

A Novel Redox-Active Conjugated Palladium Homobimetallic Complex

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The π -conjugated molecule *N,N'*-bis(4'-dimethylamino-phenyl)-1,4-benzoquinone diimine (L^2) was incorporated into the palladium(II) complex **1** bearing the *N,N'*-bis(2-phenylethyl)-2,6-pyridinedicarboxamide ligand, to afford the redox-active conjugated palladium(II) homobimetallic complex **2**. An X-ray crystal structure determination of **2** reveals that two palladium complex units are bridged by the quinone diimine moiety to form the C_2 -symmetrical 2:1 complex with an *anti* configuration, and that the bridging π -conjugated spacer moieties are aligned along a straight line almost parallel to the a axis, to form the columns of the π -conjugated molecules in the molecular packing. Variable temperature ^1H NMR studies of the conjugated complex **2** indicate that the *syn*

configuration is enthalpically more favorable than the *anti* configuration in CD_2Cl_2 by 1.0 kcal/mol, but entropically less favorable by 4.5 cal/mol from the van't Hoff plot. The redox function of the quinone diimine moiety is modulated by complexation with the palladium complex **1**. The conjugated complex **2** shows three separate redox waves assignable to the successive one-electron reduction of the quinone diimine moiety and one-electron oxidation process of the two terminal dimethylamino groups. Chemical reduction of **2** in THF with CoCp_2 resulted in the appearance of ESR signals with weak ^{105}Pd coupling centered around $g = 2.0041$. The added electrons are considered to be delocalized over the Pd^{II} -quinone diimine $d\text{-}\pi^*$ system in the complex.

Introduction

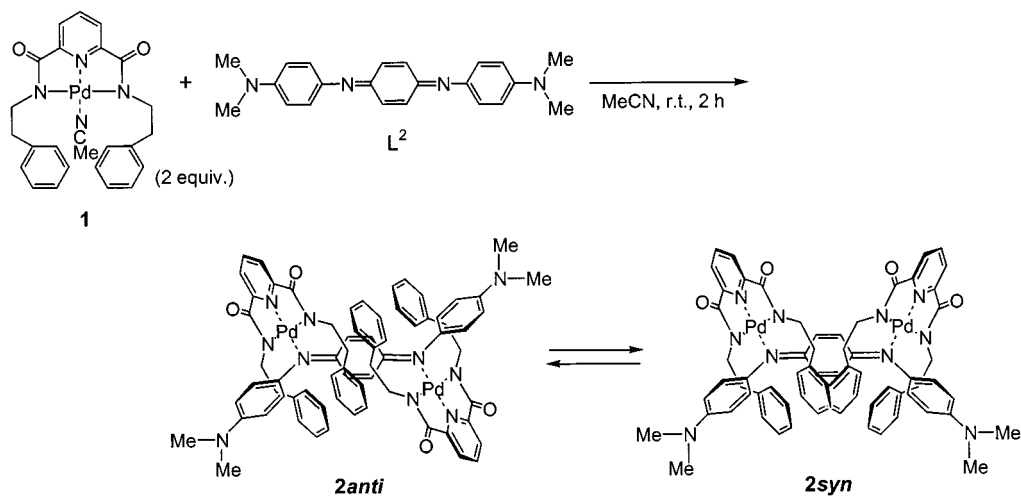
Quinone diimines can exist in three redox forms: the reduced phenylenediamide dianions, the partially reduced semiquinone diimine radical anions, and the oxidized neutral quinone diimines. The combination of this redox behavior and complexation with transition metals provides an efficient redox system. *o*-Benzoquinone diimines have attracted much attention as a redox-active compound in this context.^[1] However, transition metal complexes with *p*-benzoquinone diimine ligands have been investigated in only a few cases and the coordination behavior of *p*-benzoquinone diimine has hitherto remained unexplored.^[2] In a previous paper, the emeraldine base form of polyanilines as π -conjugated polymers, which contains a *p*-benzoquinone diimine unit, has been revealed to coordinate to transition metals, affording conjugated complex systems.^[3] The polymer complex can effectively serve as an oxidation catalyst,^[4] in which the quinone diimine moiety is considered to contribute to a reversible redox process in the catalytic cycle of a transition metal. These results prompted us to investigate the redox properties of the transition metal complexes with *p*-benzoquinone diimines and to characterize the complexes structurally. We herein report the synthesis of the palladium(II) homobimetallic complex with a bridging π -conjugated *p*-benzoquinone diimine.

