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Molecular and electronic structure of square planar complexes $[Pd^{II}(^tbpy)(L^{IP}_{N,O})]^0$, $[Pd^{II}(^tbpy)(L^{ISQ}_{N,O})](PF_6)$, and $[Pd^{II}(^tbpy)(L^{IBQ}_{N,O})](PF_6)(BF_4)\cdot 2CH_2Cl_2$: an *o*-iminophenolato based ligand centered, three-membered redox series

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Three Pd^{II} complexes which are members of the same electron-transfer series have been synthesized. Refluxing of the reaction mixture containing equimolar amounts of $PdCl_2$, 2-(2-trifluoromethyl)anilino-4,6-di-*tert*-butylphenol ($H_2L_{N,O}$), 4,4′-di-*tert*-butyl-2,2′-dipyridyl (^{t}bpy), and 3 equiv of triethylamine in MeOH under an argon atmosphere followed by exposure to air and addition of KPF_6 after cooling to room temperature yields reddish brown crystals of paramagnetic ($S = 1/2$) $[Pd(L^{ISQ}_{N,O})(^tbpy)](PF_6)$ (**2**). Reaction of **2** with one equiv of $[CoCp_2]$ in dry and degassed CH_2Cl_2 using anaerobic conditions gives diamagnetic $[Pd(L^{IP}_{N,O})(^tbpy)]$ (**1**), which is the one-electron reduced form of **2**. One-electron oxidation of **2** in CH_2Cl_2 under argon with one equiv of $NOBF_4$ affords diamagnetic $[Pd(L^{IBQ}_{N,O})(^tbpy)](PF_6)(BF_4)\cdot 2CH_2Cl_2$ (**3**). Complexes **1**, **2**, and **3** constitute three members of the same electron-transfer series. They are ideally suited to distinctly distinguish the geometrical and spectroscopic features of the *N*,*O*-coordinated, closed-shell, diamagnetic *o*-iminophenolate $(L^{IP}_{N,O})^{2-}$, the corresponding open-shell π-radical *o*-iminobenzosemiquinonate $(L^{ISQ}_{N,O})^{1-\bullet}$ ($S_{rad} = 1/2$), and the closed-shell *o*-iminobenzoquinone $(L^{IBQ}_{N,O})^0$ forms. All complexes were characterized by X-ray crystallography (100 K), cyclic voltammetry, EPR, and UV-vis spectroscopy. Complex **2** exhibits three reversible electron transfer waves in the cyclic voltammogram. Structural characterization of complex **3** reveals an interesting strong ion pairing between the BF_4 anion and the complex dication with a short C–F distance of 2.7 Å.

Introduction

It is now well established[1–10] that *o*-aminophenols are redox non-innocent and bind to transition metal ions in four forms: (1) the paramagnetic *o*-iminobenzosemiquinonate(1−) monoanionic radical ($(L^{ISQ})^{1-\bullet}$; $S_{rad} = 1/2$), (2) the diamagnetic monoanionic *o*-aminophenolate $(L^{AP})^{1-}$, (3) the dianionic *o*-iminophenolate $(L^{IP})^{2-}$, and (4) the neutral *o*-iminobenzoquinone $(L^{IBQ})^0$. Note that the o-aminophenolate(1−) anion $(L^{AP})^{1-}$ is the protonated form of the dianion $(L^{IP})^{2-}$. High-resolution low-temperature X-ray crystallography allows the assignment of the protonation and oxidation levels of such an *O*,*N*-coordinated ligand in a given complex. Average bond distances in the $(L^{ISQ})^{1-\bullet}$, $(L^{AP})^{1-}$, $(L^{IP})^{2-}$, and $(L^{IBQ})^0$ forms of the ligands in transition metal complexes have been proposed in the literature.[7,10] A number of complexes of Ni(II), Pd(II), Cu(II), Cr(III), and Co(III) containing *o*-aminophenol ligand analogues in different oxidation states, namely closed-shell *o*-iminophenolate and open-shell *o*-benzosemiquinonate π radicals, have been isolated.[2,5,7,9,10] Complexes containing closed-shell quinone type ligands like $[M^{II}(^0L^{IBQ}_{N,O})(bpy)]^{2+}$, $[M^{II}(^0L^{IBQ}_{N,O})_2]^{2+}$ have been proposed in a number of square planar complexes from spectroelectrochemical results.[2,7,9,11,12] However, only one crystal structure, namely that of $[Pd^{II}(L^{IBQ}_{N,O})_2](BF_4)_2$ containing two neutral closed-shell *o*-iminobenzoquinone ligands has been reported recently.[10]

