Metallophilic Interactions

Tri- and Tetranuclear Metal-String Complexes with Metallophilic d^{10}–d^{10} Interactions

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Dedicated to Prof. Dr. Hubert Schmidbaur on the occasion of his 85th birthday

Abstract: The reaction of 2,6-F_2C_6H_5SiMe_3 with Ph_3P*Li provided 2,6-(Ph_3P)*C_6H_5SiMe_3 (1), which can be regarded as precursor for the novel anionic tridentate ligand [2,6-(Ph_3P)*C_6H_5]^- (PCP)^-. The reaction of 1 with [AuCl(tht)] (tht = tetrahydrothiophene) afforded 2,6-(Ph_3P)*C_6H_5SiMe_3 (2). The subsequent reaction of 2 with CsF proceeded with elimination of Me_3SiF and yielded the neutral tetranuclear complex linear-[Au_4Cl_2(PCP)]_2 (3) comprising a string-like arrangement of four Au atoms. Upon chloride abstraction from 3 with NaBAr_4, (Ar’ = 3,5-(CF_3)_2C_6H_3) in the presence of tht, the formation of the dicationic tetranuclear complex linear-[Au_4(PCP),(tht)]_2(BAr_4’)]_2 (4) was observed, in which the string-like structural motif is retained. Irradiation of 4 with UV light triggered a facile rearrangement in solution giving rise to the dicaticonic tetranuclear complex cyclo-[Au_4(PCP),(tht)]_2(BAr_4’)]_2 (5), which comprises a rhomboidal motif of four Au atoms. In 3–5, the Au atoms are associated by a number of significant aurophilic interactions. The atom-economic and selective reaction of 3 with HgCl yielded the neutral trinuclear bimetallic complex [HgAu_3Cl_3(PCP)] (6) comprising significant metallophilic interactions between the Au and Hg atoms. Therefore, 6 may be also regarded as a metalloporic complex [ClHg(AuCuI)] between Hg^3 and the anionic tridentate ligand [2,6-(Ph_3P)*C_6H_5]^- (AuCuI) containing a central carbonanionic binding site and two “gold”-arms” contributing pincer-type chelation through metallophilic interactions. Compounds 1–6 were characterized experimentally by multinuclear NMR spectroscopy and X-ray crystallography and computationally using a set of real-space bond indicators (RBSIs) derived from electron density (ED) methods including Atoms In Molecules (AIM), the Electron Localizability Indicator (ELI-D) as well as the Non-Covalent Interaction (NCI) Index.

Introduction

Metallophilic interactions are structurally directing, attractive forces between two or more closed-shell metal ions that prefer low coordination numbers. From a quantum-mechanical point of view, metallophilic interactions are mostly dispersive forces that are significantly enhanced by relativistic effects. Given that relativistic effects dramatically increase for the post-lanthanide elements and reach a maximum for gold in the sixth period, linearly coordinated, 12 valence-electron complexes of Au^3 and Hg^3 both having a 5d^{10}6s^2 electron configuration are the most prominent closed-shell metal species showing metallophilic interactions. In addition to pure aurophilic [3] and mercurophilic [4] interactions, an increasing number of heteronuclear metal–metal contacts [5] for example, of the Au–Hg type [5], have been observed in recent years. Metallophilic interactions are often related to interesting photophysical phenomena such as luminescence. Since the first publication on a photoluminescent gold complex by the group of Dori in 1970 [6], numerous examples of photoluminescence based on aurophilic interactions have been reported. [7] Given that bond energies associated with metallophilic interactions rarely exceed 50 kJ mol^-1, multidentate substitutents or ligands often play a critical role to support multinuclear complexes in which the metal atoms are fixed in close proximity to each other. In this regard, the 2-diphenylphosphinophenyl ligand (I) and derivatives thereof have been frequently used to prepare a
number of dinuclear AuI–AuI complexes, which were for instance the starting materials for the preparation of interesting AuII–AuII complexes through oxidative-addition reactions (Scheme 1). In this work we report on tri- and tetranuclear AuI and HgII complexes derived from the related 2,6-bis(diphenyloxiphosphino)phenyl ligand (II, Scheme 1), which were prepared through a novel synthetic route using a trimethylsilyl substituent as protecting group. The 2,6-bis(diphenyloxiphosphino)phenyl ligand II is isoelectronic to the 2,6-bis(diphenyloxiphosphino)pyridine ligand (III), which has been utilized previously for the preparation of interesting complexes including some metallostrings complexes, which hold promise as molecular wire materials (Scheme 1). The 2,6-bis(diphenyloxiphosphino)phenyl ligand II is also closely related to the diphosphinyl NHG ligand IV and related ligand systems, which were introduced recently (Scheme 1) and were shown to stabilize poly-homo and heterometallic complexes showing metallophilic interactions.