Results and Discussion

The construction of a conjugated complex system was demonstrated by use of a redox-active π -conjugated molecule, *N,N'*-bis(4'-dimethylaminophenyl)-1,4-benzoquinone diimine (L^2).^[5] Complexation with a palladium complex bearing a tridentate ligand, which has one open coordination site, is expected to provide the bimetallic conjugated complex. In this context, the palladium(II) complex $[(L^1)\text{Pd}(\text{MeCN})]$ (**1**) bearing one interchangeable coordination site was prepared by treatment of $\text{Pd}(\text{OAc})_2$ with the *N*-heterocyclic tridentate podand ligand, *N,N'*-bis(2-phenylethyl)-2,6-pyridinedicarboxamide ($L^1\text{H}_2$).^[6] in acetonitrile. The X-ray crystal structure of **1**^[7] indicates that the open coordination site is occupied by an ancillary acetonitrile, presenting the complex **1** with one labile ligand.^[8] Treatment of the palladium(II) complex **1** with L^2 in acetonitrile led to the formation of the 2:1 complex $[(L^1)\text{Pd}(L^2)\text{Pd}(L^1)]$ (**2**, Scheme 1).

The structure of the conjugated complex **2** was confirmed by X-ray crystallography. The solid-state molecular structure reveals that the two $[(L^1)\text{Pd}]$ units are bridged by the quinone diimine moiety of L^2 to form the C_2 -symmetrical 2:1 complex *anti*-**2** with a Pd–Pd separation 8.17 Å, as depicted in Figure 1. Crystallographic data for *anti*-**2** can be found in Table 1, with selected bond lengths and bond angles listed Table 2. Each nitrogen atom of the quinone diimine moiety of L^2 is deviated from the least-squares plane of $\text{C}(37)\text{--}\text{C}(38)\text{--}\text{C}(39^*)\text{--}\text{C}(37^*)\text{--}\text{C}(38^*)\text{--}\text{C}(39)$ by 4.7° in the same direction, probably due to coordination to a palladium atom which is deviated from the plane by 10.7° . One phenyl ring of the podand moiety of $[(L^1)\text{Pd}]$ is oriented in a near face-to-face arrangement at a distance of ca. 3.9 Å with the phenyl ring of another $[(L^1)\text{Pd}]$, suggesting a weak π -stacking interaction. This interaction might cause

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Scheme 1

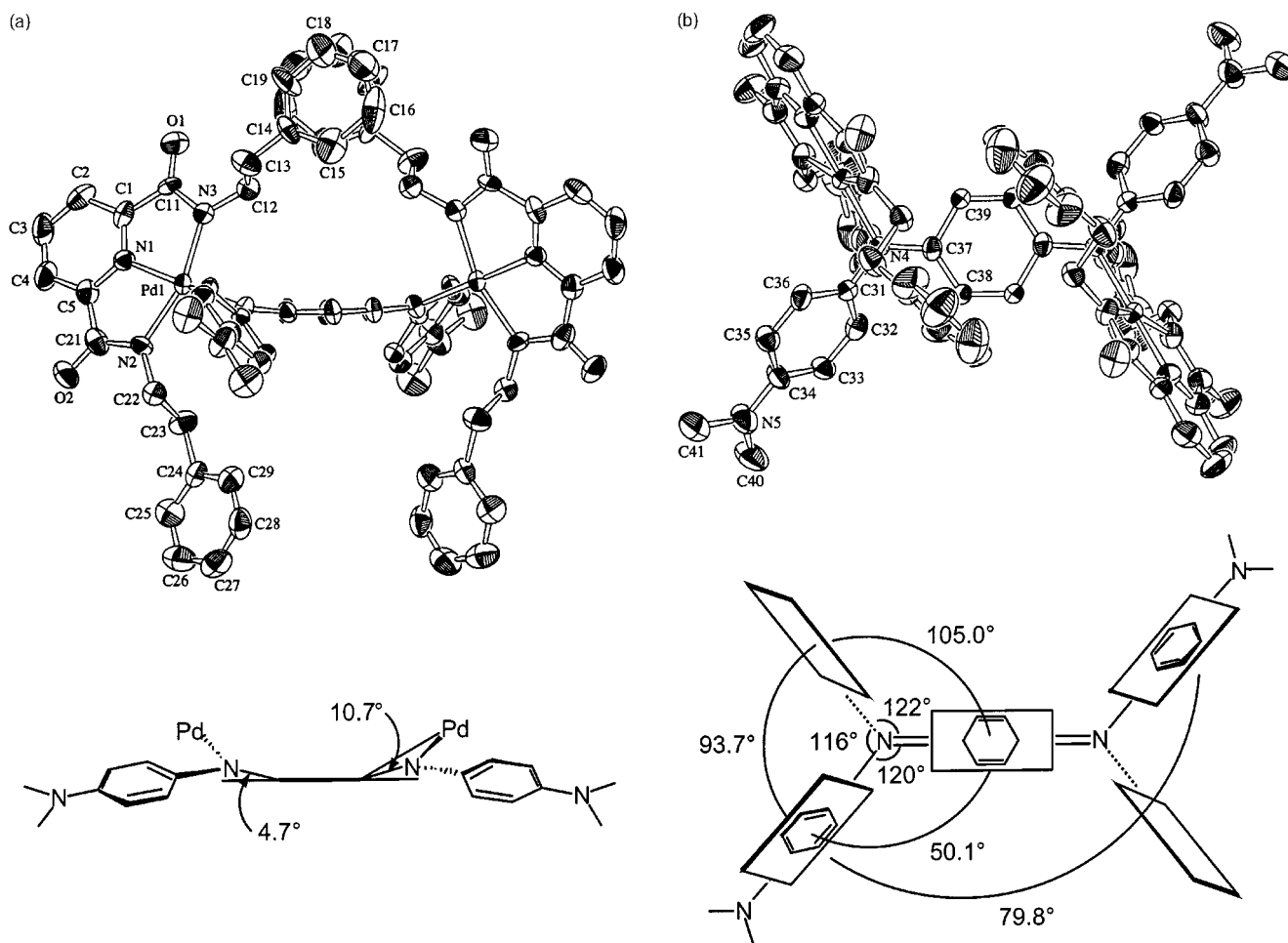
Figure 1. (a) Top view and (b) side view of the X-ray crystal structure of **anti-2** (40% probability ellipsoids; hydrogen atoms are omitted for clarity)

