H, ArH); 4.59 (s, 4H, CH_2); 2.80 (s, 6H, CH_3); 2.75 (s, 6H, CH_3); 2.55 (s, 6H, CH_3).

$^{13}C\{^1H\}$ NMR (90 MHz, D_2O), all singlets, δ [ppm]: 160.9 (HC_{im}-N); 142.4 (C_{aryl}-N); 139.5 (C-SO_3Na); 136.5 (C_{aryl}-Me); 135.2 (C_{aryl}-Me); 132.6 (C_{aryl}-H); 132.1 (C_{aryl}-Me); 51.3 (CH_{2im}); 22.3 (CH_3); 16.7 (CH_3); 15.6(CH_3). ESI-MS: m/z observed 511.090, calcd. for $C_{21}H_{25}N_2Na_2O_6S_2$ [M–Cl]$^+$ 511.094 (see Fig. S1). IR (ATR) $\nu(SO_3)$ = 1186, 1066 cm^{-1}.

2.3. Synthesis of [Ag(sIMes)₂], 2a

In a round-bottom flask, a mixture of sIMesH$^+$Cl$^-$ (465 mg, 0.85 mmol) and Ag_2O (192 mg, 0.83 mmol) in dry methanol (25 mL) was heated to reflux and stirred for 16 h at this temperature and an additional 36 h at room temperature in the dark. The solution was filtered through Celite, and the solvent was removed under vacuum to afford [Ag(sIMes)₂] as a white solid. Yield 437 mg, 93%.

^1H NMR: (360 MHz, H_2O saturated with NaCl, D_2O capillary), δ [ppm]: 7.48 (s, 2H, CH); 7.14 (s, 2H, ArH); 2.92 (s, 6H, CH_3); 2.29 (s, 6H, CH_3); 1.79 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR (90 MHz, H_2O saturated with NaCl, D_2O capillary), δ [ppm]: 182.8 (dd, $^1J_{C109Ag}$ = 205.9 Hz, $^1J_{C107Ag}$ = 178.4 Hz) (NC_{im}-N); 140.3 (s, C_{aryl}-N); 139.2 (s, C-SO_3Na); 137.7 (s, C_{aryl}-Me); 137.3 (s, C_{aryl}-Me); 136.5 (s, C_{aryl}-H); 132.3 (s, C_{aryl}-Me); 123.3 (d, $^3J_{CAg}$ = 5.4 Hz) (CH_{im}); 22.9 (s, CH_3); 16.6 (s, CH_3); 15.8 (s, CH_3). ESI-MS: m/z observed 528.038, calcd. for $C_{42}H_{44}N_4O_{12}S_4NaAg$ [M-2Na]$^{2-}$ 528.040 (see Fig. S2). IR (ATR) $\nu(SO_3)$ = 1183, 1052 cm^1.

2.4. Synthesis of [Ag(sSIMes)₂], 2b

This compound was prepared from Ag_2O and sSIMesH$^+$Cl$^-$ (450 mg, 0.82 mmol) using the same procedure as for the synthesis of [Ag(sIMes)₂]. White solid, yield 347 mg, 77%.

^1H NMR: (360 MHz, H_2O saturated with NaCl, D_2O capillary), δ [ppm]: 7.03 (s, 2H, ArH); 4.02 (s, 4H, CH_2); 2.87 (s, 6H, CH_3); 2.51 (s, 6H, CH_3); 1.90 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR (90 MHz, H_2O saturated with NaCl, D_2O capillary), δ [ppm]: 206.7 (dd, $^1J_{C109Ag}$ = 192.4 Hz, $^1J_{C107Ag}$ = 166.9 Hz) (NC_{im}-N); 139.3 (s, C_{aryl}-N); 138.5 (s, C-SO_3Na); 136.7 (s, C_{aryl}-Me); 136.4 (s, C_{aryl}-Me); 135.3 (s, C_{aryl}-H); 132.7 (s, C_{aryl}-Me); 50.8(CH_{2im}); 22.9 (s, CH_3); 16.9 (s, CH_3); 15.9 (s, CH_3). ESI-MS: m/z observed 530.055, calcd. for $C_{42}H_{48}N_4O_{12}S_4NaAg$ [M-2Na]$^{2-}$ 530.054 (see Fig. S2). IR (ATR) $\nu(SO_3)$ = 1179, 1068 cm^{-1}.

