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ARTICLE TYPE

Non-covalent interactions in coinage metal complexes of 1,2,4-triazole-based *N*-heterocyclic carbenes

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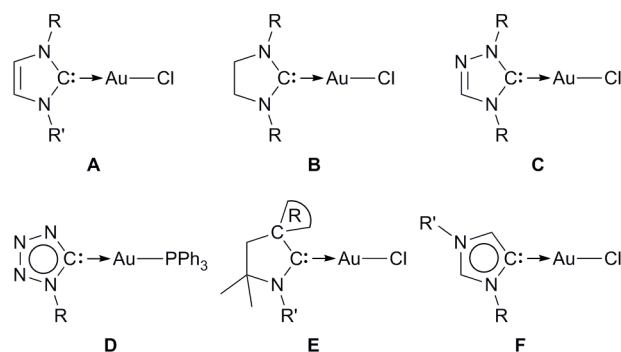
Seven coinage metal(I) complexes bearing two different triazole-based *N*-heterocyclic carbene (NHC) ligands, [1-*tert*-butyl-4-{2-[(*N,N*-dimethylamino)methyl]phenyl}-3-phenyl-1*H*-1,2,4-triazol-4-ium-5-ide and 1-*tert*-butyl-4-(4-methylphenyl)-3-phenyl-1*H*-1,2,4-triazol-4-ium-5-ide] were synthesized and fully characterized in solution by NMR spectroscopy as well as in solid state by X-ray diffraction techniques. Furthermore, the XRD analysis showed that the bidentate coordination of the amino group substituted NHC ligand, previously observed for rhodium and palladium complexes, does not take place in the solid state structure of Au(I) complexes with various halide ligands. Nevertheless, the formation of sets of two head-to-tail oriented monomers aggregated via a weak metalphilic contact was revealed for both NHC ligands as well as for all three coinage metals with different halides. These experimental data correlate quite well with the previously published theoretical study on related complexes.

Introduction

The chemistry of coinage metals, and especially of gold, has attracted a considerable attention in the past two decades. The increased interest is mostly connected with the use of gold compounds as homogenous as well as heterogeneous catalysts in transformation of organic molecules and material science including nanotechnology, supramolecular systems and medicinal chemistry.¹ In addition, several synthetic applications using gold-catalysts were developed in the field of redox reactions, addition of nucleophiles to unsaturated molecules, isomerization, cyclization, rearrangement and aldol reactions.²

The weak attractive closed-shell interactions in transition metals were first observed by Schmidbaur in the gold(I) complexes displaying short Au...Au contacts.³ Since then, compounds containing two or more metal atoms separated by a lower distance than the sum of their van der Waals radii, termed a metalphilic contact, are of great interest both in academia and industry. For example, the shortest metal-metal distance in metallic gold is 2.88 Å,⁴ whereas the corresponding distance in the gas phase Au₂ molecule is 2.47 Å⁵ and the sum of the van der Waals radii is 3.32 Å.⁶ The mainly intermolecular metalphilic contact in the complexes of weakly interacting coinage metals with formal electronic *nd*¹⁰ configuration seems to be crucial for some potential applications of metal compounds and clusters in material science.⁷ A comparison of aurophilicity with cuprophilicity and argentophilicity^{3,2e,g,8} showed that the gold-gold interaction is more acute, most likely due to a presence of relativistic effects.

The *N*-heterocyclic carbenes (NHC) literally burst onto the chemical scene after the first report of stable imidazolin-2-ylidene type of NHC by Arduengo et al.,⁹ followed by an immediate development and utilization of such species in organometallic chemistry.¹⁰ The high interest in gold(I) chemistry led to the employment of NHC as very promising stabilizing ligands. For example, Au(I)F which has been elusive in the literature, is now described as a NHC-AuF complex.¹¹ Moreover, gold(I) complexes with nearly all types of NHC ligands, including imidazole-, triazole-, or tetrazole-based carbene, mesoionic carbene, or cyclic alkylamino carbene (Scheme 1), have been



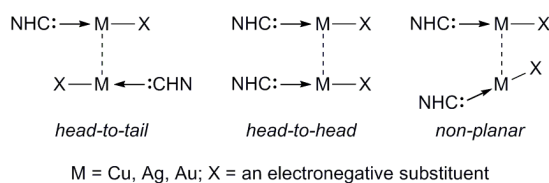
Scheme 1 Representative gold(I) complexes with various types of NHC ligands. **A** = unsaturated Arduengo-type carbene¹² (R = isopropyl, R' = phenyl), **B** = saturated Arduengo-type carbene¹³ (R = 2,6-diisopropylphenyl), **C** = triazole-based carbene¹⁴ (R = methyl), **D** = tetrazole-based carbene¹⁵ (R = 2,6-dimethylphenyl), **E** = cyclic alkylamino carbene (CAAC)¹⁶ (R = adamantyl, R' = 2,6-diisopropylphenyl), **F** = mesoionic-type carbene¹⁷ (R = adamantyl, R' = benzyl).

introduced, and with the exception of the two latter, the formation of dimers via metallophilic contact has already been observed. Besides, a thorough check of the Cambridge Structural Database¹⁸ revealed that there are many coinage metal complexes which exhibit metallophilic interactions in extended motifs, even though these are often not discussed.

The recent theoretical as well as experimental investigations of closed shell aurophilic interactions have shown a significant importance of metal-metal contacts as key intermediates in NHC- or phosphine-gold catalyzed transformations of organic molecules, such as nucleophile addition to unsaturated carbon-carbon bonds and cyclooligomerization of polyunsaturated hydrocarbons.^{2g,19} On the other hand, the study of [2.2]paracyclophanediylidiphosphane complexes of gold as possible catalysts in inter- and intramolecular hydroamination of alkynes by Roesky proved that there is no influence of the metallophilic contact on the catalytic performance of two isomers either with or without an aurophilic contact.²⁰

Many theoretical studies have been carried out on systems exhibiting a metallophilic contact,²¹ including that of the [(NHC)MX]₂ type,²² in order to characterize the strength of the interaction, preferred geometries of the complexes (Scheme 2) and to reveal the origins of such closed-shell interactions. These studies were briefly summarized in a recent review.²³ Concerning its origin, it was demonstrated already some time ago that electron correlation makes the interaction between these complexes attractive,^{21e} which was recently rationalized also by Pyykkö and co-workers as mostly coming from dispersion, quadrupole-quadrupole and induction interactions.^{22b}

Here, we present a comprehensive structural and spectroscopic study on the two series of coinage metals(I) complexes of 1,2,4-triazole-based NHC with variable halides in the gold complexes



Scheme 2 Possible structural arrangements for [(NHC)MX]₂ dimeric type complexes.

of the amino functionalized NHC ligand and with different

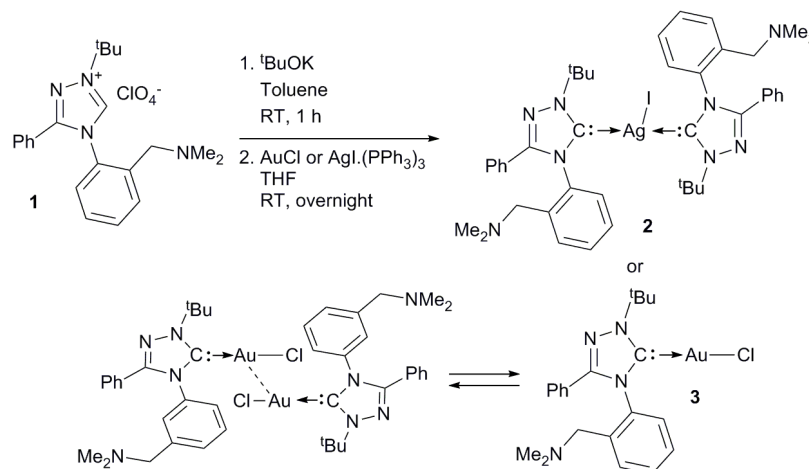
coinage metals for the analogous simplified NHC ligand. This study is closely related to our very recent detailed theoretical analysis of different model NHC-coinage metal complexes and trends in the formation of intermolecular interactions via a metal-metal contact.²⁴

Results and discussion

The first two complexes **2** and **3** were synthesized in order to distinguish whether the presence of the pendant amino group can influence the formation of presumably linear complexes of coinage metals by the intra- or intermolecular interaction, similarly as previously observed for the square planar Rh(I)²⁵ and Pd(II)²⁶ complexes. The reaction proceeds via the deprotonation of the respective triazolium perchlorate **1**²⁵ with a strong base (potassium *tert*-butoxide) affording free carbene, which was subsequently treated *in situ* with either Ag(I) or Au(I) precursors (Scheme 3).

