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Oxidative coupling of platinum arylamides: temperature dependent C–H or C–F cleavage

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The oxidation of an arylamido platinum complex leads to C–C coupling with selective C–H *versus* C–F bond cleavage depending on the reaction temperature.

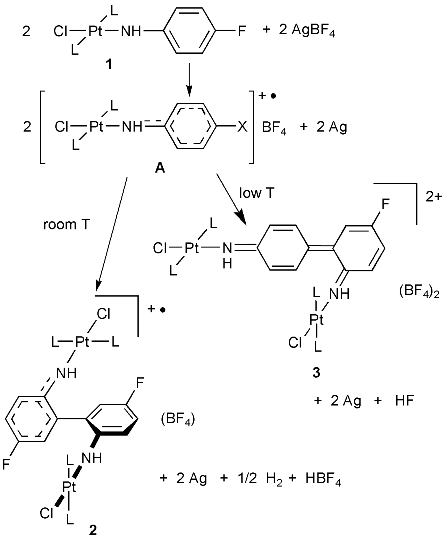
Coupling of radical cations generated by oxidation of aromatic amines is a widely used preparative method. Both electrochemical or chemical oxidation are used.[1,2] Usually the *para* positions couple to form the new C–C bond (tail to tail coupling).[1] When the *para* position is substituted, an increased stability of the radical cation is observed and a slow coupling reaction follows. Then *ortho* coupling becomes common, which has been applied to the synthesis of biaryl skeletons.[2a] In other cases (*p*-methoxy or *p*-halo substituted arylamines) 'head to tail' C–N coupling is observed to give diarylamines.[1c,d] Metal arylamido complexes (which might be looked at as *N*-substituted amines) can also undergo oxidative C–C coupling, but this reactivity has been only scarcely studied.[3–6] The oxidation of complexes [Pt(NHR)Cl(PEt$_3$)$_2$] (R = Ph, *p*-tolyl, 1-naphtyl) leads to dimerization, with formation of a new C–C bond between the *para* positions of the aryl rings or, for R = *p*-tolyl, between the *ortho* positions.[3,4] The new dimeric complexes display a rich ligand centered redox chemistry between the benzidine and biphenylene quinone diimine forms.[4–5] Sharp *et al.* have described a similar C$_{para}$–C$_{para}$ oxidative coupling in rhodium phenyl-imido/amido complexes.[6] Little is known about the oxidative coupling of other *para*-substituted arylamido complexes, although it can be presumed that the 'head to tail' C,N coupling found for some arylamines should be hampered by severe steric restrictions for arylamido complexes. We report here the behaviour of the platinum amido complex [Pt{NH(4-F–C$_6$H$_4$)}Cl(PEt$_3$)$_2$] (**1**),[7] where two different coupling modes have been found, which can be efficiently selected by simply controlling the reaction temperature. One of them is a novel C$_{ortho}$–C$_{para}$ coupling with cleavage of a C–F bond.

Upon electrochemical oxidation of **1** in a CV experiment a reversible wave is observed ($E_{1/2}$ = 0.21 V) which does not change within a wide range of scan rates (50–1000 mV s^{-1}).† This oxidation is attributed to the generation of a new species, the radical cation **A** (Scheme 1), which does not react further in the conditions of the CV experiment. When a chemical oxidation with a silver salt in acetone was carried out the monomeric radical cation could not be isolated, since coupling reactions were observed to give intensely colored dimeric products. Interestingly the nature of the product depends on the reaction temperature. At room temperature a C–C coupling at the *ortho* positions, with cleavage of two C–H bonds, was observed to give the green dimeric radical **2** (Scheme 1), a result that reflects the presence of a blocked *para* position in the ring. However, at low temperature C–F cleavage, along with C–H cleavage, was observed to give an asymmetrical bridging biphenylene quinone diimine ligand in complex **3** (Scheme 1). The reactions are remarkably selective and the radical cation **2** was obtained in 82% yield at room temperature, whereas **3** was obtained in 66% at 80 °C.‡

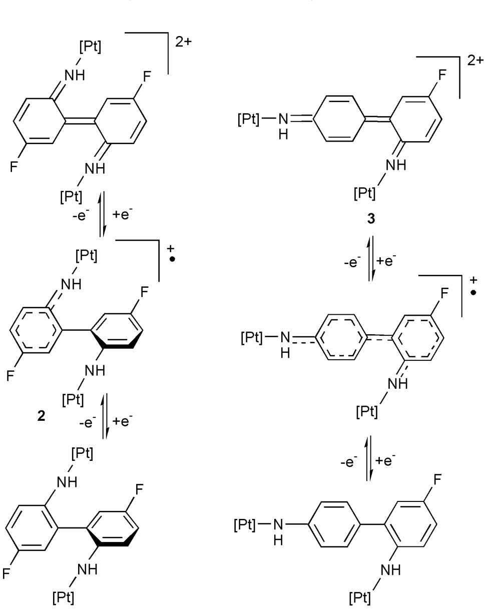
As expected for a paramagnetic complex, **2** shows no signals in the ^{19}F and ^{31}P{^{1}H} NMR spectra, and only broad signals in the ethyl region for the PEt$_3$ ligands in the ^{1}H NMR spectrum.

