Unusual transmetallation-induced formation of a C_2-symmetric tetrapallada-macrocycle†

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We report the formation of a tetrapallada-macrocycle induced by an unusual transmetallation, in which an anionic bidentate chelate ligand is replaced by a phenyl ligand from phenylboronic acid, leaving the chloride ligands intact.

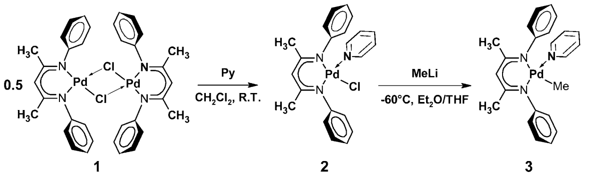
The formation of macrocycles and cages induced by organometallic transformations are emerging, where C–H activation has proved particularly fruitful.[1,2] Transmetallation-induced formation of macrocycles has not been exploited. Note that there are examples of metal-exchange processes to assemble nanostructures which have also been termed "transmetallation" reactions.[3,4] We use the term transmetallation in the typical organometallic context.[5] In this communication we describe how transmetallation of aryl groups from boronic acid to palladium(II) results in the formation of a tetrapallada-macrocycle.

In our recent investigations into palladium β-diiminate chemistry, we have explored the reactivity of [PdCl(Ph_2nacnac)L] (where L is a monodentate ligand) towards various transmetallation reagents, aiming to generate olefin polymerization pre-catalysts, [PdR(Ph_2nacnac)L], where R is an alkyl or aryl group. The precursor [[PdCl(Ph_2nacnac)L] can be synthesized by treating [Pd(Ph_2nacnac)Cl]$_2$, **1** with a monodentate ligand L.[6] Alternatively, if a suitable transmetallation reagent could replace the chloride ligands from **1** itself, the resulting coordinatively unsaturated organopalladium species [PdR(Ph_2nacnac)] or its oligomers might be used directly as activator-free olefin polymerization catalysts. Herein we report our initial discovery while exploring the two routes described above.

As shown in Scheme 1, the mononuclear complex [PdCl(Ph_2nacnac)Py], **2** can be prepared in 97% yield by treating **1** with excess pyridine. Complex **2** reacts with 1 equiv. of MeLi to afford the conventional[5] transmetallation product **3** in 40% yield. The structures of **2** and **3** have been confirmed by X-ray crystallography (Fig. 1).‡ Each [Ph_2nacnac]$^-$ ligand in **2** and **3** binds to a Pd(II) center through the two N-donor atoms in a chelating fashion. Complexes **2** and **3** feature the complete delocalization of π-electron density over the nacnac backbones and sp^2 hybridized β-carbons.

Although the treatment of the dimeric **1** with methyllithium or Grignard reagents consistently produces Pd black and complicated mixtures, from which a small amount of complex **5** was isolated,[7] a rather surprising example of transmetallation has been observed when phenylboronic acid is used as the transmetallation reagent. As shown in Scheme 2, when the mixture of **1** and ~1.3 equiv. of phenylboronic acid in a wet benzene/acetone mixed solvent is heated at 70 °C, within hours orange X-ray diffraction quality single crystals of analytically pure **4** can be isolated in 50% yield.‡ Complex **4** is slightly soluble in dichloromethane and 1,2-dichloroethane, but insoluble in benzene, acetone, hexanes, diethyl ether, THF, methanol, water, chloroform and DMSO.

