ELSEVIER

Catalysis Today 72 (2002) 29–41

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Stoichiometric and catalytic reactions of gold utilizing ionic liquids

M. Deetlefs, H.G. Raubenheimer*, M.W. Esterhuysen

Department of Chemistry, University of Stellenbosch, Private Bag X1, Matieland 7602, South Africa

Abstract

The first thiazolium gold(III) compound that qualifies as an ionic liquid has been prepared and crystallographically characterized. Hydration of phenylacetylene with this compound as catalyst precursor in ionic liquids indicates that gold(III)-based ionic liquids could serve both as solvents and catalysts for organic transformations. The potential re-use of catalysts is an advantage achieved by recycling the ionic liquid phase. Various imidazolium-derived ionic liquids as well as the new thiazolium compound can be converted into gold carbene complexes by sequential deprotonation and coordination, opening the way for in situ catalyst tailoring.

Keywords: Ionic liquids; Gold; Carbenes; Catalysis

1. Introduction

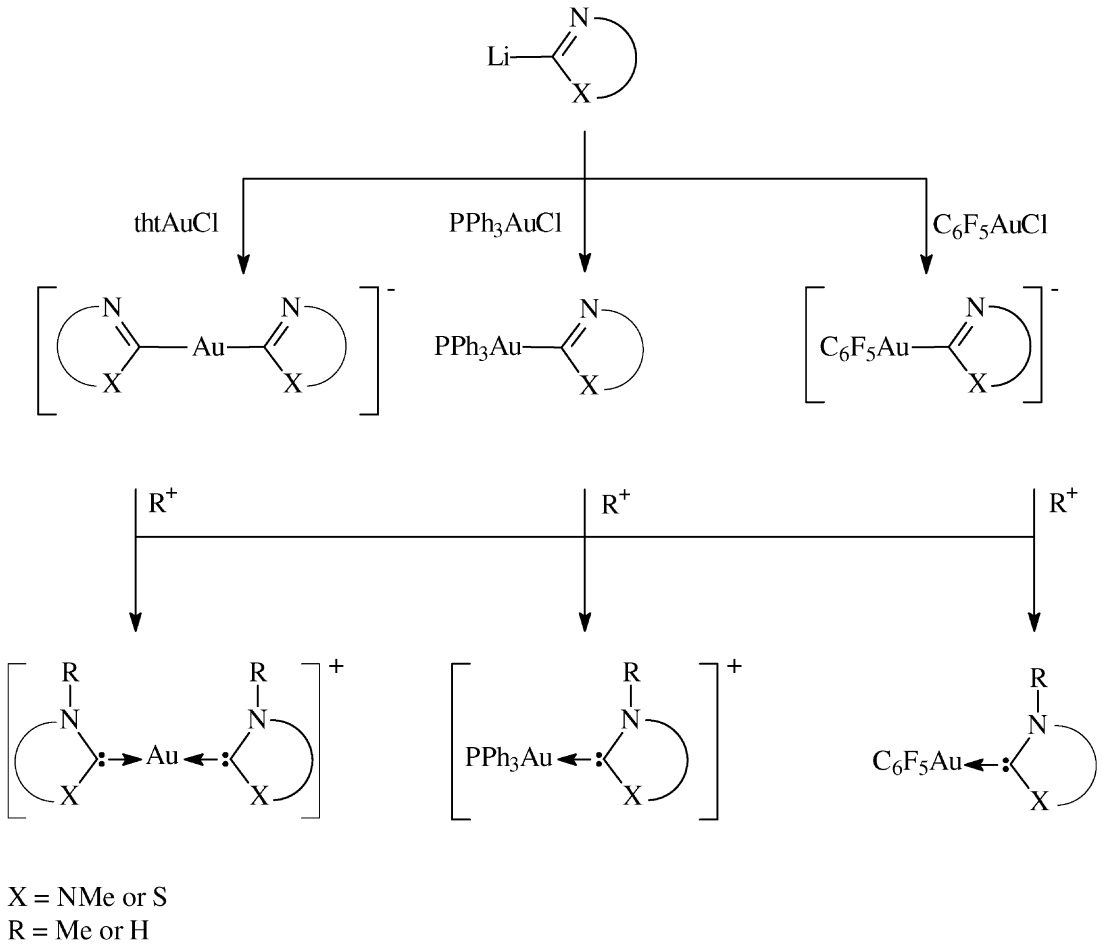
In the recent years, our research group has been interested in the synthesis of heterocyclic carbene complexes of gold [1]. Preparative procedures developed for this purpose involve the treatment of halogold compounds with lithiated azoles prior to protonation or alkylation. With the non-halide ligand labile, disubstitution occurs and predominantly bis(carbene) complexes are produced (Scheme 1). Excellent catalytic activity of such a heterocyclic gold(I) carbene complex has recently been reported [2].

Ionic liquids are presently being developed as environmentally benign solvents for homogenous catalysis [3]. The ionic liquids derived from azoles are potential precursors for free carbenes and therefore, also for carbene complexes. It would be useful in terms of product and catalyst separation in biphasic systems when the catalyst contains such non-labile, carbene ligands derived from one of the ionic solvents, or even better, when the carbene coordination can be effected in the ionic liquid medium. The first steps towards these approaches are reported here.

Thiazolium ionic liquids are alternatives to the more generally utilized imidazolium media and thus far confer only the obvious disadvantage of increased cost. Although low melting point imidazolium ionic liquids incorporating gold in the anion [4] have recently become accessible, we describe here the first example of a gold(III) thiazolium salt that qualifies as an ionic liquid. Its relatively high melting point makes it unsuitable as a solvent for the hydration of phenylacetylene, a process described here. Nevertheless, the catalytic activity of this compound was investigated in both imidazolium ionic liquids and conventional solvents and it was, furthermore, transformed into a gold(III) carbene complex by treatment with a base.

* Corresponding author. Tel.: +27-21-808-3850; fax: +27-21-808-3849.
E-mail address: hgr@maties.sun.ac.za (H.G. Raubenheimer).

0920-5861/02/$ – see front matter
PII: S0920-5861(01)00475-8



Scheme 1.

2. Results and discussion

The spectroscopic data for all the compounds are presented in Table 1 and the numbering system shown in Schemes 2 and 3 applies throughout. Counter-ions are not always indicated.

2.1. Synthesis and characterization of a free diaminocarbene and related complexes of gold(I)

Imidazolium halide salts are generally employed as free carbene precursors [5]. We could show that the ionic liquids, [BMIM][OTf] or [BMIM][PF_6] (BMIM = 1-butyl-3-methylimidazolium; OTf = triflate), are also available as substrates for free diaminocarbene generation.