Table 1. Crystallographic data for *anti-2*

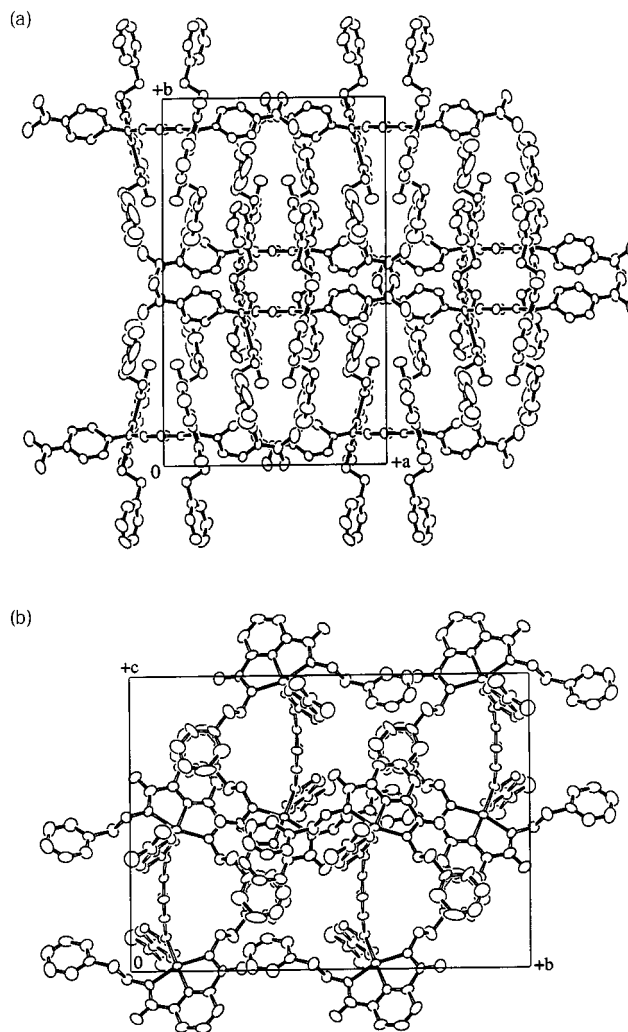
Empirical formula	C ₆₈ H ₆₆ N ₁₀ O ₄ Pd ₂
Formula mass	1300.13
Crystal system	monoclinic
Space group	C2/c (No. 15)
<i>a</i> [Å]	15.858(4)
<i>b</i> [Å]	23.955(8)
<i>c</i> [Å]	18.994(3)
β [°]	112.13(2)
<i>V</i> [Å ³]	6683(2)
<i>Z</i>	4
<i>D</i> _{calcd.} [g cm ⁻³]	1.292
μ (Mo- <i>K</i> α) [cm ⁻¹]	5.91
<i>T</i> [°C]	23
λ (Mo- <i>K</i> α) [Å]	0.71069
<i>R</i> ^[a]	0.081
<i>R</i> _w ^[b]	0.0112

[a] $R = (|F_o| - |F_c|)/|F_o|$. - [b] $R_w = [w(|F_o| - |F_c|)^2/w|F_o|^2]^{1/2}$.