In this context we have studied a series of Pd^{II} complexes where the Pd ion is *N*,*O*-coordinated to one 2-(2-trifluoromethyl)anilino-4,6-di-*tert*-butylphenol ($H_2L_{N,O}$)[9,10] and one *N*,*N*-coordinated 4,4′-di-*tert*-butyl-2,2′-dipyridyl (^{t}bpy); ^{t}bpy was used instead of simple bipyridyl (bpy) to prevent stacking of molecules in the solid state. Here, we present the syntheses, structural, and spectroscopic characterizations of the diamagnetic neutral species $[Pd(L^{IP}_{N,O})(^tbpy)]$ (**1**), the paramagnetic monocation $[Pd(L^{ISQ}_{N,O})(^tbpy)](PF_6)$ (**2**), and the diamagnetic dication $[Pd(L^{IBQ}_{N,O})(^tbpy)](PF_6)(BF_4)\cdot 2CH_2Cl_2$ (**3**), which are members of the same electron transfer series. Complexes **1**, **2** and **3** are ideally suited to establish a comparison of the structural, spectroscopic, and geometrical features of an *O*,*N*-coordinated monoanionic π radical $(L^{ISQ}_{N,O})^{1-}$ *versus* its one-electron reduced dianion $(L^{IP}_{N,O})^{2-}$, and its one-electron oxidized neutral quinone $(L^{IBQ}_{N,O})^0$. Similar neutral and monocationic complexes of Pd with one *N*,*O*-coordinated *o*-aminophenolate $(^0L^{IP}_{N,O})^{2-}$ ligand and one *N*,*N*-coordinated bpy ligand have been reported earlier.[7] The square planar, singly *N*,*O*-coordinated complexes with the complete quinone form of ligand, on the other hand, has not been structurally characterized previously, although the latter were proposed on the basis of spectroscopic data.[7]

The present X-ray diffraction study reveals that the dication in **3** exhibits an interesting, strong ion pairing interaction with the BF_4 anion.

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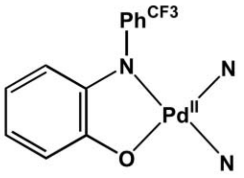
Results and discussion

Syntheses and spectroscopic characterizations

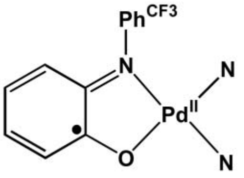
The reaction of equimolar amounts of $PdCl_2$, 4,4-di-*tert*-butyl-2,2′-dipyridyl and 2-(2-trifluoromethyl)aniline-4,6-di-*tert*-butylphenol in refluxing methanol in the presence of triethylamine (~3 equivalents) under an Ar atmosphere affords upon exposure to air and cooling to 20 °C and addition of KPF_6 crystals of $[Pd^{II}(^tbpy)(L^{ISQ}_{N,O})](PF_6)$ (**2**) in ~50% yield.

Oxidation of **2** in CH_2Cl_2 solution with one equivalent of $[NO]BF_4$ yielded brown crystals of $[Pd^{II}(^tbpy)(L^{IBQ}_{N,O})](PF_6)(BF_4)\cdot 2CH_2Cl_2$ (**3**) in ~56% yield whereas the reduction of **2** in CH_2Cl_2 with one equivalent of cobaltocene afforded the blue neutral species $[Pd^{II}(^tbpy)(L^{IP}_{N,O})]$ (**1**) in ~90% yield.

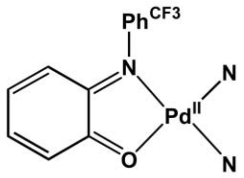
Magnetic susceptibility and ^1H NMR measurements of **1** and **3** showed that these materials are diamagnetic ($S = 0$). In contrast, for a solid sample of **2** temperature dependent (20–300 K) magnetic susceptibility measurements established a temperature independent magnetic moment of 1.72 μ_B ($g = 1.99$) per formula unit. This indicates an $S = 1/2$ ground state. The X-band EPR spectrum of **2** in CH_2Cl_2 solution at 10 K exhibits an isotropic signal at $g_{iso} = 2.0073$ without detectable Pd hyperfine splitting. This is indicative of the presence of an organic radical in **2** rather than a low spin Pd^{III} ion. Fig. 1 shows the $Pd(L_{N,O})$-fragments in **1**, **2** and **3**.



$\{(L^{IP}_{N,O})Pd^{II}\}^0$ fragment in **1**



$\{(L^{ISQ}_{N,O})Pd^{II}\}^+$ fragment in **2**



$\{(L^{IBQ}_{N,O})Pd^{II}\}^{2+}$ fragment in **3**

Fig. 1 Structural formulae of the $Pd(L_{N,O})$-fragments in **1**, **2** and **3**.

