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Metallamacrocycles

Reaction of a Metallamacrocycle Leading to a Mercury(II)···Palladium(II)···Mercury(II) Interaction[**]

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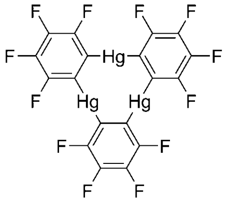
Homo- and heterometallic species that have metallophilic interactions between closed-electron-shell atoms and ions (d^{10} or s^2 systems) have attracted considerable interest owing to their unique chemical bonding, structure, reactivity, and luminescence properties.[1] In particular, the bonding and structural aspects of these complexes have been focus of several recent studies. Two or more closed-shell cations are expected to repel each other. However, recent theoretical and experimental studies provide evidence for attractive interactions arising from dispersive forces augmented by relativistic effects for heavy elements.[2] Mercury(II)[3] and gold(I)[4] ions have been recognized as "inter- and intramolecular glue". Metallophilic interactions are known to operate among closed-shell Group 11 metal ions, such as gold(I), silver(I), and copper(I).[5] The Group 12 complex, trimeric perfluoro-*o*-phenylenemercury (**1**), has been widely investigated by Gabbaï and co-workers for its Lewis acidic properties and metallophilic interactions.[1b,6] Although there are numerous reports on metallophilic interactions in homo- and heterobimetallic systems with d^{10} configurations,[3b] there are very few reports on analogous trimetallic species. The work of Catalano et al. is a notable exception, in which the metallocryptand approach was used to assemble a series of trimetallic systems (**2**).[7]



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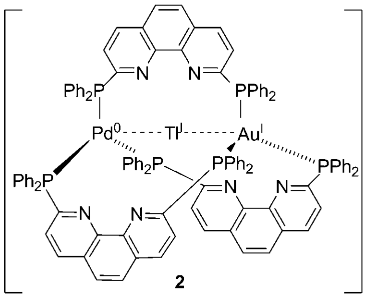

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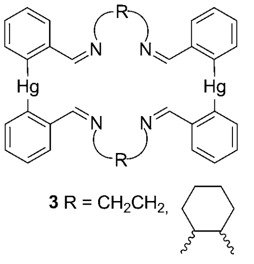
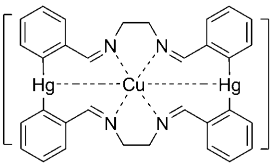


3 R = CH_2CH_2,



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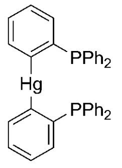

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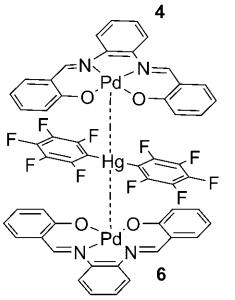

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We envisaged that use of a metallamacrocyclic ligands **3** incorporating both basic, nitrogen centers and Lewis acidic mercury as ligand to coordinate d^{10} metal ions may lead to a metallophilic interaction with $Hg^{II}\cdots M\cdots Hg^{II}$ (M = Cu, Ag, Hg, etc). The reaction of copper(I) led to isolation of species **4** with a $Hg^{II}\cdots Cu^{I}\cdots Hg^{II}\cdots Hg^{II}\cdots Cu^{I}\cdots Hg^{II}$ unit having six d^{10} ions in a chain,[8] the reaction with silver(I) led to isolation of a $Hg^{II}\cdots Ag^{I}\cdots Hg^{II}$ trimetallic species, and the reaction with mercury(II) led to cleavage of the macrocycle.[9]

