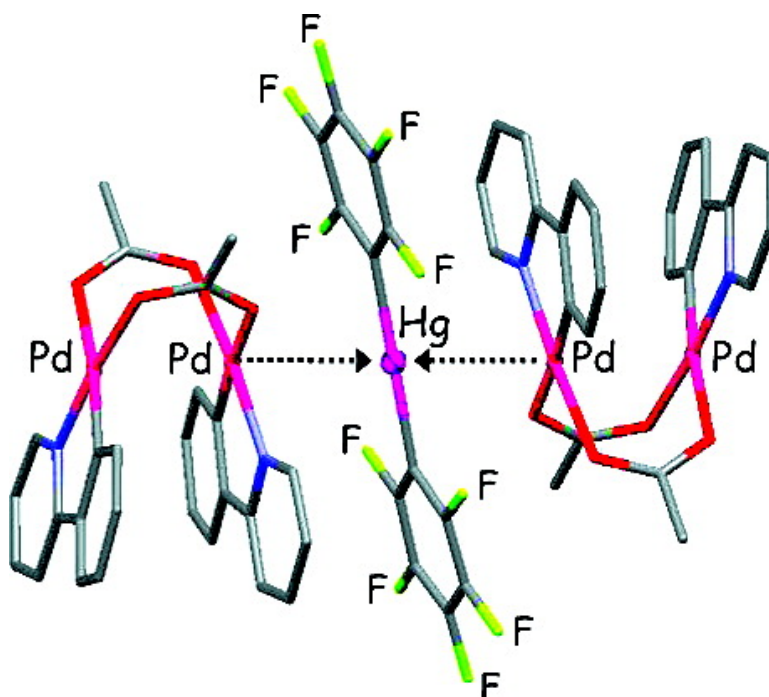


Hg(II)---Pd(II) Metallophilic Interactions

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Hg(II)⋯Pd(II) Metallophilic Interactions

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The formation of metallophilic interactions¹ between closed-shell metal atoms has become a topical area of research. From a fundamental standpoint, the forces responsible for these interactions continue to challenge existing chemical bonding paradigms. Recent theoretical advances^{2,3} suggest that dispersion forces magnified by relativistic effects play a crucial role when these interactions involve heavy ions such as Au(I)⁴ or Hg(II).¹ While much effort has been devoted to homometallic systems, the study of metallophilic bonds involving different atoms is attracting an increasing interest.⁵ In the case of mercury, documented examples of such interactions include Hg(II)⋯Au(I)⁶ and Hg(II)⋯Pt(II) bonds^{7,8} which have been shown to form in the absence of supporting ligands. Although relativistic effects are important here,⁹ the formation of these bonds is usually complemented by an acid–base or donor–acceptor component. As part of our contribution to this general area, we have focused our attention on the formation of unsupported Hg(II)⋯Pd(II) interactions. Such metallophilic bonds have remained extremely rare and have only been observed intramolecularly.^{8,10,11}

Hoping to capitalize on a possible Pd(II)→Hg(II) donor–acceptor component, we decided to consider Hg(C₆F₅)₂ (**1**, Chart 1) as a mercury-containing synthon whose Lewis acidity is enhanced by the use of fluorinated ligands.^{12–14} Interestingly, addition of **1** to a CH₂Cl₂ solution of the mononuclear palladium complex [Pd(salophen)] (**I**, Chart 1, salophen = *N,N'*-disalicylidene-*o*-phenylenediamine)¹⁵ or the dinuclear palladium complex [Pd(N[^]C)(OAc)]₂ (**II**, Chart 1, N[^]C = (2-(2-pyridyl)phenyl-*C,N*)¹⁶ results in the precipitation of the 1:2 complexes [**1**–(**I**)₂] and [**1**–(**II**)₂], respectively. These complexes, which do not luminesce when irradiated with UV light, have been characterized by elemental analysis and single-crystal X-ray diffraction but cannot be observed in solution by NMR spectroscopy because of their insolubility. Since precipitation was not observed at high dilution, we decided to study this reaction using UV–vis spectroscopy. Remarkably, incremental addition of **1** to a solution of the palladium complexes **I** in CH₂Cl₂ triggers a hypochromic response of the band at 481 nm which corresponds to a salophen centered absorption (Figure 1).¹⁷ In the case of **II**, incremental addition of **1** induces a hyperchromic response of the band centered at 404 nm (Figure 1). This band, which disappears upon dissociation of the dinuclear palladium complex **II** by addition of pyridine, is assigned to an excimeric excited state resulting from the intramolecular interaction of the two N[^]C ligands.¹⁸ While the exact origin of this hypo- or hyperchromism is difficult to assign, the observed changes clearly indicate that the organomercurial interacts with the palladium complexes in solution.

