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Competing Metal–Metal Bonding in Heterometallic Complexes of Gold and Mercury. Synthesis of Contrasting Fe–Au–Au–Fe and Fe–Hg–Fe Complexes

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By contraction of the s (and p) orbitals and expansion of the d orbitals, relativistic effects promote metal–metal interactions between gold atoms even with a $5d^{10}$ closed-shell electronic configuration.¹ Tangential bonding in gold complexes^{2a} results in the marked "aurophilic attraction"^{2b} which has become a salient feature of recent experimental³ and theoretical studies.⁴ Yet, more comparative experimental data are desirable to better understand how these effects influence the chemistry (structure and reactivity) of Au^I vs its neighbor Hg^{II} , another $5d^{10}$ closed-shell ion. Whereas Hg transition metal complexes and clusters are numerous,⁵ only few structures are known in which tangential Hg–Hg bonding occurs.⁶ We report on the marked differences observed between the new Fe–Au and Fe–Hg complexes $[AuFe\{Si(OMe)_3\}(CO)_3(\mu-dppm)]_2$ (**2**) ($dppm = Ph_2PCH_2PPh_2$) and $Hg[Fe\{Si(OMe)_3\}(CO)_3(dppm-P)]_2$ (**3**), respectively, which are due to the preference in the former for Au–Au rather than Au–Fe bonding.

We reacted $[Bu_4N][AuX_2]$ ($X = Cl, Br$) with 2 equiv of the $dppm$ -substituted silyliron metalate $K[Fe\{Si(OMe)_3\}(CO)_3(dppm-P)]$ (**1**),⁷ anticipating the formation of a $[m-Au-m]^-$ chain. However, a complex analyzing for $Au[m]$ (**2**) was obtained instead (Scheme 1)⁸ and it was also formed when only 1 equiv of **1** was used. Its $^{31}P\{^1H\}$ NMR spectrum contains a doublet of doublets, characteristic for the presence of Au- and Fe-bound P atoms coupled to each other ($^2+^3J(P,P) = 43.4$ Hz), which is further split by an additional coupling of 14.8

Hz. In addition to the methoxy resonance at δ 3.61 (1H NMR at 333 K), a broad triplet is found at δ 3.23 for the PCH_2 protons. It broadens further when the temperature is lowered, indicating a dynamic behavior for this molecule. The crystal structure of the CH_2Cl_2 solvate of complex **2**¹⁰ revealed that a dimer $(Au[m])_2$ had formed, as a result of additional Au–Au bonding and partial migration of the $dppm$ ligand (Scheme 1). The dimeric complex has an approximate C_2 symmetry, and the Fe–Au–Fe chain possesses a Z shape (Figure 1), with the pairs of atoms Fe(1) and Au(2) and Fe(2) and Au(1) each bridged by a $dppm$ ligand, thus forming two unusual, twisted six-membered rings fused along the Au–Au edge (core of a tetraphosphatetrametalladecaline). The coordination geometry about the Fe atom may be described as distorted octahedral with the P and Si atoms trans to one another and the CO ligands in a *mer* arrangement. Alternatively, if one ignores the Fe–Au bond, it may be viewed as trigonal bipyramidal, a geometry consistent with a formally zerovalent Fe center. The Au–Fe distances are in the expected

