


Cite this: *RSC Adv.*, 2023, 13, 11441

# Reactions of noble-metal oxides in ionic liquids near room temperature†

Mareike Liebertseder, Carsten Donsbach and Claus Feldmann \*

The reaction of  $\text{Ag}_2\text{O}$ ,  $\text{Au}_2\text{O}_3$ , and  $\text{HgO}$  with  $\text{CuCl}$ ,  $\text{CuI}$ ,  $\text{AgCl}$ ,  $\text{AgI}$ ,  $\text{AuCl}$ , and  $\text{AuI}$  in ionic liquids ( $[\text{EMIm}]\text{Cl}$ ,  $[\text{BMIm}]\text{Cl}$ ) near room temperature (20–80 °C) is evaluated and results in the new compounds  $(\text{C}_8\text{H}_{14}\text{N}_2)\text{CuCl}$ ,  $(\text{C}_8\text{H}_{14}\text{N}_2)\text{AgI}$ ,  $(\text{C}_6\text{H}_{10}\text{N}_2)\text{AuCl}$ ,  $[(\text{C}_8\text{H}_{14}\text{N}_2)_2\text{Hg}][\text{CuCl}_3]$ ,  $[(\text{C}_8\text{H}_{14}\text{N}_2)_2\text{Hg}][\text{AgCl}_3]$ , and  $[\text{EMIm}][\text{Ag}_2\text{I}_2\text{Cl}]$ . Thereof,  $(\text{C}_8\text{H}_{14}\text{N}_2)\text{CuCl}$ ,  $(\text{C}_8\text{H}_{14}\text{N}_2)\text{AgI}$ ,  $(\text{C}_6\text{H}_{10}\text{N}_2)\text{AuCl}$ ,  $[(\text{C}_8\text{H}_{14}\text{N}_2)_2\text{Hg}][\text{CuCl}_3]$ , and  $[(\text{C}_8\text{H}_{14}\text{N}_2)_2\text{Hg}][\text{AgCl}_3]$  are NHC complexes (NHC: N-heterocyclic carbene) with M–C bonds (M: Cu, Ag, Au, Hg). Whereas  $(\text{C}_8\text{H}_{14}\text{N}_2)\text{CuCl}$  and  $(\text{C}_8\text{H}_{14}\text{N}_2)\text{AgI}$  crystallize as single molecules,  $(\text{C}_6\text{H}_{10}\text{N}_2)\text{AuCl}$  is dimerized via aurophilic interactions.  $[(\text{C}_8\text{H}_{14}\text{N}_2)_2\text{Hg}][\text{CuCl}_3]$  and  $[(\text{C}_8\text{H}_{14}\text{N}_2)_2\text{Hg}][\text{AgCl}_3]$  exhibit Hg atoms with two Hg–C bonds. Moreover,  $(\text{C}_8\text{H}_{14}\text{N}_2)\text{AgI}$  shows intense green fluorescence at room temperature with a quantum yield of 44%, whereas all other compounds do not show any emission at room temperature. Finally,  $[\text{EMIm}][\text{Ag}_2\text{I}_2\text{Cl}]$  is not an NHC compound but contains  $\infty^1[\text{Ag}_{1/2}\text{I}_{2/4}\text{Cl}_{1/2}]^-$  chains with infinite  $d^{10}$ – $d^{10}$  interaction of the silver atoms. The title compounds are characterized by single-crystal structure analysis, infrared spectroscopy, thermogravimetry, and fluorescence spectroscopy.

Received 9th February 2023

Accepted 14th March 2023

DOI: 10.1039/d3ra00892d

rsc.li/rsc-advances

## Introduction

Ionic liquids have significantly advanced the synthesis of inorganic compounds and, in the meantime, resulted in several unique compounds that most probably would have not been obtainable in conventional solvents.<sup>1</sup> The polychloride  $[\text{Et}_4\text{N}]_2[(\text{Cl}_3)_2\cdot\text{Cl}_2]$ , the intermetalloid  $[\text{CuBi}_8]^{3+}$  cluster cation in  $[\text{CuBi}_8][\text{AlCl}_4]_2[\text{Al}_2\text{Cl}_7]$ , the heavy-metal porphyrin-analogue  $[\text{Hg}_4\text{Te}_8(\text{Te}_2)_4]^{8-}$  in  $[\text{DMIm}]_8[\text{Hg}_4\text{Te}_8(\text{Te}_2)_4]$  ( $[\text{DMIm}]^+$ : 1-decyl-3-methylimidazolium), the ligand-stabilized  $[\text{Ga}_5]^{5+}$  pentagon, the linear uranyl-type  $[\text{N}\equiv\text{U}\equiv\text{N}]$  complex and supertetrahedral selenido germanate clusters are some exemplary compounds.<sup>2</sup> We could contribute the synthesis of the three-dimensional polybromide  $[\text{C}_4\text{MPyr}]_2[(\text{Br})_2\cdot(\text{Br}_2)_9]$ , the highly coordinated  $\text{Sn}(\text{II})_8$  subunit in the carbonyl  $[\text{SnI}_8\{\text{Fe}(\text{CO})_4\}_4][\text{Al}_2\text{Cl}_7]_2$ , or crown-ether coordination compounds like  $\text{Mn}_2\text{I}_4(18\text{-crown-6})$  with unique fluorescence features such as 100% quantum yield, strong second-harmonic generation (SHG) and intense orange emission via SHG-driven excitation in the infrared spectral range.<sup>3</sup> Often, ionic-liquid-based synthesis can be performed near room temperature ( $\leq 100$  °C), which is ideal to realize new metastable compounds with kinetic control (*i.e.* at low activation energy).<sup>4</sup> Key features of ionic liquids, in this

regard, relate to the high thermal and chemical stability and the weakly coordinating properties.<sup>1,5</sup>

Until now, the synthesis of metastable compounds in ionic liquids was mainly focused on metal halides, metal selenides/tellurides or metal clusters.<sup>1–5</sup> The synthesis of new metal oxides and compounds using metal oxides as starting materials, in contrast, was barely addressed, which can be attributed to the high lattice energy of many metal oxides and their low solubility in ionic liquids. Several studies, however, have successfully shown options to dissolve metal oxides in ionic liquids.<sup>6</sup> In the course of our studies on ionic-liquid-based syntheses and the optional use of metal oxides as starting materials, we have reacted  $\text{Ag}_2\text{O}$ ,  $\text{Au}_2\text{O}_3$ , and  $\text{HgO}$  with  $\text{CuCl}$ ,  $\text{CuI}$ ,  $\text{AgCl}$ ,  $\text{AgI}$ ,  $\text{AuCl}$ , and  $\text{AuI}$  in every combination of the respective metal oxides and metal halides, whereof many lead to new compounds. As results, the novel NHC complexes (NHC: N-heterocyclic carbene)  $(\text{C}_8\text{H}_{14}\text{N}_2)\text{CuCl}$  (1),  $(\text{C}_8\text{H}_{14}\text{N}_2)\text{AgI}$  (2),  $(\text{C}_6\text{H}_{10}\text{N}_2)\text{AuCl}$  (3),  $[(\text{C}_8\text{H}_{14}\text{N}_2)_2\text{Hg}][\text{CuCl}_3]$  (4),  $[(\text{C}_8\text{H}_{14}\text{N}_2)_2\text{Hg}][\text{AgCl}_3]$  (5), as well as  $[\text{EMIm}][\text{Ag}_2\text{I}_2\text{Cl}]$  (6) with an infinite  $\infty^1[\text{Ag}_{1/2}\text{I}_{2/4}\text{Cl}_{1/2}]^-$  chain showing  $d^{10}$ – $d^{10}$  interaction of the silver atoms.

