Encapsulated, Sandwiched, or Sticking Out: Closed-Shell Interactions of d^{10} Metal Centers with Thallium(I)

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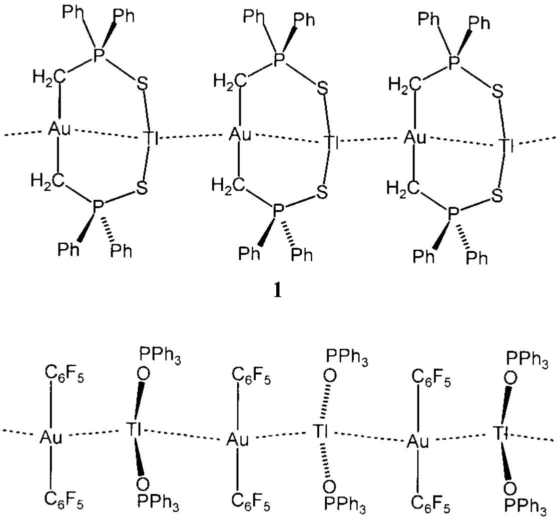
Closed-shell metal–metal contacts are ubiquitous in the structural chemistry of the heavy, late transition metal and p-block elements.[1] The attractive interaction between these heavy-metal centers in molecules and solids, which determines their structures, has early on led to the notion of significant but essentially noncovalent bonding. Phenomenologically labeled first as "aurophilic" for gold(I) compounds,[2] later more generally as "metallophilic" for the attractive forces between d^8, d^{10}, and s^2 metal centers,[1, 3] the physical interpretation of this type of interaction initially remained disputed. The work of Pyykkö and his co-workers has only recently led to a clarification of the nature of these "metallophilic" interactions. As was shown in a series of detailed theoretical studies, they represent a correlation effect which at long intermetallic distances is essentially a "classical" dispersion force.[4, 5] This dispersive (van der Waals) attraction is frequently reinforced by electrostatic components as well as a charge–transfer type dispersive contribution.[6]

Monovalent gold and thallium, possessing d^{10} and s^2 configurations and thus representing the closed-shell species referred to above, mark the two extremes of metallophilic attraction. The interaction between Au^{I} centers may be comparable to strong hydrogen bonds (up to 46 kJ mol^{-1}) and has enabled, for instance, the spectactular gold "clustering" reported by Schmidbaur's group.[2] On the other hand, the relative weakness of the attraction between Tl^{I} centers, estimated to lie below 20 kJ mol^{-1}, has lent a certain ambiguity to the interpretation of the the solid-state structures of this element.[7]

Whereas the "metallophilic" attraction between d^{10} metal centers is enhanced by the relativistic contraction of the s- and p-electron shells (along with the destabilization of the d-orbitals),[4] the relativistic contribution to the closed-shell interaction between s^2 metal centers such as Tl^{I} actually weakens their dispersive attraction.[8] It is thus not surprising that the observation of "metallophilic" attraction between thallium(I) centers strongly depends upon the absence of competing intra- and intermolecular interactions, such as electrostatic attraction or repulsion or the van der Waals interactions with aromatic rings.[9] However, combining d^{10} metal centers and Tl^{I} has led to a series of stable adducts, the metal–metal contacts for some being additionally supported by electrostatic attraction.

The first example of such a thallium(I)–d^{10} metal interaction in the infinite chains of $[\mathrm{AuTl(mtp)}]_\infty$ **1** (mtp = $\mathrm{CH_2P(S)Ph_2^-}$; Scheme 1), which are based on both dispersive and electrostatic ("acid–base") attraction between the metal centers, was reported by Fackler et al. more than a decade ago.[10] Recently, Laguna and his co-workers found a related metal chain structure **2** derived from $[\mathrm{Tl(OPPh_3)_2}]^+$ and $[\mathrm{Au(C_6F_5)_2}]^-$.[11] Whereas neither of the individual molecular components are emissive, the heterometallic aggregate displays a characteristic luminescence, similar to that of Fackler's complex **1**. The importance of the metallophilic aggregation for the photophysical properties of the compounds in question is a central aspect of current research in this area and has been reviewed previously.[12]



1

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Scheme 1. The Au–Tl chains of $[\mathrm{AuTl(mtp)}]_\infty$ (mtp = $[\mathrm{CH_2P(S)Ph_2}]^-$) **1** and $[\{\mathrm{Tl(OPPh_3)_2}\}\{\mathrm{Au(C_6F_5)_2}\}]$ **2**.

