Aurophilicity-Triggered Assembly of Novel Cyclic Penta- and Hexanuclear Gold(I) Complexes with Rigid Anionic NHC-Type Ligands

Pengfei Ai,[†] Andreas A. Danopoulos,*[,†,‡] and Pierre Braunstein*[,†]

[†]Laboratoire de Chimie de Coordination, Institut de Chimie (UMR 7177 CNRS), and [‡]Institute for Advanced Study (USIAS), Université de Strasbourg, 4 rue Blaise Pascal, 67081 Strasbourg Cedex, France

Ⓢ *Supporting Information*

ABSTRACT: The products of the reaction between *N,N*′-diphosphanylimidazol-2-ylidene (**P−C−P**) and gold-(I) precursors depend on the nature of the anions associated with the latter. In contrast to the reported reaction with [Au(tht)$_2$(OTf)], the use of [AuCl(tht)] led to the new hexanuclear complex **1**, which features a Au$_6$(μ_3-**P−C**,κC,κN,κP)$_3$ skeleton. The reaction of lithium imidazolide (**P−C−Li**) and [AuCl(tht)] also afforded **1**, together with an unusual salt of the general formula [Au$_5$Cl(μ_3-**P−C**-κP,κC,κN)$_3$]$_2$[AuCl$_2$]$_2$ (**2**), which contains [Au$_5$(μ_3-**P−C**-κP,κC,κN)]$^+$ subunits. In the solid state, one of these Au$_5$ cations is associated with an [AuCl$_2$]$^-$ anion, while two other cations interact through their unique dicoordinated N−Au−N center with a [AuCl$_2$]$^-$ anion, with the charge of the resulting monocation being compensated for by another [AuCl$_2$]$^-$ anion to give a Au$_{12}$ salt. Remarkably, the latter displays seven different bonding types at Au^I: C−Au−C, N−Au−N, P−Au−P, Cl−Au−Cl, C−Au−N, P−Au−Cl, and Au⋯Au.

Since the first report in 1970 of the cyclic trigold(I) [Au(μ-N^1,C^2-pyridyl)]$_3$,[1] similar complexes have attracted considerable attention owing to their fascinating structures and relevance to supramolecular chemistry, metallophilic interactions, and optoelectronic properties.[2] This family of complexes possesses a planar, nine-membered ring with alternating Au^I centers and bidentate C,N- or N,N-bound monoanionic ligands. In the solid state, they can assemble into 1D stacks, with or without the incorporation of electrophiles.[2c,g,i,3] The only example of a cyclic trigold(I) complex bearing N-heterocyclic carbene (NHC) ligands, [Au(μ-C^2,N^3-benzylimidazolide)]$_3$,[4] has a high π basicity,[2f] and it can sandwich Tl$^+$ and Ag$^+$ ions[3a,b] or interact with [Hg$_3$(μ-C$_6$F$_4$)$_3$], TCNQ, C$_6$F$_6$, and F$_8$-naphthalene to produce supramolecular structures with interesting luminescence properties.[2c,e,g,3c,d]

Recently, bulky *N*-phosphanyl-functionalized NHC ligands have been reported by us and others.[5] They feature two or more different coordination sites (C$_{NHC}$ and one or two P-donor functionalities) and support polynuclear complexes with promising applications.[2j,5b,c] In particular, *N,N*′-diphosphanyli-midazol-2-ylidene (**P−C−P**) led to the remarkable linear trinuclear complex [Au$_3${μ_3-κ^3(**P−C−P**)}$_2$][OTf]$_3$ (**A**), which contains a very short Au⋯Au interaction [2.7584(2) Å]. Related

P,C,P-donor ligands with a flexible ethylene spacer between the P and C donors have very recently been used to support gold complexes but with longer intermetallic distances.[6]