As shown in Fig. 2a, the molecular structure of **4** can be viewed as two [PhPd(μ-Cl)$_2$Pd(Ph_2nacnac)] units assembled *via* two Pd–C (β-carbon of [Ph_2nacnac]$^-$) bonds. Each [Ph_2nacnac]$^-$ ligand in **4** uses two N-donors to chelate to a Pd center in one [PhPd(μ-Cl)$_2$Pd(Ph_2nacnac)] unit, while the sp^3 hybridized β-carbon coordinates to a Pd center in the other unit. The six-membered chelate ring comprised of the {(Ph_2nacnac)Pd} moiety adopts a boat conformation. A similar coordination mode for [Ar_2nacnac]$^-$ has been reported by Feldman and co-workers in a dinuclear tricationic Pd(II) complex,[8] and our group in an unusual trinuclear Pd(II)–Ph_2nacnac complex with amido-chloro double-bridges.[9] The Pd2–C3A bond length in **4** is 2.099(3) Å, similar to the literature values.[8,9] The *ipso*-carbon of the phenyl ligand and the β-carbon donor of the [Ph_2nacnac]$^-$ ligand are mutually *cis* and the coordination environment around each Pd(II) center is square planar. The two methyl groups of each [Ph_2nacnac]$^-$ ligand are no longer equivalent: the methyl group containing C5 (Fig. 2a) is situated in the shielding region of a phenyl ligand, while the methyl group containing C1 has no phenyl ligand nearby. Accordingly, the two singlets at 0.87 and 2.06 ppm in the ^{1}H NMR spectrum of **4** can be assigned to the two methyl groups containing C5 and C1, respectively. As shown in Fig. 2b, complex **4** is C_2-symmetric and chiral with both phenyl ligands pointing towards the front side of the tetrapallada-macrocycle. The front opening of the macrocycle is larger than that at the back, *i.e.*, Cl2–Cl2A and Cl1–Cl1A distances are ~5.4 and ~4.0 Å, respectively. The Pd1–Pd1A and Pd1–Pd2A distances are ~4.6 and ~3.5 Å, respectively, indicating small void space inside the macrocycle.



Scheme 1 Synthesis and reactivity of **2**.

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† Electronic supplementary information (ESI) available: Experimental and spectroscopic details of **2**–**5**. CCDC 779764, 779765, 779766, and 779767. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0cc03314f

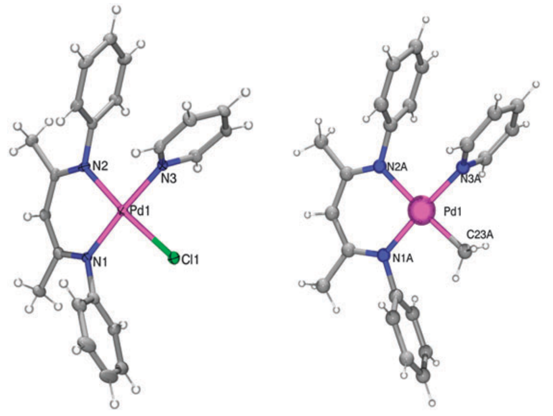


Fig. 1 X-Ray crystal structure of complexes **2** (left) and **3** (right). The thermal ellipsoids are plotted at 30% probability.

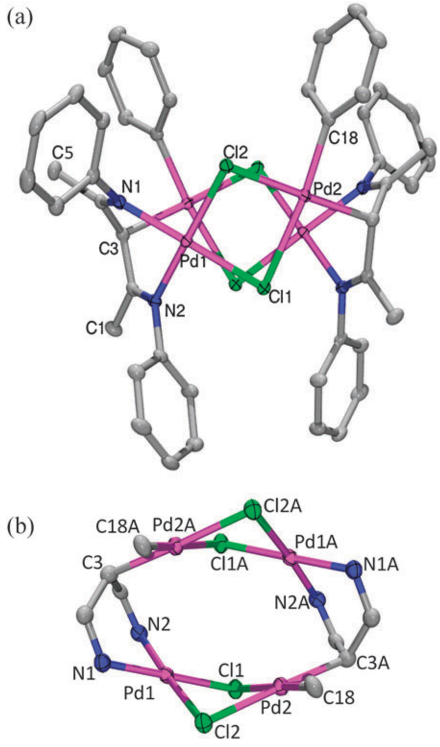
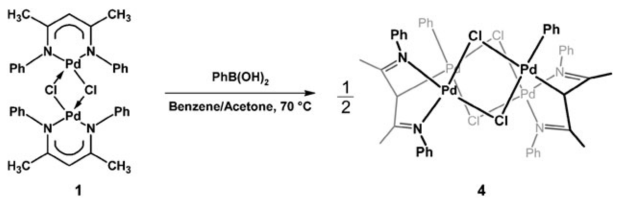


