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## Construction of modular Pd/Cu multimetallic chains via ligand- and anion-controlled metal-metal interactions

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## COMMUNICATION

## Construction of modular Pd/Cu multimetallic chains via ligand- and anion-controlled metal-metal interactions

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Accepted 00th January 20xxOrestes Rivada-Wheelaghan,<sup>a,†,§</sup> Shubham Deolka,<sup>a,§</sup> Ramadoss Govindarajan,<sup>a</sup> Eugene Khaskin,<sup>a</sup> Robert R. Fayzullin,<sup>b</sup> Shrinwantu Pal<sup>c</sup> and Julia R. Khusnutdinova<sup>\*a</sup>

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**The presence of Pd...Cu and Pd...Pd interactions as well as order of metal atoms in a chain held by a modular polynucleating ligand is controlled by coordinating ability of anions, leading to selective formation of bi- and tetranuclear Pd/Cu and Pd<sub>4</sub> chains. Metal-metal cooperative reactivity in these complexes was tested in Ar–O bond formation and alkyne activation.**

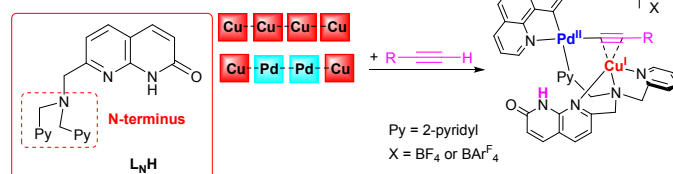
Controlled formation of well-defined multimetallic complexes showing metal-metal interactions is crucial for understanding reactivity in multimetallic catalysis by homogeneous systems, metal clusters, and heterogeneous metal surfaces.<sup>1</sup> While the synergistic effect of two (or more) metals in substrate activation or functionalization is widely employed in catalysis,<sup>2</sup> the nature of the homo- or heteromultimetallic species that may be involved often remains elusive,<sup>3</sup> although the presence of these metal-metal interactions is believed to be important.<sup>4</sup> Many currently reported ligands supporting homo- and heterobimetallic complexes that feature metal-metal interactions lack flexibility and variability in multimetal chain construction, allowing for the formation of species with fixed nuclearity and geometry.<sup>5</sup>

Recently, we reported a modular naphthyridinone-based ligand that allowed for the formation of bi-, tri- and tetranuclear copper complexes, and extended its reactivity to the selective formation of Cu...Pd...Pd...Cu chains.<sup>6</sup> The latter complexes showed a metal-metal cooperative mode for alkyne activation, which modelled the transmetalation step in Sonogashira coupling. The position of Cu<sup>I</sup> at the termini of the

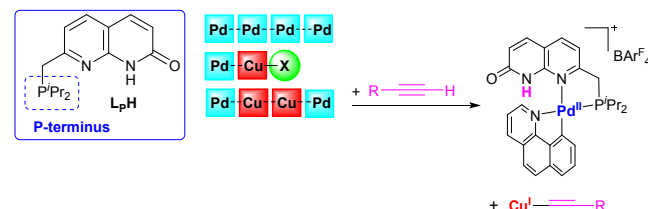
heteromultimetal chain was directed by the bis(picoyl)amine unit. We also reported a binucleating “soft”-“hard” ligand that supports Pt...Cu complexes, showing synergistic effects in the activation of alkynes and Ar–B bond.<sup>7</sup>

In this work, we found that by introducing a soft phosphine arm in ligand **L<sub>N</sub>H** (Fig. 1),<sup>8</sup> we can swap the metals' order, leading to the construction of a Pd...Cu...Cu...Pd chain. The reactivity of these inverted order chains with alkynes is different from that observed for Cu...Pd...Pd...Cu complexes. Moreover, simply by using coordinating anions or bases, we can modulate metal-metal interactions in metal chains. In the presence of chloride, an unusual binuclear Pd...Cu species is formed where the Pd atom interacts with a formally dicoordinate anionic Cu<sup>I</sup> center. The latter complex exhibits C(sp<sup>2</sup>)–O bond formation upon treatment with H<sub>2</sub>O<sub>2</sub>; this reactivity is not observed in the Pd-only aryl complex in the absence of Cu. In addition, we demonstrate the formation of Pd<sub>4</sub> chains with a doubly deprotonated, dearomatized naphthyridinone acting as a dianionic ligand with two N<sup>−</sup> amide donors.

