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Synthesis and structure of new dinuclear palladium complex containing no bridging ligands*

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Oxidation of the mononuclear semiquinonediimine complex $[(NPh)(NH)C_6H_4]_2Pd$ with silver trifluoromethanesulfonate afforded the diamagnetic dinuclear dicationic palladium complex $\{[(NPh)(NH)C_6H_4]_2Pd\}_2(O_3SCF_3)_2$ with a Pd...Pd distance of 3.267(1) Å. The complex was structurally characterized, and its spectroscopic and electrochemical properties were studied.

Key words: *o*-phenylenediamine, palladium complexes, semiquinonediimine complexes, electrochemical properties, X-ray diffraction analysis.

The ability of aromatic diamines, which are bound to Group VIII transition elements, to undergo two-step oxidation giving successively the corresponding semiquinonediimines and quinonediimines was described in the literature.[1—3] Oxidation of such diamines proceeds in the inner sphere of transition metal complexes. Although the oxidation products of free amines are very unstable, the semiquinonediimine and quinonediimine ligands form rather stable metal complexes.[4—11] Complexes with two α,β-semiquinonediimine ligands contain a planar (or nearly planar) fragment formed by the metal atom and two chelate-coordinated semiquinonediimine radical anions. The metal atom in these complexes is either in a square-planar (Pt^{II},[4] Pd^{II},[5] Ni^{II},[6,7] and Co^{II} [3,8,9]) or tetragonal-pyramidal environment (in the case of a series of Co^{III} complexes).[3,10] The Pt^{II}, Pd^{II}, Ni^{II}, and Co^{III} complexes are diamagnetic. Metals possessing one unpaired electron form both mononuclear paramagnetic and dinuclear diamagnetic complexes due to the formation of a single metal—metal bond.[11]

Earlier,[5,12] we have found that oxidation of the platinum-containing semiquinonediimine complexes $[(NR)(NH)C_6H_4]_2Pt$ (R = H (**1**) or Ph (**2**)) with 1 equiv. of silver triflate AgOTf under mild conditions afforded the diamagnetic compounds $\{[(NR)(NH)C_6H_4]_2Pt\}_2(O_3SCF_3)_2$ (R = H (**3**) or Ph (**4**)) as dinuclear dications. According to the X-ray diffraction data, there is a weak Pt—Pt interaction in these complexes (**3**, 3.031(1) Å; **4**, 3.260(1) Å). Silver triflate was chosen as an oxidizing agent for complexes **1** and **2** because of its specific properties. On the one hand, AgOTf is a rather mild oxidizing agent and, on the other hand, it is a source of weakly coordinated trifluoromethanesulfonate anions, which provide rather high solubility of the resulting ionic compounds in organic solvents. For palladium derivatives with semiquinonediimine ligands, redox transformations have been observed by electrochemical methods only in recent years.[13] However, the products of these reactions have not been isolated and structurally characterized. A possibility of the retention of the bis-chelate metal fragment upon electron transfer from ligands or the metal center remained unclear. From this viewpoint, chemical investigation of redox transformations of the palladium bis-semiquinonediimine complex $[(NPh)(NH)C_6H_4]_2Pd$ (**5**) is not only a step on the road to the synthesis of new oxidized (or reduced) forms of the bis-chelate palladium system but also allows one to elucidate how this bis-chelate system responds to the removal or addition of electrons. In the present study, oxidation of complex **5** with silver triflate was examined and the structure of this reaction product was established by X-ray diffraction analysis.

Results and Discussion

We found that the reaction of semiquinonediimine complex **5** with 1 equiv. of AgOTf in the presence of a small amount of acetone afforded silver metal in

