

# Structure and Gas-Phase Thermochemistry of a Pd/Cu Complex: Studies on a Model for Transmetalation Transition States

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**S** Supporting Information

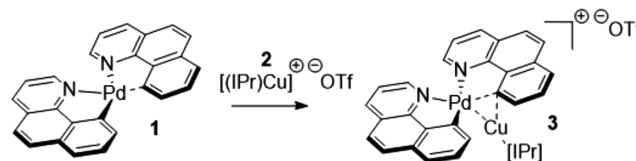
**ABSTRACT:** A heterobimetallic Pd(II)/Cu(I) complex was prepared and characterized by X-ray diffraction analysis. The crystal structure shows a remarkably short Pd–Cu bond and a trigonal ipso carbon atom. The Pd–Cu interaction, as determined by energy-resolved collision-induced dissociation cross-section experiments, models the net stabilizing energy of the Pd–Cu interaction in the transition state of the transmetalation step in Pd/Cu-catalyzed cross-coupling reactions. The bonding situation in the bimetallic dinuclear complex has been studied by atoms-in-molecules analysis.

A variety of palladium-catalyzed cross-coupling reactions between organohalides and organometal(loid)s have been developed in recent years.<sup>1</sup> Even though their organometallic coupling partners vary, it is understood that they all follow a common general catalytic cycle in which a transmetalation reaction is one of the key steps. The mechanism of transmetalation reactions has been most thoroughly studied for the Stille reaction and, more recently, for the Suzuki–Miyaura coupling,<sup>1</sup> and it has been proposed that the reaction proceeds, depending on the exact reaction conditions, via either an open or closed transition state.<sup>2</sup> For both the open and closed transition states, the d<sup>10</sup> component (Sn(IV) for the Stille coupling) is treated as the nucleophile and the d<sup>8</sup> component (Pd(II) for most cross-couplings) is the electrophile. We recently reported a study of the transmetalation step in the gas phase using ESI-MS/MS for the experimental part and density functional theory (DFT) for the computational part, which suggested that, at least for the Sonogashira coupling, the situation could be interpreted to be the opposite: M(I), the d<sup>10</sup> component, acts as the electrophile and Pd(II), the d<sup>8</sup> component, as the nucleophile,<sup>3</sup> at least within one simple, perhaps even “naïve” picture of the bonding.<sup>4</sup> Square-planar Pt(II) complexes that form metal–metal bonds to Lewis acidic d<sup>10</sup> metals have been known since the 1980s, when Van Koten first reported on Pt<sup>II</sup>–Hg<sup>II</sup> and Pt<sup>II</sup>–Ag<sup>I</sup> complexes;<sup>5,6</sup> however, it should be noted that those d<sup>8</sup>–d<sup>10</sup> bonds were supported by bridging ligands. A few years later, Puddephatt and co-workers<sup>7</sup> identified unbridged Pt<sup>II</sup>–Ag<sup>I</sup> and Pt<sup>II</sup>–Au<sup>I</sup> complexes by NMR spectroscopy. A free-standing d<sup>8</sup>–d<sup>10</sup> bond was shortly thereafter characterized crystallographically in a Pt<sup>II</sup>–Ag<sup>I</sup> complex by Usón and Cotton.<sup>8</sup> Our group recently published the X-ray structures of complexes with similarly unsupported Pt<sup>II</sup>–Cu<sup>I</sup> and Pt<sup>II</sup>–Ag<sup>I</sup> bonds.<sup>9,10</sup> We investigated

analogous Pt<sup>II</sup>–Au<sup>I</sup> complexes in the gas phase;<sup>11</sup> a related Pt<sup>II</sup>–Au<sup>I</sup> complex has recently been structurally characterized in the solid state.<sup>12</sup> Heterobimetallic complexes with a d<sup>8</sup>–d<sup>10</sup> bond to Pd(II) as the d<sup>8</sup> component are far less common, as the d<sup>8</sup>–d<sup>10</sup> interaction is much weaker. Only three examples have been reported, with Ag(I),<sup>13</sup> Au(I),<sup>14</sup> and Tl(I).<sup>15</sup> We report here the first X-ray crystal structure of a Pd<sup>II</sup>–Cu<sup>I</sup> heterobimetallic complex, its bond strength, and a first theoretical study of the bonding.