The generation of a free carbene and the subsequent formation of the NHC-metal complex can be unambiguously confirmed by the absence of the ¹H NMR resonance due to the imidazolium proton (N-CH₂-N) and by the appearance of the low field resonance of the metal-bound carbene carbon (187.2 ppm for **2**, 176.7 for **3**) in the ¹³C NMR spectra. In addition, the presence of a doublet in ¹³C NMR with the characteristic coupling constant ¹J(¹³C-^{107/109}Ag) of 178.4 Hz supports the formation of a Ag-C_{NHC} bond in **2**. The plausible interaction of the amino nitrogen atom in solution is indicated by the ¹H NMR spectra, in which the NCH₂ protons give rise to an AX spin pattern. In both cases, single crystals suitable for X-ray structure determination were obtained.

The X-ray structure of **2** reveals the formation of a C₂ symmetrical bis-carbene complex with an essentially planar arrangement of the two carbene carbons, the iodide and the silver (Fig. 1). The geometry of **2** with the tri-coordinated silver atom is comparable with the analogous imidazol derived NHC-silver(I) bromide or iodide complexes²⁷ and few other known multinuclear structures with such coordination type.²⁸ The Ag-I distance of 3.001 Å is longer than the Ag-I covalent radii (2.84 Å) and much shorter than the sum of the van der Waals radii (3.70 Å), similarly as the Ag-Br distances in the aforementioned complexes.²⁷ This Ag-I interaction causes a significant change in



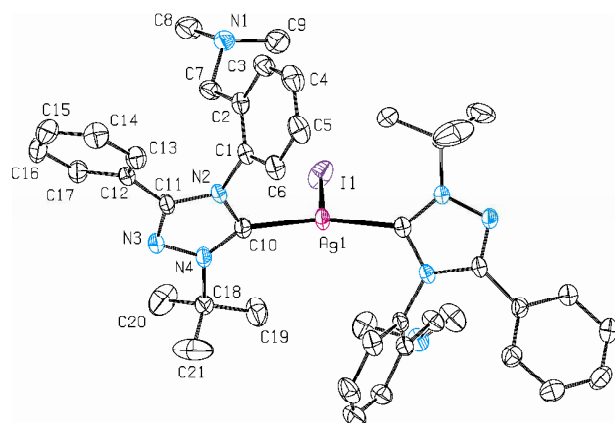
Scheme 3 Synthesis of Ag(I) and Au(I) complexes **2** and **3**.

Fig. 1 The molecular structure (ORTEP, 50% probability level) of **2**.

Hydrogen atoms have been omitted for clarity. Selected interatomic distances [Å] and angles [°]: Ag1-C10 2.131(3), Ag1-I1 3.0010(5), N4-C10 1.329(4), N2-C10 1.373(4), C10-Ag1-I1 105.13(9), C10-Ag1-C10 149.74(17), N4-C10-N2 102.3(2).

the geometrical parameters of the metal centre as revealed by the bent C–Ag–C angle (149.74(17)°). The dihedral angle between the two planes, defined by the triazole rings, is 36.01°. The complex shows no evidence neither of an intra- or intermolecular coordination of the dangling amino group (Ag–N = 5.303 Å) nor of an Ag···Ag interaction.

The repeatable and exclusive formation of the bis-carbene type of complexes even with the 1:1 stoichiometry (triazolium salt : AgI.(PPh₃)₃) was quite surprising, but is again comparable with the findings published in the literature.^{27a}

In contrast to the bis-carbene type of geometry of **2**, the X-ray structure determination of **3** showed the formation of mono-carbene linear type geometry (Fig. 2a). The carbene-metal bond ($C_{\text{carbene}}\text{-Au} = 1.976(5)$ Å) and metal-chloride bond (Au–Cl = 2.2910(14) Å) are comparable with values in other reported 1,2,4-triazole-based (NHC)AuCl.²⁹ Similarly as for **2**, the amino group of the NHC ligand is directed away from the metal centre (Ag–N = 4.707 Å), not taking part in intra- or intermolecular coordination. Another notable feature of the geometry was revealed in the packing diagram, which shows a formation of sets of two head-to-tail oriented molecules aggregated via an Au···Au interaction of 3.330 Å (Fig. 2b). We have very recently published a systematic theoretical study of such metallophilic contacts in the related [(NHC)AuCl]₂ dimers.²⁴ We found that the geometry and binding energy is determined, besides the metal–metal interaction, by the electrostatic interaction between the partially positive NHC ring (head) of one of the monomers with the partially negative halide site (tail) of the other, which results in the characteristic head-to-tail arrangement.

The chlorine atom in **3** could be exchanged for other halides. Complexes **4** and **5** were prepared by treatment of **3** with appropriate triorganotin(IV)halogenide L^{CN}Bu₂SnX³⁰ (L^{CN} = 2-(*N,N*-dimethylaminomethyl)phenyl; X = Br for **4** or I for **5**) in benzene at 55°C for 24 hours (Scheme 4). The major advantage of this organotin(IV) agent lies in the convenient monitoring of the halogen exchange completion by ¹¹⁹Sn NMR spectroscopy, where only one signal corresponding to the L^{CN}Bu₂SnCl is present when a full conversion is achieved. Besides, the high

solubility of the L^{CN}Bu₂SnCl enables its convenient separation

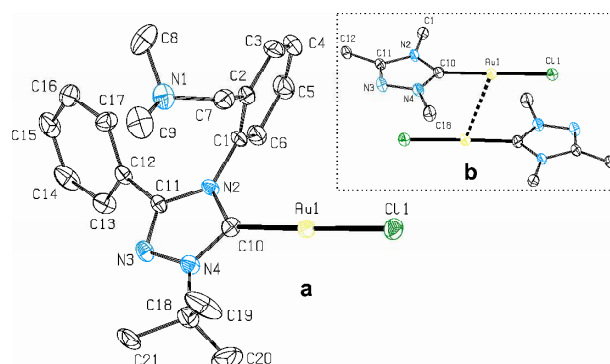
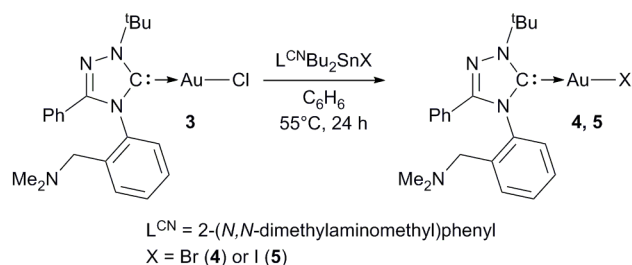


Fig. 2 (a) The molecular structure (ORTEP, 50% probability level) of **3**·C₇H₈. Hydrogen atoms and the toluene molecule have been omitted for clarity. Selected interatomic distances [Å] and angles [°]: Au1-C10 1.976(5), Au1-Cl1 2.2910(14), C10-N4 1.342(7), C10-N2 1.363(7), C10-Au1-C11 178.48(15), N4-C10-N2 103.4(4). **(b)** Au···Au metallophilic contact between two molecules of **3**. Organic substituents of the triazole rings have been omitted for clarity.



Scheme 4 Halogen exchange reactions.

from the reaction mixture after the completion of the halogen exchange. Even though the analogous L^{CN}Bu₂SnF was proven to be a very efficient fluorinating agent,³¹ all attempts to prepare appropriate gold(I) fluoride even at higher temperatures and prolonged reaction times were unsuccessful.

The formation of the desired products **4** and **5** was again elucidated by the means of ¹H and ¹³C NMR spectroscopy similarly as in the case of **3**. ¹³C NMR resonances of the carbene atom revealed comparable values of the chemical shifts (180.0 ppm for **4**, 186.5 ppm for **5**). The coordination of the dangling amino group in solution could be again suggested from the ¹H NMR spectra pattern, where methylene protons appear as an AX spin pattern.

The unambiguous proof of the formation of linear mono-carbene complexes came from the X-ray structure determination (Fig. 3 for **4**; Fig. 4 for **5**). The carbene-metal bonds ($C_{\text{carbene}}\text{-Au} = 1.980(10)$ Å for **4**; 2.020(7) Å for **5**) as well as metal-halide bonds (Au–Br = 2.3893(12) Å; Au–I = 2.5565(6) Å) are elongated in comparison to **3**, which correlates well with available structural data for this type of compounds.³² In the case of **5**, a significant deviation of the I atom from the C₂N₃ carbene plane (0.850 Å), caused most probably by the larger ionic radii of I, was observed by comparison with **3** and **4**. Similarly as for **3**, the packing diagram of both **4** and **5** revealed the formation of the head-to-tail oriented dimers connected via an aurophilic interaction (Au···Au = 3.400 Å for **4**; 3.414 Å for **5**).