## Results and discussion

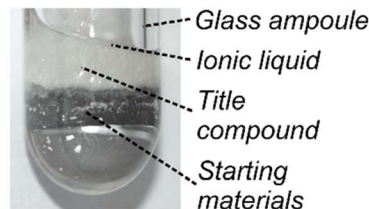
### Ionic-liquid-based synthesis

All reactions were performed using the metal oxides  $\text{Ag}_2\text{O}$ ,  $\text{Au}_2\text{O}_3$ , and  $\text{HgO}$  as well as the metal halides  $\text{CuCl}$ ,  $\text{CuI}$ ,  $\text{AgCl}$ ,  $\text{AgI}$ ,  $\text{AuCl}$ , and  $\text{AuI}$  as the starting materials.  $[\text{EMIm}]\text{Cl}$  and  $[\text{BMIm}]\text{Cl}$  ( $[\text{EMIm}]$ : 1-ethyl-3-methylimidazolium,  $[\text{BMIm}]$ : 1-butyl-3-methylimidazolium) are introduced to form ionic liquids after reaction with the aforementioned metal halides. All compounds

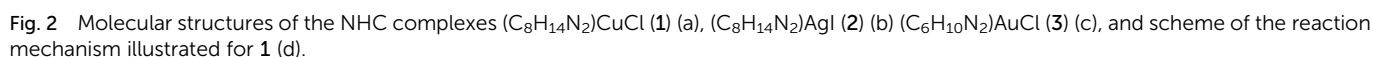
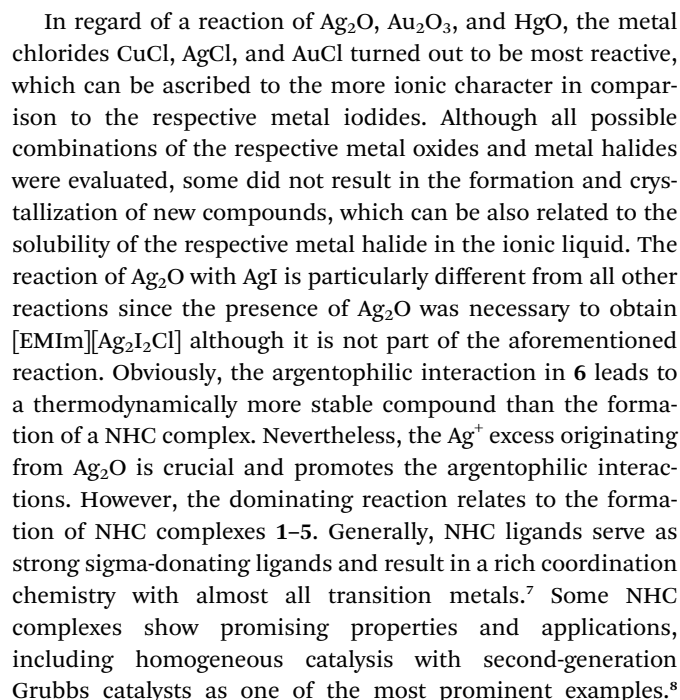
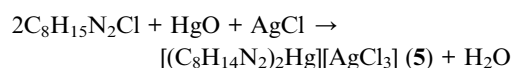
*Institute for Inorganic Chemistry, Karlsruhe Institute of Technology (KIT) Engesserstrasse 15, D-76131 Karlsruhe, Germany. E-mail: claus.feldmann@kit.edu*

† Electronic supplementary information (ESI) available: Additional data related to the analytical techniques, the crystallographic data, and the unit cells of the title compounds 1–6. CCDC 2104796–2104800 and 2220642. For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d3ra00892d>





and sample handling needs to be performed with inert conditions in order to avoid hydrolysis. Interestingly, the reactions already start at room temperature (20 °C). For **1** and **4**, leaving the ampoule at room temperature for 4 days is sufficient to grow single crystals with a yield of 40–60%. For **2**, **3**, **5**, and **6**, the reactions also start at room temperature but were accelerated and completed by slight heating to 40–80 °C. After 4 days, moisture-sensitive, colourless crystals were formed with good yield (40–60%) (Fig. 1). The synthesis of the title compounds **1–6** can be rationalized based on the following reactions:



Cu–NHC complexes have become popular due to their ability to activate C–H bonds.<sup>9</sup> Furthermore, Au– and Pt–NHC complexes received specific attention due to their potential suitability as anti-cancer agents.<sup>10</sup> Among the NHC complexes, the ligands essentially contain an imidazole or a derivative as central unit, which is usually modified by sterically demanding groups, such as in 1,3-dimesityl-imidazol-4,5-dihydro-2-ylidene (SIMes).<sup>7,11</sup> After the discovery of the very first NHC complex by Wanzlick *et al.* in 1968,<sup>12</sup> NHC complexes were prepared by different approaches, most often using transmetallation strategies.<sup>7,13</sup> In addition to these conventional approaches, few examples also show the synthesis of NHC complexes in ionic liquids,<sup>6b,14</sup> including electrochemical reduction in ionic liquids.<sup>15</sup>

### Structural characterization

(C<sub>8</sub>H<sub>14</sub>N<sub>2</sub>)CuCl (**1**) crystallizes in the form of colourless rhombuses in the orthorhombic, non-centrosymmetric and chiral space group *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> (ESI: Table S1 and Fig. S1†). Herein,

a deprotonated imidazole is connected to a CuCl unit *via* Cu–C bonding (Fig. 2a). The C–Cu–Cl arrangement is almost linear (173.7(2)°) and with a Cu–C distance of 186.9(5) pm (Table 1). Both is in good agreement with literature data (186.6–195.3 pm, 174–180°).<sup>16</sup> Similarly, the Cu–Cl distance (210.9(2) pm) is well in agreement with comparable compounds (*e.g.* 208.8 pm in (C<sub>41</sub>H<sub>32</sub>N<sub>2</sub>O<sub>2</sub>)CuCl).<sup>16a</sup> In fact, the composition of **1** was already claimed in a patent to improve bleaching agents. However, its structure and composition were not characterized.<sup>17</sup> With [Ag(EMIm-ylide)<sub>2</sub>][X] (X: SCN, CN<sub>2</sub>, OAc), Binnemans *et al.* also showed the synthesis of comparable Ag–NHC complexes in ionic liquids for the first time,<sup>6b</sup> which were obtained by reaction of Ag<sub>2</sub>O and the ionic liquid [EMIm][X] (X: SCN, CN<sub>2</sub>, OAc) only. Despite of comparable experimental conditions, the reaction of Ag<sub>2</sub>O with CuCl in [BMIm]Cl in our case did not result in an Ag–NHC compound but the Cu–NHC compound **1**, which can be ascribed to the presence of CuCl as well as of Ag<sub>2</sub>O, whereas Binnemans *et al.* examined the reaction of Ag<sub>2</sub>O

**Table 1** Comparison of selected distances in (C<sub>8</sub>H<sub>14</sub>N<sub>2</sub>)CuCl (**1**), (C<sub>6</sub>H<sub>10</sub>N<sub>2</sub>)AgI (**2**), (C<sub>6</sub>H<sub>10</sub>N<sub>2</sub>)AuCl (**3**), [(C<sub>8</sub>H<sub>14</sub>N<sub>2</sub>)<sub>2</sub>Hg][CuCl<sub>3</sub>] (**4**), and [(C<sub>8</sub>H<sub>14</sub>N<sub>2</sub>)<sub>2</sub>Hg][AgCl<sub>3</sub>] (**5**) with literature data

