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Reversible Switching of the Coordination Modes of a Pyridine-Functionalized Quinonoid Zwitterion; Its Di- and Tetranuclear Palladium Complexes†

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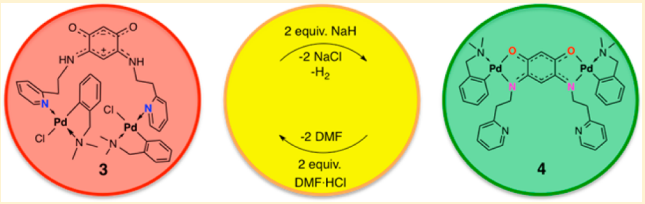
Supporting Information

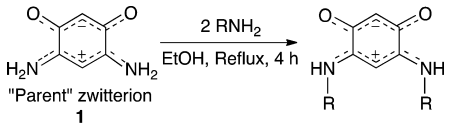
ABSTRACT: The coordination chemistry of a new functional quinonoid zwitterion (*E*)-3-oxo-4-((2-(pyridin-2-yl)ethyl)-amino)-6-((2-(pyridin-2-yl)ethyl)iminio)cyclohexa-1,4-dienolate (**2**, H_2L), in which a CH_2CH_2 spacer connects the N substituents of the quinonoid core with a pyridine group, was explored in Pd(II) chemistry. Different coordination modes have been observed, depending on the experimental conditions and the reagents. The reaction of H_2L with $[Pd(\mu\text{-Cl})(dmba)]_2$ (dmba = *o*-$C_6H_4CH_2NMe_2$-*C*,*N*) afforded the dinuclear complex $[\{PdCl(dmba)\}_2(H_2L)]$ (**3**) in which H_2L acts as a N_{Py},N_{Py} bidentate ligand. Deprotonation of this complex with NaH resulted in the formation of the dinuclear complex $[\{Pd(dmba)\}_2(\mu\text{-L})]$ (**4**) in which a shift of the Pd(II) centers from the N_{Py} sites to the N,O donor sites of the zwitterion core has occurred, resulting in a N_2O_2 tetradentate behavior of ligand L. Reaction of **4** with HCl regenerates **3** quantitatively. Chloride abstraction from **3** with AgOTf (OTf = trifluoromethanesulfonate) resulted in loss of one of the two dmba ligands and formation of an unusual tetranuclear Pd(II) complex, $[\{Pd(dmba)\}(\mu\text{-L})Pd]_2(OTf)_2$ (**5**), in which two dinuclear entities have dimerized, one pyridine donor group from each dimer forming a bridge with the other dinuclear entity. This results in a N_2, O_2, N_{Py}, N_{Py} hexadentate behavior for the ligand L. Complexes **3** and **4** constitute an unprecedented reversible, switchable system where deprotonation or protonation promotes the reversible migration of the $[Pd(dmba)]^+$ moieties, from the N_{Py} sites in **3**, to the N,O donor sites of the quinonoid core in **4**, respectively. This switch modifies the extent of π-delocalization involving the potentially antiaromatic quinonoid moiety and is accompanied by a significant color change, from red in **3** to green in **4**. The presence of uncoordinated pyridine donor groups in **4** allowed the use of this complex for the preparation of the neutral tetranuclear complex $[\{Pd(dmba)\}_2(\mu\text{-L})\{PdCl(dmba)\}_2]$ (**6**) in which **4** acts as a N_{Py},N_{Py}-bidentate metalloligand toward two PdCl(dmba) moieties. Halide abstraction from **6** afforded the monocationic, tetranuclear complex $[\{Pd(dmba)\}_2(\mu\text{-L})\{Pd(dmba)\}_2(\mu\text{-Cl})]PF_6$ (**7**) in which the two Pd(dmba) moieties are connected by ligand L and a bridging chloride. By Cl/PF_6 anion metathesis, it was possible to switch quantitatively from complex **6** to **7** and *vice versa*. All new compounds were unambiguously characterized by IR, NMR, and mass spectroscopy. Single-crystal X-ray diffraction is also available for molecules **2**–**5** and **7**.



INTRODUCTION

Quinonoid molecules have long been of special interest in coordination chemistry as O-donor and/or π-donor ligands.[1] Additional functionalities can be incorporated into these molecules, which enhance and diversify their coordination properties. This has become particularly notable with quinonoid molecules possessing N-donor groups of the enamino- or imino-type in *ortho*-position to the O-donor atoms. During the last 10 years, our group has investigated the properties of a versatile family of potentially antiaromatic[2] zwitterionic benzoquinonemonoimines derived from the "parent" zwitterion 4-(amino)-6-(iminio)-3-oxocyclohexa-1,4-dien-1-olate (**1**) (Scheme 1).[3] These molecules contain two electronically delocalized but not mutually conjugated six-π-electron systems, chemically connected by two C−C single bonds.[2] They readily form one-dimensional (1D) supramolecular associations in the solid state by virtue of NH···O intermolecular interactions.[4] Because of their ability as donor ligands to easily involve their delocalized electronic π systems with metal centers, significant synergistic effects may be anticipated in their metal complexes. Thus, such zwitterions have been used for the synthesis of functional, mixed-valence[5] and redox-active multinuclear complexes,[6] of homogeneous

Scheme 1. Transamination Reactions from the "Parent" Zwitterion 1



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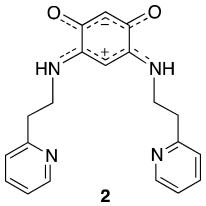
precatalysts for the oligomerization of ethylene,[6b,7] and of complexes with potential applications in optical recording.[8] These organic zwitterions can also be deposited on various metal or semiconductor surfaces and on graphene, giving rise to the occurrence of interesting physical properties.[9] Although unprecedented in quinonoid chemistry, a simple transamination reaction allows the functionalization of **1** without affecting the quinonoid core and thus allows the fine-tuning or amplification of its chemical properties (Scheme 1).[4a,10] Here we describe our first results on the coordination chemistry of the new polyfunctional zwitterionic quinonoid, potentially hexadentate N_2, O_2, N_{Py}, N_{Py} ligand, bis(2-(pyridin-2-yl)ethyl) N-substituted zwitterion **2** (H_2L) (Scheme 2). We will show how the interactions between this multidentate ligand and Pd(II) centers can be fine-tuned, by changing the experimental conditions, to result in an unexpected reversible switching of the donor sites. Coordination switching can be triggered, for example, by redox processes,[11] deprotonation and/or halide abstraction,[12] reaction with the solvent,[13] and thermal[14] or photochemical[15] activation. Because of the ease with which the coordination environment of the Pd(II) center can be modified, our observations may have relevance to *in situ* transformations occurring, for example, during Pd-catalyzed cross-coupling reactions[16] and surface functionalization.[17]

Scheme 2. Bis(2-(pyridin-2-yl)ethyl) N-substituted Zwitterion (2, H_2L)



RESULTS AND DISCUSSION

The new functional zwitterion **2** was obtained as a brown solid, in good yield (78%), from the reaction of the "parent" zwitterion **1** with 2 equiv of 2-(pyridin-2-yl)ethanamine in refluxing ethanol, following an established transamination procedure.[4a,10] Like its precursor, this zwitterion presents a planar, potentially antiaromatic core,[2] constituted by a 12-π-electron system divided into two delocalized 6-π-electron subunits, mutually connected by two C−C single bonds.[2] Each nitrogen group is functionalized by a dangling *ortho*-pyridine, and the CH_2CH_2 spacer between them offers a much better flexibility and solubility when compared to the derivative with a single CH_2 spacer.[18] The latter was indeed found to be only poorly soluble in polar solvents (e.g., MeOH, DMSO, water) and afforded insoluble complexes not suitable for our purpose. The molecular structure of **2**·CH_2Cl_2 was determined by X-ray crystallography (Figure 1).

Compound **2** crystallizes in the orthorhombic space group $Pna2_1$, and the molecule presents a symmetry axis passing through the carbon atoms C1 and C4. Selected bond lengths are listed in Table 1 (for crystal data and selected bond angles, see Supporting Information, Tables S1 and S2, respectively). The structure of **2** confirms its zwitterionic character, with a fully delocalized π system within the O1−C3−C4−C5−O2 and N1−C2−C1−C6−N3 moieties: the C═O, C═N, and C═C bond lengths are very similar, and the C2−C3 and C5−C6 distances

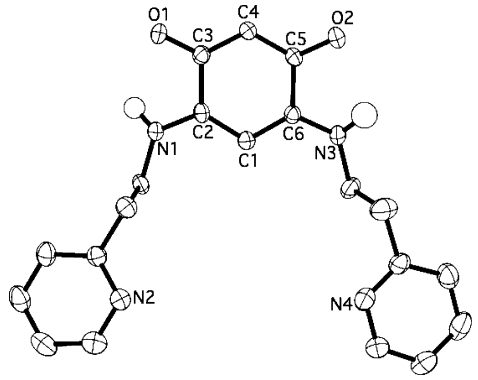


Figure 1. Crystalmaker view of **2** (H_2L) in **2**·CH_2Cl_2. Thermal ellipsoids are drawn at the 50% probability level. Only the NH protons are shown.

of 1.530(5) Å correspond to typical single bonds. In the solid state, the N1H−O2 and N3H−O1 moieties are involved in intermolecular hydrogen bonding interactions (N1···O2 = 2.862(4) Å, N3···O1 = 2.923(4) Å), resulting in a head-to-tail, zigzaglike 1D supramolecular network (Figure 2) in which a stabilizing $\pi-\pi$ stacking between the quinonoid rings of two different chains occurs, with a C1···C4 separation of 3.437(5) Å. If ligand **2** reacted with metal centers solely as a bis-pyridine-type N_{Py},N_{Py} ligand, the zwitterionic core would not be affected and would retain its strong dipolar nature. This could have a beneficial effect in subsequent reactivity studies since it has been shown recently that the addition of an ionic liquid-type zwitterion to a palladium complex improved its catalytic performance in ethylene methoxycarbonylation.[19]

When **2** was treated in CH_2Cl_2 with 1 equiv of $[Pd(\mu\text{-}Cl)(dmba)]_2$ (dmba = *o*-$C_6H_4CH_2NMe_2$-*C*,*N*), the neutral dinuclear complex $[\{PdCl(dmba)\}_2(H_2L)]$ (**3**) was obtained quantitatively (yield: 92%) (Scheme 3). The pyridine donors induce the cleavage of the chloride bridges in the dinuclear metal precursor and coordinate the two PdCl(dmba) moieties in a slightly distorted, square-planar fashion. Only the pyridine moieties are involved in metal coordination, and they adopt a *cis* arrangement and a perpendicular orientation with respect to the dmba aryl ring, as shown by an X-ray diffraction study of single crystals of **3** (Figure 3). Selected bond lengths are listed in Table 1 (for crystal data and selected bond angles see Supporting Information, Tables S1 and S2, respectively). The coordination of the Pd centers by the pyridines leads to Pd1−N2 and Pd2−N4 distances of 2.036(7) and 2.038(7) Å, respectively. As anticipated, the bonding parameters within the quinonoid core, in particular the C−O, C−C, and C−N distances, remain unaffected in comparison with **2** (Table 1). Complex **3** presents, in the solid state, the same head-to-tail, zigzag, supramolecular arrangement already displayed in the free zwitterion, owing to the formation of hydrogen bonding intermolecular interactions between the N1H−O2 and the N3H−O1 moieties (see Figure 4). Their distances of 2.783(9) Å for N1H···O2 and 2.830(9) Å for N3H···O1 are slightly shorter than they are in **2**. The resulting linear array is decorated with dangling PdCl(dmba) moieties coordinated by the pyridines, which prevent the formation of the $\pi-\pi$ stacking interaction observed in **2**. Fourier transform-far-infrared (FT-far-IR) analysis of **3** showed a typical ν(Pd−Cl) stretching vibration at 296 cm^{-1}.[20]