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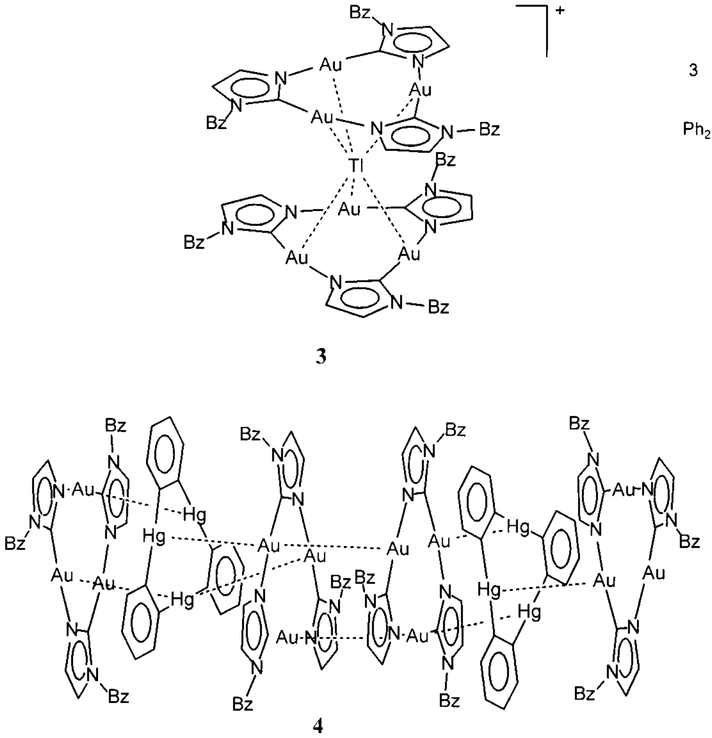
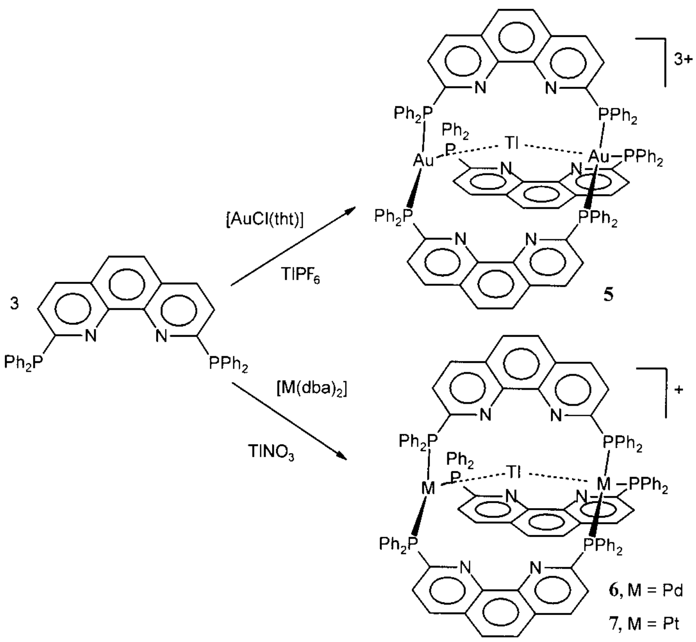
The type of aggregation through dispersive and electrostatic (Lewis acid–base) attraction observed in the metal chains discussed above has led to spectacular sandwich structures if planar trinuclear gold(I) complexes are combined with Tl^I salts. The cyclic trinuclear complex $[Au(\mu\text{-}C^2,N^3\text{-bzim})]_3$ (C^2,N^3-bzim = 1-benzylimidazolate) forms sandwich "clusters" **3** in the presence of Tl^+, in which the thallium ions are located between the planar units and form contacts with six AuI centers in a distorted trigonal-prismatic coordination (Scheme 2).[13] The sandwich units themselves further aggregate through Au–Au interactions to form infinite columnar structures obeying an Au_3-Tl-Au_3-Au_3-Tl-Au_3 stacking pattern. A related stacking pattern, based on d^{10}–d^{10} attractions, was observed upon co-crystallization of $[Au(\mu\text{-}C^2,N^3\text{-bzim})]_3$ and the trinuclear mercury complex $[Hg(\mu\text{-}C_6F_4)]_3$.[14] In the columnar structure found in a single crystal X-ray diffraction study of **4**, Hg–Au distances of as short as 3.24 Å indicate metallophillic attraction, which is additionally supported by the electrostatic attraction of the metal-basic (electron-rich) gold triangle and the metal-acidic (electron-poor) trimercury unit (Scheme 2). However, it is thought that these sandwich-type aggregates dissociate in solution and are thus only observed in the crystal, as is the case for the heterometal chains discussed above.



Scheme 2. The $(Au_3)_2Tl$ sandwich structures in $[Tl\{Au(\mu\text{-}C^2,N^3\text{-bzim})\}_3]^+$ **3** and the columnar aggregate of $[\{Au(\mu\text{-}C^2,N^3\text{-bzim})\}_3\{Hg(\mu\text{-}C_6F_4)\}_3]$ **4**.