2.5. Synthesis of [AuCl(sIMes)], 3a

In a Schlenk flask [Ag(sIMes)₂] (300 mg, 0.27 mmol) was dissolved in 36 mL deoxygenated dry methanol. A solution of [AuCl(tht)] (170 mg, 0.528 mmol) (tht = tetrahidrothiophene) in acetone (18 mL) was added and the mixture was stirred at room temperature in the dark for 72 h. The solution was filtered through Celite and the solvent was removed under vacuum to afford the crude product. The product was washed three times with cold acetone (3 × 10 mL) and dried under vacuum to afford [AuCl(sIMes)] as white powder. Yield: 340 mg, 84%.

^1H NMR (360 MHz, MeOH, D_2O capillary), δ [ppm]: 7.51 (s, 2H, CH); 7.19(s, 2H, ArH); 2.69 (s, 6H, CH_3); 2.40 (s, 6H, CH_3) 2.12 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR (90 MHz, MeOH, D_2O capillary), all singlets, δ [ppm]: 172.8 (NC_{im}-N); 142.1 (C_{aryl}-N); 139.8 (C-SO_3Na); 137.3 (C_{aryl}-Me); 137.1 (C_{aryl}-Me); 135.4 (C_{aryl}-H); 132.8 (C_{aryl}-Me); 124.3 (CH_{im}); 23.2 (CH_3); 17.7 (CH_3); 16.5 (CH_3). ESI-MS: m/z observed 347.018, calcd. for $C_{21}H_{22}N_2O_6S_2AuCl$ [M-2Na]$^{2-}$ 347.014 (see Fig. S3). IR (ATR) $\nu(SO_3)$ = 1185, 1055 cm^{-1}.

2.6. Synthesis of [AuCl(sSIMes)], 3b

This compound was prepared using 200 mg (0.18 mmol) **2b** applying the same procedure as for the synthesis of [AuCl(sIMes)]. White powder, yield 223 mg, 83%.

^1H NMR: (360 MHz, H_2O saturated with NaCl, D_2O capillary), δ [ppm]: 7.06 (s, 2H, ArH); 4.12 (s, 4H, CH_2); 2.68 (s, 6H, CH_3); 2.64 (s, 6H, CH_3); 2.33 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR (90 MHz, CD_3OD), all singlets, δ [ppm]: 194.9 (NC_{im}-N); 142.3 (C_{aryl}-N); 138.6 (C-SO_3Na); 137.9 (C_{aryl}-Me); 136.9 (C_{aryl}-Me); 136.2 (C_{aryl}-H); 132.8 (C_{aryl}-Me); 51.1 (CH_{2im}); 22.8 (CH_3); 17.7 (CH_3); 16.1 (CH_3). ESI-MS: m/z observed 348.021, calcd. for $C_{21}H_{24}N_2O_6S_2AuCl$ [M-2Na]$^{2-}$ 348.022 (see Fig. S3). IR (ATR) $\nu(SO_3)$ = 1181, 1072 cm^{-1}.

2.7. Typical procedure for the hydration of phenylacetylene with complexes 3a or 3b

A Schlenk flask equipped with a magnetic stirring bar and a reflux condenser was charged with methanol (2.5 mL), water or 0.2 M aqueous H_2SO_4 (2.5 mL) and phenylacetylene (5.0 mmol). Catalyst **3a** or **3b** (4.0 mg, 0.005 mmol) was added and the reaction mixture was stirred at reflux temperature for 3 h (reaction mixtures in 50–50 v% MeOH–H_2O solvent refluxed at 74 °C). Samples (150 μL) were periodically withdrawn and added to 1 mL water which then was extracted with 1 mL chloroform or toluene. The organic phase was dried over $MgSO_4$ and analyzed by gas chromatography.