Atoms	Compound	Distance/pm
Cu–Cl	<b>1</b>	210.9(2)
	(C <sub>41</sub> H <sub>32</sub> N <sub>2</sub> O <sub>2</sub> )CuCl <sup>16a</sup>	208.8
	CuCl <sup>27</sup>	238.2
Cu–C	<b>1</b>	186.9(5)
	(C <sub>41</sub> H <sub>32</sub> N <sub>2</sub> O <sub>2</sub> )CuCl <sup>16a</sup>	186.9
	(C <sub>21</sub> H <sub>36</sub> N <sub>2</sub> )CuCl <sup>16c</sup>	195.3
	(C <sub>27</sub> H <sub>38</sub> N <sub>2</sub> )CuCl <sup>16b</sup>	189.6
Ag–I	<b>3</b>	332.3(2)
	(C <sub>21</sub> H <sub>26</sub> N <sub>2</sub> )AgI <sup>18a</sup>	256.6
	(C <sub>27</sub> H <sub>36</sub> N <sub>2</sub> )AgI <sup>18b</sup>	254.7
	(C <sub>27</sub> H <sub>38</sub> N <sub>2</sub> )AgI <sup>18c</sup>	257.4
	AgI AgI <sub>4</sub>	281.0
Ag–C	<b>3</b>	210.0(2)
	(C <sub>21</sub> H <sub>26</sub> N <sub>2</sub> )AgI <sup>18a</sup>	211.3
Au–Cl	<b>2</b>	227.5(3), 228.1(2)
	(C <sub>7</sub> H <sub>12</sub> N <sub>2</sub> )AuCl <sup>19a</sup>	228.8
	(C <sub>5</sub> H <sub>8</sub> N <sub>2</sub> )AuCl <sup>20</sup>	228.8
	AuCl <sup>19b</sup>	230.0
Au–C	<b>2</b>	196.2(11), 197.7(9)
	(C <sub>7</sub> H <sub>12</sub> N <sub>2</sub> )AuCl <sup>19a</sup>	198.6
	(C <sub>5</sub> H <sub>8</sub> N <sub>2</sub> )AuCl <sup>20</sup>	197.9
Hg–Cl	<b>4</b>	299.4(2)
	[S <sub>4</sub> N <sub>3</sub> ][HgCl <sub>3</sub> ] <sup>26</sup>	234.5, 243.3, 248.5, 302.2, 320.4
	HgCl <sub>2</sub> <sup>32</sup>	228.4, 230.1
Hg–C	<b>4</b>	208.0(5)
	[(C <sub>15</sub> H <sub>12</sub> N <sub>2</sub> ) <sub>2</sub> Hg][ClO <sub>4</sub> ] <sub>2</sub> <sup>25a</sup>	206.0
	(C <sub>16</sub> H <sub>18</sub> N <sub>4</sub> )Hg(PF <sub>6</sub> ) <sub>2</sub> <sup>34</sup>	206.7
Cu–Cl	<b>4</b>	222.2(3), 227.5(2)
	CuCl <sup>27</sup>	238.2
Hg–Cl	<b>5</b>	304.4(1)
	[S <sub>4</sub> N <sub>3</sub> ][HgCl <sub>3</sub> ] <sup>26</sup>	234.5, 243.3, 248.5, 302.2, 320.4
	HgCl <sub>2</sub> <sup>33</sup>	228.4, 230.1
Hg–C	<b>5</b>	206.8(3)
	[(C <sub>15</sub> H <sub>12</sub> N <sub>2</sub> ) <sub>2</sub> Hg][ClO <sub>4</sub> ] <sub>2</sub> <sup>25a</sup>	206.0
	(C <sub>16</sub> H <sub>18</sub> N <sub>4</sub> )Hg(PF <sub>6</sub> ) <sub>2</sub> <sup>34</sup>	206.7
Ag–Cl	<b>5</b>	247.0(1), 250.4(1)
	CsAgCl <sub>2</sub> <sup>28a</sup>	249.2, 266.7, 287.2
	AgCl <sup>28b</sup>	277.3



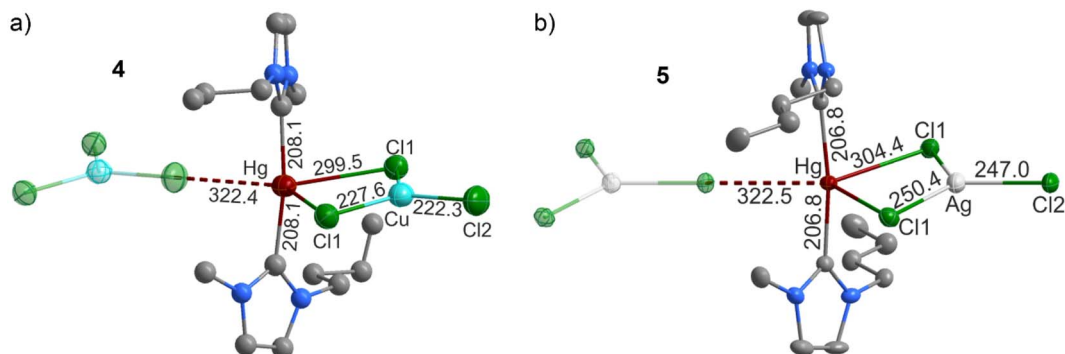


Fig. 3 Molecular structures of the NHC complexes  $[(C_8H_{14}N_2)_2Hg][CuCl_3]$  (4) (a) and  $[(C_8H_{14}N_2)_2Hg][AgCl_3]$  (5) (b).

only in the ionic liquid  $[EMIm][X]$ .<sup>6b</sup> Taking the reaction mechanism proposed by Binnemans *et al.* into account,<sup>6b</sup> we suggest a modified two-step reaction for the formation of **1** (Fig. 2d). First of all,  $Ag_2O$  as a base subtracts  $H^+$  from  $[BMIm]^+$  and  $Cl^-$  coordinates to  $Ag^+$ . Secondly, the intermediate decomposes with cleavage of the C–H bond and coordination of the carbene to  $Cu^+$ , followed by the formation of  $(C_8H_{14}N_2)CuCl$ ,  $AgCl$ , and  $H_2O$  (Fig. 2d).

Since we did not observe any crystalline Ag–NHC compound upon reacting of  $Ag_2O$  with  $AgCl$  and  $AgI$ , we have performed syntheses with  $Ag_2O$ ,  $Au_2O_3$ ,  $AuCl$ , and  $AuI$ . Here, the compounds  $(C_8H_{14}N_2)AgI$  (**2**) and  $(C_6H_{10}N_2)AuCl$  (**3**) were obtained and crystallize in the space group  $P\bar{1}$  and  $Cc$  (ESI: Table S1, Fig. S2 and S3†). The structure of **2** compares to **1** with a deprotonated imidazole connected to a  $AgI$  unit *via* Ag–C bonding (Fig. 2b). The Ag–C distance is 210.0(2) pm, the Ag–I distance is 332.3(2) pm (Table 1). Both are well in agreement with literature data (Ag–C: 206–211 pm, Ag–I: 256–257 pm).<sup>18</sup> The C–Ag–I arrangement is again almost linear ( $175.2(5)^\circ$ ). The Au–NHC compound **3** also exhibits structural features similar to **1** and **2**, however, with molecular units dimerized *via* auriphilic interactions (Fig. 2c). Here, Au–C bonding is observed with distances of 196.6(11) and 197.6(9) pm (Table 1) and almost linear C–Au–Cl arrangement ( $176.8(3)$ – $179.2(3)^\circ$ ). Distance and angle compare to literature data (Au–C: 198 pm,  $174$ – $180^\circ$ ).<sup>19</sup> Similarly, the Au–Cl distances (227.1(3), 228.1(2) pm) are well in agreement with comparable compounds, such as  $(C_7H_{12}N_2)AuCl$  (228.8 pm) or  $AuCl$  (230.0 pm).<sup>19a,20</sup> Finally, short intermolecular Au...Au distances (348.2(1) pm in **3**) are observed that are only slightly larger than the doubled van der Waals radius (332 pm) (Fig. 2c).<sup>21</sup> Such auriphilic interactions are characteristic for Au(I) and have been frequently observed.<sup>22</sup> A direct single-step formation of Au–NHC compounds such as for **3**, to the best of our knowledge, has not been shown in literature before and has yet performed by transmetalation of Ag–NHC compounds in a two-step synthesis.<sup>23</sup>

Beside using  $Ag_2O$  and  $Au_2O_3$  as a base to obtain NHC compounds, we also have evaluated the reaction of  $CuCl$  and  $AgCl$  with  $HgO$  as a base. In this context, Pelz *et al.* already pointed to the feasibility of acid–base reactions of imidazolium cations and  $HgO$ .<sup>24</sup> We have reacted  $HgO$  with  $CuCl$  or  $AgCl$  in  $[BMIm]Cl$  as the ionic liquid, which resulted in colourless

crystals of  $[(C_8H_{14}N_2)_2Hg][CuCl_3]$  (**4**) and  $[(C_8H_{14}N_2)_2Hg][AgCl_3]$  (**5**). Both crystallize in the monoclinic space group  $C2/c$  (ESI: Table S2, Fig. S4 and S5†). As the most relevant building unit, a central  $Hg^{2+}$  cation bridges two BMIm-ylide units. Furthermore, trigonal planar  $[(Cu,Ag)Cl_3]^{2-}$  units coordinate with two Cl atoms to the central  $Hg^{2+}$ . The third Cl atom of each  $[(Cu,Ag)Cl_3]^{2-}$  unit is bridging to another  $Hg^{2+}$ , so that infinite  $-[Cl_2(Cu,Ag)Cl]^- \cdots [(C_8H_{14}N_2)_2Hg^{2+}] - [Cl_2(Cu,Ag)Cl]^- \cdots$  strands are formed (Fig. 3).

