

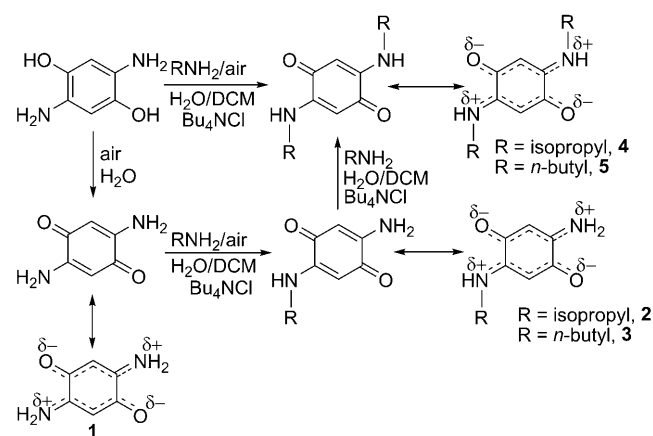
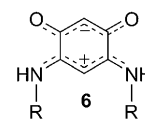
# Straightforward Synthesis of Substituted *p*-Quinones: Isolation of a Key Intermediate and Use as a Bridging Ligand in a Diruthenium Complex

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Quinones are naturally occurring redox active molecules that function in vital electron-transport processes, often in conjugation with a transition-metal center.<sup>[1]</sup> *p*-Quinones, such as vitamin K derivatives, ubiquinones or plastoquinones, play important roles in photosynthesis, respiration, and information-transfer processes.<sup>[2,3]</sup> Substituted *p*-quinones have been extensively used as ligands in coordination chemistry in recent years.<sup>[4–6]</sup> The remarkable properties that such ligands impart to their metal complexes make such compounds useful in a variety of fields, such as homogenous catalysis,<sup>[7]</sup> supramolecular chemistry,<sup>[5,8]</sup> coordination polymers,<sup>[9,10]</sup> and as bridging ligands in combination with redox active metal centers such as ruthenium.<sup>[11–14]</sup> The last field has gained tremendous attention in recent years because of ambiguities arising in oxidation-state formulations also with “organometallic-type” non-innocent ligands.<sup>[15]</sup> In addition, the creation of quinone-based molecular magnets is a lively field of research that has produced many interesting results.<sup>[16–20]</sup>

2,5-Diamino-1,4-benzoquinone **1**<sup>[21]</sup> and its substituted derivatives<sup>[22,23]</sup> have been known for decades. The synthesis of **1** has previously been reported and such syntheses are

rarely straightforward one-pot reactions.<sup>[21,24]</sup> Some years back Braunstein et al. reported a straightforward and “green” synthesis of a new class of molecules that occurs through transamination.<sup>[25,26]</sup> Such molecules, which are isomers of **1** and its derivatives, are best described as zwitterions, **6**.<sup>[25,26]</sup> Inspired by this process we looked for an elegant synthesis for the parent compound **1** and for possible intermediates formed during the transamination process. Herein we report a simple one-pot synthesis of **1** and its mono- (**2** and **3**) and dialkyl (**4** and **5**) derivatives (Scheme 1). To elucidate



Scheme 1.

the use of such ligands in coordination and redox chemistry we have prepared a diruthenium complex with the doubly deprotonated form of **4**:  $[\{\text{Ru}(\text{acac})_2\}_2(\mu\text{-4}_{-2\text{H}})]$  (**7**;  $\text{acac}^-$  = acetylacetonato). Redox processes involving multinuclear ruthenium complexes are known to display phenomena such as charge-transfer isomerism<sup>[27]</sup> and valence ambiguity when in combination with potentially non-innocent ligands.<sup>[11,13]</sup>

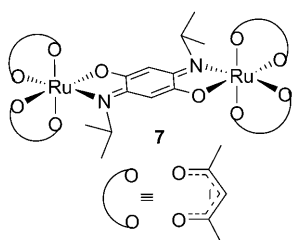
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Structural, electrochemical, magnetic, and UV/Vis-NIR and EPR spectroelectrochemical results are reported below.

