

Mixed-Metal Metallocryptands. Short Metal–Metal Separations Strengthened by a Dipolar Interaction

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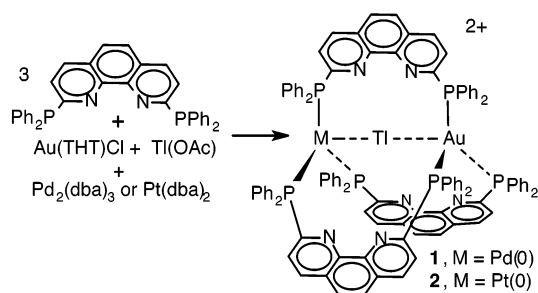
Received March 2, 2004; E-mail: vjc@unr.edu

Discrete complexes or solid-state materials containing aurophilic Au(I)–Au(I)¹ or Au(I)–Tl(I)² interactions are widely studied because of their unique metal–metal bonding properties and dramatic luminescent properties that are often exploited to produce optical sensors.³ While there are numerous reports of extended arrays of homo- and heteronuclear dimetallic systems, no reports on the interactions between three different closed-shell metals could be found. This is likely due to the difficulty in preparing discrete trimetallic systems even though the resulting species should be more stable because the added dipolar interaction of the third dissimilar metal is expected to reinforce the attractive dispersive forces believed responsible for metallophilic interactions. The incorporation of an attractive dipolar interaction was recently exemplified in a few systems where the Au–Ag interactions are noticeably shorter than the corresponding Ag–Ag or Au–Au ones.⁴

Our group has employed a cage approach to explore similar metal–metal interactions in solution whereby a guest metal atom or ion is incarcerated into the center of a metallocryptand cage.⁵ This methodology works well for a number of closed-shell M–M'–M systems where M may be Au(I), Pd(0), or Pt(0) and M' may be Tl(I), Pb(II), Hg(0), or even Hg₂²⁺. These highly stable complexes all contain short (<3 Å) metal–metal separations; however, all of them are symmetrical about the M–M'–M core. Recently, we discovered a remarkably simple reaction whereby mixed-metal metallocryptands containing Pd(0)–Tl(I)–Au(I) or Pt(0)–Tl(I)–Au(I) linkages with unusually short metal–metal separations are produced.

The deep-red, air-stable mixed-metal metallocryptands, [AuPdTl(P₂phen)₃](PF₆)₂, **1**·(PF₆)₂, or [AuPtTl(P₂phen)₃](PF₆)₂, **2**·(PF₆)₂, are easily prepared (Scheme 1) in good yield (60–70%) by reacting (regardless of order) 3 equiv of P₂phen with 1 equiv of Au(C₄H₈S)–Cl, excess thallose acetate, and the appropriate amount of either Pd₂(dba)₃ for **1** or Pt(dba)₂ for **2** in acetonitrile followed by metathesis with excess NH₄PF₆. Additionally, **1**·(BF₄)₂ and **1**·Cl₂ are produced by metathesis with the corresponding sodium salts.

Scheme 1



The ³¹P{¹H} NMR spectra (Figure 1) of **1**·(PF₆)₂ and **2**·(PF₆)₂ are consistent with their mixed-metal formulations. The spectrum (CD₂Cl₂) of **1**·(PF₆)₂ shows two broad resonances each coupled to

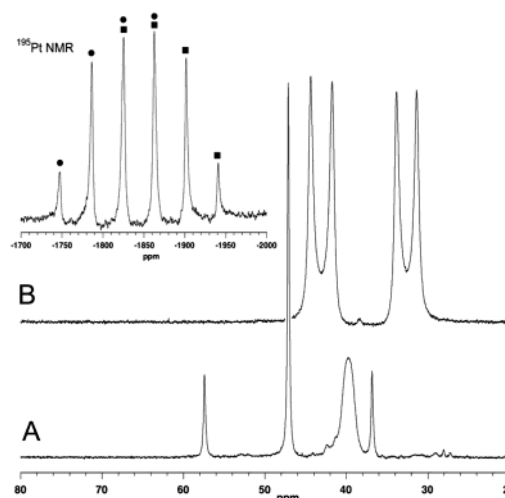


Figure 1. ³¹P{¹H} NMR spectra (CD₂Cl₂) of **1** (spectrum B) and of **2** (spectrum A) showing two independent phosphorus environments. ¹⁹⁵Pt NMR spectrum of **2** showing overlapping quartets denoted by ● and ■.