We have now found that the outcome of the reaction of **P−C−P** with gold(I) precursors dramatically depends on the nature of their associated anion. Thus, the reaction of **P−C−P** with [AuCl(tht)] (tht = tetrahydrothiophene) in tetrahydrofuran (THF) at −78 °C led to a novel cyclic hexanuclear gold(I) complex, [Au$_2$Cl(μ_3-**P−C**-κP,κC,κN)]$_3$ (**1**; eq 1 and Figure 1)
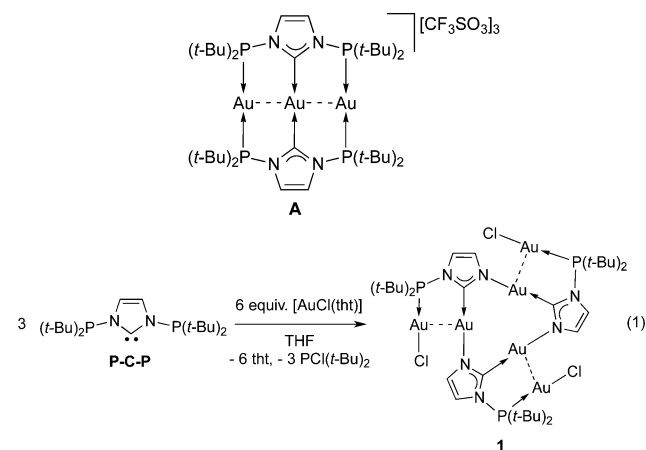
after cleavage of one *t*-Bu$_2$P−N$_{imid}$ bond of **P−C−P**. The formation of PCl(*t*-Bu)$_2$ was evidenced in the reaction mixture as the only other P-containing product (δ 145 in ^{31}P{^{1}H} NMR).

Complex **1** exhibits a cyclic structure of approximate C_3 symmetry characterized by an internal nine-membered planar ring (maximum deviation 0.109 Å for the N2 atom) formed by the assembly through N−Au bonds of three identical "modules" comprising one anionic **P−C** ligand bridging two Au atoms. The Au atoms within the internal ring form an almost equilateral triangle, in which the metal−metal separations (ave 3.491 Å) are too long to represent bonding interactions, although there is a slight inward bending of the N−Au−C angles [173.9(5)− 176.7(5)°]. The Au−N and Au−C distances are in the ranges 2.048(11)−2.056(11) and 1.974(13)−2.009(13) Å, respectively. Each P(*t*-Bu)$_2$ donor is coordinated to one Au−Cl moiety, which flanks the internal nine-membered ring (aver. P−Au−Cl 170.6°). All six Au^I centers are almost coplanar (max. deviation 0.397 Å for
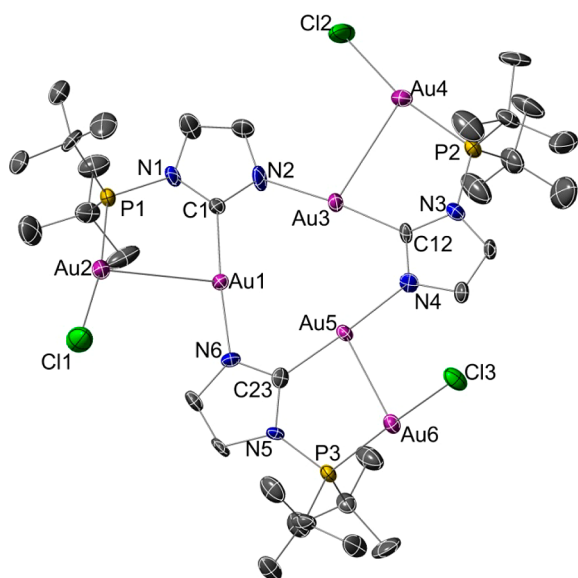
Figure 1. Structure of **1** in **1**·THF. One molecule of THF and H atoms are omitted for clarity. Selected bond distances (Å) and angles [deg]: Au1−C1 2.009(13), Au1−N6 2.048(11), Au3−C12 2.002(12), Au3−N2 2.056(12), Au5−C23 1.974(13), Au5−N4 2.056(11), Au2−P1 2.238(4), Au2−Cl1 2.284(4), Au4−P2 2.239(4), Au4−Cl2 2.294(5), Au6−P3 2.240(3), Au6−Cl3 2.300(4), Au1···Au2 3.0659(7), Au3···Au4 3.1300(8), Au5···Au6 3.0430(7); C1−Au1−N6 174.7(5), C12−Au3−N2 173.9(5), C23−Au5−N4 176.7(5), P1−Au2−Cl1 170.7(1), P2−Au4−Cl2 168.4(2), P3−Au6−Cl3 172.7(1).