The dialkylaurate, [Li(PPh_3)][$AuMe_2$], is prepared from the reaction of [Au(Cl)PPh_3] with two mole equivalents of methyllithium (MeLi) at −78 °C [6]. Treatment of the ionic liquid [BMIM][OTf] with a diethyl ether solution of the aurate at room temperature, afforded the diaminocarbene, **1** (Scheme 2). This reaction was expected to produce a neutral methylgold(I) carbene adduct but shows that the dimethylaurate functioned only as a base and not as an acid. The stoichiometric addition of MeLi to [BMIM][OTf] or [BMIM][PF_6] also furnished diaminocarbene **1** in good yield. The free carbene is extremely

Table 1
Spectroscopic data

1	δ_H[a]	7.79 (2H, d, $J = 18$, H^4, H^5), 4.38 (2H, t, $J = 15$, NCH_2–), 4.07 (3H, s, NMe), 1.92 (2H, m, NCH_2CH_2–), 1.39 (2H, m, $N(CH_2)_2CH_2$–), 0.97 (3H, t, $J = 15$, terminal CH_3)
	δ_C[a]	210.9 (C^2), 125.1 (C^4), 123.7 (C^5), 50.3 (NCH_2–), 36.7 (NCH_3), 32.8 (NCH_2CH_2–), 20.0 ($N(CH_2)_2CH_2$–), 13.7 (terminal CH_3)
	m/z	138, $[\overline{CN(Me)CH=CHN(Bu)}]^+$; 123, $[\overline{CNCH=CHN(Bu)}]^+$; 82, $[\overline{CN(Me)CH=CHN}]^+$
2	δ_H[a]	7.43 (2H, d, $J = 18$, H^4, H^5), 4.24 (2H, t, $J = 15$, NCH_2–), 3.86 (3H, s, NMe), 1.93 (2H, m, NCH_2CH_2–), 1.39 (2H, m, $N(CH_2)_2CH_2$–), 0.96 (3H, t, $J = 15$, terminal CH_3)
	δ_C[a]	171.5 (AuC), 125.0 (C^4), 123.7 (C^5), 50.2 (NCH_2–), 37.6 (NCH_3), 33.8 (NCH_2CH_2–), 20.2 ($N(CH_2)_2CH_2$–), 13.7 (terminal CH_3)
	m/z	371, $[ClAu\{\overline{CN(Me)CH=CHN(Bu)}\}]^+$; 335, $[Au\{\overline{CN(Me)CH=CHN(Bu)}\}]^+$; 138, $[\overline{CN(Me)CH=CHN(Bu)}]^+$
3	δ_H[a]	7.57 (4H, d, $J = 18$, H^4, H^5), 4.36 (4H, t, $J = 15$, NCH_2–), 4.01 (6H, s, NMe), 1.94 (4H, m, NCH_2CH_2–), 1.41 (4H, m, $N(CH_2)_2CH_2$–), 0.97 (6H, t, $J = 15$, terminal CH_3)
	δ_C[a]	185.3 (AuC), 125.2 (C^4), 123.8 (C^5), 51.6 (NCH_2–), 38.4 (NCH_3), 34.5 (NCH_2CH_2–), 20.4 ($N(CH_2)_2CH_2$–), 13.9 (terminal CH_3)
	m/z	473, $[Au\{\overline{CN(Me)CH=CHN(Bu)}_2\}]^+$; 335, $[Au\{\overline{CN(Me)CH=CHN(Bu)}\}]^+$; 138, $[\overline{CN(Me)CH=CHN(Bu)}]^+$
4	δ_H[b]	9.85 (1H, s, H^2), 7.83 (1H, s, H^5), 4.50 (2H, t, $J = 15$, NCH_2–), 2.68 (3H, s, 4-Me), 2.01 (2H, m, NCH_2CH_2–), 1.52 (2H, m, $N(CH_2)_2CH_2$–), 1.05 (3H, t, J=15, terminal CH_3)
	δ_C[b]	158.3 (C^2), 147.7 (C^4), 122.8 (C^5), 54.0 (NCH_2–), 32.3 (NCH_2CH_2–), 20.2 (4-CH_3), 14.4 ($N(CH_2)_2CH_2$–), 13.8 (terminal CH_3)
	m/z	156, $[\overline{HC=C(Me)N(Bu)CHS}]^+$; 141, $[\overline{HC=CN(Bu)CHS}]^+$; 99, $[\overline{HC=C(Me)NCHS}]^+$
5	δ_H[b]	7.45 (1H, s, H^5), 4.49 (2H, t, $J = 15$, NCH_2–), 2.48 (3H, s, 4-Me), 1.94 (2H, m, NCH_2CH_2–), 1.51 (2H, m, $N(CH_2)_2CH_2$–), 0.92 (3H, t, $J = 15$, terminal CH_3)
	δ_C[b]	173.3 (C^2), 145.3 (C^4), 119.5 (C^5), 55.9 (NCH_2–), 33.4 (NCH_2CH_2–), 20.6 (4-CH_3), 14.4 ($N(CH_2)_2CH_2$–), 14.0 (terminal CH_3)
	m/z	459, $[Cl_3Au\{\overline{HC=C(Me)N(Bu)CS}\}]^+$; 352, $[Au\{\overline{HC=C(Me)N(Bu)CS}\}]^+$; 154, $[\overline{HC=C(Me)N(Bu)CS}]^+$

[a] Recorded in $(CD_3)_2CO$.
[b] Recorded in CD_2Cl_2.

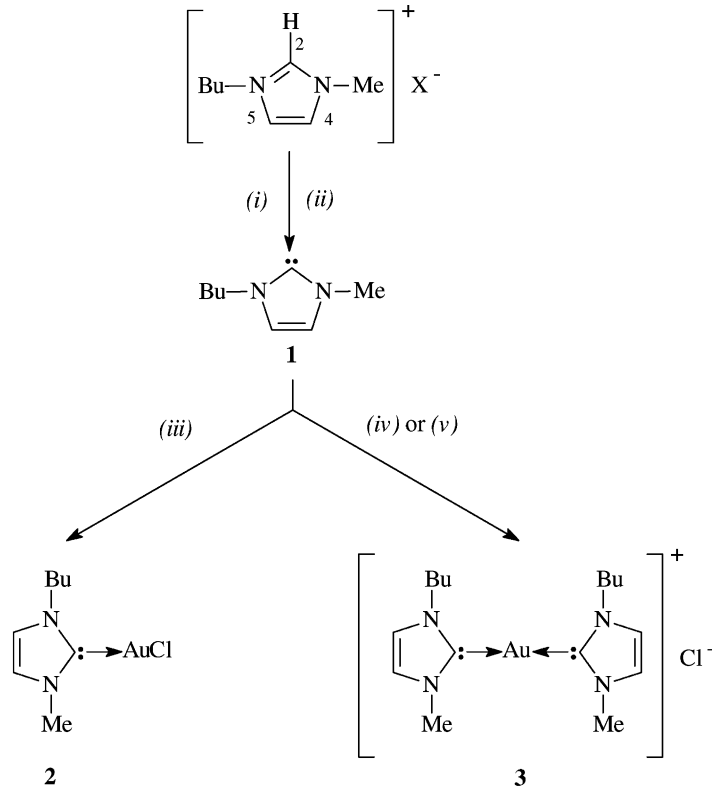
sensitive to air and moisture, but stable for prolonged periods at low temperature and under an inert atmosphere.

The proton NMR spectrum of carbene **1** displays no signal for H^2 indicating deprotonation in this position. The long-range coupling between the H^4 and H^5 ring protons and the H^2 proton in the ionic liquid precursor is also no longer visible. The remaining resonances show insignificant changes. ^{13}C–$\{^1H\}$ NMR spectroscopic data for carbene **1** displays the carbene resonance at δ 210.9, shifted downfield by $\Delta\delta$ 72.1 with respect to the precursor. The chemical shift of C^2 is similar to that found for a range of related imidazol-2-ylidene singlet carbenes that resonate between δ 205.9 and 215.2 [5]. Electron impact (EI) mass data clearly shows the molecular ion at *m*/*z* 138 as the base peak.