Tl⁶ at 42.6 (²J_{P–Tl} = 319 Hz) and 32.1 (²J_{P–Tl} = 299 Hz) ppm and an additional heptet (–143 ppm) for the PF₆[–] anion. By comparison to the symmetrical [Au₂Tl(P₂phen)₃]³⁺ and [Pd₂Tl(P₂phen)₃]⁺ metallocryptands^{7,8} which show resonances at 45.7 (²J_{P–Tl} = 186 Hz) and 27.1 ppm, respectively, the more downfield resonance in the spectrum of **1**·(PF₆)₂ is assigned to the phosphorus atoms on Au while the resonance at 32.1 ppm is assigned to Pd-bound phosphorus atoms. The ²J_{P–Tl} coupling constants are significantly larger in **1**·(PF₆)₂ than those found in [Au₂Tl(P₂phen)₃]³⁺, and the observation of coupling to Tl through Pd is noteworthy given that this coupling is noticeably absent in the closely related [Pd₂Tl(P₂phen)₃]⁺ species. Likewise in **2**·(PF₆)₂ (Figure 1, A) two broad resonances associated with the metallocryptand are observed (CD₂Cl₂, 25 °C); however, coupling to Tl through Pt is not resolved. A single, broad resonance with ¹⁹⁵Pt satellites is observed at 47.1 ppm (¹J_{P–Pt} = 4160 Hz) along with a very broad resonance for the Au-bound phosphorus atoms at 39.7 ppm. The latter resolves into a doublet (²J_{P–Tl} = 216 Hz) at –80 °C. The corresponding [Pt₂Tl(P₂phen)₃]⁺ metallocryptand has its ³¹P{¹H} resonance at 46.1 ppm with a similar ¹J_{P–Pt} of 4436 Hz and no observable P–Tl coupling. The presence of Tl in [AuPtTl(P₂phen)₃]²⁺ is supported by the ¹⁹⁵Pt NMR spectrum (Figure 1, inset) which shows the anticipated doublet of quartets at –1841 ppm with ¹J_{Pt–Tl} of 8104 Hz. This coupling is significantly larger than the 5560 Hz Pt–Tl coupling observed in [Pt₂Tl(P₂phen)₃]⁺ and suggests a stronger Pt(0)–Tl(I) interaction in the mixed metal species. The asymmetry of the complex is also expressed in the phenanthroline proton resonances with unique signals and additional coupling observed for each proton. A slight differentiation is also apparent for the phenyl protons at each end of the molecule.

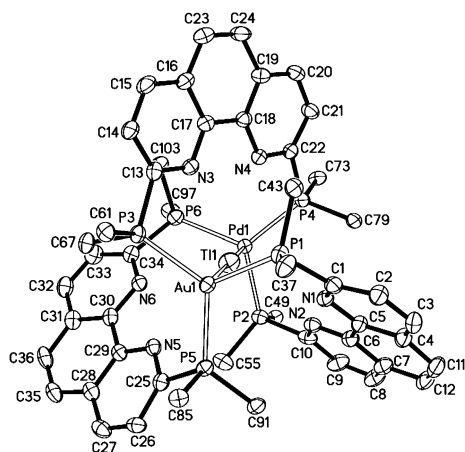


Figure 2. X-ray structural drawing showing only one portion of the disordered metal core of the cation of **1**·(PF₆)₂·3C₆H₆. Hydrogen atoms and all but the ipso carbon of the phenyl rings are removed for clarity. Selected bond distances (Å) and angles (deg): Au(1)–Ti(1) 2.811(9), Pd(1)–Ti(1) 2.796(14), Au(1)–Ti(1)–Pd(1) 177.0(4), P(1)–Au(1)–P(3) 118.3(5), P(1)–Au(1)–P(5) 116.3(4), P(3)–Au(1)–P(5) 123.4(4), P(2)–Pd(1)–P(4) 117.2(6), P(2)–Pd(1)–P(6) 120.2(6), P(4)–Pd(1)–P(6) 119.2(7).