X-ray studies of the previous three Au(I) complexes have proven that, in solid state the formation of the dimeric structure via a weak interaction of two metal centres is preferred over an

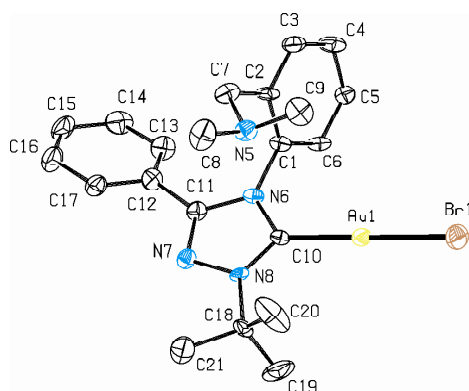


Fig. 3 The molecular structure (ORTEP, 50% probability level) of one of two independent molecules of **4**·C₆H₆. Hydrogen atoms and the benzene molecule have been omitted for clarity. Selected interatomic distances [Å] and angles [°]: Au1-C10 1.980(10) [2.005(10)], Au1-Br1 2.3893(12) [2.3957(13)], N6-C10 1.393(12) [1.363(12)], N8-C10 1.306(12) [1.332(13)], C10-Au1-Br1 174.7(3) [174.6(3)], N8-C10-N6 104.4(8) [104.9(9)].

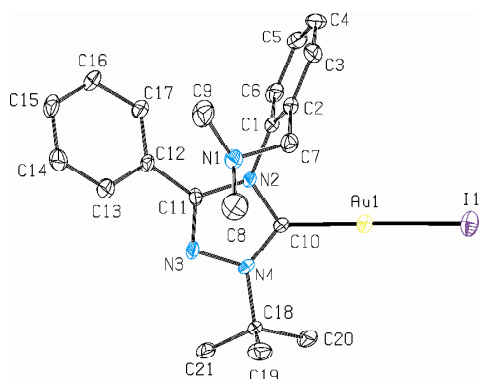
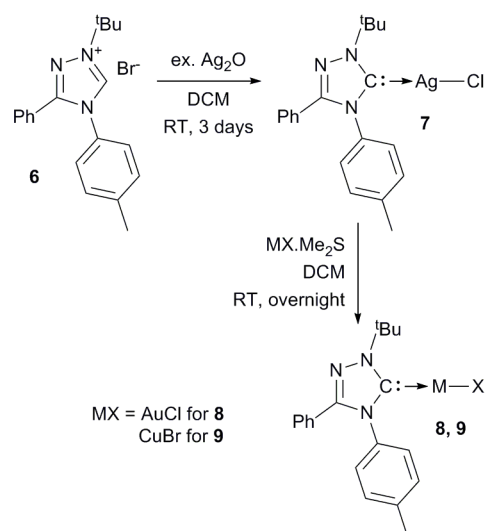


Fig. 4 The molecular structure (ORTEP, 50% probability level) of **5**·0.5 C₆H₆. Hydrogen atoms and the benzene molecule have been omitted for clarity. Selected interatomic distances [Å] and angles [°]: Au1-C10 2.020(7), Au1-I1 2.5565(6), C10-N4 1.314(9), C10-N2 1.363(8), C10-Au1-I1 173.69(19), N4-C10-N2 104.9(6).

intramolecular coordination of the donating amino group, which can only be deduced in solution from the ¹H NMR data. Therefore, a simplified 1,2,4-triazole-based ligand²⁶ was used for the next structural studies of possible metallophilic contacts of the lighter analogues of group 11 metals.

The silver(I) complex **7** was synthesized by the reaction of the 1-*tert*-butyl-3-phenyl-4-(*p*-tolyl)-4*H*-1,2,4-triazol-1-ium bromide (**6**) with silver oxide in CH₂Cl₂ according to the procedure developed by Lin and co-workers³³ (Scheme 5). As expected, the ¹H NMR spectrum of **7** lacks the resonance due to the imidazolium proton (N-CH-N), while the low field shifted resonance of the carbene carbon is seen at 182.6 ppm in the ¹³C NMR spectra. In contrast to **2**, a broad signal was observed in the ¹³C NMR spectra instead of the expected doublet with the characteristic ¹J(¹³C-^{107/109}Ag) coupling constant. This is most probably caused by the more fluxional character of the monocarbene substituted complex **7**. Moreover, the Br/Cl exchange was revealed by the X-ray structure determination, showing that the chloro complex is formed instead of the expected bromo

complex. This phenomenon has previously been observed when CH₂Cl₂, which most probably serves as the source of chloride, was used in the preparation method.³⁴



Scheme 5 Synthesis of Ag(I) complex **7** and subsequent transmetalation reactions providing complexes **8** and **9**.

The molecular structure of **7** (Fig. 5) resembles the previous linear geometries of gold(I) complexes **3-5**. The shortening of the carbene-metal bond ($C_{\text{carbene}}-\text{Ag} = 2.079(3)$ Å), in comparison to the bis-carbene complex **2**, commensurate well with the other reported silver(I) 1,2,4-triazole-based NHC complexes.^{29b,35} As for the gold(I) complexes **3-5**, a weak argentophilic interaction between two monomers can be observed with the Ag...Ag distance of 3.515 Å. Even though this value is slightly above the sum of their van der Waals radii (3.44 Å),⁶ it was shown in the literature that silver ions can exert argentophilic interactions even at such distances, maintaining the angular specificities.³⁶

Finally, the transmetalation reaction of **7** with AuCl·Me₂S and CuBr·Me₂S yielded the expected gold(I) and copper(I) complexes **8** and **9** (Scheme 5). The formation of the carbene complexes was established by the means of ¹H and ¹³C NMR in the same way as in the case of all previous complexes. The ¹³C NMR chemical shift values of signals for the carbene carbon atoms in **8** and **9** are comparable with the value found for **7** (184.2 ppm for **8**; 177.8 ppm for **9**). In both cases, single crystals suitable for X-ray structure determination were obtained and the complexes were

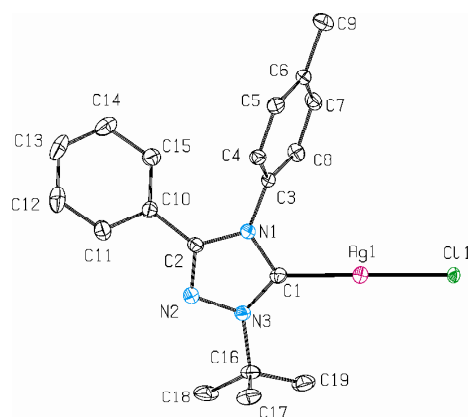


Fig. 5 The molecular structure (ORTEP, 50% probability level) of **7**. Hydrogen atoms have been omitted for clarity. Selected interatomic distances [Å] and angles [°]: Ag1-C1 2.079(3), Ag1-C11 2.3601(6), N3-C1 1.340(4), N1-C1 1.369(3), C1-Ag1-C11 174.92(7), N3-C1-N1 102.7(2).

structurally characterized.

The solid structure of **8** (Fig. 6) reveals a linear geometry very similar to that of **3**, with almost identical bond distances and angles. The unexpected and significant difference is in the length of the Au...Au metallophilic contact, which is, despite the fact that the NHC ligand is less sterically demanding, by about 0.3 Å longer than in the case of **3**.

Similarly as for **7**, the X-ray analysis of the single crystals grown from DCM solution of **9** showed a partial Br/Cl exchange and formation of a 1:1 mixture of isostructural Cu-Br (**9Br**) and Cu-Cl (**9Cl**) complexes (Fig 7). The copper(I) centre in **9** is again two-coordinate with a linear geometry as in the case of **7** and **8**. The C_{carbene}-Cu bond (1.884(3) Å) and the Cu-Br/Cl bond (2.220(10) Å and 2.16(3) Å) are within the usual range for NHC-copper(I) bromide complexes.³⁷ In line with the structural features of the former complexes, the formation of a very weak Cu...Cu interaction (3.644 Å) and thus a head-to-tail oriented dimer was observed in the packing diagram of **9**. Despite the fact that the length of the Cu...Cu interaction is well above the sum of the van der Waals radii (2.80 Å),⁶ potential energy curves

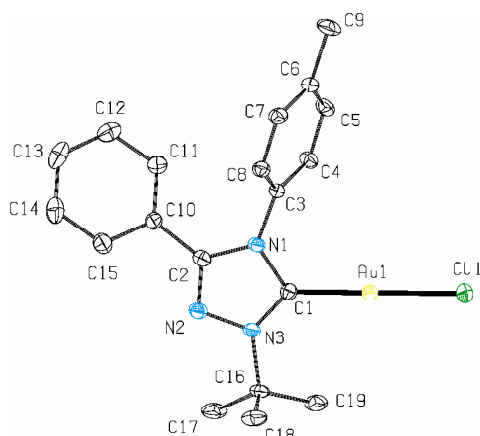


Fig. 6 The molecular structure (ORTEP, 50% probability level) of **8**. Hydrogen atoms have been omitted for clarity. Selected interatomic distances [Å] and angles [°]: Au1-C1 1.978(3), Au1-C11 2.2922(8), C3-N1 1.440(4), C1-N1 1.373(4), C1-Au1-C11 178.55(9), N3-C1-N1 103.3(3).