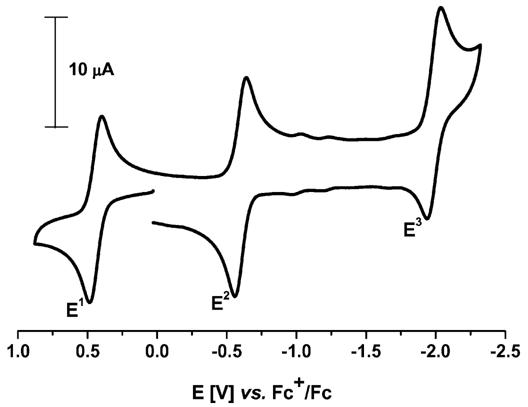


Fig. 2 Cyclic voltammogram of **2** in CH_2Cl_2 solution (0.10 M $[N(n\text{-}Bu)_4]PF_6$) at a glassy carbon working electrode recorded at a scan rate of 200 mV s^{-1}. Ferrocene was used as internal standard.

The cyclic voltammogram of **2** shown in Fig. 2 has been recorded at 20 °C in CH_2Cl_2 solution containing 0.10 M $[N(n\text{-}Bu)_4]PF_6$ as supporting electrolyte at a glassy carbon working electrode. Those of **1** and **3** have also been recorded; they are similar to that of **2** and are not shown. Ferrocene was used as internal standard, and potentials are referenced *vs.* the ferrocenium/ferrocene couple (Fc^+/Fc). The cv displays three reversible one-electron transfer waves at $E_{1/2} = +0.43$, -0.65 and -1.99 V, respectively. From controlled potential coulometric measurements it was established that the first wave corresponds to a one-electron oxidation of **2** whereas the other two correspond to two successive one-electron reductions, eqn (1).

$$[Pd^{II}(^tbpy)(L^{IBQ}_{N,O})]^{2+} \underset{E^1}{\overset{+e}{\underset{-e}{\rightleftharpoons}}} [Pd^{II}(^tbpy)(L^{ISQ}_{N,O})]^{+} \underset{E^2}{\overset{+e}{\underset{-e}{\rightleftharpoons}}}$$
$$[Pd^{II}(^tbpy)(L^{IP}_{N,O})]^{0} \underset{E^3}{\overset{+e}{\underset{-e}{\rightleftharpoons}}} [Pd^{II}(^tbpy)(L^{IP}_{N,O})]^{-} \qquad (1)$$

The above cv is very similar to that reported for $[Pd^{II}(bpy)(^0L^{ISQ}_{N,O})]PF_6$.[7] The one-electron reduction of $[Pd^{II}(^t\text{-}bpy)(L^{IP}_{N,O})]^0$ to the monoanion at −1.99 V corresponds to a ligand centered one-electron reduction of the *N*,*N*-coordinated ligand (^tbpy) to its π-radical monoanion $(^tbpy)^{1-\bullet}$. This has been reported for similar bpy complexes of Pd^{II} and Pt^{II}.[8c–d]

The electronic spectra of **1**, **2** and **3** in CH_2Cl_2 solutions at 20 °C are shown in Fig. 3. These spectra are very similar to those reported for $[Pd^{II}(bpy)(^0L^{IP}_{N,O})]$, $[Pd^{II}(bpy)(^0L^{ISQ}_{N,O})]^+$, and $[Pd^{II}(bpy)(^0L^{IBQ}_{N,O})]^{2+}$ in ref. 7 as pointed out before a single *N*,*O*-coordinated π radical anion $(L^{ISQ}_{N,O})^{1-\bullet}$ gives rise to four intraligand charge transfer bands

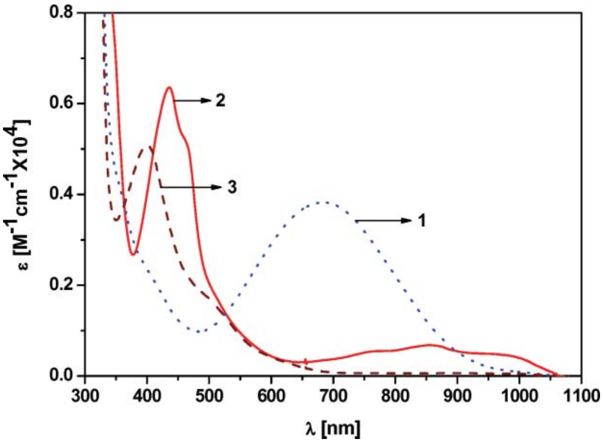
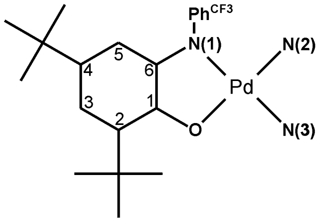


Fig. 3 Electronic spectra of **1** (dotted line), **2** (solid line) and **3** (dashed line) in CH_2Cl_2 solution (0.20 M $[N(n\text{-}Bu)_4]PF_6$).