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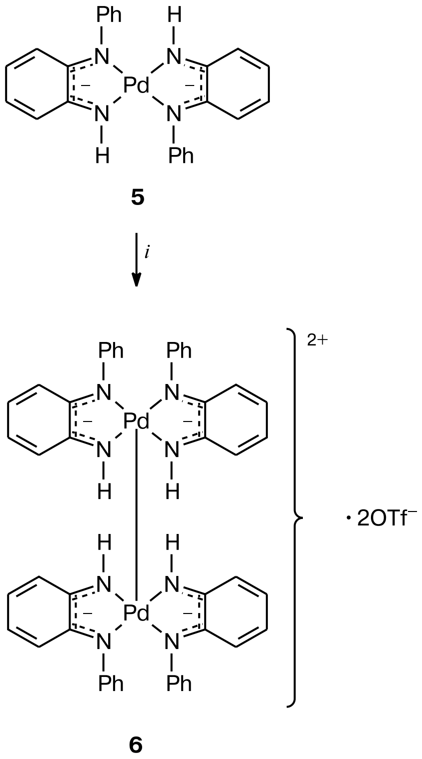
100% yield and the dinuclear diamagnetic complex $\{[(NPh)(NH)C_6H_4]_2Pd\}_2(OTf)_2$ (**6**). Similarly to the platinum analog **4**, this complex has no bridging or axial ligands (Scheme 1).

Scheme 1



i. 1) AgOTf, Me_2CO; 2) extraction with CH_2Cl_2.

According to the X-ray diffraction data, two bis-chelate metal fragments $[(NPh)(NH)C_6H_4]_2Pd$ (in composition, they are formal analogs of complex **5**) in dicationic complex **6** are separated by a distance of 3.267(1) Å, which is substantially shorter than the nonbonded distance between the palladium atoms in the structure of the starting mononuclear complex **5** (4.905(1) Å). Complex **5** differs from complex **6** also by the mutual arrangement of the mononuclear fragments in the crystal stucture. In complex **6**, these fragments adopt a distorted eclipsed conformation, whereas the corresponding fragments in complex **5** have a staggered conformation (Fig. 1). Finally, the very important difference between these complexes is that the Ph groups at the N atoms in the mononuclear fragments of compound **6** are in the *cis* configuration with respect to the metal center, whereas these groups in complex **5** are in the *trans* configuration. In addition, compound **6** contains two outer-sphere anions, which is indicative of the oxidized state of the complex.