Heavier d^8 transition-metal ions with large crystal field splitting are also considered as having a closed shell, and are expected to be involved in similar metallophilic interactions. Bennett and co-workers worked on the synthesis of trimetallic systems containing mercury(II) and palladium(0)/platinum(II) by reacting bis((*o*-diphenylphosphino)phenylmercury (**5**) with $[Pd(dba)_2]$ (dba = dibenzylideneacetone) in a 2:1 ratio, affording $[Pd((o\text{-}Ph_2PC_6H_4)_2Hg)_2]$, which contains palladium(0). The complex has not been structurally characterized, and it deposits metallic palladium and mercury in refluxing toluene.[10] Very recently, Gabbaï and co-workers have reported the presence of an intermolecular unsupported metallophilic interaction of the type $Pd^{II}\cdots Hg^{II}\cdots Pd^{II}$ (complex **6**) using $(C_6F_5)_2Hg$, which acts as acceptor to two palladium donors.[11] We wondered if **7** could be used to isolate trimetallic species that contain an interaction of the type $Hg^{II}\cdots Pd^{II}\cdots Hg^{II}$, where the palladium(II) donor interacts with two mercury(II) Lewis acid acceptors, which would be a reversal of the system reported by Gabbaï et al.[11] Herein, we present, to our knowledge, the first structurally characterized example of a metallophilic $Hg^{II}\cdots Pd^{II}\cdots Hg^{II}$ interaction.

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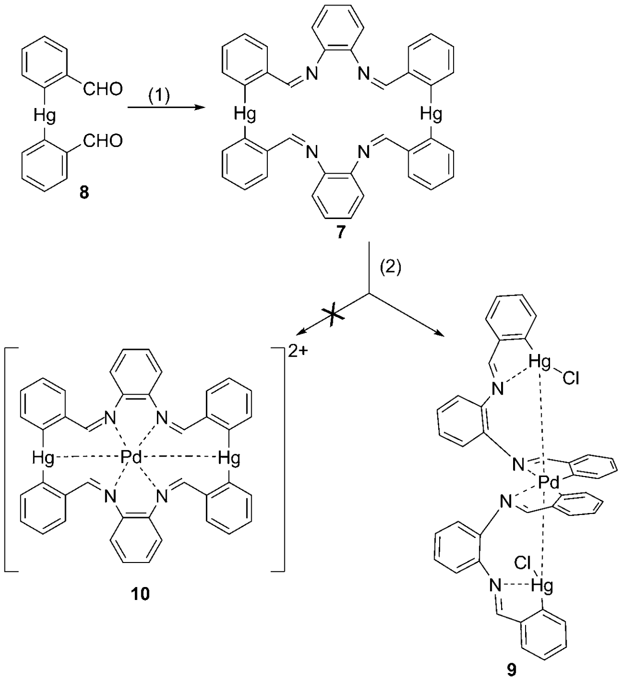
Metallamacrocycle ligand **7** was obtained in good yield by [2+2] condensation of bis(*o*-formylphenyl)mercury (**8**) with *o*-phenylenediamine (Scheme 1) without resorting to high-dilution or metal-template techniques (see Supporting Information for characterization data and structure). Intramolecular Hg···N interactions play a crucial role in the high-yield synthesis of the macrocycle, which adopts an hour-glass/figure-of-eight conformation. The transannular Hg···Hg distance is 3.654 Å. Treatment of macrocycle **7** with an equimolar amount of $[PdCl_2(PhCN)_2]$ in dichloromethane afforded a orange-colored complex, which was characterized as the product **9**[12] instead of the expected complex **10**. Facile transmetalation of the aryl group from mercury to palladium has taken precedence over coordination by nitrogen/mercury, and results in formation of cyclometalated palladium with *cis*-disposition of the aryl groups (see below). It should be noted that attempts to trap lead(II) by the metallocryptand containing cationic gold(I) by Catalano et al. were unsuccessful.[13] During crystallization, complex **9** was isolated as a solvate with dichloromethane (Figure 1) and with acetone (see the Supporting Information), which are pseudopolymorphs. A single-crystal X-ray diffraction study[14] of the dichloromethane solvate of **9** reveals several interesting features. Most notably, the trimetallic complex has a Hg^{II}···Pd^{II}···Hg^{II} (d^{10}···d^{8}···d^{10}) metallophilic interaction. The Hg···Pd distances are 3.1020(3) Å (Hg1···Pd) and 3.2337(3) Å (Hg2···Pd), which are significantly less than the sum of the van der Waals radii (3.4–3.7 Å).[11,15] These distances are close to those observed by Gabbaï et al.[11] in the Pd^{II}···Hg^{II}···Pd^{II} intermolecular system. However, the Hg1-Pd-Hg2 angle of 162.898(7)° deviates from linearity, as observed in the intermolecular system. In the crystal, the molecules are linked by hydrogen bonding to dichloromethane, resulting in chain formation along the *b* axis. Interestingly, the Hg1-Pd-Hg2 angle is 165.01(4)° in the acetone solvate of **9**. Molecules of **9** are linked by an intermolecular Hg···C=C π interaction (3.768 Å). Another interesting feature of the complex is the formation of a metallohelicate structure (Figure 2) along the Hg^{II}···Pd^{II}···Hg^{II} axis.[16] Metal-containing helical species are the focus of attention because of their similarity with bioinorganic systems and their application in asymmetric catalysis. The groove around mercury is significantly deviated from linearity owing to strong interactions with nitrogen and palladium. The C1 A-Hg1-Cl1 and C1B-Hg2-Cl2 bond angles (165.58(7)° and 169.14(7)°) deviate significantly from linearity, indicating a strong Hg–N intramolecular interaction.[6]



