Synthesis, Characterization and Luminescence of Silver(I) and Gold(I) Complexes Bearing a Diethyl Acetal Functionalized *N*-Heterocyclic Carbene

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Z. Naturforsch. **2011**, *66b,* 1255 – 1260; received November 30, 2011

1-(2,2′-Diethoxyethyl)-3-methyl-imidazolium bromide, **1**, has been prepared and used as a precursor for the synthesis of the corresponding silver bromide complex $[(NHC)_2Ag][AgBr_2]$, **2**. Transmetallation of **2** with (tht)AuBr (tht = tetrahydrothiophene) yields (NHC)AuBr, **3**. The solid-state structures of **2** and **3** have been determined by single-crystal X-ray diffraction revealing a loose aggregation of the complexes by weak metal-metal interactions. Due to the presence of these contacts, both complexes are emissive in the solid state.

Key words: Silver(I), Gold(I), *N*-Heterocyclic Carbenes, Crystal Structure, Luminescence

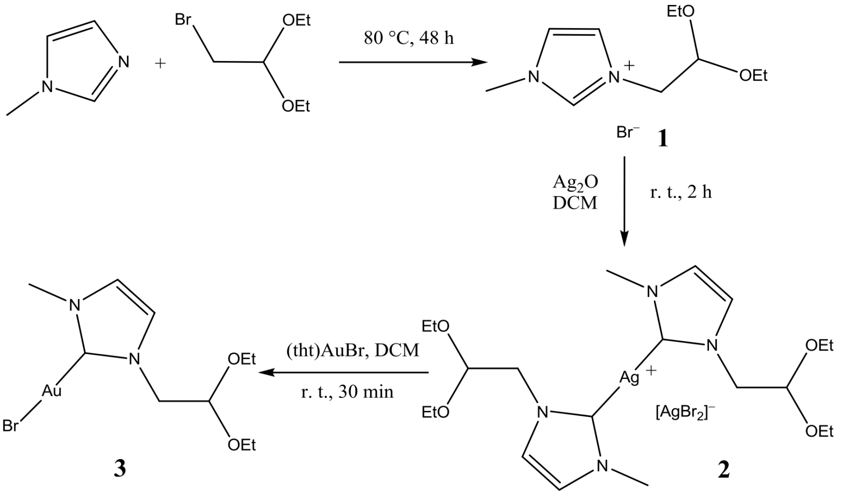
Introduction

Silver and gold complexes bearing *N*-heterocyclic carbenes (NHC) have been the focus of intense studies for over a decade [1]. Because NHC–Ag(I) complexes are versatile carbene transfer agents, they have been synthesized as stable intermediates in the course of many preparations of other transition metal NHC-complexes [2]. They are conveniently accessible by the reaction of an imidazolium salt and Ag_2O and feature a rich coordination chemistry. NHC–Au(I) complexes are investigated due to numerous applications ranging from homogeneous catalysts for unique C–C, C–O, and C–N bond forming reactions [3, 4] to pharmaceutical uses as anticancer, antiarthritis, and antibacterial agents [5, 6]. The chemistry of gold is dominated by compounds of the metal in the oxidation state $+1$ in linearly coordinated complexes of the type NHC–Au–X or $[(NHC)_2Au]X$, which are prepared by the reaction of $(R_2S)AuX$ ($R_2S = Me_2S$, tetrahydrothiophene; X = halide) with an NHC–Ag complex or the free carbene [7]. In the course of our studies on Ag(I), Au(I) and Au(III) complexes bearing NHCs functionalized with nitrogen donor atoms [8 – 10], we became also interested in examples with oxygen containing side arms at a nitrogen atom of the NHC ligands. Herein, we report the synthesis and characterization of 1-(2,2′-diethoxyethyl)-3-methyl-imidazolium bromide and the corresponding NHC–Ag(I) and –Au(I) complexes. It should be noted, that the synthesis of the related *N*,*N*′-bis-(2,2′-diethoxyethyl)-imidazolium salt and its Ag(I), Pd(II) and Ni(II) compounds has been published recently [11].