Previous work:



This work:



**Fig. 1.** Formation of Pd/Cu metal chains controlled by ligand terminus and coordinating anions.

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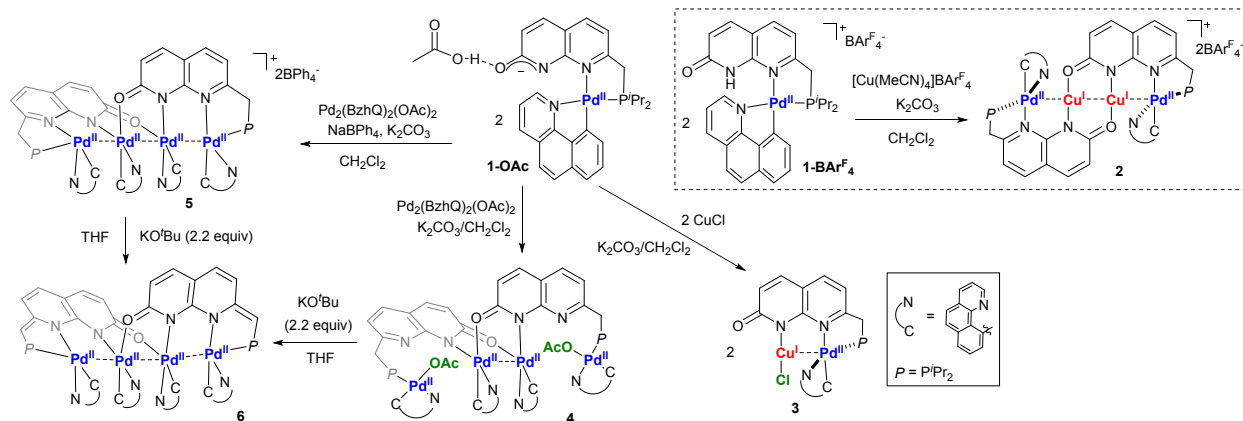
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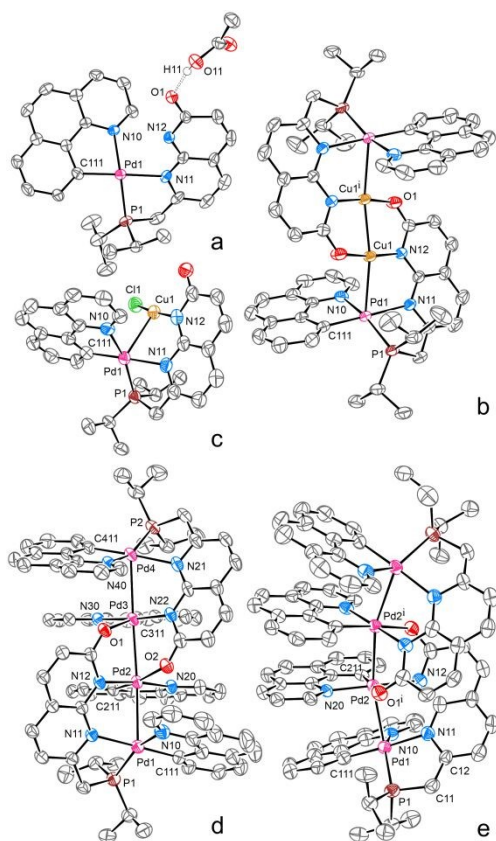
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## COMMUNICATION



Scheme 1. Synthesis of Pd and Pd/Cu complexes.



**Fig. 2.** Structures of **1-OAc** (a), **2** (b), **3** (c), **5** (d) and **6** (e) in the crystals with thermal ellipsoids at the 80 % (b) or 60 % (a, c-e) probability level. All hydrogen atoms except for [O]H, co-crystallized solvent molecules except for acetic acid in **1-OAc**, counterions  $B(Ar^f)_4$  or  $BPh_4$  and minor disorder components are omitted for clarity. In the case of **3**, only one of two symmetrically independent molecules is shown. Equivalent atoms are labelled by the superscript *i*: symmetry operations (1-*x*, 1-*y*, 1-*z*) for **2** and (*x*, ½-*y*, ½-*z*) for **6**. The structures of **1-B(Ar<sup>f</sup>)<sub>4</sub>**, the solvate form of **2** with somewhat different conformation and **4** are present in ESI.†