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- (5) See for example: (a) Charalambous, E.; Gade, L. H.; Johnson, B. F. G.; Kotch, T.; Lees, A. J.; Lewis, J.; McPartlin, M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1137. (b) Braunstein, P.; Rosé, J.; Tiripicchio, A.; Tiripicchio Camellini, M. *J. Chem. Soc., Dalton Trans.* **1992**, 911 and references cited.
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- (8) All reactions were performed under purified nitrogen, using standard Schlenk-type techniques. Complex **2**: $[n-Bu_4N][AuBr_2]$ (0.599 g, 1.0 mmol) was added at $-40^\circ C$ to a solution of **1** (0.685 g, 1 mmol) in THF (35 mL), and the mixture was stirred for 1.5 h. The yellowish solution was filtered and evaporated under reduced pressure. The residue was extracted with warm CH_2Cl_2 (30 mL), and the extract was concentrated and layered with hexane, which afforded colorless crystals after a few days at $-20^\circ C$ (0.496 g, 56%). IR (CH_2Cl_2): $\nu(CO)$ 1978 (s), 1914 (vs), 1899 (vs) cm^{-1} . 1H NMR (in $CDCl_3$, δ relative to $SiMe_4$) (333 K): 3.23 (br t, $J \approx 12$ Hz, 2 H, PCH_2), 3.61 (s, 9 H, OMe), 7.10–7.74 (m, 20 H, aromatic). $^{31}P\{^1H\}$ NMR ($CH_2Cl_2/acetone-d_6$, δ relative to external H_3PO_4): 27.9 [dd, $J(P,P) = 43.4$, 14.8 Hz, P(Au)], 58.4 (dd, $J(P,P) = 43.4$, 14.8 Hz, P(Fe)].
- (9) Braunstein, P.; Clark, R. J. H. *J. Chem. Soc., Dalton Trans.* **1973**, 1845.
- (10) Crystal structure determinations: $[AuFe\{Si(OMe)_3\}(CO)_3(\mu-dppm)]_2 \cdot CH_2Cl_2$ (**2**), $C_{62}H_{62}Au_2Fe_2O_{12}P_4Si_6 \cdot CH_2Cl_2$, $M = 1769.79$, monoclinic, space group $P2_1/a$ (the matrix /001/010/100/ must be applied to the unit cell in order to change the space group in $P2_1/c$), $a = 32.930$ (9) Å, $b = 17.826$ (7) Å, $c = 11.297$ (5) Å, $\beta = 90.57$ (2)°, $V = 6631$ (4) Å³, $Z = 4$, $D_c = 1.773$ g cm^{-3} , graphite-monochromated Mo K α radiation, $\lambda = 0.71073$ Å, $\mu = 51.02$ cm^{-1} ; $Hg[Fe\{Si(OMe)_3\}(CO)_3(dppm-P)]_2$ (**3**), $C_{62}H_{62}Fe_2HgO_{12}P_4Si_6$, $M = 1491.52$, triclinic, space group $P\bar{1}$ (the matrix /001/100/010/ must be applied to the unit cell in order to obtain the Niggli unit cell), $a = 12.706$ (6) Å, $b = 22.843$ (9) Å, $c = 12.219$ (5) Å, $\alpha = 95.79$ (2)°, $\beta = 114.15$ (2)°, $\gamma = 95.44$ (2)°, $V = 3183$ (2) Å³, $Z = 2$, $D_c = 1.556$ g cm^{-3} , niobium-filtered Mo K α radiation, $\lambda = 0.71073$ Å, $\mu = 30.47$ cm^{-1} . The intensity data were collected at room temperature on a Philips PW 1100 (2) and a Siemens AED (3) diffractometer, using the θ – 2θ scan technique. A total of 11 218 (2) and 13 985 (3) unique reflections were measured (with θ in the range 3 – 24° (2) and 3 – 27° (3), of which 5759 (2) and 8790 (3), having $I > 2\sigma(I)$, were used in the refinement. Corrections for absorption were applied. The structures were solved by Patterson and Fourier methods and refined by full-matrix least-squares procedures, with anisotropic thermal parameters in the last cycles of refinement for the Au, Fe, P, Si, and O atoms (2) and for all the non-hydrogen atom (3). The hydrogen atoms were placed at their geometrically calculated positions. The SHELX-76 and SHELXS-86 systems of computer programs were used.¹¹ The R and R_w values were 0.0665 and 0.0719 (2) and 0.0472 and 0.0510 (3), respectively. Further details of the crystal structure analyses are available as supplementary material.
- (11) Sheldrick, G. M. SHELX-76. Program for Crystal Structure Determination, University of Cambridge, U.K., 1976. SHELXS-86. Program for Crystal Structure Solution. Universität Göttingen, 1986.

