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Novel Sulfonated N-Heterocyclic Carbene Gold(I) Complexes: Homogeneous Gold Catalysis for the Hydration of Terminal Alkynes in Aqueous Media

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A series of novel water-soluble Au^I complexes using sulfonated N-heterocyclic imidazolylidene carbenes as ligands was prepared by transmetalation from the corresponding bis-carbene Ag^I complexes. Monocarbene Au^I complexes were employed as catalysts in the hydration of terminal alkynes in aqueous media. Hydrations proceeded selectively according to Markovnikov's rule with high rates and turnover numbers (up to TON 935). The highest activity was achieved in hydration of *p*-ethynylanisole (TOF = 400.2 h^{-1}). Effects of additives (H_2SO_4, AgOTs, $AgBF_4$, NaOH) were examined. Corresponding bis-carbene Au^I complexes were also isolated and characterized. However, these exhibit no catalytic activity in the explored systems.

Introduction

Following a long latent period, research into catalysis by soluble gold complexes recently entered an era of exponential expansion.[1,2] Hydration of terminal alkynes catalyzed by $Na[AuCl_4]$ reported by Fukuda and Utimoto in 1991 has initiated a rapid development of research on the use of gold in homogeneous catalysis.[3] Since then, compounds of gold have been employed as catalysts in many organic transformations, especially in reactions involving activation of CC triple bonds in unactivated alkynes, which after π-coordination to gold atoms became prone to addition of various nucleophiles.[4] Application of gold catalysts in intramolecular hydroamination,[5] hydroalkoxylation,[6] hydroacylation,[7] hydroarylation,[8] and cyclopropanation[9] of olefins as well as in rearrangements of enynes,[9,10] allenynes,[11] and alkynyl sulfoxides[12] has become a useful tool in organic synthesis.

In most cases, Au^I complexes with tertiary phosphine ligands are used for catalytic purposes.[13] However, gold complexes with N-heterocyclic carbene (NHC) ligands[14] have gained great significance in catalysis, due to the stability provided by the stronger σ-donation and weaker π-back-bonding ability of such ligands in comparison to the widely used tertiary phosphines.[15] Hydrations of alkynes catalyzed with Au^I−NHC complexes have already been reported;[16]

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(1) Li, Z.; Brouwer, C.; He, C. *Chem. Rev.* **2008**, *108*, 3239–3265.
(2) (a) Hashmi, A. S. K. *Chem. Rev.* **2007**, *107*, 3180–3211. (b) Hashmi, A. S. K.; Hutchings, G. J. *Angew. Chem., Int. Ed.* **2006**, *45*, 7896–7936. (c) Skouta, R.; Lin, C.-J. *Tetrahedron* **2008**, *64*, 4917–4938.
(3) Fukuda, Y.; Utimoto, K. *J. Org. Chem.* **1991**, *56*, 3729–3731.
(4) (a) Buzas, A.; Istrate, F.; Gagosz, F. *Org. Lett.* **2006**, *8*, 1957–1959. (b) Yu, M.; Zhang, G.; Zhang, L. *Org. Lett.* **2007**, *9*, 2147–2150. (c) Hashmi, A. S. K. *Gold Bull.* **2004**, *37*, 51.
(5) (a) Hashmi, A. S. K.; Rudolph, M.; Schymura, S.; Visus, J.; Frey, W. *Eur. J. Org. Chem.* **2006**, 4905–4909. (b) Zhang, J.; Yang, C.-G.; He, C. *J. Am. Chem. Soc.* **2006**, *128*, 1798–1799.
(6) (a) Jung, H. H.; Floreancig, P. E. *Org. Lett.* **2006**, *8*, 1945–1951. (b) Yao, X.; Li, C.-J. *Org. Lett.* **2006**, *8*, 1953–1955. (c) Hashmi, A. S. K.; Blanco, M. C.; Fischer, D.; Bats, J. W. *Eur. J. Org. Chem.* **2006**, 1387–1389. (d) Istrate, F. M.; Gagosz, F. *J. Org. Chem.* **2008**, *73*, 730–733.
(7) Harkat, H.; Weibel, J.-M.; Pale, P. *Tetrahedron Lett.* **2006**, *47*, 6273–6276.
(8) (a) Hashmi, A. S. K.; Salathé, R.; Frey, W. *Eur. J. Org. Chem.* **2007**, 1648–1652. (b) Marion, N.; Díez-González, S.; de Frémont, P.; Noble, A. R.; Nolan, S. P. *Angew. Chem., Int. Ed.* **2006**, *45*, 3647–3650.
(9) (a) López, S.; Herrero-Gómez, E.; Pérez-Galán, P.; Nieto-Oberhuber, C.; Echavarren, A. M. *Angew. Chem., Int. Ed.* **2006**, *45*, 6029–6032. (b) Ricard, L.; Gagosz, F. *Organometallics* **2007**, *26*, 4704–4707.
(10) (a) Lim, C.; Kang, J.-E.; Lee, J.-E.; Shin, S. *Org. Lett.* **2007**, *9*, 3539–3542. (b) Nieto-Oberhuber, C.; Muñoz, M. P.; Buñuel, E.; Nevado, C.; Cárdenas, D. J.; Echavarren, A. M. *Angew. Chem., Int. Ed.* **2004**, *43*, 2402–2406. (c) Nieto-Oberhuber, C.; López, S.; Jiménez-Núñez, E.; Herrero-Gómez, E.; Raducan, M.; Echavarren, A. M. *Chem. Eur. J.* **2006**, *12*, 1677–1693.
(11) Lemière, G.; Gandon, V.; Agenet, N.; Goddard, J.-P.; de Kozak, A.; Aubert, C.; Fensterbank, L.; Malacria, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 7596–7599.
(12) Shapiro, N. D.; Toste, F. D. *J. Am. Chem. Soc.* **2007**, *129*, 4160–4161.
(13) (a) Mizushima, E.; Sato, K.; Hayashi, T.; Tanaka, M. *Angew. Chem., Int. Ed.* **2002**, *41*, 4563–4565. (b) Roembke, P.; Schmidbaur, H.; Cronje, S.; Raubenheimer, H. *J. Mol. Catal. A* **2004**, *212*, 35–42.
(14) (a) Lin, I. J. B.; Vasam, C. S. *Can. J. Chem.* **2005**, *83*, 812–825. (b) Gaillard, S.; Slawin, A. M. Z.; Bonura, A. T.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2010**, *29*, 394–402. (c) Gaillard, S.; Slawin, A. M. Z.; Nolan, S. P. *Chem. Commun.* **2010**, *46*, 2742–2744. (d) Bartolomé, C.; Ramiro, Z.; Garcia-Cuadrado, D.; Pérez-Galán, P.; Raducan, M.; Bour, C.; Echavarren, A. M.; Espinet, P. *Organometallics* **2010**, *29*, 951–956. (e) Arnanz, A.; González-Arellano, C.; Juan, A.; Villaverde, G.; Corma, A.; Iglesias, M.; Sánchez, F. *Chem. Commun.* **2010**, *46*, 3001–3003.
(15) (a) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290–1309. (b) Kelly, R. A.; Clavier, H.; Giudice, S.; Scott, N. M.; Stevens, E. D.; Bordner, J.; Smardjiev, I.; Hoff, C. D.; Cavallo, L.; Nolan, S. P. *Organometallics* **2008**, *27*, 202–210.
(16) (a) Schneider, S. K.; Herrmann, W. A.; Herdtweck, E. *Z. Anorg. Allg. Chem.* **2003**, *629*, 2363–2370. (b) de Frémont, P.; Singh, R.; Stevens, E. D.; Petersen, J. L.; Nolan, S. P. *Organometallics* **2007**, *26*, 1376–1385. (c) Leyva, A.; Corma, A. *J. Org. Chem.* **2009**, *74*, 2067–2074. (d) Marion, N.; Ramón, R. S.; Nolan, S. P. *J. Am. Chem. Soc.* **2009**, *131*, 448–449.