To make the initial building block for further multi-metallic chain formation, we first treated ligand **L<sub>P</sub>H** with palladium benzo[*h*]quinoyl (BzhQ) acetate dimer,  $Pd_2(BzhQ)_2(OAc)_2$ , which led to the formation of the mononuclear Pd complex **1-OAc**, while the analogous reaction in the presence of  $NaBAr^f_4$  gave **1-BAr<sup>f</sup><sub>4</sub>** (Scheme 1). According to X-ray, **1-BAr<sup>f</sup><sub>4</sub>** is a cationic complex with a  $BAr^f_4^-$  counter anion and a protonated N-atom, while **1-OAc** is a neutral complex with a nonprotonated naphthyridonate ligand hydrogen bound to an acetic acid molecule in the solid state (Fig. 2a; see ESI for detailed discussion).

We then used these complexes as versatile blocks that could form different chains depending on the reagent identity (Scheme 1). Treatment of **1-BAr<sup>f</sup><sub>4</sub>** with 1 equiv. of  $[Cu(MeCN)_4]BAr^f_4$  in the presence of  $K_2CO_3$  base at room temperature (RT) in  $CH_2Cl_2$  solution led to its selective self-assembly into a tetranuclear dicationic  $Pd \cdots Cu \cdots Cu \cdots Pd$  complex **2** as the only product (Fig. 2b). Complex **2** is the first example of a linear  $Pd \cdots Cu \cdots Cu \cdots Pd$  chain compound; previously, only one example of a nonlinear  $Pd_2Cu_4$  arrangement was reported as a part of the Ru-containing cluster.<sup>9</sup> Interestingly, the chain length is modulated by the presence of a coordinating anion: treatment of **1-OAc** with CuCl in the presence of  $K_2CO_3$  produces a binuclear complex **3** where a formally anionic linear dicoordinate Cu center is present (Fig. 2c). The  $Pd \cdots Cu$  distances in complexes **2** and **3** are 2.71892(19) Å and 2.7809(12)–2.8182(13) Å respectively, and in both cases are shorter than the sum of van der Waals radii (3.03 Å), but somewhat longer than the sum of covalent radii (2.66 Å) of the two metals.

We then decided to explore the possibility of this ligand framework to support palladium-only chains modulated by the presence of coordinating anions. The construction of

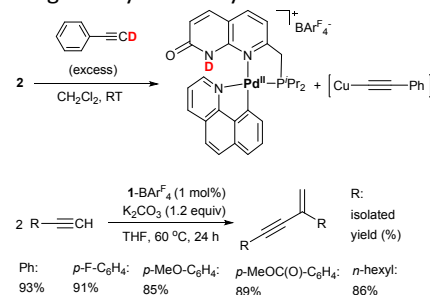
polypalladium chain has been of longstanding interest due to their implications in the design of 1D molecular devices, molecular wires, and interesting conductive properties exhibited by Pd chains.<sup>10</sup> We found that the treatment of **1**-OAc with an additional amount of Pd<sub>2</sub>(BzhQ)<sub>2</sub>(OAc)<sub>2</sub> in the presence of K<sub>2</sub>CO<sub>3</sub> led to the formation of a tetranuclear complex **4** with only two core Pd atoms showing a Pd...Pd distance of 2.8433(6) Å, shorter than the sum of their van der Waals radii (3.26 Å). The two terminal Pd atoms are located well away from the two central ones due to coordinated acetates (Fig. S77). In contrast, when the analogous reaction was performed in the presence of NaBPh<sub>4</sub> to remove acetate, the Pd<sub>4</sub> chain **5** is formed with Pd...Pd distances of 2.8187(3)–2.8956(3) Å (Fig. 2d).