3. Results and discussion

3.1. Synthesis and properties of the water-soluble NHC ligand precursors and their Ag(I)- and Au(I)-complexes

The bulky, basic N-heterocyclic ligands, IMes (1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) and SIMes (1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene) are often used in organometallic catalysis by transition metal–NHC complexes [12]. In the course of our studies on the use of NHC-complexes in aqueous catalysis we conceived that water-soluble analogs of these ligands could be successfully used in water or in biphasic systems. For that reason, disulfonated 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride (sIMesH$^+$Cl$^-$, **1a**) and disulfonated 1,3-bis(2,4,6-trimethylphenyl)imidazolinium chloride (sSIMesH$^+$Cl$^-$, **1b**) (Fig. 1) were prepared by sulfonation of the corresponding imidazolium salts, IMesH$^+$Cl$^-$ and SIMesH$^+$Cl$^-$. Sulfonation with fuming sulfuric acid proceeded cleanly at or below room temperature. Neutralization with 50% NaOH, evaporation to dryness, and extraction by dry MeOH afforded **1a** and **1b** in yields of 72% and 81%, respectively, in pure form. These compounds were previously obtained [42] by sulfonation with
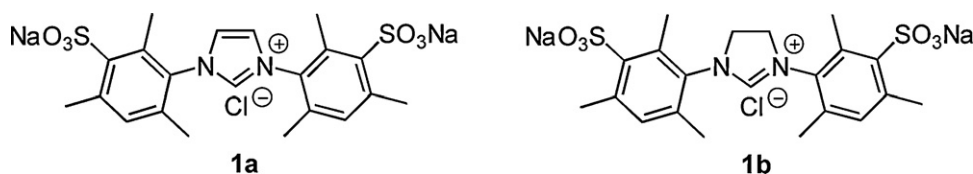
Fig. 1. 1,3-bis(2,4,6-trimethyl-3-sulfonatophenyl)imidazolium chloride (sIMesH$^+$Cl$^-$, **1a**) and 1,3-bis(2,4,6-trimethyl-3-sulfonatophenyl)imidazolinium chloride (sSIMesH$^+$Cl$^-$, **1b**).
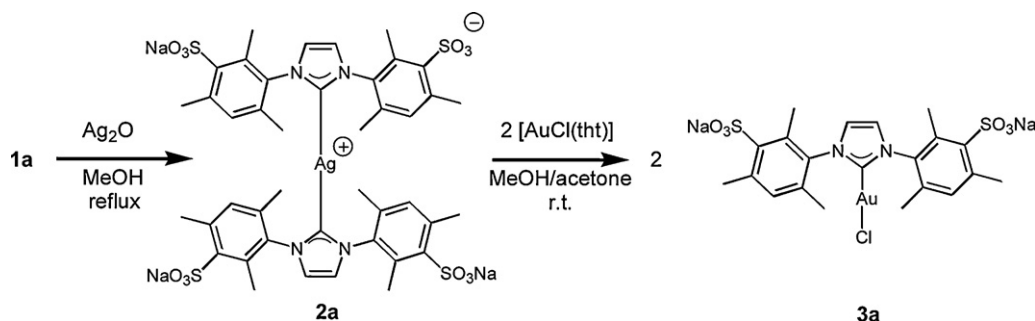

Fig. 2. Synthesis of [Ag(sIMes)$_2$] (**2a**) and [AuCl(sIMes)] (**3a**).

chlorosulfonic acid at 100 °C for 3 h. Although the ^{1}H and ^{13}C NMR data (recorded in D$_2$O) of **1a** and **1b** prepared by us agree with those of the same compounds obtained by Roy and Plenio et al. [42] the signals seemed to us unusually broad or split. Recording the spectra in H$_2$O saturated with NaCl (and using a capillary filled with D$_2$O providing a lock signal) led to sharpening of the signals and even to the collapse of the two singlets observed in D$_2$O (with no NaCl) for the unique proton on the C2 atom of the imidazolium ring (9.04 and 9.03 ppm to 8.91 ppm for **1a**; 9.23 and 9.24 ppm to 8.88 ppm for **1b**). We suppose that in solution there is an equilibrium between the closed (zwitterionic) forms of these imidazolium arylsulfonates and the fully dissociated salts where there is no specific interaction between the imidazolium cation and the pendant sulfonate anion. A high NaCl concentration is expected to favor the latter (in our case NaCl was in about 40 times excess relative to the imidazolium salts). Nevertheless, this phenomenon was not investigated further. Electrospray mass spectra (ESI-TOF MS) showed strong peaks corresponding to [M–Cl]$^+$ cations and the calculated isotope distribution pattern perfectly matched the observed ones both for **1a** and **1b** (Fig. S1).