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such reactions were performed mostly in organic solvents (THF, MeOH, MeCN) or in partially aqueous media using methanol or acetone as cosolvents, improving solubilities of the catalyst and the alkyne.

Performing the catalytic reactions in aqueous solution or in aqueous−organic biphasic media brings substantial economic as well as ecological advantages.[17] Water-soluble Au^{I}, Au^{II}, and Au^{III} phosphine complexes were introduced into homogeneous catalysis by Laguna and co-workers.[18] In these studies, solubility in aqueous media was achieved by using sulfonated triphenylphosphine ligands or PTA (1,3,5-triaza-7-phosphaadamantane). Although water-soluble NHC ligands and a few of their complexes are known,[19,20] the synthesis and catalytic application of water-soluble gold-(I) NHC complexes have not been accomplished so far. Ru, Rh, and Pd NHC complexes soluble both in water and in organic solvents were synthesized using NHC ligands derivatized by appending polyethylene glycol substituents onto the imidazolium ring.[21] Such complexes have been successfully employed in ring-closing metathesis and ring-opening metathesis polymerization reactions.[22] Water-soluble NHC complexes of Ru^{II} and Rh^{I} with imidazolylidene ligands bearing cationic ammonium groups were used in the synthesis of 2,3-dimethylfuran by intramolecular alkoxylation.[23] The first example of using remarkably water-soluble imidazolium inner salts with covalently bonded sulfonate or carboxylate anions as ligand precursors for the synthesis of Ag^{I} and Pd^{II} complexes was described by Shaughnessy and co-workers.[20] Sulfonated N,N-diarylimidazolium and N,N-diarylimidazolinium zwitterions were employed as NHC precursors in Pd^{II}-catalyzed Suzuki coupling in water.[19c] Various SO_3H-functionalized imidazolium-based ionic liquids were used as organocatalysts for the Fischer indole synthesis in water[24] and oxidative carboxylation of arylaldehydes.[25] The electrochemical properties of imidazolium sulfonate zwitterions prepared from N-alkylimidazole by N-alkylation with 1,3-propanesultone and 1,4-butanesultone were also investigated.[26]

The hydration of alkynes is an important synthetic reaction,[27] and partially or fully aqueous solvents are natural reaction media for such processes. For these reasons we synthesized a series of water-soluble Au^{I}(NHC) complexes and applied them as catalysts in the hydration of terminal alkynes in aqueous media.

Results and Discussion

For the synthesis of water-soluble gold NHC complexes, sulfonated N-alkyl- and N-arylimidazolium inner salts (Figure 1) were applied as ligands. Zwitterion **1a** has been prepared by condensation of 2-aminoethanesulfonic acid, glyoxal, and paraformaldehyde. Compound **1a** is readily soluble in water and in DMSO and is insoluble in other common organic solvents. The suitable precursor sodium 4-(imidazol-1-yl)benzenesulfonate **2** for synthesis of N-arylimidazolium sulfonates was prepared in excellent yield according to a modified procedure of Zhang and coworkers.[28] Monosodium imidazolium bis(sulfonate) zwitterions **1b**,**f** were obtained by N-alkylation of **2** with sodium 2-bromoethanesulfonate or propanesultone, respectively. Other monosulfonated structures, **1c**,**d**, were prepared by quaternization of *N*-methylimidazole and *N*-butylimidazole, respectively.[19a,24] Compound **1e** was prepared by treatment of imidazole with propanesultone according to the method of Ohno et al.[19b]

Treatment of Ag_2O with imidazolium sulfonates **1a**−**f** in water at ambient temperature provided the $[Ag(NHC)_2]$ complexes **3a**−**f** in good yields (Scheme 1). Complexes **3a**, **c**,**d** are readily soluble and stable in H_2O. On the other hand, the Ag complexes **3b**,**f** with N-aryl-substituted ligands decomposed in aqueous solution and were used for carbene transfer immediately as prepared.

Negative ion mode electrospray ionization mass spectra (ESI-MS) and X-ray structural analysis of bis-carbene silver complexes excluded the presence of halide coordinated directly to the central silver atom as well as the presence of a $[AgX_2]^-$ anion, as was observed in complexes prepared from imidazolium halide precursors.[29]

X-ray-quality crystals of complex **3a** were obtained by crystallization from H_2O/MeOH. The two carbene ligands are coplanar and are linearly coordinated to Ag, and one of the sulfonate groups serves as a counterion toward the silver(I) cation (Figure 2). The solid-phase structure is stabilized by ionic interactions and extensive hydrogen-bond network. Silver atoms are in special positions at the inversion center. The crystal lattice includes two molecules of H_2O and two types of sodium cations, mirroring the slight asymmetry of the ethylsulfonate side chains. The first type of sodium (Na1) is in a general position and is surrounded by four oxygen atoms from sulfonate groups as well as two cis-coordinated oxygen

(17) (a) Joó, F. *Aqueous-Organometallic Catalysis*; Kluwer: Dordrecht, The Netherlands, 2001. (b) Cornils, B.; Herrmann, W. A. *Aqueous-Phase Organometallic Catalysis. Concepts and Applications*; Wiley-VCH: Weinheim, Germany, 1998.

(18) (a) Sanz, S.; Jones, L. A.; Mohr, F.; Laguna, M. *Organometallics* **2007**, *26*, 952–957. (b) Mohr, F.; Cerrada, E.; Laguna, M. *Organometallics* **2006**, *25*, 644–648. (c) Mohr, F.; Sanz, S.; Tiekink, E. R. T.; Laguna, M. *Organometallics* **2006**, *25*, 3084–3087.

(19) (a) Herrmann, W. A.; Elison, M.; Fischer, J.; Köcher, C. (Hoechst AG) U.S. Patent 5,663,451, **1997**. (b) Yoshizawa, M.; Ohno, H. *Ionics* **2002**, *8*, 267–271. (c) Fleckenstein, C.; Roy, S.; Leuthäusser, S.; Plenio, H. *Chem. Commun.* **2007**, 2870–2872. (d) Zarka, M. T.; Bortenschlager, M.; Wurst, K.; Nuyken, O.; Weberskirch, R. *Organometallics* **2004**, *23*, 4817–4820. (e) Mizushima, E.; Sato, K.; Hayashi, T.; Tanaka, M. *Angew. Chem., Int. Ed.* **2002**, *41*, 4563–4565. (f) Clavier, H.; Grela, K.; Kirshing, A.; Mauduit, M.; Nolan, S. P. *Angew. Chem., Int. Ed.* **2007**, *46*, 6786–6801. (g) Gułajski, Ł.; Michrowska, A.; Narożnik, J.; Kaczmarska, Z.; Rupnicki, L.; Grela, K. *ChemSusChem* **2008**, *1*, 103–109.