Results and Discussion

Synthetic aspects

The reaction of 2,6-F2C6H4SiMe3 with Ph2PLi provided 2,6-(Ph2P)2C6H4SiMe3 (1) as a colorless solid in 54% yield (Scheme 2). The 31P(1H) NMR spectrum of 1 dissolved in CDCl3 shows a characteristic singlet at δ = −6.4 ppm. The corresponding 29Si NMR resonance is observed as a triplet (J_{Si,P} = 7.8 Hz) in the 29Si(1H) NMR spectrum at δ = −3.0 ppm. The complex [2,6-(Ph2PAuCl)2C6H4SiMe3] (2) was readily prepared through the reaction of 1 with two equivalents of [AuCl(tht)] (Scheme 2). The reaction occurred instantaneously at ambient temperature when both reactants were suspended in dichloromethane. Subsequent crystallization gave 2 as colorless crystals in 90% yield. The coordination of the two P atoms to Au gives rise to a significant shift of the 31P NMR resonance to higher frequencies than 1. The 31P(1H) NMR spectrum of 2 dissolved in [D6]DMSO reveals a singlet at δ = 33.8 ppm for two chemically equivalent 31P nuclei. Note that the poor solubility of 2, even in DMSO, precluded the acquisition of a 31Si(1H) NMR spectrum with sufficient signal intensity. However, the 1H NMR resonance associated with the (CH3)2Si group is observed at δ = 0.58 ppm. Heating a mixture of 1, [Au(tht)Cl], and anhydrous CsF as a suspension in THF/CH3CN (1:1) at 60 °C proceeded with elimination of Me3SiF and gave rise to the formation of the neutral tetranuclear complex linear-[Au2Cl(μ-P)4][(PCP)2PCP] (3, PCP = 2,6-(Ph3P)2C6H4) that was obtained as yellow prisms in 60% yield after recrystallisation from CH3Cl/n-hexane (Scheme 2). Inversion of the 31P(1H) NMR spectrum of 3 in CD2Cl2 shows two 31P NMR singlet resonances at δ = 36.6 and 36.0 ppm associated with two sets of two chemically inequivalent phosphorus nuclei. That is, two Ph2P moieties coordinate to Au atoms with Cl− ligands in mutual trans-position (inorganic coordination site) and the remaining two Ph2P donors coordinate to the two carbon-bound Au atoms in mutual trans-position (organometallic coordination site). The 29Si(1H) NMR spectrum shows no signal indicating the loss of the Me3Si group in complex 3. Coherently, no resonance corresponding to the CH3 group of the (CH3)2Si group is observed in the 1H NMR spectrum. Moreover, when the reaction was monitored in situ in a closed NMR tube, the formation of Me3SiF was observed indicated by the characteristic multiplet resonance in the 19F NMR spectrum at −159.6 ppm. Chloride abstraction from complex 3 employing NaBARF4 (ArF = 3,5-(CF3)2C6H4) in the presence of tht readily gave the dicaticonic tetranuclear complex linear-[Au2(PCP)2(μ-tht)2](BARF4)2 (4) with full conversion. Complex 4 is light sensitive and consequently, the reaction was performed in the dark. With respect to 3, the 31P(1H) NMR spectrum of 4 similarly reveals two sets of characteristic singlet resonances at δ = 39.5 and 35.1 ppm, each associated with two chemically inequivalent 31P nuclei. One set resides in the internal organometallic coordination site and one set remains in the terminal inorganic coordination site. When the reaction mixture was subsequently exposed to UV light (λmax = 366 nm), an rearrangement and thus quantitative formation of the dicaticonic tetranuclear complex cyclo-[Au2(PCP)2(μ-tht)2](BARF4)2 (5) was observed. The rearrangement coincides with an increase in symmetry as signaled by the presence of a singlet resonance at δ = 44.4 ppm in the 31P(1H) NMR spectrum (CD2Cl2). All 31P nuclei in 5 reside in an indistinguishable chemical environment with all
Ph₂P donors in mutual cis-position coordinated to a terminal Au atom. Complex 5 was isolated as colorless crystals after recrystallization from CH₂Cl₂/petroleum ether. Noteworthy, complex 5 is stable towards moisture and air and only decomposes above 218°C. The transmetalation of organogold compounds with Cu[12c] or Hg[14] salts has been previously reported. The atom-economic reaction of 3 with HgCl₂ in CH₂Cl₂ proceeded with disaggregation of the tetranuclear complex and formation of Hg@Ca and Au@Cl bonds and produced the neutral trinuclear complex [HgAu₂Cl₃(PCP)] (6) in 96% yield (Scheme 2). A ¹⁹⁹Hg{¹H} NMR spectrum of 6 was recorded in CD₂Cl₂. The observed triplet resonance at δ = -841.5 ppm shows a significant Hg–P coupling with a ¹J₃₁₉₉₋₃₈₃ coupling constant of 327 Hz. Conversely, the ³¹P{¹H} NMR spectrum has a singlet resonance at δ = 42.3 ppm, signifying two Ph₂P moieties with identical chemical environment, with ¹⁹⁹Hg satellites exhibiting a ¹J₃₁₉₉₋₃₈₃ coupling constant of 327 Hz.