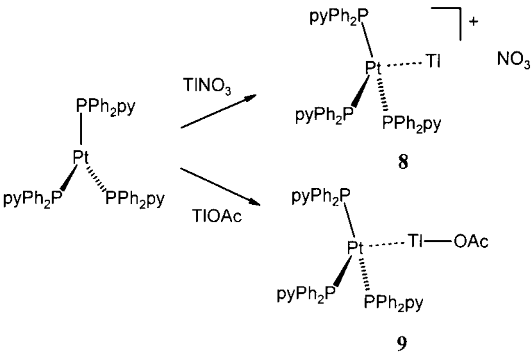
Catalano and co-workers have now shown that Tl^+ ions may bind fairly strongly to d^{10} metal centers and that this type of metal–metal contact pertains in solution. In a series of metal-binding experiments of a new class of metallocryptands, they found a facile uptake and incorporation of in particular Tl^+. In the host molecules a binding cavity is created by linking two three-coordinate Au^I, Pd^0, or Pt^0 complex fragments with three 2,9-diphosphanylphenanthrolines ("P_2phen") molecules acting as bridging ligands (Scheme 3).[15–17]



Scheme 3. Aggregation of the metallocryptates $[Tl\{Au_2(P_2phen)_3\}]^{3+}$ **5**, $[Tl\{Pd_2(P_2phen)_3\}]^+$ **6**, and $[Tl\{Pt_2(P_2phen)_3\}]^+$ **7** (tht = tetrahydrothiophene, dba = dibenzylideneacetone).

It is remarkable that Tl^+ enters the $[Au_2(P_2phen)_3]^{2+}$ cage and forms short Au–Tl contacts in **5**, in spite of the positive charges of the metal centers in both the host molecule and the guest ions. This rules out a simple electrostatic component in this attraction, which is thought to be entirely due the "metallophilic" van der Waals attraction between the metal centers. The repulsion between ionic components only becomes a destabilizing factor on going from monovalent thallium to the isoelectronic divalent lead. In order to incorporate the Pb^{2+} ions, the neutral host cages $[Pd_2(P_2phen)_3]$ and $[Pt_2(P_2phen)_3]$ were employed, in which the Pd^0 and Pt^0 centers actually bear relatively high electron densities at the metal center, in part located above and below the L_3M planes.[17]

While the complexation of Tl^+ within the cryptand cages may at first sight appear to favor the relatively strong binding and may obscure the the actual strength of the individual metal–metal interactions, a very recent study of the reaction of the three-coordinate mononuclear platinum(0) complexes $[Pt(PPh_2py)_3]$ with thallium(I) salts (Scheme 4) led to the isolation and structural characterization of the thallium adducts **8** and **9** containing direct Pt–Tl bonding in the solid (Figure 1).[18] In fact, ^{205}Tl and ^{195}Pt NMR studies in solution have established the stability of these heterometallic complexes in solution, while fast-atom bombardment (FAB) mass spectrometry established their integrity in the gas phase. That there is significant bonding interaction between Tl and Pt in these molecules is also evident from the striking changes of their chemical properties upon coordination of the thallium cations to the d^{10} metal centers. While the triphosphanepla-



Scheme 4. Formation of the Tl–Pt complexes **8** and **9** (py = pyridine).

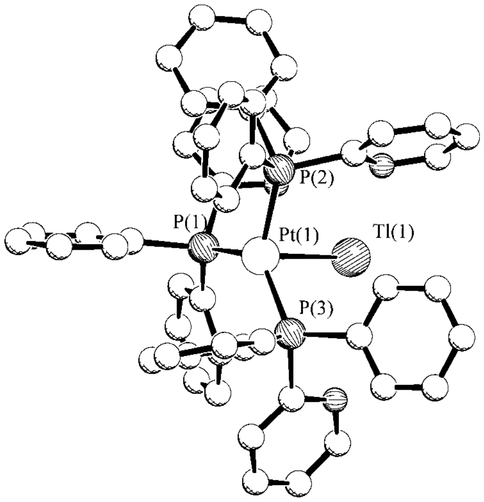


Figure 1. Molecular structure of [Tl-Pt(PPh_2py)$_3$]$^+$ in **8**.

tinum(0) compounds are highly susceptible to oxidation by O_2, this is not the case for the heterodinuclear derivatives. Further, in contrast to the trigonally coordinated platinum complexes, **8** and **9** are nonemissive.

This formation of stable adducts through metallophillic bonding of $d^{10}s^2$ ions such as Tl^+ to palladium(0) and platinum(0) makes one wonder about the generality of this phenomenon. It was therefore of interest to find out whether single mercury(0) atoms (which are isoelectronic with Tl^+) bind in a similar way to a tris(phosphane)platinum complex. Catalano and co-workers have very recently reported such an inclusion of a single mercury atom within their metallocryptand cage.[19] This exciting observation adds a new aspect to the classical experiments on the clustering of mercury metal with Pt^0 fragments bearing isocyanide, phosphane, or CO ligands reported by the groups of Yamamoto and Venanzi almost two decades ago.[20] It may also lead us to reconsider the general suitability of mercury addition to Pt and Pd catalysts in a standard experiment to distingish molecular from colloidal catalysis.[21] Strong adduct formation of a closed-shell atom or ion with a zerovalent mononuclear complex is expected to at least modify the activity of the catalytic system.

It will be interesting to see whether the metallocryptand approach developed in Catalano's group will be extended to include the complex formation of more inert closed-shell "guests" such as heavy noble-gas atoms.[22]

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