Results and Discussion

The imidazolium salt **1** is prepared by the reaction of bromoacetaldehyde diethyl acetal with 1-methylimidazole at 80 °C without solvent and obtained as a viscous oil (Scheme 1). Subsequent reaction with Ag_2O in dichloromethane (DCM) yields the complex $[(NHC)_2Ag][AgBr_2]$, **2**, in good yields and high purity as a colorless powder. The Au(I) complex **3** is obtained by the stoichiometric reaction of **2** with (tht)AuBr in DCM (Scheme 1). All complexes are stable in the dark in solution and solid state. Attempted acidic deprotection of the acetal function in complex **3** and isolation of an aldehyde-functionalized NHC–Au(I) complex failed so far.

In the NMR spectra of the ligand and its complexes, the resonance of the C2 carbon atom is most affected by the exchange of the proton by a metal atom: Whereas the C2 atom of the imidazolium salt resonates at δ = 137.5 ppm, the signal for the car-



Scheme 1.

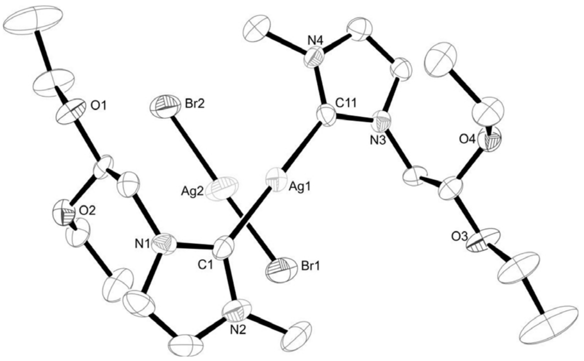


Fig. 1. Molecular structure of **2** (ORTEP; displacement ellipsoids at the 50 % probability level, H atoms omitted for clarity). Selected bond lengths (Å) and angles (deg): Ag1–C1 2.08(1), Ag1–C11 2.09(1), Ag2–Br1 2.431(1), Ag2–Br2 2.423(1), Ag1–Ag2 3.668(1); C1–Ag1–C11 179.0(2), Br1–Ag2–Br2 177.2(1).

bene carbon atom of **2** is significantly down field shifted to δ 181.1 ppm. This value is very similar to that of analogous NHC–Ag complexes of the type $[(NHC)_2Ag][AgBr_2]$ [7, 10]. The chemical shift of the C2 carbene carbon atom of the gold complex **3** is 184.3 ppm, which is at the down field limit of comparable NHC–Au–Br complexes [7]. The ESI mass spectra of **2** and **3** are each dominated by the signal representing the cationic species $[(NHC)_2M]^+$. Particularly NHC–Ag(I), but also NHC–Au(I) complexes, are generally prone to ligand scrambling reactions [1e, 12], albeit to our knowledge no crystal structures are known of the ionic form $[(NHC)_2Au][AuX_2]$ (X = halide). Astonishingly, no elimination of ethanol from the acetal group could be detected in the mass spectra.

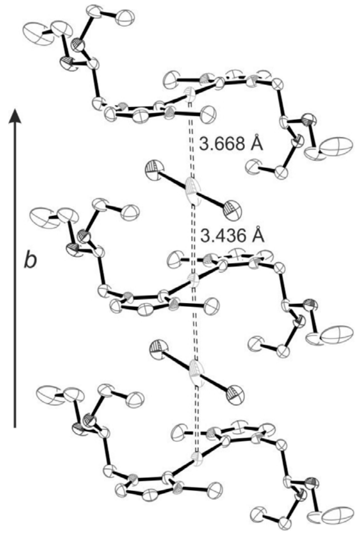


Fig. 2. Excerpt of a cell plot of the crystalline phase of compound **2** depicting the aggregation to linear chains parallel to the *b* axis.

Crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of diethyl ether into solutions of **2** and **3** in chloroform at 5 °C. Compound **2** crystallizes in the monoclinic space group $P2_1/c$ ($Z = 2$) in an ionic form with linearly coordinated $[(NHC)_2Ag]^+$ cations and $[AgBr_2]^-$ anions aggregated alternatingly to infinite, almost linear chains (Figs. 1, 2; Ag1–Ag2–Ag1^{ii} 177.9°). Neighboring ions do not feature a perpendicular but a slightly twisted arrangement to each other (C1–Ag1–Ag2–Br2 74.7°) with two different Ag···Ag distances of 3.436(1) for Ag1–Ag2 and 3.668(1) Å for Ag2–Ag1^{ii}. Taking into account the sum of the van der Waals radii of silver (3.44 Å [13]) these distances are indicative of only weak or even insignificant attractive argentophilic interactions. Therefore, this aggregation might be governed mainly by Coulombic or multipolar interactions (*e. g.* quadrupole-quadrupole interactions which in certain cases can even outperform metallophilic interactions [14]). It should be noted that this aggregation pattern is frequently found for silver halide complexes bearing NHC ligands, but is rarely observed with other ligands [7]. The imidazolyl ring planes are almost exactly coplanar (N1–C1–C11–N3 178.2°) which results from an increased π backbonding contribution compared to a perpendicular orientation [15]. Both Ag–C bond lengths are almost identical [Ag1–C1 2.08(1) Å, Ag1–C11 2.09(1) Å] and fall in the range typical for other silver-carbene complexes [16].