Molecular structures

Precise structural information was obtained from X-ray crystallography. The molecular structures of 1–6 are shown in Figure 1–Figure 5. Selected bond lengths are collected in the caption of the figures. In all structures the Au¹ and Hg² atoms adopt almost linear spatial arrangements as anticipated for complexes with a 14 valence-electron count. The related Au–C, Au–P, Au–S, Au–Cl, Hg–C, and Hg–Cl bond distances exhibit typical lengths.[5,6,9] In the structure of 2 the Me₃Si group is still present after the complexation of the two Au atoms (Figure 1). However, the displacement of the Si atom from the plane defined by the central phenyl ring increases notably upon going from 1 (0.072(1)) to 2 (0.219(1) Å), which might be a sign for the Si–C bond activation in 2. However, the Si–C bond lengths of 1 (1.8721(1)) and 2 (1.878(6) Å) are indistinguishable within the experimental error. The molecular structures of 3 and 4 (Figure 2 and Figure 3) reveal a string arrangement of four Au atoms, which are associated by three Au–Au contacts (2.8280(5) to 3.0567(4) Å). The contact distances between the inner Au1 and Au3 atoms in 3, 2.8280(5) Å are significantly shorter than the intermetallic distances in similar cationic or neutral string gold complexes that display aurophilic interactions (e.g. for [Au₄(dpmp)₂(SCN)]²⁺ the distance between the inner Au atoms is 3.0049(8) Å (dpmp = bis(diphenylphosphinomethyl)phosphine).[15] The neutral complex 3 entails two sets of two Au atoms in equivalent chemical environment: the organometallic coordination site encompasses two Au atoms each coordinated by a phenylate—and the Ph₂P donor moiety in mutual trans-position (Au1 and Au3). This pattern gives rise to a linear coordination sphere around Au atoms located in the center of the Au₄ string. The second set