Au1), as a result of aurophilic interactions between the "internal" and "external" Au[I] centers (aver. Au···Au = 3.080 Å).[7] No intermolecular Au···Au contacts were observed (the closest intermolecular Au···Au distance is 6.258 Å).

Although details of the formation of **1** are not yet clear, it is plausible that the chloride ligand displaced from [AuCl(tht)] acted as a nucleophile toward the uncoordinated P−N bond of a partially (i.e. via one P and/or C) coordinated **P−C−P** ligand (neither the free **P−C−P** ligand nor **A** is degraded by chloride ions) and led to the formation of PCl(t-Bu)₂ and Au{P−C}⁻ moieties, with the latter assembling to give **1**. We thus envisaged a more direct access to **1** from lithium imidazolide (**P−C−Li**), preformed by the deprotonation of 1-(di-*tert*-butylphosphanyl)-imidazole with *n*-BuLi (see the Supporting Information, SI).

Interestingly, the reaction of preisolated **P−C−Li** with [AuCl(tht)] in THF indeed afforded **1**, but a new gold complex, **2**, was also obtained (Scheme 1) in a ca. 1:1 ratio (from ³¹P NMR spectra). Pure **2** was obtained by repeated washing of the precipitate obtained from the reaction mixture with THF, in which **2** is much less soluble than **1**. As solids, **1** and **2** are air-stable for several hours but are better stored under an inert atmosphere. Reactions of [AuCl(tht)] with a mixture of 1-(di-

Scheme 1. Synthesis of 1 and 2
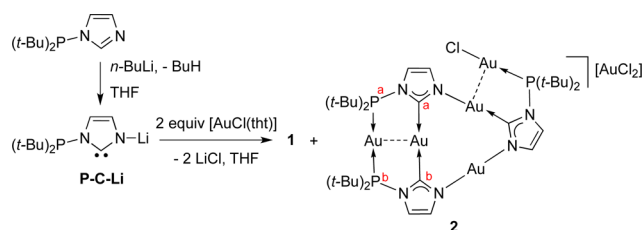
tert-butylphosphanyl)imidazole and *n*-BuLi in THF failed because of the competing reduction of [AuCl(tht)] by *n*-BuLi.

In the solid state, the structure of **2**·CH₂Cl₂ can be described as containing, first, one pentanuclear cation of the formula [Au₅(μ₃-**P**−**C**-κP,κC,κN)]⁺ (Figure 2), the positive charge of which
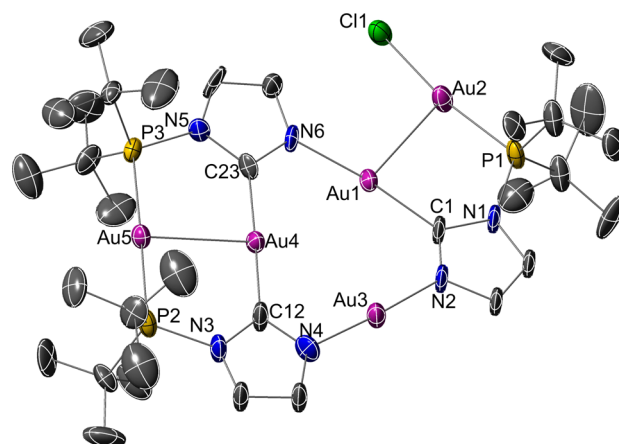