The gold complex crystallizes in the monoclinic space group $P2_1/n$ with $Z = 4$. The coordination of the gold atom is linear [C1–Au1–Br1 175.8(2)°] with Au–C and Au–Br distances of 1.98(1) and 2.394(1) Å, respectively. Two complex molecules are loosely associated in an antiparallel mode into dimers with a relatively long Au···Au distance of 3.598(1) Å, *i. e.* too far to suggest significant aurophilic interactions [17] (Fig. 3). Interestingly, the Au1···C1^i distance of 3.498(1) Å is significantly shorter than the Au···Au distance and in the range of reported π(C)–Au(I) interactions [12]. Therefore, it is tempting to speculate that the dimerization is synergetically governed by both closed-shell d^{10}-d^{10} as well as cation-π interactions. Albeit not explicitly described in previous publications about NHC–Au–X (X = Cl, Br) complexes, an analysis of their crystal structures revealed that this loose aggregation pattern is not unusual for functionalized NHC ligands [18]. A similar aggregation has also been reported for some compounds of the type L–Au–SR (L = phosphane, isonitrile; SR = SCN, thiolate, thioacetate), where the Au and S atoms form a parallelogram with Au···S edges and an Au···Au′ diagonal with dominating thiophilic interactions [19].

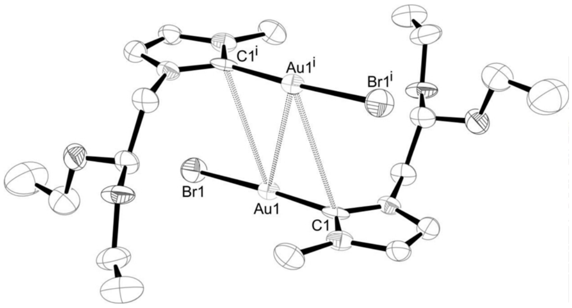


Fig. 3. Dimers in crystals of **3**. Selected bond lengths (Å) and angles (deg): Au1–C1 1.98(1), Au1–Br1 2.394(1), Au1–Au1^i 3.598(1), Au1–C1^i 3.498(1); C1–Au1–Br1 175.8(2).

Closed-shell d^{10}-d^{10} interactions of coinage metals frequently give rise to luminescence in the solid state and under special conditions also in solution. Albeit not always unambiguous, the emission from complexes with gold-gold interactions are usually assigned to a $^3[5d\sigma^*6p\sigma]$ excited state, which has a formal metal-metal bond reminiscent of the formation of excimers or exciplexes of organic molecules [20]. Compared to gold(I) complexes, the luminescence mechanisms of complexes featuring silver-silver contacts are not equally well established but mostly explained in analogy to gold(I) also by an excimer/exciplex model [21]. For the present results no direct correlation between the metal-metal distances determined by X-ray diffraction and the emission wavelength could be formulated, because the bonded M-M distance in the excited state is responsible for the emission properties and usually not known. Therefore, the photoluminescent behavior is possible even if the distance in the ground state is of the order of the sum of the van der Waals radii or slightly above. The distortion of the complexes in the excited state are reflected by the Stokes shift which in the case of metallophilicity-based emission is very large.