Scheme 1. Synthetic route to the macrocycle **7** and palladium complex **9**. 1) *o*-Phenylenediamine, ethanol, reflux; 2) $[PdCl_2(C_6H_5CN)_2]$, CH_2Cl_2, RT.

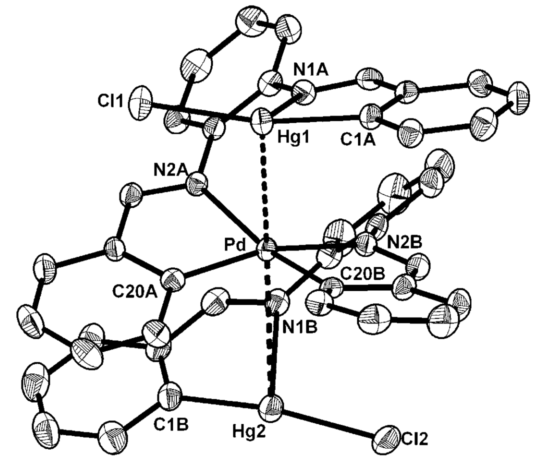


Figure 1. Molecular structure of compound **9** (ellipsoids set at 50 % probability, hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: Hg1–Pd 3.1020(3), Hg2–Pd 3.2337(3), Hg1–N1A 2.6662(19), Hg2–N1B 2.647(2), Pd–N2A 2.1611(18), Pd–N2B 2.1602(19); Hg1-Pd-Hg2 162.898(7), C1A-Hg-Cl1 165.58(7), C1B-Hg-Cl2 169.14(7).

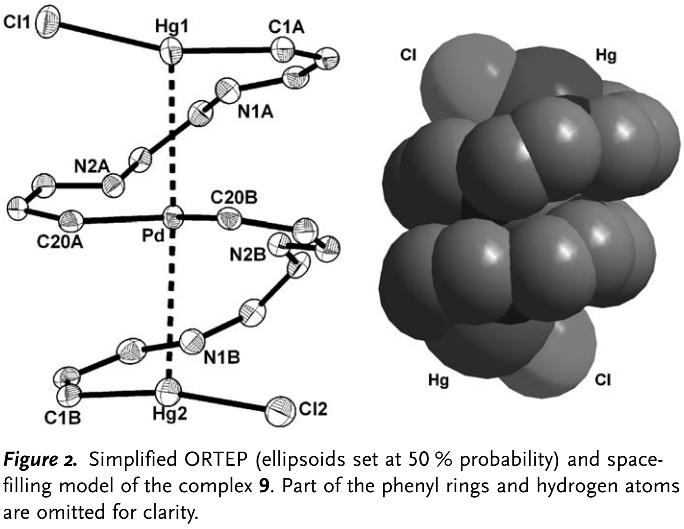


Figure 2. Simplified ORTEP (ellipsoids set at 50 % probability) and space-filling model of the complex **9**. Part of the phenyl rings and hydrogen atoms are omitted for clarity.