In methanolic suspensions **1a** and **1b** react readily with Ag$_2$O leading to the formation of the corresponding silver(I)–NHC complexes [Ag(sIMes)$_2$] (**2a**) and [Ag(sSIMes)$_2$] (**2b**) (Fig. 2) which can be isolated by filtration followed by evaporation of the filtrate to dryness. Chloride removal is facilitated by the excess of silver, and in these compounds one of the sulfonate groups acts as a counter-ion to Ag$^+$. These zwitterionic complexes are stable in the solid form for long periods in the dark and can be used for carbene transfer reactions. NMR parameters are very similar to those of close analogs described in the literature. For example, Arduengo et al. reported [63] for [Ag(IMes)$_2$]CF$_3$SO$_3$ the following ^{13}C NMR signals (δ/ppm): 183.6 (dd, $^1J_{C109Ag}$ = 208.57 Hz, $^1J_{C107Ag}$ = 187.95) (NC$_{im}$-N); 124.1 (d $^3J_{CAg}$ = 5.39 Hz) (CH$_{im}$), while those for [Ag(sIMes)$_2$] were observed at 182.8 ppm (dd $^1J_{C109Ag}$ = 205.9 Hz, $^1J_{C107Ag}$ = 178.4 Hz) (NC$_{im}$-N); 123.3 (d, $^3J_{CAg}$ = 5.4 Hz) (CH$_{im}$). These compounds were also characterized by ESI-TOF mass spectrometry and peaks of [M-2Na]$^{2-}$ ions where detected with complete match of the observed and calculated isotope distribution pattern (Fig. S2).

[AuCl(sIMes)] (**3a**) and [AuCl(sSIMes)] (**3b**) were obtained by carbene transfer [64] from **2a** and **2b**, respectively to [AuCl(tht)] in dry methanol/acetone (Fig. 2). After filtration and evaporation to dryness, **3a** and **3b** were obtained in 84% and 83% yields, respec-

tively. These complexes are well soluble in water. Their ^{13}C NMR spectra compare well to those of analogous complexes described in the literature. For example, Nolan and co-workers reported the characteristic ^{13}C resonances for the carbene and imidazole carbon atoms in [AuCl(IMes)] and [AuCl(SIMes)], respectively (all singlets, δ/ppm): 173.4, 122.17 and 195.0, 50.67 [65]. The same values for **3a** and **3b** are 172.8, 124.3 and 194.9, 51.1, respectively. ESI-TOF MS showed peaks for [M-2Na]$^{2-}$ ions with precise match of the observed and calculated isotope distribution patterns (Fig. S3).

3.2. Hydration of water-insoluble alkynes with [AuCl(sIMes)] (3a) and [AuCl(sSIMes)] (3b) as catalysts

In order to compare the catalytic properties of **3a** and **3b** to those of the sulfoalkyl-substituted Au–NHC complexes investigated by us earlier [61] we attempted hydration of several aromatic and aliphatic alkynes (Fig. 3), mostly terminal ones but hydration of diphenylacetylene, as a representative internal alkyne was also examined.

It was found, that both **3a** and **3b** were highly active catalysts in these reactions. The reactions proceeded according to Markovnikov's rule and afforded methyl-ketones as sole products. Fig. 4 shows the time-course of hydration of 4-ethynylanisole, while Table 1 contains characteristic data of the reactions with **3a** as catalyst. It should be mentioned here, that although the catalysts work in purely aqueous solutions with the water-soluble alkyne, propargyl alcohol, for solubility reasons in most cases methanol/water 1/1 mixtures were used as solvent for the largely water-insoluble aromatic alkynes.

It can be seen from Table 1, that all three alkynes reacted cleanly with 4-ethynylanisole being the most reactive (see also Fig. S4).
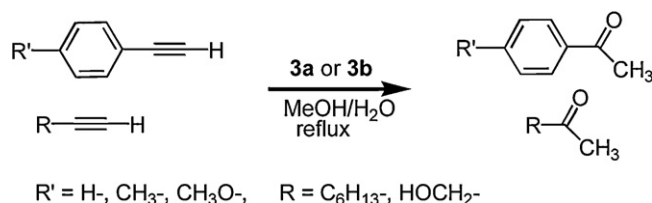

R' = H-, CH$_3$-, CH$_3$O-,　　R = C$_6$H$_{13}$-, HOCH$_2$-

Fig. 3. Hydration of alkynes catalyzed by **3a** and **3b**.

Table 1
Hydration of aromatic alkynes with **3a** as catalyst with and without acid co-catalyst[a].