Although they are weak, the metal-metal interactions of both complexes **2** and **3** give rise to lumi-

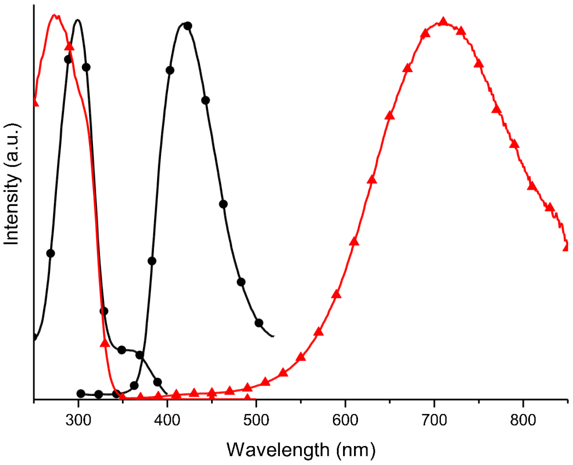


Fig. 4 (color online). Excitation (left) and emission (right) spectra of solid **2** (●) and **3** (▲) at 20 °C (emission spectra: **2** λ_{ex} = 280 nm, **3** λ_{ex} = 300 nm; excitation spectra: **2** λ_{det} = 420 nm, **3** λ_{det} = 700 nm).

nescence in the solid state upon excitation with UV light (Fig. 4). At r. t., the gold complex shows a broad, low-energy emission band around 709 nm. In the excitation spectrum a signal at 275 nm and a shoulder at 305 nm are detected. These values are in the standard range of other gold complexes with aurophilic contacts in the solid state [22]. The silver complex features an unstructured, broad emission band at 419 nm. Two bands appear in the excitation spectra at 300 and 360 nm. Interestingly, these values are very similar to those of Tl[Ag(CN)$_2$], where the arrangement of silver atoms (also with two different silver-silver distances) has been held responsible for the emission behavior [21]. As solutions of **2** and **3** are not absorbing above 250 nm, the bands in the excitation spectra are indicative of electronic transitions originating from the aggregation *via* metal-metal interactions in the solid state. The very large Stokes shifts of $\sim$ 9470 cm^{-1} (**2**) and $\sim$ 22260 cm^{-1} (**3**) indicate severe distortions of the structures in the excited state. These observations are in accordance with an excimer/exciplex model.

Conclusion

In this contribution we describe the synthesis of 1-(2,2′-diethoxyethyl)-3-methyl-imidazolium bromide as a precursor for the synthesis of the silver(I) and gold(I) complexes of the corresponding carbene. The single crystal structure analysis of the silver compound revealed the formation of an ionic complex of the form [(NHC)$_2$Ag][AgBr$_2$], whose ions are aggregated alternatingly to infinite chains *via* loose silver-silver contacts. Transmetallation with (tht)AuBr (tht = tetrahydrothiophene) yields (NHC)AuBr which dimerizes in an anti-parallel fashion in the solid state. Although the metal-metal distances are large, the presence of M-M contacts gives rise to photo-luminescence in the solid state at r. t. with very large Stokes shifts indicative of strong geometric distortion in the excited state.

Experimental Section

General information

All solvents and reagents were commercially available and used as received. The gold precursor (tht)AuBr was prepared following the procedure described by Usón *et al.* [23]. NMR spectra were recorded either on a Bruker Digital Avance DPX 300 (300 MHz) or on an Avance DRX 500 (500 MHz) spectrometer. ^{1}H and ^{13}C shifts are reported in ppm relative to Si(CH$_3$)$_4$ referring internally to the residual signal of the deuterated solvent. Mass spectra were collected on a Finnigan LCQ DecaXPplus ion trap mass spectrometer with ESI ion source. The electronic spectra were recorded on a Horiba Jobin Yvon Fluorolog-3 spectrofluorometer. All emission spectra were corrected for wavelength-dependent instrument and detector response.

Table 1. Crystal structure data for **2** and **3**.

	2	**3**
Formula	$C_{20}H_{36}N_4O_4Ag_2Br_2$	$C_{10}H_{18}N_2O_2AuBr$
M_r	772.09	475.14
Crystal size, mm^3	0.71 × 0.49 × 0.35	0.61 × 0.61 × 0.60
Crystal system	monoclinic	monoclinic
Space group	$P2_1$	$P2_1/n$
a, Å	11.172(2)	7.739(1)
b, Å	7.103(1)	14.839(2)
c, Å	18.459(3)	12.664(1)
β, deg	105.916(4)	93.034(4)
V, Å^3	1408.6(4)	1452.2(3)
Z	2	4
D_{calcd}, g cm^{-3}	1.82	2.17
μ(MoK_α), mm^{-1}	4.3	12.9
hkl range	±13, ±8, ±22	±9, −17→+15, ±15
Refl. measured / unique	24983 / 5178	8897 / 2556
R_{int}	0.044	0.085
Refl. observed [$I \geq 2\sigma(I)$]	4807	2090
Absorption correction	multi-scan	multi-scan
T_{min} / T_{max}	0.22 / 0.32	0.05 / 0.05
Param. refined	296	149
Restraints	0	0
R_1 [$I \geq 2\sigma(I)$]	0.040	0.044
wR_2 (all data)	0.096	0.115
x (Flack)	0.19(1)	–
$\Delta\rho_{\text{fin}}$ (max / min), e Å^{-3}	1.28 / −0.77	2.18 / −2.70
CCDC number	854542	854543