The **L<sub>p</sub>H** ligand possesses a CH<sub>2</sub> bridging moiety that can be deprotonated, leading to dearomatization of the pyridine, a strategy that has been used in metal-ligand cooperation catalysis.<sup>11</sup> In our case the potential to form a dearomatized pyridine would significantly change the coordinating behavior of the chain. When either **4** or **5** are treated with 2.2 equiv of the strong base KO<sup>t</sup>Bu, deprotonation of CH<sub>2</sub>P arms leads to neutral Pd<sub>4</sub> chain **6** with two dearomatized ligands **L<sub>p</sub><sup>\*-</sup>**. The dearomatized ligand **L<sub>p</sub><sup>\*-</sup>** shows an unusual coordination mode, acting as a dianionic fragment that provides two amide N<sup>-</sup> donors to bridge Pd atoms. Interestingly, the orientation of benzoquinolyl ligands in **6** is also different from that in **5**, with all four benzoquinolyls aligned, displaying a four-layer stack, while in complex **5** the benzoquinolyls are aligned only for the two central Pd atoms. Although complex **6** can potentially demonstrate both metal-metal and metal-ligand cooperation, its extremely low stability prevented us from studying its reactivity as complex **6** decomposed even in the absence of protic additives in toluene solution and was stable only when crystallized at low temperature.

The presence of short Pd...Cu distances in **2** and **3** prompted us to analyze heterobimetallic d<sup>8</sup>-d<sup>10</sup> interactions by Quantum Theory of Atoms in Molecules (QTAIM) and Natural Bond Orbital (NBO) analysis (Tables S4–S7, Fig. S80–S81). Structures of **2** and **3** were optimized using the ωB97XD functional. The metal centres (Cu, Pd) were described by the SDD basis sets while the remaining atoms were described by the 6-31++G(d,p) basis set. QTAIM analysis of optimized structures showed the presence of bond critical points (bcp) between Pd and Cu both in **2** and **3**, and between two Cu atoms in **2**. The characteristics of bcp's (positive values of the Laplacian of electron density ∇<sup>2</sup>ρ<sub>b</sub>, and negative but close to zero values of total electronic energy density H<sub>b</sub>) are typical for closed-shell, metal-metal interactions.<sup>12–14</sup> The Pd...Cu in **2** is characterized by a somewhat larger value of electron density at the bcp (ρ<sub>b</sub> 2.87·10<sup>-2</sup> and 2.94·10<sup>-2</sup> a.u.), compared to **3** (ρ<sub>b</sub> 2.55·10<sup>-2</sup> a.u.), suggesting a stronger interaction and consistent with a shorter Pd...Cu distance in **2** compared to **3**. NBO analysis of **2** showed moderate electron density donation to an empty s-type orbital on Cu from σ(Pd–C<sub>Ar</sub>) (E<sup>(2)</sup> = 14.29 kcal mol<sup>-1</sup>) and from σ(Pd–P) (E<sup>(2)</sup> = 8.41 kcal mol<sup>-1</sup>) orbitals. Moderate donation of electron density from Pd-based d-orbital to a Cu-based s orbital (E<sup>(2)</sup> = 6.06 kcal mol<sup>-1</sup>) is also present. The NBO analysis of **3** shows comparatively weaker donation from Pd(d) to Cu(s) orbital (E<sup>(2)</sup>

= 2.52 kcal mol<sup>-1</sup>). Overall, the Pd...Cu interactions in **2** and **3** resemble those reported earlier for a Pt/Cu complex and in other d<sup>8</sup>-d<sup>10</sup> complexes with metallophilic interactions,<sup>15</sup> while the characteristics of Cu...Cu interactions are similar to those observed in multicopper chains with naphthyridinone-based ligands.<sup>6a</sup>