Free diaminocarbenes are described as better σ-donors than the best phosphine donors [7] and both compounds readily displace weakly coordinated thioether ligands such as dimethylsulphide (SMe_2) and tetrahydrothiophene (tht). The neutral gold(I) adduct, **2** (Scheme 2), was easily prepared by treatment of a diethyl ether suspension of $[Au(Cl)SMe_2]$ or [Au(Cl)tht] with one mole equivalent of carbene **1** at –50 °C. Gold(I) compounds regularly exhibit homoleptic rearrangement (Eq. (1), in which charges are omitted) [8,9], but this behavior was not observed for compound **2**:

$$2AuL^1L^2 \rightarrow AuL^1_2 + AuL^2_2 \quad (1)$$

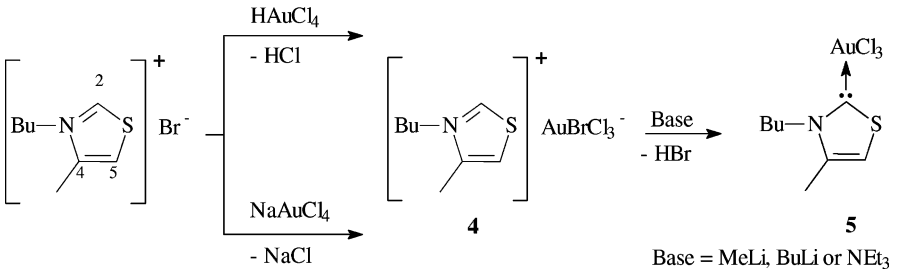
In contrast to Fischer-type carbenes, imidazol-2-ylidenes bind to transition metals mainly by σ-donation with π-back bonding negligible [10]. The slight upfield shift noted for H^4 and H^5 at δ 7.43 is therefore surprising, but similar to that observed for a similar neutral cyano-carbenegold(I) complex at δ 7.38 [11]. The positive upfield shift of C^2 ($\Delta\delta$ 39.4) with



Reagents: *(i)* $[Li(PPh_3)][AuMe_2]$; X = OTf *(ii)* MeLi; X = OTf, PF_6
(iii) [Au(Cl)tht] or $[Au(Cl)SMe_2]$ *(iv)* $[AuMe_2]Li$
(v) $[Au(Cl)PPh_3]$

Scheme 2.

respect to its resonance in carbene **1** cannot readily be explained. The carbene carbon in neutral as well as cationic gold(I) carbene complexes generally resonates at δ ca. 180 [1] and the present chemical shift of δ 171.5 seems rather low. Mass spectral data display the molecular ion at *m*/*z* 371 and the fragmentation pattern shows sequential loss of chloride and gold.



Scheme 3.

Addition of free carbene **1** to a solution containing two molar amounts of MeLi and one molar amount of [Au(Cl)tht] afforded predominantly the bis(carbene) complex **3** (Scheme 2) and a low concentration of the mono(carbene) compound, **2**. Evidenced by both deposition of gold and the fact that [BMIM][OTf] was only deprotonated to a limited extent in a parallel reaction, we concluded that a stable aurate complex, [Li(tht)][$AuMe_2$], had not formed. The formation of the mono(carbene) **2** was, therefore, ascribed to the reaction of the free carbene **1** and unconverted [Au(Cl)tht]. The formation of complex **3** is reminiscent of a reaction between ylides of the type $R_2{}^3C{=}PR_3{}^2$ and halogold(I) phosphine compounds that form mono(ylide) species, converting into a bis(ylide) gold(I) complex with an excess of the ligand (Eq. (2)) [12].

$$(\mathrm{Au(Cl)PR_3{}^1}) \overset{\mathrm{R_3{}^2P{=}CR_2{}^3}}{\rightarrow} [\mathrm{Au(CR_2{}^3PR_3{}^2)(PR_3{}^1)}] \times \mathrm{Cl} \underset{-\mathrm{PR_3{}^1}}{\overset{\mathrm{R_3{}^2P{=}CR_2{}^3}}{\rightarrow}} [\mathrm{Au(CR_2{}^3PR_3{}^2)_2}]\mathrm{Cl} \quad (2)$$

In the current reaction, the free diaminocarbene was present in excess since some [Au(Cl)tht] decomposed upon treatment with MeLi. Furthermore, the *trans* influence of free imidazol-2-ylidene carbenes is greater than that of PPh_3 [13] and the Au–Cl bond is labilized. Due to the positive charge on the final complex, the remaining proton resonances are all shifted downfield with respect to the neutral complex **2**. $^{13}C–\{^1H\}$ NMR spectroscopic data for complex **3** display a downfield shift for C^2 ($\Delta\delta$ 13.8) with respect to the coordinated carbon in compound **2**. The resonance of the carbene atom at δ 185.3 is similar to the chemical shift observed for an analogous gold(I) bis(imidazol-2-ylidene) complex (δ 185.7) [11] Mass spectral data does not exhibit a peak for the molecular ion, but the cationic fragment is observed at *m*/*z* 473. The fragmentation pattern shows sequential loss of one carbene fragment followed by gold to give the molecular ion of the free carbene at *m*/*z* 138 as the base peak.

Stoichiometric addition of [Au(Cl)PPh_3] in a 1:1 ratio to a tetrahydrofuran (thf) solution of carbene **1** at room temperature, furnished mainly the cationic bis(carbene) complex **3** and an unidentified phosphine-containing product. Three possible pathways could account for the result obtained: (a) ligand displacement of PPh_3 by carbene **1** that furnishes the adduct **2** followed by rapid homoleptic rearrangement to give complex **3**, but with $AuCl_2{}^-$ as counterion; (b) ligand displacement of chloride by carbene **1** to afford a cationic complex, followed by rapid homoleptic rearrangement to give complex **3** and [$Au(PPh_3)_2$]Cl; (c) sequential substitution (compare Eq. (2)) as a result of the addition of [Au(Cl)PPh_3] to a local excess of carbene **1** where half of the original [Au(Cl)PPh_3] remains unreacted. The first pathway is not feasible since solutions of complex **2** did not exhibit homoleptic rearrangement and no free PPh_3 was present in the reaction mixture. The third pathway is unlikely since the product mixture contained very little unreacted [Au(Cl)PPh_3]. The second pathway is the most convincing and is supported by a previous report from our group [9] where a rapid disproportionation is suggested for a cationic triphenylphosphine gold(I) isothiazolylinylidene complex to afford the corresponding bis(carbene) complex.