Both complexes crystallize in the *P*2₁/*n* monoclinic space group with two centrosymmetrical molecules of the complex per unit cell (Figure 2). The crystal structure of complex [**1**–(**I**)₂] consists of two molecules of the palladium complex sandwiching the organomercurial. As indicated by the short centroid–centroid distances of 3.41 and 3.57 Å occurring between the C₆F₅ ring and the flanking phenyl groups of the salophen ligand, formation of this complex

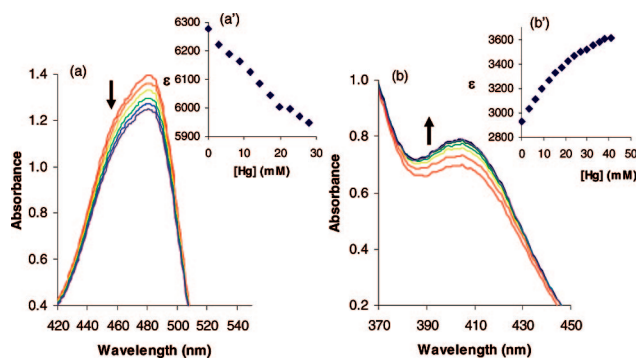
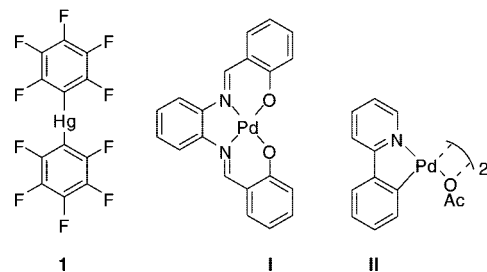


Figure 1. Changes observed in the UV spectrum of **I** (a, [**I**] = 2.22×10^{-4} M) and **II** (b, [**II**] = 2.38×10^{-4} M) upon incremental addition of **1** ($0 \sim 4.1 \times 10^{-2}$ M) in CH₂Cl₂. Molar absorptivity change of [**I**] at 481 nm (a') and [**II**] at 404 nm (b') are shown in the insets.

Chart 1



benefits from arene–fluoroarene interactions.¹⁹ Further inspection of the structure indicates that the mercury atom Hg(1), which sits on the inversion center, is separated from the two palladium atoms of the adjacent molecules of **I** by 3.2841(2) Å. With a C(1)–Hg(1)–Pd(1) angle of 81.8°, the palladium atoms are well positioned to engage in secondary interactions with the mercury centers. However, the Pd(1)–Hg(1) distance is not significantly shorter than the sum of the van der Waals radii of the two elements (3.4–3.7 Å),^{1,20,21} suggesting that the Hg–Pd interactions bear a small donor–acceptor component and are mostly of dispersive nature.

The structure of complex [**1**–(**II**)₂] is similar to that of [**1**–(**I**)₂]. However, the Hg(1)–Pd(1) bond of 3.1065(8) Å in [**1**–(**II**)₂] is notably shorter, suggesting a stronger Pd(II)→Hg(II) donor–acceptor interaction. This bond length, which can be compared to the sum of the covalent radii of Pd and Hg (2.77 Å), is only slightly longer or comparable to existing intramolecular Pd(II)→Hg(II) bonds (2.88–3.10 Å).^{8,10,11} The C(1)–Hg(1)–Pd(1) angle of 104.0(2)° indicates that the Pd(1) and Pd(1A) palladium atoms remain close to the direction that is perpendicular to the C(1)–Hg–C(1A) vector. Another important difference is the apparent absence of strong arene–fluoroarene interactions in this structure, with the centroid of the C₆F₅ ring separated by more than 4 Å from the centroid of the phenyl or pyridyl rings of the N[^]C ligand. Altogether, these