(20) (a) Moore, L. R.; Cooks, S. M.; Anderson, M. S.; Schanz, H.-J.; Griffin, S. T.; Rogers, R. D.; Kirk, M. C.; Shaughnessy, K. H. *Organometallics* **2006**, *25*, 5151–5158. (b) da Costa, A. P.; Mata, J. A.; Royo, B.; Peris, E. *Organometallics* **2010**, *29*, 1832–1838.

(21) Herrmann, W. A.; Goossen, L. J.; Spiegler, M. *J. Organomet. Chem.* **1997**, *547*, 357–366.

(22) (a) Gallivan, J. P.; Jordan, J. P.; Grubbs, R. H. *Tetrahedron Lett.* **2005**, *46*, 2577–3580. (b) Hong, S. H.; Grubbs, R. H. *J. Am. Chem. Soc.* **2006**, *128*, 3508–3509.

(23) Özdemir, İ.; Yiğit, B.; Çetinkaya, B.; Ulkü, D.; Tahir, M. N.; Arıcı, C. *J. Organomet. Chem.* **2001**, *633*, 27–32.

(24) Xu, D.-Q.; Wu, J.; Luo, S.-P.; Zhang, J.-X.; Wu, J.-Y.; Du, X.-H.; Xu, Z.-Y. *Green Chem.* **2009**, *11*, 1239–1246.

(25) Yoshida, M.; Katagiri, Y; Zhu, W.-B.; Shishido, K. *Org. Biomol. Chem.* **2009**, *7*, 4062–4066.

(26) Yoshizawa, M.; Narita, A.; Ohno, H. *Aust. J. Chem.* **2004**, *57*, 139–144.

(27) (a) Hintermann, L.; Labonne, A. *Synthesis* **2007**, 1121–1150. (b) Beller, M.; Seayad, J.; Tillack, A.; Jiao, H. *Angew. Chem., Int. Ed.* **2004**, *43*, 3368–3398.

(28) Liu, J.; Chen, J.; Zhao, J.; Zhao, Y.; Li, L.; Zhang, H. *Synthesis* **2003**, *17*, 2661–2666.

(29) (a) Kwang, M. L.; Harrison, M. J. W.; Lin, I. J. B. *Dalton Trans.* **2002**, 2852–2856. (b) Sentman, A. C.; Csihony, S.; Waymouth, R. M.; Hedrick, J. L. *J. Org. Chem.* **2005**, *70*, 2391–2393. (c) Newman, C. P.; Clarkson, G. J.; Rourke, J. P. *J. Organomet. Chem.* **2007**, *692*, 4962–4968.

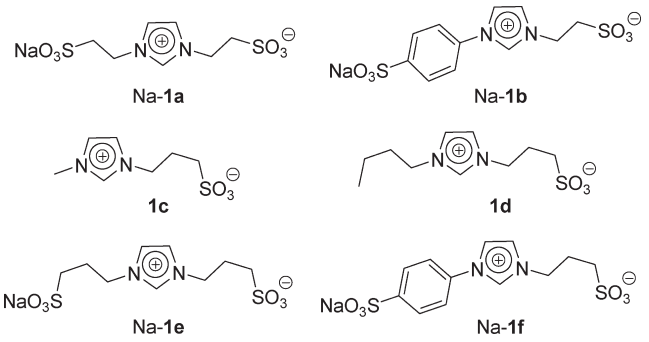
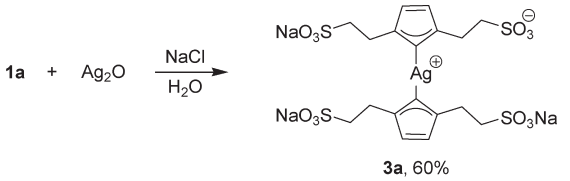


Figure 1. Imidazolium sulfonate zwitterions **1a**−**f**.

Scheme 1. Preparation of Bis-Carbene Silver(I) Zwitterionic Complexes 3a−f



3a, 60%

1b **3b**, not isolated
1c **3c**, 43%
1d **3d**, 56%
1e **3e**, not isolated
1f **3f**, not isolated

atoms of water. The second type (Na2) is in a special position and is surrounded by two trans-coordinated oxygen atoms from sulfonate groups and four oxygen atoms of water, forming an infinite polymeric network, with abundance of Na1/Na2 = 2/1 (Figure 3). The distance between two adjacent silver atoms is 5.638 Å, and the Ag−C(2) bond length is 2.066(5) Å, similar to the bond lengths of other $[Ag(NHC)_2]$ complexes reported.[20,30] A search of the Cambridge Structural Database[31] (CSD, Version 5.31, November 2009) resulted in 28 hits for mononuclear NHC−Ag−NHC compounds with an average Ag−C distance of 2.088(8) Å.

The target Au^I−NHC complexes were obtained by carbene transfer from complexes **3a**−**f** following the procedure of Wang and Lin.[32] Reaction of complexes **3a**−**e** with $[AuCl(SMe_2)]$ or [AuCl(tht)] (tht = tetrahydrothiophene) provided mixtures of the mono-carbene chloro complexes [AuCl(NHC)] (**4a**−**e**) and corresponding bis-carbene complexes (**5a**−**e**) (Scheme 2, Table 1). Bis-carbene complexes are, in general, less soluble in MeOH and EtOH. Complexes **4a**−**e** were characterized by ^1H and ^{13}C NMR and ESI-MS. Bis-carbene complexes were characterized by ^1H and ^{13}C NMR as byproducts. ^{13}C NMR signals of Au−*C* atoms of bis-carbene complexes **5a**−**f** are found between 184.2 and 182.9 ppm and in mono-carbene complexes **4a**−**e** between 168.1 and 166.0 ppm. These signals are shifted around 10 ppm upfield compared to the signals for the corresponding dimethylimidazolium- and diethylimidazolium-derived Au^I mono-carbene complexes.[33]

X-ray-quality crystals of complex **5a** were obtained by crystallization from H_2O/MeOH. Complex **5a** is isostructural

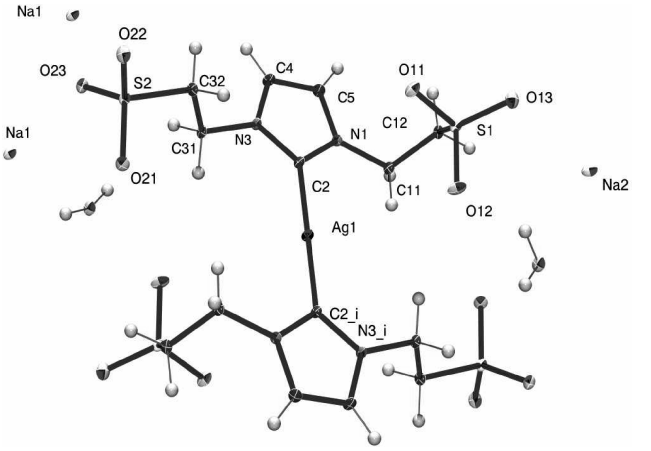


Figure 2. ORTEP diagram (50% probability ellipsoids) of the complex $Na_3[Ag(\mathbf{1a})_2]\cdot 2H_2O$ in the crystal state. Selected bond lengths (Å) and angles (deg): Ag−C2, 2.066(5); N1−C2−N3, 103.7(4); N1−C2−Ag, 127.7(3); N3−C2−Ag, 128.4(3); C2−Ag−C2′, 180.0; C2−N1−C11−C12, −117.8; C2−N3−C31−C32, 105.8; N1−C11−C12−S1, 73.1; N3−C31−C32−S2, −177.8.

