# Redox Properties of Zerovalent Palladium Complexes Containing α-Diimine and *p*-Quinone Ligands

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The redox behavior of zerovalent palladium complexes of the types (i) Pd(N⌒N)(Q) (N⌒N = 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen), 1,4-dicyclohexyl-1,4-diaza-1,3-butadiene (chexDAB), bis(arylimino)acenaphthene (aryl = *o*,*o*-*i*Pr$_2$-C$_6$H$_3$; *o*,*o*-*i*Pr$_2$-BIAN), 2,2′-bipyrimidine (bpym); Q = 1,4-benzoquinone (pbq), 1,4-naphthoquinone (nq), duroquinone (dq)) and (ii) Pd$_2$(*μ*-N⌒N)(*μ*-pbq)$_2$ (N⌒N = 4,5-diazafluorene (dafe), 4,5-diazafluoren-9-one (dafo)) was investigated by cyclic voltammetry and, in selected cases, by UV−vis spectroelectrochemistry and EPR spectroscopy. The character of the one-electron reduction of these complexes strongly depends on the *π*-acceptor properties of both types of redox-active ligands. The Q-localized reduction of Pd(N⌒N)(pbq) (N⌒N = chexDAB, phen, bpy) and Pd(bpy)(nq) leads to reversible dissociation of the *p*-semiquinone ligand, whereas the stable radical anion [Pd(bpym)(pbsq)]$^{\bullet-}$ is produced on coordination of the stronger *π*-acceptor bpym ligand. The predominant localization of the electron transfer on the Q ligand is also evidenced by the strongly Q-dependent reduction potentials of the complexes Pd(bpym)(Q) (Q = pbq, dq) and Pd(bpy)(Q) (Q = pbq, nq). In contrast to this behavior, the one-electron reduction of Pd(*o*,*o*-*i*Pr$_2$-BIAN)(Q) (Q = pbq, nq) and Pd$_2$(*μ*-dafo)(*μ*-pbq)$_2$ is most likely localized on *o*,*o*-*i*Pr$_2$-BIAN and dafo, respectively, the strongest *π*-acceptor α-diimine ligands used. Oxidation of all Pd(N⌒N)(Q) complexes under study is chemically irreversible and only slightly depends on the combination of the N⌒N and Q ligands.



## Introduction

The study of coordination with zerovalent group 10 metals (M = Ni, Pd, Pt) *versus* the reactivity of *π*-bound unsaturated hydrocarbons has attracted increasing attention, particularly in the field of organic synthesis and homogeneous catalysis.[1] Among factors influencing the reactivity, electronic effects are of great importance, namely oxidizing of the metal center and tuning the donor/acceptor properties of the *π*-coordinated unsaturated hydrocarbon ligand(s) and other coligands to vary the distribution of the electron density in the complexes. In this field one of the most challenging systems to study is that involving complexes with coordinated redox-active *p*-quinone ligands which can also be considered as having two activated olefinic functions. Bäckvall and co-workers[2] demonstrated the importance of *p*-quinone coordination to a Pd$^0$ center for the mechanism of Pd$^{II}$-catalyzed oxidations of conjugated dienes, where a transformation of the Pd$^0$(*p*-quinone) moiety to a Pd$^{II}$ complex and hydroquinone plays a key role. The feasibility of the latter electron-transfer step appears to be strongly determined by the redox properties of the *p*-quinone ligands.

In general, thorough electrochemical studies of the d$^{10}$ M$^0$(*p*-quinone) complexes will significantly advance our understanding of their bonding properties and reactivity, with possible utilization in catalytic systems. The electrochemical behavior of free quinones has perhaps been studied most thoroughly in organic redox couples.[3] In contrast to this, and also to a large number of reports on redox series based on complexes with chelated *o*-quinone ligands and their reduced forms,[4] only very few electrochemical studies of metal complexes containing *p*-quinones have been published.[5] The reduction potential of the *π*-bound *p*-quinone ligands, that is known to be shifted[5] more negatively with respect to the noncoordinated *p*-quinone ligands, has been shown to depend strongly on their *π*-acceptor properties. Electrochemical investigation of two series of Pd(L$_2$)(*p*-quinone) (L$_2$ = 1,5-cyclooctadiene (COD) or L = PPh$_3$)

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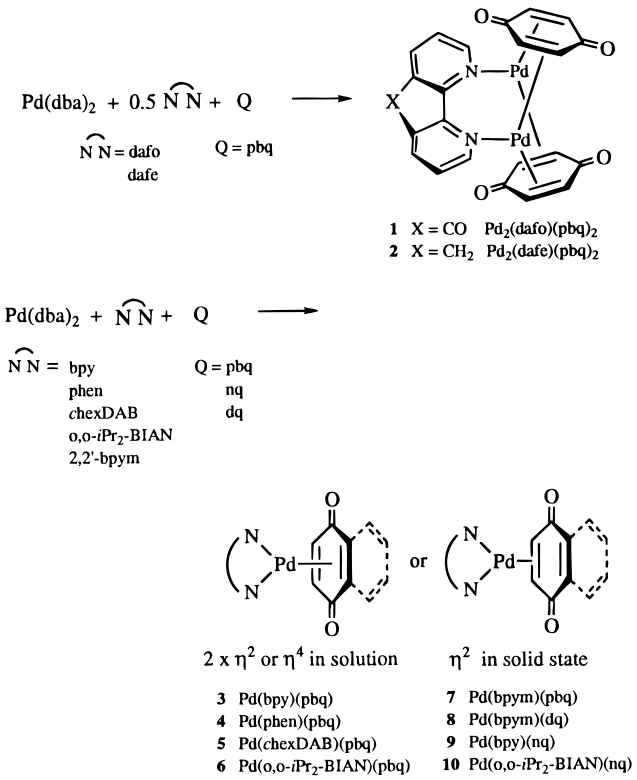
**Scheme 1**



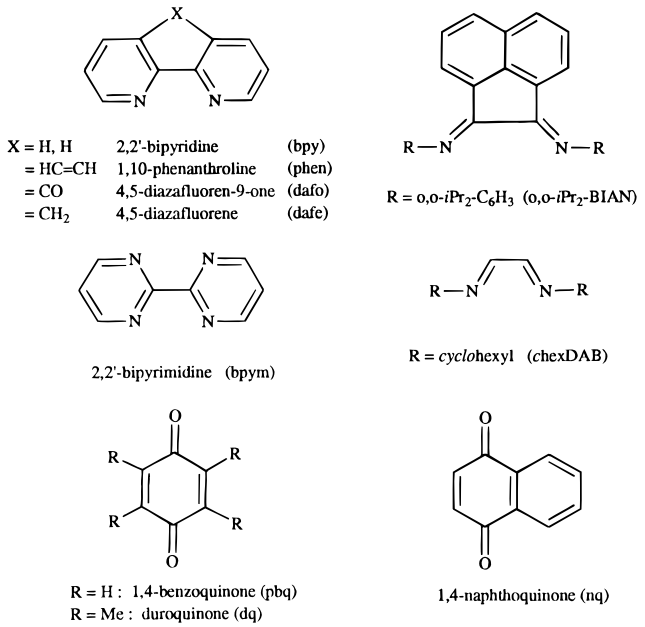




**Figure 1.** α-Diimine (N^N) and *p*-quinone ligands used.



complexes also pointed to an apparent influence of the coligand L on the reduction potentials.[5b,c]