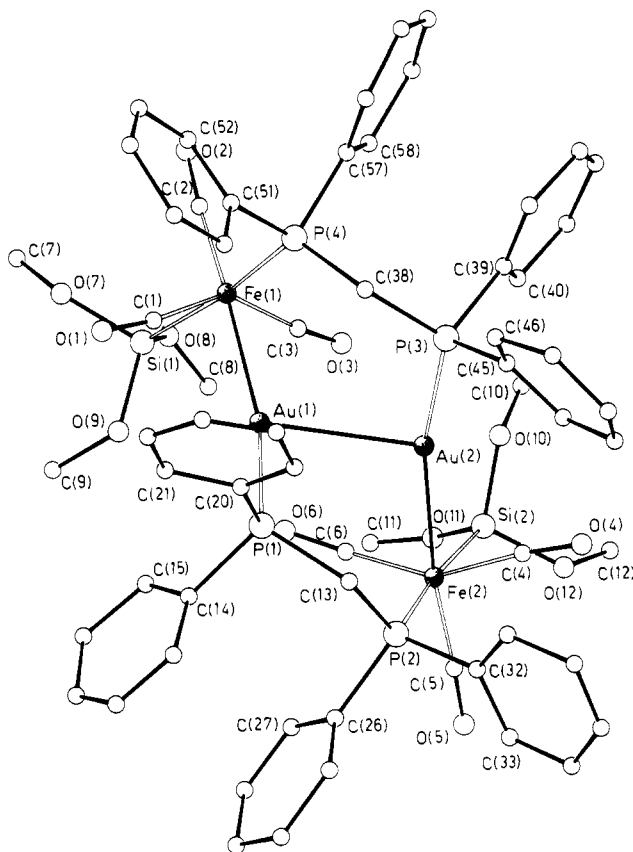
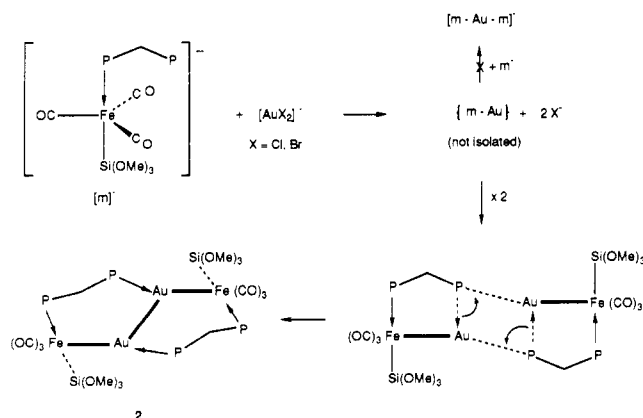


Figure 1. View of the molecular structure of the complex $[\text{AuFe}\{\text{Si}(\text{OMe})_3\}(\text{CO})_3(\mu\text{-dppm})]_2 \cdot \text{CH}_2\text{Cl}_2$ (**2**) together with the atomic numbering system. Selected bond distances (Å) and angles (deg): $\text{Au}(1)\text{--}\text{Au}(2) = 2.962$ (1), $\text{Au}(1)\text{--}\text{Fe}(1) = 2.535$ (3), $\text{Au}(2)\text{--}\text{Fe}(2) = 2.562$ (3), $\text{Au}(1)\text{--}\text{P}(1) = 2.266$ (6), $\text{Au}(2)\text{--}\text{P}(3) = 2.294$ (6), $\text{Fe}(1)\text{--}\text{Si}(1) = 2.268$ (8), $\text{Fe}(1)\text{--}\text{P}(4) = 2.226$ (6), $\text{Fe}(2)\text{--}\text{Si}(2) = 2.282$ (7), $\text{Fe}(2)\text{--}\text{P}(2) = 2.244$ (6); $\text{Fe}(1)\text{--}\text{Au}(1)\text{--}\text{P}(1) = 161.7$ (2), $\text{Fe}(2)\text{--}\text{Au}(2)\text{--}\text{P}(3) = 164.0$ (2), $\text{Fe}(1)\text{--}\text{Au}(1)\text{--}\text{Au}(2) = 107.2$ (1), $\text{P}(1)\text{--}\text{Au}(1)\text{--}\text{Au}(2) = 87.3$ (1), $\text{Fe}(2)\text{--}\text{Au}(2)\text{--}\text{Au}(1) = 104.8$ (1), $\text{P}(3)\text{--}\text{Au}(2)\text{--}\text{Au}(1) = 88.6$ (1), $\text{C}(1)\text{--}\text{Fe}(1)\text{--}\text{C}(3) = 143$ (1), $\text{C}(1)\text{--}\text{Fe}(1)\text{--}\text{C}(2) = 108$ (1), $\text{C}(2)\text{--}\text{Fe}(1)\text{--}\text{C}(3) = 106$ (1), $\text{P}(4)\text{--}\text{Fe}(1)\text{--}\text{Si}(1) = 171.4$ (3), $\text{C}(4)\text{--}\text{Fe}(2)\text{--}\text{C}(6) = 150$ (1), $\text{C}(4)\text{--}\text{Fe}(2)\text{--}\text{C}(5) = 103$ (1), $\text{C}(5)\text{--}\text{Fe}(2)\text{--}\text{C}(6) = 105$ (1), $\text{P}(2)\text{--}\text{Fe}(2)\text{--}\text{Si}(2) = 174.3$ (3).