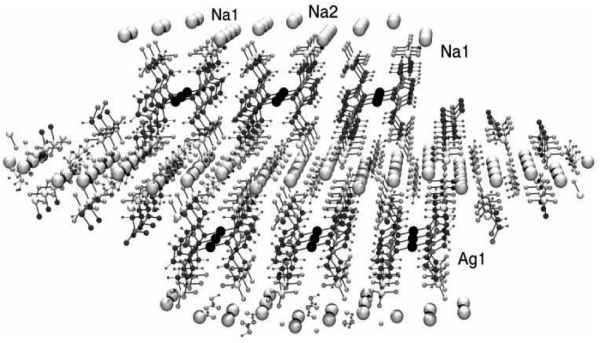


Figure 3. Packing diagram showing the arrangement of $Na_3[Ag(\mathbf{1a})_2]\cdot 2H_2O$ units connected by infinite chains of sodium cations. All hydrogen atoms have been omitted for clarity.

with **3a** and has almost identical unit cell dimensions (for details of the X-ray structure analysis see the Supporting Information). The distance between two adjacent gold atoms is 5.594 Å; therefore, there is no evidence for the aurophilic interaction reported for similar Au^I bis-carbene complexes.[14,34] The Au−C(2) distance is 2.025(10) Å, in good agreement with the average of 23 hits in the CSD of 2.026(15) Å.

Alkyl-substituted mono-carbene complexes in aqueous solution convert slowly to the corresponding bis-carbene complexes. This change is accompanied by a violet coloration of the solutions, which may be due to the presence of gold nanoparticles. However, the mono-carbene species are perfectly stable in the presence of electrolytes such as $NaPF_6$, NaCl, NaOH, and H_2SO_4. Conversion of aryl-substituted monocarbene complexes proceeds more quickly. Complex **4b** converts completely to the bis-carbene complex within 24 h in D_2O at room temperature. The monomeric complex **4f** [AuCl(**1f**)] was not observed at all, and only bis-carbene complex **5f** was isolated.

(30) dit Dominique, F. J.-B.; Gornitzka, H.; Hemmert, C. *J. Organomet. Chem.* **2008**, *693*, 579–583.
(31) Allen, F. H. *Acta Crystallogr.* **2002**, *B58*, 380–388.
(32) Wang, H. M. J.; Lin, I. J. B. *Organometallics* **1998**, *17*, 972–975.
(33) Wang, H. M. J.; Chen, C.Y. L.; Lin, I. J. B. *Organometallics* **1999**, *18*, 1216–1223.
(34) (a) Catalano, V. J.; Moore, A. L. *Inorg. Chem.* **2005**, *44*, 6558–6566. (b) Wang, H. M. J.; Vasam, C. S.; Tsai, T. Y. R.; Chen, S.-H.; Chang, A. H. H.; Lin, I. J. B. *Organometallics* **2005**, *24*, 486–493.

Scheme 2. Formation of Mono-Carbene Complex 4a and Bis-Carbene Au^{I} Complex 5a by Transmetalation from Silver Carbene Transfer Complexes 3a and [AuCl(tht)]

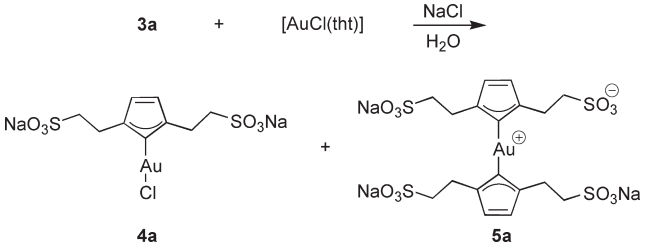


Table 1. Composition of Mixtures of Mono-Carbene/ Bis-Carbene Au^{I} Complexes

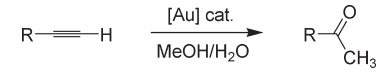
[Ag(NHC)$_2$]	[AuCl(NHC)]/[Au(NHC)$_2$][a]	overall yield (%)
3a	**4a**/**5a** 89/11	78
3b	**4b**/**5b** 83/17	82
3c	**4c**/**5c** 82/18	80
3d	**4d**/**5d** 80/20	47
3e	**4e**/**5e** 91/9	59
3f	**4f**/**5f** 0/100	34

[a] Determined by ^{1}H NMR.

Complexes **4a**−**e** were found to be active catalysts of the hydration of aromatic and aliphatic terminal alkynes in refluxing MeOH/H_2O solutions (Table 2). In order to make a direct comparison of the catalytic properties of the new Au NHC complexes to those of known Au tertiary phosphine catalysts, the reaction conditions were chosen to be identical with those used by Laguna and co-workers.[18] It is remarkable that—although sulfuric acid could be used beneficially (vide infra)—the reactions proceed with high rates and high conversions (Table 2, entries 3 and 5 and Figure S3 in the Supporting Information) also in the absence of an acid cocatalyst. This is a definite advantage in the case of acid-sensitive substrates. These reactions could be run also in *neat water* with considerably lower rate due to the low solubility of the substrates. Such biphasic systems allow the easy separation of the catalyst from the products (and unreacted substrates). Addition of H_2O proceeded selectively following Markovnikov's rule. Internal alkynes did not react at all. With ethynylbenzene as substrate and 2.0 mol % of [AuCl(NHC)], conversions in the range of 79−94% could be achieved with all catalysts except **4d**, the most active being **4c**,**e** (Table 2, entries 1−5). Although these activities (a time-average TOF of 13−16 h^{-1}) are substantially smaller than those obtained by Tanaka and co-workers with the [Au(CH$_3$)(PPh$_3$)] + acid catalyst,[13a] they are in the range of those determined under comparable conditions with the water-soluble Au phosphine catalysts [AuCl(P)]: P = TPPMS (2), TPPDS (10), TPPTS (25) (TPPMS, TPPDS, TPPTS = mono-, di-, and trisulfonated triphenylphosphine, respectively; TOFs for hydration of phenylacetylene in parentheses).[18]

Complex **4a** was used as a catalyst to explore the reactivity of various substrates. The highest TOFs were obtained with electron-rich aliphatic and aromatic alkynes (Table 2, entries 6, 7, and 10−12). This is in accord with π-coordination of the alkyne on a Lewis acidic catalytic species in the initial step of the catalytic cycle. In the hydration of *p*-ethynylanisole using 0.1 mol % of catalyst **4a**, a TOF of 400.2 h^{-1} was achieved (Table 2, entry 12), showing again the reactivity of the [AuCl(NHC)] catalysts being approximately the same as