Crystal structure determination

Single-crystal structure analyses were carried out on a Bruker Smart X2S diffractometer operating with MoK_α radiation (λ = 0.71073 Å). Crystal data and numbers pertinent to data collection and structure refinement can be found in Table 1. The structures were solved by Direct Methods (SHELXS-97 [24]) and refined by full-matrix least-squares on F^2 (SHELXL-97 [25]). The H atoms were calculated geometrically, and a riding model was applied during the refinement process.

CCDC 854542 and 854543 contain the supplementary crystallographic data for **2** and **3**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

1-(2,2′-Diethoxyethyl)-3-methyl-imidazolium bromide, ***1***

A Pyrex tube was charged with 1-methyl-imidazole (1.08 g, 13.2 mmol) and bromoacetaldehyde diethyl acetal (2.39 g, 12.2 mmol). The mixture was heated to 80 °C and stirred for 2 d. The reaction mixture was cooled to r. t. and washed three times with 10 mL toluene. The highly viscous brownish oil was dried *in vacuo*. Yield: 87.7 % (3.00 g, 10.7 mmol). – ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, 30 °C): δ = 9.64 (s, 1H, $\mathrm{C2_{Im}}H$), 6.64 (s, 1H, $\mathrm{C_{Im}}H$), 6.58 (s, 1H, $\mathrm{C_{Im}}H$), 4.50 (t, $^3J_{\mathrm{HH}}$ = 4.25 Hz, 1H, C*H*OO), 4.13 (d, $^3J_{\mathrm{HH}}$ = 4.25 Hz, 2H, $\mathrm{NC}H_2$), 3.90 (s, 3H, $\mathrm{NC}H_3$), 3.55 (m, 4H, $\mathrm{OC}H_2$), 0.83 (t, $^3J_{\mathrm{HH}}$ = 7.01 Hz, 6H, $\mathrm{C}H_3$). – ^{13}C NMR (300 MHz, $\mathrm{CDCl_3}$, 30 °C): δ = 137.5, 123.4, 122.9, 99.1, 63.8, 51.5, 36.4, 14.9. – MS ((+)-ESI): m/z = 199.13 $[\mathrm{M}]^+$. – Due to the hygroscopicity of the product no reliable elemental analysis could be obtained.

Bromo-[1-(2,2′-diethoxyethyl)-3-methyl-imidazol-2-ylidene]silver(I), ***2***

In a Pyrex tube a sample of **1** (2.95 g, 10.6 mmol) was dissolved in 5 mL of dichloromethane (DCM). To the resulting solution was added dry $\mathrm{Ag_2O}$ (1.70 g, 7.33 mmol) with stirring. After a stirring time of about 3 h at r. t. the reaction mixture was filtered over Celite. The solvent was removed *in vacuo*, and recrystallization of the product from DCM/diethyl ether afforded colorless needles. Yield: 84.5 % (3.46 g, 8.96 mmol). – ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, 30 °C): δ = 7.05 (s, 1H, $\mathrm{C_{Im}}H$), 6.87 (s, 1H, $\mathrm{C_{Im}}H$), 4.58 (t, $^3J_{\mathrm{HH}}$ = 5.00 Hz, 1H, C*H*OO), 4.11 (d, $^3J_{\mathrm{HH}}$ = 4.98 Hz, 2H, $\mathrm{NC}H_2$), 3.78 (s, 3H, $\mathrm{NC}H_3$), 3.66 (m, 2H, $\mathrm{OC}H_2$a), 3.46 (m, 2H, $\mathrm{OC}H_2$b), 1.13 (t, $^3J_{\mathrm{HH}}$ = 7.07 Hz, 6H, $\mathrm{C}H_3$). – ^{13}C NMR (300 MHz, $\mathrm{CDCl_3}$, 30 °C): δ = 182.2, 123.0, 121.6, 101.7, 64.2, 54.4, 39.1, 15.3. – MS ((+)-ESI): m/z = 505.33 $[(\mathrm{NHC})_2\mathrm{Ag}]^+$. – $\mathrm{C_{10}H_{18}N_2O_2AgBr}$ (386.04): calcd. C 31.11, H 4.70, N 7.26; found C 31.31, H 4.72, N 7.30.