Solution NMR analyses of **3** revealed a temperature-dependent dynamic behavior. In particular, room-temperature

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Table 1. Selected Bond Distances (Å) in 2−5 and 7

	2·CH_2Cl_2	3	4	5	7·CH_2Cl_2
O1−C3	1.250(4)	1.230(1)	1.273(5)	1.268(8)	1.268(8)
C3−C4	1.391(4)	1.390(1)	1.384(5)	1.414(9)	1.360(1)
C4−C5	1.395(4)	1.390(1)	1.382(5)	1.363(9)	1.390(1)
C2−O5	1.248(4)	1.260(1)	1.273(4)	1.307(8)	1.278(9)
C2−C3	1.530(5)	1.560(1)	1.509(6)	1.498(9)	1.520(1)
C5−C6	1.530(5)	1.510(1)	1.502(6)	1.497(9)	1.540(1)
N1−C2	1.309(4)	1.270(1)	1.322(5)	1.325(8)	1.341(9)
C1−C2	1.394(4)	1.410(1)	1.400(5)	1.417(9)	1.400(1)
C1−C6	1.400(4)	1.390(1)	1.393(5)	1.405(9)	1.390(1)
N3−C6	1.315(4)	1.310(1)	1.332(5)	1.320(8)	1.314(9)
Pd1−N4		2.038(7)		2.038(6)	
Pd1−Cl1		2.431(3)			
Pd1−N5		2.078(7)	2.067(3)		2.081(6)
Pd1−C21		1.870(1)	1.979(4)		1.981(7)
Pd1−N3			2.027(3)	1.969(6)	2.033(6)
Pd1−O2			2.103(3)	1.998(5)	2.115(4)
Pd1−N2				2.033(5)	
Pd2−N2		2.036(7)			
Pd2−Cl2		2.412(3)			
Pd2−C30		1.970(1)	1.995(4)	1.972(9)	1.991(9)
Pd2−N6		2.068(7)	2.067(3)	2.074(6)	2.083(6)
N1−Pd2			2.049(3)	2.026(6)	2.031(6)
O1−Pd2			2.101(3)	2.142(5)	2.147(6)
Pd3−N4					2.033(1)
Pd3−C39					1.964(1)
Pd3−N7					2.064(1)
Pd3−Cl1					2.380(2)
N2−Pd4					2.030(1)
Pd4−C48					1.978(9)
Pd4−N8					2.068(1)
Pd4−Cl1					2.435(2)

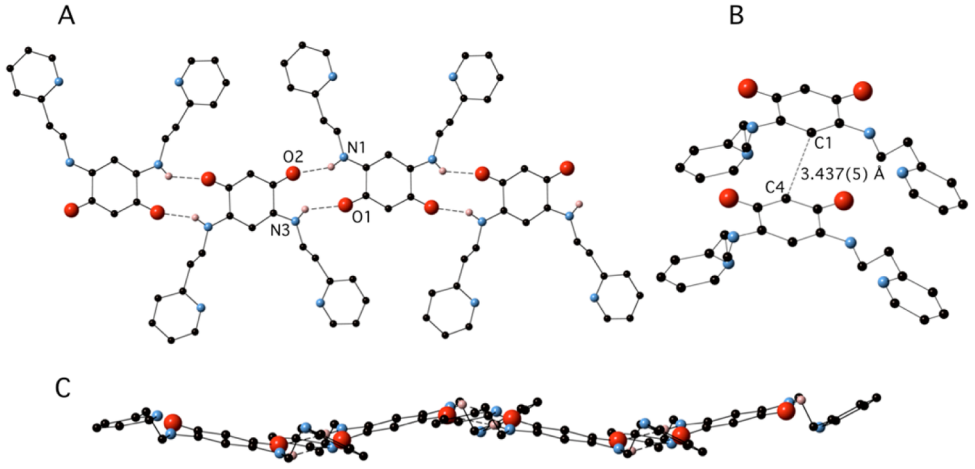

Figure 2. Crystalmaker views of the supramolecular array generated by **2** in 2·CH_2Cl_2, in the solid state. (A) Top view. (B) Interchain $\pi-\pi$ stacking view. (C) Side view. Color coding: nitrogen, blue; oxygen, red; hydrogen, pink.

rotating frame nuclear Overhauser effect spectroscopy (ROESY) (see Supporting Information, Figure S8) indicated a chemical exchange between two conformers involving the hydrogen atoms on each CH_2 group of the CH_2CH_2 spacers linking the quinonoid nitrogen atoms and the pyridyl rings. This interconversion was slowed down by lowering the temperature and suppressed at 263 K (see Supporting Information, Figure S9), where integration of the ^{1}H NMR signals at this temperature indicated a 1:1 ratio between the two conformers. Therefore, ^{13}C, ^{1}H/^{13}C heteronuclear single quantum correlation (HSQC), and ^{1}H correlation spectroscopy (COSY) spectra were also recorded at this temperature and allowed the complete discrimination of the signals belonging to each conformer (named **3a** and **3b** in the Experimental Section) (see Supporting Information, Figures S1−S7). Both conformers show the typical chemical shifts of the zwitterionic quinonoid core[7b] and a signal for the *ortho* H7 hydrogen of the dmba phenyl (see Experimental Section, Scheme 9) at 5.61

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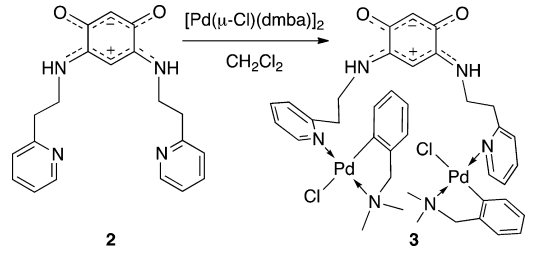
Scheme 3. Synthesis of the Dipalladium Complex 3



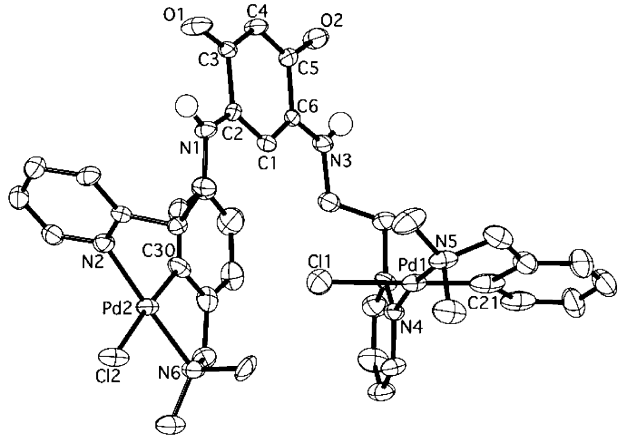


Figure 3. Crystalmaker view of **3**. Thermal ellipsoids are drawn at the 50% probability level. Only the NH protons are shown.

ppm. Such a low value is typical for a dmba phenyl ring *cis* and orthogonal to a pyridine ring.[21] An equilibrium between possible conformers **3a** and **3b** is shown in Scheme 4, where nonequivalent orientations of the metal centers are made possible by the high flexibility of the CH_2CH_2 spacers, resulting from easy rotation about their C−N and C−C bonds.

Addition of 2 equiv of NaH to a solution of complex **3** in CH_2Cl_2 led to deprotonation and loss of the chloride ligands, with formation of the neutral complex $[\{Pd(dmba)\}_2(\mu\text{-L})]$ (**4**) (Scheme 5). We shall see below that this transformation is fully reversible.

The green complex **4** was isolated in good yield (72%), and crystals suitable for X-ray diffraction were obtained by stratification of a toluene solution of the complex with *n*-pentane. Selected bond lengths are listed in Table 1 (for crystal data and selected bond angles see Supporting Information, Tables S1 and S2, respectively). Complex **4** crystallizes in the *Pbca* orthorhombic space group, and the molecule possesses a C_2 symmetry axis passing through C1 and C4. The structure of **4** depicted in Figure 5 shows that the deprotonation of **3** has formally resulted in the migration of the two cationic $[Pd(dmba)]^+$ moieties from the pyridine to the quinonoid site, which now acts as a bis(N,O)-chelating, bridging ligand connected to two free dangling pyridines. As will be shown below, these latter can act as donors for additional metal centers.

Both metal centers in **4** display a distorted square planar coordination geometry. The values of the bond distances within the O1−C3−C4−C5−O2 and N1−C2−C1−C6−N3 moieties indicate notable bond equalization, which is a clear indication that the electronic delocalization within these π systems results in bond orders intermediate between one and two. The C2−C3 and C5−C6 distances of 1.509(6) and 1.502(6) Å, respectively, confirm the lack of electronic conjugation between the two π systems. The pattern of the ^1H and ^{13}C NMR signals of **4** is consistent with the high molecular symmetry found in the solid

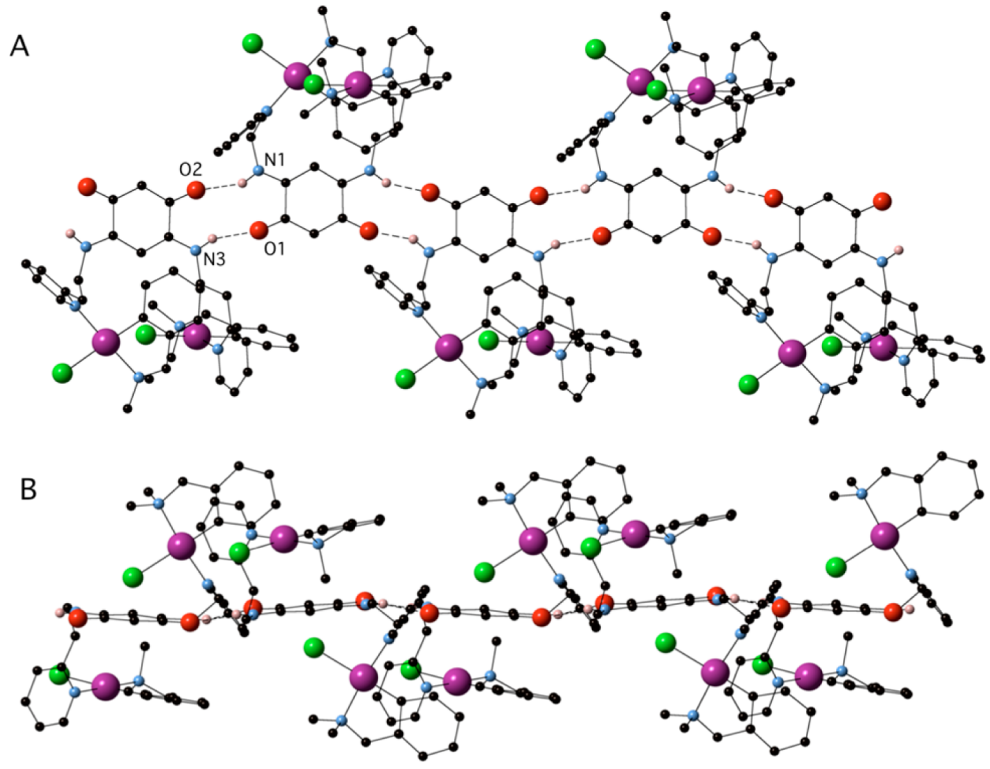


Figure 4. Crystalmaker view of the supramolecular array generated by **3** in the solid state. (A) Top view. (B) Side view. Color coding: nitrogen, blue; oxygen, red; hydrogen, pink; palladium, magenta; chlorine, green.