Table 2. Selected bond lengths [Å] and bond angles [deg] for *anti-2*

Bond lengths			
Pd–N(1)	1.93(2)	C(37)–C(38)	1.40(2)
Pd–N(2)	2.02(1)	C(37)–C(39)	1.45(2)
Pd–N(3)	2.03(2)	C(38)–C(39*)	1.33(2)
Pd–N(4)	2.05(1)	C(31)–C(36)	1.39(2)
N(4)–C(31)	1.42(2)	C(31)–C(32)	1.40(2)
N(4)–C(37)	1.35(2)		
Bond angles			
N(1)–Pd–N(2)	80.1(7)	N(3)–Pd–N(4)	98.5(6)
N(1)–Pd–N(3)	80.7(7)	Pd–N(4)–C(31)	116(1)
N(1)–Pd–N(4)	179.0(6)	Pd–N(4)–C(37)	122(1)
N(2)–Pd–N(3)	160.8(6)	C(31)–N(4)–C(37)	120(1)
N(2)–Pd–N(4)	100.7(6)		

the above-mentioned deviation of the palladium atoms. Due to π -conjugation of L², the orientation of each phenylene ring should be within a limited range of locations parallel to the quinone diimine moiety. The steric interaction between the hydrogen atom at C(32) and the hydrogen atom at C(38), however, causes the phenylene ring of L² to rotate away from this orientation, resulting in a conformation with a dihedral angle of 50.1° between the phenylene and quinone planes. Each phenylene ring of L² has an opposite dihedral angle with respect to the quinone plane, causing a propeller twist of 79.8° between the planes of the two phenylene rings. The least-squares plane of N(1)–N(2)–N(3)–Pd is at an angle of 109.7° instead of 90° from the plane of C(31)–N(4)–C(37) as a result of the twist of the π -conjugated plane of L². Another interesting feature is that the bridging π -conjugated molecules L² are aligned along a straight line almost parallel to the *a* axis in the molecular packing (Figure 2a). The coordination planes of palladium composed of the pyridyl and two amide moieties occupy nearly the *bc* plane (Figure 2b).

Figure 2. (a) Projection down the *c* axis and (b) projection down the *a* axis of the molecular packing of *anti-2*

Variable temperature ¹H NMR studies of the conjugated complex **2** indicated interesting molecular dynamics in solution (Figure 3). As the temperature was lowered, the peaks of the *syn* conformer *syn-2* appeared and increased gradually. It should be noted that the conjugated complex **2** prefers the *anti* configuration at temperatures above 220 K and the *syn* configuration below this temperature. The equilibrium constant *K*_{eq} between *anti-2* and *syn-2* was calculated from variable temperature ¹H NMR spectra (Scheme 2). The temperature dependence of *K*_{eq} is used to construct the van't Hoff plot of ln*K*_{eq} vs. *T*⁻¹ (Figure 4). The *syn* configuration is enthalpically more favorable than the *anti* configuration in CD₂Cl₂ by 1.0 kcal/mol, but entropically less favorable by 4.5 cal/mol from the van't Hoff plot.

The interesting redox properties of **2** were disclosed by cyclic voltammetry. The conjugated complex **2** in CH₂Cl₂ shows three separate redox waves (*E*_{1/2} = −1.49 V, −0.85 V, and 0.20 V vs. Fc/Fc⁺) as depicted in Figure 5. The waves at −1.49 V and −0.85 V are assigned to the successive one-electron reduction of the quinone diimine moiety to give

