

Palladium Homobimetallic Complexes with Bridging π -Conjugated Ligands

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The palladium homobimetallic complexes **2a** and **2b** with a bridging π -conjugated molecule, *N,N'*-bis(4'-pyridylmethylidene)-1,4-phenylenediamine (L^{2a}) and 2'-pyridyl derivative L^{2b} , were respectively synthesized and characterized by X-ray crystal structure analysis and cyclic voltammetry. $^1\text{H-NMR}$ of **2b** indicates the five-coordinate geometry on the palladium center.

π -Conjugated ligands have been attracting much interest in a variety of applications depending on their electrical properties.¹ The incorporation of more than two transition metal complexes into such π -conjugated ligands is envisaged to provide efficient redox systems with novel physical properties based on electronic communication between transition metal centers. From these points of view, bimetallic complexes composed of π -conjugated bridging spacers and terminal redox-active transition metals have currently received much attention as functional materials and the importance of π -conjugated molecules in electronic communication has been highlighted.² In this context, we embarked upon a program of research aimed at constructing a novel redox system composed of bimetallic and π -conjugated metal-assembled complexes. This paper describes the crystallographical and spectroscopical characterization of the π -conjugated palladium homobimetallic complexes with *N,N'*-bis(pyridylmethylidene)-1,4-phenylenediamines.

It has been demonstrated that the palladium(II) complex $[(L^1)\text{Pd}(\text{MeCN})]$ (**1**) bearing the *N*-heterocyclic tridentate podand ligand, *N,N'*-bis(2-phenylethyl)-2,6-pyridinedicarboxamide ($L^1\text{H}^2$),³ offers one interchangeable coordination site as a metalloceptor. Treatment of the palladium(II) complex **1** with 0.5 equiv of a π -conjugated molecule, *N,N'*-bis(4'-pyridylmethylidene)-1,4-phenylenediamine (L^{2a}),⁴ in acetonitrile led to the formation of the 2:1 complex $[(L^1)\text{Pd}(L^{2a})\text{Pd}(L^1)]$ (**2a**, 92% yield, Scheme 1).⁵ The structure of the isolated complex **2a** was elucidated by $^1\text{H-NMR}$. Notably, the upfield shift of the pyridyl proton on the 3'-carbon of L^{2a} was observed upon complexation (L^{2a} : 8.78 ppm; **2a**: 8.18 ppm) although the

pyridyl proton on the 2'-carbon exhibited the downfield shift (L^{2a} : 7.78 ppm; **2a**: 7.82 ppm). These findings indicate that the pyridyl nitrogen coordinates to the palladium center, in which the pyridine ring seems to be almost perpendicular to the coordination plane of palladium, to locate the pyridyl proton on the 3'-carbon above the coordination plane.⁶

Further structural information of **2a** was obtained by the single-crystal X-ray structure determination.⁷ Two palladium complex units are bridged by L^{2a} to form the C_2 symmetrical 2:1 complex with the Pd-Pd separation 19.51 Å, as depicted in Figure 1. The pyridyl nitrogen of L^{2a} , which was slightly deviated from the square planar coordination plane (N(1)-Pd-

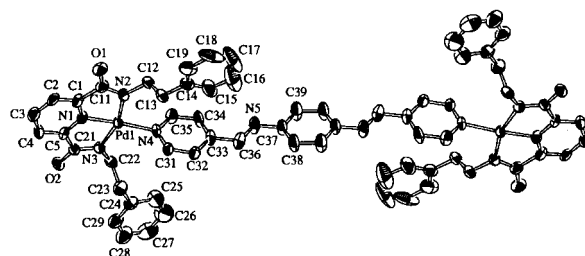
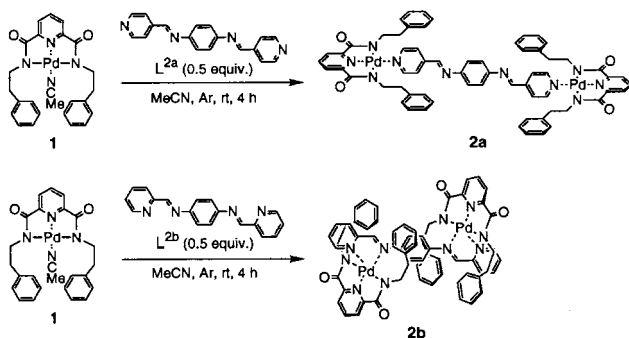