Scheme I



range,^{3d} and the $\text{Au}(1)\text{--}\text{Au}(2)$ separation of 2.962 (1) Å is typical for such interactions that are perpendicular (tangential) to the $\text{Fe}\text{--}\text{Au}\text{--}\text{P}$ bonding axis [$\text{P}(1)\text{--}\text{Au}(1)\text{--}\text{Fe}(1) = 161.7$ (2)°; $\text{P}(3)\text{--}\text{Au}(2)\text{--}\text{Fe}(2) = 164.0$ (2)°].³ It is interesting to note that **2** forms a 10-membered-ring structure in which the $\text{Au}\text{--}\text{Au}$ interaction is reminiscent of the transannular interactions which occur in organic cycles of middle size (8–12).

But why could the trinuclear chain complex $[\text{m}\text{--}\text{Au}\text{--}[\text{m}]]^-$ not be isolated in contrast to the behavior observed with other

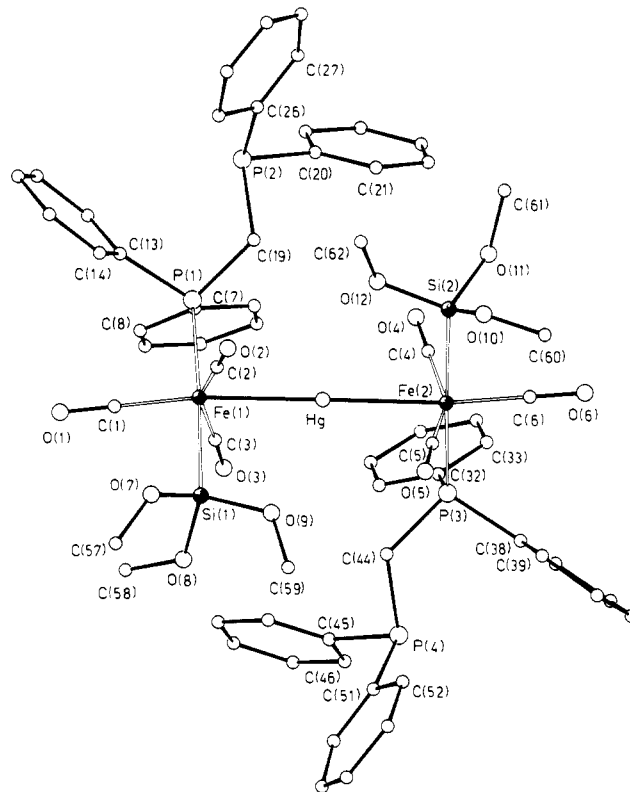
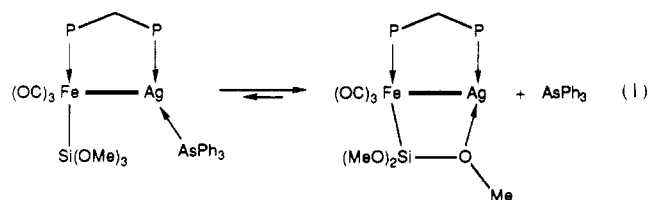