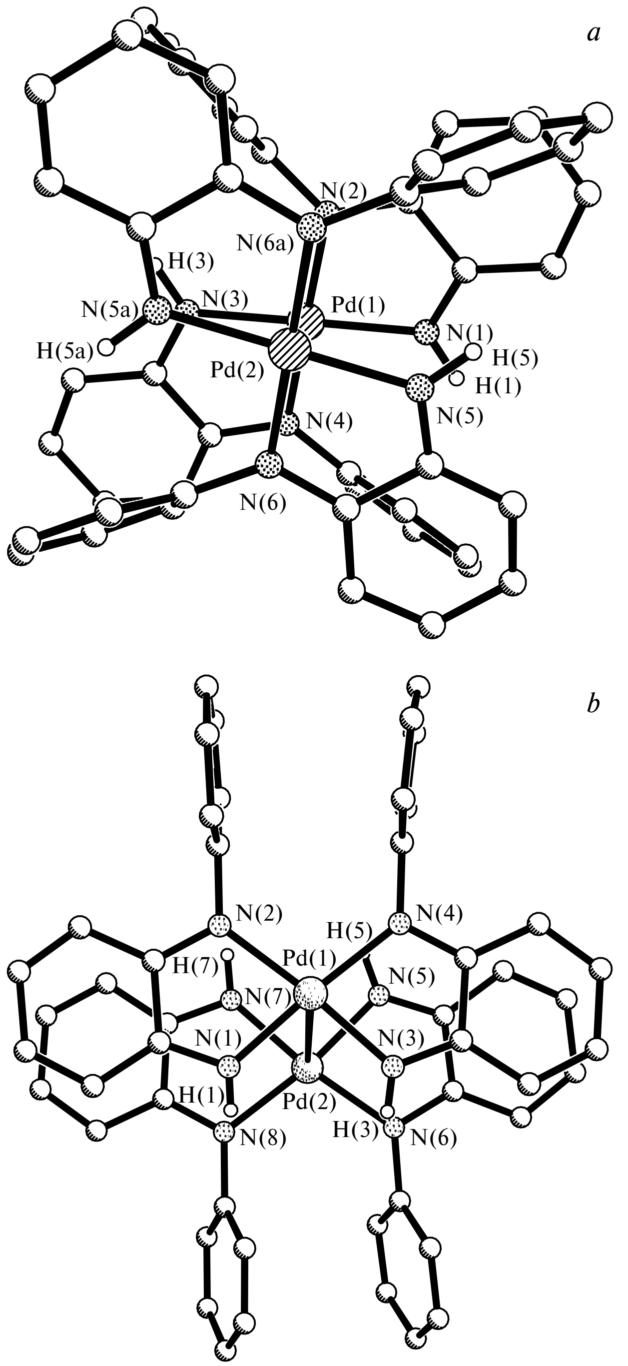


Fig. 1. Geometric arrangement of the mononuclear fragments with respect to each other in the crystals of **5** (*a*) and **6** (*b*).

Analogous differences between the mononuclear and dinuclear dications were observed in the case of mono- and dinuclear platinum derivatives **2** and **4**, respectively. In dinuclear dication **4**, the Pt—Pt distance (3.260(1) Å) is virtually equal to that in complex **6**, and it is only slightly larger than the sum of the covalent radii. Hence, it was assumed[5] that there is a somewhat weakened single bond between the metal atoms. In palladium dication **6**, this distance is also close to the formal sum of the covalent radii of the Pd atoms (~3.0 Å)[14] and approaches the values known for the mixed-valence dinuclear cations $[NMe_4][Pd(C_3S_3Se_2)_2]_2$ and $[PMe_4][Pd(C_3S_5)_2]_2$ (3.174(3) and 3.176(9) Å, respectively[15]). The interactions between two equivalent Pd atoms in the bis-chelate fragments and the *cis*-phenyl substituents, which are virtually orthogonal to the plane of the metallocycle (angle between the plane of the phenyl ring and the plane passing through the Pd(1), C(1), and N(1) atoms is 86.1(2)°), results in steric hindrance. To overcome this hindrance, the bis-chelate mononuclear fragments are forced to shift relative to each other (Pd atoms are not located strictly one above the other; the angle between the Pd—Pd line and the plane of the bis-chelate metal fragment is 116.0(2)°) (Fig. 2). This arrangement of the mononuclear fragments at least substantially hinders the occurrence of stacking interaction between the planar pseudoaromatic metallocycles in the mononuclear fragments. An analogous situation has been observed earlier in platinum complex **4** (angle between the Pt—Pt line and the plane of the bis-chelate metal fragment is 108.04(1)°).[5] This leads to a substantial distortion of the geometry of the dications in complexes **4** and **6** compared to platinum dication **3** containing the unsubstituted bis-semiquinonediimine ligands. For example, the Pd—N(H) and Pd—N(Ph) bonds in complex **6** are nonequivalent (Pd—N(H), 1.958(5) and 1.963(5) Å; Pd—N(Ph), 2.023(5) and 2.021(5) Å) although the ligands retain the initial semiquinoid structure (in the Pd(1)N(1)N(2)C(1)C(6) ring, C—N, 1.309(7)—1.327(7) Å; C—C, 1.459(6) Å). In complex **6**, the Pd atoms only slightly deviate (by ~0.07 Å) from the corresponding PdN_4 planes (Table 1).