Figure 2. Structure of one of the pentanuclear cations present in the asymmetric unit of **2**·CH₂Cl₂. Selected bond distances (Å) and angles [deg]: Au1−C1 2.01(1), Au1−N6 2.044(11), Au3−N2 2.001(11), Au2−P1 2.232(4), Au3−N4 2.01(1), Au4−C12 2.00(1), Au4−C23 2.03(1), Au5−P2 2.305(4), Au5−P3 2.314(4), Au1···Au2 3.0846(8), Au4···Au5 2.7523(7). In the other pentanuclear cation present in the asymmetric unit of **2**·CH₂Cl₂, a contact is established between the unique N−Au−N atom and one of the [AuCl₂]⁻ anions (Scheme 2).

(formally associated with the P → Au ← P unit) is compensated for by a [AuCl₂]⁻ anion, and second, a centrosymmetric Au₁₁ monocation, balanced by another [AuCl₂]⁻ anion. The Au₁₁ monocation comprises two pentanuclear cations connected through their unique dicoordinated N−Au−N center to the Au atom of one linear [AuCl₂]⁻ anion. The latter Au atom occupies a center of symmetry (Scheme 2 and Figure S1 in the SI). Overall,

Scheme 2. Representation of 2 in 2·CH₂Cl₂ Containing Two [Au₅(μ₃-P−C-κP,κC,κN)]⁺ Cations That Establish d¹⁰−d¹⁰ Interactions with a Central [AuCl₂]⁻ Anion [Au8···Au11 = 3.0863(5) Å; Au11 Occupies a Center of Symmetry]
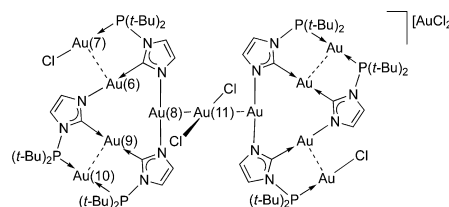
this gives for **2** a formulation corresponding to [Au₅Cl(μ₃-**P**−**C**-κP,κC,κN)₃]₂[AuCl₂]₂. The metrical data within the Au₅ units are almost identical. The Au8···Au11 distance of 3.0863(5) Å is consistent with aurophilic interactions.[7] Like in **1**, in each pentanuclear unit, there are three N_imidazolide−Au bonds. Whereas the internal Au[I] centers in **1** were all in the same coordination environment (with three C−Au−N vectors forming a topologically oriented nine-membered ring), the different assembling orientations of the bridging ligand in **2** result in three different environments for the Au[I] centers: C−Au−C, N−Au−N, and C−Au−N. The Au−Cl distances in the two types of [AuCl₂]⁻ anions present (ave. 2.248 Å) are very similar to that in [*n*-

$Bu_4N][AuCl_2]$ [2.257(4) Å].[8] The Au8−Au11−Cl plane makes an angle of 75.63° with the Au6−Au8−Au9 plane.

Although the alternating assembly of mononuclear cationic and anionic gold(I) complexes resulting from electrostatic interactions is well-known,[7a,d] we are not aware of literature precedents for the arrangements displayed by **2**.

It is worth noting that **1** and **2** are actually formula isomers, but whereas in **1** there are only two types of gold(I) coordination environments (neglecting the aurophilic interactions), i.e., P−Au−Cl and C−Au−N, six different types are present in **2**: C−Au−C, N−Au−N, P−Au−P, Cl−Au−Cl, C−Au−N, and P−Au−Cl. This remarkable diversity within the same complex appears unprecedented. The shorter Au⋯Au distances in **2** are associated with the $\kappa C,\kappa N,\kappa P$ bonding mode of the μ_3-**P**−**C** ligand [2.7523(7) and 2.7608(7) Å for Au4⋯Au5 and Au9⋯Au10, respectively] and are similar to those observed in the linear trinuclear gold complex **A** [2.7584(2) Å].[5c] However, these short distances cannot be solely ascribed to the short-bite effect of the ligand because the longer Au1⋯Au2 and Au6⋯Au7 separations [3.0846(8) and 3.0863(5) Å, respectively] are also spanned by this ligand in the same bridging mode. The latter values are similar to those for the "peripheral" Au⋯Au interactions in **1**.