In regard of the distances, Hg–C distances of 208.0(5) pm (**4**) and 206.8(3) pm (**5**) fit well with known Hg–NHC compounds (204.6(5)–209.2(5) pm).<sup>25</sup> The Hg–Cl distances are 227.6(1) and 299.5(2) pm in **4** as well as 250.4(1) pm and 304.4(1) pm in **5** for the

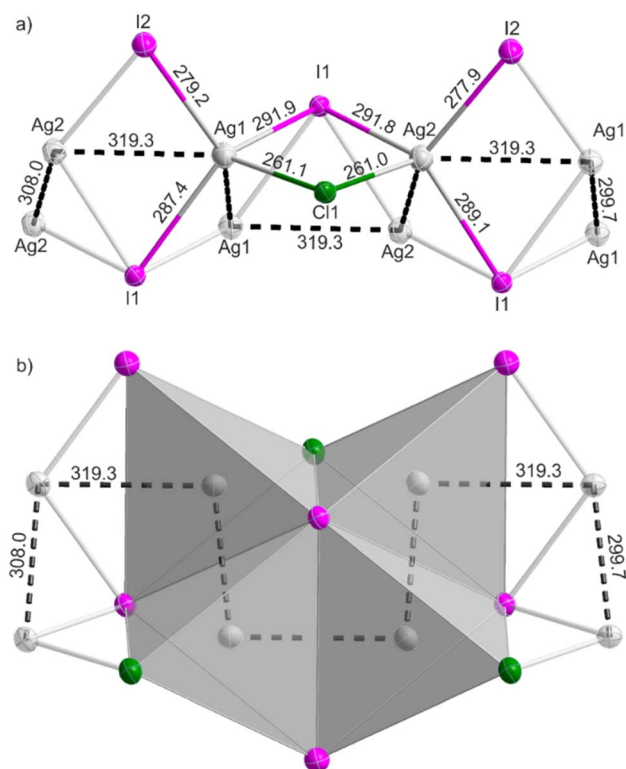


Fig. 4  $\infty [AgI_{2/4}I_{1/2}Cl_{1/2}]^-$  chain with  $d^{10}$ – $d^{10}$  interaction in  $[EMIm][Ag_2I_2Cl]$  (**6**).

$\mu_2$ -binding  $[(\text{Cu},\text{Ag})\text{Cl}_3]^{2-}$  units, which compares to  $[\text{S}_4\text{N}_3][\text{HgCl}_3]$  (234.5–320.4 pm).<sup>26</sup>  $\mu_1$ -Binding is accompanied with longer  $\text{Hg}\cdots\text{Cl}$  distances of 322.4(1) pm in **4** and 322.5(1) pm in **5** (Table 1). The  $\text{Cu}-\text{Cl}$  distances in the  $[\text{CuCl}_3]^{2-}$  unit of **4** with 222.2(3)–227.5(2) pm and are slightly shorter than in  $\text{CuCl}$  (238.2 pm),<sup>27</sup> which reflects the threefold coordination in the title compound as compared to a tetrahedral coordination of  $\text{Cu}^+$  cation in  $\text{CuCl}$ . For similar reasons, the  $\text{Ag}-\text{Cl}$  distances of the  $[\text{AgCl}_3]^{2-}$  unit in **5** with 247.0(1)–250.4(1) pm are slightly shorter than in  $\text{CsAgCl}_2$  (249.2–287.2 pm) or  $\text{AgCl}$  (277.3 pm).<sup>28</sup> Interestingly, for **5** a comparably short  $\text{Hg}\cdots\text{Ag}$  distance of 334.5(1) pm is observed, which is slightly above the van der

Waals distance (327 pm) but still points to a weak interaction.<sup>21</sup> Finally, it needs to be noticed that the butyl chain of the BMIm-ylide in **4** is disordered, which was tackled by split positions for all carbon atoms with a probability of 33 and 67%. Although  $\text{Hg}-\text{NHC}$  complexes are amongst the first described for this class of compounds,<sup>7,13,25</sup> the here observed structure and coordination, to the best of our knowledge, are described for the first time. Thus, a coordination of trigonal planar  $[\text{CuCl}_3]^{2-}/[\text{AgCl}_3]^{2-}$  units in a  $\text{Hg}-\text{NHC}$  complex is new. Trigonal planar  $[\text{CuCl}_3]^{2-}/[\text{AgCl}_3]^{2-}$  units are rarely observed in general and typically require sterical stabilization by sterically demanding organic ligands,<sup>29</sup> or hydrogen bonds.<sup>30</sup> In the case of  $\text{Ag}^+$ , such

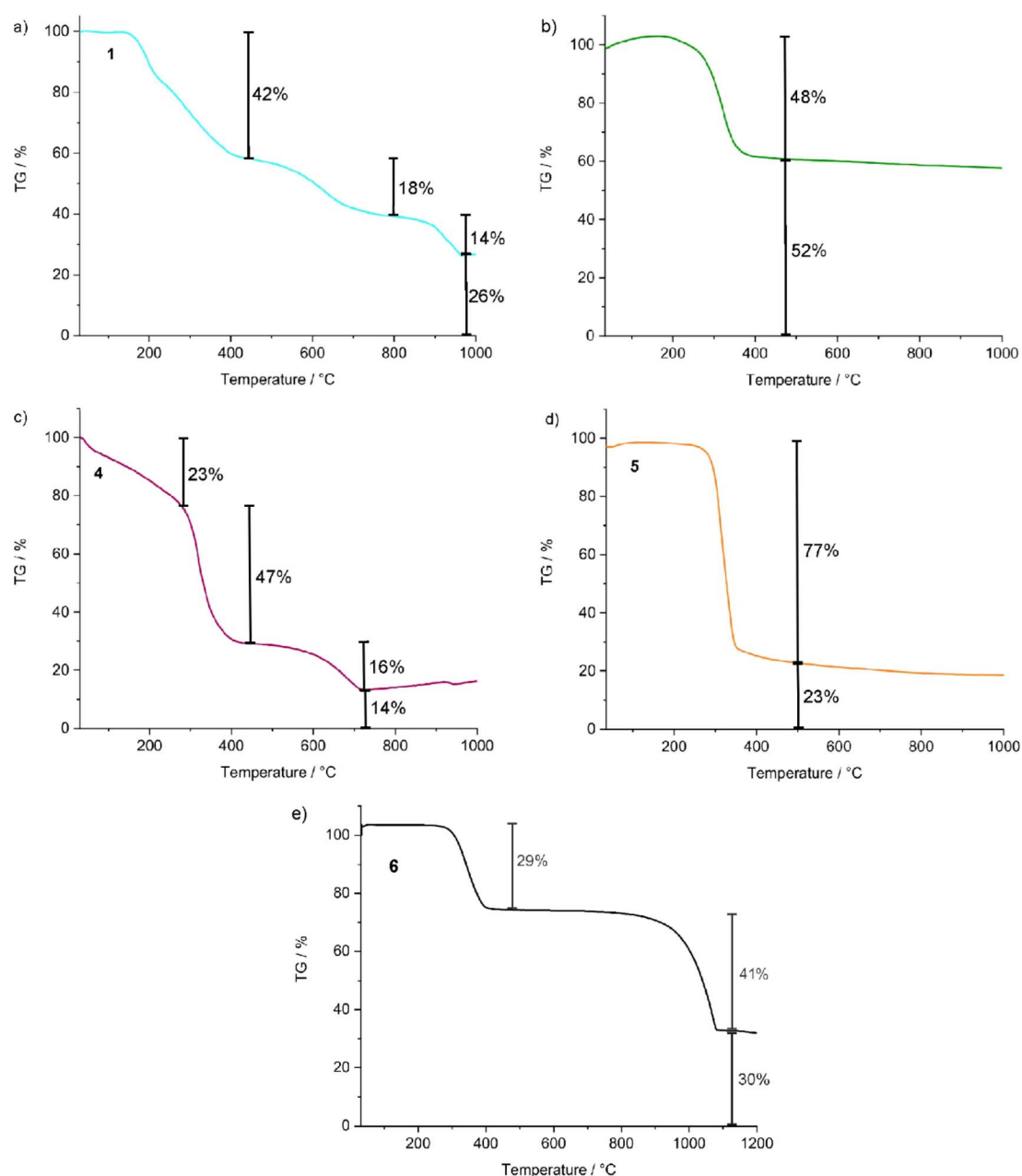


Fig. 5 TG analysis of the compounds  $(\text{C}_8\text{H}_{14}\text{N}_2)\text{CuCl}$  (**1**),  $(\text{C}_6\text{H}_{10}\text{N}_2)\text{AuCl}$  (**3**),  $[(\text{C}_8\text{H}_{14}\text{N}_2)_2\text{Hg}][\text{CuCl}_3]$  (**4**),  $[(\text{C}_8\text{H}_{14}\text{N}_2)_2\text{Hg}][\text{AgCl}_3]$  (**5**), and  $[\text{C}_6\text{H}_{11}\text{N}_2][\text{Ag}_2\text{I}_2\text{Cl}]$  (**6**).