2.2. Synthesis and characterization of a thiazolium-based gold(III) ionic liquid and carbene complex

3-Butyl-4-methylthiazolium bromide, [BMTz][Br], was prepared by refluxing an equimolar mixture of 4-methyl thiazole and 1-bromobutane [14]. Treatment of [BMTz][Br] dissolved in methanol with $HAuCl_4$ or $NaAuCl_4$ furnished compound **4** in good yield (Scheme 3). Formation of the mixed anion is due to the substitution of chloride by the softer bromide ion present in the reaction mixture. Suitable crystals for structure determination by X-ray methods were obtained by vapor diffusion. Compound **4** meets the requirement of melting below 100 °C and is classified as an ionic liquid [3]. The proton spectrum shows an insignificant upfield shift for the H^2 proton with respect to [BMTz]Br. $^{13}C–\{^1H\}$ NMR spectroscopic data also display small upfield shifts for C^2 ($\Delta\delta$ 3.5) and C^4 ($\Delta\delta$ 7.0) with respect to the precursor. The molecular ion of **4** was not observed in fast atom bombardment (FAB) or EI mass spectra. A high intensity signal for the thiazolium cation is, however, present at *m*/*z* 156.

Dissolution of compound **4** in thf, cooling to −78 °C and subsequent treatment with a base yielded the neutral mono(carbene) complex, **5** (Scheme 3).

The formation of **5** implies that substitution of bromide by the free thiazolylinylidene has occurred. The orange carbene complex cannot be handled in air and shows limited stability under an inert atmosphere. The most prominent feature of the ^{13}C–$\{^1H\}$ NMR spectra is the significant upfield shift of C^2 ($\Delta\delta$ 52) with respect to the precursor compound. This effect is opposite to that usually observed when azolium halide salts are transformed into free carbenes [5]. Resonance of this carbene carbon at δ 173.3 is comparable to a chemical shift at δ 167.8 for a related halogold(III) complex [15]. The molecular ion of the neutral complex appears as a strong signal in fast atom bombardment (FAB) spectra at *m/z* 459 and the $[M]^+$, $[M + 2]^+$, $[M + 4]^+$ and $[M + 6]^+$ isotope lines for $\{Cl_3\}$ are unmistakable.

2.3. Crystal structure determination of *[BMTz][AuBrCl$_3$]*, *4*

The crystal data as well as collection and refinement details for complex **4** are given in Table 2 and selected bond lengths and angles in Table 3. The molecular structure is shown in Fig. 1 and the unit cell packing showing Au–halide interactions, in Fig. 2.

Complex **4** crystallizes in the monoclinic space group $P2_1/n$ as dark red crystals and consists of a 3-butyl-4-methylthiazolium cation with $AuBrCl_3^-$ as counterion (Fig. 1). The Au–Au distances exclude any metal–metal interactions and, both the cation as well as the square planar anion exhibit disorder. The $AuBrCl_3^-$ anion exhibits positional disorder of the halogen atoms with the occupancy of the bromine atom distributed over positions 1–4

Table 2
Crystal data, collection and refinement details for **4**

Formula	$C_8H_{14}NSAuBrCl_3$
Formula weight	539.41
Crystal system, space group	Monoclinic, $P2_{1/n}$
Radiation	Mo Kα (0.71073 Å)
T (°C)	−123(2)
a, b, c (Å)	8.2241 (3), 9.6725 (3), 18.5555 (8)
α, β, γ (°)	90, 93.6050 (10), 90
Z	4
U (Å^3)	1473.12 (9)
Crystal size	$0.13 \times 0.20 \times 0.20\,mm^3$
Calculated density (D_c) (g cm^{-3})	2.232
Absorption coefficient (μ)	$13.356\,mm^{-1}$
Absorption correction method	Empirical (Scalepack)
T_{min}	0.1753
T_{max}	0.2756
F(0 0 0)	1000
Diffractometer	Enraf Nonis Kappa CCD
Scan type	ϕ and ω to fill an Ewald sphere
Scan range, θ (°)	$2.38 \le \theta \le 27.52$
$h\,k\,l$ ranges	$-10 \le h \le 9$, $-12 \le k \le 11$, $-24 \le l \le 17$
Reflections collected/unique	7160/2603 [R(int) = 0.0328]
Data/restraints/parameters	3357/32/178
Refinement method	Full-matrix least-squares on F^2
Final R indices [$I > 2$ sigma(I)]	$R_1 = 0.0446$, $wR_2 = 0.0978$
R indices (all data)	$R_1 = 0.0639$, $wR_2 = 0.1054$
Maximum scan rate (°min^{-1})	0.2207
Maximum scan time per reflection (s)	0.3335
Weighting scheme	Calc. $w = 1/[\sigma^2(Fo^2)] + [(0.0290)^2 + 13.1169P]$, where $P = (Fo^2 + 2Fc^2)/3$
Goodness of fit on F^2	1.061
Largest peak, deepest hole (e$^-$/Å^3)	1.56, −1.73 (0.72 from Au)
Maximum shift (esd)	0.001

Table 3
Selected bond lengths (Å) and angles (°) for **4**[a]

Au1–Cl1	2.260 (3)	Au1–Br1	2.39 (3)
Au1–Cl2	2.27 (2)	Au1–Br2	2.41 (4)
Au1–Cl3	2.39 (3)	Au1–Br3	2.37 (15)
Au1–Cl4	2.26 (9)	Au1–Br4	2.48 (3)
C1a–N1a	1.32 (2)	C5–N1a	1.48 (2)
C1b–N1b	1.38 (4)	C5–N1b	1.43 (2)
C1a–S1a	1.67 (2)		
C1b–S1b	1.56 (3)		
Cl1–Au1–Cl2	87.3 (7)	Cl1–Au1–Br2	81.7 (13)
Cl1–Au–Cl3	170.9 (7)	Cl1–Au–Br3	178.1 (6)
Cl1–Au1–Cl4	93.0 (6)	Cl1–Au1–Br4	95.5 (11)
Cl3–Au1–Cl4	95.1 (6)	Cl3–Au1–Br4	92.9 (11)
S1a–C1a–N1a	113.4 (19)		
S1b–C1b–N1b	116.0 (2)		

[a] e.s.d.s. in parentheses.

with site occupancies of 0.30, 0.16, 0.42, and 0.12, respectively.

The disorder in the thiazolium ring of the cation was modeled as a disordered pair of rings lying across each other at an angle of approximately 174° (least square planes through disordered rings) in a 59% (a) to 41% (b) percentage ratio. The *N*-butyl chain in **4** exhibits dynamic disorder, which could not be modeled successfully. The chain, however, lies roughly in the plane of the thiazolium ring, unlike the *N*-butyl chain in the known structure of [BMIM][$AuCl_4$] which is nearly perpendicular to the ring plane [4]. In [BMIM][$AuCl_4$], two crystallographically independent $AuCl_4^-$ anions are arranged perpendicular to each other in an infinite anionic chain pattern of alternating corner-to-face $AuCl_4^-$ units. In the present structure, the anions are arranged with a halide–Au–halide angle of 108° (mean) also producing infinite anion chain but in a zigzag pattern as every $AuBrCl_3^-$ unit has one interacting halide atom (Fig. 2). Gold–halide distances between the anions of **4** is ca. 3.57 Å (mean value for Br and Cl), which is longer than the gold–chloride separation of 3.45 Å in [BMIM][$AuCl_4$].