Scheme 2. Synthesis and ³¹P NMR chemical shifts in ppm of 1–6.
of Au atoms terminate the Au string and reside likewise in a linear coordination motif. A P donor and a Cl ligand in mutual trans-position build this linear coordination pattern (Au2 and Au4). The related dicationic complex 4 is centrosymmetric but retains the string-like Au motif with its internal organometallic coordination site around Au1 and Au1a and the terminal inorganic coordination site. Due to the abstraction of both Cl ligands and the introduction of tht, the terminal Au moieties (Au2/Au2a) are coordinated by the P donor of the PCP ligand and the sulfur donor stemming from the thioether (tht), both in mutual trans-arrangement. Two weakly coordinating [BAR4]− anions maintain the charge compensation for the dicationic complex. In contrast, the molecular structure of 5 (Figure 4) shows a planar rhomboidal motif with five significant Au–Au interactions (2.9980(3) to 3.1356(3) Å) in the cycle defined by Au1, Au2, Au1a, and Au2a, that are comparable to other similar complexes stabilized by tripodal phosphine ligands (dpmp) reported recently. The increase in number of aurophilic contacts is due to the rhomboidal arrangement and the additional trans-annular contact Au1···Au1a (3.1118(5) Å), which might be the thermodynamic driving force for the rearrangement of 4 into 5. This rearrangement results into a redistribution of the ligands in organometallic and inorganic coordination sites. The gold atoms Au2 and Au2a show a homoleptic linear coordination of two Ph2P donors in mutual trans-position, whereas the organometallic coordination site shows a mutual trans-arrangement of a phenylate and a tht moiety to each gold atom of this site (Au1 and Au1a). The crystal structure of 6 comprises two crystallographically independent conformers, in which the two Au atoms chelate the central Hg atom (Figure 5). In this way, the two conformers adopt Au–Hg–Au transoid and cisoid arrangements, respectively. Overall, the Au–Hg contacts of 6 (3.0253(4) to 3.4082(4) Å) are somewhat longer than the Au–Au contacts in 3–5, but are close to intermolecular Au–Hg distances (3.097(2)–3.498(3) Å) observed recently for a number of so called molecular Au–Hg amalgams, as well as the intramolecular Au–Hg distances (3.112(1)–3.2940(9) Å) observed for some similar complexes. Complex 6 may be also regarded as a metallo-pincer
complex $[\text{ClHg(AuCAu)}]$ between $\text{Hg}^{II}$ and the anionic tridentate ligand $[2,6-(\text{Ph}_2\text{PAuCl})_2\text{C}_6\text{H}_3]^-$ ($\text{AuCAu}^-$) containing a central carbanionic binding site and two “gold-arms” contributing pincer-type chelation through metallophilic interactions. In a more general way, the ($\text{PCP}$)-ligand II is extended by two metal units, which are coordinated to the $\text{PPh}_2$ moieties in a linear fashion giving rise to an ($\text{MCM}$)-metallo pincer ligand V comprised of a central carbanionic donor and two “metal-arms” providing pincer-type chelation through metallophilic interactions (Scheme 1).

**Photophysical properties**

Only in case of 3, bright luminescence can be observed upon exposure to UV-A light. The UV/Vis absorption spectrum and the emission spectrum of 3 in $\text{CH}_2\text{Cl}_2$ solution are shown in Figure 6a. An absorption maximum at 365 nm and another strong absorption band reaching into the UV region below 250 nm are observed. The emission spectra in $\text{CH}_2\text{Cl}_2$ solution and in the solid state reveal maxima at 538 and 539 nm, respectively, which is associated with the emission of yellow-
green light. Photoluminescence quantum yields of 4.3% in dichloromethane solution and 17% in the solid state were found. Similar emissive properties although at higher quantum yields in solution or solid state, have been reported for linear polynuclear string gold complexes.[17]

The photoluminescence spectrum of 3 in the solid state is shown in Figure 6b.

DFT analysis

Complementing the interpretation of the structural parameters, electronic bond characteristics of the metallophilic Au···Au and Au···Hg interactions were examined in terms of computed real-space bonding indicators (RSBI). All calculations are based on the experimentally obtained XRD structures with C–H distances corrected in order to obey neutron diffraction results.[19] The RSBI set comprises parameters extracted from topological analysis of the electron and pair densities according to the Atoms In Molecules (AIM)[20] and Electron Localizability Indicator (ELI-D)[21] space-partitioning schemes as well as a surface study within the framework of the recently introduced Non-Covalent Interactions (NCI) index,[22] which is based on the reduced density gradient (s) of the electron density (ED) and unravels noncovalent interaction areas. Thus, the NCI transcend topological approaches, which mainly rely on stationary point analysis as it also detects weak intra- and intermolecular interactions, such as London dispersion,[23] for which not essentially bond-critical points (bcp) are detectable in the underlying ED. By mapping the second Eigenvalue (λ2) of the ED-Laplacian (\(\nabla^2p = \lambda_1 + \lambda_2 + \lambda_3\)) on s, bonding (\(\lambda_2 < 0\)) can be distinguished from weak Van der Waals (VdW) forces (\(\lambda_2 \approx 0\)), or steric repulsion (\(\lambda_2 > 0\)). The topological AIM bond paths’ motifs, which are typically referred to resemble the molecular structures, are displayed in Figures 7–Figure 9 for compounds 3, 4, 5, as well as the transoid and cisoid conformers of 6. For all cases, metallophilic Au···Au or Au···Hg attraction is disclosed by formation of corresponding bcp in the ED, the topological parameters of which are typical for this kind of interactions (Table 1).[6,24] The low value of the ED at the bcp (\(\rho_{bcp}\) approx. 0.1–0.3 e Å\(^{-3}\)), the positive but close to zero value of the Laplacian (\(\nabla^2\rho\) approx. 1–3 e Å\(^{-5}\)), as well as the dominance of the kinetic energy density over ED ratio (\(G/\rho_{bcp}\) approx. 0.6–0.8 e Å\(^{-1}\)) against the total energy density over ED ratio (\(H/\rho_{bcp}\) approx. −0.2–0.0 e Å\(^{-1}\)) uncovers these contacts to be mainly noncovalent.