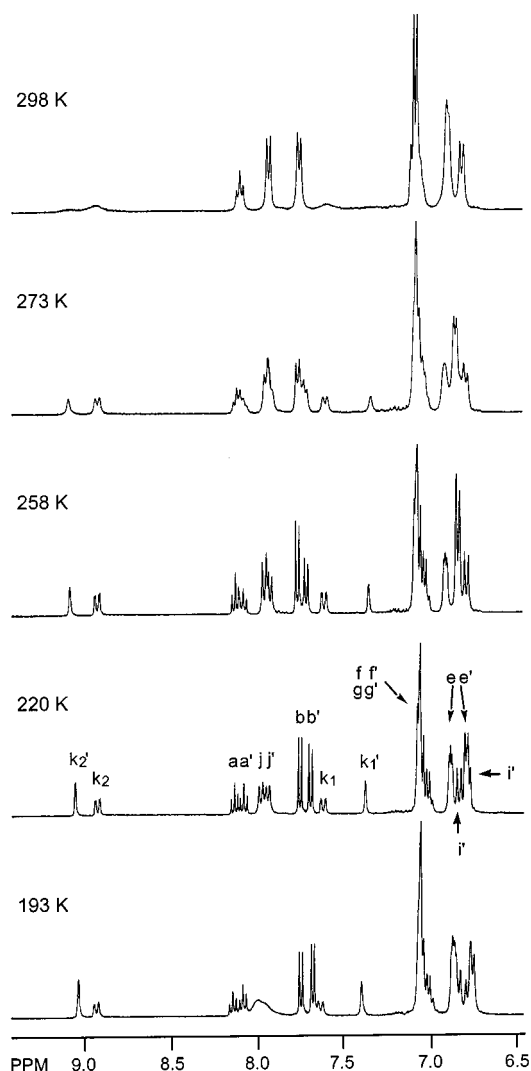


Figure 3. Variable temperature ^1H NMR spectrum of **2** in CD_2Cl_2

the corresponding reduced species. This result is in sharp contrast to the redox behavior of L^2 in CH_2Cl_2 , in which an irreversible reduction wave is observed at -1.67 V. Generally, the generated radical anion appears to be unstable, although this depends on the availability of a proton source.^[9] In the case of reduction of the complex **2**, the

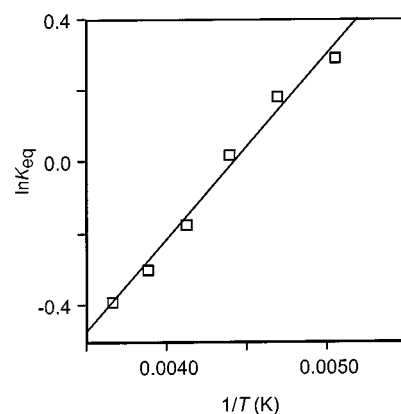


Figure 4. Plot of $\ln K_{\text{eq}}$ vs. T^{-1} for **2** in CD_2Cl_2

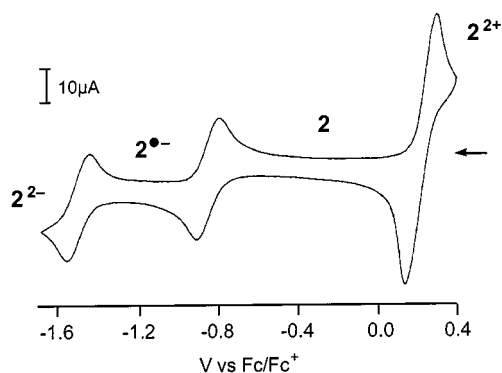
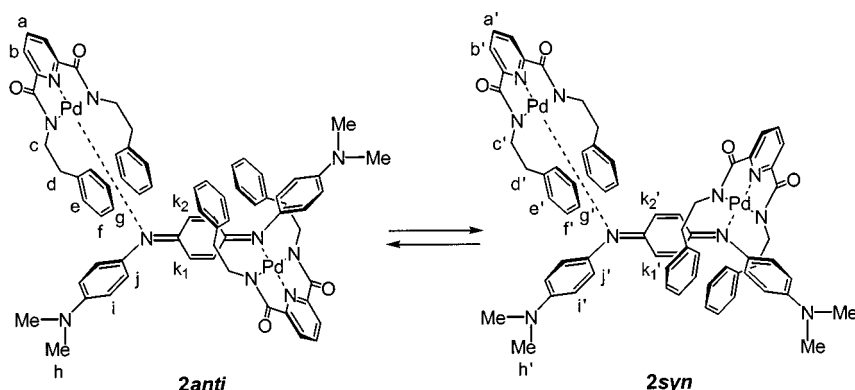
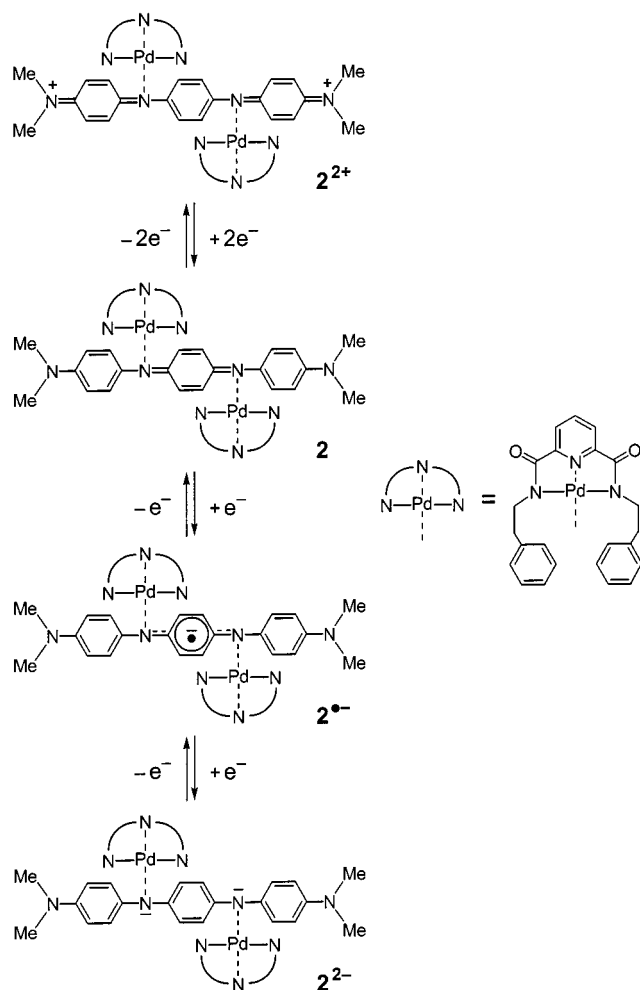