The closest cationic–anionic contacts involve thiazolium C-bound hydrogens and halogen atoms (H2a–Br1 = 2.73 Å). Although closer CH–halide contacts of 2.53 Å are observed between H4b3 and Br4, they have to be disregarded as H4b3 is a methyl

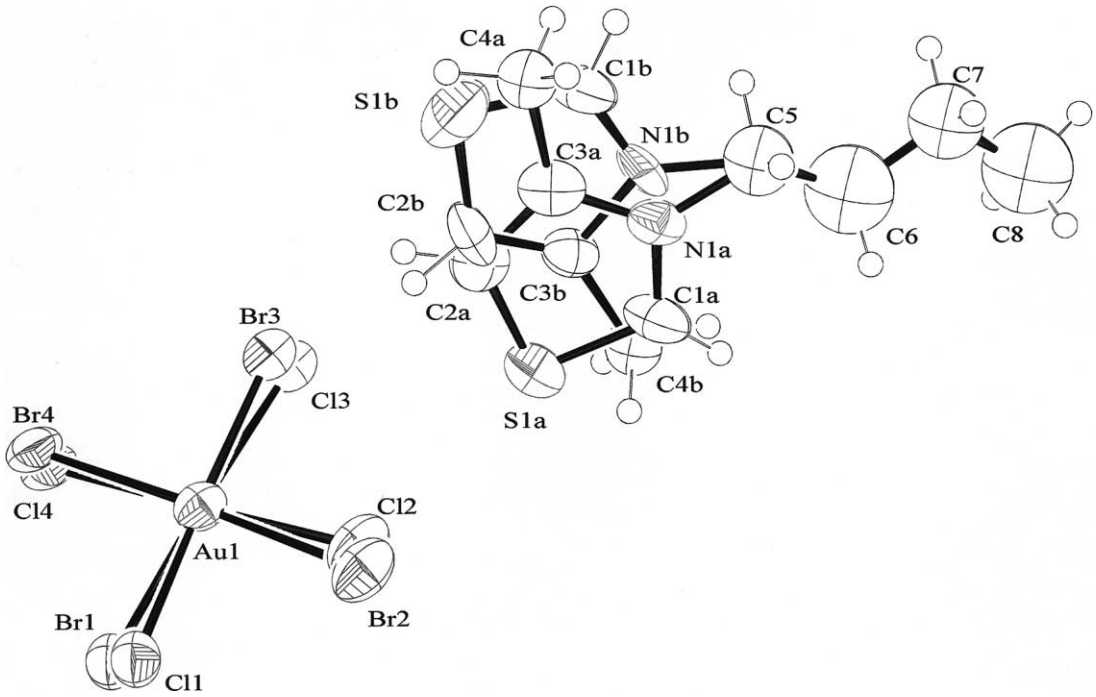


Fig. 1. Crystal structure of **4** showing disordered atom positions and numbering scheme.

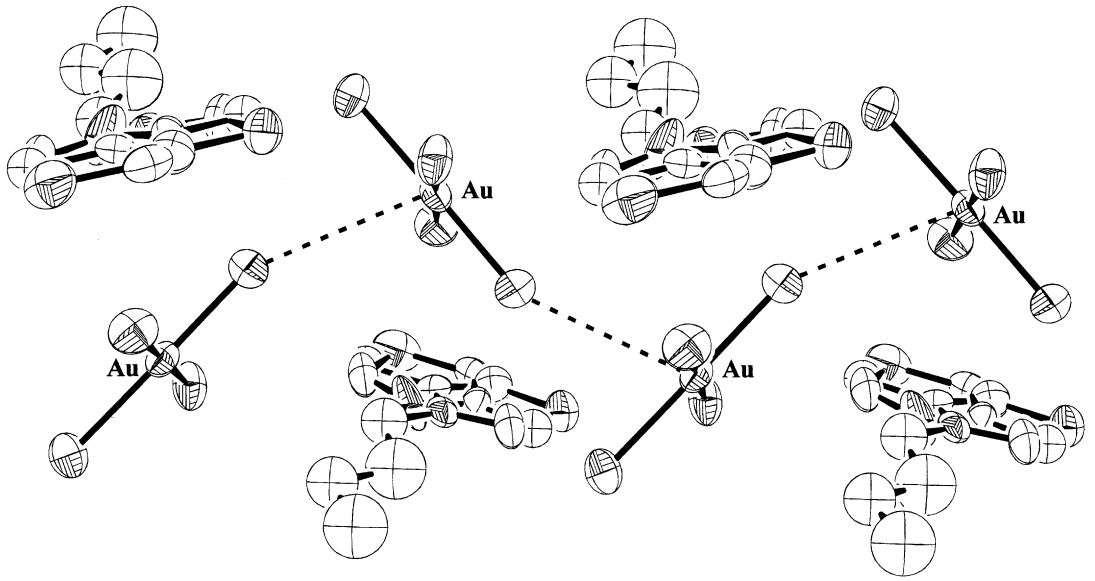


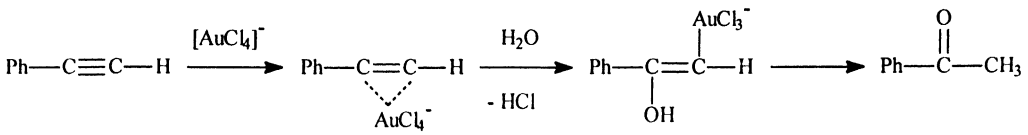
Fig. 2. Packing diagram of **4**, viewed along the a-axis, showing Au–halide interaction (hydrogen atoms and second disordered halide position omitted for clarity).

proton in an unreliable calculated position. The interpretation of CH–halide interactions in **4** should in general be treated with extreme caution as none of the positions of the hydrogen atoms could be determined directly from the Fourier synthesis. Furthermore, the thiazolium rings to which the calculated hydrogens are connected are disordered and could only be refined with both rigid body and planarity restraints. Their positions are thus not reliable and can certainly not be employed in accurately describing interionic Coulomb interactions. In addition, the fact that such a high degree of disorder, with little preference for specific conformations, exists suggests that the aforementioned Coulombic interactions probably play a negligible role in stabilizing the crystalline phase of **4**. It is more likely that the observed Au–halide interactions could direct the orientation of the ions and perhaps govern the overall assembly in the crystalline phase.

2.4. Catalytic hydration of phenylacetylene

First catalytic results are presented here. Histograms using the mean of the values given in Table 4 appear in Figs. 3 and 4.

The hydration of phenylacetylene (Eq. (3)) in refluxing aqueous methanol with $NaAuCl_4$ as catalyst has been reported by Fukuda and Utimoto [16]:



(3)

We investigated the same reaction in, methanol, [BMIM][OTf], [BMIM][BF_4] or [BMIM][PF_6] with $NaAuCl_4$ and [BMTz][$AuBrCl_3$] (2.4 mol%), respectively as catalysts. The reaction time was 24 h at temperatures of 30, 40 and 60 °C. Blank reactions were performed in the ionic liquids and showed no conversion of phenylacetylene.