trigonal planar arrangement is known from  $[\text{PPh}_4]_2[\text{Ag}_2\text{Cl}_4]$ , but only with a strongly distorted  $[\text{Ag}_2\text{Cl}_4]^{2-}$  unit,<sup>31</sup> or from the rigid network in the Zintl phase  $\text{Li}_{17}\text{Ag}_3\text{Sn}_6$ .<sup>32</sup>

In difference to the formation of NHC complexes by the reaction of  $\text{Ag}_2\text{O}$ ,  $\text{Au}_2\text{O}_3$ ,  $\text{HgO}$  with  $\text{CuCl}$ ,  $\text{AgCl}$ ,  $\text{AuCl}$ , the reaction of  $\text{Ag}_2\text{O}$  and  $\text{AgI}$  in  $[\text{EMIm}]\text{Cl}$  did not result in an NHC compound but in the formation of  $[\text{EMIm}][\text{Ag}_2\text{I}_2\text{Cl}]$ . **6** crystallizes with colourless needles in the triclinic space group  $P\bar{1}$  (ESI: Table S2 and Fig. S6†). The compound is composed of infinite anionic  $\infty^1[\text{AgI}_{2/4}\text{I}_{1/2}\text{Cl}_{1/2}]^-$  chains, which are separated by  $[\text{EMIm}]^+$  cations (Fig. 4). In these chains, the Ag atoms are coordinated by three I and one Cl atom to form distorted  $\text{Ag}(1)\text{I}_3\text{Cl}$  and  $\text{Ag}(2)\text{I}_3\text{Cl}$  tetrahedra with two crystallographically independent Ag sites. All  $\text{AgI}_3\text{Cl}$  tetrahedra are connected *via* edge-sharing over all edges to four adjacent  $\text{AgI}_3\text{Cl}$  tetrahedra (Fig. 4a). Such edge-sharing is rare and in difference, for instance, to the corner-sharing  $\text{AgI}_4$  tetrahedra in the binary sphalerite-type  $\text{AgI}$ .<sup>35</sup> Most remarkably, two I atoms in **6** belong to four different  $\text{AgI}_3\text{Cl}$  tetrahedra. The Ag–I distances in **6** range from 277.9(1) to 291.9(1) pm, which is comparable to  $\text{AgI}$  (281.4 pm). Due to the edge-sharing of tetrahedra in **6**, the longer Ag–I distances in comparison to  $\text{AgI}$  with corner-sharing tetrahedra are to be expected. In contrast, the Ag–Cl distances (261.0(2), 261.1(2) pm) in **6** are slightly shorter than in  $\text{AgCl}$  (277.2 pm),<sup>35</sup> which can be attributed to the lower coordination in comparison to NaCl-type  $\text{AgCl}$ .

Due to the edge-sharing  $\text{AgI}_3\text{Cl}$  tetrahedra, moreover, short Ag–Ag distances are observed in the  $\infty^1[\text{AgI}_{2/4}\text{I}_{1/2}\text{Cl}_{1/2}]^-$  chains of **6** (Fig. 4b). Thus, the Ag–Ag distances are at 299.7(1), 308.0(1), and 319.3(1) pm. All of them are below 330 pm, which was considered as attractive  $d^{10}$ – $d^{10}$  interaction by Jansen.<sup>36</sup> Hence, an infinite zig-zag chain of attractive Ag–Ag distances is present in **6**. These Ag–Ag distances are of course longer than in elemental silver (288.9 pm), which reflects the positive charge of the  $\text{Ag}^+$  cations. In principle, compounds with chain-like  $[\text{Ag}_2\text{I}_3]^-$  anions were already described in the literature.<sup>37</sup> However, a formation of infinite  $\text{Ag}^+$  chains with attractive  $d^{10}$ – $d^{10}$  interaction was only discussed for  $[\text{C}_8\text{H}_9\text{N}_2][\text{Ag}_2\text{I}_3]$  by

Zhang.<sup>38</sup> This compound has a comparable connectivity of  $\text{AgI}_4$  tetrahedra as in **6** but only contains iodine and exhibits significantly longer Ag–Ag distances (322.9–334.9 pm) than in **6**. Moreover, this compound requires a synthesis in concentrated HI.<sup>38</sup> A combination of chlorine and iodine in chain-like halido argentates (I) is generally rare and does not result in Ag chains with attractive  $d^{10}$ – $d^{10}$  interactions.<sup>39</sup> In sum, a compound like **6** with infinite  $\infty^1[\text{AgI}_{2/4}\text{I}_{1/2}\text{Cl}_{1/2}]^-$  chains and zig-zag-shaped Ag–Ag chains was obtained for the first time and prepared by ionic-liquid-based synthesis.

## Material properties

Beside the structural properties, chemical composition, thermal stability and fluorescence properties of the title compounds were examined by Fourier-transformed infrared (FT-IR) spectroscopy, thermogravimetry (TG), and photoluminescence spectroscopy (PL). FT-IR spectra of the NHC compounds **1**, **3**–**5** are dominated by the imidazolium cations with characteristic vibrations of  $\nu(\text{C–H})$ : 3300–2800  $\text{cm}^{-1}$ ,  $\nu(\text{C=N})$ : 1650–1600  $\text{cm}^{-1}$ , as well as the fingerprint area at 1500–500  $\text{cm}^{-1}$  (ESI: Fig. S7†). Moreover, the Hg–C stretching vibration at 720–680  $\text{cm}^{-1}$  is observed in the spectra of **4** and **5**. Similarly, the characteristic vibrations of the  $[\text{EMIm}]^+$  cation are observed for **6** (ESI: Fig. S8†). The absence of O–H-related vibrations at 3600–3000  $\text{cm}^{-1}$  confirms the absence of moisture.

TG analysis was performed, on the one hand, to examine the thermal stability of the title compounds, and on the other hand, to confirm the chemical composition *via* total organic combustion analysis (Fig. 5). All title compounds show thermal decomposition with 1 to 3 decompositions steps, which are summarized in Table 2. Except for **4**, which starts to decompose already slightly above room temperature, the inset of thermal decomposition is at 150 to 200 °C and is initiated by the decomposition of the  $\text{EMIm}/\text{BMIm}$ -ylides of **1** and **3**–**5** as well as the  $[\text{EMIm}]^+$  cation in **6**. At higher temperature,  $\text{HCl}$ ,  $\text{I}_2$ ,  $\text{CuCl}$ ,  $\text{AgCl}$ , or  $\text{HgCl}_2$  evaporate (Table 2). The decomposition ends with the metals (Cu, Ag, Au) or metal halides ( $\text{CuCl}$ ,  $\text{AgCl}$ ) as

Table 2 TG analysis of the compounds **1**, **2**, **4**, **5** and **6**

Compound	Temperature range/°C	Mass loss/%	Calculated mass loss/%
$(\text{C}_8\text{H}_{14}\text{N}_2)\text{CuCl}$ ( <b>1</b> )	140–450	42	
	450–800	18	58 ( $\text{C}_8\text{H}_{13}\text{N}_2$ )
	800–960	14	15 ( $\text{HCl}$ )
		26 (residue)	27 ( $\text{Cu}$ )
$(\text{C}_6\text{H}_{10}\text{N}_2)\text{AuCl}$ ( <b>2</b> )	200–400	42	42 ( $\text{C}_6\text{H}_{10}\text{N}_2$ )
		58 (residue)	58 ( $\text{Au}$ )
$[(\text{C}_8\text{H}_{14}\text{N}_2)_2\text{Hg}][\text{CuCl}_3]$ ( <b>4</b> )	20–270	23	22 ( $2\text{C}_5\text{H}_{10}$ )
	270–420	47	42 ( $\text{HgCl}_2$ )
	500–750	16	21 ( $2\text{C}_3\text{H}_4\text{N}_2$ )
		14 (residue)	15 ( $\text{CuCl}$ )
$[(\text{C}_8\text{H}_{14}\text{N}_2)_2\text{Hg}][\text{AgCl}_3]$ ( <b>5</b> )	250–500	77	79 ( $2\text{C}_8\text{H}_{14}\text{N}_2$ , $\text{HgCl}_2$ )
		23 (residue)	21 ( $\text{AgCl}$ )
$[\text{C}_6\text{H}_{11}\text{N}_2][\text{Ag}_2\text{I}_2\text{Cl}]$ ( <b>6</b> )	260–420	29	24 ( $\text{C}_6\text{H}_{10}\text{N}_2$ , $\text{HCl}$ )
	800–1100	41	41 ( $\text{I}_2$ )
		30 (residue)	35 ( $2\text{Ag}$ )