As a part of a continuing research program in our laboratory on palladium complexes containing rigid bidentate ligands,[6] the literature survey has stimulated us to explore the redox behavior of a series of $Pd^0$ complexes with two different redox-active ligands, *viz.* Pd(N^N)(Q) and $Pd_2(\mu\text{-N^N})(\mu\text{-Q})_2$ (Scheme 1), where N^N = α-diimine and Q = *p*-quinone (Figure 1). The syntheses and characterization of a majority of the mixed-ligand complexes shown in Scheme 1 have been reported previously.[7] In Pd(N^N)(Q) the α-diimine acts as a bidentate ligand. The *p*-quinone coordinates in the solid complexes as a monofunctional ligand through one of its C=C double bonds, whereas both olefinic functions were found to coordinate to the palladium center in solution. X-ray structure determinations revealed that in $Pd_2(\mu\text{-N^N})(\mu\text{-Q})_2$ the α-diimine and the two *p*-quinone ligands form bridges between the two palladium atoms. In this case, the *p*-quinone acts as a bifunctional ligand.

Our primary interest in undertaking this (spectro)-electrochemical study was to evaluate the influence of the α-diimine ligands on the character of the reduction, *viz.* the location and reversibility of the electron-transfer step, and to compare it with that of the ligands L in the corresponding complexes Pd($L_2$)(*p*-quinone) ($L_2$ = 1,5-cyclooctadiene (COD) or L = $PPh_3$).[5b,c] The complexes under study also provide an interesting opportunity to tune their redox properties by independent variation of the $\pi$-acceptor capacity of the N^N and Q ligands and to probe the electronic communication between these redox-active ligands through the palladium center.

## Experimental Section

**Materials.** The solvents THF and $CH_2Cl_2$ (both Janssen) were distilled from a sodium-benzophenone mixture and $P_2O_5$, respectively. Dibenzylideneacetone[8] (dba) and $Pd(dba)_2$[9] (the latter complex being in fact the dimer $Pd_2(dba)_3$·dba[7a]), *o,o*-$iPr_2$-BIAN[6e] (Figure 1), 1,4-dicyclohexyl-1,4-diaza-1,3-butadiene[10] (chexDAB), 4,5-diazafluoren-9-one[11] (dafo), and 4,5-diazafluorene[11] (dafe) were synthesized according to published procedures. The *p*-quinones (Q) 1,4-benzoquinone (pbq) (Merck), 1,4-naphthoquinone (nq) (Fluka), and duroquinone (dq) (Aldrich) and 2,2′-bipyridine (bpy) (Merck), 2,2′-bipyrimidine (bpym) (Johnson Matthey GmbH), 1,10-phenanthroline (phen) (Fluka), cobaltocene ($CoCp_2$) (Aldrich), and ferrocene ($FeCp_2$ or Fc) (BDH) were used as received. $Bu_4NPF_6$ (Fluka) was dried *in vacuo* at 80 °C for 10 h. The complexes **1**−**7**, **9**, and **10** were synthesized as described elsewhere.[7]

**Synthesis of Pd(bpym)($\eta^2$-dq) (8).** $Pd(dba)_2$ (124.3 mg, 0.22 mmol), bpym (35.8 mg, 0.23 mmol), and dq (41 mg, 0.25 mmol) were dissolved in acetone (60 mL) and stirred for 30 min. The color of the solution changed from dark purple to red. The solution was then filtered through Celite to remove metallic palladium and concentrated to ca. 5 mL. The product was precipitated on addition of hexane (30 mL). The red-brown precipitate was filtered off, washed twice with diethyl ether (30 mL) and twice with hexane (30 mL), and dried under vacuum. The yield was 82%.

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**Table 1. Cyclic Voltammetric Data for the Palladium Complexes 1−10,[a] Uncoordinated *p*-Quinones (Q) and α-Diimine (N⁀N) Ligands Used, and Related $Pd^0$ Complexes**

| compd | $E_p{}^a$ | $E_p{}^c(1)$ ($\Delta E_p$) | $E_p{}^c(2)$ | $\Delta E_p$(Fc/Fc$^+$) |
|---|---|---|---|---|
| $Pd_2$(dafo)(pbq)$_2$ (**1**) | +0.52[d,e] | −1.33[d,f] (130) | | 130 |
| | +0.52[d,f,g] | −1.19[d,f,g] (120) | | 120 |
| $Pd_2$(dafe)(pbq)$_2$ (**2**) | *b* | *b* | | |
| Pd(bpy)(pbq) (**3**) | +0.49[e] | −1.87[e] | | |
| | | −1.90[e,h] | | |
| Pd(phen)(pbq) (**4**) | +0.44[e] | −1.75[e] | | |
| Pd(chexDAB)(pbq) (**5**) | +0.55[e] | −1.87[e] | | |
| Pd(*o*,*o*-*i*Pr$_2$-BIAN)(pbq) (**6**) | +0.60[e] | −1.50 (110)[f] | | 110 |
| | +0.58[e,h] | −1.43 (110)[f,h] | −2.34[e,h] | 120 |
| | *c* | −1.35 (110)[f,g,h] | −2.33[e,g,h] | 100 |
| Pd(bpym)(pbq) (**7**) | +0.50[e,h] | −1.13 (120)[f,h] | −1.83[e,h] | 120 |
| Pd(bpym)(dq) (**8**) | *c* | −1.79[e,h] | | |
| Pd(bpy)(nq) (**9**) | +0.40[e,h] | −2.04[e,h] | | |
| Pd(*o*,*o*-*i*Pr$_2$-BIAN)(nq) (**10**) | +0.60[e,h] | −1.43 (120)[f,h] | −2.39[e,h] | |
| Pd(COD)(pbq) | +0.50[e,i] | −1.59[e,i] | | |
| Pd(PPh$_3$)$_2$(pbq) | +0.48[e,i] | −1.67[e,i] | | |
| Pd(*p*Tol-BIAN)(MA)[k] | | −1.38 (80)[f,h,j] | −1.86[f,h,j] | |
| dafo | | −1.55 (100)[f] | | 100 |
| | | −1.66 (120)[f,h] | −2.34[f,h] | 120 |
| dafe | | −2.51[e,h] | | |
| bpy | | −2.78 (120)[f,h] | −3.29 [e,h] | 120 |
| phen | | −2.62 (90)[f,h] | −3.21 [e,h] | 70 |
| bpym | | −2.40 (120)[f,h] | −2.93 [e,h] | 120 |
| chexDAB | | −2.96[e,h] | | |
| *o*,*o*-*i*Pr$_2$-BIAN | | −2.14 (120)[f,h] | | 120 |
| Ph-BIAN | | −1.84 (130)[f,h,j] | | |
| pbq | | −0.93 (120)[f,h] | −1.52[e,h] | 120 |
| nq | | −1.30 (120)[f,h] | −1.94[e,h] | 120 |
| dq | | −1.43 (150)[f,h] | −2.10[e,h] | 150 |