The hydration reaction is temperature dependent and the best conversions were obtained at 30 °C for both catalyst precursors in methanol and the respective ionic liquid solvents (Figs. 3 and 4). The activities

Table 4
Catalytic results for the hydration of acetylene

Temperature (°C)	Yield (%)													
	Methanol		[BMIM][BF_4]		[BMIM][PF_6]		[BMIM][OTf]		[BMIM][BF_4][a]		[BMIM][PF_6][a]		[BMIM][OTf][a]	
	A[b]	B[c]	A[b]	B[c]	A[b]	B[c]	A[b]	B[c]	A[b]	B[c]	A[b]	B[c]	A[b]	B[c]
30	65	60	68	66	65	64	75	74	28	27	30	28	34	30
	63	61	66	65	60	63	70	72	31	29	33	30	32	32
	64	59	65	66	61	63	72	74	33	32	33	26	32	29
40	42	40	45	43	49	50	55	56	20	17	20	22	21	19
	41	41	45	43	48	51	54	56	20	18	22	20	20	18
	40	39	43	43	50	47	55	54	23	22	23	18	24	21
60	16	12	18	19	21	20	23	22	8	11	10	9	11	12
	17	13	16	17	19	21	23	22	8	9	13	13	10	8
	15	11	16	19	18	17	22	22	10	7	15	9	13	9

[a] Recycled ionic liquid phases.
[b] $NaAuCl_4$.
[c] [BMTz][$AuBrCl_3$].

of the gold complexes were similar at the chosen temperatures but a decrease in the total yield of acetophenone (65%) was obtained compared to the previous study (91%). Nevertheless, employing extended reaction times in conjunction with milder temperatures, decreased the catalyst deactivation rate and thereby increased phenylacetylene conversion. Acetophenone formation ceased after 24 h (as determined by GC–MS) and the deposition of gold became visible.

Catalytic hydration of phenylacetylene with two mole equivalents of wet methanol also proceeded with the individual catalysts in a biphasic mixture of ionic liquid and toluene. Catalyst dissolution in the ionic liquid, introduction of phenylacetylene and methanol and heating to 30, 40 and 60 °C respectively, afforded acetophenone in various yields. The introduction of toluene eliminated the need for a final product extraction procedure. A number of reactions were performed with only toluene as solvent, the catalysts showed limited solubility and the yield of acetophenone was much lower than in the corresponding reactions in the ionic liquids. Conversions, TONs and activities followed the order [BMIM][OTf] > [BMIM][PF_6] ≈ [BMIM][BF_4]

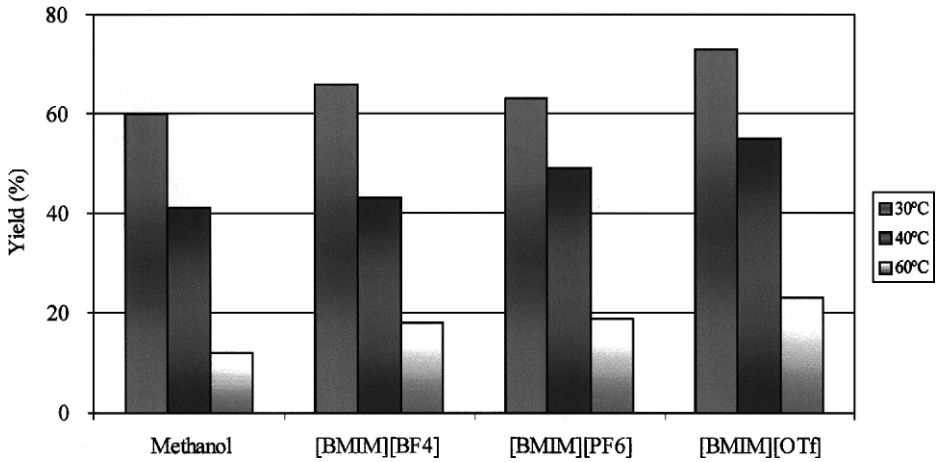


Fig. 3. Percentage yield of acetophenone with [BMTz][$AuBrCl_3$].

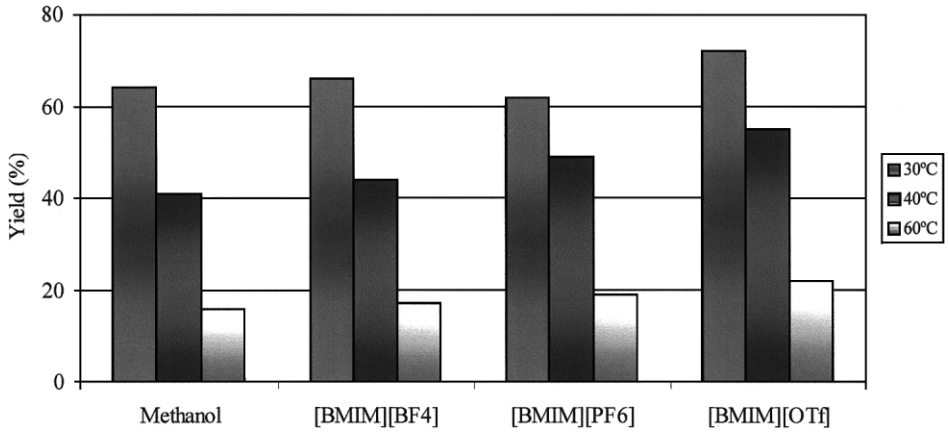


Fig. 4. Percentage yield of acetophenone with $NaAuCl_4$.

and deposition of gold metal was again evident. In [BMIM][BF_4] and [BMIM][PF_6], the yield of acetophenone was the same as in methanol, whereas the reaction in [BMIM][OTf] gave a slight increase (ca. 10%). Performing the reaction at the melting point of [BMTz][$AuBrCl_3$] (80 °C) afforded significantly lower yields (ca. 10%). Nonetheless, catalysis of the hydration reaction by [BMTz][$AuBrCl_3$] indicates that gold(III)-based ionic liquids could serve as both solvents and catalysts for organic transformations, but that further work is necessary.

One of the reported advantages of utilizing ionic liquids as opposed to conventional solvents, is their capacity to be re-cycled [3]. The potential re-use of catalysts within the ionic liquid phase could then also be an advantage. Filtering off deposited gold, repeatedly washing the ionic liquid phase with toluene and drying in vacuo removed deposited gold metal and traces of acetophenone present due to the original hydration reactions. Fresh phenylacetylene and methanol were introduced and the reactions repeated. At the three temperatures, the conversions were now 50% lower, but, nevertheless, indicating the need for further work. The conversion of phenylacetylene showed a similar dependency on the ionic liquids as before with the best yields obtained in [BMIM][OTf].

3. Conclusion

We could show that ionic liquids derived from imidazole are precursors for free carbenes and for gold(I) carbene complexes, indicating that in situ metal–carbene coordination is possible. Since free imidazolinylidenes generally exhibit greater stability than their thiazolinylidene counterparts [17], in situ benzoin condensation catalysis [16] with the latter compounds in the parent ionic liquids is being investigated.

The first thiazolium gold(III) ionic liquid was crystallographically characterized and used to prepare a rather unstable carbene complex. Low melting ionic liquids incorporating gold in the anion have lately become accessible, potentially eliminating the need for a conventional and thereby promoting the "green chemistry" aspect of catalysis [4]. With a melting point of nearly 100 °C, the new ionic liquid was unsuitable as a medium for studying the hydration of acetylenes. It, nevertheless, catalyses this reaction in other imidazolium ionic liquids, which could be regenerated and re-used. Future prospects include in situ generation of more stable imidazolinylidene gold, and other metal complexes and their direct utilization in catalysis.