Reaction of 2,5-diamino-1,4-dihydroxybenzene in water with air leads to the formation of **1**. This is a one-pot reaction and, in stark contrast to the synthetic procedures known in the literature for **1**, does not require any further purification.<sup>[21,24]</sup>

When the same reaction was carried out in the presence of isopropylamine or *n*-butylamine we observed “double” transamination leading to the formation of **4** or **5**, respectively. Such transamination reactions have been observed previously, but this is only the second example of transamination reactions in quinonoid chemistry.<sup>[25]</sup> However, in contrast to reference [25] the yields of **4** and **5** were unsatisfactory. Careful examination of the reaction mixture showed that the formation of the parent compound **1**, which is poorly soluble in water, is extremely fast and its precipitation limits the yield of the transamination. To circumvent this problem, we carried out the transamination reactions in a mixture of water, dichloromethane, and THF with Bu<sub>4</sub>NCl as a phase-transfer catalyst (see Supporting Information). These reaction conditions not only led to higher yields, but also to the formation of a second product. Analysis of the products showed it to be a mixture of the monosubstituted products, **2** or **3**, and the disubstituted products, **4** or **5**. Thus, the monosubstituted compounds **2** and **3** are key intermediates in the transamination reactions leading to the formation of the disubstituted products **4** and **5**, respectively, as has been proposed for the formation of compounds of type **6**. However, in these cases they could not be isolated due to the extremely fast second transamination reaction leading to the disubstituted products.<sup>[25,26]</sup> To the best of our knowledge, examples of asymmetrically substituted *p*-quinones, such as **2** and **3**, are extremely rare in the literature.<sup>[28]</sup>

Compounds **1–5** were characterized by <sup>1</sup>H- and <sup>13</sup>C NMR spectroscopy, elemental analysis, and mass spectrometry. Whereas compounds **4** and **5** showed only one N–H signal in their <sup>1</sup>H NMR spectra, compounds **2** and **3** showed two N–H signals, which was the first evidence for the formation of these monosubstituted species. To elucidate the bonding situation within these compounds, we determined, through X-ray diffraction, the crystal structure of **4** (see Figure S1 in the Supporting Information). Even though the crystal structure of **4** has been reported previously, no detailed analysis of the bonding situation, with respect to localization and delocalization of electrons, was presented.<sup>[23]</sup> A look at the bond lengths within **4** (see Figure S1 in the Supporting Infor-

mation) shows that there is extensive delocalization within the O1–C1–C2–C3'–N1' and N1–C3–C2'–C1'–O1' sections of the molecule and these are connected by authentic C–C single bonds with C1–C3 distances of 1.519(2) Å (see Table S2 in the Supporting Information). These molecules can thus be considered as two merocyanine units connected by C–C single bonds as has been observed before.<sup>[29]</sup> Cyclic voltammetry experiments on **2–5** in CH<sub>2</sub>Cl<sub>2</sub> with 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> showed one oxidation and two reduction processes (see Figure S2 in the Supporting Information). While the first reduction is reversible, the oxidation and second reduction are irreversible processes. The influence of double-alkyl, rather than single-alkyl, substitution is shown by slightly more negative reduction potentials for **4** and **5** compared with **2** and **3**, respectively. The influence of *n*-butyl versus isopropyl groups on the reduction potentials is negligible (Table 1).

Table 1. Redox potentials of the ligands **2–5** and complex **7**.<sup>[a]</sup>

|          | $E_{1/2}^{\text{ox1}} (\Delta E_p)^{[b]}$ | $E_{1/2}^{\text{ox2}} (\Delta E_p)^{[b]}$ | $E_{1/2}^{\text{red1}} (\Delta E_p)^{[b]}$ | $E_{1/2}^{\text{red2}} (\Delta E_p)^{[b]}$ |
|----------|-------------------------------------------|-------------------------------------------|--------------------------------------------|--------------------------------------------|
| <b>2</b> | 1.04 <sup>[c]</sup>                       | n.o. <sup>[e]</sup>                       | −1.43 (70)                                 | −1.88 <sup>[d]</sup>                       |
| <b>3</b> | 1.01 <sup>[c]</sup>                       | n.o.                                      | −1.48 (65)                                 | −1.92 <sup>[d]</sup>                       |
| <b>4</b> | 1.00 <sup>[c]</sup>                       | n.o.                                      | −1.50 (73)                                 | −2.10 <sup>[d]</sup>                       |
| <b>5</b> | 0.95 <sup>[c]</sup>                       | n.o.                                      | −1.56 (75)                                 | −2.05 <sup>[d]</sup>                       |
| <b>7</b> | 0.11 (60)                                 | 0.76 (65)                                 | −1.09 (65)                                 | −1.72 (62)                                 |

[a] Electrochemical potentials in V from cyclic voltammetry in CH<sub>2</sub>Cl<sub>2</sub> with 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> at 298 K; scan rate: 100 mV s<sup>−1</sup>; ferrocene/ferrocenium was used as the internal standard. [b]  $\Delta E_p$  = difference between peak potentials in mV. [c] Anodic peak potential for irreversible oxidation. [d] Cathodic peak potential for irreversible reduction. [e] n.o. = not observed.