[a] Conditions and definitions: $10^{-3}$ M solutions in $CH_2Cl_2$ (containing $10^{-1}$ M $Bu_4NPF_6$) at 293 K unless stated otherwise; Pt-disk electrode; $v$ = 100 mV/s; redox potentials in V against $E_{1/2}$(Fc/Fc$^+$), $E_p{}^a$ = anodic peak potential for oxidation of the parent complex; $E_p{}^c$ = cathodic peak potential for reduction of the parent compound (1) and its radical anion (2), $\Delta E_p$ = cathodic-to-anodic peak separation in mV. [b] Not possible to measure due to complete decomposition in solution. [c] Not recorded. [d] $v$ = 50 mV/s. [e] Chemically irreversible. [f] Chemically reversible. [g] 223 K. [h] THF. [i] Potentials (determined in acetone) taken from ref 5c, using $E_{1/2}$(Fc/Fc$^+$) = +0.40 V *vs* SCE. The reduction potentials are $E_{1/2}$ values. [j] Potentials taken from ref 14, using $E_{1/2}$(Fc/Fc$^+$) = +0.575 V *vs* SCE in THF. [k] MA = maleic anhydride.

**Spectroscopic Characterization of 8.** $^1$H NMR ($CDCl_3$, 293 K): $\delta$ 9.14 (dd, 4.8, 2.2, 2H), 8.67 (dd, 5.1, 2.2, 2H), 7.65 (pst, 5.0, 2H), 1.94 (s, 12H). $^{13}$C NMR ($CDCl_3$, 213 K): $\delta$ 187.7 (s, *C*═O), 159.4 (d), 158.8 (s), 154.7 (d), 115.2 (s), 13.5 (q). Abbreviations used: s = singlet, d = doublet, pst = pseudo-triplet, q = quartet. Multiplicity, coupling constants (Hz), and number of protons are given in parentheses. IR (KBr pellet): strong band due to $\nu$(C═O) at 1568 cm$^{-1}$. Mass: found for $M^{\bullet+}$ = $m/z$ 429.0490 (calcd 429.732).

**Instrumentation.** All experiments were carried out under an atmosphere of dry nitrogen, using standard Schlenk techniques. $^1$H NMR and $^{13}$C NMR measurements were carried out on a Bruker AMX 300 spectrometer at 300.13 and 75.48 MHz, respectively. Chemical shifts ($\delta$, ppm) are given relative to TMS. Electronic absorption spectra were recorded on a Perkin-Elmer Lambda 5 UV−vis spectrophotometer connected to a Model 3600 data station. A Bio-Rad FTS-7 FTIR spectrometer was used to measure the IR spectra. Mass spectra (FAB) were recorded at the Institute of Mass Spectroscopy of the University of Amsterdam using a JEOL JMS SX/SX 102 A four-sector mass spectrometer coupled to a JEOL MS-MP7000 data system. A Varian E6 X-band spectrometer with 100 kHz field modulation was used to measure EPR spectra. 2,2′-Diphenyl-1-picrylhydrazyl (DPPH) was employed as an external "*g*-mark".

**(Spectro)electrochemistry.** Cyclic voltammograms were recorded in a gastight three-electrode cell equipped with Pt-disk working (apparent surface area of 0.38 mm$^2$), Pt-gauze auxiliary, and Ag-wire pseudoreference electrodes. The working electrode was carefully polished with a 0.25 $\mu$m grain diamond paste. All potentials are reported against the ferrocene/ferrocenium (Fc/Fc$^+$) redox couple used as an internal standard.[12] Spectroelectrochemical experiments at 293 K were performed in a previously described OTTLE cell[13] equipped with a Pt-minigrid working electrode (32 wires/cm) and quartz windows. Bulk electrolyses were carried out in a gastight cell that consisted of three electrode compartments separated at the bottom by frits (S4), with a Pt-flag working electrode (120 mm$^2$ surface) in the middle compartment and with Ag-wire pseudoreference and Pt-gauze auxiliary electrodes in the lateral compartments. The concentrations used were ($5 \times 10^{-3}$) − ($1 \times 10^{-4}$) M Pd complex/$10^{-1}$ M $Bu_4NPF_6$ (cyclic voltammetry) or $5 \times 10^{-3}$ M Pd complex/$3 \times 10^{-1}$ M $Bu_4NPF_6$ (spectroelectrochemistry, bulk electrolysis). The potential control was achieved in all cases by using a PA 4 potentiostat (EKOM, Polnà, Czech Republic). Chemical reduction was accomplished with 1% Na/Hg or with $CoCp_2$.

## Results

**Cyclic Voltammetry.** Cyclic voltammograms of the compounds **1**−**10** were recorded in $CH_2Cl_2$ or THF at 293 or 223 K. The redox potentials as listed in Table 1 are given *vs* the standard[12] Fc/Fc$^+$ redox couple. *Caution!* The study of the redox behavior of the palladium complexes **1**−**5**, **8**, and **9** was complicated by inevitable partial dissociation of the *p*-quinone ligand. The complex **2** decomposed completely. In contrast to this, the complexes **6**, **7**, and **10** could be studied without any disturbing decomposition. The dissociation of the pbq and nq ligands *prior* to the reduction of the complexes **1**, **3**−**5**, and **9** could largely be suppressed on using THF instead of more polar $CH_2Cl_2$. This phenomenon is not uncommon for the complexes Pd(L$_2$)(Q), as it was also

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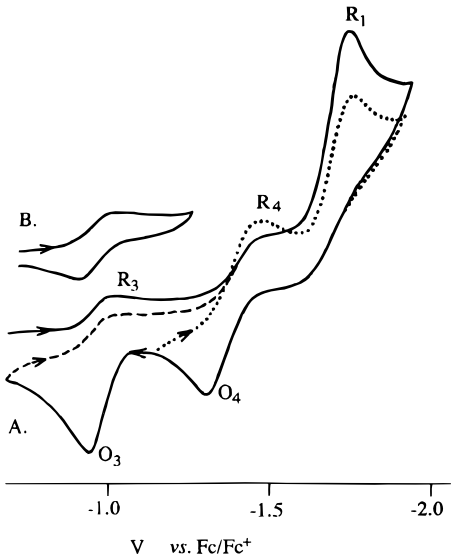



**Figure 2.** Cyclic voltammogram of $10^{-3}$ M Pd(phen)(pbq) (**4**): (A) $R_1$ = reduction of **4**, $R_3/O_3$ = the redox couple pbq/pbsq; $R_4/O_4$ = the redox couple pbsq/pbhq; (B) $R_3/O_3$ recorded *prior* to the reduction of **4**. Conditions: $N_2$-saturated solution in $CH_2Cl_2$ containing 0.1 M $Bu_4NPF_6$, Pt-disk electrode, 100 mV/s scan rate, 293 K.

reported[5b] for L = $PPh_3$. In the latter case, the decomposition could also be minimized by using less polar solvents: *viz.*, acetone instead of acetonitrile.