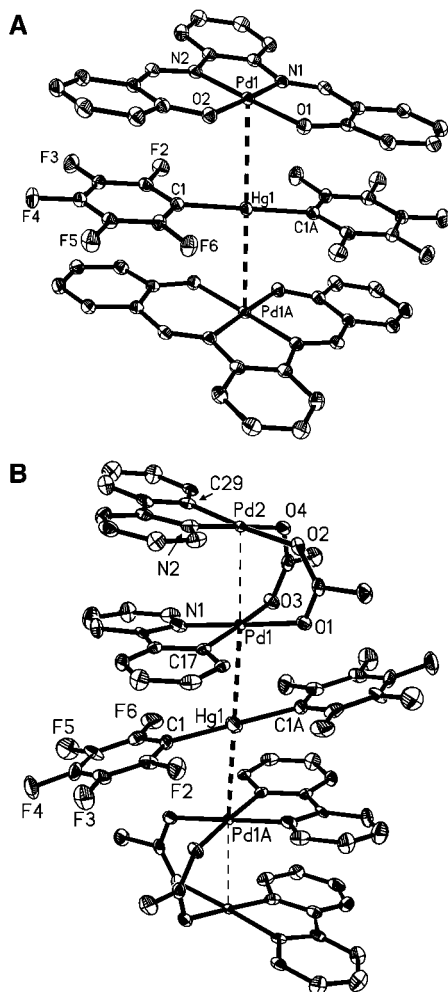


Figure 2. Crystal structures of [I-(I)₂] (A) and [I-(II)₂] (B) (50% ellipsoid, H atoms omitted). Selected bond lengths (Å) and angles (°): [I-(I)₂] Hg(1)–C(1) 2.0681(18), Hg(1)–Pd(1) 3.2841(2), C(1)–Hg(1)–C(1A) 180.0, C(1)–Hg(1)–Pd(1) 81.85(5), Pd(1)–Hg(1)–Pd(1A) 180.0; [I-(II)₂] Hg(1)–C(1) 2.071(9), Hg(1)–Pd(1) 3.1065(8), C(1)–Hg(1)–C(1A) 180.0, C(1)–Hg(1)–Pd(1A) 76.0(2), C(1)–Hg(1)–Pd(1) 104.0(2), Pd(1)–Hg(1)–Pd(1A) 180.0, Pd(2)–Pd(1)–Hg(1) 170.82(2).

structural features suggest that the Pd(II)–Hg(II) bonds present in [I-(II)₂] are unsupported and certainly stronger than those in [I-(I)₂].

The electronic structure of **I** and **II** may be at the origin of these structural differences. In **I**, the palladium 4d_{z²} orbital may be too low in energy to strongly interact with the mercury atoms. In **II**, the two palladium atoms are forced into proximity by the bridging acetate ligands. As a result, the filled 4d_{z²} orbitals of each palladium center interact to form filled σ and σ^* orbitals, the latter being oriented outward along the Pd–Pd axis. The presence of a filled σ^* orbital whose energy is higher than that of the mononuclear unit should result in a substantial increase in the basicity of this molecule and make it a better donor, leading to shorter Pd(II)–Hg(II) distances. In agreement with this view, we note that the Pd(1)–Pd(2) distance of 2.8394(9) Å in [I-(II)₂] is slightly shorter than that in

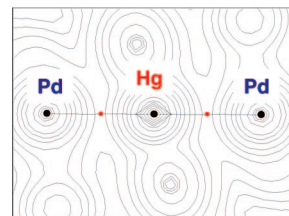


Figure 3. View of computed electron density map of [I-(II)₂]. The bond paths and bond critical points are also shown.

pure **II** (2.8664(6) Å) whose structure has also been determined. For both compounds, an AIM analysis carried out at the crystal geometry (B3LYP, basis sets: WTBS for Hg and Pd, 6-31g for H, C, N, O, and F) indicates the presence of a bond path connecting the Hg atom to each Pd atom (Figure 3). The electron density at the Hg–Pd bond critical point is significantly greater for [I-(II)₂] ($1.7 \times 10^{-2} \text{ e}^-/\text{bohr}^3$) than for [I-(I)₂] ($1.0 \times 10^{-2} \text{ e}^-/\text{bohr}^3$).

In conclusion, we report structural evidence for the formation of unsupported Hg(II)···Pd(II) interactions. We propose that these interactions originate from favorable dispersion forces complemented, at least for [I-(II)₂], by a Pd(II)→Hg(II) donor–acceptor component.

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Supporting Information Available: Experimental details, spectral data, and crystallographic data of **II**, [I-(I)₂], and [I-(II)₂]. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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