Figure 5. Molecular structures of the two independent conformers of 6 showing 50% probability ellipsoids and the crystallographic numbering Scheme. Selected bond lengths (Å): Hg1–Cl10 2.072(7), Hg2–C60 2.076(8), Hg1–C13 2.307(2), Hg2–C16 2.302(2), Au1–P1 2.235(2), Au2–P2 2.238(2), Au3–P3 2.239(2), Au4–P4 2.232(2), Au1–C11 2.283(2), Au2–C12 2.295(2), Au3–C14 2.284(2), Au4–C15 2.284(2), Au1–Hg1 3.287(4), Au2–Hg1 3.099(5), Au3–Hg2 3.408(2), Au4–Hg2 3.025(3).

Figure 6. (a) Absorption (solid line) and emission (dashed line, a.u.) spectrum of 3 in CH\(_2\)Cl\(_2\) solution. (b) Emission spectrum of 3 in the solid state (excitation at 365 nm).
lent (Table 1). This is supported by the integrated delocalization
index, $\delta(A,B)$, which quantifies the number of electron
pairs shared between two adjacent or distant atoms and lies in
the range of 0.2 to 0.4. Similar values are typically observed for
ionic atom-atom contacts with the only difference that $\nabla^2\rho_{\text{bcp}}$
and $G/\rho_{\text{bcp}}$ values are larger positive for the latter. Consequent-
ly, the NCI surface analysis of 3–6 shows pronounced features
along the Au···Au and Au···Hg interaction axes in terms of disc-
shaped reduced density gradient basins with highly negative
$\lambda_2$ values on the surface suggesting attractive metallophilic in-
teractions (Figures 7), whereas no corresponding ELI-D basins
are formed (Figure 8, Figure 9). In the NCI, weaker attractive
or even repelling H···H and H···$\pi$ interactions are also observed,
which determine the spatial orientation of the different molec-
ular fragments (e.g. phenyl groups) and thus the three-dimen-
sional appearance of the molecule in the crystal. With a consid-
erably higher ED at the bcp of about 0.7–0.9 Å$^{-3}$ but Laplac-
ian values (approx. 1–5 Å$^{-5}$) similar to the Au···Au and Au···Hg
bonds the Au/Hg–Cl/P/C bonds combine covalent as well as
noncovalent bonding aspects and may thus be regarded as polarized covalent.

Accordingly, both $G/\rho_{\text{bcp}}$ (approx. 0.6–0.9 ke$^{-1}$) and $H/\rho_{\text{bcp}}$
(approx. −0.5–0.4 ke$^{-1}$), show strongly positive and negative
values, respectively. The covalent character is further supported
by $\delta(A,B)$ being close to or even above 1 and the formation of
Au–Cl/P and Hg–Cl/C bonding basins in the ELI-D (Figure 8).
Due to the higher Pauling electronegativity of Au atoms (2.4)
compared with Hg atoms (1.9) the AIM atomic charges are
close to zero for the former ($Q_{\text{AIM}}(\text{Au}) = 0.09–0.07$ e), but posi-
tive for the latter ($Q_{\text{AIM}}(\text{Hg}) = 0.64–0.65$ e), which confirms previ-
sous results. As anticipated, Cl atomic charges are negative
(approx. −0.5 e), whereas P atomic charges are highly positive
(approx. 1.8 e) within AIM space-partitioning (see the Support-
ing Information, Tables S3–S6 for a full list).