Table 1 Electronic spectra of complexes in CH_2Cl_2 solution at 25 °C

Complex	λ_{max}/nm (10^4 ε/L mol^{-1} cm^{-1})
1	350sh(1.0), 400sh(0.75), 708(1.08)
2	436(0.59), 460sh(~0.5), 770sh(~0.05), 850(0.07), 950sh
3	385(0.73), 549sh(~0.11)

Table 2 Selected bond lengths (Å) in **1**, **2** and **3**



	1	**2**	**3**
Pd–N_1	1.981(1)	2.021(2)	2.050(3)
Pd–N_2	2.042(1)	2.009(2)	2.012(3)
Pd–N_3	2.011(1)	1.994(2)	1.989(3)
Pd–O	1.969(1)	1.983(2)	2.024(2)
N_1–C_6	1.387(2)	1.360(4)	1.306(4)
O–C_1	1.353(1)	1.307(4)	1.242(4)
N_1–C_{Ph}	1.404(2)	1.424(4)	1.439(4)
C_1–C_6	1.415(2)	1.439(4)	1.499(4)
C_1–C_2	1.404(2)	1.422(4)	1.458(4)
C_2–C_3	1.413(2)	1.381(4)	1.354(5)
C_3–C_4	1.395(2)	1.439(4)	1.466(5)
C_4–C_5	1.399(2)	1.355(4)	1.345(5)
C_5–C_6	1.396(2)	1.422(4)	1.428(4)

>450 nm with molar extinction coefficients of 0.5–7.0 × 10^3 L mol^{-1} cm^{-1} (see Table 1).

The X-band EPR spectrum of **2** in CH_2Cl_2 solution at 298 K is shown in Fig. 4. It displays a hyperfine split $S = 1/2$ signal at $g_{iso} = 2$. A satisfactory simulation was obtained by using the following parameters: $a(^{14}N) = 19.6$ MHz (6.99 G), $a(^1H) = 13.4$ MHz (4.78 G), $a(^{105}Pd, I = 2.5, 22.2\%) = 9.0$ MHz (3.21 G), and a line width of 2.0 G. These data show the iminosemiquinone character of the ligand $(L^{ISQ})^{1-\bullet}$ *N*,*O*-coordinated to a diamagnetic Pd(II) center. The spectrum is again very similar to that reported for $[Pd^{II}(bpy)(L^{ISQ})]^+$.

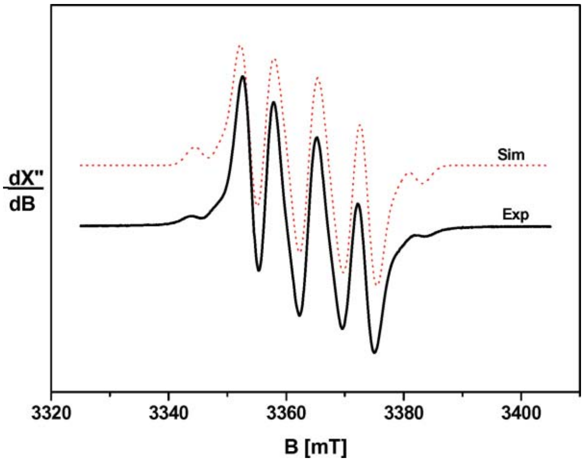


Fig. 4 X-Band EPR spectrum of **2** in CH_2Cl_2 solution at 298 K (conditions: frequency 9.4328 GHz, power 8.0 mW, modulation amplitude 1.0 G).

Crystal structures

From previous work we have identified the following structural markers for the *N*,*O*-coordinated *o*-iminophenolate dianion, $(L^{IP}_{N,O})^{2-}$, the *o*-iminosemiquinonate radical monoanion, $(L^{ISQ}_{N,O})^{1-\bullet}$, and the neutral *o*-iminebenzoquinone, $(L^{IBQ}_{N,O})^0$: (a) the C–N bond length of the respective iminophenolate ring system decreases from 1.37 ± 0.01 to 1.35 ± 0.01, and finally to 1.30 ± 0.01 with increasing oxidation level; (b) similarly, the corresponding C–O bond length decreases from 1.35 ± 0.01 to 1.30 ± 0.01 to 1.24 ± 0.01 Å; and (c) the six C–C bonds of the iminophenolate six-membered ring are nearly equidistant at 1.407 ± 0.01 Å in $(L^{IP}_{N,O})^{2-}$ indicating the aromatic, closed shell character of this phenyl ring. One-electron oxidation to $(L^{ISQ}_{N,O})^{1-\bullet}$ yields two alternating short C–C bonds at ~1.36 ± 0.01 Å of partially double bond character and four longer ones at 1.438 ± 0.01 Å. This characteristic distortion is labelled "quinoid-like". In the neutral quinone form, $(L^{IBQ}_{N,O})^0$, this distortion is even more pronounced.