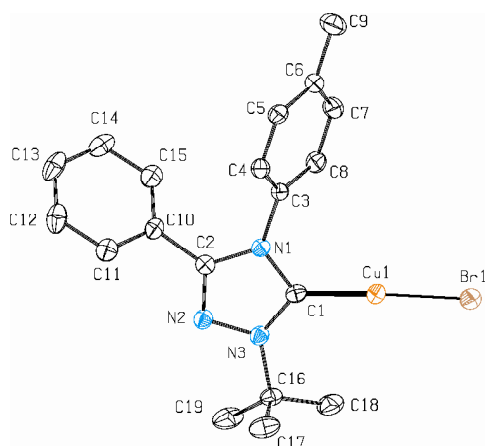


Fig. 7 The molecular structure (ORTEP, 50% probability level) of **9Br**-C₄H₈O. Hydrogen atoms and the THF molecule have been omitted for clarity. Selected interatomic distances [Å] and angles [°]: Cu1-C1 1.884(3), Cu1-Br1 2.220(10), N3-C1 1.336(4), N1-C1 1.372(4), C1-Cu1-Br1 173.8(2), N3-C1-N1 102.6(2).

Table 1. Summary of the selected NMR [ppm] and XRD [Å] parameters

	$\delta(\text{C}_{\text{carb}})^{\text{a}}$	$d(\text{M}-\text{C}_{\text{carb}})$	$d(\text{M}-\text{X})$	$d(\text{M}\cdots\text{M})$
(NHC)AuCl ^b	176.7	1.976(5)	2.2910(14)	3.33
(NHC)AuBr ^{b,c}	180.6	1.980(10) 2.005(10)	2.3893(12) 2.3957(13)	3.40
(NHC)AuI ^b	186.5	2.020(7)	2.5565(6)	3.41
(NHC)CuBr ^d	177.8	1.884(3)	2.220(10)	3.65
(NHC)AgCl ^d	182.6	2.079(3)	2.3601(6)	3.52
(NHC)AuCl ^d	184.2	1.978(3)	2.2922(8)	3.63
(NHC)CuCl ^e		1.83	2.09	3.34
(NHC)AgCl ^e		2.04	2.32	3.16
(NHC)AuCl ^e		1.95	2.28	3.19

^aMeasured in CDCl₃; ^bNHC = 1-*tert*-butyl-4-{2-[(dimethylamino)methyl]phenyl}-3-phenyl-1*H*-1,2,4-triazol-4-ium-5-ide; ^cStructural data for two independent molecules; ^dNHC = 1-*tert*-butyl-3-phenyl-4-(*p*-tolyl)-1*H*-1,2,4-triazol-4-ium-5-ide; ^eTheoretical data,²⁴ NHC = 1,3,4-trimethyl-1*H*-1,2,4-triazol-4-ium-5-ide

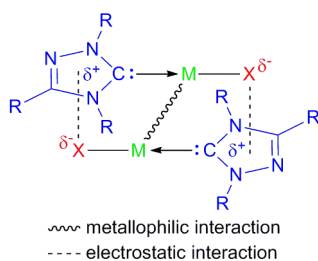
obtained by Pyykkö at the *ab initio* MP2 level of calculation with very large basis sets display energy minima for Cu at 3.137 Å.^{21b} Moreover, the curve is extremely shallow, showing that a separation of 4.5 Å still provides a favourable interaction which amounts to -1.2 kcal.mol⁻¹ compared to the stabilization energy of -3.07 kcal.mol⁻¹ computed at the minimum.

The close resemblance of the ¹³C NMR spectral features summarized in Table 1 for all mono-carbene complexes points towards their structural similarities. Next to that, the ¹³C NMR data shows that in both Cl-Br-I as well as Cu-Ag-Au series, the carbene carbon atoms are slightly less shielded in the order Cl<Br<I and Cu<Ag<Au, respectively. Furthermore, the selected structural data correlate quite well with the theoretical data for analogous simplified systems.²⁴

As discussed earlier, it is worth mentioning that, according to the energy-decomposition analysis along with the calculations of the molecular electrostatic potential, the weakening of the metal...metal bond in the dimer is compensated by the electrostatic interaction between the negatively charged halide ion of one of the monomers and moderately positively charged carbene ring of the other monomer and vice versa (Scheme 6).²⁴ This relatively strong interaction results most probably in the characteristic head-to-tail arrangement.

Conclusions

Seven novel coinage metal complexes containing two different triazole-based NHC ligands were synthesized and structurally



Scheme 6 Schematic representation of the interactions in the investigated complexes.

characterized in order to compare the experimental data with previous theoretical studies on related complexes. As expected, the formation of a linear type of monocarbene complexes was revealed with only one exception of a Ag(I) silver biscarbene complex. Even though the ^1H NMR data suggested a possible interaction of the pendant amino donor group of one of the NHC ligands in the Au(I) complexes with various halogens, the X-ray diffraction analysis showed no signs of any inter- or intramolecular coordination. On the other hand, a weak metallophilic interaction between two monomers with the $\text{M}\cdots\text{M}$ separation of 3.33 – 3.65 Å can be observed in the packing diagram of NHC complexes of all three coinage metals. This relatively weak interaction is furthermore stabilized by the electrostatic interaction between the negatively charged halide ion of one of the monomers and moderately positively charged carbene ring of the other monomer and vice versa, which results in a typical head-to-tail conformation. The experimental data correlates quite well with the previous detailed theoretical survey on the set of analogous coinage metal(I) NHC complexes.

Experimental section

General Comments

All reactions leading to free carbenes and their $\text{M}(\text{I})$ complexes ($\text{M} = \text{Cu}, \text{Ag}, \text{Au}$) were performed under an argon atmosphere using standard Schlenk techniques. Solvent purification system PureSolv MD 7 by Innovative Technology, Inc. was used to dry the solvents which were then degassed by the freeze-pump-thaw method and stored under an argon atmosphere.

Materials

1-*tert*-butyl-4-{2-[(dimethylamino)methyl]phenyl}-3-phenyl-4*H*-1,2,4-triazol-1-ium perchlorate (**1**),²⁵ 1-*tert*-butyl-3-phenyl-4-(*p*-tolyl)-4*H*-1,2,4-triazol-1-ium bromide (**6**),²⁶ [2-(*N,N*-dimethylaminomethyl)phenyl]di-*n*-butyltin(IV) bromide,^{30a} [2-(*N,N*-dimethylaminomethyl)phenyl]di-*n*-butyltin(IV) iodide,^{30b} and tris-(triphenylphosphine)silver(I) iodide³⁸ were prepared according to literature procedures. Potassium *tert*-butoxide, gold(I) chloride, silver(I) oxide, chloro(dimethylsulfide)gold(I) and bromo(dimethylsulfide)copper(I) were purchased from Sigma-Aldrich and used as received.

NMR Spectroscopy

NMR spectra were recorded from solutions in C_6D_6 and CDCl_3 on Bruker Avance II 500 and 400 spectrometers (equipped with Z -gradient 5 mm probe) operating at frequencies 500.13 MHz and 400.13 MHz for ^1H and 125.76 MHz and 100.62 for $^{13}\text{C}\{^1\text{H}\}$. All

deuterated solvents were distilled under reduced pressure, degassed by the freeze-pump-thaw method and finally stored over K-mirror (C_6D_6) or molecular sieves (CDCl_3) under an argon atmosphere. Solutions were obtained by dissolving of approximately 20 mg of the analyzed compound in ca. 0.7 ml of deuterated solvent. The ^1H chemical shift values are given relative to internal tetramethylsilane ($\delta(^1\text{H}) = 0.00$) or to residual solvent signals (C_6D_6 , $\delta(^1\text{H}) = 7.16$ and CDCl_3 , $\delta(^1\text{H}) = 7.26$). The ^{13}C chemical shifts were calibrated similarly (C_6D_6 , $\delta(^{13}\text{C}) = 128.06$ and CDCl_3 , $\delta(^{13}\text{C}) = 77.16$). All ^{13}C NMR spectra were measured using the standard proton-decoupled experiment and CH and CH_3 vs. C and CH_2 groups were distinguished by the APT method.³⁹

Elemental Analysis

Elemental compositions were determined under an argon atmosphere using the automatic combustion analyzer EA 1108 by FISON Instruments.