Figure 2. View of the molecular structure of the complex $\text{Hg}[\text{Fe}\{\text{Si}(\text{OMe})_3\}(\text{CO})_3(\text{dppm-P})]_2$ (**3**) along the pseudo- C_2 axis, together with the atomic numbering system. Selected bond distances (Å) and angles (deg): $\text{Hg}\text{--}\text{Fe}(1) = 2.574$ (1), $\text{Hg}\text{--}\text{Fe}(2) = 2.576$ (1), $\text{Fe}(1)\text{--}\text{Si}(1) = 2.290$ (3), $\text{Fe}(1)\text{--}\text{P}(1) = 2.247$ (2), $\text{Fe}(2)\text{--}\text{Si}(2) = 2.285$ (3), $\text{Fe}(2)\text{--}\text{P}(3) = 2.235$ (2); $\text{Fe}(1)\text{--}\text{Hg}\text{--}\text{Fe}(2) = 178.0$ (1), $\text{P}(1)\text{--}\text{Fe}(1)\text{--}\text{Si}(1) = 177.3$ (1), $\text{C}(1)\text{--}\text{Fe}(1)\text{--}\text{C}(2) = 102.6$ (4), $\text{C}(2)\text{--}\text{Fe}(1)\text{--}\text{C}(3) = 154.9$ (4), $\text{C}(1)\text{--}\text{Fe}(1)\text{--}\text{C}(3) = 99.7$ (4).

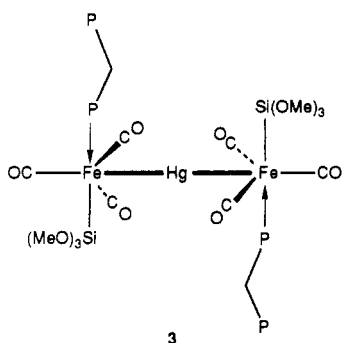
carbonylmatalates?¹² Possibly its $\text{Fe}\text{--}\text{Au}$ bond would be sufficiently labile for dissociation in $[\text{m}]^-$ and $\text{Au}[\text{m}]$, in which the gold atom obviously prefers to increase its coordination by formation of a new $\text{Au}\text{--}\text{Au}$ bonding interaction. This dimerization process would be assisted by the phosphorus atoms $\text{P}(1)$ and $\text{P}(3)$, which could be either bonded to gold in $\text{Au}[\text{m}]$ or pendent, resulting for the first time, we believe, in dppm ligands bridging the *termini* atoms of a trinuclear chain. This is supported by the observation that **2** formed in small amounts (5%, $^{31}\text{P}\{^1\text{H}\}$ NMR) upon dissolution of pure $[\text{Fe}\{\text{Si}(\text{OMe})_3\}(\text{CO})_3(\mu\text{-dppm})\text{Au}(\text{PPh}_3)]$,^{7a} owing to partial dissociation of PPh_3 . The $\text{Ag}\text{--}\text{AsPh}_3$



analogue of the latter complex readily dissociates AsPh_3 in solution,^{7a} resulting instead in the occurrence of an unusual $\mu_2\text{--}\eta^2\text{--}\text{SiO}$ bridge (eq 1). The preference for intramolecular stabilization of the electron-deficient Ag center over a dimerization of the type observed above with gold nicely illustrates the much lower affinity of silver for making $\text{Ag}\cdots\text{Ag}$ contacts. On electronic grounds, $\text{Au}\leftarrow\text{O}(\text{Si})$ interactions are therefore not needed in **2**. Note also that excess PPh_3 breaks the $\text{Au}\text{--}\text{Au}$ bond of **2**, yielding quantitatively $[\text{Fe}\{\text{Si}(\text{OMe})_3\}(\text{CO})_3(\mu\text{-dppm})\text{Au}(\text{PPh}_3)]$.

(12) Braunstein, P.; Schubert, U.; Burgard, M. *Inorg. Chem.* **1984**, *23*, 4057 and references cited.