Table 2. Hydration of Terminal Alkynes[a]



entry	cat. (amt (mol %))	R	time (h)	conversn (%)[c]	TOF (h^{-1})
1	**4a** (2.0)[b]	Ph	3.0	88.4	14.7
2	**4b** (2.0)[b]	Ph	3.0	78.8	13.1
3	**4c** (2.0)[b]	Ph	3.0	92.5	15.4
4	**4d** (2.0)[b]	Ph	3.0	61.4	10.2
5	**4e** (2.0)[b]	Ph	3.0	93.6	15.6
6	**4a** (0.5)	$CH_3(CH_2)_3$	0.5	50.9[d]	203.7
7	**4a** (0.5)	$CH_3(CH_2)_5$	0.5	23.4[d]	93.6
8	**4a** (2.0)	4-CH_3-Ph	0.5	19.3	19.3
9	**4a** (0.5)	4-CH_3-Ph	1.5	21.5	28.6
10	**4a** (2.0)	4-CH_3O-Ph	0.5	55.1	55.1
11	**4a** (0.5)	4-CH_3O-Ph	0.5	35.1	140.3
12	**4a** (0.1)	4-CH_3O-Ph	0.5	20.0	400.2

[a] Conditions (except where noted): substrate, 1.00 mmol; H_2O/MeOH 1/5, 5 mL; reflux. [b] H_2O/MeOH 1/1, 5 mL. [c] Conversion determined by GC. [d] Conversion determined by ^{1}H NMR.

that with tertiary phosphine ligands (substrate phenylacetylene, [Au(OTf)(TPPTS)] 0.1 mol %, H_2SO_4 10 mol %, TOF 427 h^{-1}).[18]

Catalytic activity in hydration of alkynes can be improved by the addition of appropriate cocatalysts such as Lewis and Brønsted acids[13,16,35] or silver salts,[36] generating active [Au]$^+$ species by exchange of chloro ligand for a noncoordinating anion. We explored the effect of cocatalysts on the hydration of phenylacetylene catalyzed by complex **4a** (Table 3 and Figure S3 (Supporting Information)). Addition of 10 mol % of H_2SO_4 doubled the reaction rate; however, 20 mol % of H_2SO_4 led to only a slight further increase in activity (Table 3, entries 2 and 3). The catalyst is quite robust, since with a [substrate]/[catalyst] ratio of 1000, 93.5% conversion (TON = 935) was obtained (Table 3, entries 4−6). Sulfuric acid itself is catalytically inactive under the same reaction conditions (entry 9). Surprisingly, silver triflate decreased the activity of the catalyst (entry 7). Addition of AgOTf to an aqueous solution of complex **4a** resulted in precipitation of AgCl, together with a violet coloration of the solution and formation of metal particles, indicating decomposition of the catalyst. Reaction of **4a** with $AgBF_4$ in the presence of phenylacetylene also yielded an AgCl precipitate; however, in this case a stable strong yellow solution was formed and the hydration reaction did not proceed at all. Different effects of AgOTf and $AgBF_4$ are not unprecedented, due to the somewhat stronger coordination ability of triflate ion. It is also noted here that hydration of phenylacetylene did not proceed in the presence of NaOH. It is tempting to speculate that this inhibition may be due to the formation of a stable Na$_2$[Au(OH)(**1a**)] species similar to [Au(OH)(IPr)] described recently by Nolan and co-workers.[14c]

Concerning the mechanism of gold-catalyzed alkyne hydrations, two possible pathways have been suggested in the literature: one involving enol ethers and ketals[16d,34] and the other procceding by direct attack of water on the coordinated alkyne.[13a,35] A recent detailed study by Leyva and

(35) Teles, J. H.; Brode, S.; Chabanas, M. *Angew. Chem., Int. Ed.* **1998**, *37*, 1415–1418.
(36) Casado, R.; Contel, M.; Laguna, M.; Romero, P.; Sanz, S. *J. Am. Chem. Soc.* **2003**, *125*, 11925–11935.

Table 3. Hydration of Phenylacetylene Catalyzed by 4a: Effect of Additives[a]

entry	amt of **4a** (mol %)	cocat. (amt (mol %))	time (h)	conversn (%)[b]	TOF (h^{-1})
1	2.0		0.5	20.1	20.1
2	2.0	H_2SO_4 (10.0)	0.5	39.7	39.7
3	2.0	H_2SO_4 (20.0)	0.5	43.5	43.5
4	0.1	H_2SO_4 (10.0)	3.0	30.7	102.2
5	0.1	H_2SO_4 (10.0)	6.0	43.2	72.0
6	0.1	H_2SO_4 (10.0)	48.0	93.5	19.5
7	1.0	AgOTf (1.0)	1.0	5.0	5.0
8	1.0	AgOTf (1.0) H_2SO_4 (20.0)	4.0	1.6	0.4
9		H_2SO_4 (20.0)	4.0	n/a	n/a

[a] Conditions: substrate, 1.00 mmol; H_2O/MeOH 1/5, 5 mL; reflux. [b] Conversion determined by GC.

Corma[16c] has revealed that with an [Au(L)NTf_2] (L = 2-(dicyclohexylphosphino)-2′,6′-dimethoxybiphenyl, NTf_2 = bis(trifluoromethanesulfonyl)imidate) catalyst in water/methanol mixtures hydration of phenylacetylene involved the active role of methanol, and this favors the enol ether/ketal route. At this point in our investigations we do not have enough data to draw sound conclusions in this respect. Although no intermediates or products other than methyl ketones have been observed in the hydration of terminal alkynes in water−methanol mixtures with our catalysts, this does not rule out the intermediate formation of enol ethers and ketals. However, the effect of changing solvent composition is worth considering. In general, hydrations proceeded with high conversions in MeOH/H_2O mixtures with compositions from 1/5 to 5/1, while in the hydration of phenylacetylene catalyzed by complex **4a** in refluxing water 17% conversion was achieved after 3 h. Even lower conversions were obtained under the same conditions in neat (undried) methanol (2.7%) or in a MeOH/H_2O 98/2 mixture (6.4%). Considering these results, we suppose that hydration proceeds through the direct addition of water instead of formation of methanol adducts.

In summary, we have prepared for the first time several water-soluble gold(I) N-heterocyclic carbene complexes with N-sulfoalkyl- and N-sulfoarylimidazolylidene ligands which showed high activity in the catalysis of alkyne hydration, even in the absence of an acid cocatalyst. Such complexes provide a new entry to homogeneous and biphasic gold catalysis in aqueous systems.