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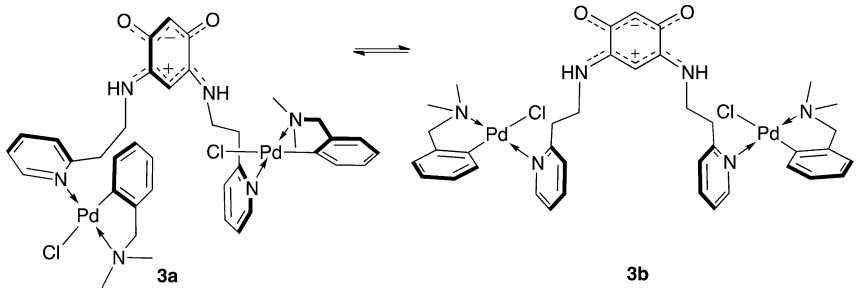
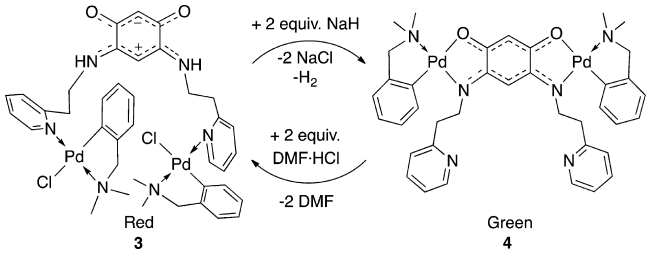
Scheme 4. Two Possible Conformers, 3a and 3b, Present in Solution[a]



[a]Conformer **3a** is taken arbitrarily as corresponding to the structure of the complex in the solid state.

Scheme 5. Deprotonation−Reprotonation-Triggered Transformations Involving 3 and 4 Leading to a Reversible, Switchable System



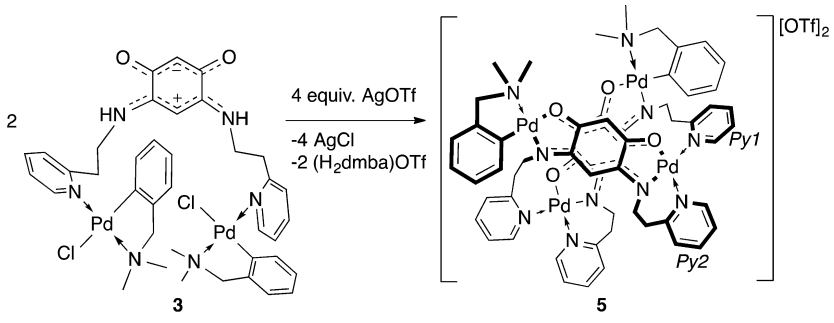
state. The chemical shifts of the N=C and O=C carbon nuclei at 188.30 and 164.87 ppm, respectively, support the presence of the delocalized π systems.[7b] All the data are consistent with the fact that deprotonation of **3** has led to a new neutral dinuclear complex **4** in which a direct interaction occurs between the Pd centers and the quinonoid core. This results in an extension of the two delocalized π systems that now involve the quinonoid moiety and the metal centers. The associated modification in the electronic structure is accompanied by a color change from red, for **3**, to green, for **4**.[7b] The ultraviolet−visible (UV−vis) spectra of complexes **3** and **4** are shown in Figure 6. Compound **3** displays a broad absorption band at 518 nm, which is assigned to intraquinone transitions of the zwitterionic part.[5c] The spectrum of complex **4** exhibits an absorption band and a shoulder at 430 and 454 nm, respectively, consistent with a ligand-to-metal charge transfer transition (LMCT), and a broad absorption band at 628 nm, assigned to intraquinone transitions.[5c] The pronounced red shift of the intraquinone transition absorptions between **3** (518 nm) and **4** (628 nm) is consistent with an increase of the delocalization of the conjugated π system.[22]

Interestingly, the deprotonation-induced conversion of **3** in **4** is reversible, and reaction of the latter complex with 2 equiv of DMF·HCl[23] allowed quantitative recovery of complex **3** (Scheme 5). Complexes **3** and **4** thus define an unprecedented switchable system, in which deprotonation or protonation of the complex allows a reversible change of the donor atoms and of the position of the metal centers on the functional ligand (Scheme 5). Accordingly, the spatial extension of the π delocalization involving the quinonoid ring is modified. Preliminary cyclic voltammetric measurements were carried out in CH_2Cl_2 on complex **4**, but unfortunately most processes were irreversible, and the sample underwent decomposition during analysis (see Supporting Information, Figures S10−S14), even upon increasing the scan rate.

The discovery of this tunable metal migration prompted us to investigate the reactivity of **3** toward simple halide abstraction (without deprotonation). We thus reacted complex **3** with 2 equiv of AgOTf in MeOH. Rapid precipitation of AgCl occurred with formation of a red intermediate that was not isolated and is likely to be a solvento species where MeOH coordinates the metal in place of Cl. The color of the solution progressively changed from red to green, and the dicationic complex $[\{Pd(dmba)\}(\mu\text{-L})Pd]_2(OTf)_2$ (**5**) was isolated as a green solid in 68% yield (Scheme 6).

Green crystals of **5** suitable for X-ray diffraction analysis were obtained by stratification of an acetone solution of the complex with *n*-pentane. The structure of **5** is shown in Figure 7, and selected bond lengths are listed in Table 1 (for crystal data and selected bond angles see Supporting Information, Tables S1 and S2, respectively). Both metal centers present a distorted square-planar coordination geometry. The structural parameters within the quinonoid core are still consistent with the presence of two, nonconjugated, delocalized π systems, and the two Pd centers are involved in the electronic delocalization. This is also confirmed by ^1H and ^{13}C NMR spectroscopy, in

Scheme 6. Synthesis of the Tetranuclear Pd(II) Complex 5



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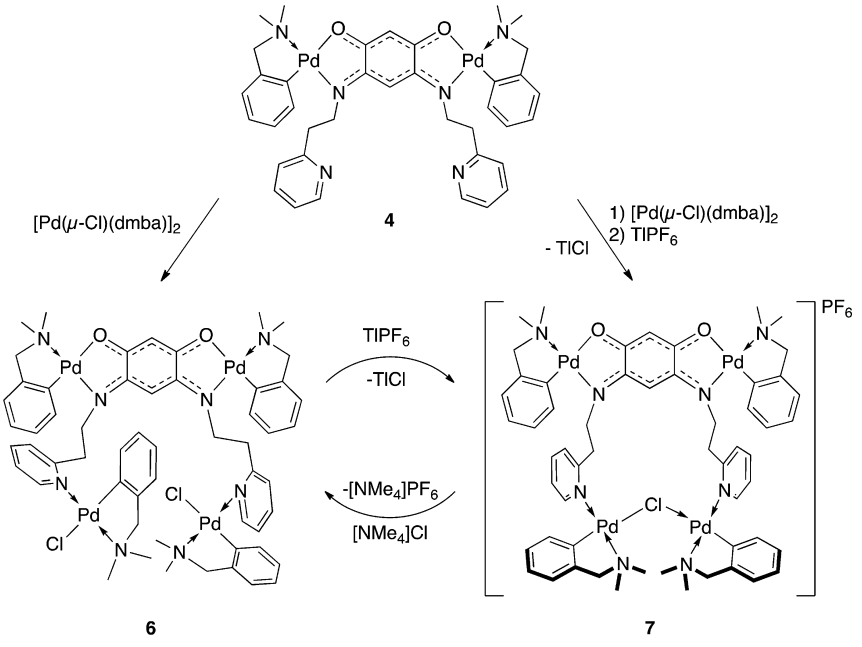
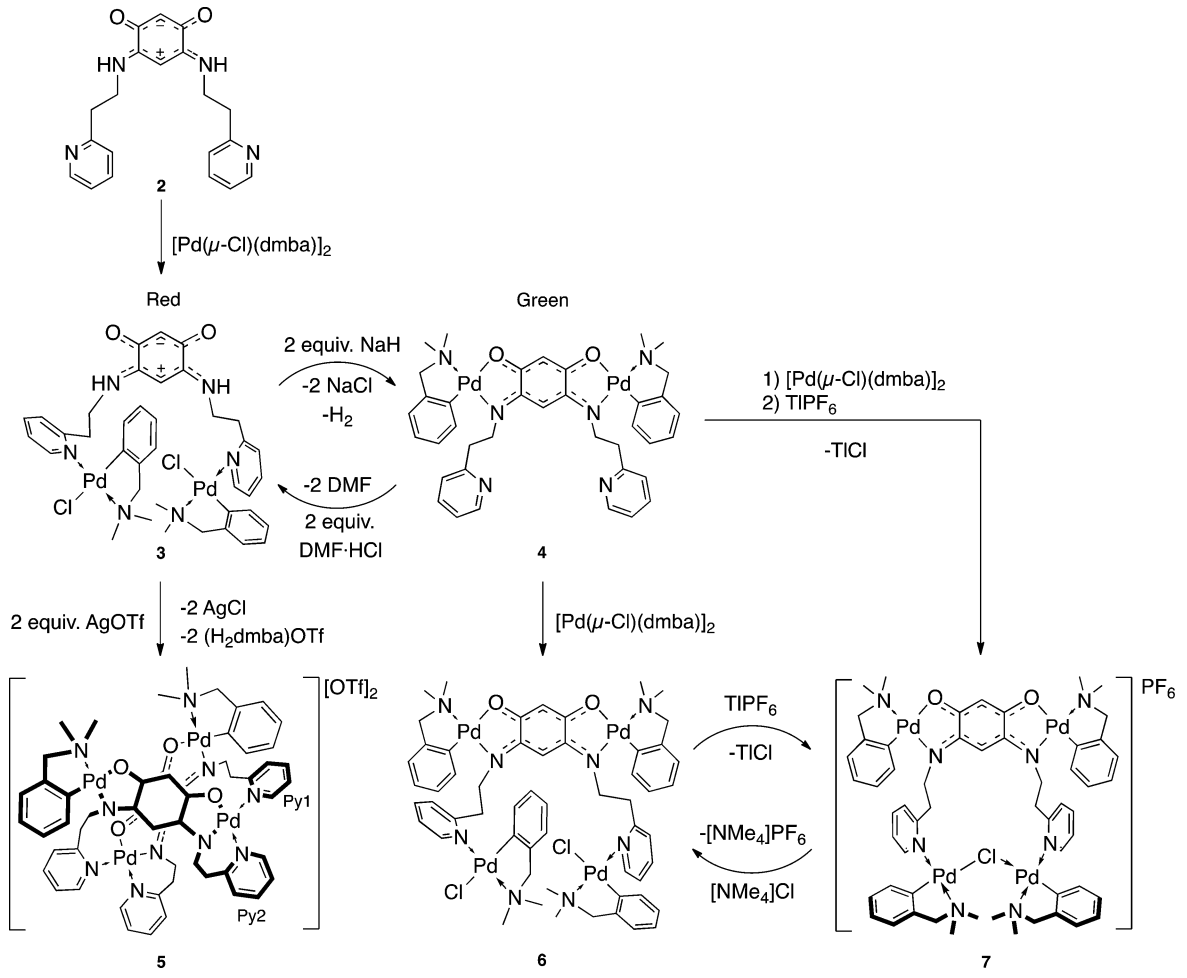
Scheme 7. Synthesis of the Tetranuclear Pd(II) Complexes 6 and 7



Scheme 8. Overview of the Synthetic Transformations Involving Ligand 2



particular by the ^{13}C chemical shifts of the O2=C5 and O1=C3 carbons at 189.63 and 189.86 ppm, respectively, and by the signals of the C6=N2 and C2=N1 carbons at 165.94 and 165.04 ppm, respectively.[7b] The green color of the complex is very similar to that of **4** and appears typical for the electronic delocalization involving two metal centers and the quinonoid

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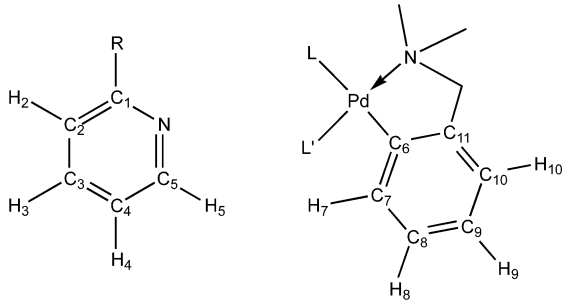
Scheme 9. Atom Numbering Scheme Used for NMR Description[a]



[a]In case of complex **5**, the two non-equivalent pyridines (Py1 and Py2) are named as in Scheme 6.