Bromo-[1-(2,2′-diethoxyethyl)-3-methyl-imidazol-2-ylidene]gold(I), ***3***

A 10 mL round bottom flask was charged with a sample of **2** (0.19 g, 0.49 mmol) and 5 mL of DCM. Solid (tht)AuBr (0.18 g, 0.49 mmol) was added to the solution with stirring whereupon a precipitate of AgBr was formed immediately. After further stirring for about 30 min at ambient temperature and filtation the solvent was removed *in vacuo*, and the remaining solid was recrystallized from DCM/*n*-pentane generating colorless needles. Yield 77.6 % (0.18 g, 0.38 mmol). – ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, 30 °C): δ = 7.20 (s, 1H, $\mathrm{C_{Im}}H$), 7.01 (s, 1H, $\mathrm{C_{Im}}H$), 4.85 (t, $^3J_{\mathrm{HH}}$ = 5.05 Hz, 1H, C*H*OO), 4.16 (d, $^3J_{\mathrm{HH}}$ = 5.04 Hz, 2H, $\mathrm{NC}H_2$), 3.94 (s, 3H, $\mathrm{NC}H_3$), 3.69 (m, 2H, $\mathrm{OC}H_2$a), 3.51 (m, 2H, $\mathrm{OC}H_2$b), 1.13 (t, $^3J_{\mathrm{HH}}$ = 7.05 Hz, 6H, $\mathrm{C}H_3$). – ^{13}C NMR (300 MHz, $\mathrm{CDCl_3}$, 30 °C): δ = 184.5, 122.9, 122.5, 101.3, 64.0, 54.0, 38.6, 15.5. – MS ((+)-ESI): m/z = 593.47 $[(\mathrm{NHC})_2\mathrm{Au}]^+$. – $\mathrm{C_{10}H_{18}N_2O_2AuBr}$ (475.14): calcd. C 25.28, H 3.82, N 5.90; found C 25.35, H 3.72, N 5.93.

Acknowledgement

We thank Prof. G. Knör for fruitful discussions and generous support of the experimental work.

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[1] a) F. Mohr (Ed.), *Gold Chemistry: Applications and Future Directions in the Life Sciences*, Wiley-VCH, Weinheim, **2009**; b) A. Laguna (Ed.), *Modern Supramolecular Gold Chemistry*, Wiley-VCH, Weinheim, **2008**; c) M. C Jahnke, F. E. Hahn, *Top. Organomet. Chem.* **2010**, *30*, 95 – 129; d) M. C. Jahnke, F. E. Hahn in *N-Heterocyclic Carbenes: From Laboratory Curiosities to Efficient Synthetic Tools*, (Ed.: S. Díez-González), RSC Publishing, Cambridge, **2011**, pp. 1 – 41; e) J. G. Garrison, W. J. Youngs, *Chem. Rev.* **2005**, *105*, 3978 – 4008; f) J. C. Y. Lin, R. T. W. Huang, C. S. Lee, A. Bhattacharyya, W. S. Hwang, I. J. B. Lin, *Chem. Rev.* **2009**, *109*, 3561 – 3598; g) I. J. B. Lin, C. S. Vasam, *Can. J. Chem.* **2005**, *83*, 812 – 825; h) H. Schmidbaur, *Gold: Chemistry, Biochemistry and Technology*, Wiley, Chichester, **1999**.

[2] a) A. Rit, T. Pape, A. Hepp, F. E. Hahn, *Organometallics* **2011**, *30*, 334 – 347; b) A. Rit, T. Pape, F. E. Hahn, *J. Am. Chem. Soc.* **2010**, *132*, 4572 – 4573; c) H. M. J. Wang, I. J. B. Lin, *Organometallics* **1998**, *17*, 972 – 975.