Thus, the observed C–N, C–O and C–C bond lengths summarized in Table 2 for the respective *o*-iminophenolate derivative in **1**, **2** and **3** clearly allow their identification as a dianion $(L^{IP}_{N,O})^{2-}$ in neutral **1**, a π radical monoanion $(L^{ISQ}_{N,O})^{1-\bullet}$ in the monocation of **2**, and as a neutral *o*-iminobenzoquinone $(L^{IBQ}_{N,O})^0$ in the dication in **3**. It is revealing that the (^{t}bpy) ligand in the three structures have identical corresponding C–C and C–N bond lengths within experimental error (3σ). Thus, the geometrical parameters of the (^{t}bpy)Pd^{II}-fragments are nearly identical in the three structures and the redox processes are predominantly localized on the *o*-iminophenolate ligand. Fig. 5 displays the structure of the dication (top) and the ion pair $\{[Pd^{II}({}^t bpy)(L^{IBQ}_{N,O})](BF_4)\}^+$ (bottom) in crystals of **3**. The structures of the neutral molecules in **1** and of the monocation in crystals of **2** are similar and not shown. The structure of **1** consists of well separated, square-planar molecules of $[Pd^{II}({}^t bpy)(L^{IP}_{N,O})]$. The C–C, C–N and C–O bond distances (Table 2) are clearly those of a closed shell, diamagnetic dianion $(L^{IP}_{N,O})^{2-}$ which renders the central metal ion a Pd(II) ion (d^8) which is coordinated to a neutral closed shell ^{t}bpy ligand.

The structure of **2** consists of the monocation $[Pd^{II}({}^t bpy)\,(L^{ISQ}_{N,O})]^+$ and well separated PF_6^- anions. The C–C, C–N, and C–O distances of the *o*-iminophenolate derivative are indicative of the open-shell π radical monoanion $(L^{ISQ}_{N,O})^{1-\bullet}$. The geometry of the Pd^{II}(^{t}bpy) fragment is as in **1**. Thus, an organic π radical monoanionic ligand ($S_{rad} = 1/2$) is *N*,*O*-coordinated to the diamagnetic fragment $[Pd^{II}({}^t bpy)]^{2+}$ yielding an $S_t = 1/2$ ground state.

Finally, the structure of **3** is interesting (Fig. 5). It consists of the dication $[Pd^{II}({}^t bpy)(L^{IBQ}_{N,O})]^{2+}$, BF_4^- and PF_6^- monoanions (1 : 1) and dichloromethane solvent molecules. Fig. 5 (bottom) exhibits the structure of the dication. The very short C–N and C–O bond lengths indicate double bond character in both cases. In addition, the alternating two short C–C bonds in the corresponding six-membered ring system are in excellent agreement with a neutral, diamagnetic *o*-iminoquinone ligand $(L^{IBQ}_{N,O})^0$. Interestingly, the dication forms unique ion pairs with the BF_4^- anions, namely $\{[Pd^{II}({}^t bpy)\,(L^{IBQ}_{N,O})]BF_4\}^+$. The PF_6^- ions balance the charge; they are well separated from the above ion pairs. As shown in Fig. 5 (bottom) in the solid state there are two structurally slightly