Entry	Alkyne	**3a** (mol%)	H_2SO_4 (mol%)	Time (min)	Conv. (%)	TOF (h^{-1})
1	Phenylacetylene	0.1	–	30	13	260
2	Phenylacetylene	0.1	–	90	31	206
3	Phenylacetylene	0.1	–	120	36	180
4	Phenylacetylene	0.2	–	120	52	130
5	Phenylacetylene	0.4	–	120	95	119
6	Phenylacetylene[b]	0.1	10	30	83	1660
7	Phenylacetylene[b]	0.1	10	90	99	660
8	4-Ethynyltoluene	0.1	-	90	28	187
9	4-Ethynyltoluene[b]	0.1	10	30	80	1600
10	4-Ethynyltoluene[b]	0.1	10	90	95	633
11	4-Ethynylanisole	0.1	–	30	38	760
12	4-Ethynylanisole	0.1	-	90	98	653
13	4-Ethynylanisole[b]	0.1	10	30	78	1560
14	4-Ethynylanisole[b]	0.1	10	90	100	666

[a] *Conditions*: 5 mmol alkyne, 0.005 mmol **3a**, 2.5 mL MeOH, 2.5 mL H_2O.
[b] 2.5 mL 0.2 M H_2SO_4, reflux.
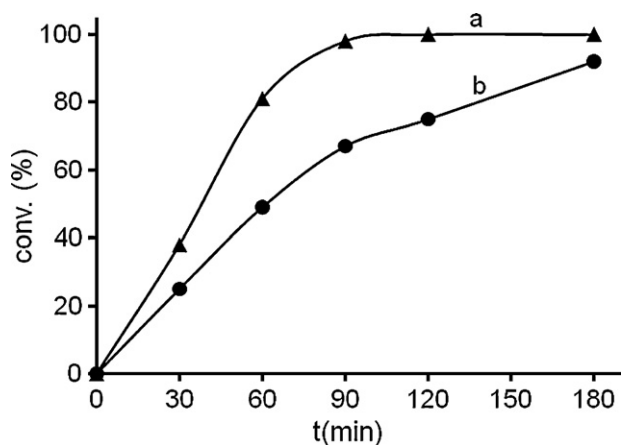
Fig. 4. Hydration of 4-ethynylanisole catalyzed by **3a**. Conditions: (▲) 5.0 mmol 4-ethynylanisole, 0.005 mmol **3a**, 2.5 mL MeOH, 2.5 mL H_2O, reflux; (●) 0.5 mmol 4-ethynylanisole, 6.5×10^{-4} mmol **3a**, 2.5 mL MeOH, 2.5 mL H_2O, reflux.

An important feature of the reaction is in that neither an acid co-catalyst nor a silver(I) activating agent for chloride removal is needed. For example, 98% conversion was achieved in case of 4-ethynylanisole without addition of an acid (entry 12) at a substrate/catalyst ratio of 1000. In this respect **3a** (and also **3b**, see later) belong to the very few Au(I)-based hydration catalysts which are active in acid-free solutions [58,59]. Nevertheless, sulfuric acid has a beneficial effect on the conversions with all three substrates (entries 6, 7, 9, 10, 13, 14), while it is completely ineffective in the absence of the Au(I)–NHC catalyst. Increased catalyst concentrations led to faster reactions, and close to quantitative conversion could be achieved with 0.4 mol% catalyst even with the less reactive phenylacetylene (entry 5). The effect of dilution is also shown

in Fig. 4, where the substrate/catalyst concentration ratio was 1000 (curve a) and 770 (curve b), however, the absolute concentrations of the substrate and catalyst were much different in the two experiments (1.0 mM and 0.13 mM catalyst, respectively). The latter concentration corresponds to as little as 97 ppm **3a** in the reaction mixture so this catalyst belongs to the most active Au(I)–NHC complexes known for alkyne hydration [59,60]. Remarkably, although the reaction slowed down in dilute solution, still the conversion was close to quantitative at longer reaction times. Initial turnover frequencies of the catalyst (TOF = (mol reacted substrate) (mol catalyst)$^{-1}$h^{-1}, calculated from the conversion in the first 30 min) are very high ranging from 260 h^{-1} (entry 1) to 760 h^{-1} (entry 11) under acid-free conditions, and are in the range of 1560–1660 h^{-1} in the presence of sulfuric acid (entries 6, 9, 13; see also Fig. S4).

[AuCl(sSIMes)], **3b**, also showed high catalytic activities in hydration of aromatic alkynes (Table 2). Again, an acid co-catalyst was not necessary (see e.g. entry 8), however, 10 mol% sulfuric acid increased the rate so much that 99% conversions were achieved in 30 min with all three substrates, corresponding to an average turnover frequency of 1980 h^{-1} (entries 3, 6, 9; see also Tables S1 and S2).