The reaction of 2 equiv of **1** with HgCl_2 or of 1 equiv of **1** with the intermediate $[\text{Fe}\{\text{Si}(\text{OMe})_3\}(\text{CO})_3(\mu\text{-dppm})\text{HgCl}]^{7b}$ afforded in high yield the expected¹³ chain complex $[\text{m}]\text{-Hg-}[\text{m}]$ (**3**).¹⁴



Its X-ray structure shows that it has approximate C_2 symmetry¹⁰ and confirms the linearity of the Fe–Hg–Fe array (Figure 2). The Fe–Hg bond distances are slightly longer than those found

in neutral or anionic complexes showing a linear Fe–Hg–Fe array.¹⁵ The pendent nature of two P atoms in **3** is maintained in solution, since, even at -30°C , no $^1J(\text{PHg})$ coupling could be detected in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. The formation and structure of **3** clearly show that there were no obvious reasons (e.g. steric) why its gold analogue would not form. A comparison of closely related Fe–Ag^I, Fe–Au^I, and Fe–Hg^{II} systems demonstrates that the Au^I–Au^I attraction (recent estimations are of about $-30\text{ kJ/mol}^{3a,16}$) represents a decisive component to the dramatic structural reorganization leading to **2**.

An interesting feature of complex **3** is the orientation of the pendent P atoms. We are currently evaluating the potential of this molecule as an assembling "ligand" of which the trinuclear core could act as a rigid spacer, imparting unique stereochemical features to its complexes.

Acknowledgment. Financial support from the CNRS (Paris) and the "Commission of the European Communities" (Contract No. ST2J-0347-C) is gratefully acknowledged.

Supplementary Material Available: Tables of crystal data and data collection and refinement details, positional parameters, anisotropic thermal parameters, and bond distances and angles for **2** and **3** (26 pages). Ordering information is given on any current masthead page.

Registry No. **1**, 123674-03-3; **2**, 142563-98-2; **2**· CH_2Cl_2 , 142632-19-7; **3**, 142563-99-3; $[\text{Bu}_4\text{N}][\text{AuCl}_2]$, 50480-99-4; $[\text{Bu}_4\text{N}][\text{AuBr}_2]$, 50481-01-1; $[\text{Fe}\{\text{Si}(\text{OMe})_3\}(\text{CO})_3(\mu\text{-dppm})\text{HgCl}]$, 142632-20-0; Fe, 7439-89-6; Au, 7440-57-5; Hg, 7439-97-6.

(13) Kunz, E.; Schubert, U. *Chem. Ber.* **1989**, *122*, 231.

(14) Complex **3**: HgCl_2 (0.135 g, 0.5 mmol) was added at 0°C to a solution of $\text{K}[\text{m}]$ (0.685 g, 1 mmol) in THF (25 mL), and the mixture was stirred for 1.5 h. The yellow solution was filtered and evaporated under reduced pressure. The residue was recrystallized from toluene/hexane at -20°C , affording yellow, air-stable crystals of **3** (0.545 g, 73%). IR (THF): $\nu(\text{CO})$ 1994 (m), 1965 (sh), 1939 (vs) cm^{-1} . ^1H NMR (CD_2Cl_2): δ 3.22 (br d, $^2J(\text{P,H}) = 4.6\text{ Hz}$, 2 H, PCH_2), 3.56 (s, 9 H, OMe), 7.10–7.53 (m, 20 H, aromatic). $^{31}\text{P}\{^1\text{H}\}$ NMR (THF/acetone- d_6 , 298 K): -22.4 (d, $^2J(\text{P,P}) = 59\text{ Hz}$, P), 51.4 (d, $^2J(\text{P,P}) = 59\text{ Hz}$, $^2J(\text{P,Hg}) = 173\text{ Hz}$, P(Fe)). ^{199}Hg NMR (Bruker WP 200 SY, $\text{CH}_2\text{Cl}_2/\text{C}_6\text{D}_6$, δ relative to external HgMe_2), (312 K): -658 (t, $^2J(\text{P,Hg}) = 180\text{ Hz}$) (we thank P. Maltese and M. Strampfer for these data).

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