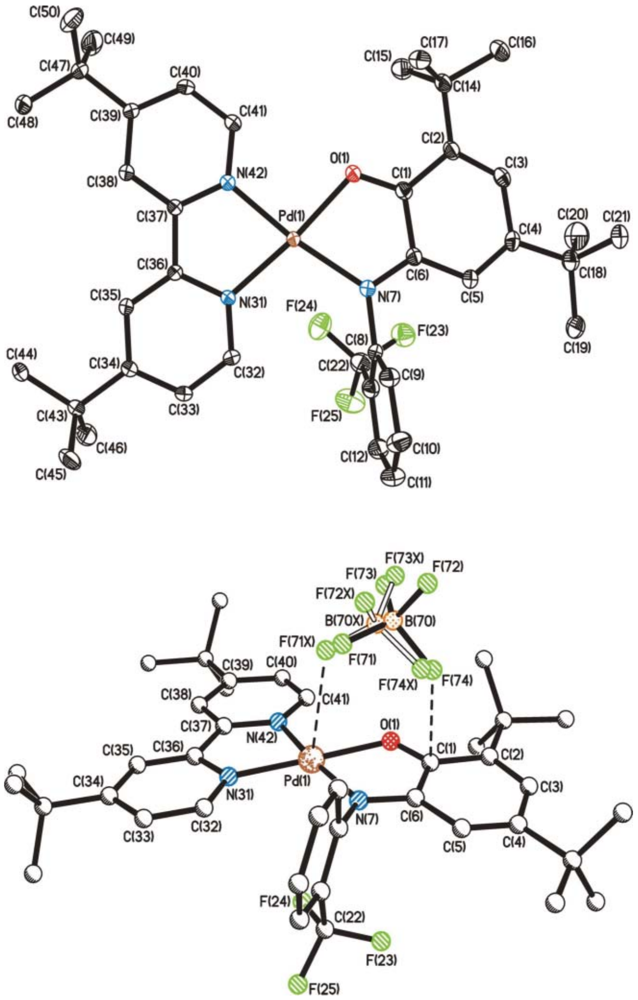


Fig. 5 Structure of the dicationic complex **3** (top) (50% probability for ellipsoids). The bottom structure represents the two forms of the ion pair $\{[\mathrm{Pd^{II}}(^t\mathrm{bpy})(\mathrm{L}^{\mathrm{IBQ}}_{\mathrm{N,O}})](\mathrm{BF_4})\}^+$ in **3** (see text).

different ion pairs present. One fluorine atom F(74) of the $\mathrm{BF_4}^-$ forms a short contact to the carbon atom C(1) at 2.700 Å. The resulting ion pair is present in 69%. On the other hand, in the second ion pair (31%) fluorine atom F(71X) forms a relatively short contact to the palladium ion at 2.795 Å. The quinone ligand $(\mathrm{L}^{\mathrm{IBQ}}_{\mathrm{N,O}})^0$ and the Pd(II) ion are obviously relatively electron poor and carry partial positive charges. As has been noted before, paramagnetic $[\mathrm{Pd^{II}}(\mathrm{L}^{\mathrm{ISQ}}_{\mathrm{N,O}})(\mathrm{L}^{\mathrm{IBQ}}_{\mathrm{N,O}})]^+$ also forms an ion pair with a $\mathrm{BF_4}^-$ counteranion in the solid state.[10] This is shown in Fig. 6. The asymmetric F(63) · · · C contact is at 2.710 Å and localizes the unpaired electron of $(\mathrm{L}^{\mathrm{ISQ}}_{\mathrm{N,O}})^{1-\bullet}$ at this site. It is the $(\mathrm{L}^{\mathrm{IBQ}}_{\mathrm{N,O}})$ site which is electron poor and, consequently, forms the C · · · F contact.

Experimental

Synthesis

The ligand 2-(2-trifluoromethyl)aniline-4,6-di-*tert*-butylphenol, $\mathrm{H_2}(\mathrm{L}^{\mathrm{IP}}_{\mathrm{N,O}})$ has been prepared as is described in ref. 9.

$[\mathrm{Pd^{II}}(^t\mathrm{bpy})(\mathrm{L}^{\mathrm{IP}}_{\mathrm{N,O}})]$ (1). To a dry, deaerated solution of $[\mathrm{Pd^{II}}(^t\mathrm{bpy})(\mathrm{L}^{\mathrm{ISQ}}_{\mathrm{N,O}})](\mathrm{PF_6})$ (**2**) (0.26 g; 0.29 mmol) in $\mathrm{CH_2Cl_2}$ (8 mL) was added cobaltocene, $[\mathrm{Cp_2Co}]$, (0.06 g; 0.295 mmol) under an argon blanketing atmosphere with stirring for 1 h at 20 °C. The solvent was then removed by evaporation *in vacuo* and the resulting blue powder was redissolved in $\mathrm{CH_3OH}$ (6 mL). A yellow solid material, $[\mathrm{CpCo}]\mathrm{PF_6}$ was filtered off. Slow evaporation of the solvent produced blue crystals of **1** suitable for X-ray crystallography. Yield: 0.20 g (92%). Elemental analysis: C, 63.5; H, 6.6; N, 5.6; Pd, 14.4%. Calculated ($\mathrm{C_{39}H_{48}F_3N_3OPd}$): C, 63.4; H, 6.6; N, 5.7; Pd, 14.4%. ESI-MS ($\mathrm{CH_2Cl_2}$), *m*/*z*: 737 $\{\mathrm{M}\}^+$.

