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Editor's Choice paper

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.

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_2O 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 $Ph_2PC_6H_4$-*2* or *3*-CH_2NHR ($R = Pr^i$ 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 $[Ru(NH_3)_5(H_2O)]^{2+}$. 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_2CO_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_2O [21] or Cu_2O [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 $[RuCl_2L(\eta^6\text{-}p\text{-cymene})]$ (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_2PdCl_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, *m*tppms (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 = *m*tppms, *m*tppds and *m*tppts, 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(trifluoromethanesulfonyl)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_2O 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. ^1H 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_2SO_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_2SO_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%.

^1H NMR (360 MHz, H_2O saturated with NaCl, D_2O 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,