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Architectural formation of a conjugated bimetallic Pd(II) complex *via* oxidative complexation and a tetracyclic Pd(II) complex *via* self-assembling complexation†

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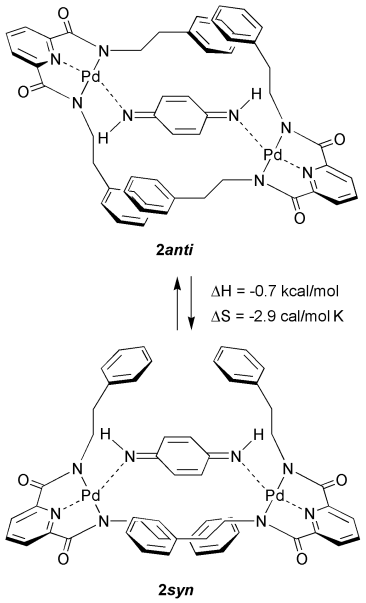
The conjugated homobimetallic palladium(II) complex [(L¹)Pd(qd)Pd(L¹)] (qd = quinonediimine) was obtained in a one-pot reaction by the *in-situ* oxidative complexation of 1,4-phenylenediamine with the palladium(II) complex [(L¹)Pd(MeCN)] (H_2L^1 = *N*,*N*′-bis(2-phenylethyl)-2,6-pyridinedicarboxamide) while in the absence of an additional ligand [(L¹)Pd(MeCN)] was converted to the amide-bridged macrocyclic tetramer $[Pd(L^1)]_4$.

π-Conjugated ligands have been attracting much interest in a variety of applications owing to their electronic characteristics.[1] The incorporation of transition metal complexes into such π-conjugated ligands is envisaged to provide efficient redox systems based on the redox properties of both moieties. From these points of view, bimetallic complexes composed of π-conjugated bridging spacers and terminal redox-active transition metals have received much attention as functional materials, in which electronic communication through a π-conjugated spacer can operate.[2] In a previous paper, controlled complexation with the redox-active π-conjugated ligand, *N*,*N*′-bis(4′-dimethylaminophenyl)-1,4-benzoquinonediimine, has been achieved to afford the conjugated polymeric complex, the conjugated trimetallic macrocycle, or the conjugated bimetallic complex depending on the coordination mode.[3] Architectural control of transition metal-directed assembly to construct well-arranged metallomacrocycles is one of the current research areas to create organized nanostructures for advanced materials.[4] Metal-directed assembly using a labile coordination site is a useful approach to such metal-assembled complexes.[5] We herein report a one-pot preparation of a conjugated homobimetallic palladium(II) complex and a macrocyclic tetrameric palladium(II) complex from a palladium(II) complex bearing the tridentate ligand.

The palladium(II) complex [(L¹)Pd(MeCN)] (**1**) composed of the *N*-heterocyclic tridentate podand ligand, *N*,*N*′-bis(2-phenylethyl)-2,6-pyridinedicarboxamide (H_2L^1), possesses one labile coordination site through removal of the acetonitrile ligand.[3a,6] π-Conjugated ligands with potential metal-coordination sites are expected to coordinate to the palladium center of **1** by displacing this labile ligand. The redox properties of 1,4-phenylenediamine and high coordination ability of the corresponding oxidized quinonediimine prompted us to investigate the *in-situ* oxidative complexation of 1,4-phenylenediamine with **1** to form a conjugated bimetallic complex. One-pot treatment of the palladium(II) complex **1** with 0.5 equiv. of 1,4-phenylenediamine in the presence of 3.0 equiv. of iodosobenzene led to the formation of the conjugated homobimetallic palladium(II) complex [(L¹)Pd(qd)Pd(L¹)] (**2**) (qd = quinonediimine) in a one-pot reaction in 85% yield (Scheme 1). In the ^{1}H NMR spectrum of the conjugated complex **2**, two sets of peaks based on *syn* and *anti* quinonediimine isomers were observed at 298 K in DMSO-d_6. The *syn* isomer is enthalpically more favorable than the *anti* one in DMSO-d_6 by 0.7 kcal mol^{-1}, but is entropically less favored by 2.9 cal mol^{-1} K^{-1} from the van't Hoff plot.