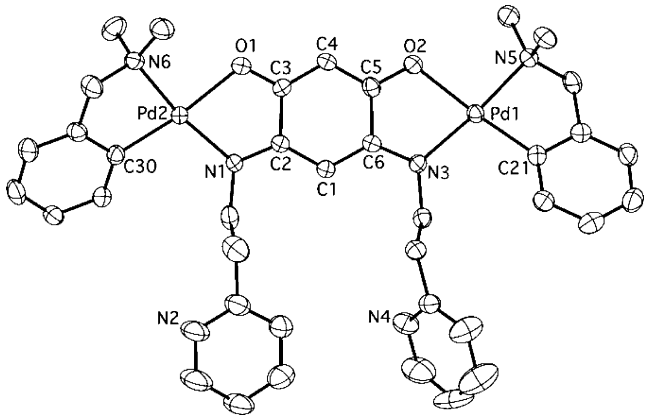


Figure 5. Crystalmaker view of **4** (H atoms not shown). Thermal ellipsoids are drawn at the 50% probability level.

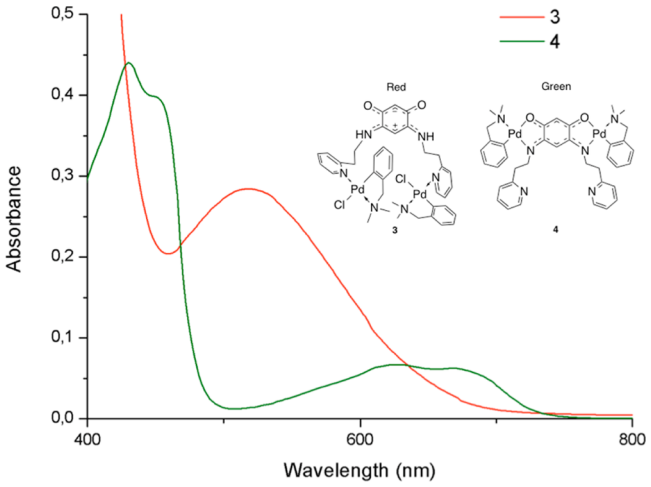


Figure 6. UV−vis absorption spectra of compounds **3** ($c = 1.1 \times 10^{-3}$ M) and **4** ($c = 1.1 \times 10^{-5}$ M) in CH_2Cl_2 at room temperature.

core, as observed previously with Ni(II), Pd(II), and Pt(II) dinuclear complexes.[5a,7b,24]

This new complex results from an interesting transformation of **3** upon chloride abstraction: despite the lack of an external base, spontaneous deprotonation occurred by elimination of one equivalent of $(H_2dmba)OTf$, which resulted in the formation of a dicationic, tetranuclear dimeric complex, formed by two dipalladium moieties mutually connected by two pyridine arms. Within each dinuclear moiety, the quinonoid core acts again as a bis(N,O)-chelating, bridging ligand for two Pd centers, which then complete their coordination spheres in two different ways. While Pd2 retains its chelating dmba ligand and displays a coordination environment similar to that in complex **4**, Pd1 has lost its dmba chelate and completes its coordination sphere with two inequivalent pyridines: one originates from the ligand itself (intramolecular Py2), while the other is shared by the other half of the dimer (intermolecular Py1) and becomes part of a bridge between the two dinuclear moieties. The resulting double positive charge is balanced by two triflate anions.

Because of its two uncoordinated pyridines, complex **4** could still react with metal centers and act as a pyridinic N_{Py},N_{Py}-bidentate metalloligand.[25] Thus, the reaction of **4** with $[Pd(\mu\text{-}Cl)(dmba)]_2$ in a L/Pd ratio of 1:2 afforded the neutral tetranuclear complex $[\{Pd(dmba)\}_2(\mu\text{-}L)\{PdCl(dmba)\}_2]$ (**6**) (Scheme 7) in 71% yield. NMR data of **6** in solution suggested that this reaction did not affect the quinonoid part with respect to the precursor metalloligand **4**, while the two pyridines coordinate the Pd centers in a similar way to what is observed in complex **3**. In particular, **6** displayed only one conformer constituted by two inequivalent pyridinic arms, each bearing a PdCl(dmba) moiety. The chemical shift of the *ortho*-H of the dmba phenyl (H7, see Experimental Section and Scheme 9) at 5.73 ppm confirmed the *cis* and orthogonal orientation of the pyridine rings with respect to the dmba phenyls (see above). Furthermore, in the far-IR spectrum, the ν(Pd−Cl) stretching vibration of 299 cm^{-1} is consistent with the value found in complex **3** (295 cm^{-1}).

The reaction of **6** with 1 equiv of $TlPF_6$ resulted in the abstraction of one chloride ligand and the formation of the monocationic tetranuclear complex $[\{Pd(dmba)\}_2(\mu\text{-}L)\{Pd(dmba)\}_2(\mu\text{-}Cl)]PF_6$ (**7**) (Scheme 7) in 83% yield.

As established by an X-ray diffraction on single crystals obtained by layering a CH_2Cl_2 solution of the complex with pentane, the assembling ligand L in **7** acts as a N_2, O_2, N_{Py}, N_{Py} hexadentate donor where the dinuclear quinonoid moiety of the precursor complex **4** remains unaffected, while the two pyridines are involved in coordination to two additional metal centers from the cationic $[(dmba)Pd(\mu\text{-}Cl)Pd(dmba)]^+$ moiety (Figure 8). The resulting positive charge is balanced by one PF_6^- anion. All the metal centers present a distorted square planar coordination geometry. Selected bond lengths for **7** are listed in Table 1 (for crystal data and selected bond angles see Supporting Information, Tables S1 and S2, respectively). As confirmed by the X-ray diffraction analysis, the two pyridine rings are orthogonal and *cis* to the dmba aryls, as found for complex **3** (see above). This is consistent with the NMR data in solution (δ of H7 (*ortho* H of the dmba phenyl) = 5.35 ppm, see Experimental Section and Scheme 9). The average Pd−(μ-Cl) distance of 2.407 Å is similar to values found in the literature for a related complex (average 2.443 Å).[26] The presence of a bridging μ-Cl ligand between the Pd centers results in a shift of the ν(Pd−Cl) stretching vibration, from 299 cm^{-1} for complex **6** to 246 cm^{-1} for **7**. The latter value is typical for a $\nu[Pd(\mu\text{-}Cl)]$ vibration involving a chloride ligand in *trans* position to a σ-bonded carbon, and this absorption disappears upon LiBr metathesis.[27] Furthermore, as depicted in Scheme 7, it was possible via Cl/PF_6 anion exchange to switch quantitatively from complex **6** to **7** and *vice versa*. Complex **7** could also be obtained (in lower yield: 57%) by the one-pot reaction of **4** with $[Pd(\mu\text{-}Cl)(dmba)]_2$ and $TlPF_6$ in 1:1:1 ratio. By analogy with the formation of **7**, we reacted complex **3** with

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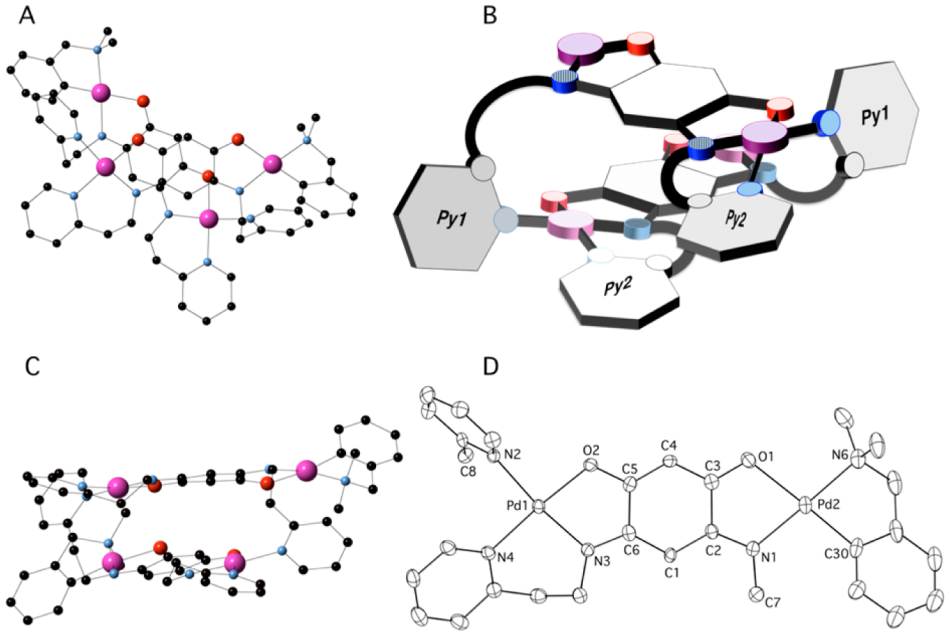

Figure 7. Views of the crystal structure of **5**. The OTf^- anions were omitted for clarity. (A) and (C) Perspective views. (B) Simplified perspective model, dmba ligands omitted for clarity. (D) Dinuclear fragment constitutive of **5**, thermal ellipsoids are drawn at the 50% probability level. Color coding: nitrogen, blue; oxygen, red; palladium, magenta.

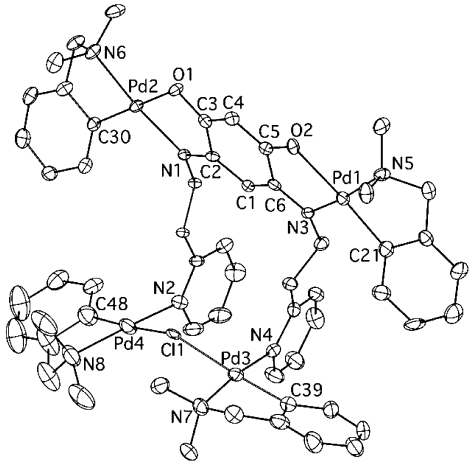

Figure 8. Crystalmaker view of **7** in **7**·CH_2Cl_2. The PF_6^- anion is omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

only 1 equiv AgOTf in CH_2Cl_2 or MeOH. Although a reaction took place (^{1}H and IR monitoring), we could not characterize the species formed, and far-IR data indicated the presence of terminal chloride(s).