Experimental Section

Ag_2O was prepared by the reaction of $AgNO_3$ and NaOH. The precursor [AuCl(tht)] was prepared from Na[$AuCl_4$]·H_2O and tetrahydrothiophene according to a literature procedure.[37] All other reagents were obtained commercially and used as received. Reactions of organometallic compounds as well as catalytic experiments were performed in Schlenk tubes with deaerated solvents under a nitrogen atmosphere. ^1H and ^{13}C NMR spectra were recorded on Bruker Avance 360 MHz spectrometer. Coupling constants are reported in Hz. ESI mass spectra were recorded on a Bruker BioTOF II. ESI-TOF spectrometer. Reaction mixtures in hydrations of arylacetylenes were analyzed by gas chromatography (HP5890 Series II; Chrompack WCOT Fused Silica 30 m × 32 mm CP WAX52CB; FID; carrier gas argon). X-ray diffraction data of **3a** and **5a** were collected at 293(1) K on Enraf-Nonius MACH3 diffractometer (Mo Kα radiation, λ = 0.710 73 Å, ω motion). The structures were solved using SIR-92 software[38] and refined on F^2 using SHELX-97 program;[39] publication material was prepared with the WINGX-97 suite.[40] Significant residual electron density remained close (< 1 Å) to the gold or silver atom. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed into geometric positions, except water hydrogen atoms, which could be found in the difference electron density map but their distances from the oxygen atom had to be constrained. However, the orientation of some of the water molecules is ambiguous because heavy elements of Ag or Au made it impossible to determine the exact positions of water protons. This fact also suggests that strong electrostatic interactions and coordinative bonds have a much greater role in the stabilization of the lattice than do hydrogen bonds. Further details of the structure determination can be found in the Supporting Information.

Preparation of Sodium 2,2′-(Imidazolium-1,3-diyl)bisethanesulfonate (Na-1a). A mixture of taurine (10.00 g, 80.0 mmol) and glyoxal (4.2 mL, 36.3 mmol, 40% aqueous solution) in H_2O (100 mL) was stirred and heated to 75 °C for 24 h. Paraformaldehyde (4.36 g, 145.3 mmol) and HCl (12 mL, 145.3 mmol, 37% aqueous solution) were added, and the mixture was stirred and heated to 75 °C for 92 h. Water was evaporated under vacuum. The product was dissolved in boiling MeOH (60 mL), and excess taurine was filtered off. The filtrate was evaporated under vacuum, and the product H-**1a** was recrystallized from EtOH. The corresponding sodium salt Na-**1a** was prepared by neutralization with an equimolar amount of $NaHCO_3$: white crystalline solid, yield 60%. ^1H NMR (D_2O, 360 MHz): δ 8.89 (s, 1H, H−C(2)), 7.53 (s, 2H, H−C(4,5)), 4.56 (t, ^3J = 6.5 Hz, 4H, H_2C−N), 3.38 (t, ^3J = 6.5 Hz, 4H, H_2C−S). ^{13}C NMR (D_2O, 75 MHz): δ 136.8, 122.6, 49.7, 45.1.

Preparation of 4-(Imidazol-1-yl)benzenesulfonic Acid (H-2). A solution of sulfanilic acid (3.00 g, 17.22 mmol) in H_2O (220 mL) was cooled in an ice bath. Glyoxal (2.50 g, 17.2 mmol, 40% aqueous solution) was added, and the mixture was stirred at room temperature for 28 h. Aqueous NH_3 (2.35 g, 34.4 mmol, 25% aqueous solution) and paraformaldehyde (1.03 g, 34.4 mmol) were added. The mixture was stirred and heated to 70 °C for 2 h; then it was removed from the heating bath and HCl (30 mL, 18.5% aqueous solution) was added slowly over 5 min. The mixture was stirred and heated to 70 °C for 60 h. The solvent was evaporated under vacuum, EtOH (40 mL) was added, and the resulting precipitate was filtered off, washed with EtOH (2 × 10 mL), and dried under vacuum. The product was obtained as a brownish solid, yield 94%. ^1H NMR (D_2O, 360 MHz): δ 9.25 (s, 1H, H−C(2)), 8.00 (m, 2H, H−C^{Ph}), 7.94 (s, 1H, H−C^{Im}), 7.78 (m, 2H, H−C^{Ph}), 7.68 (s, 1H, H−C^{Im}). ^{13}C NMR (D_2O, 75 MHz): δ 144.0, 136.8, 134.0, 127.6, 122.9, 121.3, 120.6. Sodium 4-(imidazol-1-yl)benzenesulfonate (**2**) was prepared by neutralization of the acid H-**2** with an equimolar amount of $NaHCO_3$.

General Procedure for the Alkylation of Sodium 4-(Imidazol-1-yl)-benzenesulfonate. To a solution of propanesultone or sodium 2-bromoethanesulfonate (3.0 mmol) in DMF (4 mL) was added compound **2** (0.50 g, 2.0 mmol), and the reaction mixture was stirred at reflux for 3 h. The resulting precipitate was filtered, washed with acetone (2 × 10 mL), and dried under vacuum. Sodium imidazolium bis(sulfonate) zwitterion Na-**1b** was obtained as a brownish solid, yield 57%. ^1H NMR (D_2O, 360 MHz): δ 9.39 (s, 1H, H−C(2)), 7.93 (m, 2H, H−C^{Ph}), 7.88 (d, ^3J = 1.6 Hz, 1H, H−C^{Im}), 7.72 (d, ^3J = 1.6 Hz, 1H, H−C^{Im}), 7.69 (m, 2H, H−C^{Ph}), 4.67 (t, ^3J = 5.8 Hz, 2H, H_2C−N), 3.45 (t, ^3J = 5.8 Hz, 2H; H_2C−S). ^{13}C NMR (D_2O, 75 MHz): δ 144.0, 136.7, 127.6, 123.4, 122.9, 121.8, 49.7, 45.7.

(37) Usón, R.; Laguna, A.; Laguna, M. *Inorg. Synth.* **1989**, *26*, 86.
(38) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallogr.* **1993**, *26*, 343.
(39) Sheldrick, G. M. *Programs for Crystal Structure Analysis (Release 97-2)*; Institut für Anorganische Chemie der Universität, Göttingen, Germany, 1998.
(40) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837.

Sodium imidazolium bis(sulfonate) zwitterion Na-**1f** was obtained as a brownish solid, yield 79%. ESI-MS for $C_{12}H_{13}N_2NaO_6S_2$ (*m*/*z*): 345.031 ($M - Na^+$). ^1H NMR (D_2O, 360 MHz): δ 9.35 (s, 1H, $H-C(2)$), 7.94 (m, 2H, $H-C^{Ph}$), 7.89 (s, 1H, $H-C^{Im}$), 7.70 (m, 2H, $H-C^{Ph}$), 7.69 (s, 1H, $H-C^{Im}$), 4.42 (t, ^3J = 7.2 Hz, 2H, H_2C-N), 2.92 (t, ^3J = 7.4 Hz, 2H, H_2C-S), 2.33 (tt, ^3J = 7.4 Hz, ^3J = 7.2 Hz, 2H, H_2C). ^{13}C NMR (D_2O, 75 MHz): δ 143.9, 136.7, 127.6, 123.2, 122.8, 121.9, 48.4, 47.2, 25.0.

General Procedure for the Preparation of Ag(NHC)$_2$ Complexes. A mixture of imidazolium sulfonate **1a**−**f** (2.0 mmol), Ag_2O (0.46 g, 2.0 mmol), and H_2O (3 mL) was stirred at room temperature in darkness for 3.5 h. NaCl (0.12 g, 2.0 mmol) was added, and the mixture was passed through a short Super-Cel pad. Solvent was evaporated under vacuum. Products were crystallized from H_2O/MeOH or H_2O/EtOH.