Table 1. Principal bond lengths (*d*) and bond angles (ω) in complex **6**

Bond	*d*/Å	Angle	ω/deg
Pd(1)—N(1)	1.958(5)	N(1)—Pd(1)—N(2)	78.6(2)
Pd(1)—N(2)	2.023(5)	N(1)—Pd(1)—N(3)	96.6(2)
Pd(1)—N(3)	1.963(5)	N(1)—Pd(1)—N(4)	176.2(2)
Pd(1)—N(4)	2.021(5)	N(2)—Pd(1)—N(3)	172.1(2)
Pd(2)—N(5)	1.955(5)	N(2)—Pd(1)—N(4)	104.9(2)
Pd(2)—N(6)	2.030(5)	N(3)—Pd(1)—N(4)	79.8(2)
Pd(2)—N(7)	1.966(5)	N(5)—Pd(2)—N(6)	79.9(2)
Pd(2)—N(8)	2.031(5)	N(5)—Pd(2)—N(7)	93.3(2)
N(1)—C(1)	1.310(8)	N(5)—Pd(2)—N(8)	171.7(2)
N(2)—C(6)	1.327(8)	N(6)—Pd(2)—N(7)	171.7(2)
N(3)—C(13)	1.304(8)	N(6)—Pd(2)—N(8)	107.5(2)
N(4)—C(18)	1.332(8)	N(7)—Pd(2)—N(8)	79.1(2)
N(4)—C(19)	1.436(7)	Pd(1)—N(1)—C(1)	118.7(4)
N(5)—C(25)	1.308(8)	Pd(1)—N(2)—C(6)	114.9(4)
N(6)—C(30)	1.341(8)	Pd(1)—N(3)—C(13)	117.4(4)
N(6)—C(31)	1.443(8)	Pd(1)—N(4)—C(18)	114.1(4)
N(7)—C(37)	1.314(8)	Pd(1)—N(4)—C(19)	129.7(4)
N(8)—C(42)	1.335(7)	C(18)—N(4)—C(19)	116.2(5)
C(1)—C(6)	1.459(9)	Pd(2)—N(5)—C(25)	117.6(4)
C(13)—C(18)	1.467(9)	Pd(2)—N(6)—C(30)	113.8(4)
C(25)—C(30)	1.467(9)	Pd(2)—N(6)—C(31)	129.5(4)
C(37)—C(42)	1.460(9)	C(30)—N(6)—C(31)	116.3(5)
		Pd(2)—N(7)—C(37)	118.5(4)
		Pd(2)—N(8)—C(42)	114.1(4)
		N(1)—C(1)—C(6)	112.9(5)
		N(2)—C(6)—C(1)	114.5(5)
		N(3)—C(13)—C(18)	114.3(5)
		N(4)—C(18)—C(13)	114.5(5)
		N(5)—C(25)—C(30)	114.5(5)
		N(6)—C(30)—C(25)	114.2(5)

It should be noted that both dinuclear dications (with the Pt (**4**) and Pd (**6**) atoms) were completely transformed into the starting mononuclear complexes **2** and **5**, respectively, by a reducing agent, *viz.*, dispersed sodium metal in benzene. This fact indicates that the mononuclear fragments with the *cis* arrangement of the Ph groups underwent the reverse transformation into the *trans*-substituted metallocycles, which is, apparently, caused by the cleav-