We chose to synthesize *cis*-bis(1,10-benzo[*h*]quinolino)-palladium, [(bhq)<sub>2</sub>Pd<sup>II</sup>] (**1**),<sup>16</sup> because it is structurally and electronically similar to proposed intermediates in Pd-catalyzed cross-coupling reactions yet more stable than other L<sub>2</sub>Pd<sup>II</sup>R<sub>2</sub> (R = alkyl, alkenyl, alkynyl) complexes, the reductive elimination being sterically blocked in the bischelate. Complex **1** was mixed with an equimolar amount of (IPr)Cu<sup>I</sup>OTf, [2(–OTf)]<sup>17</sup> (IPr = [1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]) (Scheme 1), and the solution was cooled to –35 °C; the thereby-

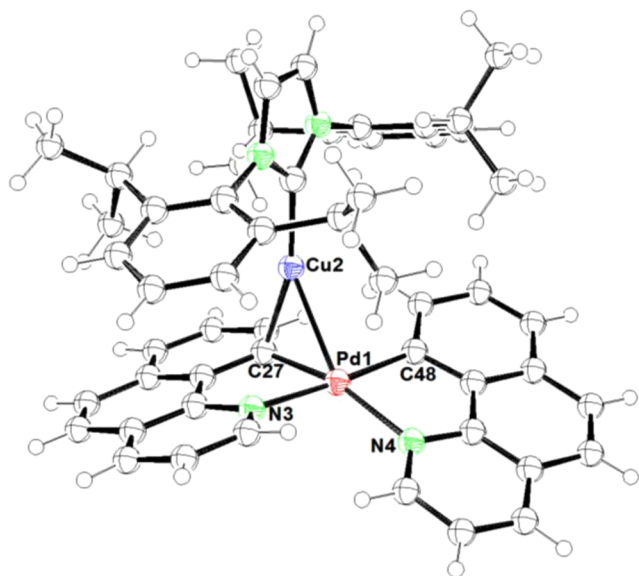
**Scheme 1. Synthesis of the Heterobimetallic Complex [3(–OTf)]**



formed colorless crystals of [3(–OTf)] were analyzed by X-ray diffraction. The measured crystal structure (Figure 1) shows a short Pd<sup>II</sup>–Cu<sup>I</sup> distance of only 2.55 Å, which is significantly shorter than the sum of the covalent radii (2.71 Å),<sup>18</sup> this criterion having been justified previously as an indication of an attractive bonding interaction.<sup>19</sup> Also striking is the strong interaction between Cu and one of the carbons of the bhq ligand (Cu2–C27: 2.025 Å) leading to an enhancement of a slight, already present,<sup>20</sup> out-of-plane distortion of the bhq ligand (N4–Pd1–C27: 162.6°) and the formation of a trigonal ipso carbon. The observed geometry, with the metal–metal bond not standing perpendicular to the coordination plane of the d<sup>8</sup> metal (i.e., sitting on the Pd atom’s d<sub>z<sup>2</sup></sub> orbital) but instead tilted toward one (or two) of the ligands, had been observed previously in some Pt<sup>II</sup>–M<sup>I</sup> complexes by us and others.<sup>10,12,21</sup> Theoretical studies of d<sup>8</sup>–d<sup>10</sup> (and the related d<sup>8</sup>–d<sup>8</sup>) bonding attribute the attractive interaction variously to

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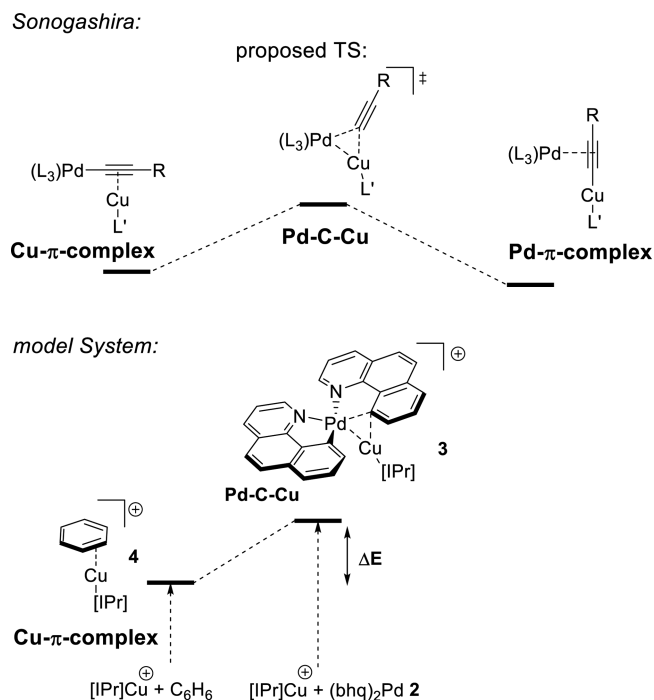
**Figure 1.** Crystal structure of cationic complex **3**. Selected bond distances (Å) and angles (deg): Pd1–Cu2 2.554, Pd1–C27 2.072, Pd1–C48 2.018, Pd1–N3 2.148, Pd1–N4 2.124, Cu2–C27 2.025, N4–Pd1–C27 162.6, N3–Pd1–C48 175.3, N4–Pd1–Cu2 146.5.