Complex 3a, Na$_3$[Ag(1a)$_2$]. White solid, yield 60%. ESI-MS for $C_{14}H_{20}AgN_4Na_3O_{12}S_4$ (*m*/*z*): 716.901 ($M - Na^+$). ^1H NMR (D_2O, 360 MHz): δ 7.22 (s, 4H, $H-C^{Im}$), 4.53 (t, ^3J = 6.6 Hz, 8H, H_2C-N), 3.38 (t, ^3J = 6.6 Hz, 8H, H_2C-S). ^{13}C NMR (D_2O, 75 MHz): δ 180.8, 121.7, 49.8, 45.2.

Complex 3b, Na$_3$[Ag(1b)$_2$]. Unstable and was not isolated. ^1H NMR (D_2O, 360 MHz): δ 7.77 (d, ^3J = 8.3 Hz, 4H, $H-C^{Ph}$), 7.57 (d, ^3J = 8.3 Hz, 4H, $H-C^{Ph}$), 7.37 (s, 2H, $H-C^{Im}$), 7.36 (s, 2H, $H-C^{Im}$), 4.44 (t, ^3J = 6.4 Hz, 4H, H_2C-N), 3.30 (t, ^3J = 6.4 Hz, 4H, H_2C-S). ^{13}C NMR (D_2O, 75 MHz): δ 142.7, 142.2, 127.0, 124.8, 122.7, 121.7, 51.3, 47.3. The signal of carbon $C(2)-Ag$ was not resolved.

Complex 3c, Na[Ag(1c)$_2$]. White solid, yield 43%. ^1H NMR (D_2O, 360 MHz): δ 7.18 (d, ^3J = 1.8 Hz, 2H, $H-C^{Im}$), 7.12 (d, ^3J = 1.8 Hz, 2H, $H-C^{Im}$), 4.20 (t, ^3J = 6.8 Hz, 4H, H_2C-N), 3.75 (s, 6H, H_3C-N), 2.82 (t, ^3J = 7.6 Hz, 4H, H_2C-S), 2.22 (tt, ^3J = 7.6 Hz, ^3J = 6.8 Hz, 4H, H_2C). ^{13}C NMR (D_2O, 75 MHz): δ 179.7, 122.7, 121.3, 49.6, 47.8, 38.1, 26.5.

Complex 3d, Na[Ag(1d)$_2$]. White solid, yield 56%. ^1H NMR (D_2O, 360 MHz): δ 7.19 (s, 2H, $H-C^{Im}$), 7.17 (s, 2H, $H-C^{Im}$), 4.19 (t, ^3J = 6.6 Hz, 4H, H_2C), 4.06 (t, ^3J = 6.8 Hz, 4H, H_2C), 2.77 (t, ^3J = 7.7 Hz, 4H, H_2C), 2.20 (m, 4H, H_2C), 1.73 (m, 4H, H_2C), 1.21 (m, 4H, H_2C), 0.81 (t, ^3J = 7.0 Hz, 6H, H_3C). ^{13}C NMR (D_2O, 75 MHz): δ 178.9, 121.8, 121.3, 51.3, 49.8, 47.9, 33.0, 26.6, 19.2, 13.0.

Complexes **3e**, $Na_3[Ag(\mathbf{1e})_2]$ and **3f**, $Na_3[Ag(\mathbf{1f})_2]$ are unstable and were not isolated.

General Procedure for Preparation of [AuCl(NHC)] Complexes. .A solution of $Ag[(NHC)_2]$ **3a**−**f** (0.5 mmol) in H_2O (2 mL) was added dropwise to a mixture of [AuCl(tht)] (0.34 g, 1.05 mmol) and H_2O (2 mL). The reaction mixture was stirred at room temperature for 3 h. NaCl (0.30 g, 0.5 mmol) was added, and the mixture was passed through a short Super-Cel pad, followed by vacuum evaporation of the solvent.

Mixtures of mono- and bis-carbene Au^I complexes were obtained, except that complex **3f** provided exclusively bis-carbene complex **5f**. Mono-carbene complexes were isolated by precipitation of the bis-carbene minor product from the concentrated aqueous solution of a product mixture by addition of a small amount of methanol. For yields and compositions of product mixtures, see Table 1. Bis-carbene complexes can be prepared by using an equimolar amount of [AuCl(tht)].

Complex 4a, Na$_2$[AuCl(1a)]. ESI-MS for $C_7H_{10}AuClN_2Na_2O_6S_2$ (*m*/*z*): 536.925 ($M - Na^+$), 256.9654 ($M - 2Na^+$). ^1H NMR (D_2O, 360 MHz): δ 7.22 (s, 2H, $H-C^{Im}$), 4.50 (t, ^3J = 6.9 Hz, 4H, H_2C-N), 3.41 (t, ^3J = 6.9 Hz, 4H, H_2C-S). ^{13}C NMR (D_2O, 75 MHz): δ 168.1, 121.7, 51.1, 46.6. Solubility: 320 mg/1 mL of H_2O (20 °C).

Complex 5a, Na$_3$[Au(1a)$_2$]. ESI-MS for $C_{14}H_{20}AuN_4Na_3O_{12}S_4$ (*m*/*z*): 806.956 ($M - Na^+$). ^1H NMR (D_2O, 360 MHz): δ 7.25 (s, 4H, $H-C^{Im}$), 4.60 (t, ^3J = 6.7 Hz, 8H, H_2C-N), 3.46 (t, ^3J = 6.7 Hz, 8H, H_2C-S). ^{13}C NMR (D_2O, 75 MHz): δ 184.2, 122.0, 51.5, 46.5. Solubility: 300 mg/1 mL H_2O (20 °C).

Complex 4b, Na$_2$[AuCl(1b)]. ESI-MS for $C_{11}H_{10}AuClN_2Na_2O_6S_2$ (*m*/*z*): 584.931 ($M(^{35}Cl) - Na^+$), 281.971 ($M(^{37}Cl) - 2Na^+$), 280.973 ($M(^{35}Cl) - 2Na^+$). ^1H NMR (D_2O, 360 MHz): δ 7.86 (d, ^3J = 8.5 Hz, 2H, $H-C^{Ph}$), 7.79 (d, ^3J = 8.7 Hz, 2H, $H-C^{Ph}$), 7.41 (m, 2H, $H-C^{Im}$), 4.59 (t, ^3J = 6.7 Hz, 2H, H_2C-N), 3.46 (t, ^3J = 6.7 Hz, 2H, H_2C-S). ^{13}C NMR (D_2O, 75 MHz): δ 166.0, 139.4, 133.9, 127.0, 126.8, 125.8, 125.5, 51.1, 46.7.

Complex 5b, Na$_3$[Au(1b)$_2$]. ^1H NMR (D_2O, 360 MHz): δ 7.77 (d, ^3J = 8.3 Hz, 4H, $H-C^{Ph}$), 7.57 (d, ^3J = 8.3 Hz, 4H, $H-C^{Ph}$), 7.36 (m, 4H, $H-C^{Im}$), 4.44 (t, 4H; ^3J = 6.4 Hz, H_2C-N), 3.30 (t, ^3J = 6.4 Hz, 4H, H_2C-S). ^{13}C NMR (D_2O, 75 MHz): δ 182.9, 142.7, 142.2, 127.0, 124.8, 122.7, 121.7, 51.3, 47.3.