Figure 5. Cyclic voltammogram of **2** (1.0×10^{-3} M) in CH_2Cl_2 (0.1 M $n\text{Bu}_4\text{NClO}_4$) at a glassy carbon working electrode with scan rate = 100 mV/s under Ar

added electrons are considered to be delocalized over the Pd^{II} -quinone diimine $d-\pi^*$ system. Compared with the uncomplexed one, the complexed quinone diimine becomes stabilized as an electron sink. Accordingly, the redox properties of the quinone diimine moiety are modulated by complexation with the palladium complex **1**, affording a multi-redox complex system. Furthermore, the most positive anodic peak with twice height ($E_{1/2} = 0.20$ V) is attributable to a one-electron oxidation process of the two terminal dimethylamino groups.^[10] A substantial positive shift of this



Scheme 2. Numbering of carbon atoms of the conjugated complex **2**; the left palladium complex moiety in each isomer is moved for labelling



Scheme 3. Schematic representation of the redox behavior of the conjugated complex **2**

oxidation wave compared with the free quinone diimine L^2 ($E_{1/2} = -0.08$ V) is consistent with the coordination of L^2 to palladium. The redox behavior of the conjugated complex **2** is depicted schematically in Scheme 3.

To gain insight into the redox properties of the conjugated complex **2**, the redox behavior was investigated spectroscopically. The chemical reduction of **2** in THF with CoCp₂ resulted in the appearance of the ESR signals centered around $g = 2.0041$, with hyperfine coupling to two equivalent nitrogen nuclei and four equivalent protons and weak coupling to the ^{105}Pd nucleus (natural abundance 22.2%, $I = 5/2$) as shown in Figure 6, indicating that the unpaired electron is located mostly on the quinone diimine moiety. Some delocalization onto the metal is revealed by the weak satellite lines due to ^{105}Pd coupling. The ESR signal could be approximately simulated by assuming the following parameters: $A_N = 6.6$ G; $A_H = 1.6$ G; $A_{Pd} = 3.4$ G.

The electronic spectrum of a solution of **2** in THF exhibits a strong broad absorption around 806 nm ($\log \varepsilon = 4.82$), probably assignable to a low-energy charge-transfer transition with significant Pd content (Figure 7). The generated semiquinone diimine complex $2^{\bullet-}$ could be characterized by a broad absorption around 931 nm ($\log \varepsilon = 4.16$)