generalized Lewis acid–Lewis base effects,<sup>22</sup> specific frontier orbital overlap,<sup>23</sup> or even predominantly London dispersion (van der Waals) interactions.<sup>24</sup> While we make no definite claim concerning the bonding model in this report—we characterize the attractive interaction as a first step toward working out a bonding model—the experimentally observed geometry can be understood in terms of bonding to the locus of maximum electron density.

Our previous DFT studies of the transmetalation step in the Sonogashira reaction suggested that the reaction starts from a Cu acetylide with Pd coordinated to the  $\pi$  bond and goes through a transition state with a close Pd<sup>II</sup>–Cu<sup>I</sup> contact and a trigonal ipso carbon to a Pd acetylide with Cu coordinated to the triple bond (Figure 2).<sup>3</sup> Experimental results as well as DFT calculations showed that the barrier for the internal rearrangement is exceptionally low, leading us to propose that the favorable metal–metal interaction, which occurs in the transition state but not in either of the  $\pi$  complexes, lowers the barrier to rearrangement with respect to the reactant and product. As may be seen in Table 1, the crystal structure of **3** strongly resembles the calculated structure of the transition state of the rearrangement in the Sonogashira transmetalation, specifically with regard to the short Pd<sup>II</sup>–Cu<sup>I</sup> distance and the trigonal ipso carbon, from which we claim that **3** can model the transition state. The transmetalation process has been identified by Lei and co-workers<sup>26</sup> to be rate-limiting in the overall Sonogashira reaction.

Therefore, the quantification of the net stabilization of the transition state due to the close Pd<sup>II</sup>–Cu<sup>I</sup> contact would not only improve the understanding of the mechanism of transmetalation reactions in general but also help to develop more efficient catalytic systems, especially given the close similarity of computed structures along the reaction coordinate of the transmetalation step in the Sonogashira coupling to those computed by Espinet for the Negishi coupling,<sup>19c,25,27</sup> as also seen in Table 1.

Cationic complex **3** is well-suited for ESI-MS investigations (Figure 3), and its composition was confirmed by the  $m/z$  ratio

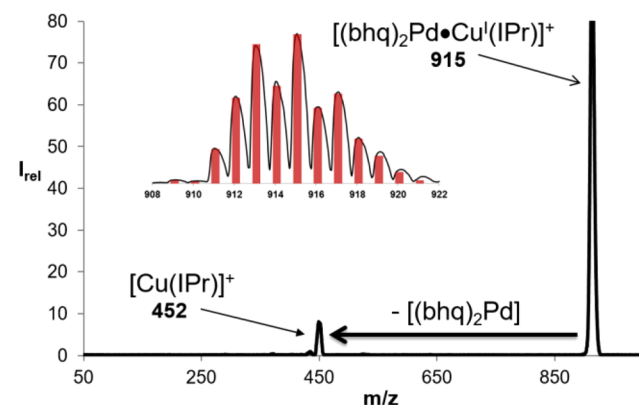


**Figure 2.** Schematic comparison of the proposed mechanism for the transmetalation step in Sonogashira reaction (top) with the model system (bottom).

**Table 1.** Comparison of Selected Bond Lengths (Å) in the X-ray Structure of **3** and Three Isoelectronic DFT-Calculated Transmetalation TSs

Pd/M (M = Cu <sup>I</sup> , Zn <sup>II</sup> )	Pd–M	Pd–C <sub>ipso</sub>	M–C <sub>ipso</sub>
Pd/Cu (complex <b>3</b> , X-ray)	2.55	2.07	2.03
Pd/Cu (Sonogashira TS) <sup>a</sup>	2.69	2.14	1.91
Pd/Zn-1 (Negishi TS) <sup>b</sup>	2.47	2.27	2.16
Pd/Zn-2 (Negishi TS) <sup>b</sup>	2.65	2.39	2.21