The complexes Pd(N⌒N)(pbq) (**3**−**5**) are reduced at 293 K in a chemically irreversible step at 20−500 mV/s, as indicated by the complete absence of an anodic counterpeak (see Figure 2). The reduction of these complexes takes place at a potential more negative than the successive one-electron reductions of the free pbq, producing pbsq (sq = semiquinone radical anion) and pbhq (hq = hydroquinone, the pbq dianion) (Table 1). This negative potential shift agrees with the $\pi$-coordination of pbq to the $Pd^0$ center through the C=C double bond(s),[5,7b,c] if we consider the reduction of Pd(N⌒N)(pbq) to be localized on the pbq ligand. Switching the scan direction beyond the cathodic peak of the complex (*e.g.* **4**; see Figure 2) results in a considerable increase of the anodic current due to the successive reoxidation of free pbhq and pbsq. This implies that the concentration of the reduced forms of pbq increases on passing the reduction potentials of **3**−**5**. It is thus obvious that, in a manner identical with the reduction pathways of the related complexes Pd($PPh_3$)(pbq) and Pd(COD)(pbq),[5b,c] the irreversible character of the reduction of **3**−**5** can be ascribed to the dissociation of the pbsq ligand, which is instantaneously further reduced at the applied reduction potential of the parent complexes to give free pbhq (Table 1).

Figure 2 also documents that, in contrast to the chemically reversible character of the reduction of free pbq initially present in the solution due to the partial dissociation of **4**, the reoxidation of free pbsq liberated from reduced $[Pd(phen)(pbsq)]^{\bullet-}$ completely lacks the reversibility, leaving in the solution only the original amount of free pbq. The rest of pbq is therefore assumed to re-enter the coordination sphere of $Pd^0$ in the "Pd(phen)" secondary reduction product, which leads to the complete recovery of **4**. The same route applies for the complex **3**, whereas no recoordination of pbq was observed for the complex **5**. The corresponding sequence

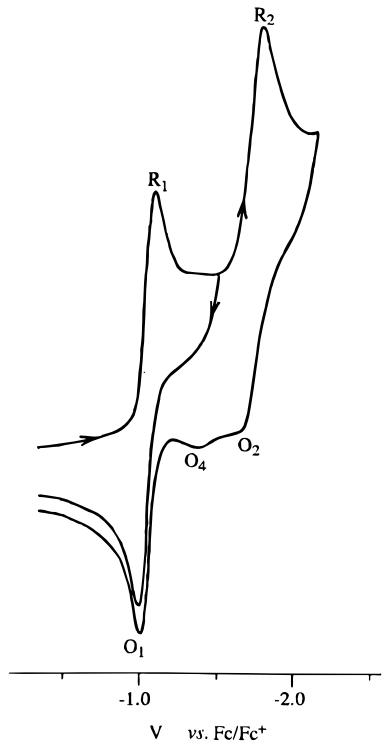
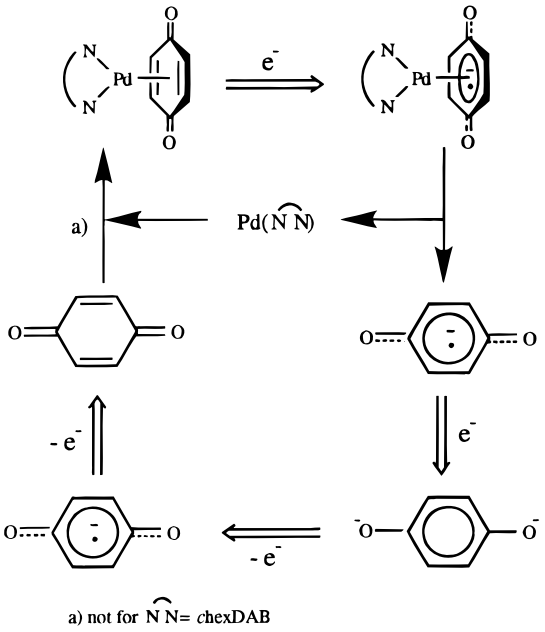



**Figure 3.** Cyclic voltammogram of $10^{-3}$ M Pd(bpym)(pbq) (**7**) in THF: $R_1/O_1$ = **7**/**7**$^{\bullet-}$, $R_2/O_2$ = **7**$^{\bullet-}$/**7**$^{2-}$, $O_4$ = oxidation of uncoordinated pbhq. Experimental conditions correspond to those in Figure 2.

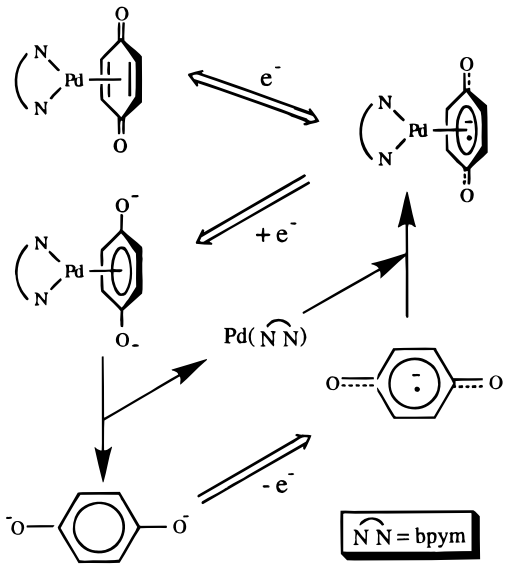
**Scheme 2**




of the electron transfer and secondary chemical steps is summarized in Scheme 2.

In contrast, coordination of strong $\pi$-acceptor α-diimine ligands makes the reduction of the pbq-complexes **1**, **6** and **7** fully chemically and electrochemically reversible on the time scale defined by scan rates $v \geq 50$ mV/s (see Figure 3). In comparison with the reduction of **3**−**5**, the $E_p^c$ values become considerably positively shifted toward the $E_{1/2}$ potential of the pbq/pbsq redox couple, which particularly applies for the complex **7** (Table 1). Corresponding UV−vis OTTLE and ESR measurements, described in more detail in the following section,

**Scheme 3**




proved that the reduction of **7** involved transfer of 1e into the lowest empty orbital localized largely on the pbq ligand, *i.e.* the $\pi^*$(pbq) LUMO. This interpretation also explains the large negative shift of the reduction potential when pbq in **7** is replaced by the less electron-withdrawing dq in **8** (see Table 1). The magnitude of the shift corresponds reasonably well with the difference between the reduction potentials of free pbq and dq (Table 1), which therefore does not favor the reduction of the bpym ligand. The reduction of **8** is chemically irreversible, probably following the reaction sequence presented in Scheme 2.