The aliphatic terminal alkyne, 1-octyne also reacted smoothly and with catalyst loadings of 0.5–1 mol% was converted to 2-octanone with 89–100% conversions in 30–90 min reaction times with no acid co-catalyst added. **3a** and **3b** showed about the same catalytic activity (Table S3). The highest turnover frequencies (average for the first 30 min, no acid) were 400 h^{-1} (**3a**) and 354 h^{-1} (**3b**).

Hydration of diphenylacetylene was also attempted with the new water-soluble Au–NHC catalysts. The reactions proceeded slowly both with **3a** and **3b** even at high catalyst loadings with acid co-catalyst (maximum conversion to 2-phenylacetophenone was 38% with 5 mol% **3b** in 6h; see also Table S4). Nevertheless,

Table 2
Hydration of aromatic alkynes with **3b** as catalyst, with and without acid co-catalyst[a].

Entry	Alkyne	H_2SO_4 (mol%)	Time (min)	Conv. (%)	TOF (h^{-1})
1	Phenylacetylene	–	30	12	240
2	Phenylacetylene	–	90	45	300
3	Phenylacetylene[b]	10	30	99	1980
4	4-Ethynyltoluene	–	30	30	600
5	4-Ethynyltoluene	–	90	64	349
6	4-Ethynyltoluene[b]	10	30	99	1980
7	4-Ethynylanisole	–	30	53	1060
8	4-Ethynylanisole	–	90	91	606
9	4-Ethynylanisole[b]	10	30	99	1980

[a] *Conditions*: 5 mmol alkyne, 0.005 mmol **3b** (0.1 mol%), 2.5 mL MeOH, 2.5 mL H_2O.
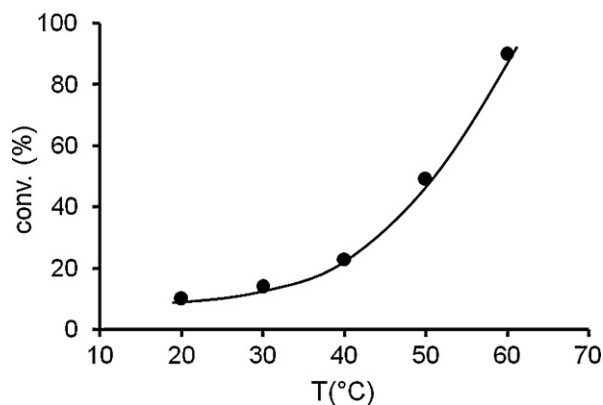[b] 2.5 mL 0.2 M H_2SO_4, reflux.

Fig. 5. Temperature dependence of the hydration of phenylacetylene catalyzed by **3a**. Conditions: 5.0 mmol phenylacetylene, 0.005 mmol **3a**, 2.5 mL MeOH, 2.5 mL 0.2 M H_2SO_4, 3 h.

Table 3
Hydration of phenylacetylene in water-methanol mixtures of various composition[a].

H_2O (v/v %)	Conversion (%)	TOF (h^{-1})
~0[b]	98	49
25	91	46
50	99	50
75	97	49
100	90	45

[a] *Conditions*: 0.5 mmol phenylacetylene, 2 mol% **3a**, 1 h, V(MeOH + H_2O) = 3.0 mL, reflux.
[b] Wet (undried) methanol.

this low but distinct catalytic activity makes **3a** and **3b** superior in comparison with the analogous Au(I) complexes with NHC-ligands derived from sulfoalkylimidazolium precursors [61] which did not catalyze the hydration of diphenylacetylene at all.

Below 40 °C the hydration of phenylacetylene catalyzed by **3a** was very slow but the conversion increased exponentially as a function of the temperature (Fig. 5). From the corresponding Arrhenius plot a virtual activation energy of 45.6 kJ/mol can be calculated. However, since the reaction mechanism is not known in detail, but certainly consists of several steps, this value can be taken only as the average temperature coefficient of the reaction rate.

We studied the effect of the water concentration in methanolic solutions on the hydration of phenylacetylene to see whether **3a** and **3b** are could be used in purely aqueous solutions. The results are collected in Table 3.