[3] a) X. Zeng, R. Kinjo, B. Donnadieu, G. Bertrand, *Angew. Chem.* **2010**, *122*, 954 – 957; *Angew. Chem. Int. Ed.* **2010**, *49*, 942 – 945; b) A. S. K. Hashmi, A. M. Schuster, F. Rominger, *Angew. Chem.* **2009**, *121*, 8396 – 8398; *Angew. Chem. Int. Ed.* **2009**, *48*, 8247 – 8249; c) N. Marion, R. S. Ramón, S. P. Nolan, *J. Am. Chem. Soc.* **2009**, *131*, 448 – 449; d) N. Marion, G. Lemiére, A. Correa, C. Costabile, R. S. Ramón, X. Moreau, P. de Frémont, R. Dahmane, A. Hours, D. Lesage, J.-C. Tabet, J.-P. Goddard, V. Gandon, L. Cavallo, L. Fensterbank, M. Malacria, S. P. Nolan, *Chem. Eur. J.* **2009**, *15*, 3243 – 3260; e) R. S. Paton, F. Maseras, *Org. Lett.* **2009**, *11*, 2237 – 2240; f) S. Díez-González, N. Marion, S. P. Nolan, *Chem. Rev.* **2009**, *109*, 3612 – 3676; g) J. Urbano, A. J. Hormigo, P. de Frémont, S. P. Nolan, M. M. Díaz-Requejo, P. J. Pérez, *Chem. Commun.* **2008**, 759 – 761; h) N. Marion, S. P. Nolan, *Chem. Soc. Rev.* **2008**, *37*, 1776 – 1782; i) N. Marion, P. Carlqvist, R. Gealageas, P. de Frémont, F. Maseras, S. P. Nolan, *Chem. Eur. J.* **2007**, *13*, 6437 – 6451; j) S. M. Kim, J. H. Park, S. Y. Choi, Y. K. Chung, *Angew. Chem.* **2007**, *119*, 6284 – 6287; *Angew. Chem. Int. Ed.* **2007**, *46*, 6172 – 6175.

[4] M. Pažický, A. Loos, M. J. Ferreira, D. Serra, N. Vinokurov, F. Rominger, C. Jäkel, A. S. K. Hashmi,

M. Limbach, *Organometallics* **2010**, *29*, 4448–4458.

[5] a) P. de Frémont, N. Marion, S. P. Nolan, *J. Organomet. Chem.* **2009**, *694*, 551–560; b) H. G. Raubenheimer, S. Cronje, *Chem. Soc. Rev.* **2008**, *37*, 1998–2011; c) J. L. Hickey, R. A. Ruhayel, P. J. Barnard, M. V. Baker, S. J. Berners-Price, A. Filipovska, *J. Am. Chem. Soc.* **2008**, *130*, 12570–12571; d) M. M. Jellicoe, S. J. Nichols, B. A. Callus, M. V. Baker, P. J. Barnard, S. J. Berners-Price, J. Whelan, G. C. Yeoh, A. Filipovska, *Cancinogenesis* **2008**, *29*, 1124–1133; e) I. J. Lin, C. S. Vasam, *Coord. Chem. Rev.* **2007**, *251*, 642–670; f) M. V. Baker, P. J. Barnard, S. J. Berners-Price, S. K. Brayshaw, J. L. Hickey, B. W. Skelton, A. H. White, *Dalton Trans.* **2006**, 3708–3715; g) M. V. Baker, P. J. Barnard, S. J. Berners-Price, S. K. Brayshaw, J. L. Hickey, B. W. Skelton, A. H. White, *J. Organomet. Chem.* **2005**, *690*, 5625–5635; h) P. J. Barnard, M. V. Baker, S. J. Berners-Price, D. A. Day, *J. Inorg. Biochem.* **2004**, *98*, 1642–1647.

[6] J. Lemke, A. Pinto, P. Niehoff, V. Vasylyeva, N. Metzler-Nolte, *Dalton Trans.* **2009**, 7063–7070.

[7] C. Hirtenlehner, C. Krims, J. Hölbling, M. List, M. Zabel, M. Fleck, R. J. F. Berger, W. Schoefberger, U. Monkowius, *Dalton Trans.* **2011**, *40*, 9899–9910.

[8] C. Topf, C. Hirtenlehner, M. Zabel, M. List, M. Fleck, U. Monkowius, *Organometallics* **2011**, *30*, 2755–2764.