The cyclic voltammogram of **7** recorded in THF also exhibited a second cathodic peak that was negatively shifted with respect to the reduction potential of **7** by $\Delta E_p^c = 0.70$ V (Figure 3). This potential difference is similar to $\Delta E_p^c = 0.59$ V between the free pbq/pbsq and pbsq/pbhq redox couples (Table 1). We therefore suggest that the second cathodic step produces the dianion $[Pd(bpym)(pbhq)]^{2-}$ ($\mathbf{7}^{2-}$). This step is chemically irreversible (the $I_p^a/I_p^c$ ratio is ~0.7 at $v = 100$ mV/s), probably due to the dissociation of the pbhq ligand whose reoxidation was observed on the reverse positive scan at $E_p^a = -1.35$ V, producing free pbsq (Figure 3). The latter anodic step is probably followed by a complete recovery of $[Pd(bpym)(pbsq)]^{\bullet-}$, as no reoxidation of free pbsq at $E_p^a \approx -0.8$ V (Table 1) could be detected on the continued reverse scan. The reduction pathway of **7** is summarized in Scheme 3.

The cyclic voltammogram of the complex **6** resembles that of **7**. On closer inspection, however, it reveals two striking differences. First, the chemically reversible reduction of **6** ($I_p^a/I_p^c = 1$ at $v > 50$ mV/s) occurs more *negatively* by 300 mV than was found for the reduction of **7**, although the reversible reduction of free *o,o-i*Pr$_2$-BIAN was found to be more *positive* by 260 mV than that of free bpym (Table 1). It is obvious that just the opposite trend should be observed, taking into account the apparently stronger $\pi$-acceptor character of *o,o-i*Pr$_2$-BIAN relative to that of 2,2′-bipyrimidine. Second, the difference between the reduction potentials of **6** and $\mathbf{6}^{\bullet-}$ is apparently larger than that found for **7** and $\mathbf{7}^{\bullet-}$; *viz.*, $\Delta E_p^c$(**6** *vs* $\mathbf{6}^{\bullet-}$) = 0.91 V (Table 1). The reduction of $\mathbf{6}^{\bullet-}$ to give $\mathbf{6}^{2-}$ is totally chemically irreversible at room temperature and at $v \leq 1$ V/s. It produces a species that becomes reoxidized at $E_p^a = -1.96$ V, probably free $[o,o\text{-}i\text{Pr}_2\text{-BIAN}]^{\bullet-}$ (see Table 1), and thus is not free pbhq, found as the secondary product of the irreversible reduction of $[Pd(bpym)(pbsq)]^{\bullet-}$.

The last mononuclear Pd(N⌒N)(Q) complexes studied by cyclic voltammetry were **9** and **10**, *i.e.* the nq derivatives of **3** and **6**, respectively (see Table 1). In general, there is no substantial difference between the voltammetric responses of **3** and **6** (see above) and those of **9** and **10**, respectively. Thus, the oxidations of the latter compounds are chemically irreversible, and the $E_p^a$ potentials again fall within the range of +0.6−0.4 V *vs* Fc/Fc$^+$. The one-electron reduction of **9** results in rapid dissociation of free nsq according to Scheme 2, whereas **10** is reduced to stable $\mathbf{10}^{\bullet-}$. Importantly, the replacement of pbq in **3** and **6** by less electron-withdrawing nq (see Table 1) in **9** and **10**, respectively, shifts the reduction potential negatively only in the case of **9**. The reduction potentials of **6** and **10** are identical, which also applies for the one-electron reduction of $\mathbf{6}^{\bullet-}$ and $\mathbf{10}^{\bullet-}$. It is noteworthy that the 2e-reduced complex $\mathbf{10}^{2-}$ is significantly more stable ($I_p^a/I_p^c = 0.95$ at $v =$ 100 mV/s; electrochemically quasireversible step with $\Delta E_p = 150$ mV *vs* 120 mV for Fc/Fc$^+$) than the corresponding $\mathbf{6}^{2-}$ (see above).

The dafo ligand in the dinuclear complex Pd$_2$($\mu$-dafo)-($\mu$-pbq)$_2$ (**1**) is the strongest $\pi$-acceptor α-diimine used for this study, as evidenced by its rather positive reduction potential (Table 1). It is therefore not surprising that, when its cyclic voltammogram is recorded in $CH_2Cl_2$ at $v \geq 50$ mV/s, **1** is reduced in a chemically reversible step. Similarly to **6**, the reduction potential of **1** is more negative than that of Pd(bpym)(pbq) (**7**). Table 1 documents that this result is again in contradiction with the much higher $\pi$-acceptor capacity of the dafo ligand with respect to that of 2,2′-bipyrimidine.

In contrast to the apparent N⌒N- and Q-ligand dependence of the reduction potentials, the complexes under study are irreversibly oxidized within a rather narrow $\Delta E_p^a$ interval of 200 mV (see Table 1). The intrinsic instability of the oxidized complexes may have its origin in rapid dissociation of the Q ligand, as was documented[5b] for the Pd(PPh$_3$)$_2$(pbq) derivative. We did not investigate the oxidation processes in detail. The only slight variation of the anodic potentials, albeit with neglect of the influence of the chemically irreversible nature of the Pd$^0$ oxidation, nevertheless testifies to a strong buffer effect of the electron-withdrawing Q ligand, largely compensating for the increased $\sigma$-donation from more basic α-diimine or PPh$_3$[5b] ligands.

**UV−Vis and EPR Spectroscopy.** The conventional cyclic voltammetry on the time scale of seconds indicated that the complex **7** undergoes one-electron reduction, producing the stable radical anion $\mathbf{7}^{\bullet-}$. The thin-layer cyclic voltammogram of **7** recorded within the OTTLE cell at $v = 2$ mV/s confirmed the chemical and electrochemical reversibility of the reduction step at longer times. No anodic peak due to the reoxidation of the free pbsq was observed after the scan direction had been reversed beyond the cathodic peak of **7**. The same result was obtained when **7** was kept singly reduced for 10 min prior to the scan reversal. The UV−vis spectrum of $\mathbf{7}^{\bullet-}$ in THF exhibited an intense UV band at 320 nm and visible bands at 403 (sh), 427, and 445 nm. These