CONCLUSIONS

The synthesis and coordination chemistry of the new zwitterionic, multidentate ligand **2** (H_2L) have further demonstrated the tunability of this class of quinonoid-type ligands. Its reactivity with various Pd(II) complexes has led to di- and tetranuclear complexes, and the corresponding transformations are summarized in Scheme 8. Modulation of the ligand denticity and the chemoselectivity of its coordination led to various situations in which **2** acts as a N_{Py}, N_{Py} bidentate ligand, as in complex **3**, and L acts as a N_2O_2 tetradentate (complex **4**) or N_2, O_2, N_{Py}, N_{Py} hexadentate (complexes **5**, **6**, and **7**) ligand, respectively.

Complexes **3** and **4** constitute a novel reversible switchable system, triggered by protonation or deprotonation, which allows the selection of the chemoselective binding of the cationic moiety $[Pd(dmba)]^+$ on the ligand and, consequently, the modification of the extent of π delocalization in the quinonoid π system. Simple dehalogenation of **3** led to a spontaneous deprotonation of the complex by elimination of 1 equiv of (H_2dmba)OTf and formation of the dicationic, dimeric, tetranuclear quinonoid complex **5**, where the ligand acts as N_2, O_2, N_{Py}, N_{Py} hexadentate. The presence of uncoordinated pyridine donor groups in **4** opens the possibility of using this complex as a metalloligand, and this was demonstrated by the isolation of the neutral tetranuclear complex **6** and the monocationic, tetranuclear complex **7**, in which complex **4** act as a N_{Py}, N_{Py} pyridinic bidentate metalloligand and, respectively, coordinates two PdCl(dmba) fragments (**6**) and chelates the $[(dmba)Pd(\mu\text{-}Cl)Pd(dmba)]^+$ moiety (**7**). Furthermore, complexes **3** and **4** represent potential candidates for deposition and anchoring on surfaces, and this will be examined in future work.

EXPERIMENTAL SECTION

General Procedure. All operations were carried out by using standard Schlenk techniques under an inert atmosphere. Solvents were purified and dried under a nitrogen atmosphere by using conventional methods. CD_2Cl_2 and $CDCl_3$ were dried over 4 Å molecular sieves, degassed by performing freeze−pump−thaw cycles, and stored under an argon atmosphere. ^{1}H and ^{13}C NMR spectra were recorded at room temperature, unless specified, on Bruker AVANCE 400, 500, or 600 spectrometers and referenced to the residual solvent resonance. Assignments are based on ^{1}H, ^{1}H COSY, ^{1}H/^{13}C HSQC, ROESY, and ^{13}C NMR experiments. Chemical shifts (δ) are given in ppm, coupling constants are in Hz, and the atom numbering used is shown in Scheme 9. IR spectra were recorded within the region of 4000−100 cm^{-1} on a Nicolet 6700 FTIR spectrometer (ATR mode, SMART ORBIT accessory, Diamond crystal). Elemental analysis was performed by the

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"Service de Microanalyses," Université de Strasbourg, or by the "Service Central d'Analyse," USR-59/CNRS, Solaize. Electrospray mass spectroscopy was performed on a microTOF (Bruker Daltonics, Bremen, Germany) instrument by using a flow of nitrogen gas as a drying agent and nebulizing gas. Matrix-assisted laser desorption-ionization time-of-flight mass spectrometry (MALDI-TOF-MS) spectra were acquired on a TOF mass spectrometer (MALDI-TOF-TOF Autoflex II TOF-TOF, Bruker Daltonics, Bremen, Germany) equipped with a nitrogen laser (λ = 337 nm). An external multipoint calibration was carried out before each measurement. Scan accumulation and data processing were performed with FlexAnalysis 3.0 software. Matrix solutions were freshly prepared: α-cyano-4-hydroxycinnamic acid (CHCA) was dissolved to saturation in a H_2O/CH_3CN/HCOOH (50/50, 1%) solution, and Dithranol was dissolved in tetrahydrofuran (THF) to obtain a 20 mg/mL solution. Typically, 0.5 μL of a mixture containing the sample solution and the matrix (1/1) was deposited on the stainless steel plate. The UV−vis spectra were recorded on an Analytic Jena Specord 205 spectrophotometer, using optically transparent glass cells. The complex $[Pd(\mu\text{-}Cl)(dmba)]_2$ was synthesized according to the literature.[28] Other chemicals were commercially available and were used as received.

Synthesis of Zwitterion **2**. To a dispersion of **1** (0.607 g, 4.40 mmol) in 10 mL of EtOH was added 2-(pyridin-2-yl)ethanamine (0.950 g, 7.91 mmol). The reaction mixture was heated to reflux for 4 h and then cooled to room temperature. Volatiles were removed under vacuum, the dark purple solid obtained was dissolved in CH_2Cl_2, and the solution was filtered through Celite. Addition of *n*-pentane to the filtrate led to the precipitation of a brown powder of **2**. Red crystals suitable for X-ray diffraction were grown by slow diffusion of *n*-pentane into a solution of **2** in CH_2Cl_2. Yield: 1.204 g, 3.45 mmol (78%). Anal. Calcd for $C_{20}H_{20}N_4O_2$ (348.40): C, 68.95; H, 5.79; N, 16.08. Found: C, 68.60; H, 5.80; N, 15.74%. FTIR: ν_{max}(solid)/cm^{-1}: 3184 ms, 3047vw, 3015vw, 1644w, 1535vs, 1477s, 1461w, 1432s, 1387w, 1356m, 1311w, 1285m, 1261w, 1205w, 1186w, 1148mw, 1103w, 1050w, 998m, 887vw, 848w, 821vw, 767vs, 746vs, 724vs, 684vw, 631mw. ^{1}H NMR (CD_2Cl_2, 400 MHz) δ: 8.90 (br, 2H, NH), 8.69 (br-d, 2H, $^3J_{H,H}$ = 4.6 Hz, H^{5}Py), 7.77 (dt, 2H, $^3J_{H,H}$ = 7.6, $^4J_{H,H}$ = 1.9 Hz, H_3Py), 7.34−7.31 (m, 4H, H^{2,4}Py), 5.39 (s, 1H, N=C−CH), 5.32 (s, 1H, O=C−CH), 3.94 (t, 4H, $^3J_{H,H}$ = 6.7 Hz, HNCH_2CH_2Py), 3.29 (t, 4H, $^3J_{H,H}$ = 6.7 Hz, HNCH$_2$CH_2Py) ppm.^{13}C{^{1}H} NMR (CD_2Cl_2, 75.5 MHz) δ: 172.51 (s, C=O), 158.12 (s, C^{1}Py), 157.01 (s, C=N), 149.94 (s, C^{5}Py), 137.15 (s, C^{3}Py), 123.88 (s, C^{2}Py), 122.41 (s, C^{4}Py), 98.01 (s, O=C−*C*), 81.37 (s, HN=C−*C*), 42.79 (s, HNCH$_2$CH$_2$Py), 36.29 (s, HNCH$_2$CH$_2$Py) ppm.

Synthesis of Complex **3**. To a solution of **2** (0.098 g, 0.28 mmol) in 10 mL of CH_2Cl_2 was added $[Pd(\mu\text{-}Cl)(dmba)]_2$ (0.155 g, 0.28 mmol). The reaction mixture was stirred for 4 h. Addition of *n*-pentane to this solution led to the precipitation of a red solid of **3** that was filtered and washed with THF. Red crystals suitable for X-ray diffraction were grown by slow diffusion of *n*-pentane into a solution of **3** in CH_2Cl_2. Yield: 0.232 g, 0.26 mmol (92%). Anal. Calcd for $C_{38}H_{44}Cl_2N_6O_2Pd_2$ (900.49): C: 50.68; H: 4.92; N: 9.33. Found: C, 50.75; H, 5.20; N, 8.84%. FTIR: ν_{max}(solid)/cm^{-1}: 3168w, 3050w, 2975w, 2910vw, 2886vw, 1534vs, 1476m, 1449w, 1437m, 1352w, 1313vw, 1289w, 1260vw, 1207vw, 1178vw, 1107w, 1065vw, 1046vw, 1018mw, 983w, 968mw, 930vw, 901vw, 866mw, 850mw, 798vw, 769vw, 738vs, 658vw, 518m, 479vw, 445w, 423mw, 398m, 362s, 334vw, 296s (ν(Pd−Cl)), 226vs, 151vw, 126s, 108vw. An equilibrium is present in solution between two conformers **3a** and **3b** in ca. 1:1 ratio (see text), which can be discriminated by low temperature combined ^{1}H, ^{13}C, ^{1}H COSY, and HSQC NMR analysis. ^{1}H NMR ($CDCl_3$, 500 MHz, 263 K) δ: 9.01 (d, 2H, $^3J_{H,H}$ = 5.7 Hz, H^{5}Py of **3a**), 8.97 (d, 2H, $^3J_{H,H}$ = 5.7 Hz, H^{5}Py, **3b**), 8.53 (t, 2H, $^3J_{H,H}$ = 6.8 Hz, NH, **3a**), 8.43 (t, 2H, $^3J_{H,H}$ = 6.8 Hz, NH, **3b**), 7.80−7.75 (m, 4H, $^3J_{H,H}$ = 7.8 Hz, $^4J_{H,H}$ = 1.5 Hz, H_3Py, **3a**+**3b**), 7.56−7.52 (m, 4H, H^{2}Py, **3a**+**3b**), 7.33−7.30 (m, 2H, H^{4}Py, **3b**), 7.27−7.25 (m, 2H, H^{4}Py, **3a**), 6.99−6.95 (m, 8H, H^{8,10}Ph, **3a**+**3b**), 6.70−6.67 (m, 4H, H^{9}Ph, **3a**+**3b**), 5.87 (s, 1H, N=C−CH, **3a**), 5.64 (s, 1H, N=C−CH, **3b**), 5.61 (d, 4H, $^3J_{H,H}$ = 7.6 Hz, H^{7}Ph, **3a**+**3b**), 5.38 (s, 1H, O=C−CH, **3a**), 5.37 (s, 1H, O=C−CH, **3b**), 4.37−4.08 and 3.60−3.52 (m, 12H + 4H, NCH_2CH_2Py, **3a**+**3b**), 4.08−3.96 (m, 8H, NCH$_2$Ph, **3a**+**3b**), 2.97, 2.95, and 2.93 (s, 12H, 6H, 6H, NCH$_3$, **3a**+**3b**) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 150.9 MHz, 263 K) δ: 172.79 (s, C=O, **3a**), 172.75 (s, C=O, **3b**), 158.51 (s, C^{1}Py, **3a**), 158.49 (s, C^{1}Py, **3b**), 156.76 (s, N=C, **3a**), 156.72 (s, N=C, **3b**), 153.29 (s, C^{5}Py, **3a**), 153.25 (s, C^{5}Py, **3b**), 147.63 (s, C^{6}Ph, **3a**), 147.61 (s, C^{6}Ph, **3b**), 146.64 (s, C^{11}Ph, **3a**+**3b**), 138.40 (s, C^{3}Py, **3a**), 138.38 (s, C^{3}Py, **3b**), 131.27 (s, C^{7}Ph, **3a**), 131.23 (s, C^{7}Ph, **3b**), 127.01 (s, C^{2}Py, **3a**), 126.95 (s, C^{2}Py, **3b**), 125.63 (s, C^{9}Ph, **3a**+**3b**), 124.97 (s, C^{8}Ph, **3a**+**3b**), 123.75 (s, C^{4}Py, **3a**), 123.73 (s, C^{4}Py, **3b**), 122.07 (s, C^{10}Ph, **3a**+**3b**), 99.14 (s, O=C=*C*, **3a**), 99.03 (s, O=C=*C*, **3b**), 82.68 (s, N=C=*C*, **3a**), 82.64 (s, N=C=*C*, **3b**), 73.93 (s, NCH$_2$Ph, **3a**), 73.92 (s, NCH$_2$Ph, **3b**), 52.93 and 52.79 (s, N(CH$_3$)$_2$, **3a**), 52.91 and 52.76 (s, N(CH$_3$)$_2$, **3a**), 42.20 (s, NCH$_2$CH$_2$Py, **3a**), 42.10 (s, NCH$_2$CH$_2$Py, **3b**), 40.75 (s, NCH$_2$CH$_2$Py, **3a**), 40.69 (s, NCH$_2$CH$_2$Py, **3b**) ppm. MS (ESI): *m*/*z* = 865.13 $[M - Cl]^+$.