X-Ray Crystallography

The diffraction data (see Supporting Information, Table S1) were obtained at 150(2) K with an Oxford Cryostream low-temperature device on a Nonius KappaCCD diffractometer with MoK_α radiation ($\lambda = 0.71073$ Å) using a graphite monochromator, and the ϕ and χ scan mode. Data reductions were performed with DENZO-SMN.⁴⁰ The data were corrected for absorption by integration methods.⁴¹ The structures were solved by direct methods (SIR92)⁴² and refined by full matrix least-squares based on F^2 (SHELXL97).⁴³ Hydrogen atoms could be mostly localized on the difference Fourier maps. However, to ensure uniformity of the treatment of the crystal structures, all hydrogen atoms were recalculated into their idealized positions (riding model) and assigned temperature factors of $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}$ (pivot atom) or of $1.5 U_{\text{eq}}$ for the methyl moiety with C-H = 0.96, 0.97, and 0.93 Å for methyl, methylene and hydrogen atoms in aromatic rings or allyl moiety, respectively.

Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EY, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>). CCDC deposition numbers 1011243-1011249.

General Procedure for Free Carbene Generation and for the Preparation of Complexes 2 and 3.

Free carbene was generated at room temperature from the reaction of **1** with $^t\text{BuOK}$ (molar ratio $1:^t\text{BuOK} = 1.05:1$) in dry toluene (ca. 30 ml). After stirring for one hour, the resulting precipitate was filtered off and the colourless to light-yellow filtrate was evaporated to dryness to afford yellow oily free carbene. Another Schlenk tube was charged with the precursor coinage metal(I) complex ($\text{AgI}(\text{PPh}_3)_3$ or AuCl), which was mixed with dry THF (ca. 10 ml). The solution of the freshly prepared free carbene dissolved in 20 ml of dry THF was added dropwise to a stirred suspension of the coinage metal(I) complex at room temperature (molar ratio $1:\text{M}(\text{I})$ complex = 1:1.9 for **2** and 1:0.9 for **3**). The reaction mixture was stirred overnight and the solid residues were afterwards filtered off and the filtrate was evaporated to dryness. The crude products were washed with

hexane to give pure **2** and **3** as off-white powders. Single crystals suitable for X-ray diffraction were obtained by slow cooling of a saturated toluene solution at $-30\text{ }^{\circ}\text{C}$.

Bis[1-tert-butyl-4-{2-[(dimethylamino)methyl]phenyl}-3-phenyl-1H-1,2,4-triazol-4-ium-5-yl]iodoaurate(I) (2) Yield: 86 %. ^1H NMR (500 MHz, CDCl_3): δ 7.92 (br, 1H, ArH), 7.58 (br, 1H, ArH), 7.49-7.42 (m, 6H, ArH), 7.34-7.27 (m, 6H, ArH), 7.20 (t, 4H, $^3J = 7.6$ Hz, ArH), 3.27 (br, 1H, NCH_2), 3.08 (br, 2H, NCH_2), 2.87 (br, 1H, NCH_2), 1.84 (br, 12H, $\text{N}(\text{CH}_3)_2$), 1.45 (br, 18H, $\text{C}(\text{CH}_3)_3$). ^{13}C NMR (125 MHz, CDCl_3): δ 187.2 ($\text{NC}_{\text{carb}}\text{N}$), $^1J(^{13}\text{C}-^{107/109}\text{Ag}) = 178.4$ Hz), 152.2 (NCN), 137.5 (ArC), 136.5 (ArC), 131.1 (ArC), 130.6 (ArC), 130.0 (ArC), 129.5 (ArC), 128.9 (ArC), 128.5 (ArC), 128.3 (ArC), 126.3 (ArC), 61.0 ($\text{C}(\text{CH}_3)_3$), 60.1 (br, NCH_2), 45.3 ($\text{N}(\text{CH}_3)_2$), 30.4 ($\text{C}(\text{CH}_3)_3$). Anal. Calcd. (%) for $\text{C}_{42}\text{H}_{52}\text{AuN}_8$: C, 55.82; H, 5.80; N, 12.40. Found: C, 55.84; H, 5.83; N, 12.43. Mp 143-146 $^{\circ}\text{C}$.

[1-tert-butyl-4-{2-[(dimethylamino)methyl]phenyl}-3-phenyl-1H-1,2,4-triazol-4-ium-5-yl]chloroaurate(I) (3) Yield: 95 %. ^1H NMR (500 MHz, C_6D_6): δ 7.30 (d, 2H, $^3J = 7.9$ Hz, ArH), 7.06 (d, 1H, $^3J = 7.8$ Hz, ArH), 7.01 (br, 2H, ArH), 6.94-6.91 (m, 1H, ArH), 6.88 (t, 1H, $^3J = 7.5$ Hz, ArH), 6.81 (t, 2H, $^3J = 7.7$ Hz, ArH), 3.13, 2.79 (AX spin system, $^2J = 13.4$ Hz, 2H, NCH_2), 1.75 (s, 9H, $\text{C}(\text{CH}_3)_3$), 1.68 (s, 6H, $\text{N}(\text{CH}_3)_2$). ^{13}C NMR (125 MHz, C_6D_6): two ^{13}C resonances of ArC obscured by C_6D_6 , δ 176.7 ($\text{NC}_{\text{carb}}\text{N}$), 151.3 (NCN), 137.2 (ArC), 131.5 (ArC), 130.5 (ArC), 130.4 (ArC), 129.2 (ArC), 128.9 (ArC), 128.6 (ArC), 126.4 (ArC), 62.6 (NCH_2), 61.1 ($\text{C}(\text{CH}_3)_3$), 45.2 ($\text{N}(\text{CH}_3)_2$), 31.0 ($\text{C}(\text{CH}_3)_3$). Anal. Calcd. (%) for $\text{C}_{21}\text{H}_{26}\text{AuClN}_4$: C, 44.28; H, 4.62; N, 9.88; Cl, 6.25. Found: C, 44.22; H, 4.59; N, 9.86; Cl, 6.21. Mp 215-218 $^{\circ}\text{C}$.

General Procedure for Halogen Exchange Reactions.

Complex **2** (0.27 mmol) and [2-(*N,N*-dimethylamino-methyl)-phenyl]di-*n*-butyltin(IV) bromide or [2-(*N,N*-dimethylamino-methyl)phenyl]di-*n*-butyltin(IV) iodide (0.27 mmol) were dissolved in benzene (ca. 30ml) and the reaction mixture was stirred at $55\text{ }^{\circ}\text{C}$ for 24 hours. After cooling down to room temperature, the reaction mixture was evaporated to dryness and the resulting crude products were washed with hexane to give off-white powders of **4** and **5**. Single crystals suitable for X-ray diffraction were obtained from a saturated benzene solution at room temperature.

Bromo[1-tert-butyl-4-{2-[(dimethylamino)methyl]phenyl}-3-phenyl-1H-1,2,4-triazol-4-ium-5-yl]aurate(I) (4) Yield: 82 %. ^1H NMR (500 MHz, C_6D_6): δ 7.30 (d, 2H, $^3J = 7.5$ Hz, ArH), 7.03 (d, 1H, $^3J = 7.7$ Hz, ArH), 6.98 (br, 2H, ArH), 6.92-6.85 (m, 2H, ArH), 6.80 (t, 2H, $^3J = 7.6$ Hz, ArH), 3.11, 2.78 (AX spin system, $^2J = 13.6$ Hz, 2H, NCH_2), 1.75 (s, 9H, $\text{C}(\text{CH}_3)_3$), 1.67 (s, 6H, $\text{N}(\text{CH}_3)_2$). ^{13}C NMR (125 MHz, C_6D_6): δ 180.0 ($\text{NC}_{\text{carb}}\text{N}$), 151.2 (NCN), 137.1 (ArC), 136.3 (ArC), 131.4 (ArC), 130.5 (ArC), 130.4 (ArC), 129.2 (ArC), 128.8 (ArC), 128.6 (ArC), 128.4 (ArC), 126.4 (ArC), 62.6 (NCH_2), 61.1 ($\text{C}(\text{CH}_3)_3$), 45.2 ($\text{N}(\text{CH}_3)_2$), 31.0 ($\text{C}(\text{CH}_3)_3$). Anal. Calcd. (%) for $\text{C}_{21}\text{H}_{26}\text{AuBrN}_4$: C, 41.26; H, 4.29; N, 9.16. Found: C, 41.23; H, 4.25; N, 9.14. Mp 212-214 $^{\circ}\text{C}$.