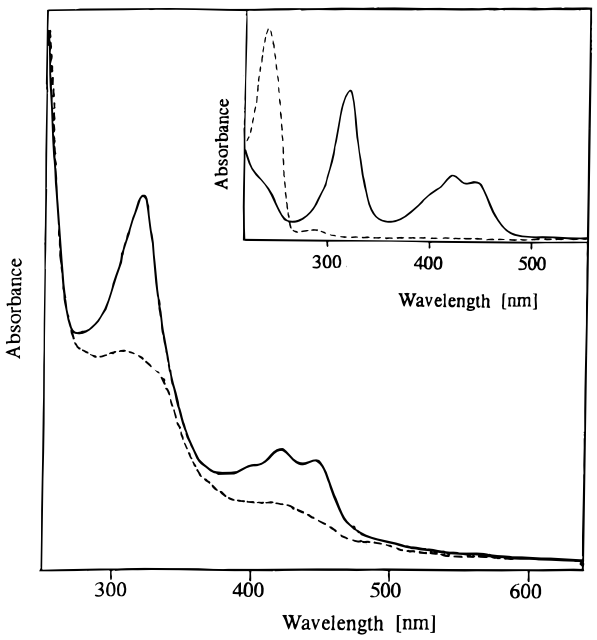



**Figure 4.** Reduction of Pd(bpym)(pbq) (**7**) in THF/0.3 M $Bu_4NPF_6$ within the OTTLE cell[13] at 293 K monitored by UV−vis spectroscopy: (dashed line) **7**; (solid line) **7**$^{\bullet-}$. Insert: (dashed line) uncoordinated pbq; (solid line) uncoordinated pbsq.

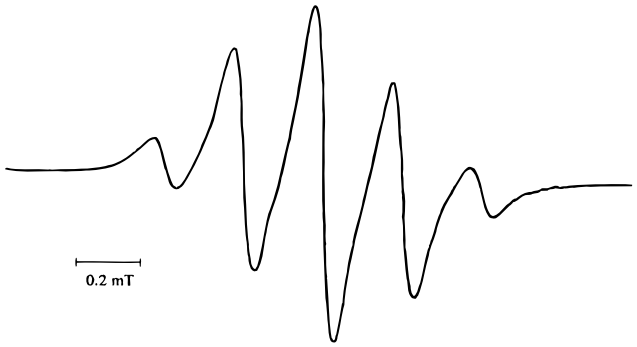



**Figure 5.** EPR spectrum of $[CoCp_2]^+$[Pd(bpym)(pbsq)]$^{\bullet-}$ (**7**$^{\bullet-}$) in THF at 293 K.

band maxima are practically identical with those of free pbsq (see Figure 4). This result thus proves that the reduction of **7** is largely localized on the pbq ligand, producing [Pd(bpym)(pbsq)]$^{\bullet-}$ (**7**$^{\bullet-}$) (see Scheme 3). Similarly, a negligible difference was found between the UV−vis spectra of the radical complex $[Co(CN)_5(pbsq)]^{3-}$ and free pbsq in DMF.[14]

Chemical reduction of **7** in THF by $CoCp_2$ ($E_{1/2}(CoCp_2^{+/0}) = -1.33$ V *vs* $Fc/Fc^+$) resulted in a concomitant appearance of a five-line EPR spectrum of $CoCp_2^+$**7**$^{\bullet-}$ at $g = 2.0049$ and with the line-intensity pattern 1:4:6:4:1 as a result of the hyperfine splitting due to four equivalent $^1H$ nuclei of the pbsq ligand ($a_H = 0.248$ mT) (Figure 5). The EPR spectrum of free pbsq in THF is very similar ($g = 2.0046$, $a_H = 0.252$ mT), although an apparent difference exists in the line width ($\Delta H = 0.08$ mT for **7**$^{\bullet-}$ but only 0.025 mT for free pbsq under the same experimental conditions). No hyperfine splitting due to the $^{105}Pd$ nucleus (natural abundance 22.2%, $I = {}^5/_2$)[15] was observed in the EPR spectrum of

(14) Vlček, A., Jr.; Klíma, J.; Vlček, A. A. *Inorg. Chim. Acta* **1983**, *69*, 191.
(15) Senftleber, F. C.; Geiger, W. E., Jr. *Inorg. Chem.* **1978**, *17*, 3615.

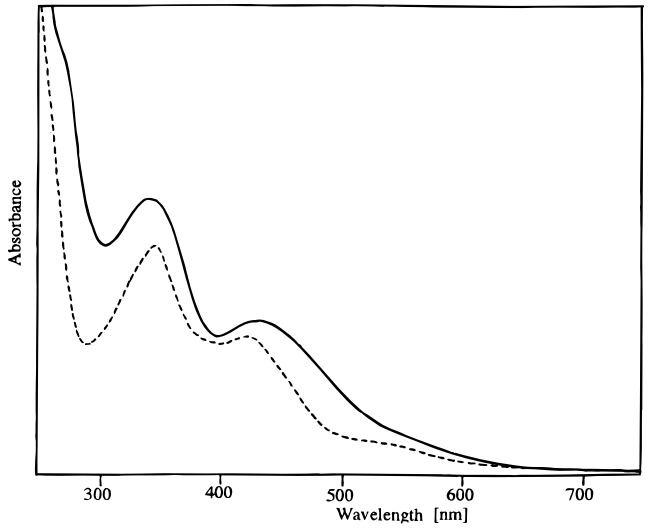



**Figure 6.** Reduction of Pd(*o,o-i*$Pr_2$-BIAN)(pbq) (**6**) in $CH_2Cl_2$/0.3 M $Bu_4NPF_6$ within the OTTLE cell[13] at 293 K monitored by UV−vis spectroscopy: (dashed line) **6**; (solid line) **6**$^{\bullet-}$.

$CoCp_2^+$**7**$^{\bullet-}$. These features, together with almost identical UV−vis spectra of **7**$^{\bullet-}$ and free pbsq (see Figure 4), indicate that the pbsq ligand in **7**$^{\bullet-}$ is only weakly bound to the $Pd^0$ center, resembling significantly free pbsq in the orbital energies of its $\pi$-MO levels and in the spin density distribution. The equivalent $^1H$ hyperfine splitting, together with the electrochemical reversibility of the reduction step (see above), implies that the pbsq ligand remains linked to palladium in an almost unaltered manner as pbq in **7**, *i.e.* through the aromatic ring (see Schemes 2 and 3). The relatively broad lines in the ESR spectrum of **7**$^{\bullet-}$ point to a dynamic behavior of the $\pi$-bound pbsq ligand. The nature of this process may be very similar to the rearrangement of the alternatively $\eta^2$-bound pbq ligand in **7**, as evidenced by NMR spectroscopy at variable temperatures.[7b,c]

The reduction of the complex **6** in $CH_2Cl_2$ was also followed *in situ* by UV−vis spectroscopy (Figure 6). In contrast to the reduction of **7**, the UV−vis spectrum of singly reduced **6** does not exhibit the distinct absorption bands belonging to free or coordinated pbsq (see Figure 4). This result implies that the electron-transfer step is not predominantly localized on the pbq ligand in **6**, as was already indicated by cyclic voltammetry (see above). The UV−vis OTTLE experiment with **6** was also performed in THF and led to a result very similar to that as shown in Figure 6. Subsequent reoxidation of **6**$^{\bullet-}$, controlled by the reverse thin-layer cyclic voltammetric response, led in both solvents to the complete reappearance of the initial UV−vis spectrum of parent **6**. The absence of free pbsq in the reduced solution witnessed to the stability of the radical **6**$^{\bullet-}$ on the time scale of minutes.