Synthesis of Complex **4**. Solid NaH (0.012 g, 0.51 mmol) was added to a solution of **3** (0.230 g, 0.25 mmol) in 15 mL of CH_2Cl_2. The reaction mixture was stirred for 2 h, during which it changed color from red to bright green. After filtration, the volatiles were removed under vacuum, and the green solid obtained was redissolved in toluene. Addition of *n*-pentane to this solution led to the precipitation of a dark green solid of **4**, which was filtered and washed with *n*-pentane. Green crystals suitable for X-ray diffraction were grown by stratification of a solution of **4** in toluene with *n*-pentane. Yield: 0.151 g, 0.18 mmol (72%). Anal. Calcd for $C_{38}H_{42}N_6O_2Pd_2{\cdot}H_2O$ (845.63): C, 53.97; H, 5.24; N, 9.93. Found: C, 54.03; H, 5.29; N, 9.53%. FTIR: selected ν_{max}(solid)/cm^{-1}: 3043vw, 2970vw, 2915w, 2801vw, 1589m, 1570w, 1493vs, 1439w, 1402w, 1361w, 1292s, 1266vw, 1203w, 1180w, 1148w, 1104vw, 1075w, 1043w, 1021w, 990w, 969vw, 926w, 905w, 863mw, 848mw, 827mw, 773m, 742s, 697vw, 659w, 635w, 615m, 567w, 534m, 520s, 505vw, 494vw, 479vw, 466vw, 457w, 442w, 427w, 402m, 365s, 340vw, 311vw, 277vw, 246vw, 222vw, 172vs, 141vw, 128vw, 121w, 106w. ^{1}H NMR (CD_2Cl_2, 400 MHz) δ: 8.40 (br-d, 2H, $^3J_{H,H}$ = 4.5 Hz, H^{5}Py), 7.50 (dt, 2H, $^3J_{H,H}$ = 7.6, $^4J_{H,H}$ = 1.8 Hz, H^{3}Py), 7.35−7.34 (m, 2H, H^{8}Ph), 7.19 (d, 2H, $^3J_{H,H}$ = 7.6 Hz, H^{2}Py), 7.05−7.03 (m, 2H, H^{4}Py), 6.98 (m, 4H, H^{9,7}Ph), 6.95 (m, 2H, H^{10}Ph), 5.50 (s, 1H, N=C−CH), 5.41 (s, 1H, O=C−CH), 3.90 (m, 6H, NCH_2Ph + NCH_2CH$_2$Py), 3.14 (m, 4H, NCH$_2$CH_2Py), 2.78 (s, 12H, NCH$_3$) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 75.5 MHz) δ: 188.30 (s, O=C), 164.87 (s, N=C), 159.88 (s, C^{1}Py), 149.35 (s, C^{5}Py), 148.06 (s, C^{11}Ph), 147.37 (s, C^{6}Ph), 135.92 (s, C^{3}Py), 133.34 (s, C^{8}Ph), 125.37 (s, C^{7}Ph), 124.02 (s, C^{9}Ph), 123.31 (s, C^{2}Py), 121.65 (s, C^{4}Py), 121.01 (C^{10}Ph), 102.23 (s, O=C=*C*), 85.41 (s, N=C=*C*), 72.62 (s, NCH$_2$Ph), 51.29 (s, NCH$_3$), 50.79 (s, NCH$_2$CH$_2$Py), 37.4 (s, NCH$_2$CH$_2$Py) ppm. MS (ESI): *m*/*z* = 829.15 $[M + H]^+$.

Synthesis of Complex **5**. To a dispersion of **3** (0.230 g, 0.25 mmol) in 15 mL of MeOH was added solid AgOTf (0.131 g, 0.51 mmol). Precipitation of AgCl started rapidly. The reaction mixture was stirred for 2 h and then filtered; the filtrate was allowed to stand overnight at room temperature. During this time, the color of the solution changed from red to bright green, and a green crystalline solid of **5** precipitated. The product was isolated by filtration, dissolved in the minimum amount of CH_2Cl_2, precipitated by addition of *n*-pentane, and collected by filtration. Green crystals suitable for X-ray diffraction were grown by stratification of a solution of **5** in acetone with *n*-pentane. Yield: 0.282 g, 0.17 mmol (68%). Anal. Calcd for $C_{60}H_{60}F_6N_{10}O_{10}Pd_4S_2{\cdot}CH_2Cl_2$ (1769.93): C, 41.39; H, 3.53; N, 7.91. Found: C, 41.25; H, 3.58; N, 8.04%. FTIR: selected ν_{max}(solid)/cm^{-1}: 3361w, 2972vw, 2941vw, 2901vw, 1610w, 1581vw, 1548m, 1497vw, 1484mw, 1440mw, 1413w, 1371w, 1340w, 1261vs, 1225w, 1159m, 1140m, 1113w, 1073w, 1029s, 967w, 908vw, 890vw, 873vw, 823mw, 804w, 788w, 769m, 756w, 720vw, 660vw, 636s, 584s, 572s, 559s, 532w, 512vs, 488w, 458mw, 437 ms, 390m, 350m, 334w, 324w, 315w, 280w, 265m, 255w, 247vw, 227w, 208 ms, 172m, 158vw, 151w, 140vw, 132vw, 125vw, 121vw, 105ms. ^{1}H NMR (CD_2Cl_2, 500 MHz) δ: 8.88 (br d, 1H, $^3J_{H,H}$ = 5.6 Hz, H$_5$Py1), 7.91 (dt, 1H, $^3J_{H,H}$ = 7.6, $^4J_{H,H}$ = 1.4 Hz, H^{4}Py2), 7.72 (d, 1H, $^3J_{H,H}$ = 7.6 Hz, H^{2}Py2), 7.55−7.52 (m, 1H, H^{4}Py1), 7.45 (dt, 1H, $^3J_{H,H}$ = 7.8, $^4J_{H,H}$ = 1.4 Hz, H^{3}Py1), 7.20 (br-d, 1H, $^3J_{H,H}$ = 7.6 Hz, H^{5}Py2), 7.16−7.14 (m, 1H, H^{8}Ph), 7.10−7.08 (m,

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3H, H^3Py2 + $H^{7,8}$Ph), 6.99−6.97 (m, 1H, H^{10}Ph), 6.93 (d, 1H, $^3J_{H,H}$ = 7.8 Hz, H^2Py1), 5.72 (s, 1H, N−C−CH), 5.16 (s, 1H, O−C−CH), 4.96 (dt, 1H, $^2J_{H,H}$ = 14.2 $^3J_{H,H}$ = 4.5 Hz, $NCH_2CHHPy1$), 4.47 (dt, 1H, $^2J_{H,H}$ = 12.8 and 3.6 Hz, $NCH_2CHHPy2$), 4.24 (br-d, 1H, $^2J_{H,H}$ = 12.8 Hz,, $NCH_2CHHPy2$), 3.95 (d, 1H, A part of an AB system, $^2J_{H,H}$ = 13.5 Hz, NCHPh), 3.71−3.63 (m, 2H, $NCHHCH_2Py1$−2), 3.36 (d, 1H, $^2J_{H,H}$ = 12.8 Hz, $NCHHCH_2Py1$), 3.31 (d, 1H, B part of an AB system, $^2J_{H,H}$ = 13.5 Hz, NCHPh), 3.17 (d, 1H, $^2J_{H,H}$ = 12.5 Hz, $NCHHCH_2Py2$), 2.96 (br-d, 1H, $^2J_{H,H}$ = 14.2 Hz, $NCH_2CHHPy1$), 2.68 (s, 3H, $N(CH_3)CH_3$), 2.43 (s, 3H, $N(CH_3)CH_3$) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125.7 MHz) δ: 189.63 (s, (dmba)PdO−C), 189.86 (s, $(Py)_2$PdO−C), 165.94 (s, (dmba)PdN−C), 165.04 (s, $(Py)_2$PdN−C), 161.26 (s, C^1Py2), 159.22 (s, C^1Py1), 150.48 (s, C^5Py2 + C^6Ph), 150.23 (s, C^5Py1), 147.91 (s, C^{11}Ph), 141.08 (s, C^3Py2), 139.17 (s, C^3Py1), 133.33 (s, C^8Ph), 128.32 (s, C^2Py1), 128.00 (s, C^2Py2), 126.41 (s, C^4Py2), 124.66 (s, C^4Py1), 125.10 (s, C^7Ph), 124.66 (s, C^9Ph), 122.56 (s, C^{10}Ph), 105.08 (s, O−C−C), 85.84 (s, N−C−C), 72.81 (s, NCH_2Ph), 52.00 and 50.52 (s, $N(CH_3)_2$), 48.42 (s, NCH_2CH_2Py2), 45.34 (s, NCH_2CH_2Py2), 41.85 (s, NCH_2CH_2Py1), 37.79 (s, NCH_2CH_2Py1) ppm. MS (ESI): m/z = 693.53 $[M]^{2+}$.