Scheme 1

The X-ray crystal structure of **2**‡ revealed that the two [(L¹)Pd] units are bridged by the quinonediimine spacer to form the C_2-symmetrical 2 : 1 complex *anti*-**2** in *anti* configuration as shown in Fig. 1. An interesting feature is that each benzene ring of the podand moiety of [(L¹)Pd] is oriented in a near face-to-face arrangement at a distance of *ca.* 3.8 Å with the benzene ring of another [(L¹)Pd] to form a pseudo-macrocycle.

The cyclic voltammogram of the conjugated complex **2** in DMSO exhibited two separate redox waves at $E_{1/2}$ = −1.52 and −0.78 V *vs.* Fc/Fc$^+$, which are assignable to the successive one-

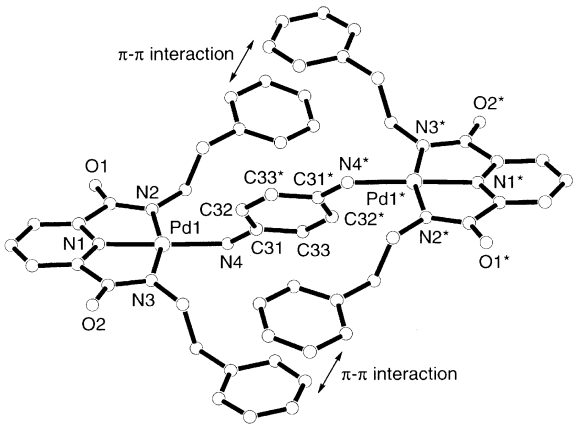


Fig. 1 Molecular structure of *anti*-**2** (hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (°): Pd(1)–N(1) 1.922(8), Pd(1)–N(2) 2.015(9), Pd(1)–N(3) 2.035(9), Pd(1)–N(4) 1.998(8), N(4)–C(31) 1.30(1), C(31)–C(32) 1.44(1), C(32)–C(33*) 1.33(1); N(1)–Pd(1)–N(2) 80.7(3), N(2)–Pd(1)–N(3) 161.8(3), N(2)–Pd(1)–N(4) 97.3(3), Pd(1)–N(4)–C(31) 131.2(7), N(4)–C(31)–C(32) 119.5(9).

† Electronic supplementary information: experimental section and crystallography. Figs. S1–6. See http://www.rsc.org/suppdata/cc/b2/b203726m/

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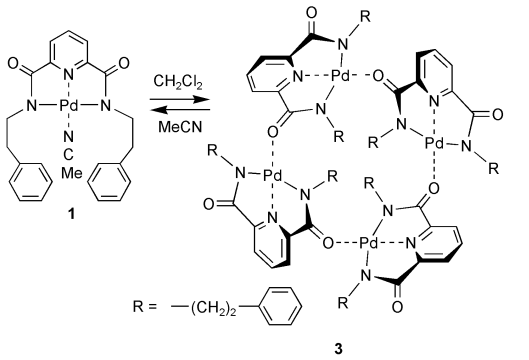
electron reduction of the quinonediimine moiety. The EPR spectrum of $\mathbf{2}^{\cdot-}$ in DMSO showed the signals centered at g = 2.004 accompanied by hyperfine coupling (A_N = 6.7 G; A_H = 7.2 G; A_H = 1.6 G; A_{Pd} = 4.0 G). The unpaired electron appears to locate mostly on the quinonediimine moiety although some delocalization onto the metal is indicated by the weak satellite lines due to ^{105}Pd coupling.

It should be noted that the macrocyclic tetramer $[(L^1)Pd]_4$ (**3**) was obtained quantitatively by treatment of **1** in dichloromethane or chloroform at reflux temperature (Scheme 2). No other products were formed. This stable self-assembled complex is considered to be formed through removal of a labile acetonitrile ligand in the absence of an additional ligand. The structure of **3** was elucidated by spectral data. In the ^{1}H NMR spectra, the signals attributable to the methylene protons of the phenylethyl moieties exhibited nonequivalent resonances in CD_2Cl_2, indicating unsymmetrical coordination to the palladium center. By contrast, those of **1** are magnetically equivalent with the expected triplet in CD_3CN. The ESI-MS spectrum also supported the formation of **3** (*m*/*z* 1912.4 $[M + H]^+$). Interestingly, treatment of **3** with acetonitrile led to the dissociative formation of **1**. The transformation between **1** and **3** was found to be reversible, which can be controlled by the solvent exchange. Reversible formation of the metal-assembled complex by solvent exchange provides a strategy to construct switchable nanostructures.