Four unique X-ray crystal structures of **1** (Figure 2) were obtained.⁹ Each one contains the C₃-symmetric cation, varying number of solvent molecules and two independent anions, verifying the overall dicationic charge. In all four structures the capping Pd and Au atoms are positionally disordered; however, simple models produce satisfactory refinements, and reliable metal–metal separations can be measured. The Pd–Ti(1) separations range from 2.673–(5) to 2.796(14) Å (average = 2.743 Å) while the Au–Ti(1) separations are slightly longer and range from 2.793(6) to 2.8865–(16) Å with an average value of 2.831 Å. These values are somewhat shorter than the corresponding Pd–Ti separation of 2.7914(6) Å found in [Pd₂Tl(P₂phen)₃]⁺ and noticeably shorter than the Au–Ti separations of 2.9171(5) and 2.9190(5) Å measured in [Au₂Tl(P₂phen)₃]³⁺. Both Pd and Au atoms are displaced relative to their P₃-planes toward Ti(I) ion by 0.324 and 0.209 Å, respectively.

Unlike **1**, the X-ray structure of **2**·(PF₆)₂⁹ (Supporting Information) is not disordered and also contains short metal–metal separations with a Au(1)–Ti(1) separation of 2.9000(6) Å and a Pt(1)–Ti(1) separation of 2.7712(6) Å. The assignment of Pt and Au in the X-ray structure is based upon a comparison of metal–phosphorus bond distances and the relative metal–Ti separations. For comparison, the corresponding [Pt₂Tl(P₂phen)₃]⁺ metallocryptand contains Pt–Ti separations of 2.7907(9) and 2.7919(9) Å and the unconstrained Pt–Ti separation in [Pt(PPh₂py)₃Tl]⁺ measures 2.8888(5) Å.¹⁰

The electronic absorption spectra (CH₂Cl₂) for **1** and **2** are nearly identical with high-energy π–π* transitions at 230 and 279 nm, a shoulder at ~325 nm, and a broad low-energy band at 400 nm (ε = 40 300 M⁻¹ cm⁻¹) for **1** and 397 nm for **2** (ε = 29 900 M⁻¹ cm⁻¹). Excitation into these low-energy bands produces very weak photoluminescence at ~425 nm. This is in contrast to the [M₂Tl(P₂phen)₃]⁺ (M = Pt or Pd) metallocryptands where no emission was detected and to [Au₂Tl(P₂phen)₃]³⁺ species which shows an intense, long-lived (10 μs), and large Stokes-shifted emission band at 580 nm.

The shortened intermetallic separations observed in **1** and **2** relative to their symmetrical counterparts likely result from the introduction of the dissimilar capping metals, producing a dipole

moment. This feature is expected to reinforce the dispersion forces resulting in a stronger closed-shell, metal–metal interactions. The role of dispersion forces stabilizing metal–metal interactions has been elucidated theoretically¹¹ and has been exemplified in our previous work⁵ where shorter intermetallic separations follow a trend based on increasing dispersion. Single-point energy DFT calculations for the crystal structures of **1** and **2** show that these molecules possess dipole moments of 4.14 and 5.31 D, respectively, and these values are significantly larger than the dipole moment of 0.40 D calculated from the crystal structure of [Pt₂Tl(P₂phen)₃]⁺. Although the mixed-metal species are the thermodynamic products, refluxing a mixture of [M₂Tl(P₂phen)₃]⁺ (M = Pt or Pd) and [Au₂Tl(P₂phen)₃]³⁺ does not produce **1** or **2**, suggesting that the relative kinetic inertness of P₂phen-based metallocryptands prevents the comproportionation reaction.

The successful preparation and enhanced stability of the mixed, closed-shell metal metallocryptands described above illustrates the importance of simple bonding concepts (dipole– and induced dipole–ion interactions) in stabilizing multimetal cores. A similar approach could be applied to developing unsupported multimetallic systems with a variety of metal compositions that may have interesting bonding, structural, luminescent, or compositional properties.