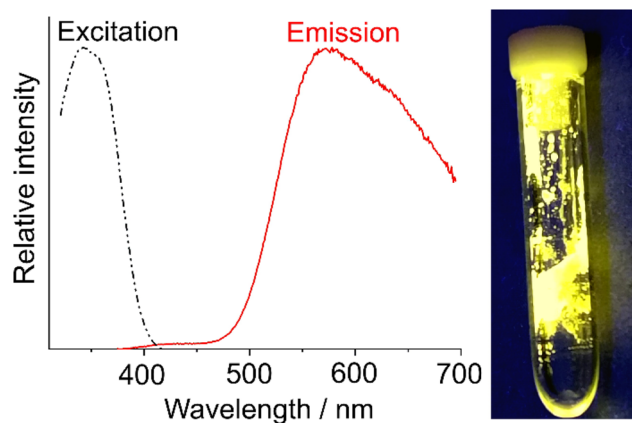


Fig. 6 PL spectra with excitation and emission of  $(\text{C}_8\text{H}_{14}\text{N}_2)\text{AgI}$  (2) as well as a photo of the sample.

solid residues. The observed mass loss fits well with the calculated values, and thus, also confirms the composition and purity of the title compounds.

Whereas the compounds **1** and **3–6** do not show any PL at room temperature, intense yellow emission is observed for  $(\text{C}_8\text{H}_{14}\text{N}_2)\text{AgI}$  (**2**), which is visible for the naked eye under UV-excitation (Fig. 6). Excitation and emission spectra indicate strong absorption below 400 nm and intense emission at 400–550 nm with a maximum at 572 nm. The efficiency of the photoluminescence processes was quantified with an absolute quantum yield of 44%, following the method given by Friend *et al.*<sup>40</sup> A comparable luminescence was frequently observed for coinage metal complexes but predominately for Cu(I) and Au(I) compounds.<sup>41</sup> In contrast, a luminescence of molecular Ag(I) complexes was rarely reported and is usually limited to quantum yields <20% at room temperature.<sup>42</sup>

## Conclusions

The noble metal oxides  $\text{Ag}_2\text{O}$ ,  $\text{Au}_2\text{O}_3$ , and  $\text{HgO}$  are reacted with the respective noble metal halides  $\text{CuCl}$ ,  $\text{CuI}$ ,  $\text{AgCl}$ ,  $\text{AgI}$ ,  $\text{AuCl}$ , and  $\text{AuI}$  in ionic liquids ( $[\text{EMIm}]\text{Cl}$ ,  $[\text{BMIm}]\text{Cl}$ ) near room temperature (20–80 °C). Most often, the reactions start already at room temperature. Certain heating accelerates and completes the reaction. As a result, the NHC complexes  $(\text{C}_8\text{H}_{14}\text{N}_2)\text{CuCl}$ ,  $(\text{C}_8\text{H}_{14}\text{N}_2)\text{AgI}$ ,  $(\text{C}_6\text{H}_{10}\text{N}_2)\text{AuCl}$ ,  $[(\text{C}_8\text{H}_{14}\text{N}_2)_2\text{Hg}][\text{CuCl}_3]$  and  $[(\text{C}_8\text{H}_{14}\text{N}_2)_2\text{Hg}][\text{AgCl}_3]$  are formed as new compounds. They contain EMIm- and BMIm-ylides with Cu–C, Ag–C, Au–C, and Hg–C bonds.  $(\text{C}_6\text{H}_{10}\text{N}_2)\text{AuCl}$  is dimerized *via* aurophilic interactions.  $[(\text{C}_8\text{H}_{14}\text{N}_2)_2\text{Hg}][\text{CuCl}_3]$  and  $[(\text{C}_8\text{H}_{14}\text{N}_2)_2\text{Hg}][\text{AgCl}_3]$  contain central Hg atoms with two Hg–C bonds of BMIm-ylides. Furthermore, trigonal planar  $[\text{CuCl}_3]^-$  and  $[\text{AgCl}_3]^-$  connect the  $[(\text{C}_8\text{H}_{14}\text{N}_2)_2\text{Hg}]^+$  cations *via* alternating  $\mu_1$ - and  $\mu_3$ -binding to infinite chains. The reaction of  $\text{Ag}_2\text{O}$  with  $\text{AgI}$  in  $[\text{EMIm}]\text{Cl}$  does not result in an NHC compound but yields  $[\text{EMIm}][\text{Ag}_2\text{I}_2\text{Cl}]$ , which exhibits  $\infty^1[\text{AgI}_{1/2}\text{I}_{2/4}\text{Cl}_{1/2}]^-$  chains with infinite d<sup>10</sup>–d<sup>10</sup> interaction of silver atoms. Structure, composition, and thermal properties of all compounds were examined by single-crystal structure analysis,

infrared spectroscopy, and thermogravimetry. Finally,  $(\text{C}_8\text{H}_{14}\text{N}_2)\text{AgI}$  shows intense green fluorescence at room temperature with a quantum yield of 44%. Metal oxides, in general, were rarely used as starting materials in ionic-liquid-based synthesis until now, which can be related to their low solubility and reactivity. The here presented reactions and compounds, however, show that metal oxides nevertheless can be used for reactions already at room temperature, which offers various options for chemical synthesis and the formation of new compounds.

## Experimental

### Synthesis

**General.** All reactions and sample handling were carried out under dried argon atmosphere using standard Schlenk techniques or glove boxes. Reactions were performed in Schlenk flasks and glass ampoules. The starting materials  $\text{AgCl}$  (99.9%, Alfa Aesar),  $\text{Ag}_2\text{O}$  ( $\geq 99\%$ , Alfa Aesar),  $\text{AuCl}$  (99.9%, Sigma Aldrich),  $\text{Au}_2\text{O}_3$  (99%, abcr),  $\text{CuCl}$  ( $\geq 99\%$ , Alfa Aesar), and  $\text{HgO}$  (99%, Alfa Aesar) were used as received. The ionic liquid  $[\text{BMIm}]\text{Cl}$  (99.9%, IoLiTec) was dried at 130 °C at reduced pressure ( $1 \times 10^{-3}$  mbar) for 3 days. All compounds were handled and stored in argon-filled glove boxes ( $\text{MBraun Unilab}$ ,  $c(\text{O}_2, \text{H}_2\text{O}) < 0.1$  ppm).

**$(\text{C}_8\text{H}_{14}\text{N}_2)\text{CuCl}$  (1).** 100.0 mg (0.573 mmol) of  $[\text{BMIm}]\text{Cl}$ , 57.0 mg (0.573 mmol) of  $\text{CuCl}$ , and 50.0 mg (0.216 mmol) of  $\text{Ag}_2\text{O}$  were mixed and filled in a glass ampoule. After 4 days at room temperature, colourless rod-like crystals were obtained with a yield of about 40%. The compound is sensitive to moisture and must be handled under inert gas conditions.

**$(\text{C}_6\text{H}_{10}\text{N}_2)\text{AgI}$  (2).** 100 mg (0.374 mmol) of  $[\text{BMIm}]\text{Cl}$ , 121 mg  $\text{AuI}$  (0.376 mmol), and 50 mg of  $\text{Ag}_2\text{O}$  (0.216 mmol) were mixed and filled in a glass ampoule. This mixture was heated to 80 °C, and the temperature was kept for 96 h. After cooling to room temperature with a rate of 1 K per h, colourless crystals were obtained with a yield of about 40%. These crystals are stable in air.