According to the data, with low substrate amount (0.5 mmol) and with 2 mol% of **3a** already in wet (undried) methanol the reaction gave high conversion and the same was observed on increasing the water concentration in the solvent up to 100%. This shows that the catalyst is active in neat water. However, with high amount (5 mmol) of substrate and with only 0.1 mol% catalyst, increasing the water concentration in the solvent led to gradual decrease of conversion and in pure water only 0.06% conversion was observed instead of 22% detected under the same conditions but with methanol/water 1/1 mixtures. We attribute this low conversion to the very low solubility (456 mg/L [66]) of phenylacetylene in water which leads to the formation of a two-phase reaction mixture in which the catalyst and the substrate are confined to different phases. Since the reaction in such systems can take place only in the interphase region the relative concentration of the catalyst in the aqueous phase may become the governing factor of the reaction rate.

It is of interest that in solid state the catalysts are stable on air for long times. Hydration of phenylacetylene was repeated with the same batch of catalyst (**3a**) stored for eight month on air; the two
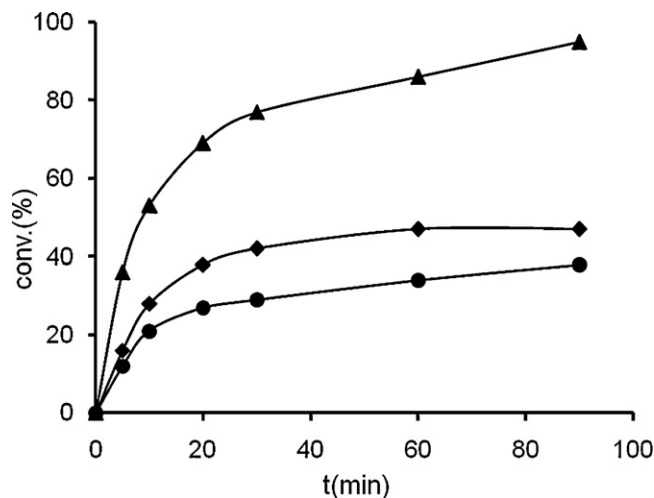

Fig. 6. Hydration of propargyl alcohol in aqueous solution, catalyzed by **3b**. Conditions: 5 mmol propargyl alcohol, 2.5 mL 0.2 M H_2SO_4, 60 °C. Concentration of catalyst: 0.1 mol% (●), 0.2 mol% (♦), 1.0 mol% (▲).

reactions showed the same time course and led to the same high conversions (Fig. S5).

3.3. Hydration of propargyl alcohol

Propargyl alcohol is soluble in water and its catalytic hydration was studied without organic co-solvents. The reaction gave hydroxyacetone (Fig. 3) as the sole product. The reaction was followed by ^1H NMR and the product was also identified by ^{13}C NMR spectroscopy. Both **3a** and **3b** catalyzed the reaction although in this case **3a** was markedly less active than **3b**. (Fig. S6). The time-course of the reaction with different amounts of **3b** as catalyst is shown in Fig. 6.

As can be seen in Fig. 6, the reactions started with a fast initial phase which turned into saturation at medium conversions (30–40%) at small catalyst concentrations. Conversely, with 1 mol% of **3b**, 5 mmol propargyl alcohol was hydrated to hydroxyacetone with 95% conversion in 90 min at 60 °C, demonstrating the synthetic utility of the new water-soluble Au(I)–NHC catalysts in neat water as solvent.

3.4. General discussion

The new Au(I)–NHC complexes **3a** and **3b** showed excellent catalytic properties in hydration of terminal alkynes, both aromatic and aliphatic, in methanol–water mixtures as solvent. The catalytic activities compare favourably to those reported for other water-soluble gold(I) catalysts in the literature. For example, Laguna and co-workers observed a TOF of 1000 h^{-1} and 1060 h^{-1} in the hydration of phenylacetylene using the preformed alkynyl-gold(I) complexes [Au(C≡CR$_1$)(mtppts)] and [Au(C≡CR$_2$)(mtppts)] (R$_1$ = *tert*-butyl, R$_2$ = 3-thiophenyl), respectively [47]. Under closely comparable conditions **3a** and **3b** catalyzed the same reaction with TOFs 1660 h^{-1} and 1980 h^{-1}. These activities are also much higher than those obtained with sulfoalkyl-substituted imidazolylidene complexes of gold(I) studied by us earlier which generally showed turnover frequencies in the range of 20–140 h^{-1} and only in case of 4-ethynylanisole was an initial TOF 400 h^{-1} determined [61]. Conversely, the catalytic activities of **3a** and **3b** fall behind those of preformed cationic [Au(PR$_3$)]$^+$ catalysts [58] or behind those of Au(I)-precatalysts transformed to [Au(NHC)]$^+$ [59,60] or [Au(PR$_3$)]$^+$ [49] species under reaction conditions (although in the first two cases much different reaction conditions were applied). However,