Further structural information of **3** was obtained by X-ray crystallography.‡ The coordination of the amide oxygen to the palladium center affords a tetrametallic macrocyclic skeleton as depicted in Fig. 2, which is consistent with the spectroscopically nonequivalent protons of the phenylethyl moieties of **3** in the ^{1}H NMR spectrum. A remarkable feature in the structure is that the coordination plane of palladium is composed of the pyridine and two amide moieties which are orientated in up and down fashion to create an open cavity with a cone conformation. The coordination planes of the palladium centers are inclined in a range of 51.4°–60.5° from the plane defined by the four coordinated amide oxygen atoms.



Scheme 2

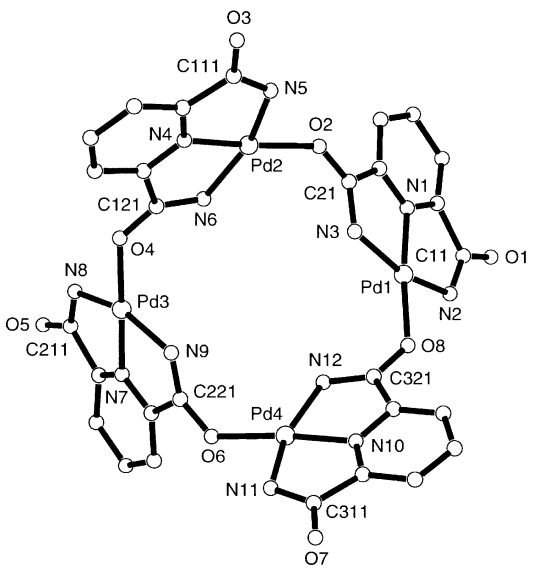


Fig. 2 Molecular structure of **3** (phenylethyl moieties and hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (°): Pd(1)–N(1) 1.913(9), Pd(1)–N(2) 2.00(1), Pd(1)–N(3) 2.06(1), Pd(1)–O(8) 2.064(8), O(1)–C(11) 1.27(2), O(2)–C(21) 1.27(2); N(1)–Pd(1)–N(2) 81.2(5), N(2)–Pd(1)–N(3) 161.3(4), N(1)–Pd(1)–O(8) 174.2(5), N(2)–Pd(1)–O(8) 96.3(4), N(3)–Pd(1)–O(8) 102.4(4), Pd(1)–O(8)–C(321) 134.3(8).

In conclusion, a conjugated homobimetallic palladium(II) complex was formed by one-pot oxidative complexation of 1,4-phenylenediamine with a palladium(II) complex bearing the tridentate ligand, which, in the absence of a ligand undergoes controlled formation of a macrocyclic tetramer *via* removal of a labile solvent ligand.

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Notes and references

‡ *Crystal data*: for *anti*-**2**: $C_{52}H_{48}N_8O_4Pd_2\cdot 2CH_3CN$, M = 1143.91, monoclinic, space group $P2_1/c$ (no. 14), a = 13.959(2), b = 9.828(3), c = 19.603(2) Å, β = 91.41(1)°, V = 2688.6(8) Å^3, Z = 2, T = 23.0 °C, D_c = 1.413 g cm^{-3}, μ(Mo-Kα) = 7.24 cm^{-1}, Mo-Kα radiation (λ = 0.71069 Å), R = 0.041, R_w = 0.071.

For **3**: $C_{92}H_{84}N_{12}O_8Pd_4\cdot CHCl_3$, M = 2030.73, triclinic, space group $P\bar{1}$ (no. 2), a = 17.6912(5), b = 19.1708(3), c = 16.5754(7) Å, α = 107.276(4), β = 101.263(4), γ = 78.927(3)°, V = 5210.4(3) Å^3, Z = 2, T = 23.0 °C, D_c = 1.294 g cm^{-3}, μ(Mo-Kα) = 8.10 cm^{-1}, Mo-Kα radiation (λ = 0.71069 Å), R = 0.132, R_w = 0.374. Chloroform solvent molecule was treated isotropically. Despite modelling the disorder, a good result was not obtained probably due to the data quality. In this context, C214, C219, C316 and C317 carbon atoms were refined isotropically.

CCDC reference numbers 178475 and 178476. See http://www.rsc.org/suppdata/cc/b2/b203726m/ for crystallographic data in CIF or other electronic format.

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