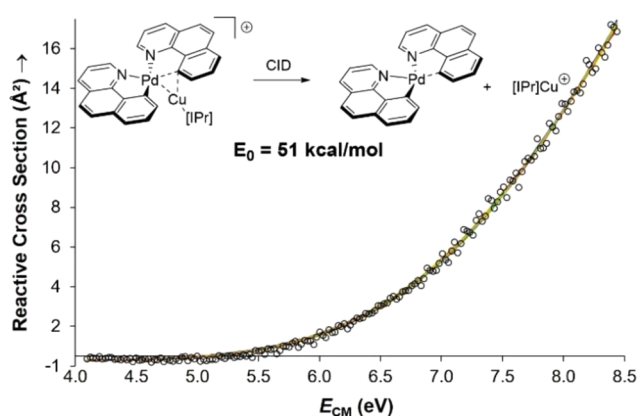
<sup>a</sup>Geometric parameters were taken from our study of the transmetalation step in the Sonogashira reaction.<sup>3</sup> <sup>b</sup>Geometric parameters were extracted from Espinet's study of the transmetalation between *cis*-[PdArMe(PMe<sub>3</sub>)<sub>2</sub>] and ZnMe<sub>2</sub>.<sup>25</sup>



**Figure 3.** Mass spectrum upon CID of [(bhq)<sub>2</sub>Pd<sup>II</sup>·Cu<sup>I</sup>(IPr)]<sup>+</sup> (**3**) at 0.1 mTorr and a collision of offset 70 V, showing the clean dissociation to [(bhq)<sub>2</sub>Pd<sup>II</sup>] (not visible because it is uncharged) and [Cu<sup>I</sup>(IPr)]<sup>+</sup>. Inset: Experimental (black) and calculated (red) isotope patterns of **3**.

as well as its isotope pattern. Upon collision-induced dissociation (CID), [(bhq)<sub>2</sub>Pd<sup>II</sup>·Cu<sup>I</sup>(IPr)]<sup>+</sup> (**3**) gave a single

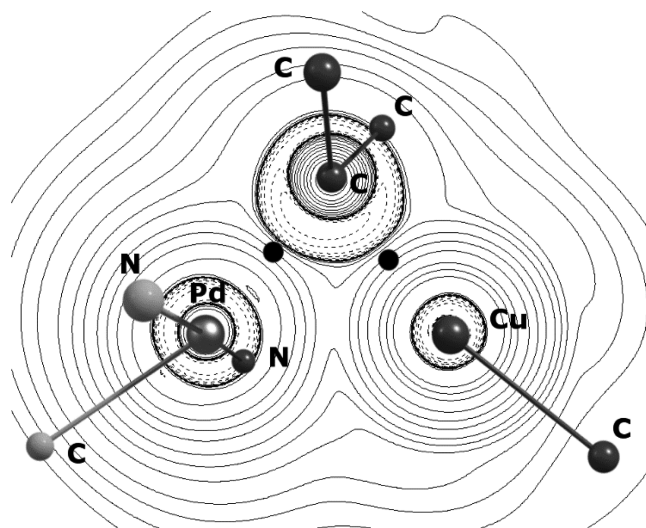
product corresponding to  $[\text{IPr}]\text{Cu}^+$ . The activation energy for the gas-phase reaction was determined experimentally by measurement of the energy-resolved CID cross section in our customized Finnigan-MAT TSQ-700 ESI-MS/MS mass spectrometer. Reactant and product ion intensities were recorded at different CID gas (Xe) pressures (20 to 110  $\mu\text{Torr}$ ) as a function of the collision offset, extrapolated to zero pressure, and subsequently fit with the L-CID program<sup>3,28</sup> as a dissociation through a “loose” transition state (Figure 4). The threshold energy for the dissociation of **3** was determined to be 51 kcal mol<sup>-1</sup>.



**Figure 4.** Zero-pressure-extrapolated cross sections (circles) with L-CID-fitted curves (lines). Inset: Reaction scheme for CID of complex  $[(\text{bhd})_2\text{Pd}^{\text{II}}\text{-Cu}^{\text{I}}(\text{IPr})]^+$  with the corresponding activation energy ( $E_0$ ).