[1-tert-butyl-4-{2-[(dimethylamino)methyl]phenyl}-3-phenyl-1H-1,2,4-triazol-4-ium-5-yl]iodoaurate(I) (5) Yield: 90 %. ^1H NMR (500 MHz, C_6D_6): δ 7.30 (d, 2H, $^3J = 7.5$ Hz, ArH), 6.99-6.97 (m, 3H, ArH), 6.92-6.85 (m, 2H, ArH), 6.79 (t, 2H, $^3J = 7.6$

Hz, ArH), 3.08, 2.77 (AX spin system, $^2J = 13.5$ Hz, 2H, NCH_2), 1.73 (s, 9H, $\text{C}(\text{CH}_3)_3$), 1.67 (s, 6H, $\text{N}(\text{CH}_3)_2$). ^{13}C NMR (125 MHz, C_6D_6): δ 186.5 ($\text{NC}_{\text{carb}}\text{N}$), 151.1 (NCN), 137.0 (ArC), 136.3 (ArC), 131.4 (ArC), 130.5 (ArC), 130.4 (ArC), 129.1 (ArC), 128.8 (ArC), 128.6 (ArC), 128.4 (ArC), 126.3 (ArC), 62.7 (NCH_2), 61.1 ($\text{C}(\text{CH}_3)_3$), 45.3 ($\text{N}(\text{CH}_3)_2$), 30.9 ($\text{C}(\text{CH}_3)_3$). Anal. Calcd. (%) for $\text{C}_{21}\text{H}_{26}\text{AuIN}_4$: C, 38.31; H, 3.98; N, 8.51. Found: C, 38.28; H, 3.96; N, 8.49. Mp 197-198 $^{\circ}\text{C}$.

Preparation of [1-tert-butyl-3-phenyl-4-(*p*-tolyl)-1H-1,2,4-triazol-4-ium-5-yl]chloroaurate(I) (7)

A solution of **6** (1.61 mmol) in 20 ml of dry DCM was added to the suspension of Ag_2O (8.20 mmol) in 10 ml of DCM at room temperature. The reaction mixture was stirred for three days at room temperature under exclusion of light and the solid residues were afterwards filtered off and the filtrate was evaporated to dryness. The crude product was finally washed with hexane to afford pure **7** in form of a yellow-brown powder. Yield: 87 %. ^1H NMR (500 MHz, CDCl_3): δ 7.43-7.40 (m, 1H, ArH), 7.35-7.30 (m, 4H, ArH), 7.25 (br, 4H, ArH), 2.41 (s, 3H, CH_3), 1.79 (s, 9H, $\text{C}(\text{CH}_3)_3$). ^{13}C NMR (125 MHz, CDCl_3): δ 182.6 (br, $\text{NC}_{\text{carb}}\text{N}$), 151.7 (NCN), 140.3 (ArC), 134.9 (ArC), 130.8 (ArC), 130.7 (ArC), 128.9 (ArC), 128.8 (ArC), 126.6 (ArC), 125.0 (ArC), 61.8 ($\text{C}(\text{CH}_3)_3$), 31.0 ($\text{C}(\text{CH}_3)_3$), 21.3 (CH_3). Anal. Calcd. (%) for $\text{C}_{19}\text{H}_{21}\text{AgClN}_3$: C, 52.50; H, 4.87; N, 9.67. Found: C, 52.47; H, 4.85; N, 9.64. Mp 253-255 $^{\circ}\text{C}$.

General Procedure for Transmetallation Reactions.

To a Schlenk tube charged with the starting coinage metal(I) complex ($\text{AuCl}\cdot\text{Me}_2\text{S}$ or $\text{CuBr}\cdot\text{Me}_2\text{S}$; 0.35 mmol) and a small amount of dry DCM (approx. 5 ml), a solution of **7** (0.35 mmol) in 20 ml of DCM was added at room temperature. The reaction mixture was stirred overnight and the solid residues were afterwards filtered off and the filtrate was evaporated to dryness. The crude products were washed with hexane to give pure **8** and **9** as off-white powders. Single crystals suitable for X-ray diffraction were obtained by slow cooling of a saturated DCM solution at $-30\text{ }^{\circ}\text{C}$.

[1-tert-butyl-3-phenyl-4-(*p*-tolyl)-1H-1,2,4-triazol-4-ium-5-yl]chloroaurate(I) (8) Yield: 82 %. ^1H NMR (500 MHz, CDCl_3): δ 7.43-7.40 (m, 1H, ArH), 7.34 (br, 4H, ArH), 7.33-7.31 (m, 4H, ArH), 2.46 (s, 3H, CH_3), 1.57 (s, 9H, $\text{C}(\text{CH}_3)_3$). ^{13}C NMR (125 MHz, CDCl_3): δ 184.2 ($\text{NC}_{\text{carb}}\text{N}$), 151.8 (NCN), 141.0 (ArC), 134.4 (ArC), 131.2 (ArC), 131.0 (ArC), 128.9 (ArC), 128.8 (ArC), 127.5 (ArC), 124.4 (ArC), 62.8 ($\text{C}(\text{CH}_3)_3$), 31.0 ($\text{C}(\text{CH}_3)_3$), 21.4 (CH_3). Anal. Calcd. (%) for $\text{C}_{19}\text{H}_{21}\text{AuClN}_3$: C, 43.57; H, 4.04; N, 8.02; Cl, 6.77. Found: C, 43.60; H, 4.06; N, 8.04; Cl, 6.80. Mp 239 $^{\circ}\text{C}$ (dec.).

Bromo[1-tert-butyl-3-phenyl-4-(*p*-tolyl)-1H-1,2,4-triazol-4-ium-5-yl]cuprate(I) (9) Yield: 87 %. ^1H NMR (400 MHz, CDCl_3): δ 7.44-7.40 (m, 1H, ArH), 7.37-7.30 (m, 4H, ArH), 7.23 (br, 4H, ArH), 2.39 (s, 3H, CH_3), 1.88 (s, 9H, $\text{C}(\text{CH}_3)_3$). ^{13}C NMR (125 MHz, CDCl_3): δ 177.8 ($\text{NC}_{\text{carb}}\text{N}$), 151.4 (NCN), 140.0 (ArC), 134.4 (ArC), 130.7 (ArC), 130.5 (ArC), 128.9 (ArC), 128.7 (ArC), 126.4 (ArC), 125.0 (ArC), 61.6 ($\text{C}(\text{CH}_3)_3$), 31.1 ($\text{C}(\text{CH}_3)_3$), 21.3 (CH_3). Anal. Calcd. (%) for $\text{C}_{19}\text{H}_{21}\text{BrCuN}_3$: C, 52.48; H, 4.87; N, 9.66. Found: C, 52.50, H, 4.91, N, 9.68. Mp 234-236 $^{\circ}\text{C}$.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Crystallographic tables and details (CIF) for compounds 2-5 and 7-9. See DOI: 10.1039/b000000x/