it should be noted that while the in situ [AuCl(IPr)]/AgSbF$_6$ catalyst proved extremely efficient for hydration of a variety of aliphatic and aromatic, terminal and internal alkynes including diphenylacetylene, reaction of this latter substrate was not catalyzed at all by the strictly analogous [AuCl(IMes)]/AgSbF$_6$ catalyst (2 mol%) in 1,4-dioxane/water 2/1 solvent, at 120 °C in 20 h [59]. In this comparison the 38% conversion of diphenylacetylene to 2-phenylacetophenone with 5 mol% **3b** in 6 h (methanol/water 2/1, 50 mol% H$_2$SO$_4$ co-catalyst, reflux at 74 °C) signals a moderate catalytic activity. It is also remarkable that the neutral **3a** and **3b** showed outstanding activity at 74 °C allowing catalyst loadings down to the 100 ppm level. Formation of cationic [Au(sIMes)]$^+$ and [Au(sSIMes)]$^+$ is very likely in the polar aqueous media, and catalytic hydrations can be run in the absence of a silver(I) salt for chloride abstraction.

An important question on the mechanism of catalytic hydrations in methanol–water mixtures is whether methanol takes part in the reaction [58]. One possible pathway involves the formation of enol ethers and ketals hydrolysis of which leads to ketones. The other possibility is the direct addition of water on the coordinated alkyne. The recent findings of Leyva and Corma with the cationic [Au(L)]NTf$_2$ catalyst (L = 2-(dicyclohexylphosphino)-2',6'-dimethoxybiphenyl), NTf$_2$ = bis(trifluoromethansulfonyl)imidate support the enol ether/ketal route [58]. We have found that fast hydration of propargyl alcohol could be carried out with both **3a** and **3b** as catalysts in homogeneous aqueous solution in the absence of methanol. Besides, we have not detected intermediates or products other than methyl ketones in any of the reactions studied. These findings show that the route with direct attack of water on the coordinated alkyne is possible, in fact it can be the only pathway in exclusively aqueous systems; nevertheless, they do not rule out the participation of methanol in reactions run in methanol–water mixtures. Taking all evidence we believe that in neat aqueous solutions the most probable route involves direct attack of water on the alkyne moiety in a [Au(sIMes)(alkyne)]$^+$ or [Au(sSIMes)(alkyne)]$^+$ cationic complex, however, such intermediates have not been identified and their kinetic role needs further scrutiny.

In most catalytic hydrations acid co-catalysts are required to achieve reasonable or high catalytic activities and there are only a few catalyst known [58,59] which do not necessitate the addition of acids. Importantly, both **3a** and **3b** performed well also in the absence of acid as shown by the TOF 760 h^{-1} determined for the first 30 min of the hydration of 4-ethynylanisole catalyzed by **3a** (Table 1, entry 11). This is an obvious asset in case of acid-sensitive substrates.

4. Conclusion

Direct sulfonation of the appropriate imidazolium salts with fuming sulfuric acid allowed an easy and high yield access to **1a** and **1b** the reaction of which with Ag$_2$O afforded the corresponding water-soluble **2a** and **2b**. These silver(I)–NHC complexes served as carbene transfer agents in the synthesis of water-soluble gold(I)-N-heterocyclic carbene complexes, namely [AuCl(sIMes)] (**3a**) and [AuCl(sSIMes)] (**3b**). The new Ag(I)- and Au(I)–NHC complexes contain the disulfonated derivatives of IMes and SIMes which are useful ligands in many transition-metal NHC-complexes. Characterization of the complexes by ^{1}H- and ^{13}C-NMR spectroscopy as well as by ESI-TOF mass spectrometry revealed structural parameters close to those of the analogous IMes and SIMes complexes of Ag(I) and Au(I). The new water-soluble gold(I)-N-heterocyclic carbene complexes showed high catalytic activity (down to 0.07 mol% or 97 ppm catalyst loading) in the hydration of alkynes in methanol–water mixtures or in purely aqueous solutions. A particularly useful feature of alkyne hydrations catalyzed by **3a** and **3b** is that high reaction rates and conversions can be achieved also in the absence of acid co-catalysts with no need for activation by silver(I) additives. These findings show that the environmentally benign water is a suitable solvent for transition metal–NHC complexes and encourage further research on the use of such complexes in aqueous organometallic catalysis.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2011.03.009.

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