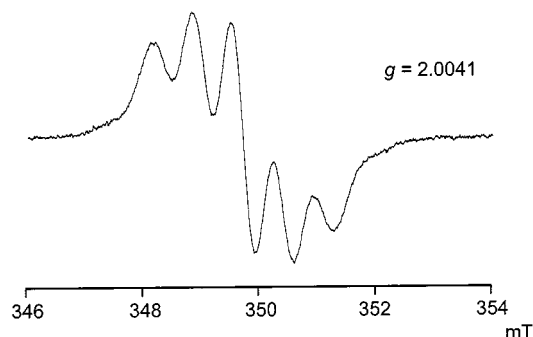


Figure 6. ESR spectrum of $2^{\bullet-}$ in THF at 290 K

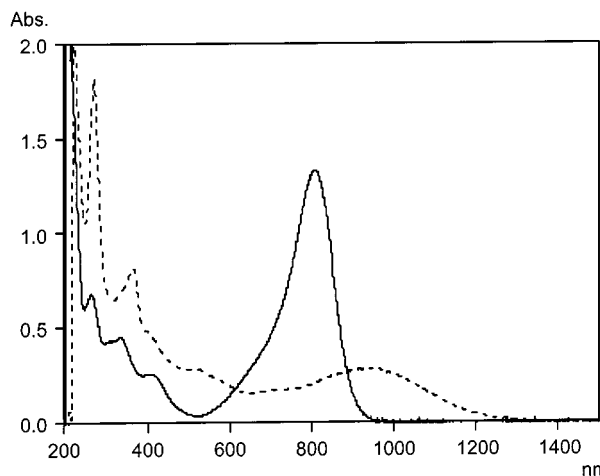


Figure 7. Electronic spectra of **2** (—) and $2^{\bullet-}$ (---) (2.0×10^{-5} M) in THF

as illustrated in Figure 7. This broad absorption, the assignment of which is not yet clear, might be a charge-transfer transition or an internal transition with significant Pd content.

Conclusion

Two palladium atoms were demonstrated to be bridged by the quinone diimine moiety of the π -conjugated molecule L^2 to afford the novel redox-active conjugated homobimetallic complex system, in which the complexed quinone diimine becomes stabilized as an electron sink. The *syn* configuration of the conjugated complex **2** is enthalpically more favorable than the *anti* one in CD_2Cl_2 , but entropically less favorable. These results are related to the conjugated complexes with polyanilines. Bimetallic complexes composed of π -conjugated bridging spacers and terminal redox-active transition metals have currently received much attention as functional materials.^[11] From this point of view, the potential use of the present bimetallic complex characterized by the redox-active π -conjugated bridging spacer appears to be promising.

Experimental Section

General Methods: All reagents and solvents were purchased from commercial sources and were further purified by the standard

methods, if necessary. Melting points were determined on a Yanagimoto Micromelting Point Apparatus and were uncorrected. Infrared spectra were obtained with a Perkin–Elmer Model 1605 FT-IR. ^1H NMR spectra were recorded on a JEOL JNM-GSX-400 (400 MHz) spectrometer with tetramethylsilane as an internal standard. Mass spectra were run on a JEOL JMS-DX303HF mass spectrometer. Electronic spectra were obtained using a Hitachi U-3500 spectrophotometer.

N,N'-Bis(2-phenylethyl)-2,6-pyridinedicarboxamide (L^1H_2) was prepared according to the method reported in a previous paper.^[6b] *N,N'*-Bis(4'-dimethylaminophenyl)-1,4-benzoquinone diimine (L^2) was prepared by the literature method.^[5]

Preparation of $[(\text{L}^1)\text{Pd}(\text{MeCN})]$ (1): A mixture of L^1H_2 (18.7 mg, 0.05 mmol) and $\text{Pd}(\text{OAc})_2$ (11.2 mg, 0.05 mmol) in acetonitrile (5 mL) was stirred under argon at room temperature for 2 h. After evaporation of the solvent, the palladium complex **1** was isolated in 96% yield (24.9 mg) as yellow crystals by recrystallization from acetonitrile. M.p. 165–167 °C (uncorrected). – IR (KBr): $\tilde{\nu}$ = 1590, 1388 cm^{-1} . – ^1H NMR (400 MHz, CD_3CN , 298 K): δ = 2.78 (t, J = 7.3 Hz, 4 H), 3.40 (t, J = 7.3 Hz, 4 H), 7.19–7.33 (m, 10 H), 7.56 (d, J = 7.7 Hz, 2 H), 8.01 (t, J = 7.7 Hz, 1 H). – MS (FAB): m/z = 478 $[(\text{M} - \text{CH}_3\text{CN})^+ + 1]$. – $\text{C}_{25}\text{H}_{24}\text{N}_4\text{O}_2\text{Pd}$ (518.91): calcd. C 57.87, H 4.66, N 10.80; found C 57.83, H 4.75, N 10.76.