Figure 1. ORTEP view of the X-ray crystal structure of **2a**: (40% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pd(1)-N(1) 1.93(1), Pd(1)-N(2) 2.02(2), Pd(1)-N(3) 2.01(1), Pd(1)-N(4) 2.03(1); N(1)-Pd(1)-N(2) 80.2(6), N(1)-Pd(1)-N(3) 80.3(6), N(1)-Pd(1)-N(4) 172.6(7), N(2)-Pd(1)-N(3) 160.4(6), N(2)-Pd(1)-N(4) 98.2(6), N(3)-Pd(1)-N(4) 101.3(6).

N(4), 172.6°), coordinated to the palladium center at the interchangeable coordination site of **1**. Noteworthy, the dihedral angle between the least-square planes of the pyridine ring of L^{2a} and Pd-N(1)-N(2)-N(3) was found to be 94.3°, being consistent with the above-mentioned shift of the pyridyl proton in $^1\text{H-NMR}$. Another interesting feature is that the π -conjugated molecule units are aligned along nearly to the *ac* plane and arrange in a herringbone motif in the crystal packing (Figure 2).

The imine nitrogen of a π -conjugated molecule, *N,N'*-bis(2'-pyridylmethylidene)-1,4-phenylenediamine (L^{2b}),⁴ is expected to participate in the coordination. The tridentate palladium(II) complex **1** was also found to form the 2:1 complex $[(L^1)\text{Pd}(L^{2b})\text{Pd}(L^1)]$ (**2b**) with L^{2b} in 91% yield (Scheme 1).⁸ In $^1\text{H-NMR}$, the upfield shift of the pyridyl proton on the 3'-carbon of L^{2b} was detected as observed in **2a**. Furthermore, the -N=CH- protons of L^{2b} appeared at the lower field (L^{2b} : 8.67 ppm; **2b**: 9.79 ppm). These results suggest the coordination of the imine nitrogen to the palladium center to form the five-coordinate palladium complex.⁹ The upper-field shift of the phenylene protons of L^{2b} (7.39 ppm) compared with those of **2a** (7.49 ppm), which is probably due to the location below the coordination plane of palladium, also supports the coordination of the imine nitrogen. Another interesting feature is that the signals attributable to the methylene protons of L^1 exhibit-



Scheme 1.

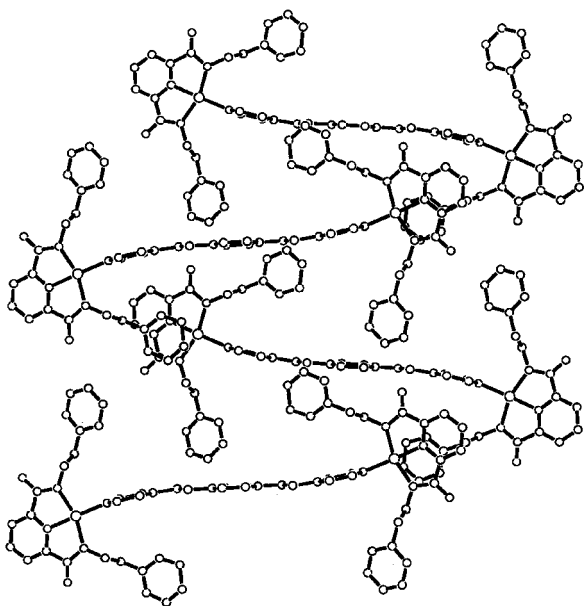


Figure 2. Crystal packing of **2a**.

ed nonequivalent resonances in the region 3.24–3.17, 2.79–2.72, 2.70–2.63, and 2.51–2.45 ppm although those of **2a** are magnetically equivalent and in the expected form of a triplet. The upper and lower sides of the coordination plane of the five-coordinate geometry are unsymmetrical.