- (a) *Modern Gold Catalyzed Synthesis*, ed. A. S. K. Hashmi and F. D. Toste, WILEY-VCH, Weinheim, 2012; (b) *Gold: Science and Applications*, ed. C. Corti and R. Holliday, CRC Press, 2009; (c) *Gold Chemistry*, ed. F. Mohr, WILEY-VCH, Weinheim, 2009; (d) A. Laguna, T. Lasanta, J. M. López-de-Luzuriaga, M. Monge, P. Naumov and M. E. Olmos, *J. Am. Chem. Soc.*, 2010, **132**, 456; (e) J. C. Garrison and W. J. Youngs, *Chem. Rev.*, 2005, **105**, 3978; (f) I. J. B. Lin and C. S. Vasam, *Coord. Chem. Rev.*, 2007, **251**, 642; (g) J. C. Y. Lin, R. T. W. Huang, C. S. Lee, A. Bhattacharyya, W. S. Hwang and I. J. B. Lin, *Chem. Rev.*, 2009, **109**, 3561.
- For primary as well as recent references see: (a) Y. Fukuda and K. Utimoto, *J. Org. Chem.*, 1991, **56**, 3729; (b) J. H. Teles, S. Brode and M. Chabanas, *Angew. Chem. Int. Ed.*, 1998, **37**, 1415; (c) A. S. K. Hashmi and G. J. Hutchings, *Angew. Chem. Int. Ed.*, 2006, **45**, 7896; (d) A. Furstner and P. W. Davies, *Angew. Chem. Int. Ed.*, 2007, **46**, 3410; (e) A. S. K. Hashmi, *Chem. Rev.*, 2007, **107**, 3180; (f) A. S. K. Hashmi, *Angew. Chem. Int. Ed.*, 2010, **49**, 5232; (g) D. J. Gorin and F. D. Toste, *Nature*, 2007, **446**, 395; (h) C. Aubert, L. Fensterbank, P. Garcia, M. Malacria and A. Simonneau, *Chem. Rev.*, 2011, **111**, 1954; (i) N. Krause and C. Winter, *Chem. Rev.*, 2011, **111**, 1994; (j) T. C. Boorman and I. Larrosa, *Chem. Soc. Rev.*, 2011, **40**, 1910; (k) M. Rudolph and A. S. K. Hashmi, *Chem. Soc. Rev.*, 2012, **41**, 2448; (l) C. Nieto-Oberhuber, M. P. Munoz, S. Lopez, E. Jimenez-Nuner, C. Nevado, E. Herrero-Gomez, M. Raducan and A. M. Echavarren, *Chem. Eur. J.*, 2006, **12**, 1677; (m) C. Sperger and A. Fiksdahl, *Org. Lett.*, 2009, **11**, 2449; (n) M. Rudolph and A. S. K. Hashmi, *Chem. Commun.*, 2011, **47**, 6536.
- (a) P. D. Harvey, *Coord. Chem. Rev.*, 1996, **153**, 175; (b) H. Schmidbaur, F. Scherbaum, B. Huber and G. Mueller, *Angew. Chem., Int. Ed.*, 1988, **27**, 419; (c) F. Scherbaum, B. Huber, G. Mueller and H. Schmidbaur, *Angew. Chem., Int. Ed.*, 1988, **27**, 1542; (d) F. Scherbaum, A. Grohmann, B. Huber, C. Krueger and H. Schmidbaur, *Angew. Chem., Int. Ed.*, 1988, **27**, 1544.
- A. Maeland and T. B. Flanagan, *Can. J. Phys.*, 1964, **42**, 2364.
- G. A. Bishea and M. D. Morse, *J. Chem. Phys.*, 1991, **95**, 5646.
- A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441.
- (a) A. S. K. Hashmi and M. Rudolph, *Chem. Soc. Rev.*, 2008, **37**, 1766; (b) M. Chen and D. W. Goodman, *Chem. Soc. Rev.*, 2008, **37**, 1860; (c) R. Coquet, K. L. Howard and D. J. Willock, *Chem. Soc. Rev.*, 2008, **37**, 2046; (d) P. Pyykkö, *Chem. Soc. Rev.*, 2008, **37**, 1967; (e) V. W.-W. Yam and E. C.-C. Cheng, *Chem. Soc. Rev.*, 2008, **37**, 1806; (f) H. G. Raubenheimer and S. Cronje, *Chem. Soc. Rev.*, 2008, **37**, 1998; (g) H. Schmidbaur and A. Schier, *Chem. Soc. Rev.*, 2008, **37**, 1931; (h) M. J. Katz, K. Sakaib and D. B. Leznoff, *Chem. Soc. Rev.*, 2008, **37**, 1884; (i) N. Marion and S. P. Nolan, *Chem. Soc. Rev.*, 2008, **37**, 1776; (j) R. A. Sperling, P. R. Gil, F. Zhang, M. Zanella nad W. J. Parak, *Chem. Soc. Rev.*, 2008, **37**, 1896; (k) H. Häkkinen, *Chem. Soc. Rev.*, 2008, **37**, 1847; (l) G. J. Hutchings, M. Brust and H. Schmidbaur, *Chem. Soc. Rev.*, 2008, **37**, 1759; (m) D. J. Gorin, B. D. Sherry and F. D. Toste, *Chem. Rev.*, 2008, **108**, 3351; (n) M.-C. Daniel and D. Astruc, *Chem. Rev.*, 2004, **104**, 293; (o) A. Kishimura, T. Yamashita, K. Yamaguchi and T. Aida, *Nature*, 2005,

- 4, 546; (p) M. Enomoto, A. Kishimura and T. Aida, *J. Am. Chem. Soc.*, 2001, **123**, 5608; (q) A. Kishimura, T. Yamashita and T. Aida, *J. Am. Chem. Soc.*, 2005, **127**, 179; (r) V. W.-W. Yam, C.-L. Chan, C.-K. Li, and K. M.-C. Wong, *Coord. Chem. Rev.*, 2001, **216-217**, 173; (s) A. A. Mohamed, M. A. Rawashdeh-Omary, M. A. Omary and J. P. Frackler, Jr., *Dalton Trans.*, 2005, 2597; (t) A. Burini, A. A. Mohamed and J. P. Frackler, Jr., *Comm. Inorg. Chem.*, 2003, **24**, 253.
- For selected references see: (a) H. Schmidbaur, S. Cronje, B. Djordjevic and O. Schuster, *Chem. Phys.*, 2005, **311**, 151; (b) H. Schmidbaur, *Nature*, 2001, **413**, 31; (c) H. Schmidbaur, *Gold Bull.*, 2000, **33**, 3; (d) H. Schmidbaur, *Chem. Soc. Rev.*, 1995, 391; (e) P. Pyykkö, *Inorg. Chim. Acta*, 2005, **358**, 4113; (f) P. Pyykkö, *Angew. Chem., Int. Ed.*, 2004, **43**, 4412; (g) P. Pyykkö, *Chem. Rev.*, 1997, **97**, 597; (h) C.-M. Che and S.-W. Lai, *Coord. Chem. Rev.*, 2005, **249**, 1296; (i) M. A. Omary, M. A. Rawashdeh-Omary, M. W. A. Gonsler, O. Elbjairami, T. Grimes, T. R. Cundari, H. V. K. Diyabalanage, C. S. P. Gamage and H. V. Rasika Dias, *Inorg. Chem.*, 2005, **44**, 8200; (j) A. Sundararaman, L. N. Zakharov, A. L. Rheingold and F. Jäkle, *Chem. Commun.*, 2005, 1708; (k) J.-P. Zhang, Y.-B. Wang, X.-C. Huang, Y.-Y. Lin and X.-M. Chen, *Chem. Eur. J.*, 2005, **11**, 552; (l) W.-F. Fu, X. Gan, C.-M. Che, Q.-Y. Cao, Z.-Y. Zhou and N.-Y. N. Zhu, *Chem. Eur. J.*, 2004, **10**, 2228; (m) H. L. Hermann, G. Boche and P. Schwerdtfeger, *Chem. Eur. J.*, 2001, **7**, 5333; (n) C. Y. Chen, J. Y. Zeng and H. M. Lee, *Inorg. Chim. Acta*, 2007, **360**, 21; (o) X. Liu, G.-C. Guo, M.-L. Fu, X.-H. Liu, M.-S. Wang and J.-S. Huang, *Inorg. Chem.*, 2006, **45**, 3679; (p) L. Dobrzanska, H. G. Raubenheimer and L. J. Barbour, *Chem. Commun.*, 2005, 5050-5052; (q) A. A. Mohamed, L. M. Pérez and J. P. Frackler, Jr., *Inorg. Chim. Acta*, 2005, **358**, 1657.
- (a) A. J. Arduengo III, R. L. Harlow and M. Kline, *J. Am. Chem. Soc.*, 1991, **113**, 361. (b) A. J. Arduengo III, *Acc. Chem. Res.*, 1999, **32**, 913.
- (a) W. A. Herrmann and C. Köcher, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2162. (b) F. E. Hahn, *Angew. Chem., Int. Ed.*, 2006, **45**, 1348.
- D. S. Laitar, P. Müller, T. G. Gray and J. P. Sadighi, *Organometallics*, 2005, **24**, 4503.
- X. Xu, S. H. Kim, X. Zhang, A. K. Das, H. Hirao and S. H. Hong, *Organometallics*, 2013, **32**, 164.
- P. de Frémont, N. M. Scott, E. D. Stevens, S. P. Nolan, *Organometallics*, 2005, **24**, 2411.
- H. M. J. Wang, C. S. Vasam, T. Y. R. Tsai, S.-H. Chen, A. H. H. Cahng and I. J. B. Lin, *Organometallics*, 2005, **24**, 486.
- W. F. Gabrielli, S. D. Nogai, J. M. McKenzie, S. Cronje and H. G. Raubenheimer, *New J. Chem.*, 2009, **33**, 2208.
- G. D. Frey, R. D. Dewhurst, S. Kousar, B. Donnadiou and G. Bertrand, *J. Organomet. Chem.*, 2008, **693**, 1674.
- A. S. K. Hashmi, D. Riedel, M. Rudolph, F. Rominger and T. Oeser, *Chem. Eur. J.*, 2012, **18**, 3827.
- F. H. Allen, *Acta Cryst.*, 2002, **B58**, 380.
- (a) E. Tkatchouk, N. P. Mankad, D. Benitez, W. A. Goddard, III and F. D. Toste, *J. Am. Chem. Soc.*, 2011, **133**, 14293; (b) D. Wang, R. Cai, S. Sharma, J. Jirak, S. K. Thummanapelli, N. G. Akhmedov, H. Zhang, X. Liu, J. L. Petersen and X. Shi, *J. Am. Chem. Soc.*, 2012, **134**, 9012; (c) D. Weber and M. R. Gagné, *Chem. Sci.*, 2013, **4**, 335; (d) J. Roithová, Š. Janková, L. Jašíková, J. Váňa and S. Hybelbauerová, *Angew. Chem., Int. Ed.*, 2012, **51**, 8378; (e) P. H.-Y. Cheong, P. Morganelli, M. R. Luzung, K. N. Houk and F. D. Toste, *J. Am. Chem. Soc.*, 2008, **130**, 4517; (f) A. S. K. Hashmi, I. Braun, M. Rudolph and F. Rominger, *Organometallics* 2012, **31**, 644; (g) A. S. K. Hashmi, M. Wietek, I. Braun, P. Nosel, L. Jongbloed, M. Rudolph and F. Rominger, *Adv. Synth. Catal.*, 2012, **354**, 555; (h) A. S. K. Hashmi, I. Braun, P. Nosel, J. Schadlich, M. Wietek, M. Rudolph and F. Rominger, *Angew. Chem., Int. Ed.*, 2012, **51**, 4456; (i) L. Ye, Y. Wang, D. H. Aue and L. Zhang, *J. Am. Chem. Soc.*, 2012, **134**, 31.