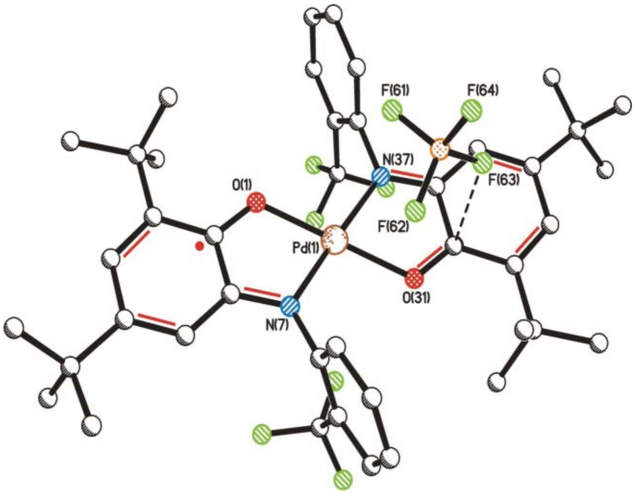


Fig. 6 Structure of the ion pair $[\mathrm{Pd}(\mathrm{L}^{\mathrm{ISQ}}_{\mathrm{N,O}})(\mathrm{L}^{\mathrm{IBQ}}_{\mathrm{N,O}})](\mathrm{BF_4})$ from ref. 10.

$[\mathrm{Pd^{II}}(^t\mathrm{bpy})(\mathrm{L}^{\mathrm{ISQ}}_{\mathrm{N,O}})](\mathrm{PF_6})$ (2). To a solution of $\mathrm{PdCl_2}$ (0.18 g; 1.0 mmol) in $\mathrm{CH_3OH}$ (20 mL) was added triethylamine (0.8 mL), the ligand $\mathrm{H_2}(\mathrm{L}^{\mathrm{IP}}_{\mathrm{N,O}})$ (0.37 g; 1.0 mmol) and 4,4′-di-*tert*-butyl-2,2′-dipyridyl (^{t}bpy) (0.27 g; 1.0 mmol). The mixture was heated to reflux under Ar for 1 h. The solution was allowed to cool to 20 °C in an open vessel in the presence of air. Then $\mathrm{KPF_6}$ (0.8 g) dissolved in $\mathrm{CH_3OH}$ (10 mL) was added. After stirring for 3 h, the filtered, reddish-brown solution was allowed to stand in an open vessel for 12 h after which time X-ray quality crystals of **2** were obtained. Yield: 0.46 g (53%). Elemental analysis: C, 53.2; H, 5.3; N, 4.6; Pd, 12.0. Calculated ($\mathrm{C_{39}H_{48}F_9N_3OPPd}$): C, 53.0; H, 5.5; N, 4.8; Pd, 12.0. ESI-MS ($\mathrm{CH_2Cl_2}$), *m*/*z*: 882 $\{\mathrm{Pd}(^t\mathrm{bpy})(\mathrm{L}^{\mathrm{ISQ}}_{\mathrm{N,O}})\mathrm{PF_6}\}^+$.

$[\mathrm{Pd^{II}}(^t\mathrm{bpy})(\mathrm{L}^{\mathrm{IBQ}}_{\mathrm{N,O}})](\mathrm{PF_6})(\mathrm{BF_4})\cdot2\mathrm{CH_2Cl_2}$ (3). To a dry, deaerated solution of **2** (0.10 g; 0.11 mmol) in $\mathrm{CH_2Cl_2}$ (7 mL) was added $[\mathrm{NO}]\mathrm{BF_4}$ (0.013 g; 0.11 mmol) under an Ar blanketing atmosphere at 20 °C. After stirring for 2 h, a brown solution was obtained which was filtered and topped with a layer of *n*-heptane. The solvents were allowed to slowly evaporate which gave rise to X-ray quality brown crystals of **3**. Yield: 0.07 g (56%). Elemental analysis: C, 43.9; H, 4.7; N, 3.7; Pd, 8.7. Calculated ($\mathrm{C_{41}H_{52}F_{13}N_3Cl_2OBPPd}$): C, 43.2; H, 4.6; N, 3.7; Pd, 9.25.