AIM analysis[17,18] of **9**, performed with AIM2000[19] on the crystal geometry, confirms the presence of bond critical points between palladium and mercury atoms. The values of electron density (ρ) at bond critical points for the Hg1···Pd and Pd···Hg2 interactions are obtained as 0.017 a.u. and 0.013 a.u., respectively. These values suggest weak metal–metal interactions. To gain an idea about the strength of metallophilic interaction, Wiberg indices at the B3LYP/SDD, 6-31G(d) level of theory were computed. The bond order for Hg1···Pd was found to be 0.12 and 0.09 for the Hg2···Pd interaction. The bond order, along with the electron density at the bond critical point of the Hg–Pd bond, is suggestive of a stronger Hg1···Pd interaction compared to Hg2···Pd interaction. To get an idea about the nature of orbitals involved the in Hg···Pd interaction, natural bond orbital (NBO) analyses[20] were carried out using B3LYP and SV-LDF methods.

The SV-LDF method has been recently used by Schwarz and Wang to study aurophilic interactions and is found to be acceptable for qualitative investigations.[21] NBO analysis identifies the origin of the Hg···Pd···Hg interaction to be 1) donation of electron density from the palladium 4d orbital to the antibonding σ* orbital of the Hg–C bond (Figure 3), and 2) donation from the σ orbital of the Pd–C bond to the antibonding σ* orbital of the Hg–C bond (Supporting Information, Figure S21). The sum of deletion energy of the major orbital interaction for Hg1···Pd and Hg2···Pd was found to be 12.52 and 9.12 kcal mol^{-1}, respectively (B3LYP), whereas a value of 15.16 and 10.75 kcal mol^{-1} was obtained by the SV-LDF method. (Supporting Information, Table S3).

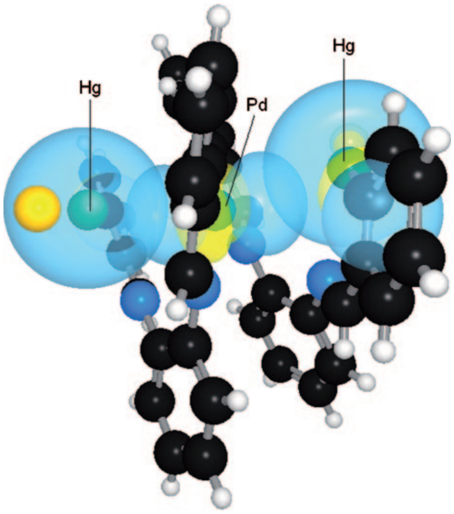


Figure 3. NBO overlap model, showing the $\text{lp(4d)}_{\text{Pd}}\rightarrow\sigma^*_{\text{Hg-C}}$ interaction. Opposing signs of orbitals indicated in yellow and blue. C black, H white, N dark blue, Cl dark yellow.

The electronic absorption spectrum of **7** has a strong absorption at 418 nm in the solid state, whereas complex **9** has a broad absorption in the range of 460–480 nm in the solid state. Although macrocycle **7** is luminescent at room temperature in the solid state and has strong emissions at 484 and 529 nm ($\lambda_{\text{ex}} = 418$ nm), complex **9** is weakly luminescent in solid state, with a macrocycle-**7**-based emission band at 530 nm ($\lambda_{\text{ex}} = 477$ nm).

In conclusion, we have isolated a trimetallic complex with a Hg$^{\text{II}}$···Pd$^{\text{II}}$···Hg$^{\text{II}}$ metallophilic interaction in which cyclometalated palladium(II) acts as a donor. We are extending this approach for the isolation of other helical trimetallic systems with dipositive d^8 and d^{10} metal ions.