[9] C. Topf, C. Hirtenlehner, U. Monkowius, *J. Organomet. Chem.* **2011**, *696,* 3274–3278.

[10] C. Topf, C. Hirtenlehner, M. Fleck, M. List, U. Monkowius, *Z. Anorg. Allg. Chem.* **2011**, doi: 10.1002/zaac.201100341.

[11] W.-H. Yang, C.-S. Lee, S. Pal, Y.-N. Chen, W.-S. Hwang, I. J. B. Lin, J.-C. Wang, *J. Organomet. Chem.* **2008**, *693*, 3729–3740.

[12] U. Monkowius, M. Zabel, H. Yersin, *Inorg. Chem. Commun.* **2008**, *11*, 409–412 and refs. therein.

[13] A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441–451.

[14] R.-Y. Liau, T. Mathieson, A. Schier, R. J. F. Berger, N. Runeberg, H. Schmidbaur, *Z. Naturforsch.* **2002**, *57b*, 881–889.

[15] D. Nemcsok, K. Wichmann, G. Frenking, *Organometallics* **2004**, *23*, 3640–3646.

[16] P. de Frémont, N. M. Scott, E. D. Stevens, T. Ramnial, O. C. Lightbody, C. L. B. Macdonald, J. A. C. Clyburne, C. D. Abernethy, S. P. Nolan, *Organometallics* **2005**, *24*, 6301–6309.

[17] H. Schmidbaur, A. Schier, *Chem. Soc. Rev.* **2008**, *37*, 1931–1951.

[18] a) M. K. Samantaray, K. Pang, M. M. Shaikh, P. Ghosh, *Dalton Trans.* **2008**, 4893–4902; b) L. Ray, V. Katiyar, M. J. Raihan, H. Nanavati, M. M. Shaikh, P. Ghosh, *Eur. J. Inorg. Chem.* **2006**, 3724–3730; c) B. Bovio, A. Burini, B. R. Pietroni, *J. Organomet. Chem.* **1993**, *452*, 287–291; d) L. Ray, V. Katiyar, S. Barman, M. J. Raihan, H. Nanavati, M. M. Shaikh, P. Ghosh, *J. Organomet. Chem.* **2007**, *692*, 4259–4269; e) V. W. W. Yam, J. K.-W. Lee, C.-C. Ko, N. Zhu, *J. Am. Chem. Soc.* **2009**, *131*, 912–913; f) X. Zhang, S. Gu, Q. Xia, W. Chen, *J. Organomet. Chem.* **2009**, *694*, 2359–2367.

[19] a) T. Mathieson, A. Schier, H. Schmidbaur, *J. Chem. Soc., Dalton Trans.* **2001**, 1196–1200; b) D. Schneider, S. Nogai, A. Schier, H. Schmidbaur, *Inorg. Chim. Acta* **2003**, *352*, 179–187; c) J. D. E. T. Wilton-Ely, A. Schier, N. W. Mitzel, H. Schmidbaur, *J. Chem. Soc., Dalton Trans.* **2001**, 1058–1062.

[20] C.-M. Che, S.-W. Lai in *Gold Chemistry: Applications and Future Directions in the Life Sciences*, (Ed.: F. Mohr), Wiley-VCH, Weinheim, **2009**, pp. 249–281.

[21] a) M. A. Rawashdeh-Omary, M. A. Omary, H. H. Patterson, J. P. Fackler, Jr., *J. Am. Chem. Soc.* **2001**, *123*, 11237–11247; b) M. A. Omary, H. H. Patterson, *J. Am. Chem. Soc.* **1998**, *120*, 7696–7705; c) M. A. Omary, H. H. Patterson, *Inorg. Chem.* **1998**, *37*, 1060–1066.

[22] U. Monkowius, M. Zabel, M. Fleck, H. Yersin, *Z. Naturforsch.* **2009**, *64b*, 1513–1524.

[23] R. Usón, A. Lagúna, M. Lagúna, *Inorg. Synth.* **1989**, *26*, 85.

[24] G. M. Sheldrick, SHELXS-97, Program for the Solution of Crystal Structures, University of Göttingen, Göttingen (Germany) **1997**. See also: G. M. Sheldrick, *Acta Crystallogr.* **1990**, *A46*, 467–473.

[25] G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen (Germany) **1997**. See also: G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112–122.