Preliminary experiments have not led to the observation of any remarkable photophysical properties for **1** and **2**, despite the presence of numerous Au⋯Au interactions. This is probably related to the presence of bulky *t*-Bu groups on the P atoms that prevent the establishment of closer intermolecular contacts.

The Au_6 and Au_5 cores found in **1** and **2**, respectively, are retained in solution, as evidenced by NMR spectroscopy. Particularly diagnostic in this respect are (i) the $^{31}P\{^1H\}$ NMR singlet at δ 111 for **1**, in contrast to the AB pattern (δ 126.5, 124.8; $^2J_{AB}$ = 289.5 Hz) for the two trans atoms P_a and P_b (the AB pattern originating from the lack of any symmetry element relating these two nuclei) and a singlet at δ 115.1 in **2** and (ii) the equivalence of all three C_{NHC} atoms in **1**, which gives rise to a doublet at δ 178.6 (d, $^2J_{CP}$ = 30.5 Hz), whereas in **2**, the C_{NHC} atoms C_a and C_b appear as dd at δ 193.8 (dd, $^2J_{CP}$ = 25.9 Hz, $^4J_{CP}$ = 2.7 Hz) and 192.1 (dd, $^2J_{CP}$ = 25.4 Hz, $^4J_{CP}$ = 2.3 Hz), and the C_{NHC} atom trans to N appears at δ 179.0 (d, $^2J_{CP}$ = 30.9 Hz), a value very similar to the corresponding one in **1**.

In conclusion, the nucleophilic Cl^- liberated from the precursor [AuCl(tht)] is thought to be responsible for the change of the reaction course of the **P**−**C**−**P** ligand with [AuCl(tht)] compared to $[Au(tht)_2](OTf)$. While the rational synthesis of **1** based on the use of the isolated **P**−**C**−**Li** as a ligand source was successful, it also afforded the unusual Au_{12} complex **2**, which exhibits seven different types of coordination environments for Au^I. Significant energetic contributions responsible for the assembly of these remarkable complexes are thought to involve aurophilic interactions.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, NMR data, and crystal data for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org. CIF files have been deposited with the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K., and can be obtained upon request free of charge by quoting the publication citation and deposition numbers 1046767 and 1046768.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: danopoulos@unistra.fr.

*E-mail: braunstein@unistra.fr.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ DEDICATION

Dedicated to Prof. H. Schmidbaur on the occasion of his 80th birthday (December 31, 2014), with our warmest congratulations.

■ REFERENCES

(1) Vaughan, L. G. *J. Am. Chem. Soc.* **1970**, *92*, 730−731.

(2) (a) Minghetti, G.; Bonati, F. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 429−429. (b) Olmstead, M. M.; Jiang, F.; Attar, S.; Balch, A. L. *J. Am. Chem. Soc.* **2001**, *123*, 3260−3267. (c) Fackler, J. P., Jr. *Inorg. Chem.* **2002**, *41*, 6959−6972. (d) Burini, A.; Mohamed, A. A.; Fackler, J. P., Jr. *Comments Inorg. Chem.* **2003**, *24*, 253−280. (e) Omary, M. A.; Mohamed, A. A.; Rawashdeh-Omary, M. A.; Fackler, J. P., Jr. *Coord. Chem. Rev.* **2005**, *249*, 1372−1381. (f) Tekarli, S. M.; Cundari, T. R.; Omary, M. A. *J. Am. Chem. Soc.* **2008**, *130*, 1669−1675. (g) Elbjeirami, O.; Rashdan, M. D.; Nesterov, V.; Rawashdeh-Omary, M. A. *Dalton Trans.* **2010**, *39*, 9465−9468. (h) Hettiarachchi, C. V.; Rawashdeh-Omary, M. A.; Korir, D.; Kohistani, J.; Yousufuddin, M.; Dias, H. V. R. *Inorg. Chem.* **2013**, *52*, 13576−13583. (i) Ni, W.-X.; Li, M.; Zheng, J.; Zhan, S.-Z.; Qiu, Y.-M.; Ng, S. W.; Li, D. *Angew. Chem., Int. Ed.* **2013**, *52*, 13472−13476. (j) Visbal, R.; Gimeno, M. C. *Chem. Soc. Rev.* **2014**, *43*, 3551−3574.