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[1] a) P. Pyykkö, *Chem. Rev.* **1997**, *97*, 597–636; b) M. R. Haneline, R. E. Taylor, F. P. Gabbaï, *Chem. Eur. J.* **2003**, *9*, 5188–5193; c) P. Pyykkö, *Angew. Chem.* **2004**, *116*, 4512–4557; *Angew. Chem. Int. Ed.* **2004**, *43*, 4412–4456; d) A. Barbieri, G. Accorsi, N. Armaroli, *Chem. Commun.* **2008**, 2185–2193.

[2] a) J. S. Thayer, *J. Chem. Educ.* **2005**, *82*, 1721–1727, and references therein; b) P. Pyykkö, *Inorg. Chim. Acta* **2005**, *358*, 4113–4130.

[3] a) P. Pyykkö, M. Straka, *Phys. Chem. Chem. Phys.* **2000**, *2*, 2489–2493; b) W. Schuh, P. Braunstein, M. Bénard, M.-M. Rohmer, R. Welter, *J. Am. Chem. Soc.* **2005**, *127*, 10250–10258, and references therein.

[4] M. O. Hakala, P. Pyykkö, *Chem. Commun.* **2006**, 2890–2892.

[5] a) M. A. Rawashdeh-Omary, M. A. Omary, J. P. Fackler, Jr., R. Galassi, B. R. Pietroni, A. Burini, *J. Am. Chem. Soc.* **2001**, *123*, 9689–9691; b) A. Hayashi, M. M. Olmstead, S. Attar, A. L. Balch, *J. Am. Chem. Soc.* **2002**, *124*, 5791–5795; c) H. V. R. Dias, H. V. K. Diyabalanage, M. A. Rawashdeh-Omary, M. A. Franzman, M. A. Omary, *J. Am. Chem. Soc.* **2003**, *125*, 12072–12073; d) H. L. Hermann, G. Boche, P. Schwerdtfeger, *Chem. Eur. J.* **2007**, *7*, 5333–5342; e) Y. Zhou, W. Chen, D. Wang, *Dalton Trans.* **2008**, 1444–1453, and references therein.

[6] T. J. Taylor, C. N. Burress, F. P. Gabbaï, *Organometallics* **2007**, *26*, 5252–5263, and references therein.

[7] a) V. J. Catalano, B. L. Bennett, M. A. Malwitz, R. L. Yson, H. M. Kar, S. Muratidis, S. J. Horner, *Comments Inorg. Chem.* **2003**, *24*, 39–68; b) V. J. Catalano, M. A. Malwitz, *J. Am. Chem. Soc.* **2004**, *126*, 6560–6561, and references therein.

[8] U. Patel, H. B. Singh, G. Wolmershäuser, *Angew. Chem.* **2005**, *117*, 1743–1745; *Angew. Chem. Int. Ed.* **2005**, *44*, 1715–1717.

[9] U. Patel, H. B. Singh, S. Dey, V. K. Jain, G. Wolmershäuser, R. J. Butcher, unpublished results.

[10] M. A. Bennett, M. Contel, D. C. R. Hockless, L. L. Welling, *Chem. Commun.* **1998**, 2401–2402.

[11] M. Kim, T. J. Taylor, F. P. Gabbaï, *J. Am. Chem. Soc.* **2008**, *130*, 6332–6333.