X-Ray crystallographic data collection and refinement of the structures

A deep green single crystal of **1**, an orange brown crystal of **2**, and a red crystal of **3** was coated with perfluoropolyether and picked up with a glass fibers. The crystals were immediately mounted in the nitrogen cold stream (100 K) of a Nonius Kappa-CCD diffractometer equipped with a Mo-target rotating-anode X-ray source and a graphite monochromator (Mo-Kα, $\lambda = 0.71073$ Å). Final cell constants were obtained from least squares fits of all

Table 3 Crystallographic data for **1**, **2** and **3**·$2CH_2Cl_2$

	1	**2**	**3**
Chemical formula	$C_{39}H_{48}F_3N_3OPd$	$C_{39}H_{48}F_9N_3OPPd$	$C_{41}H_{52}BCl_4F_{13}N_3OPPd$
FW	738.20	883.17	1139.84
Space group	$P2(1)/c$, No. 14	$Pbca$, No. 61	$C2/c$, No. 15
a/Å	14.8500(4)	17.7791(5)	37.901(2)
b/Å	19.2194(6)	20.9990(7)	11.5338(6)
c/Å	13.7915(4)	21.6489(7)	26.740(2)
β/°	110.538(5)	90	124.352(6)
V/Å	3686.0(2)	8082.5(4)	9650.4(10)
Z	4	8	8
T/K	100(2)	100(2)	100(2)
ρ calcd/g cm^{-3}	1.330	1.452	1.569
Refl. collected/$2\theta_{max}$	62 403/62.04	88 473/52.0	76 981/58.0
Unique refl./$I > 2\sigma(I)$	11 678/10 737	7921/5657	12 804/9741
No. of param./restr.	452/31	499/0	614/94
μ/cm^{-1}/λ/Å	5.52/0.71073	5.74/0.71073	7.26/0.71073
$R1^a$/goodness of fit^b	0.0261/1.075	0.0417/1.037	0.0536/1.043
$wR2^c$ ($I > 2\sigma(I)$)	0.0603	0.0803	0.1201
Residual density/e Å^{-3}	+0.73/−0.60	+0.68/−0.60	+1.59/−1.14

[a] Observation criterion: $I > 2\sigma(I)$. $R1 = \sum\|F_o| - |F_c\|/\sum|F_o|$. [b] GooF $= [\sum[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$. [c] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$ where $w = 1/\sigma^2(F_o^2) + (aP)^2 + bP$, $P = (F_o^2 + 2F_c^2)/3$.

measured reflections. Crystallographic data of the compounds are listed in Table 3. The Siemens ShelXTL[13] software package was used for solution and artwork of the structure, ShelXL97[14] was used for the refinement. The structures were readily solved by direct and Patterson methods and subsequent difference Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at calculated positions and refined as riding atoms with isotropic displacement parameters. The BF_4-anion in **3** was found to be disordered and was split on two positions in a ratio of 69 : 31. B–F and F–F distances were restrained to be equal within errors (SADI). Equal thermal displacement parameters were given to the corresponding parts (EADP). The disorder of a *t*-butyl group (C(43)–C(46)) in **1** was treated the same way adopting a ratio of 83 : 17.

CCDC reference numbers 281237–281239.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b614745c

Conclusions

In summary, a series of square planar complexes **1**, **2** and **3** containing one *N*,*N*-coordinated neutral ^{t}bpy and a *N*,*O*-coordinated non-innocent 2-(2-trifluoromethyl)anilino-4,6-di-*tert*-butylphenol derivative ligand each bound to a diamagnetic, divalent Pd centre have been isolated. It has been shown that the paramagnetic monocation in **2** contains an *o*-iminobenzosemiquinonate(1−) π radical. The most salient structural features to identify the radical character are (i) C–O and C–N bond lengths at 1.30 ± 0.01 Å and 1.36 ± 0.01 Å, respectively, and (ii) quinoid type distortion in the aminophenolate ring. A sharp EPR signal at 10 K with a $g = 2.0073$ value indicates the presence of organic, *i.e.*, ligand centred, radical. Neutral diamagnetic **1** contains the dianionic *o*-iminophenolate ligand. Important structural features include (i) C–O and C–N bond lengths at 1.35 ± 0.01 Å and 1.39 ± 0.01 Å, and (ii) six nearly equidistant C–C ring bond lengths. An intense, broad band at 685 nm is assigned as an inter-ligand charge transfer transition (LLCT). The dicationic diamagnetic complex **3** with a neutral *o*-iminobenzoquinone ligand has been isolated for the first time. Identification of $(L^{IBQ})^0$ has been achieved by the observation of (i) very short C–O and C–N bond lengths at 1.24 ± 0.01 Å and 1.30 ± 0.01 Å, (ii) a pronounced quinone type distortion with two alternating short C=C and four long C–C in the aminophenolate ring, and (iii) a quinone charge transfer bands in the UV-vis spectrum between 350–550 nm. Thus, it is clear that the oxidation levels of *O*,*N*-coordinated *o*-aminophenolate derivatives can be established primarily from their high quality crystal structures and electronic spectra.

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