To test the utility of such ligands in coordination and redox chemistry we prepared a dinuclear complex, **7**, with the doubly deprotonated form of **4**. It was discovered that compound **7** is paramagnetic, with two Ru<sup>III</sup> centers. This compound was characterized by elemental analysis and mass spectrometry. The Ru<sup>III</sup> complexes of this family are known to show temperature-independent paramagnetism (TIP).<sup>[13,30]</sup> The magnetic susceptibility of compound **7** was measured with a SQUID setup (see Figure S3 in the Supporting Information). As in previously reported cases,<sup>[11,13,30]</sup> the spectrum was fitted by considering the system as composed of dimers with a small fraction, *P*, of defective paramagnetic sites<sup>[11,31]</sup> and using *g*, TIP, and the magnetic exchange, *J*, as free parameters; this yielded TIP = 0.01 ± 0.01 cm<sup>3</sup> mol<sup>−1</sup>, *g* = 2.1 ± 0.1, and *J* = −19 ± 3 cm<sup>−1</sup>. This anti-ferromagnetic behavior is in agreement with previous reports<sup>[11,13]</sup> and is also visible from the nonsaturated value attained by the low-temperature *M* versus *H* curves. The obtained value is comparable to those previously reported for similar compounds and its slightly diminished magnitude can probably be attributed to the reduced twisting induced by the isopropyl substituents on the imino nitrogen atoms. The discrepancy from the fit at lower temperatures can probably be attributed to the presence of either the onset of interdimer interactions or a zero-field splitting effect.<sup>[32]</sup>

While the latter case cannot be excluded, our attempt at a fit with the same parameters as above, but adding interdimer interactions,  $J'$ , obtained satisfactory agreement at low  $T$  when  $J' = -4 \pm 1 \text{ cm}^{-1}$ . The magnetic interaction pathway for  $J'$  is not purely dipolar in origin, since its magnitude is higher than that expected for a dipolar interaction transmitted by the interdimer  $\text{Ru}^{\text{III}}\text{-Ru}^{\text{III}}$  distance of  $7.649(1) \text{ \AA}$ . However this can be considered an indicative value, since single-crystal measurements would be needed for a complete determination of the local anisotropic axes of  $\text{Ru}^{\text{III}}$  and an accurate evaluation of the interdimer interactions.

The EPR spectra of all species showed no signal at room temperature. This can be attributed to the  $^2T_{2g}$  state of  $\text{Ru}^{\text{III}}$ , which leads, as in low-spin  $\text{Fe}^{\text{III}}$ , to three closely spaced Kramers doublets.<sup>[19]</sup> Thus, fast relaxation makes the system EPR silent until the solution is frozen. The observation of the signal only in a frozen matrix can perhaps be linked to the anisotropy expected for  $\text{Ru}^{\text{III}}$ <sup>[19,31,32]</sup> with tumbling processes incapable of merging the very different  $g$  values. At 110 K the EPR spectrum of **7** in  $\text{CH}_2\text{Cl}_2$  showed a weak signal (Figure 1a) and could be simulated using  $g_1 = 2.33$ ,

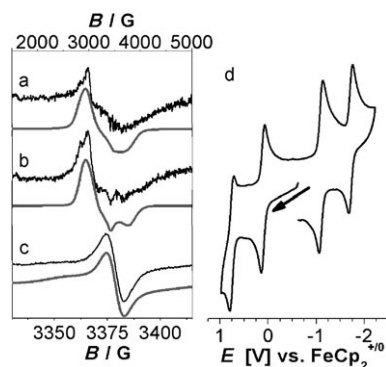


Figure 1. Left: EPR investigation of the compounds, with the upper scale referring to spectra a) and b) and the lower scale to spectrum c). All spectra have been vertically shifted for clarity and the gray lines are the corresponding simulations (see text). a) EPR spectrum of **7** at frequency  $f = 9.6722 \text{ GHz}$  in  $\text{CH}_2\text{Cl}_2$  at 110 K; b) EPR spectrum of  $\mathbf{7}^+$  at  $f = 9.6949 \text{ GHz}$ , in  $\text{CH}_2\text{Cl}_2$  with  $0.1 \text{ M Bu}_4\text{NPF}_6$  at 110 K; c) EPR spectrum of  $\mathbf{7}^-$  at  $f = 9.4741 \text{ GHz}$  in  $\text{CH}_2\text{Cl}_2$  with  $0.1 \text{ M Bu}_4\text{NPF}_6$  at 110 K; d) Cyclic voltammogram of **7** in  $\text{CH}_2\text{Cl}_2$  with  $0.1 \text{ M Bu}_4\text{NPF}_6$  at 295 K. Ferrocene/ferrocenium was used as the internal standard.