Figure 7. AIM bond paths’ motifs and NCI isosurfaces ($s = 0.5$) of compounds 3 (left) and 4 (right). Atom colors are as follows: Au = gold, Cl = green, P = pink, C = grey, H = white.
Table 1. Topological bond descriptors and delocalization index of prominent bonds of 3–6.

| Bond | \(d\) [Å] | \(d_i/d\) | \(\rho_{bcp}\) [e Å\(^{-3}\)] | \(\nabla^2 \rho_{bcp}\) [e Å\(^{-5}\)] | \(\varepsilon\) | \(G/\rho_{bcp}\) [a.u.] | \(H/\rho_{bcp}\) [a.u.] | \(\delta(A,B)\) |
|------|------------|----------|-------------------------------|-------------------------------|--------|----------------|----------------|--------|
| 3    | Au1–Au2   | 2.983    | 0.50                          | 0.23                          | 1.9    | 0.05           | 0.70           | –0.12  | 0.36    |
|      | Au3–Au4   | 2.945    | 0.50                          | 0.25                          | 2.1    | 0.06           | 0.72           | –0.13  | 0.38    |
|      | Au1–Au3   | 2.843    | 0.50                          | 0.30                          | 2.5    | 0.03           | 0.76           | –0.17  | 0.43    |
|      | Au2–Cl1   | 2.292    | 0.50                          | 0.70                          | 5.3    | 0.00           | 0.90           | –0.37  | 1.01    |
|      | Au2–P1    | 2.238    | 0.52                          | 0.85                          | 1.7    | 0.01           | 0.64           | –0.50  | 1.02    |
|      | Au1–C\(\text{ch}\) | 2.068 | 0.54                          | 0.90                          | 4.0    | 0.04           | 0.78           | –0.46  | 0.91    |
| 4    | Au1–Au2   | 2.910    | 0.50                          | 0.27                          | 2.2    | 0.04           | 0.73           | –0.15  | 0.41    |
|      | Au1–Au1a  | 2.827    | 0.50                          | 0.31                          | 2.6    | 0.04           | 0.76           | –0.18  | 0.44    |
|      | Au1a–Au2a | 2.910    | 0.50                          | 0.27                          | 2.2    | 0.04           | 0.73           | –0.15  | 0.41    |
|      | Au2–S1    | 2.338    | 0.50                          | 0.69                          | 4.2    | 0.03           | 0.80           | –0.38  | 0.87    |
|      | Au1–C\(\text{ch}\) | 2.052 | 0.54                          | 0.93                          | 4.0    | 0.03           | 0.77           | –0.48  | 0.92    |
| 5    | Au1a–Au2a | 2.998    | 0.50                          | 0.22                          | 1.9    | 0.10           | 0.72           | –0.11  | 0.31    |
|      | Au1–Au1a  | 3.111    | 0.50                          | 0.18                          | 1.6    | 0.10           | 0.69           | –0.07  | 0.25    |
|      | Au1a–Au2  | 3.135    | 0.50                          | 0.17                          | 1.5    | 0.16           | 0.67           | –0.07  | 0.24    |
|      | Au1–Au2   | 2.998    | 0.50                          | 0.22                          | 1.9    | 0.10           | 0.72           | –0.11  | 0.31    |
|      | Au2–P1a   | 2.319    | 0.51                          | 0.75                          | 1.7    | 0.01           | 0.60           | –0.45  | 0.88    |
|      | Au1–S1    | 2.339    | 0.50                          | 0.69                          | 4.3    | 0.02           | 0.82           | –0.38  | 0.84    |
|      | Au1–C\(\text{ch}\) | 2.024 | 0.55                          | 0.99                          | 3.7    | 0.04           | 0.76           | –0.50  | 0.95    |
|      | Au2–H\(\text{tht}\) | 2.952 | 0.63                          | 0.96                          | 0.5    | 0.17           | 0.59           | 0.08   | 0.04    |
| trans-6 | Au1–Hg1  | 3.288    | 0.51                          | 0.13                          | 1.1    | 0.33           | 0.61           | –0.01  | 0.18    |
|        | Au2–Hg1   | 3.099    | 0.51                          | 0.18                          | 1.6    | 0.14           | 0.67           | –0.05  | 0.25    |
|        | Hg1–C\(\text{ph}\) | 2.073 | 0.55                          | 0.90                          | 3.0    | 0.04           | 0.70           | –0.46  | 0.88    |
|        | Au1–C\(\text{ph}\) | 2.262 | 0.50                          | 0.72                          | 5.3    | 0.00           | 0.90           | –0.38  | 1.06    |
|        | Au1–P1    | 2.236    | 0.52                          | 0.85                          | 1.6    | 0.01           | 0.64           | –0.50  | 1.03    |
| cis-6 | Au3–Hg2   | 3.408    | 0.52                          | 0.11                          | 0.9    | 0.87           | 0.58           | 0.03   | 0.15    |
|        | Au4–Hg2   | 3.026    | 0.51                          | 0.20                          | 1.8    | 0.10           | 0.70           | –0.08  | 0.28    |
|        | Hg1–C\(\text{ph}\) | 2.075 | 0.55                          | 0.90                          | 3.0    | 0.04           | 0.70           | –0.46  | 0.88    |
|        | Au3–Cl1   | 2.285    | 0.50                          | 0.72                          | 5.3    | 0.00           | 0.89           | –0.38  | 1.07    |
|        | Au3–F3    | 2.239    | 0.52                          | 0.84                          | 1.8    | 0.00           | 0.64           | –0.50  | 1.03    |