The electrochemical properties of **2** were studied by cyclic voltammetry. The palladium homobimetallic complex **2** in dichloromethane exhibited two separate redox waves (**2a**: -1.61 and -1.72 V; **2b**: -1.69 and -1.79 V vs. Fc/Fc⁺) assignable to the redox of two carbaldiminopyridyl moieties as shown in Figure 3. Two redox couples suggest that there is electronic communication between the carbaldiminopyridyl moieties through the π -conjugated spacer L². Since the binding to palladium lowers the energy of the π^* orbital of the π -conjugated molecule, the difference in the redox potentials between **2a** and **2b** is accounted for by the difference of the coordination mode.

In conclusion, complexation of the π -conjugated molecule L² with the palladium complex **1** led to the formation of the π -conjugated palladium homobimetallic complex **2**, in which

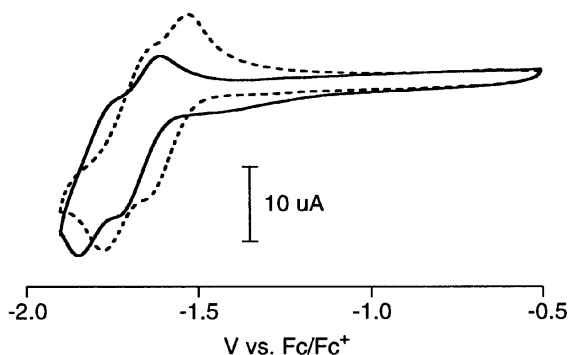


Figure 3. Cyclic voltammograms of **2a** (---) and **2b** (—). [2] = 1.0×10^{-3} M; [*n*-Bu₄ClO₄] = 0.1 M; solv., CH₂Cl₂; under Ar; scan rate = 100 mV/s.

electronic communication is possible through the π -conjugated spacer. The control of electronic and magnetic interactions between redox centers is considered to partly depend on the coordination properties of the π -conjugated bridging ligands. ¹H-NMR studies of **2b** indicate the unique five-coordinate geometry on the palladium center.

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- 2a**: ¹H-NMR (CDCl₃): δ 8.58 (s, 2H), 8.18 (d, J = 6.6 Hz, 4H), 8.08 (t, J = 7.8 Hz, 2H), 7.82 (d, J = 6.6 Hz, 4H), 7.81 (d, J = 7.8 Hz, 4H), 7.49 (s, 4H), 7.24–7.18 (m, 12H), 6.92–6.90 (m, 8H), 3.04 (t, J = 7.2 Hz, 8H), 2.68 (t, J = 7.2 Hz, 8H). Anal. Found: C, 60.41; H, 4.70; N, 10.68%. Calcd for C₆₄H₅₆N₁₀O₄Pd₂·2H₂O: C, 60.15; H, 4.73; N, 10.96%.
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- Crystal data for **2a**: C₆₄H₅₆N₁₀O₄Pd₂, *M* = 1242.01, monoclinic, space group *P2₁/a* (#14), *a* = 15.524(6) Å, *b* = 14.794(3) Å, *c* = 14.838(3) Å, β = 90.01(2)°, *V* = 3407(1) Å³ *Z* = 2, *T* = 23.0 °C, *D*_{calc} = 1210 g cm⁻³, μ (MoK α) = 5.66 cm⁻¹, MoK α radiation (λ = 0.71069 Å), *R* = 0.086, *R*_w = 0.126 for 3368 observed reflections ($2\theta_{\max}$ = 55.1°).
- 2b**: ¹H-NMR (CDCl₃): δ 9.79 (s, 2H), 8.50 (dd, J = 8.1, 1.5 Hz, 2H), 8.28 (dd, J = 5.6, 1.4 Hz, 2H), 8.09 (t, J = 7.8 Hz, 2H), 8.08–8.04 (m, 2H), 7.79 (d, J = 7.8 Hz, 4H), 7.43 (ddd, J = 7.7, 5.6, 1.5 Hz, 2H), 7.39 (s, 4H), 7.16–7.10 (m, 12H), 6.79–6.77 (m, 8H), 3.24–3.17 (m, 4H), 2.79–2.72 (m, 4H), 2.70–2.63 (m, 4H), 2.51–2.45 (m, 4H). Anal. Found: C, 59.97; H, 4.59; N, 11.04%. Calcd for C₆₄H₅₆N₁₀O₄Pd₂·2H₂O: C, 60.15; H, 4.73; N, 10.96%.
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