(3) (a) Burini, A.; Fackler, J. P., Jr.; Galassi, R.; Pietroni, B. R.; Staples, R. J. *Chem. Commun.* **1998**, 95−96. (b) Burini, A.; Bravi, R.; Fackler, J. P., Jr.; Galassi, R.; Grant, T. A.; Omary, M. A.; Pietroni, B. R.; Staples, R. J. *Inorg. Chem.* **2000**, *39*, 3158−3165. (c) Burini, A.; Fackler, J. P., Jr.; Galassi, R.; Grant, T. A.; Omary, M. A.; Rawashdeh-Omary, M. A.; Pietroni, B. R.; Staples, R. J. *J. Am. Chem. Soc.* **2000**, *122*, 11264−11265. (d) Rawashdeh-Omary, M. A.; Omary, M. A.; Fackler, J. P., Jr.; Galassi, R.; Pietroni, B. R.; Burini, A. *J. Am. Chem. Soc.* **2001**, *123*, 9689−9691.

(4) Bonati, F.; Burini, A.; Pietroni, B. R.; Bovio, B. *J. Organomet. Chem.* **1989**, *375*, 147−160.

(5) (a) Gaillard, S.; Renaud, J.-L. *Dalton Trans.* **2013**, *42*, 7255−7270. (b) Marchenko, A. P.; Koidan, H. N.; Hurieva, A. N.; Gutov, O. V.; Kostyuk, A. N.; Tubaro, C.; Lollo, S.; Lanza, A.; Nestola, F.; Biffis, A. *Organometallics* **2013**, *32*, 718−721. (c) Ai, P.; Danopoulos, A. A.; Braunstein, P.; Monakhov, K. Yu. *Chem. Commun.* **2014**, *50*, 103−105. (d) Marchenko, A.; Koidan, H.; Hurieva, A.; Kurpiieva, O.; Vlasenko, Y.; Kostyuk, A.; Tubaro, C.; Lenarda, A.; Biffis, A.; Graiff, C. *J. Organomet. Chem.* **2014**, *771*, 14−23. (e) Wang, T.; Stephan, D. W. *Chem.—Eur. J.* **2014**, *20*, 3036−3039. (f) Brill, M.; Marrwitz, D.; Rominger, F.; Hofmann, P. *J. Organomet. Chem.* **2015**, *775*, 137−151.

(6) Bestgen, S.; Gamer, M. T.; Lebedkin, S.; Kappes, M. M.; Roesky, P. W. *Chem.—Eur. J.* **2015**, *21*, 601−614.

(7) (a) Katz, M. J.; Sakai, K.; Leznoff, D. B. *Chem. Soc. Rev.* **2008**, *37*, 1884−1895. (b) Schmidbaur, H.; Schier, A. *Chem. Soc. Rev.* **2008**, *37*, 1931−1951. (c) Sculfort, S.; Braunstein, P. *Chem. Soc. Rev.* **2011**, *40*, 2741−2760. (d) Schmidbaur, H.; Schier, A. *Chem. Soc. Rev.* **2012**, *41*, 370−412. (e) Tiekink, E. R. T. *Coord. Chem. Rev.* **2014**, *275*, 130−153.

(8) Braunstein, P.; Müller, A.; Bögge, H. *Inorg. Chem.* **1986**, *25*, 2104−2106.