\(\rho_{bcp}\): electron density, \(\nabla^2 \rho_{bcp}\): Laplacian, \(d_i/d\): ratio, \(\varepsilon\): bond ellipticity, \(G/\rho_{bcp}\) and \(H/\rho_{bcp}\): kinetic and total energy density over \(\rho_{bcp}\) ratios, \(\delta\): delocalization index.

Figure 8. AIM bond paths' motifs and NCI isosurfaces (s = 0.5) of compound 5. Atom colors are as follows: Au = gold, Cl = green, P = pink, C = grey, H = white.
Summary and Conclusions

The synthesis and characterization of the tetranuclear gold complexes $\text{linear-}[\text{Au}_4\text{Cl}_2(\text{PCP})_2]$ (3), $\text{linear-}[\text{Au}_4(\text{PCP})_2(\text{tht})_2][\text{BAR}_4]^-$ (4), $\text{cyclo-}[\text{Au}_4(\text{PCP})_2(\text{tht})][\text{BAR}_4]^-$ (5), and the trinuclear bimetallic complex $[\text{HgAu}_2\text{Cl}_3(\text{PCP})]$ (6) were reported, whereby ($\text{PCP}$) comprises the novel tridentate carbanionic ligand $[2,6-(\text{Ph}_2\text{P})_2\text{C}_6\text{H}_3]^-$ (II). Compounds 4 and 5 are metal-string complexes in which four Au atoms are associated by three aurophilic interactions in very similar linear chain arrangements. Compound 3 shows yellow-green photoluminescence both in dichloromethane solution and in the solid state ($\lambda_{\text{max}} = 538$ and 539 nm, respectively). UV-light triggers an irreversible rearrangement from 4 into the isomer 5 in which four Au atoms are associated by five aurophilic interactions in a rhomboidal arrangement. Compound 6 can be regarded as metallo-pincer complex $[\text{ClHg(AuCAu)}]$, whereby (AuCAu)$^-$ comprises the novel tridentate carbanionic ligand $[2,6-(\text{Ph}_2\text{P})_2\text{AuCl}_2]\text{C}_6\text{H}_3]^-$ (V) containing a central carbanionic binding site and two “gold-arms” contributing pincer-type chelation through two metalophilic Au–Hg interactions (Scheme 1). All metalophilic interactions of 3–6 give rise to AIM bond paths and bond critical points. Typically for noncovalent interactions, the NCI shows contact patches where the Au–Au and Au–Hg interac-

Figure 9. AIM bond paths’ motifs, NCI isosurfaces ($s = 0.5$), and ELI-D isosurfaces ($Y = 1.3$) of the cis- and trans-conformers of 6. Atom colors are as follows: Au = gold, Hg = light gray, Cl = green, P = pink, C = grey, H = white.
tions occur, while the ELI-D remains featureless demonstrating the complementarity of these real-space bond indicators.\textsuperscript{[20]}

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\section*{Conflict of interest}

The authors declare no conflict of interest.

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