4. Experimental

4.1. General

The ionic liquids [BMIM][OTf] [18], [BMIM][PF_6] [19], [BMIM][BF_4] [20] and the gold compounds [Au(Cl)tht], [Au(Cl)PPh_3] [21], [Au(Cl)SMe_2] [22]

and [Li(PPh_3)][$AuMe_2$] [23] were all prepared according to literature procedures. The thiazolium based ionic liquids, [BMTz][Br] and [BMTz][BF_4], were prepared according to the procedures employed for [BMIM][Cl] [24] and [BMIM][BF_4]. Thf, hexane, toluene and diethyl ether were distilled under nitrogen from sodium diphenylketyl and dichloromethane from CaH_2. Methanol was distilled from magnesium methanolate and stored over 3 Å molecular sieves. All reactions involving organometallic and free carbene reagents were performed under an atmosphere of argon using standard vacuum-line and Schlenk techniques. Melting points were determined on a standardized Buchi 535 apparatus. EI mass spectra were recorded on a Finnigan Matt 8200 instrument at ca. 70 eV (1.12×10^{-17} J) and FAB mass spectra were recorded on a VGA70-70E mass spectrometer at 70 eV with xenon as bombardment gas and *m*-nitrobenzylalcohol as matrix. NMR spectra were recorded on a Varian 300 FT spectrometer.

4.2. Preparation of [$CN(\overline{Me})CH = CHN(Bu)$], **1**

[Li(PPh_3)][$AuMe_2$] was prepared by the treatment of [Au(Cl)PPh_3] (494 mg, 1 mmol) in thf or diethyl ether (20 ml) at −78 °C with 1.4 M MeLi (1.4 ml, 2 mmol). The prepared [Li(PPh_3)][$AuMe_2$] was filtered at −78 °C in an adapted filtration apparatus into [BMIM][OTf] (288 mg, 1 mmol) dissolved in diethyl ether (10 ml) at −78 °C. The reaction mixture was stirred for 30 min, warmed to room temperature and the solvent removed to give the pale yellow, oily product. Yield 86 mg (0.62 mmol, 62%); m.p. 110–112 °C. Calc. for $C_8H_{14}N_2$ (138.21 g mol^{-1}): C, 69.5; H, 10.2; N, 20.2. Anal. Found: C, 69.8; H, 10.2; N, 20.1.

[BMIM][OTf] (577 mg, 2 mmol) or [BMIM][PF_6] (506 mg, 2 mmol) was treated with 1.4 M MeLi (1.4 ml, 2 mmol) at room temperature. The reaction mixture was stirred for 15 min, 15 ml diethyl ether added, the reaction mixture filtered through Celite and the solvent removed. Yield 118 mg (0.85 mmol, 85%); m.p. 110–112 °C. Calc. for $C_8H_{14}N_2$ (138.21 g mol^{-1}): C, 69.5; H, 10.2; N, 20.2. Anal. Found: C, 69.8; H, 10.2; N, 20.1.

4.3. Preparation of [$ClAu\{CN(\overline{Me})CH = CHN(Bu)\}$], **2**

1-Butyl-3-methylimidazol-2-ylidene (**1**) (371 mg, 1 mmol) dissolved in thf (20 ml) was added to [Au(Cl)SMe_2] (295 mg, 1 mmol) or [Au(Cl)tht] (321 mg, 1mmol) in thf (20 ml) at −50 °C. The reaction mixture was stirred for 30 min, warmed to room temperature, filtered through Celite and the solvent removed to give the product as a white powder. Yield 315 mg (0.85 mmol, 85%); m.p. 192–193 °C. Calc. for $C_8H_{14}N_2AuCl$ (370.64 g mol^{-1}): C, 25.9; H, 3.8; N, 7.6. Anal. Found: C, 25.9; H, 4.0; N, 7.4.

4.4. Preparation of [$Au\{CN(\overline{Me})CH = CHN(Bu)\}_2$][$Cl$], **3**

[Au(Cl)tht] (321 mg, 1 mmol) dissolved in thf (20 ml) at −78 °C was treated with 1.4 M MeLi (1.4 ml, 2 mmol), stirred for 20 min and 1-butyl-3-methylimidazol-2-ylidene (**1**) (371 mg, 1 mmol) dissolved in thf (20 ml) added. The reaction mixture was stirred for 30 min, warmed to room temperature and the solvent removed to give the product as a white powder. Yield 208 mg (0.41 mmol, 41%, according to NMR). A suitably pure sample could not be obtained and elemental analyses and the melting point were, therefore, not performed.

4.5. Preparation of [*BMTz*][$AuBrCl_3$], **4**, by halide displacement

3-Butyl-4-methylthiazolium bromide (605 mg, 2.56 mmol) was dissolved in methanol (10 ml) and $HAuCl_4$ (1 g, 2.56 mmol) dissolved in methanol (10 ml) added dropwise over 10 min. The reaction mixture was stirred for 2 h, the methanol removed in vacuo and the ionic liquid dried under high vacuum (1 mm Hg) at 30 °C for 24 h. Yield 1133 mg (2.1 mmol, 82%); m.p. 80–82 °C; Calc. for $C_8H_{14}NSAuBrCl_3$ (539.50 g mol^{-1}): C, 17.9; H, 2.5; N, 2.6. Anal. Found: C, 17.8; H, 2.6; N, 2.6.

4.6. Preparation of [*BMTz*][$AuBrCl_3$], **4**, by halide exchange

3-Butyl-4-methylthiazolium bromide (525 mg, 2.22 mmol) was dissolved in methanol (10 ml) and

$NaAuCl_4$ (963 mg, 2.22 mmol) dissolved in methanol (10 ml) added dropwise over 10 min. The reaction mixture was stirred for 2 h and the methanol removed in vacuo. The product was redissolved in dichloromethane, the precipitated NaCl filtered off and the ionic liquid dried under high vacuum (1 mm Hg) at 30 °C for 24 h. A crystal suitable for X-ray crystallographic studies was obtained by dissolving the compound in methylene chloride and layering with pentane. Yield 1018 mg (1.9 mmol, 85%); m.p. 80–82 °C. Calc. for $C_8H_{14}NSAuBrCl_3$ (539.50 g mol^{-1}): C, 17.9; H, 2.5; N, 2.6. Anal. Found: C, 17.8; H, 2.6; N, 2.6.

4.7. Preparation of $[Cl_3Au\{HC=\overline{C(Me)N(Bu)}CS\}]$, **5**

[BMTz][$AuBrCl_3$] (539 mg, 1 mmol) was dissolved in thf (15 ml) and cooled to 78 °C. MeLi, 1.4 M (0.7 ml, 1 mmol), 1.6 M butyllithium (BuLi) (0.6 ml, 1 mmol) or NEt_3 (101 mg, 1 mmol) was added and stirring continued for 2 h with gradual warming to room temperature. The mixture was filtered through Celite and the solvent removed. Yield 1018 mg (1.9 mmol, 85%); m.p. 115 °C, decomposition. The product slowly decomposes and elemental analyses could not be performed.