Acknowledgment. This work and the X-ray diffractometer purchase were supported by the National Science Foundation (CHE-0091180 and CHE-0226402). We are grateful to Prof. Brian J. Frost for the DFT calculations and to Dr. Charles Campana (Bruker-AXS) for crystallographic support.

Supporting Information Available: Experimental procedures and thermal ellipsoid plot of **2** (pdf) and crystallographic data in CIF format for **1**·(PF₆)₂·3C₆H₆, **1**·(PF₆)₂·2CHCl₃·2CH₂Cl₂, **1**·(BF₄)₂·2.5CH₂Cl₂, **1**·Cl₂·4.5CH₂Cl₂, and **2**·(PF₆)₂·3CHCl₃·6H₂O. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) (a) Schmidbaur, H., Ed. *Gold: Progress in Chemistry, Biochemistry and Technology*; Wiley: New York, 1999. (b) Schmidbaur, H. *Nature* **2001**, *413*, 31. (c) Schmidbaur, H. *Gold Bull.* **1990**, *23*, 11.
- (2) (a) Fernández, E. J.; López-de-Luzuriaga, J. M.; Monge, M.; Olmos, M. E.; Pérez, J.; Laguna, A.; Mohamed, A. A.; Fackler, J. P., Jr. *J. Am. Chem. Soc.* **2003**, *125*, 2022. (b) Fernández, E. J.; Laguna, A.; López-de-Luzuriaga, J. M.; Mendizabal, F.; Monge, M.; Olmos, M. E.; Pérez, J. *Chem. Eur. J.* **2003**, *9*, 456. (c) Fernández, E. J.; Laguna, A.; López-de-Luzuriaga, J. M.; Olmos, M. E.; Pérez, J. *Chem. Commun.* **2003**, 1760.
- (3) Bardají, M.; Laguna, A. *Eur. J. Inorg. Chem.* **2003**, 3069.
- (4) (a) Rawashdeh-Omary, M. A.; Omary, M. A.; Fackler, J. P., Jr. *Inorg. Chim. Acta* **2002**, *334*, 376. (b) Fernández, E. J.; Laguna, A.; López-de-Luzuriaga, J. M.; Monge, M.; Pyykkö, P.; Runeberg, N. *Eur. J. Inorg. Chem.* **2002**, 750. (c) Usón, R.; Laguna, A.; Laguna, M.; Usón, A.; Jones, P. G.; Erdbrügger, C. F. *Organometallics* **1987**, *6*, 1778. (d) Usón, R.; Laguna, A.; Laguna, M.; Usón, A.; Jones, P. G.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1984**, 285. (e) Catalano, V. J.; Horner, S. J. *Inorg. Chem.* **2003**, *42*, 8430.
- (5) Catalano, V. J.; Bennett, B. L.; Malwitz, M. A.; Yson, R. L.; Kar, H. M.; Muratidis, S.; Horner, S. J. *Comment. Inorg. Chem.* **2003**, *24*, 39.
- (6) Both ²⁰³Tl (29.5% abundant) and ²⁰⁵Tl (70.5% abundant) are I = 1/2 and have nearly identical gyromagnetic ratios. Their individual couplings are not resolved.
- (7) Catalano, V. J.; Bennett, B. B.; Kar, H. M.; Noll, B. C. *J. Am. Chem. Soc.* **1999**, *121*, 10235.
- (8) Catalano, V. J.; Bennett, B. B.; Yson, R. L.; Noll, B. C. *J. Am. Chem. Soc.* **2000**, *122*, 10056.
- (9) Complete crystal data for all structures are provided as Supporting Information.
- (10) Catalano, V. J.; Bennett, B. L.; Muratidis, S.; Noll, B. C. *J. Am. Chem. Soc.* **2001**, *123*, 173.
- (11) (a) Mendizabal, F.; Pyykkö, P.; Runeberg, N. *Chem. Phys. Lett.* **2003**, *370*, 733. (b) Runeberg, N.; Schütz, M.; Werner, H.-J. *J. Chem. Phys.* **1999**, *110*, 7210.

JA048800N