$g_2 = 2.24$  and  $g_3 = 1.91$  ( $g_{\text{av}} = 2.16$ ) in overall agreement with the extracted susceptibility value. Hyperfine interaction with the  $^{99}\text{Ru}$  and  $^{101}\text{Ru}$  isotopes (natural abundances of 13 and 17%, respectively) was considered for the simulation and gave  $A_{\parallel} = 260 \text{ MHz}$  and  $A_{\perp} = 150 \text{ MHz}$ , similar to reported literature values.<sup>[33]</sup> The weakness of the signal may indicate the detection of the fraction,  $P$ , of single  $\text{Ru}^{\text{III}}$  centers in defective dimers that would otherwise be silent due to antiferromagnetic coupling (as in the case of Cu acetate).<sup>[34]</sup> It is worth noting that  $g_1$  is slightly lower than expected for  $\text{Ru}^{\text{III}}$  centers in this type of environment, a fact that can be attributed to orbital reduction factors  $< 1$ , that is, to partial electronic delocalization onto the ligand.<sup>[19]</sup> We also obtained

crystals for compound **7** and determined its X-ray structure. A perfectly statistic disorder is present, with all  $\text{acac}^-$  and bridging ligands occupying two sets of positions around the same Ru center and 50% occupancy of each position was used in the refinements (see Experimental Section). Nonetheless the connectivity within the molecule has been unambiguously determined to be the *meso*-isomer (Figures 2 and 3). The Ru centers are in a distorted octahedral environ-

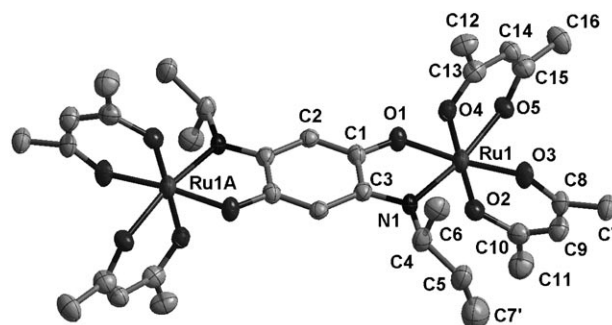


Figure 2. ORTEP view of **7** (occupancy of each set of ligands assigned to 50%).

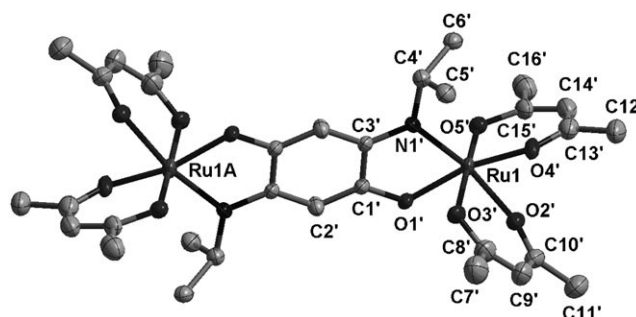


Figure 3. ORTEP view of **7'** (occupancy of each set of ligands assigned to 50%).

ment as it is coordinated by one oxygen and one nitrogen atom from the bridging ligand and four oxygen atoms from the two  $\text{acac}^-$  ligands. The bonding situation within the bridging ligand in **7** shows higher localization of the double bonds compared with free ligand **4** (see Table S2 in the Supporting Information), possibly as a result of the aforementioned delocalization of  $\text{Ru}^{\text{III}}$  electrons.<sup>[19]</sup> The C1–C3 bond, at  $1.48(3)$  ( $1.46(2)$ )  $\text{\AA}$ , remains an authentic single bond as in the case of the free ligand **4**. Such localization of bonds within a substituted *p*-quinone ligand has been observed previously in the doubly deprotonated form of **1**.<sup>[13]</sup> Thus, the bridging ligand binds to the Ru centers through  $\text{O}^-$  and imino nitrogen donors (see image of **7**). The Ru–Ru distance in **7** is  $7.840(1) \text{ \AA}$ .