Synthesis of Complex ***6****.* To a solution of **4** (0.190 g, 0.21 mmol) in 10 mL of CH_2Cl_2 was added $[Pd(\mu\text{-}Cl)(dmba)]_2$ (0.116 g, 0.21 mmol). The reaction mixture was stirred for 4 h. Addition of *n*-pentane to this solution led to the precipitation of a green solid of **6** that was filtered and washed with *n*-pentane. Yield 0.206 g, 0.15 mmol (71%). Anal. Calcd for: $C_{56}H_{66}Cl_2N_8O_2Pd_4{\cdot}CH_2Cl_2$ (1464.71): C, 46.74; H, 4.68; N, 7.30. Found: C, 46.76; H, 5.11; N, 7.65%. FTIR: selected ν_{max}(solid)/cm^{-1}: 3044vw, 2969vw, 2909vw, 2886vw, 2856vw, 1502vs, 1441w, 1400w, 1295s, 1201w, 1179vw, 1156vw, 1106w, 1045w, 1022m, 987mw, 969w, 891vw, 863mw, 847m, 832vw, 771w, 738vs, 520vs, 477vw, 443w, 425s, 365vs, 299s (Pd−Cl), 270vw, 260vw, 226vs, 219vs, 192m, 185vw, 175vs, 157w, 142vw, 128vs, 122vw, 106s. ^{1}H NMR (CD_2Cl_2, 500 MHz) δ: 8.81 and 8.77 (br-d, 1H +1H, $^3J_{H,H}$ = 5.4 Hz, H^5Py), 7.68 (t, 2H, $^3J_{H,H}$ = 7.9 H^3Py), 7.33 and 7.30 (d, 1H+1H, $^3J_{H,H}$ = 7.9 Hz, H^2Py), 7.19−7.13 (overlapping multiplet, 4H, H^4Py + H^7PhPd(O,N)), 7.01−6.91 (m, 10H, H^{8-10}PhPd(O,N) + H^{9-10}PhPd(Cl)), 6.50 and 6.44 (t, 1H + 1H, $^3J_{H,H}$ = 7.5 Hz, H^8PhPd(Cl)), 5.73 (d, 2H, $^3J_{H,H}$ = 7.5 Hz, H_7PhPd(Cl)), 5.66 (s, 1H, N−C−CH), 5.21 (s, 1H, O−C−CH), 3.99−3.84 and 3.80−3−66 (overlapping multiplets, 8H + 8H, NCH_2CH_2Py + NCH_2PhPd(O,N) + NCH_2PhPd(Cl)), 2.84, 2.77, 2.73, 2.71, and 2.69 (s, 6H + 3H + 3H + 6H + 6H, $N(CH_3)_2$Pd(Cl) + $N(CH_3)_2$Pd(N,O)) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125.7 MHz) δ: 188.23 (s, O−C), 164.64 (s, N−C), 161.19 (s, C^1Py), 152.19 (s, C^5Py), 152.53 and 152.48 (s, C^5Py), 148.63 (s, C^{11}PhPd(O,N)), 147.93 (s, C^6PhPd(O,N)), 147.80 (s, C^6PhPd(Cl)), 137.31 and 137.20 (s, C^3Py), 133.27 and 133.18 (s, C^7PhPd(O,N)), 132.01 and 131.82 (s, C^7PhPd(Cl)), 125.66 and 125.55 (s, C^8PhPd(Cl)), 125.10 (s, C^2Py), 121.84 (C^4Py), 125.20, 125.16, 124.21, 124.07, 124.03, 123.99, 122.54, 122.24, 121.26, and 121.18 (s, C^{8-10}PhPd(O,N) + C^{9-10}PhPd(Cl)), 101.78 (s, O−C−C), 87.12 (s, N−C−C), 73.79 (s, NCH_2Pd(Cl)), 72.30 (s, NCH_2Pd(O,N)), 52.54, 52.45, 52.18, and 52.09 (s, $N(CH_3)_2$Pd-(Cl)), 50.93 (br s, $N(CH_3)_2$Pd(O,N)), 48.01 and 47.89 (s, NCH_2CH_2Py), 42.21 and 42.14 (s, NCH_2CH_2Py) ppm. MS (ESI): m/z = 865.12 $[M + H - (Pd(dmba)) - PdCl(dmba)]^+$, 588.01 $[M + H - (Pd(dmba)) - (PdCl(dmba))_2]^+$, 516.19 $[(dmba)Pd(\mu\text{-}Cl)Pd$-$(dmba)]^+$.

Synthesis of Complex ***7****.* To a solution of **6** (0.290 g, 0.21 mmol) in 10 mL of CH_2Cl_2, was added $TlPF_6$ (0.073 g, 0.21 mmol). The reaction mixture was stirred for 4 h at room temperature. After filtration, addition of *n*-pentane led to the precipitation of a green solid of **7**, which was filtered and washed with *n*-pentane. Green crystals suitable for X-ray diffraction were grown by stratification of a solution of **7** in CH_2Cl_2 with *n*-pentane. Yield: 0.259 g, 0.17 mmol (83%). Anal. Calcd for: $C_{56}H_{66}ClN_8O_2Pd_4F_6P$ (1489.29): C, 45.16; H, 4.67; N, 7.52. Found: C, 45.32; H, 4.64; N, 7.59%. FTIR: selected ν_{max}(solid)/cm^{-1}: 3049vw, 2974vw, 2914brw, 1604w, 1580vw, 1509s, 1485vw, 1468vw, 1450mw, 1403mw, 1288m, 1206vw, 1181vw, 1161vw, 1110vw, 1064vw, 1044mw, 1023mw, 987mw, 969w, 834vs, 776w, 734s, 659w, 579vw, 555vs, 518m, 469mw, 455vw, 438vw, 420m, 398w, 359m, 342vw, 327vw, 314w, 302w, 289vw, 280mw, 266w, 246s (ν(Pd−μ-Cl)), 225vs, 209vw, 202w, 177m, 158w, 151s, 140w, 133w, 121m, 104m. ^{1}H NMR (CD_2Cl_2, 500 MHz) δ: 8.62 (dd, 2H, $^3J_{H,H}$ = 4.7 Hz, $^4J_{H,H}$ = 1.5 Hz, H^5Py), 7.79 (dt, 2H, $^3J_{H,H}$ = 7.7, $^4J_{H,H}$ = 1.5 Hz, H^3Py), 7.47 (d, 2H, $^3J_{H,H}$ = 7.7 Hz, H^2Py), 7.28 (overlapping ddd, 2H, $^3J_{H,H}$ = 7.7, 4.7 Hz, $^4J_{H,H}$ = 1.5 Hz, H^4Py), 7.15 (d, 2H, $^3J_{H,H}$ = 7.6 Hz, H^7PhPd(O,N)), 7.03−6.99 and 6.96−6.93 (m, 4H + 6H, $H^{9,10}$PhPd-(μ-Cl) + $H^{8,9,10}$PhPd(O,N)), 6.58−6.54 (m, 2H, H^8PhPd(μ-Cl)), 5.35 (d, 2H, $^3J_{H,H}$ = 7.8 Hz, H^7PhPd(μ-Cl)), 5.28 (s, 1H, O−C−CH), 4.64 (s, 1H, N−C−CH), 4.10 and 3.88 (4H, AB system, $^2J_{H,H}$ = 14.2 Hz, NCHPhPd(μ-Cl)), 3.99 and 3.93 (4H, AB system, $^2J_{H,H}$ = 13.0 Hz, NCHPhPd(O,N)), the signals for the NCH_2CH_2Py protons overlap with the signals in the 4.12−3.81 range, 2.94 and 2.90 (s, 6H + 6H, $N(CH_3)_2$Pd(μ-Cl)), 2.75 (s, 12H, $N(CH_3)_2$Pd(O,N)) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125.7 MHz) δ: 187.92 (s, O−C), 165.19 (s, N−C), 161.43 (s, C^1Py), 152.19 (s, C^5Py), 148.89 (s, C^{11}PhPd(O,N)), 147.08 (s, C^6PhPd(O, N)), 146.67 (s, C^{11}PhPd(μ-Cl)), 143.63 (s, C^6PhPd(μ-Cl)), 138.38 (s, C^3Py), 132.39 (s, C_7PhPd(O,N)), 131.02 (s, C^7PhPd(μ-Cl)), 127.93 (s, C^2Py), 125.70, 125.18, 124.42, 123.22, and 122.28 (s, $C^{8,9,10}$PhPd(O,N)+$C_{9,10}$PhPd(μ-Cl)), 125.39 (s, C_8PhPd(μ-Cl)), 101.58 (s, O−C−C), 86.00 (s, N−C−C), 73.00 (s, NCH_2Pd(μ-Cl)), 72.56 (s, NCH_2Pd(O,N)), 52.86 and 52.57 (s, $N(CH_3)_2$Pd(μ-Cl)), 51.15 and 51.08 (s, $N(CH_3)_2$Pd(O,N)), 49.38 (s, NCH_2CH_2Py), 42.40 (s, NCH_2CH_2Py) ppm. MS (ESI): m/z = 829.15 $[4 + H]^+$, 516.97 $[(dmba)Pd(\mu\text{-}Cl)Pd(dmba)]^+$. MALDI-TOF-MS: m/z = 1068.14 $[4{\cdot}Pd(dmba)]^+$, 829.12 $[4 + H]^+$.

X-ray Data Collection, Structure Solution, and Refinement for All Compounds. Suitable crystals for the X-ray diffraction analysis of all compounds were obtained as described above. The intensity data for **2** and **3** were collected on a Nonius Kappa CCD diffractometer (graphite monochromated Mo Kα radiation, λ = 0.710 73 Å) at 173(2) K.[22] Data for **4**−**7** were collected on a Bruker APEX-II Kappa CCD (triumph monochromated Mo Kα radiation, λ = 0.710 73 Å). Crystallographic and experimental details for the structures are summarized in Supporting Information, Table S1. The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares procedures (based on F^2, SHELXL-97)[23] with anisotropic thermal parameters for all the non-hydrogen atoms. The hydrogen atoms were introduced into the geometrically calculated positions (SHELXL-97 procedures) and refined riding on the corresponding parent atoms. Except for complex **2** where the NH protons were located from Fourier difference maps and refined isotropically, for **3**, **4**, **5**, and **7** semiempirical absorption correction was applied using the MULTISCAN-ABS in PLATON[24] or SAD-ABS in APEX-II.[25] For complex **3** a SQUEEZE procedure[24] was applied, and the residual electron density was assigned to five molecules of disordered pentane. In **5**, there is half a molecule in the asymmetric unit, and a SQUEEZE procedure was also applied; the residual electron density was assigned to one molecule of acetone. In **7** a SQUEEZE procedure was also applied, and the residual electron density was assigned to one molecule of CH_2Cl_2. The thermal ellipsoid of Cl1 is flattened, but the nature of this atom was confirmed by other analytical methods.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic data, including selected bond angles and CIF files, NMR characterization of conformers **3a** and **3b**, and cyclic voltammetry for complex **4**. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic information files (CIF) of the compounds **2**·CH_2Cl_2, **3**−**5**, and **7**·CH_2Cl_2 were deposited with the CCDC, 12 Union Road, Cambridge, CB2 1EZ, U.K., and can be obtained on request free of charge, by quoting the publication citation and deposition numbers 982040−982044.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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DEDICATION

[†]Dedicated to Prof. Barry Lever, Distinguished Research Professor Emeritus at York University in Toronto, for his numerous and outstanding contributions to inorganic chemistry.

REFERENCES

(1) (a) Vigalok, A.; Milstein, D. *Acc. Chem. Res.* **2001**, *34*, 798. (b) Reingold, J. A.; Uk Son, S.; Bok Kim, S.; Dullaghan, C. A.; Oh, M.; Frake, P. C.; Carpenter, G. B.; Sweigart, D. A. *Dalton Trans.* **2006**, 2385. (c) Dei, A.; Gatteschi, D.; Sangregorio, C.; Sorace, L. *Acc. Chem. Res.* **2004**, *37*, 827. (d) Agarwala, H.; Das, D.; Mobin, S. M.; Mondal, T. K.; Lahiri, G. K. *Inorg. Chim. Acta* **2011**, *374*, 216. (e) Das, D.; Agarwala, H.; Chowdhury, A. D.; Patra, T.; Mobin, S. M.; Sarkar, B.; Kaim, W.; Lahiri, G. K. *Chem.—Eur. J.* **2013**, *19*, 7384. (f) Kim, S. *J. Inorg. Organomet. Polym. Mater.* **2013**, 1. (g) Schweinfurth, D.; Khusniyarov, M. M.; Bubrin, D.; Hohloch, S.; Su, C.-Y.; Sarkar, B. *Inorg. Chem.* **2013**, *52*, 10332. (h) Damas, A. l.; Ventura, B.; Axet, M. R.; Esposti, A. D.; Chamoreau, L.-M.; Barbieri, A.; Amouri, H. *Inorg. Chem.* **2010**, *49*, 10762. (i) Al-Jibori, S. *Transition Met. Chem.* **1995**, *20*, 120. (j) Das, D.; Mondal, T. K.; Chowdhury, A. D.; Weisser, F.; Schweinfurth, D.; Sarkar, B.; Mobin, S. M.; Urbanos, F. a.; Jiménez-Aparicio, R.; Lahiri, G. K. *Dalton Trans.* **2011**, *40*, 8377. (k) T. Moriuchi, T. W.; Ikeda, I.; Ogawa, A.; Hirao, T. *Eur. J. Inorg. Chem.* **2001**, 277.