4.8. Hydration of phenylacetylene in methanol

$NaAuCl_4$ (87 mg, 0.24 mmol) or [BMTz][$AuBrCl_3$] (129 mg, 0.24 mmol) was dissolved in methanol (15 ml) in a glass bomb and phenylacetylene (1 g, 0.93 ml, 10 mmol) added. The bomb was sealed and heated to 30, 40 or 60 °C for 24 h. The vessel was allowed to cool to room temperature, the reaction mixture filtered and the excess methanol removed in vacuo.

4.9. Hydration of phenylacetylene in ionic liquids

$NaAuCl_4$ (87 mg, 0.24 mmol) or [BMTz][$AuBrCl_3$] (119 mg, 0.24 mmol) was dissolved in [BMIM][BF_4], [BMIM][PF_6] or [BMIM][OTf] (10 ml) and layered with toluene (10 ml) in a glass bomb. Phenylacetylene (1 g, 0.93 ml, 10 mmol) and methanol (160 mg, 5 mmol) was added, the bomb was sealed and heated to 30, 40 or 60 °C for 24 h. The vessel was allowed to cool to room temperature, the toluene layer decanted and the excess toluene removed in vacuo.

4.10. Hydration of phenylacetylene in recycled ionic liquid phases

After the original reaction, the ionic liquid was filtered (porosity 4 filter) washed repeatedly with toluene (3 ml × 10 ml) and dried under high vacuum (3 mm Hg) for 24 h at room temperature. The hydration reaction was then performed as before.

4.11. X-ray crystallography of **4**

X-ray diffraction data were collected on an Enraf-Nonius Kappa CCD diffractometer at 150(2) K using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) [25] and corrected for Lorenz and absorption effects using the Scalepack package [26]. Structure solution and refinement was carried out using the program SHELX-97 [27]. ORTEP-3 for Windows was used to generate the figures at 50% probability level [28]. The structure was solved by direct methods and completed by full-matrix least-squares refinement against F^2. All non-hydrogen atoms were refined anisotropically, except those in the *N*-butyl chain (C5, C6, C7, C8), which exhibited dynamic disorder. Equal bond length restraints with an effective standard deviation of 0.02 Å were applied to the C_{sp3}–C_{sp3} bonded carbon atoms in the *N*-butyl chain in order to obtain sensible bond lengths. The disorder in the thiazolium ring was resolved by identifying disordered atom pairs for the components of the ring from the difference Fourier map and restraining the sum of their common site occupancy factors to 1. Rigid body and planarity restraints were applied to the disordered ring pair after which the atoms involved were allowed anisotropic motion. Final refined occupation factors gave a disordered ring ratio of 0.59 (a):0.41 (b). The positional disorder found for the bromine atom in the $AuBrCl_3^-$ anion was dealt with as follows: The halide positions around the gold atom were each split into a chlorine and bromine atom with the sum of their respective site occupancy factors independently restrained to 1. Refinement of these halide positions yielded a total site occupancy of exactly 1

for the bromine atom over all 4 halide positions in the ratio 0.30:0.16:0.42:0.12 for halide positions 1–4, respectively, thus crystallographically confirming the $AuBrCl_3^-$ empirical formula for the anion. Hydrogen positions were calculated with C–H distances of 0.98 (methyl C–H) and 0.95 (methylene C–H) and assigned isotropic thermal parameters 1.5 (methyl H) and 1.2 (methylene H) times the equivalent isotropic displacement parameters of their parent atoms.

References

[1] H.G. Raubenheimer, S. Cronje, J. Organomet. Chem. 617–618 (2001) 170.
[2] J.H. Teles, S. Brode, M. Chabanas, Angew. Chem., Int. Ed. Engl. 37 (1998) 1415.
[3] K.R. Seddon, J. Chem. Biotechnol. 68 (1997) 351;
K.R. Seddon, Kinet. Catal., Engl. Transl. 37 (1996) 693.
[4] M. Hasan, I.V. Kozhevnikov, M.R.H. Siddiqui, A. Steiner, N. Winterton, Inorg. Chem. 38 (1999) 5637.
[5] D. Bourissou, O. Guerret, F.P. Gabbaï, G. Bertrand, Chem. Rev. 100 (2000) 39.
[6] A. Tamaki, J.K. Kochi, J. Organomet. Chem. 51 (1973) C39.
[7] J. Huang, E.D. Stevens, S.P. Nolan, J.L. Peterson, J. Am. Chem. Soc. 121 (1999) 2674.
[8] A.L. Hormann-Arendt, C.F. Shaw, Inorg. Chem. 29 (1990) 4683;
P.N. Dickson, A. Wehrli, G. Geier, Inorg. Chem. 27 (1988) 2921.
[9] H.G. Raubenheimer, M. Desmet, G.J. Kruger, J. Chem. Soc., Dalton Trans. (1995) 2067.
[10] J.C. Green, R.G. Scurr, P.L. Arnold, F.G.N. Cloke, J. Chem. Soc., Chem. Commun. (1997) 1963.
[11] H.G. Raubenheimer, L. Lindeque, S. Cronje, J. Organomet. Chem. 511 (1996) 177.
[12] H. Schmidbaur, A. Grohmann, M.E. Olmos, in: H. Schmidbaur (Ed.), Gold Progress in Chemistry, Biochemistry and Biotechnology, Wiley, West Sussex, 1999.
[13] H.M.J. Wang, C.Y.L. Chen, I.J.B. Lin, Organometallics 18 (1999) 1216.
[14] J.H. Davis Jr., K.J. Forrester, Tetrahedron Lett. 40 (1999) 1621.
[15] H.G. Raubenheimer, P.J. Olivier, L. Lindeque, M. Desmet, J. Hrušak, G.J. Kruger, J. Organomet. Chem. 544 (1997) 91.
[16] A.J. Arduengo, J.R. Goerlich, W.J. Marshall, Liebigs Ann. Recueil (1997) 365.
[17] Y. Fukuda, K. Utimoto, J. Org. Chem. 56 (1991) 3729.
[18] P. Bonhôte, A.-P. Dias, N. Papegeorgiou, N. Kalyanasundaram, M. Grätzel, Inorg. Chem. 35 (1996) 1168.
[19] P.A.Z. Suarez, J.E.L. Dullius, S. Einloft, R.F. de Souza, J. du Pont, Polyhedron 15 (1996) 1217.
[20] J.S. Wilkes, M.J. Zawarotko, J. Chem. Soc., Chem. Comm. (1992) 965.
[21] A. Hass, J. Helmbrecht, U. Niemann, Handbuch der Prapärativen Anorganischen Chemie, Ferdinand Enke, Stuttgart, 1974, p. 1014.
[22] P.C. Rây, D.C. Chen, J. Indian Chem. Soc. (1930) 67.
[23] J. Stein, J.P. Fackler, C. Paparizos, H.-W. Chen, J. Am. Chem. Soc. 103 (1981) 2192.
[24] J.S. Wilkes, J.A. Levisky, R.A. Wilson, C.L. Hussey, Inorg. Chem. 21 (1982) 1263.
[25] Nonius, COLLECT, Nonius BV, Delft, The Netherlands, 1999.
[26] Z. Otwinowski, W. Minor, Methods Enzymol. 276 (1997) 307.
[27] G.M. Sheldrick, SHELX-97—Program for Crystal Structure Analysis, Institüt für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, 1998.
[28] L.J. Farrugia, J. Appl. Cryst. 30 (1997) 565.