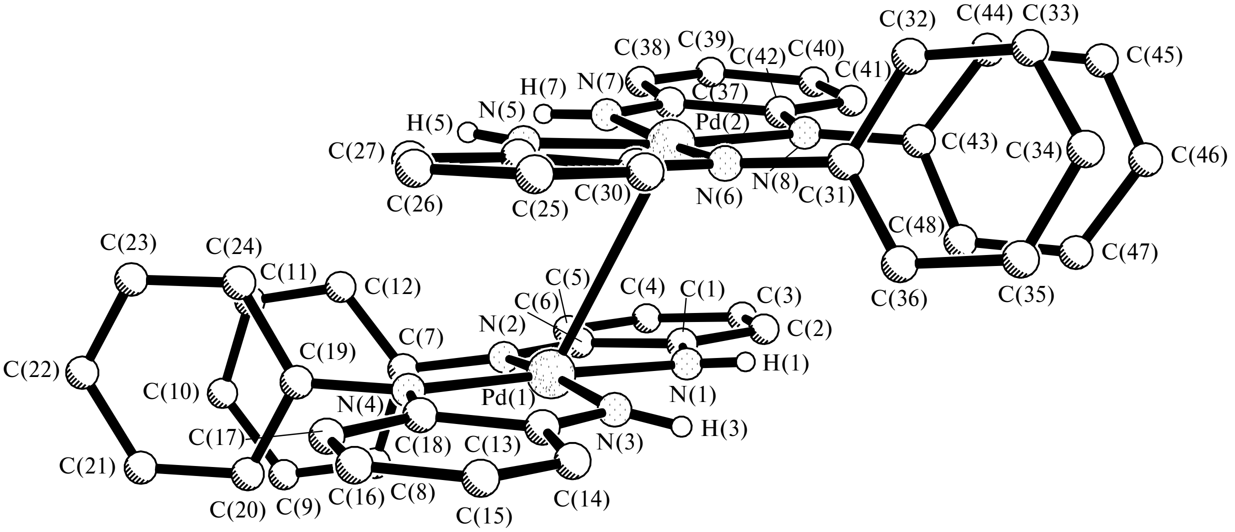


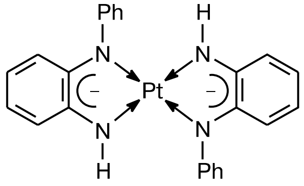
Fig. 2. Structure of the dication in complex **6**.

age of the M—N bonds, taking into account that Pd^{II} or Pt^{II} derivatives with a tetrahedral or octahedral environment (as possible intermediates) involving the chelate N-donor ligands have been found in neither the solid state nor solutions. However, the result of the action of the redox agent can vary depending on the oxidation potential and the chemical activity of the chosen compound. For example, the reaction of mononuclear platinum complex **2** with Cu^{II} as an oxidizing agent (as $CuBr_2$) led to oxidation of the semiquinonediimine ligand to the diimine ligand, the second ligand being eliminated due to the migration of the Br atoms to the platinum center giving rise to the neutral mononuclear complex $[(NPh)(NH)C_6H_4]PtBr_2$ (**7**). The structure of the latter was established by X-ray diffraction analysis.[5]

The electronic state of the metal atoms in the dinuclear complexes $\{[(NPh)(NH)C_6H_4]_2M\}_2(OTf)_2$ (M = Pt (**4**) or Pd (**6**)) and the nature of the metal—metal bonds in these complexes remain open questions. In recent studies, the results of calculations[16] and ESR data[13] for the $\{[1,2\text{-}(NH)_2C_6H_4]_2Pt\}^n$ compounds (n = 0, –1, or +1) demonstrated that the highest MOs b_{2g} and b_{1u} are active in redox transformations of neutral mononuclear complexes. These orbitals are primarily the symmetrical and antisymmetrical combinations of MOs of the free semiquinone ligand occupied by the unpaired electron, *i.e.*, the spin-occupied MO (SOMO). Therefore, the d electrons of the metal atom are not involved in oxidation and the metal atom retains the formal oxidation state 2+. The authors of the study[13] believed that the dicationic nickel complex $\{[1,2\text{-}(NH)_2C_6H_2Bu^t{}_2]_2Ni\}_2{}^{2+}$, which is an isoelectronic analog of the palladium and platinum dinuclear dications, has a single bond between the Ni^{II} atoms with a length of 2.800(1) Å. Electrochemical study of mononuclear complexes **2** and **5** as well as of dinuclear dications **4** and **6** (Table 2) demonstrated that oxidation of the mononuclear complexes proceeded somewhat differently compared to oxidation of the dinuclear systems. Based on the electronic structures of the mononuclear fragments,[13,16] it can be concluded that the removal of electrons from SOMOs of the ligands (b_{1u}) upon oxidation should depend only slightly on the nature of the metal center, because these orbitals have no contribution of the metallic character. In this situation, the second potentials for the mononuclear complexes and the first potentials of the anodic peaks for the dinuclear dications should have close values. This condition is met only for mononuclear complex **2** and dinuclear dication **4** (see Table 2). For the corresponding palladium derivatives (compounds **5** and **6**), the potentials are substantially different (0.58 and 0.72 V, respectively). Presumably, this is indicative of the involvement of the d electrons of the Pd atoms in the formation of a dinuclear structure of the dication.