The reduction of **6** was further investigated by EPR spectroscopy. Prior to the EPR measurement bulk electrolysis of **6** was carried out in THF at $E = -1.70$ V *vs* $Fc/Fc^+$. The electrolysis was stopped after the cathodic current had dropped to *ca.* 85% of its initial value, *i.e.* after *ca.* 30 min. Comparison of cyclic voltammograms recorded before and directly after the electrolysis revealed approximately 30% decomposition of **6**$^{\bullet-}$. Besides peaks belonging to the reduction and oxidation of free pbsq (see Table 1), a new, chemically

reversible redox couple was found in the resulting cyclic voltammogram at $E_{1/2} = -2.05$ V *vs* $Fc/Fc^+$, which could be assigned according to the data in Table 1 to free *o,o*-*i*$Pr_2$-$BIAN^{0/\bullet-}$. The concentration of free pbsq and *o,o*-*i*$Pr_2$-BIAN in the electrolyzed solution corresponded well with the degree of the decomposition of $\mathbf{6}^{\bullet-}$. The liberation of free *o,o*-*i*$Pr_2$-BIAN (primarily produced in the form of the radical anion and concomitantly reoxidized at the applied reduction potential of **6**) is thus in sharp contrast to the chemically irreversible reduction of the complexes **3**−**5** (see above), which only led to the dissociation of free pbsq (see Scheme 2). The EPR spectrum of the electrolyzed solution confirmed the presence of free pbsq. Most importantly, another EPR signal, probably belonging to $\mathbf{6}^{\bullet-}$, was also observed at $g = 2.0033$ as a quintet of the 1:2:3:2:1 line-intensity pattern, caused by hyperfine splitting due to the two $^{14}N$ (99.63%, $I = 1$) nuclei of the [*o,o*-*i*$Pr_2$-BIAN]$^{\bullet-}$ ligand ($a_N = 0.633$ mT, line width $\Delta H = 0.33$ mT). The latter result is thus consistent with the conclusion drawn from the cyclic voltammetric and UV−vis OTTLE experiments that the one-electron reduction of **6** is likely not localized on the pbq ligand but largely on *o,o*-*i*$Pr_2$-BIAN.

The last redox couple that was found chemically reversible on the time scale of cyclic voltammetry, *i.e.* $\mathbf{1}/\mathbf{1}^{\bullet-}$, was also investigated by the UV−vis OTTLE technique. The reduction of $Pd_2(\mu\text{-dafo})(\mu\text{-pbq})_2$ (**1**) resulted in the disappearance of its broad absorption band at 291 nm tailing down to 400 nm. A new intense band arose at 240 nm, accompanied by a less intense, structured one with maxima at 299 and 315 nm. A weak absorption was also observed between 500 and 800 nm. These features strongly resemble intraligand (IL) electronic transitions of the free radical anion [dafo]$^{\bullet-}$, generated in $CH_3CN$, that absorbs strongly at 251, 300 (sh), and 318 nm and weakly at 425, 529 (sh), 554 (sh), 595, 647, 726, and 800 nm. This, of course, points to the dafo-localized one-electron reduction of **1**, in agreement with the cyclic voltammetric information and with the comparable reduction path of the complex **6**. Unfortunately, the radical anionic complex $[Pd_2(\mu\text{-dafo})(\mu\text{-pbq})_2]^{\bullet-}$ ($\mathbf{1}^{\bullet-}$) decomposed in the course of the UV−vis OTTLE experiment. The decomposition was indicated, besides the diminished absorption of $\mathbf{1}^{\bullet-}$, by constantly growing visible absorption bands at 420 and 445 nm belonging to free pbsq. Indeed, free pbsq was the only radical product detected by ESR spectroscopy after **1** had been electrolyzed in the bulk solution.



## Discussion

The complexes Pd(N⌒N)(Q) are stabilized by $\pi$-back-donation from the electron-rich $Pd^0$ center to the empty $\pi^*$ orbitals of both noninnocent α-diimine and *p*-quinone ligands. Increasing the basicity of the N⌒N ligand in the series of Pd(N⌒N)(pbq) (N⌒N = bpy (**3**), phen (**4**), chexDAB (**5**), bpym (**7**)) complexes does not influence significantly the oxidation potentials of the complexes. The outflow of the electron density from the N⌒N ligands is directed toward the pbq ligand *via* the Pd → pbq $\pi$-back-donation. As a consequence, the energy of the largely Pd-localized HOMO is rather invariable, whereas the energy of the LUMO, which is assumed on the basis of our cyclic voltammetric, UV−vis OTTLE, and EPR results to have a predominant $\pi^*$(pbq) character, considerably increases in the order of the increasing basicity of N⌒N, *i.e.* bpym < phen < bpy ≈ chexDAB. The reduction potentials of Pd(N⌒N)(Q) therefore shift negatively in the same order. The absolute values of the potential shifts should be considered, however, with care due to the chemically irreversible character of the redox steps, with the exception of the reversible 1e reductions of **6**, **7**, and **10.** The fact that the reduction potentials are more negative with respect to the value for free pbq is in agreement with the $\pi$-coordination of pbq through its olefinic part.[7b,c] The same trend applies for the $\pi$-Q complexes CpM(Q) (M = Rh, Ir; Q = dq, 2,6-*t*$Bu_2$bq)[5a] and Pd($L_2$)(Q) (L = $PPh_3$,[5b] $L_2$ = COD;[5c] Q = pbq, dq, nq). The conformity of the oxidation potentials of Pd($PPh_3$)$_2$(pbq) and Pd(COD)(pbq) with those of **3**−**5** and **7** (see Table 1) nicely documents the buffer effect of the pbq ligand on the variation of the HOMO energy, which remains almost unchanged regardless of the substitution of the N⌒N ligands by different bases.