Preparation of $[(\text{L}^1)\text{Pd}(\text{L}^2)\text{Pd}(\text{L}^1)]$ (2): A mixture of **1** (20.8 mg, 0.04 mmol) and L^2 (6.9 mg, 0.02 mmol) was stirred in acetonitrile (20 mL) under argon at room temperature for 2 h. After evaporation of the solution, the conjugated palladium complex **2** was isolated in 73% yield as dark green crystals by recrystallization from chloroform/hexane. M.p. 227–229 °C (decomp.). – IR (KBr): $\tilde{\nu}$ = 1588, 1359, 1161 cm^{-1} . – UV/Vis (THF): λ_{max} (log ϵ) = 806 (4.82) nm. – ^1H NMR (400 MHz, CD_2Cl_2 , 220 K, *antisyn* = 1:1): δ = 2.15–2.30 (m, 8 H, *syn* and *anti*), 2.38–2.50 (m, 8 H, *syn* and *anti*), 2.76–2.90 (m, 8 H, *syn* and *anti*), 3.00–3.10 (m, 8 H, *syn* and *anti*), 3.13 (s, 12 H, *anti*), 3.20 (s, 12 H, *syn*), 6.75–6.92 (m, 24 H, *syn* and *anti*), 6.97–7.10 (m, 24 H, *syn* and *anti*), 7.38 (s, 2 H, *syn*), 7.62 (dd, J = 10.3, 2.2 Hz, 2 H, *anti*), 7.70 (d, J = 8.1 Hz, 4 H, *syn*), 7.76 (d, J = 8.1 Hz, 4 H, *anti*), 7.95 (d, J = 8.8 Hz, 4 H, *syn*), 7.99 (d, J = 8.8 Hz, 4 H, *anti*), 8.10 (t, J = 8.1 Hz, 2 H, *syn*), 8.15 (t, J = 8.1 Hz, 2 H, *anti*), 8.95 (dd, J = 10.3, 2.2 Hz, 2 H, *anti*), 9.08 (s, 2 H, *syn*). – MS (FAB): m/z = 1301 $[\text{M}^+ + 1]$. – $\text{C}_{68}\text{H}_{66}\text{N}_{10}\text{O}_4\text{Pd}_2$ (1300.18): calcd. C 62.82, H 5.12, N 10.77; found C 62.50, H 5.11, N 10.60.

Generation of $[(\text{L}^1)\text{Pd}(\text{L}^2)^-\text{Pd}(\text{L}^1)]$ (2^{2-}): For spectroscopic purposes, 2^{2-} was generated by treatment of **2** with 1 equiv. of cobaltocene in THF. The cobaltocene and cobaltocenium ion present in the reaction mixture did not significantly interfere with the electronic spectrum because of their low extinction coefficient below 400 nm.

Equilibrium Measurement for 2: Measurement of the equilibrium constants at various temperatures was carried out by integration of the appropriate peaks during ^1H NMR spectroscopy. Spectra were taken in CD_2Cl_2 at 15 K intervals from 198 to 273 K. The thermodynamic parameters were determined from the van't Hoff plot of $\ln K_{\text{eq}}$ vs. T^{-1} .

Electrochemical Experiments: The cyclic voltammetry measurements were performed on a BAS CV-50 W voltammetry analyzer in deaerated acetonitrile containing 0.1 M $n\text{Bu}_4\text{NClO}_4$ as a supporting electrolyte at 298 K with a three-electrode system consisting of a highly polished glassy carbon working electrode (BAS), a platinum

auxiliary electrode (BAS), and an Ag/AgCl (0.01 M) reference electrode (BAS) at 100 mV/s scan rate. Potentials are given vs. Fc/Fc $^{+}$.

X-ray Crystal Structure Determination of *anti*-2: A dark green crystal of the conjugated palladium complex *anti*-**2** with approximate dimensions of 0.20 $\times$ 0.20 $\times$ 0.30 mm was mounted on a glass fiber. The measurement was made on a Rigaku AFC5R diffractometer with graphite monochromated Mo- K_α radiation and a rotating anode generator. The cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $22.81 < 2\theta < 27.12^\circ$. The data were collected at a temperature of 23 ± 1 °C using the ω - 2θ scan technique to a maximum 2θ value of 55.1° . Totals of 8202 independent reflections were obtained and 7912 were unique. The structure was solved by heavy-atom Patterson methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 2875 observed reflections [$I > 3\sigma(I)$] and 379 variable parameters. R = 0.081, R_w = 0.112. Crystallographic details are given in Table 1. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-152467 for *anti*-**2**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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