The electronic absorption spectra (EAS) of complex **5** in a solution in CH_2Cl_2 are identical to the spectra recorded earlier.[13] The absorption spectrum of dication **6**

Table 2. Electrochemical characteristics* of the mono- and dinuclear Pt (**2**, **4**) and Pd (**5**, **6**) complexes ($MeCN—CH_2Cl_2$ (1 : 1), Pt, Ag/AgCl, 0.1 *M* NBu_4ClO_4)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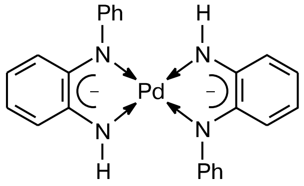
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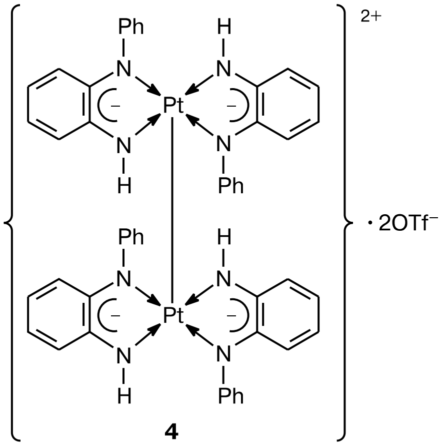
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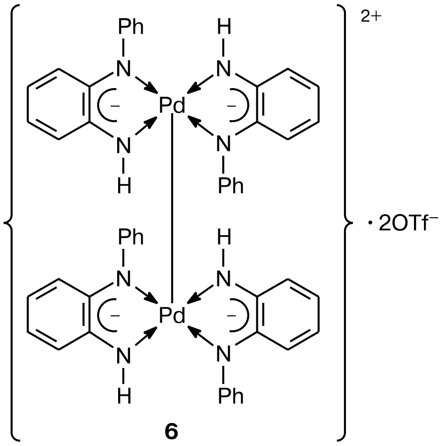
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Compound	E_{pa}	$-E_{pc}$
	V	
2	0.42, 0.84	0.82, 1.50
4	0.89, 1.52	0.54, 1.03
5	0.30, 0.58	0.72, 1.20
6	0.72, 1.24	0.38, 0.68

* E_{pa} and E_{pc} are the potentials of the anodic and cathodic peaks, respectively.

dissolved in CH_2Cl_2 is virtually identical to the spectrum of cation $[\mathbf{5}]^+$ generated electrochemically[13] in a solution in CH_2Cl_2. These facts provide evidence that the electrochemical one-electron oxidation of mononuclear complex **5** and the dissolution of dimeric dication **6** prepared by the chemical reaction afforded identical species in solution. However, the Ph groups at the N atoms in complex **5** are in the *trans* configuration, whereas these substituents in complex **6** are in the *cis* configuration. Therefore, the *trans—cis* isomerization of the mononuclear fragment occurs upon the removal of one electron and is, apparently, associated with the cleavage of the Pd—N bond. This is not surprising if oxidation of complex **5** is accompanied by the removal of the electron from the bonding orbital with a contribution of the orbital of the metal atom. If this orbital were occupied only by electrons of the ligand, the mechanism of the *trans—cis* transformation would be unreasonable.

Experimental

The IR spectra were measured on a Specord M-80 instrument in KBr pellets. The EAS spectra of complexes **5** and **6** in CH_2Cl_2 were recorded on Specord M-400 (in the region of 240—900 nm) and Specord 61 NIR spectrophotometers (in the region of 740—2860 nm) in 0.1-cm quartz cells. The concentrations of the solutions of the complexes were varied in the range of 10^{-3}—10^{-4} mol L^{-1}.

The redox potentials of complexes **2**, **4**, **5**, and **6** in a MeCN—CH_2Cl_2 solvent mixture (1 : 1) were studied using a system for electrochemical measurements consisting of a PI-50 potentiostat, a PR-8 diaphragmless three-electrode cell (operating volume was 2 mL), a PR-8 programmator, and a recorder. A 2-mm stationary platinum disk electrode was used as the working electrode, and a platinum plate with a surface area of 70 mm^2 served as the auxiliary electrode. A silver-silver chloride electrode with a water-impermeable diaphragm was used as the reference electrode. A solution of tetrabutylammonium perchlorate ($5 \cdot 10^{-1}$ mol L^{-1}) served as the supporting electrolyte. The concentration of the complexes was 0.005 mol L^{-1}. The potential scan rate on the programmator was 0.5 V s^{-1}. The oxidation and reduction processes of the mono- and dinuclear complexes were monitored in the potential ranges from 0 to 2.0 V and from 0 to −2.0 V, respectively. Reduction of the compounds under study was carried out under a stream of argon.