The reduction potential of **7** only deviates by 200 mV from that of free pbq. This small potential difference may indicate only a slight perturbation of the pbq ligand. This is in line with its relatively large $\tilde{\nu}$(C═O) wavenumber (1645 $cm^{-1}$),[7b,c] which is close to that of uncoordinated pbq (1662 $cm^{-1}$). For instance, the stronger Pd → pbq back-donation in Pd(bpy)(pbq) (**3**) relative to that in **7** is reflected in the considerably more negative reduction potential (Table 1) and in the $\tilde{\nu}$(C═O) wavenumber diminished to 1602 $cm^{-1}$. Considering the rather loosely bound pbq in **7**, it is therefore not surprising that the UV−vis and EPR spectra of $\mathbf{7}^{\bullet-}$ are almost unaltered in comparison with those of the uncoordinated pbq. The Pd−pbsq bond is apparently weak, which accounts for rapid dissociation of the pbsq radical anion on coordination of stronger bases such as 2,2′-bipyridine, 1,10-phenathroline, and $PPh_3$.[5b]

The predominant localization of the one-electron reduction of **3**−**5** and **7** on the pbq ligand is further corroborated by the observed negative shifts of the $E_p^c$ values on replacement of pbq in **7** and **3** by less electron-withdrawing dq in **8** and nq in **9**, respectively, which are close to the $\Delta E_{1/2}$ shifts for the uncoordinated *p*-quinones. According to the reduction potentials of the α-diimines in Table 1, the *o,o*-*i*$Pr_2$-BIAN ligand in **6** and the dafo ligand in **1** are significantly stronger $\pi$-acceptors than the bpym ligand in **7**. In sharp contrast to this, the complexes **1** and **6** are reduced at potentials more negative than for **7**, whereas an opposite trend might be anticipated. The singly reduced species $\mathbf{1}^{\bullet-}$ and $\mathbf{6}^{\bullet-}$ live long enough to be detected by UV−vis and, in the latter case, by EPR spectroscopy. The spectroscopic results, in particular the $^{14}N$ hyperfine splitting of the EPR signal of $\mathbf{6}^{\bullet-}$, the presence of the IL bands due to the [dafo]$^{\bullet-}$ radical anion in the UV−vis spectrum of $\mathbf{1}^{\bullet-}$, and the absent IL bands of pbsq in the UV−vis spectra of both $\mathbf{1}^{\bullet-}$ and $\mathbf{6}^{\bullet-}$ (Figure 6) indicate that the unpaired electron in these radical anions largely resides on the α-diimine ligand. As anticipated, the reduction potentials of the complexes Pd(*o,o*-*i*$Pr_2$-BIAN)(Q) (Q = pbq (**6**), nq (**10**)) are not sensitive to the variation of the Q ligand, which does not apply for the bpy derivatives **3** and **9** (see Table 1), belonging to the group of Q-reducible complexes. Our explanation also agrees with the results of van Asselt *et al.*,[16] who studied

(16) van Asselt, R.; Elsevier, C. J.; Amatore, C.; Jutand, A. *Organometallics* **1997**, *16*, 317.

reduction of the closely related complex Pd(*p*Tol-BIAN)(MA) (MA = maleic anhydride). The authors also argued that the first, chemically reversible reduction step at $E_{1/2}$, which is quite similar to $E_{1/2}$(**6**/**6**$^{\bullet-}$) (see Table 1), involves electron transfer to the *p*Tol-BIAN ligand.

The striking difference in the character of the reduction between the series of the complexes **3**−**5** and **7**−**9** and, on the other side, **1**, **6**, and **10** cannot be clearly explained on the basis of the existing experimental data. The fact that the SOMO's of **1**$^{\bullet-}$ and **6**$^{\bullet-}$ appear to possess a major contribution from the $\pi$*(N⌒N) orbital does not correspond to the more electron-withdrawing nature of uncoordinated pbq relative to that of *o*,*o*-*i*Pr$_2$-BIAN and dafo. In this instance it is particularly important to note that a similar situation applies for the tetracyanoethylene (tcne) and 2,2′-bipyridine ligands in Pd$^0$(bpy)(tcne).[17] The one-electron reduction of this complex was postulated as bpy-localized, regardless of the much stronger $\pi$-acceptor character of the uncoordinated tcne in comparison with that of 2,2′-bipyridine: $E_{1/2}$(tcne$^{0/\bullet-}$) − $E_{1/2}$(bpy$^{0/\bullet-}$) = 2.4 V.[17] The strong destabilization of the $\pi$*(tcne) LUMO and stabilization of the $\pi$*(bpy) LUMO on coordination of the ligands to the palladium center may reasonably account for this intriguing behavior. In this respect it should be recalled that 0.1 V corresponds only to roughly 2.5 kcal, so that very subtle energetic changes may result in drastic changes of the voltammetric response within a series of complexes. The actual bonding situation in **1**, **3**, and **6** and in their radical anions needs to be the subject of further investigation, in particular by the DFT-MO method, which can provide[18] a revealing information about the character of the frontier orbitals of these complexes.

The difference in the stability between the dinuclear complexes **1** and **2** also deserves attention. The complex **2** thermally decomposes in solution *prior* to its reduction, whereas **1** is relatively stable and can be reduced in a chemically reversible step on the subsecond time scale. The reversibility of the redox couple **1**/**1**$^{\bullet-}$ can reasonably be ascribed to the pronounced $\pi$-acceptor ability of the dafo ligand, whose low-lying $\pi$* LUMO has been shown by EHT calculations[19] to reside 60% on the bridging carbonyl group. The SLUMO of dafo then resembles in energy the corresponding LUMO's of 2,2′-bipyridine and the dafe ligands. The EHT calculations thus account well for the observed large difference between the reduction potentials of the uncoordinated dafo and dafe (Table 1). The chemical irreversibility of the dafe reduction can be explained by facile dissociation of one of the bridgehead hydrogen atoms from [dafe]$^{\bullet-}$. It was documented[20] that 2,2′-bipyridine reacts with the (Cp′)$_2$Ti($\eta^2$-C$_2$(SiMe$_3$)) complex to give (Cp′)$_2$Ti(bpy), whose electronic structure can be discussed in terms of a Ti$^{III}$ center with bound [bpy]$^{\bullet-}$, arising from the electron transfer Ti$^{II}$ → bpy. In contrast to this, the reaction of (Cp′)$_2$Ti($\eta^2$-C$_2$(SiMe$_3$)$_2$) with 4,5-diazafluorene (dafe) is followed by a decomposition of the transient [dafe]$^{\bullet-}$ ligand, producing the dafe anion and dihydrogen.

## Conclusions

We have shown that the character of the one-electron reduction of the complexes **1**−**10** strongly depends on the $\pi$-acceptor capacity of the α-diimine (N⌒N) and *p*-quinone ligands. On coordination of strong N⌒N bases in Pd(N⌒N)(pbq) (N⌒N = chexDAB, bpy, phen), the pbq-localized reduction leads to reversible dissociation of the pbsq ligand, whereas the radical anion [Pd(bpym)(pbsq)]$^{\bullet-}$ is inherently stable. The character of the reduction becomes drastically changed on coordination of strong $\pi$-acceptor α-diimine ligands such as dafo and *o*,*o*-*i*Pr$_2$-BIAN. The one-electron reduction of the complexes Pd$_2$($\mu$-dafo)($\mu$-pbq) and Pd(*o*,*o*-*i*Pr$_2$-BIAN)(Q) (Q = pbq, nq) can be regarded as localized on the α-diimine ligand.

The oxidation potential of the Pd center in the complexes under study is hardly influenced by the basicity of the α-diimine ligand. This property is in sharp contrast to the observed variability of the reduction potentials. The small range of anodic potentials may explain the barely noticeable difference in reactivity of several PdCl$_2$(α-diimine) complexes toward homogeneously catalyzed C−C cross-coupling reactions.[21]

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