Fig. 2 X-Ray crystal structure of complex **4**. (a) Side view; (b) Top view (down the C_2 axis): the phenyl and methyl groups of nacnac ligands are omitted and the phenyl ligands are reduced to the *ipso*-carbons for clarity. The thermal ellipsoids are plotted at 30% probability. For clarity all H atoms are omitted. Selected bond lengths (Å) and angles (°): Pd1–N1, 2.009(3); Pd1–N2, 2.012(2); Pd1–Cl1, 2.3347(8); Pd1–Cl2, 2.3371(8); Pd2–C18, 1.988(3); Pd2–C3A, 2.099(3); Pd2–Cl2, 2.3851(8); Pd2–Cl1, 2.5101(8); N1–Pd1–N2, 85.87(10); N2–Pd1–Cl1, 93.75(8); N1–Pd1–Cl2, 93.79(7); Cl1–Pd1–Cl2, 86.63(3); C18–Pd2–C3A, 87.41(13); C18–Pd2–Cl2, 91.39(9); C3A–Pd2–Cl1, 99.47(9); Cl2–Pd2–Cl1, 81.75(3); Pd1–Cl1–Pd2, 85.15(2); Pd1–Cl2–Pd2, 88.00(3).

The macrocycle can be described as being ‘crown-shaped’, similar to other cyclic hosts such as cyclodextrins and calixarenes. Similarly designed platforms may find use in chiral recognition or as receptors.

The direct transmetallation of an aryl group from an arylboronic acid to a palladium(II) centre is an important step in the catalytic cycle of Suzuki-Miyaura cross-coupling reactions. The direct observation of diorganopalladium(II) intermediates resulting from transmetallation using boronic acids is rare given that the subsequent reductive elimination is usually quite facile, unless the Pd–C bond is strengthened by fluorine substitution on the C-donor ligands.[10] In contrast, complex **4**, which is formed from the direct transmetallation using a boronic acid at an elevated temperature, has remarkable thermal stability and is inert towards air and moisture. Furthermore, **4** contains mutually *cis* aryl and alkyl ligands on Pd(II) centers, which are neither supported by carbene or phosphine ligands nor stabilized by fluorine substitution on the aryl or alkyl ligands. The formation of **4** is presumably driven by the poor solubility. The fates of the displaced $[\text{Ph}_2\text{nacnac}]^-$ ligand and the $[\text{B(OH)}_2]^+$ fragment are yet to be determined, and the formation of certain highly stable species from these fragments might also contribute to the driving force for the formation of **4**. The ring restraint in **4** may also retard the reductive elimination process.



Scheme 2 Synthesis of complex **4**.

In summary, we have shown two types of reactivities between Pd-nacnac complexes and transmetallation reagents: the conventional transmetallation between **2** and MeLi and the unusual transmetallation between **1** and phenylboronic acid, where the anionic chelating $[\text{Ph}_2\text{nacnac}]^-$ ligand instead of a simple chloride is replaced from a Pd(II) center, leading to the subsequent formation of a tetrapallada-macrocycle, **4**. Current efforts are focused on expanding this methodology to form other discrete molecular architectures (including larger macrocycles), investigating the fate of the displaced $[\text{Ph}_2\text{nacnac}]^-$ ligand and the $[\text{B(OH)}_2]^+$ fragment, and inducing reductive elimination of **4** to form C–C bonds.

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Notes and references

‡ Selected crystallographic data, for **2**: a = 6.4520(5) Å, b = 10.7360(10) Å, c = 29.278(4) Å, V = 2028.0(4) Å^3, Z = 4, space group $Pc2_1b$, T = 150 K, total data 6717, unique data 2883, parameters 246, R_1 = 0.0370 (observed data), wR_2 = 0.0769 (all data); for **3**: a = 11.1137(6) Å, b = 23.4596(15) Å, c = 11.9041(6) Å, β = 98.157(2)°, V = 3072.3(3) Å^3, Z = 8, space group $C2/c$, T = 150 K, total data 12476, unique data 3530, parameters 688, R_1 = 0.0371 (observed data), wR_2 = 0.0967 (all data); for **4**: a = 21.5383(8) Å, b = 13.6270(3) Å, c = 18.8184(6) Å, β = 124.5226(11)°, V = 4550.6(2) Å^3, Z = 4, space group $C2/c$, T = 150 K, total data 17143, unique data 5211, parameters 264, R_1 = 0.0334 (observed data), wR_2 = 0.0881 (all data).

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7 In one attempted reaction with PhMgBr, a new coordination mode for the β-diimine ligand was observed (see supporting information† for experimental details and X-ray structure of complex **5**).

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