Considering that a Pd/Cu combination is commonly used in terminal alkyne activation, we decided to compare the reactivity of the previously published Cu...Pd...Pd...Cu complex with **L<sub>N</sub><sup>-</sup>** ligand<sup>6b</sup> and the “swapped order” Pd...Cu...Cu...Pd complex **2** (Fig. 1). Our previous study of the Cu...Pd...Pd...Cu complex showed that its reaction with a terminal alkyne leads to deprotonation of a terminal CH bond by an N-atom of naphthyridonate and the formation of a Pd/Cu complex with acetylide σ-bound to Pd and π-bound to Cu (Fig. 1).<sup>6b</sup> When we reacted **2** with phenylacetylene in DCM solution at RT, it led to breaking the tetranuclear chain and the formation of **1**-BARF<sub>4</sub> (Scheme 2). No Pd σ-acetylide was present in the reaction mixture. The deprotonation of the terminal CH group by N-atom of naphthyridonate was confirmed by reacting **2** with phenylacetylene-*d*, which gave complex **1**-BARF<sub>4</sub>-*d*, whose ND group was observed as a broad singlet at 9.63 ppm by <sup>2</sup>H NMR. We hypothesized that the other product is likely an oligomeric Cu acetylide complex not containing ligand **L<sub>p</sub>**. Treatment of the reaction mixture with aqueous ammonia led to precipitation of an insoluble yellow solid, which was identified as a Cu phenylacetylide complex by comparison of its IR spectrum with the literature. Therefore, the nature of the ligand terminus and order of metals in a chain led to contrasting reactivity with terminal alkynes: while the previously reported Cu<sub>2</sub>Pd<sub>2</sub> complex led to transmetalation, complex **2** undergoes disassembly of its polymetallic core, presumably due to the Cu<sub>2</sub> core's greater lability compared to a Pd<sub>2</sub> core and stronger P,N-chelate coordination to Pd (Fig. 1). When we further studied the reactivity with terminal alkynes, we found that complex **2** used in catalytic amounts led to alkyne dimerization. Further studies showed that the reaction is likely catalyzed by complex **1**-BARF<sub>4</sub> alone, formed *in situ* from **2** and alkyne. This is confirmed by observation of facile and selective alkyne dimerization catalyzed by 1 mol% of independently prepared **1**-BARF<sub>4</sub> even in the absence of Cu, leading to exclusive formation of head-to-tail alkyne dimerization product in good to excellent yields for a range of aryl- and alkyl-substituted terminal alkynes (Scheme 2).

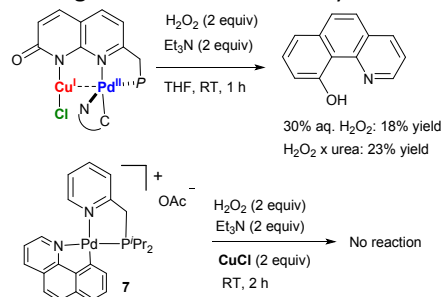


**Scheme 2.** Reactivity of **2** with a terminal alkyne and catalytic alkyne dimerization.

During an evaluation of cooperativity between Pd and Cu, we also tested the reactivity of complex **3** in Ar–O bond formation



using common oxidants. C(sp<sup>2</sup>)–O bond elimination at a Pd center commonly requires strong oxidants such as hypervalent iodine derivatives<sup>16</sup> and only limited examples are known for C(sp<sup>2</sup>)–O formation at Pd using H<sub>2</sub>O<sub>2</sub>.<sup>17</sup> Treatment of **3** with an aqueous solution of H<sub>2</sub>O<sub>2</sub> led to elimination of 10-hydroxybenzo[*h*]quinoline, which was isolated in a pure form in 18% yield. A similar yield, 23%, was obtained when H<sub>2</sub>O<sub>2</sub> × urea adduct was used as an oxidant. Importantly, treatment of complex **1** with H<sub>2</sub>O<sub>2</sub>/Et<sub>3</sub>N in the absence of Cu did not lead to elimination of Ar–O bond and the complex remained mostly unreacted. No reaction was observed when complex **7** was reacted with H<sub>2</sub>O<sub>2</sub> in the presence of added CuCl. Therefore, this reactivity shows a possible synergistic effect of the two metals in C(sp<sup>2</sup>)–O bond formation induced by H<sub>2</sub>O<sub>2</sub> oxidation, although the reaction selectivity needs to be further improved.



**Scheme 3.** Reactivity of **3** and **7** with H<sub>2</sub>O<sub>2</sub>.

In summary, we demonstrated that selective Pd/Cu and Pd<sub>4</sub> chain construction is achieved by using multinucleating ligands with a modular terminal chelating group, and this reactivity is further attenuated by adding coordinating anions. Using a P-terminus ligand, we obtained Pd...Cu...Cu...Pd as well as Pd...CuX chains. By contrast, swapped order Cu...Pd...Pd...Cu chains are obtained when the earlier reported N-terminus ligand is used. The difference in metal chain architecture led to contrasting reactivity with a terminal alkyne, leading to deconstruction of the multimetal chain in the Pd...Cu...Cu...Pd complex. We also demonstrated a synergistic effect of Cu in C(sp<sup>2</sup>)–O bond formation using H<sub>2</sub>O<sub>2</sub> as an oxidant.

## Conflicts of interest

There are no conflicts to declare.

## Notes and references

†R.R.F. performed crystal structure determination within the government statements for Kazan Scientific Center of RAS. We acknowledge OIST IAS and Engineering Section for technical support.

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