Cyclic voltammetry of **7** in  $\text{CH}_2\text{Cl}_2$  with  $0.1 \text{ M Bu}_4\text{NPF}_6$  reveals two oxidation and two reduction processes (Figure 1d) that are all completely reversible. This is also authenticated by spectroelectrochemical measurements (vide infra). The

difference between the two oxidation potentials of 650 mV translates to a comproportionation constant  $K_c$  ( $K_c = 10^{\Delta E/59}$  at 298 K)<sup>[35]</sup> of the order of  $10^{11}$  for the one-electron oxidized species. The corresponding difference in the reduction potentials is 630 mV (Table 1) and the  $K_c$  value is of the order of  $10^{10}$ .

The Ru<sup>III</sup>–Ru<sup>III</sup> species **7** shows an intense LMCT ( $4_{-2H} \rightarrow Ru^{III}$ ) transition at 534 nm ( $\epsilon = 19900 M^{-1} cm^{-1}$ ; see Figure S4 in the Supporting Information). In addition, there are further ligand-centered transitions in the UV region. In the one-electron oxidized form **7**<sup>+</sup>, the LMCT band is red-shifted to 708 nm with the intensity remaining almost unchanged. Furthermore, a new band grows in the near IR region at 1515 nm with  $\epsilon$  of  $5000 M^{-1} cm^{-1}$  that disappears on second oxidation (see Figures S4 and S5 in the Supporting Information). Thus, the UV/Vis/NIR measurements of **7**<sup>+</sup> point to a mixed-valent situation leading to the formation of a Ru<sup>III</sup>–Ru<sup>IV</sup> species on one-electron oxidation. The EPR signal of **7**<sup>+</sup> at 110 K (Figure 1b) is very similar to that of **7**, strengthening the hypothesis of the detection of defective dimers for **7**. The spectrum can be simulated well with the same  $g$  and  $A$  parameters by using a narrower linewidth. The  $\Delta\nu_{1/2}$  of the IVCT (intervalence charge transfer) band at 1515 nm is measured at about  $1475 cm^{-1}$ . The Hush formulation gives  $\Delta\nu_{1/2} = (2310\nu_{IVCT})^{1/2} \approx 3905 cm^{-1}$ .<sup>[36]</sup> This points to delocalization in the mixed-valent form and hence **7**<sup>+</sup> belongs to the strongly-coupled Class III system. The one-electron reduced form **7**<sup>−</sup> shows a very strong band at 750 nm ( $\epsilon = 31700 M^{-1} cm^{-1}$ ). In addition, this species shows absorptions in the near IR region at 1725 nm ( $\epsilon = 1100 M^{-1} cm^{-1}$ ). Since the starting Ru<sup>III</sup>–Ru<sup>III</sup> compound can, in principle, be reduced to the Ru<sup>III</sup>–Ru<sup>II</sup> form, these near IR bands can be taken as evidence for a mixed-valent species. However, the EPR spectrum of **7**<sup>−</sup> at 110 K (Figure 1c) shows a strong quinone signal that shadows the much weaker Ru<sup>III</sup> line. The spectrum is well reproduced by using an isotropic signal with  $g = 2.004$ , and considering hyperfine coupling to the N nuclei. This points to a reduction of the bridging ligand leading to a three-spin situation, Ru<sup>III</sup>–( $4_{-2H}^{-\cdot}$ )Ru<sup>III</sup> ( $\uparrow, \uparrow, \downarrow$ ), with antiferromagnetic coupling between the Ru<sup>III</sup> spins. This contrasts with what has been observed for the reduced state of the compound, analogous to **7**<sup>−</sup>, with the doubly deprotonated form of **1** as the bridging ligand. In that case the metal-centered spin was observed by EPR spectroscopy.<sup>[13]</sup> This shows the subtle changes in orbital coupling pattern that can be brought about by simple substitutions on the nitrogen atoms of *p*-quinones.

In summary, we have reported a new, one-pot, synthetic route to **1** and its transaminated analogues **4** and **5**. We also detected compounds **2** and **3** as key intermediates in the transamination reaction step. Asymmetrically substituted *p*-quinones, such as **2** and **3**, are rare in the literature. Compound **4** was used then to prepare the diruthenium complex **7**. Oxidation of this compound leads to a Ru<sup>III</sup>–Ru<sup>IV</sup>-containing mixed-valent species and its reduction leads to a quinonoid radical-containing Ru<sup>III</sup>–Ru<sup>III</sup> species. Future efforts will be directed towards a target-oriented expansion of the

ligand library, tuning of the redox properties, and the use of asymmetric ligands such as **2** and **3** in coordination chemistry.

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**Keywords:** cyclic voltammetry • quinones • ruthenium • spectroelectrochemistry • synthetic methods

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