**$(\text{C}_6\text{H}_{10}\text{N}_2)\text{AuCl}$  (3).** 100 mg (0.682 mmol) of  $[\text{EMIm}]\text{Cl}$ , 158 mg (0.682 mmol) of  $\text{AuCl}$ , and 80 mg (0.181 mmol) of  $\text{Au}_2\text{O}_3$  were mixed and filled in a glass ampoule. This mixture was heated to 60 °C, and the temperature was kept for 96 h. After cooling to room temperature with a rate of 1 K per h, colourless, moisture-sensitive crystals were obtained with a yield of about 40%.

**$[(\text{C}_8\text{H}_{14}\text{N}_2)_2\text{Hg}][\text{CuCl}_3]$  (4).** 100.0 mg (0.573 mmol) of  $[\text{BMIm}]\text{Cl}$ , 57.0 mg (0.576 mmol) of  $\text{CuCl}$ , and 50.0 mg of (0.231 mmol) of  $\text{HgO}$  were mixed and filled into a glass ampoule. Again, the reaction occurred already at room temperature. After 4 days, rhombic, colourless crystals were obtained with a yield of about 60%. The crystals are highly moisture sensitive and must be handled under inert gas atmosphere.

**$[(\text{C}_8\text{H}_{14}\text{N}_2)_2\text{Hg}][\text{AgCl}_3]$  (5).** 100.0 mg (0.573 mmol) of  $[\text{BMIm}]\text{Cl}$ , 82.0 mg (0.573 mmol) of  $\text{AgCl}$ , and 50 mg (0.231 mmol) of  $\text{HgO}$  were mixed and filled in a glass ampoule. The reaction again started at room temperature. The growth of suitable single crystals was promoted by heating to 80 °C. The ampoule



was kept at 80 °C for 96 h and then cooled to room temperature with a rate of 1 K per h. Colourless, moisture-sensitive, rhombic crystals were obtained with a yield of about 50%.

**[EMIm][Ag<sub>2</sub>I<sub>2</sub>Cl] (6).** 100.0 mg (0.682 mmol) of [EMIm]Cl, 160.0 mg (0.682 mmol) of AgCl and 50 mg (0.32 mmol) of Ag<sub>2</sub>O were mixed in a glass ampoule. The ampoule was heated to 45 °C and kept at this temperature for 96 h. Subsequently, the ampoule was cooled to room temperature with a rate of 1 K per h. Crystals of **5** were obtained as colourless needles with a yield of about 40%. The compound is sensitive to moisture and needs to be handled under inert gas conditions.

## Analytical equipment

Detailed information on the analytical equipment can be obtained from the ESI.† Further details of the crystal structure investigation may be obtained from the joint CCDC/FIZ Karlsruhe deposition service on quoting the depository number CSD-No. 2104796–2104800 and 2220642.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

The authors acknowledge the Deutsche Forschungsgemeinschaft (DFG). Furthermore, the authors thank Prof. Dr Dieter Fenske, Prof. Dr Peter Roesky, and Dr Michael Garmer for data collection on the gallium-jet Stoe StadiVari diffractometer as well as on Stoe Stadi Vari diffractometer.

## References

- (a) T. Zhang, T. Doert, H. Wang, S. Zhang and M. Ruck, *Angew. Chem., Int. Ed.*, 2021, **60**, 22148–22165; (b) D. Freudenmann, S. Wolf, M. Wolff and C. Feldmann, *Angew. Chem., Int. Ed.*, 2011, **50**, 11050–11060.
- (a) R. Brueckner, H. Haller, S. Steinhauer, C. Mueller and S. Riedel, *Angew. Chem., Int. Ed.*, 2015, **54**, 15579–15583; (b) M. Knies, M. Kaiser, A. Isaeva, U. Mueller, T. Doert and M. Ruck, *Chem. - Eur. J.*, 2018, **24**, 127–132; (c) C. Donsbach, K. Reiter, D. Sundholm, F. Weigend and S. Dehnen, *Angew. Chem., Int. Ed.*, 2018, **57**, 8770–8774; (d) K. Gloatz, D. Himmel, D. Kratzert, B. Butschke, H. Scherer and I. Krossing, *Angew. Chem., Int. Ed.*, 2019, **58**, 14162–14166; (e) S. S. Rudel, H. L. Deubner, M. Mueller, A. J. Karttunen and F. Kraus, *Nat. Chem.*, 2020, **12**, 962–967; (f) Z. Wu, I. Nussbruch, S. Nier and S. Dehnen, *J. Am. Chem. Soc.*, 2022, **2**, 204–213.
- (a) M. Wolff, J. Meyer and C. Feldmann, *Angew. Chem., Int. Ed.*, 2011, **50**, 4970–4973; (b) S. Wolf, R. Köppe, T. Block, R. Pöttgen, P. W. Roesky and C. Feldmann, *Angew. Chem., Int. Ed.*, 2020, **59**, 5510–5514; (c) E. Merzlyakova, S. Wolf, S. Lebedkin, L. Bayarjargal, B. L. Neumeier, D. Bartenbach, C. Holzer, W. Kloppe, B. Winkler, M. Kappes and C. Feldmann, *J. Am. Chem. Soc.*, 2021, **143**, 798–804.
- C. Feldmann, *Angew. Chem., Int. Ed.*, 2013, **52**, 7610–7611.
- (a) P. Wasserscheid and T. Welton, *Ionic Liquids in Synthesis*, Wiley-VCH, Weinheim, 2008; (b) B. Kirchner, J. Blasius, V. Alizadeh, A. Gansaeuer and O. Holloczki, *J. Phys. Chem. B*, 2022, **126**, 766–777.
- (a) P. Nockemann, B. Thijs, T. N. Parac-Vogt, K. Van Hecke, L. Van Meervelt, B. Tinant, I. Hartenbach, T. Schleid, V. T. Ngan, M. T. Nguyen and K. Binnemans, *Inorg. Chem.*, 2008, **47**, 9987–9999; (b) S. Wellens, N. R. Brooks, B. Thijs, L. Van Meervelt and K. Binnemans, *Dalton Trans.*, 2014, **43**, 3443–3452; (c) J. Richter and M. Ruck, *RSC Adv.*, 2019, **9**, 29699–29710; (d) S. Wolf, S. Seidel, J. Treptow, R. Köppe, P. Roesky and C. Feldmann, *Inorg. Chem.*, 2022, **61**, 4018–4023.
- (a) P. P. Nair, A. Jayaraj and C. A. Swamy, *ChemistrySelect*, 2022, **7**, e202103517; (b) Q. Zhao, G. Meng, M. Szostak and S. P. Nolan, *Chem. Rev.*, 2020, **120**, 1981–2048; (c) W. A. Herrmann and C. Kocher, *Angew. Chem., Int. Ed.*, 1997, **36**, 2162–2187.
- (a) S. S. Bera and M. Szostak, *ACS Catal.*, 2022, **12**, 3111–3137; (b) P. Schwab, R. H. Grubbs and J. W. Ziller, *J. Am. Chem. Soc.*, 1996, **118**, 100–110.
- (a) Y.-H. Wen, Z.-J. Zhang, S. Li, J. Song and L.-Z. Gong, *Nat. Commun.*, 2022, **13**, 1344; (b) W. Xie and S. Chang, *Angew. Chem., Int. Ed.*, 2016, **55**, 1876–1880.
- (a) S. K. Goetzfried, P. Kapitza, C. M. Gallati, A. Nindl, M. Czipferszky, M. Hermann, K. Wurst, B. Kircher and R. Gust, *Dalton Trans.*, 2022, **51**, 1395–1406; (b) M. Bian, R. Fan, Z. Yang, Y. Chen, Z. Xu, Y. Lu and W. Liu, *J. Med. Chem.*, 2022, **65**, 1848–1866.
- M.-M. Gan, J.-Q. Liu, L. Zhang, Y. Y. Wang, F. E. Hahn and Y.-F. Han, *Chem. Rev.*, 2018, **118**, 9587–9641.
- H.-W. Wanzlick and H.-J. Schönherr, *Angew. Chem., Int. Ed.*, 1968, **7**, 141–142.
- F. E. Hahn and M. C. Jahnke, *Angew. Chem., Int. Ed.*, 2008, **47**, 3122–3172.
- C. Donsbach and S. Dehnen, *Eur. J. Inorg. Chem.*, 2018, 4429–4433.
- (a) I. Chiarotto, M. Feroci and A. Inesi, *New J. Chem.*, 2017, **41**, 7840–7843; (b) I. Chiarotto, M. Feroci, G. Sotgiu and A. Inesi, *Eur. J. Org. Chem.*, 2013, 326–331.
- (a) C. Liu, H.-Q. Shen, M.-W. Chen and Y.-G. Zhou, *Organomet.*, 2018, **37**, 3756–3769; (b) S. Díez-González, E. D. Stevens and S. P. A. Nolan, *Chem. Commun.*, 2008, 4747–4749; (c) H. Kaur, F. K. Zinn, E. D. Stevens and S. P. Nolan, *Organomet.*, 2004, **23**, 1157–1160.
- M. B. Abrams and X. Zhang, *Metallocarbene Complex Peroxideactivators*, *US pat.* 8414793B, 2013.
- (a) M. Iglesias, D. J. Beetstra, J. C. Knight, L.-L. Ooi, A. Stasch, S. Coles, L. Male, M. B. Hursthouse, K. J. Cavell, A. Dervisi and I. A. Fallis, *Organomet.*, 2008, **27**, 3279–3289; (b) D. V. Partyka and N. Deligonul, *Inorg. Chem.*, 2009, **48**, 9463–9475; (c) V. H. L. Wong, A. J. P. White, T. S. A. Hor and K. K. M. Hii, *Chem. Commun.*, 2015, **51**, 17755; (d) R. Bloch and H. Möller, *Z. Phys. Chem. A*, 1930, **152**, 245–248.