- 20 C. Sarcher, A. Lühl, F. C. Falk, S. Lebedkin, M. Kühn, C. Wang, J. Paradies, M. M. Kappes, W. Klopffer and P. W. Roesky, *Eur. J. Inorg. Chem.*, 2012, 5033.
- 21 (a) J. Li and P. Pyykkö, *Chem. Phys. Lett.*, 1992, **197**, 586; (b) P. Pyykkö, N. Runeberg and F. Mendizabal, *Chem. Eur. J.*, 1997, **3**, 1451; (c) P. Pyykkö and F. Mendizabal, *Chem. Eur. J.*, 1997, **3**, 1458; (d) N. Runeberg, M. Schütz and H.-J. Werner, *J. Chem. Phys.*, 1999, **110**, 7210; (e) P. Pyykkö and Y. Zhao, *Angew. Chem., Int. Ed.*, 1991, **30**, 604; (f) P. Pyykkö and M. Straka, *Phys. Chem. Chem. Phys.*, 2000, **2**, 2489; (g) S.-L. Sun, G.-C. Yang, C.-S. Qin, Y.-Q. Qiu, L.-K. Yan, Z.-M. Su and R.-S. Wang, *Int. J. Quantum Chem.*, 2010, **110**, 865.
- 22 (a) L. Ray, M. M. Shaikh and P. Ghosh, *Inorg. Chem.*, 2008, **47**, 230; (b) J. Muñoz, C. Wang and P. Pyykkö, *Chem. Eur. J.*, 2011, **17**, 368.
- 23 H. Schmidbaur and A. Schier, *Chem. Soc. Rev.*, 2012, **41**, 370.
- 24 B. Pinter, L. Broeckaert, J. Turek, A. Růžička and F. De Proft, *Chem. Eur. J.*, 2014, **20**, 734.
- 25 J. Turek, I. Panov, M. Horáček, Z. Černošek, Z. Padělková and A. Růžička, *Organometallics*, 2013, **32**, 7234.
- 26 J. Turek, I. Panov, M. Semler, P. Štěpnička, F. De Proft, Z. Padělková and A. Růžička, *Organometallics*, 2014, **33**, 3108.
- 27 (a) C. P. Newman, G. J. Clarkson and J. P. Rourke, *J. Organomet. Chem.*, 2007, **692**, 4962; (b) W.-H. Yang, C.-S. Lee, S. Pal, Y.-N. Chen, W.-S. Hwang, I. J. B. Lin and J.-C. Wang, *J. Organomet. Chem.*, 2008, **693**, 3729; (c) H.-L. Su, L. M. Pérez, S.-J. Lee, J. H. Reibenspies, H. S. Bazzi and D. E. Bergbreiter, *Organometallics*, 2012, **31**, 4063.
- 28 (a) X. Wang, S. Liu, L.-H. Weng and G.-X. Jin, *Organometallics*, 2006, **25**, 3565; (b) Q.-X. Liu, H.-L. Li, X.-J. Zhao, S.-S. Ge, M.-C. Shi, G. Shen, Y. Zang and X.-G. Wang, *Inorg. Chim. Acta*, 2011, **376**, 437; (c) C. Topf, S. Leitner and U. Monkowius, *Acta Crystallogr. Sect. E: Struct. Rep. Online*, 2012; **68**, m272.
- 29 (a) T. Sato, Y. Hirose, D. Yoshioka, T. Shimojo and S. Oi, *Chem. Eur. J.*, 2013, **19**, 15710; (b) C. Dash, M. M. Shaikh, R. J. Butcher and P. Ghosh, *Inorg. Chem.*, 2010, **49**, 4972; (c) L. Ray, M. M. Shaikh and P. Ghosh, *Organometallics*, 2007, **26**, 958.
- 30 (a) A. Růžička, V. Pejchal, J. Holeček, A. Lyčka and K. Jacob, *Collect. Czech. Chem. Commun.*, 1998, **63**, 977; (b) T. Weidlich, L. Dušek, B. Vystrčilová, A. Eisner, P. Švec and A. Růžička, *Appl. Organomet. Chem.*, 2012, **26**, 293.
- 31 (a) P. Švec, P. Novák, M. Nádvořník, Z. Padělková, I. Císařová, A. Růžička and J. Holeček, *J. Fluorine Chem.*, 2007, **128**, 1390; (b) P. Švec, A. Eisner, L. Kolářová, T. Weidlich, V. Pejchal and A. Růžička, *Tetrahedron Lett.*, 2008, **49**, 6320; (c) P. Švec, A. Růžička, *Main Group Met. Chem.*, 2011, **34**, 7.
- 32 (a) C. Hirtenlehmer, C. Krims, J. Hölbling, M. List, M. Zabel, M. Fleck, R. J. F. Berger, W. Schoeferberger and U. Mokowius, *Dalton Trans.*, 2011, **40**, 9899; (b) M. V. Baker, P. J. Barnard, S. K. Brayshaw, J. L. Hickey, B. W. Skelton and A. H. White, *Dalton Trans.*, 2005, 37.
- 33 H. M. J. Wang and I. J. B. Lin, *Organometallics*, 1998, **17**, 972.
- 34 (a) K. M. Lee, H. M. J. Wang and I. J. B. Lin, *J. Chem. Soc., Dalton Trans.*, 2002, 2852; (b) X.-Q. Xiao and G.-X. Jin, *Dalton Trans.*, 2009, 9298; (c) W. Huang, R. Zhang, G. Zou, J. Tang and J. Sun, *J. Organomet. Chem.*, 2007, **692**, 3804; (d) A. A. D. Tulloch, A. A. Danopoulos, S. Winston, S. Kleinhenz and G. Eastham, *J. Chem. Soc., Dalton Trans.*, 2000, 4499; (e) Y. Li, X. Chen, Y. Song, L. Fang and G. Zou, *Dalton Trans.*, 2011, **40**, 2046.
- 35 O. Guerret, S. Solé, H. Gornitzka, M. Teichert, G. Trinquier and G. Bertrand, *J. Am. Chem. Soc.*, 1997, **119**, 6668.
- 36 (a) X.-F. Zheng and L.-G. Zhu, *Cryst. Growth Des.*, 2009, **9**, 4407; (b) R. Santra and K. Biradha, *Cryst. Growth Des.*, 2010, **10**, 3315.
- 37 (a) B. R. M. Lake and C. E. Willans, *Chem. Eur. J.*, 2013, **19**, 16780; (b) S. Diez-González, E. C. Escudero-Adán, J. Benet-Buchholz, E. D. Stevens, A. M. Z. Slawin and S. P. Nolan, *Dalton Trans.*, 2010, **39**, 7595; (c) A. A. D. Tulloch, A. A. Danopoulos, S. Kleinhenz, M. E. Light, M. B. Hurthouse and G. Eastham, *Organometallics*, 2001, **20**, 2027.
- 38 M. Camalli and F. Caruso, *Inorg. Chim. Acta*, 1987, **127**, 209.
- 39 S. Patt and J. N. Shoolery, *J. Magn. Reson.*, 1982, **46**, 535.
- 40 Z. Otwinowski and W. Minor, *Methods Enzymol.*, 1997, **276**, 307.
- 41 P. Coppens, in *Crystallographic Computing*, ed. F. R. Ahmed, S. R. Hall and C. P. Huber, Munksgaard, Copenhagen, 1970, pp. 255.
- 42 A. Altomare, G. Casciarano, C. Giacovazzo and A. Guagliardi, *J. Appl. Crystallogr.*, 1993, **26**, 343.
- 43 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **64**, 112.