An estimate of the net stabilization of the transition state for transmetalation attributable to the close  $\text{Pd}^{\text{II}}\text{-Cu}^{\text{I}}$  contact can be made by subtracting the binding energy of  $[(\text{IPr})\text{Cu}^{\text{I}}]^+$  to benzene in  $[(\text{IPr})\text{Cu}^{\text{I}}(\eta^2\text{-C}_6\text{H}_6)]^+$  (**4**) from the binding energy of  $[(\text{IPr})\text{Cu}^{\text{I}}]^+$  to  $[(\text{bhd})_2\text{Pd}^{\text{II}}]$  in our model complex **3** (see Figure 2, bottom), with complex **4** being the closest, if nevertheless imperfect, model for the interaction without Pd. We note that a  $\sigma$ -bonded  $\text{Cu}^{\text{I}}\text{-vinyl}$  species has been reported<sup>29</sup> in which the  $\text{Cu}\text{-C}$  bond length of 1.919 Å is only marginally shorter than that of 2.025 Å in **3**, but the angle of the  $\text{Cu}\text{-C}$  bond in **3** with respect to the plane of the aromatic ring, 119°, suggests that a  $\pi$ -bonded reference molecule (e.g., **4**) would be at least as appropriate for the thermochemical comparison. As an electrospray study requires a charged species, we prepared **4** by electrospray of  $[2(\text{-OTf})]$  in benzene and found a CID threshold of 42 kcal mol<sup>-1</sup>. Although the comparison of **3** to **4** is admittedly imperfect, the result suggests that the  $\text{Pd}^{\text{II}}\text{-Cu}^{\text{I}}$  contact gives an additional stabilization energy of about 9 kcal mol<sup>-1</sup>, which is consistent with the expectation based on the single comparable value of 11–12 kcal mol<sup>-1</sup> determined experimentally for a  $\text{Pd}^{\text{II}}\text{-Au}^{\text{I}}$   $d^8\text{-d}^{10}$  system.<sup>24b</sup> While 9 kcal mol<sup>-1</sup> may not appear to be a large stabilization energy, it should be considered that the alternative is no stabilization at all (e.g., in a linear transition state), from which one would infer an acceleration of transmetalation by about 6 orders of magnitude, *ceteris paribus*.

To further characterize the bonding in bimetallic dinuclear complex **3**, we calculated the electron density at the experimental geometry<sup>30</sup> by DFT (TPSS/cc-pVTZ), which we proceeded to analyze with the atoms-in-molecules (AIM) method.<sup>31</sup> As expected, the contour plot (Figure 5) shows a bond path and a bond critical point (BCP) between Pd and the



**Figure 5.** Contour-line diagram of  $\nabla^2\rho(r)$  for  $[(\text{bhd})_2\text{Pd}^{\text{II}}\text{-Cu}^{\text{I}}(\text{IPr})]^+$ , **3**, with nuclei and bond critical points (small black spheres) in the  $\text{Pd}\text{-Cu}\text{-C}$  plane.

adjacent carbon atom as well as between Cu and the neighboring carbon atom. However, no bond path and no BCP were located between Pd and Cu in **3**, even though the  $\text{Pd}\text{-Cu}$  distance in the crystal structure indicates that there must be an interaction. A similar finding was reported in the AIM analysis of a  $\text{Pt}\text{-Au}$  complex by Martín and co-workers,<sup>12</sup> where the AIM analysis also did not find a BCP between the metal centers. Preliminary work in our group indicates that a BCP can indeed be recovered with further analysis of the electron density (to be described separately), which supports the contention that the treatment of the metallophilic interactions is not simple.<sup>24a,c</sup>

In conclusion, we have reported the first crystal structure of a bimetallic complex with a  $\text{Pd}^{\text{II}}\text{-Cu}^{\text{I}}$   $d^8\text{-d}^{10}$  bond. The measured structure resembles our previously proposed transition state of the Sonogashira transmetalation step, for which we take **3** to be a model, as well as the isoelectronic transition state for the transmetalation step in the Negishi coupling as computed by Espinet.<sup>19c,25,27</sup> From **3**, we were able to estimate the net stabilization energy of the transition state due to the close  $\text{Pd}^{\text{II}}\text{-Cu}^{\text{I}}$  interaction. The concept of transmetalation steps being facilitated by metal–metal interactions might be applicable to other bimetallic transition-metal-catalyzed reactions, and a detailed knowledge about this phenomenon can potentially lead to the development of more efficient catalytic reactions. This study is a continuation of the exploration of favorable metal–metal interactions, which are currently investigated within our research group.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b12152.

Sample preparation, computational details, energies and geometries, experimental distribution of ion kinetic energies, mass spectra, and energy-resolved collision-induced dissociation experimental data (PDF)

Crystallographic data for  $[3(\text{-OTf})]\cdot 2\text{CH}_2\text{Cl}_2$  (CIF)

Crystallographic data for **1** (CIF)



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## Notes

The authors declare no competing financial interest.

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