- 19 (a) P. de Frémont, N. M. Scott, E. D. Stevens and S. P. Nolan, *Organomet.*, 2005, **24**, 2411–2418; (b) J. Strähle and K.-P. Lörcher, *Naturforsch. B*, 1974, **29**, 266–267.
- 20 H. M. J. Wang, C. S. Vasam, T. Y. R. Tsai, S.-H. Chen, A. H. H. Chang and I. J. B. Lin, *Organomet.*, 2005, **24**, 486–493.
- 21 A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441–451.
- 22 H. Schmidbaur and A. Hubert, *Chem. Soc. Rev.*, 2012, **41**, 370–412.
- 23 K. U. N. Sheikh, H. Amin, R. A. Haque, A. S. Abdul Majid, M. Yaseen and M. A. Iqbal, *J. Coord. Chem.*, 2021, **74**, 467–542.
- 24 S. Pelz and F. Mohr, *Organomet.*, 2011, **30**, 383–385.
- 25 (a) A. J. Arduengo, R. L. Harlow, W. J. Marshall and T. K. Prakasha, *Heteroat. Chem.*, 1996, **7**, 421–426; (b) A. J. Arduengo, D. Tapu and W. J. Marshall, *Angew. Chem., Int. Ed.*, 2005, **44**, 7240–7244; (c) S.-C. Chen, H.-H. Hsueh, C.-H. Chen, C. S. Lee, F.-C. Liu, I. J. B. Lin, G.-H. Lee and S.-M. Peng, *Inorg. Chim. Acta*, 2009, **362**, 3343–3350.
- 26 K. Weidenhammer and M. L. Ziegler, *Z. Anorg. Allg. Chem.*, 1977, **434**, 152–156.
- 27 R. W. G. Wyckoff and E. Posnjak, *J. Am. Chem. Soc.*, 1922, **44**, 30–36.
- 28 (a) H.-C. Gaebell, G. Meyer and R. Hoppe, *Z. Anorg. Allg. Chem.*, 1983, **497**, 199–205; (b) S. Hull and D. A. Keen, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1999, **59**, 750–761.
- 29 (a) A. Beheshti, W. Clegg, V. Nobakht, M. Panahi Mehra and L. Russo, *Dalton Trans.*, 2008, 6641–6646; (b) R. Balamurugan, M. Palaniandavar and R. S. Gopalan, *Inorg. Chem.*, 2001, **40**, 2246–2255; (c) M. R. Churchill and F. J. Rotella, *Inorg. Chem.*, 1979, **18**, 166–171; (d) O. Crespo, M. C. Gimeno, P. G. Jones and A. Laguna, *J. Chem. Soc., Dalton Trans.*, 1996, 4583–4588; (e) S. Y. Lee, S. Parka and S. S. Lee, *Inorg. Chem.*, 2009, **48**, 11335–11341; (f) C.-Y. Su, Y.-P. Cai, C.-L. Chen, M. D. Smith, W. Kaim and H.-C. zur Loye, *J. Am. Chem. Soc.*, 2003, **125**, 8595–8613.
- 30 (a) L. Xian, T.-B. Wei and Y.-M. Zhang, *J. Coord. Chem.*, 2004, **57**, 453–457; (b) F. A. Devillanova, A. Diaz, F. Isaia, G. Verani, L. P. Battaglia and A. B. Corradi, *J. Coord. Chem.*, 1986, **15**, 161–172.
- 31 G. Helgesson and S. Jagner, *J. Chem. Soc., Dalton Trans.*, 1988, 2117–2120.
- 32 C. Lupu, C. Downie, A. M. Guloy, T. A. Albright and J.-G. Mao, *J. Am. Chem. Soc.*, 2004, **126**, 4386–4397.
- 33 V. Subramanian and K. Seff, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1980, **36**, 2132–2135.
- 34 R. A. Haque, A. W. Salman, T. S. Guan and H. H. Abdallah, *J. Organomet. Chem.*, 2011, **696**, 3507–3512.
- 35 S. Hull and D. A. Keen, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1999, **59**, 750–761.
- 36 M. Jansen, *Angew. Chem.*, 1987, **26**, 1098–1110.
- 37 (a) T. Sörgel and M. Jansen, *Z. Kristallogr. NCS*, 2007, **222**, 20–22; (b) Y.-K. Wang, L.-M. Zhao, Y.-Q. Fu, Z. Chen, X.-Y. Lin, D.-H. Wang, Y. Li, H.-H. Li and Z.-R. Chen, *Cryst. Growth Des.*, 2018, **18**, 3827–3840; (c) B. Xu, R. Wang and X. Wang, *Nanoscale*, 2012, **4**, 2713–2719.
- 38 C. Zhang, J. Shen, Q. Guan, T. Yu and Y. Fu, *Solid State Sci.*, 2015, **46**, 14–18.
- 39 (a) G. A. Bowmaker, Y. Effend, J. D. Kildea, B. W. Skelton and A. H. White, *Aust. J. Chem.*, 1990, **43**, 2113; (b) R. Frydrych, T. Muschter, I. Brüdgam and H. Hartl, *Z. Naturforsch.*, 1990, **45b**, 679–688; (c) K. Rosenstengel, A. Schulz, O. Niehaus, O. Janka, R. Pöttgen and A. Villinger, *Eur. J. Inorg. Chem.*, 2018, 778–790.
- 40 J. C. de Mello, H. F. Wittmann and R. H. Friend, *Adv. Mater.*, 1997, **9**, 230–232.
- 41 (a) J. M. Lopez-de-Luzuriaga, M. Monge and M. E. Olmos, *Dalton Trans.*, 2017, **46**, 2046–2067; (b) R. C. Evans, P. Douglas and C. J. Winscom, *J. Coord. Chem. Rev.*, 2006, **250**, 2093–2126.
- 42 (a) H.-M. Pan, Y.-Y. Ma, D.-Y. Li, S. Wu and Z. Jing, *J. Solid State Chem.*, 2022, **307**, 122814; (b) M. Klein, N. Rau, M. Wende, J. Sundermeyer, G. Cheng, C.-M. Che, A. Schinabeck and H. Yersin, *Chem. Mater.*, 2020, **32**, 10365–10382; (c) T. Teng, K. Li, G. Cheng, Y. Wang, J. Wang, J. Li, C. Zhou, H. Liu, T. Zou, J. Xiong, C. Wu, H.-X. Zhang, C.-M. Che and C. Yang, *Inorg. Chem.*, 2020, **59**, 12122–12131; (d) R. Hamze, S. Shi, S. C. Kapper, D. S. Muthiah Ravinson, L. Estergreen, M.-C. Jung, A. C. Tadler, R. Haiges, P. I. Djurovich, J. L. Peltier, R. Jazsar, G. Bertrand, S. E. Bradforth and M. E. Thompson, *J. Am. Chem. Soc.*, 2019, **141**, 8616–8626; (e) M. Z. Shafikov, R. Czerwieniec and H. Yersin, *Dalton Trans.*, 2019, **48**, 2802–2806.