[12] Synthesis of palladium complex **9**: Bis(benzonitrile)palladium(II) chloride (0.081 g, 0.21 mmol) was added to a solution of macrocycle **7** (0.203 g, 0.21 mmol) in dichloromethane (25 mL), and the reaction mixture was stirred for five hours at room temperature. The yellow precipitate obtained was filtered, and the filtrate was kept at room temperature. Slow evaporation resulted in the formation of orange-colored crystals of **9**. The yellow precipitate was recrystallized from dichloromethane (100 mL) to obtain pure **9**. Yield (0.060 g, 60 %), m.p. 202–204 °C. ^{1}H NMR (CD_2Cl_2, 400 MHz): $\delta = 8.19$ (s, 2H), 7.95 (d, $^3J_{\text{HH}} = 7.3$ Hz, 2H), 7.62 (s, 4H), 7.36–7.30 (m, 4H), 7.27–7.17 (m, 4H), 7.09–6.99 (m, 4H), 6.87 (dd, $^3J_{\text{HH}} = 7.9$ Hz, $^4J_{\text{HH}} = 1.2$ Hz, 2H), 6.81–6.71 (m, 4H), 6.52 (d, $^3J_{\text{HH}} = 7$ Hz, 2H). IR (KBr pellet) $\tilde{\nu} = 1621, 1599$ cm^{-1} (C=N). ES-MS: *m*/*z* (%) 1104.9 (37),

947.4 (100), 873.0 (66). Elemental analysis (%) calcd for $C_{41}H_{30}Cl_4Hg_2N_4Pd$: C 40.10, H 2.46, N 4.56; found: C 39.96, H 2.23, N 4.53. UV/Vis: λ_{max} (solid) 467 nm; Emission (solid) 530 nm ($\lambda_{ex} = 477$ nm).

[13] V. J. Catalano, B. L. Bennett, B. C. Noll, *Chem. Commun.* **2000**, 1413–1414.

[14] Crystal structure data for **9**: $C_{41}H_{30}Cl_4Hg_2N_4Pd$, $M_w = 1228.07$, triclinic, space group $P\bar{1}$, $a = 12.1959(10)$, $b = 13.4828(10)$, $c = 14.2258(8)$ Å, $\alpha = 75.804(5)$, $\beta = 65.258(7)$, $\gamma = 63.424(8)°$, $V = 1895.2(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 2.152$ mg m^{-3}, $4.44 < \theta < 34.95$, crystal dimensions $0.41 \times 0.36 \times 0.30$ mm, $\mu = 8.869$ mm^{-1}, $T = 200(2)$ K. A total of 31285 reflections were measured in the range $4.44 < \theta < 34.95$ ($-18 < h < 19$, $-21 < k < 20$, $-22 < l < 19$) with 15312 unique reflections ($R_{int} = 0.\ 0291$). Full-matrix least-squares refinement on F^2 $R1 = 0.0260$, ($I > 2\sigma(I)$) $R1 = 0.0471$ (all data); $wR2 = 0.0415$ ($I > 2\sigma(I)$), $wR2 = 0.0435$. Further details are given in the Supporting Information. CCDC-696373 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif..

[15] a) A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441–451; b) S. Nag, K. Banerjee, D. Datta, *New J. Chem.* **2007**, *31*, 832–834.

[16] F. E. Hahn, M. Offermann, C. S. Isfort, T. Pape, R. Fröhlich, *Angew. Chem.* **2008**, *120*, 6899–6902; *Angew. Chem. Int. Ed.* **2008**, *47*, 6794–6797.

[17] R. F. W. Bader, *Atoms in Molecules: A Quantum Theory*, Oxford University Press, New York, **1990**.

[18] Single-point density-functional calculations and NBO analyses on the crystal geometry were performed with the GAUSSIAN 03 program by the B3-LYP and SV-LDF methods (see the Supporting Information). The SDD basis set with corresponding relativistic effective core potential was employed for Hg and Pd, whereas the 6-31G(d) basis set was employed for remaining atoms in single-point calculations and NBO analyses. AIM analysis was performed with the WTBS basis set on Hg and Pd, and 6-31G(d) for remaining atoms.

[19] F. Beigler-König, J. Schönbohm, D. Bayles, *J. Comput. Chem.* **2001**, *22*, 545–559.

[20] a) A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.* **1988**, *88*, 899–926; b) E. D. Glendening, A. E. Reed, J. E. Carpenter, F. Weinhold, NBO Version 3.1.

[21] S. G. Wang, W. H. E. Schwarz, *J. Am. Chem. Soc.* **2004**, *126*, 1266–1276.