Complex **6** was synthesized in air using freshly distilled solvents. The starting complex **5** was prepared according to a known procedure.[5] EAS of complex **5**, λ/nm ($\varepsilon \cdot 10^{-4}$/L mol^{-1} cm^{-1}): 332 (1.53), 419 sh (0.23), 469 (0.22), 542 (0.34), 598 (0.44), 650 (0.61), 838 (2.31).

Synthesis of tetrakis[η^2-*N,N′*-(*N*-phenyl-*o*-benzosemiquinonediimine)]palladium(II) di(trifluoromethanesulfonate), disolvate with dichloromethane, $\{[(NPh)(NH)C_6H_4]_2Pd\}_2(O_3SCF_3)_2 \cdot 2CH_2Cl_2$ (6). A mixture of complex **5** (0.102 g, 0.217 mmol) and AgOTf (0.056 g, 0.217 mmol) with acetone (1—2 mL) was ground in an agate mortar at ~20 °C for 20 min with the gradual addition of 3—5 drops of acetone. The green-brown solid mixture that formed was extracted with dichloromethane (4×10 mL). The resulting solution was concentrated (0.1 Torr, 20 °C) to 30 mL and kept at −18 °C for 24 h. Green-brown crystals of **6** that precipitated were filtered off, washed with hexane, and dried *in vacuo* (0.1 Torr). The yield of compound **6** was 0.054 g (35.5% with respect to **5**). Found (%): C, 44.32; H, 3.35; N, 8.05. $C_{52}H_{44}Cl_4F_6N_8O_6Pd_2S_2$. Calculated (%): C, 44.26; H, 3.12; N, 7.94. IR, ν/cm^{-1}: 3440 w, 3257 w, 3280 w, 2991 w, 2960 w, 2948 w, 1716 w, 1644 w, 1504 m, 1484 w, 1436 v.s, 1356 v.s, 1284 s, 1224 w, 1100 w, 1028 s, 1000 w, 912 w, 860 w, 804 w, 756 w, 688 s, 628 s, 580 w, 516 w, 428 w. EAS of complex **6**, λ/nm ($\varepsilon \cdot 10^{-4}$/L mol^{-1} cm^{-1}): 266 sh (5.85), 305 sh (3.16), 394 (2.41), 434 sh (1.90), 458 (1.81), 529 sh (0.75), 623 (0.46), 869 sh (1.09), 1101 (4.03), 1639 (2.67).

Crystals of **6** were suitable for X-ray diffraction study.

X-ray diffraction study. The X-ray diffraction data for complex **6** were collected on an automated Bruker AXS SMART diffractometer equipped with a CCD detector (graphite monochromator, 110 K, ω scanning technique, scan step was 0.3°, frames were exposed for 30 s) using a standard procedure.[17] The semiempirical absorption correction was applied.[18] The structure of complex **6** was solved by direct methods with the use of the SHELXS-97 program package[19] and refined anisotropically by the full-matrix least-squares method using the SHELXL-97 program package.[20] The H atoms of the NH groups of the semiquinonediimine ligands were revealed from the difference Fourier synthesis and refined isotropically. The remaining H atoms were generated geometrically and refined using the riding model. The molecular formula $C_{52}H_{44}Cl_4F_6N_8O_6Pd_2S_2$, M = 1409.67, space group $P2_1/n$, a = 15.063(3), b = 20.985(4), c = 17.302(3) Å, β = 100.526(4)°, V = 5377.2(17) Å^3, Z = 4, 19392 measured reflections, of which 11288 reflections were with $F^2 > 2\sigma(I)$, ρ_{calc} = 1.741 g cm^{-3}, μ = 1.025 cm^{-1}, R_1 = 0.0493, wR_2 = 0.0850. The complete tables of the atomic coordinates, bond lengths, and bond angles were deposited with the Cambridge Structural Database (No. 188990).

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