Complex 4c, Na[AuCl(1c)]. ESI-MS for $C_7H_{11}AuClN_2NaO_3S$ (*m*/*z*): 434.995 ($M(^{35}Cl) - Na^+$). ^1H NMR (D_2O, 360 MHz): δ 7.18 (d, ^3J = 1.6 Hz, 1H, $H-C^{Im}$), 7.12 (d, ^3J = 1.6 Hz, 1H, $H-C^{Im}$), 4.21 (t, ^3J = 6.9, ^3J = 6.9 Hz, 2H, H_2C). ^{13}C NMR (D_2O, 75 MHz): δ 167.5, 122.7, 121.0, 49.2, 47.8, 37.7, 26.0. Solubility: 680 mg/1 mL of H_2O (20 °C).

Complex 5c, Na[Au(1c)$_2$]. ESI-MS for $C_{14}H_{22}AuN_4NaO_6S_2$ (*m*/*z*): 603.007 ($M - Na^+$). ^1H NMR (D_2O, 360 MHz): δ 7.18 (d, ^3J = 1.4 Hz, 2H, $H-C^{Im}$), 7.15 (d, ^3J = 1.4 Hz, 2H, $H-C^{Im}$), 4.28 (t, ^3J = 6.9 Hz, 4H, H_2C-N), 3.81 (s, 6H, H_3C-N), 2.87 (t, ^3J = 6.8 Hz, 4H, H_2C-S), 2.21 (tt, ^3J = 7.7 Hz, ^3J = 6.8 Hz, 4H, H_2C). ^{13}C NMR (D_2O, 75 MHz): δ 183.7, 123.0, 121.4, 49.1, 47.9, 37.5, 26.4.

Complex 4d, Na[AuCl(1d)]. ESI-MS for $C_{10}H_{17}AuClN_2NaO_3S$ (*m*/*z*): 477.039 ($M - Na^+$). ^1H NMR (D_2O, 360 MHz): δ 7.19 (s, 1H, $H-C^{Im}$), 7.17 (s, 1H, $H-C^{Im}$), 4.19 (t, 2H, ^3J = 6.6 Hz, H_2C-N), 4.05 (t, 2H, ^3J = 6.8 Hz, H_2C-N), 2.82 (t, 2H, ^3J = 7.0 Hz, H_2C-S), 2.20 (m, 2H, H_2C), 1.72 (m, 2H, H_2C), 1.22 (m, 2H, H_2C), 0.82 (t, 3H, ^3J = 7.0 Hz, H_3C). ^{13}C NMR (D_2O, 75 MHz): δ 166.9, 121.6, 121.2, 50.8, 49.3, 47.8, 32.5, 26.1, 19.0, 13.0.

Complex 5d, Na[Au(1d)$_2$]. ESI-MS for $C_{20}H_{34}AuN_4NaO_6S_2$ (*m*/*z*): 687.166 ($M - Na^+$). ^1H NMR (D_2O, 360 MHz): δ 7.24 (d, ^3J = 1.4 Hz, 2H, $H-C^{Im}$), 7.23 (d, ^3J = 1.4 Hz, 2H, $H-C^{Im}$), 4.27 (t, ^3J = 6.6 Hz, 4H, H_2C-N), 4.15 (t, ^3J = 6.7 Hz, 4H, H_2C-N), 2.82 (t, 4H, H_2C-S), 2.67 (m, 4H, H_2C), 1.80 (t, ^3J = 7.0 Hz, 4H, H_2C), 1.26 (m, 4H, H_2C), 0.84 (t, ^3J = 7.0 Hz, 6H, H_3C). ^{13}C NMR (D_2O, 75 MHz): δ 182.9, 122.3, 122.0, 50.9, 49.3, 47.9, 33.0, 26.5, 19.3, 13.1.

Complex 4e, Na$_2$[AuCl(1e)]. ^1H NMR (D_2O, 360 MHz): δ 7.18 (s, 2H, $H-C^{Im}$), 4.22 (t, ^3J = 6.9 Hz, 4H, H_2C-N), 2.82 (t, ^3J = 7.8 Hz, 4H, H_2C-S), 2.20 (tt, ^3J = 7.8 Hz, ^3J = 6.9 Hz, 4H, H_2C). ^{13}C NMR (D_2O, 75 MHz): δ 167.1, 121.5, 49.4, 47.8, 26.0. Solubility: 355 mg/1 mL of H_2O (20 °C).

Complex 5e, Na$_3$[Au(1e)$_2$]. ^1H NMR (D_2O, 360 MHz): δ 7.21 (s, 2H, $H-C^{Im}$), 4.28(t, ^3J = 6.3, 4H, H_2C-N), 2.84 (t, ^3J = 7.2 Hz, 4H, H_2C-S), 2.27 (tt, ^3J = 7.2 Hz, ^3J = 6.3 Hz, 4H, H_2C). ^{13}C NMR (D_2O, 75 MHz): δ 183.3, 121.5, 49.3, 47.8, 26.4.

Complex 5f, Na$_3$[Au(1f)$_2$]. ESI-MS for $C_{24}H_{26}AuN_4Na_3O_{12}S_4$ (*m*/*z*): 930.982 ($M - Na^+$). ^1H NMR (D_2O, 360 MHz): δ 7.86 (m, 4H, $H-C^{Ph}$), 7.62 (m, 4H, $H-C^{Ph}$), 7.45 (d, ^3J = 1.9 Hz, 2H, $H-C^{Im}$), 7.42 (d, ^3J = 1.9 Hz, 2H, $H-C^{Im}$), 4.11 (t, ^3J = 6.7 Hz, 4H, H_2C-N), 2.79 (t, ^3J = 7.7 Hz, 4H, H_2C-S), 2.24 (tt, ^3J = 7.7 Hz, ^3J = 6.7 Hz, 4H, H_2C). ^{13}C NMR (D_2O, 75 MHz): δ 181.9, 143.5, 141.1, 127.0, 125.7, 125.3, 122.8, 49.6, 47.7, 26.2.

Typical Terminal Alkyne Hydration Experiment. A solution of the catalyst (0.02 mmol) in H_2O (2.5 mL) was added to a solution of the terminal alkyne (1.0 mmol) in MeOH (2.5 mL). The reaction mixture was stirred and heated to reflux for 3 h. Samples (300 μL) were extracted with toluene (1 mL), dried over $MgSO_4$, and subjected to gas chromatography. In the hydration of aliphatic alkynes, the samples were extracted with $CDCl_3$ (1 mL), washed with H_2O (3 × 1 mL), and dried over $MgSO_4$. The composition was determined by ^1H NMR.

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Supporting Information Available: CIF files, figures, and tables giving details of the X-ray structure analysis of complexes **3a** and **5a** and the time course of hydration of phenylacetylene catalyzed by **4a** with and without additives. This material is available free of charge via the Internet at http://pubs.acs.org.