(2) Braunstein, P.; Siri, O.; Taquet, J.-P.; Rohmer, M.-M.; Bénard, M.; Welter, R. *J. Am. Chem. Soc.* **2003**, *125*, 12246.

(3) Siri, O.; Braunstein, P. *Chem. Commun.* **2002**, *379*, 208.

(4) (a) Yang, Q.-Z.; Siri, O.; Braunstein, P. *Chem.—Eur. J.* **2005**, *11*, 7237. (b) Oh, M.; Carpenter, G. B.; Sweigart, D. A. *Acc. Chem. Res.* **2003**, *37*, 1. (c) Moussa, J.; Amouri, H. *Angew. Chem., Int. Ed.* **2008**, *47*, 1372.

(5) (a) Siri, O.; Taquet, J.-P.; Collin, J.-P.; Rohmer, M.-M.; Bénard, M.; Braunstein, P. *Chem.—Eur. J.* **2005**, *11*, 7247. (b) Cotton, F. A.; Jin, J.-Y.; Li, Z.; Murillo, C. A.; Reibenspies, J. H. *Chem. Commun.* **2008**, 211. (c) Schweinfurth, D.; Rechkemmer, Y.; Hohloch, S.; Deibel, N.; Peremykin, I.; Fiedler, J.; Marx, R.; Neugebauer, P.; Slageren, J. V.; Sarkar, B. *Chem.—Eur. J.* **2014**, *20*, 3475.

(6) (a) Siri, O.; Braunstein, P.; Taquet, J.-P.; Collin, J.-P.; Welter, R. *Dalton Trans.* **2007**, 1481. (b) Hohloch, S.; Braunstein, P.; Sarkar, B. *Eur. J. Inorg. Chem.* **2012**, *2012*, 546. (c) Das, H. S.; Das, A. K.; Pattacini, R.; Hübner, R.; Sarkar, B.; Braunstein, P. *Chem. Commun.* **2009**, *70*, 4387. (d) Das, D.; Mondal, T. K.; Mobin, S. M.; Lahiri, G. K. *Inorg. Chem.* **2009**, *48*, 9800. (e) Deibel, N.; Schweinfurth, D.; Huebner, R.; Braunstein, P.; Sarkar, B. *Dalton Trans.* **2011**, *40*, 431. (f) Braunstein, P.; Bubrin, D.; Sarkar, B. *Inorg. Chem.* **2009**, *48*, 2534. (g) Deibel, N.; Hohloch, S.; Sommer, M. G.; Schweinfurth, D.; Ehret, F.; Braunstein, P.; Sarkar, B. *Organometallics* **2013**, *32*, 7366.

(7) (a) Yang, Q.-Z.; Kermagoret, A.; Agostinho, M.; Siri, O.; Braunstein, P. *Organometallics* **2006**, *25*, 5518. (b) Taquet, J.-P.; Siri, O.; Braunstein, P.; Welter, R. *Inorg. Chem.* **2004**, *43*, 6944.

(8) Braunstein, P.; Siri, O.; Steffanut, P.; Winter, M.; Yang, Q. *C. R. Chim.* **2006**, *9*, 1493.

(9) (a) Simpson, S.; Kunkel, D. A.; Hooper, J.; Nitz, J.; Dowben, P. A.; Routaboul, L.; Braunstein, P.; Doudin, B.; Enders, A.; Zurek, E. *J. Phys. Chem. C* **2013**, *117*, 16406. (b) Dowben, P. A.; Kunkel, D. A.; Enders, A.; Rosa, L. G.; Routaboul, L.; Doudin, B.; Braunstein, P. *Top. Catal.* **2013**, *56*, 1096. (c) Routaboul, L.; Braunstein, P.; Xiao, J.; Zhang, Z.; Dowben, P. A.; Dalmas, G.; Da Costa, V.; Félix, O.; Decher, G.; Rosa, L. G.; Doudin, B. *J. Am. Chem. Soc.* **2012**, *134*, 8494. (d) Rosa, L. G.; Velev, J.; Zhang, Z.; Alvira, J.; Vega, O.; Diaz, G.; Routaboul, L.; Braunstein, P.; Doudin, B.; Losovyj, Y. B.; Dowben, P. A. *Phys. Status Solidi B* **2012**, *249*, 1571. (e) Kong, L.; Perez Medina, G. J.; Colón Santana, J. A.; Wong, F.; Bonilla, M.; Colón Amill, D. A.; Rosa, L. G.; Routaboul, L.; Braunstein, P.; Doudin, B.; Lee, C.-M.; Choi, J.; Xiao, J.; Dowben, P. A. *Carbon* **2012**, *50*, 1981. (f) Xiao, J.; Zhang, Z.; Wu, D.; Routaboul, L.; Braunstein, P.; Doudin, B.; Losovyj, Y. B.; Kizilkaya, O.; Rosa, L. G.; Borca, C. N.; Gruverman, A.; Dowben, P. A. *Phys. Chem. Chem. Phys.* **2010**, *12*, 10329. (g) Kong, L.; Routaboul, L.; Braunstein, P.; Park, H.-G.; Choi, J.; Cordova, J. P. C.; Vega, E.; Rosa, L. G.; Doudin, B.; Dowben, P. A. *RSC Adv.* **2013**, *3*, 10956. (h) Fang, Y.; Nguyen, P.; Ivasenko, O.; Aviles, M. P.; Kebede, E.; Askari, M. S.; Ottenwaelder, X.; Ziener, U.; Siri, O.; Cuccia, L. A. *Chem. Commun.* **2011**, *47*, 11255.

(10) (a) Yang, Q.-Z.; Siri, O.; Braunstein, P. *Chem. Commun.* **2005**, *5*, 2660. (b) Tamboura, F. B.; Cazin, C. S. J.; Pattacini, R.; Braunstein, P. *Eur. J. Org. Chem.* **2009**, *2009*, 3340.

(11) (a) McNitt, K. A.; Parimal, K.; Share, A. I.; Fahrenbach, A. C.; Witlicki, E. H.; Pink, M.; Bediako, D. K.; Plaisier, C. L.; Le, N.; Heeringa, L. P.; Griend, D. A. V.; Flood, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 1305. (b) Kalny, D.; Elhabiri, M.; Moav, T.; Vaskevich, A.; Rubinstein, I.; Shanzer, A.; Albrecht-Gary, A.-M. *Chem. Commun.* **2002**, 1426. (c) Bofinger, R.; Ducrot, A.; Jonusauskaite, L.; McClenaghan, N. D.; Pozzo, J.-L.; Sevez, G.; Vives, G. *Aust. J. Chem.* **2011**, *64*, 1301. (d) Kuwamura, N.; Kitano, K. i.; Hirotsu, M.; Nishioka, T.; Teki, Y.; Santo, R.; Ichimura, A.; Hashimoto, H.; Wright, L. J.; Kinoshita, I. *Chem.—Eur. J.* **2011**, *17*, 10708. (e) Murahashi, T.; Shirato, K.; Fukushima, A.; Takase, K.; Suenobu, T.; Fukuzumi, S.; Ogoshi, S.; Kurosawa, H. *Nat. Chem.* **2012**, *4*, 52. (f) Zelikovich, L.; Libman, J.; Shanzer, A. *Nature* **1995**, *374*, 790.

(12) (a) Schuster, E. M.; Botoshansky, M.; Gandelman, M. *Organometallics* **2009**, *28*, 7001. (b) Chao, S. T.; Lara, N. C.; Lin, S.; Day, M. W.; Agapie, T. *Angew. Chem., Int. Ed.* **2011**, *50*, 7529.

(13) Knight, J. C.; Amoroso, A. J.; Edwards, P. G.; Prabaharan, R.; Singh, N. *Dalton Trans.* **2010**, *39*, 8925.

(14) Beves, J. E.; Blanco, V.; Blight, B. A.; Carrillo, R.; D'Souza, D. M.; Howgego, D.; Leigh, D. A.; Slawin, A. M. Z.; Symes, M. D. *J. Am. Chem. Soc.* **2014**, *136*, 2094.

(15) Kojima, T.; Sakamoto, T.; Matsuda, Y. *Inorg. Chem.* **2004**, *43*, 2243.

(16) Chen, X.; Engle, K. M.; Wang, D.-H.; Yu, J.-Q. *Angew. Chem., Int. Ed.* **2009**, *48*, 5094.

(17) (a) Croizat, P.; Müller, F.; Mantz, H.; Englisch, A.; Welter, R.; Hüfner, S.; Braunstein, P. *C. R. Chim.* **2009**, *12*, 1228. (b) Soriaga, M. P.; Binamira-Soriaga, E.; Hubbard, A. T.; Benziger, J. B.; Pang, K. W. P. *Inorg. Chem.* **1985**, *24*, 65.

(18) Yang, Q.-Z.; Siri, O.; Brisset, H.; Braunstein, P. *Tetrahedron Lett.* **2006**, *47*, 5727.

(19) Khokarale, S. G.; García-Suárez, E. J.; Xiong, J.; Mentzel, U. V.; Fehrmann, R.; Riisager, A. *Catal. Commun.* **2014**, *44*, 73.

(20) Clark, R. J. H.; Natile, G.; Belluco, U.; Cattalini, L.; Filippin, C. *J. Chem. Soc. A* **1970**, 659.

(21) Deeming, A. J.; Rothwell, I. P.; Hursthouse, M. B.; New, L. *Dalton Trans.* **1978**, *7*, 1490.

(22) Siri, O.; Braunstein, P.; Rohmer, M.-M.; Bénard, M.; Welter, R. *J. Am. Chem. Soc.* **2003**, *125*, 13793.
(23) Roberts, D. A.; Steinmetz, G. R.; Breen, M. J.; Shulman, P. M.; Morrison, E. D.; Duttera, M. R.; Debrosse, C. W.; Whittle, R. R.; Geoffroy, G. L. *Organometallics* **1983**, *2*, 846.
(24) Siri, O.; Braunstein, P. *Chem. Commun.* **2000**, 2223.
(25) Das, M. C.; Xiang, S.; Zhang, Z.; Chen, B. *Angew. Chem., Int. Ed.* **2011**, *50*, 10510.
(26) Dai, L.-X.; Zhou, Z.-H.; Zhang, Y.-Z.; Ni, C.-Z.; Zhang, Z.-M.; Zhou, Y.-F. *Chemm. Commun.* **1987**, 1760.
(27) (a) Braunstein, P.; Dehand, J.; Pfeffer, M. *Inorg. Nucl. Chem. Lett.* **1974**, *10*, 521. (b) Crociani, B.; Boschi, T.; Pietropaolo, R.; Belluco, U. *J. Chem. Soc. A* **1970**, 531.
(28) Cope, A. C.; Friedrich, E. C. *J. Am. Chem. Soc.* **1968**, *90*, 909.