Complex **2** is redox active and its cyclic voltamogram shows two reversible processes corresponding to the reduction to the benzidine complex ($E_{1/2}$ = −0.06 V) and the oxidation to the quinone diimine form ($E_{1/2}$ = 0.81 V) (Scheme 2).[4]

The high potential needed for oxidation of **2** is in accordance with its remarkable stability in the air both in solution and in the solid state. Molecular models and analysis of the posible conformations of the two rings by molecular mechanics indicate that there are severe steric restrictions to adopt a planar structure in this system. This explains the reluctance of **2** to undergo oxidation to a planar quinone diimine derivative, and the fact



Scheme 1 Synthesis of **2** and **3** by oxidation of **1**.



Scheme 2 Redox activity of complexes **2** and **3**.

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that, according to the ESR spectrum of **2**, the unpaired electron is mainly delocalized over only one half of the bridging ligand. The ESR spectrum shows a signal (g = 2.0451) split by hyperfine coupling to one N and its substituents (H and ^{195}Pt) and the *ortho* H and *para* F of one ring (Fig. 1). Among the possible resonance structures, those that would delocalize the unpaired electron on the second arylamido group need a planar arrangement of the ligand and are much less contributing, so the corresponding H(meta) hyperfine couplings are small (Fig. 1).

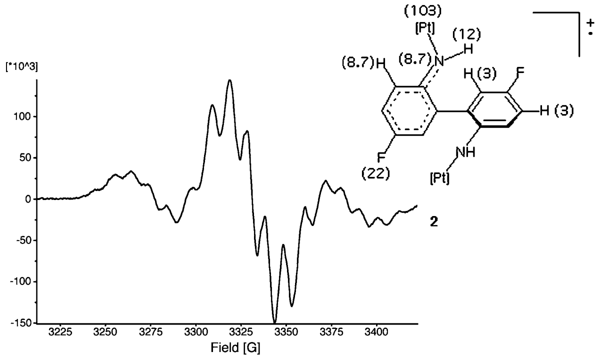

Fig. 1 Experimental ESR spectrum of **2** at 260 K (recorded in a Bruker ER83CS/ER 041 X6). The hyperfine couplings, *a* (G), were determined by simulation of the spectrum and are given in parentheses in the inset.

The X-ray crystal structure of complex **3** is shown in Fig. 2.§ There is some disorder affecting the anions and ethyl groups of the phosphines. The bridging ligand is clearly a quinone dimine derivative with a short C4–C7 distance (1.387(15) Å) and bond lengths in the rings that alternate long and short values reflecting the loss of aromaticity. Both rings define a small dihedral angle of 20.9°. When a CV experiment was carried out on a solution of complex **3** in CH_2Cl_2, two reversible processes were observed corresponding to the reduction of **3** to the radical monocation ($E_{1/2}$ = 0.39 V) and the benzidine form ($E_{1/2}$ = 0.00 V), a behaviour analogous to complex **2** (Scheme 2).

The temperature is the main factor that determines the outcome of the oxidation reaction of **1**. The same results were obtained with Ag$^+$ in different solvents (NCMe, THF), or using $[Fe(Cp)_2]PF_6$ as oxidant. The experimental results rule out a direct attack of **A** to a molecule of the amido complex **1** as the origin of **2** or **3** since reactions carried out at room temperature varying the concentration of the oxidant and **1**, and the addition rate of the silver salt to a solution of **1**, do not show significant change in product composition. Consequently, a mechanism that generates **2** or **3** by coupling of two radical cations **A** in a competitive way seems plausible. Cleavage of a C–F bond in this way is unusual. Among the C–F activation routes described,[8] electron transfer to a fluorinated derivative which gives a radical anion, usually leads to defluorination.[9] Examples of radical aromatic substitution of F in fluoroaryls have also been reported.[10] C–F cleavage by direct coupling of radicals following oxidation is however rare.

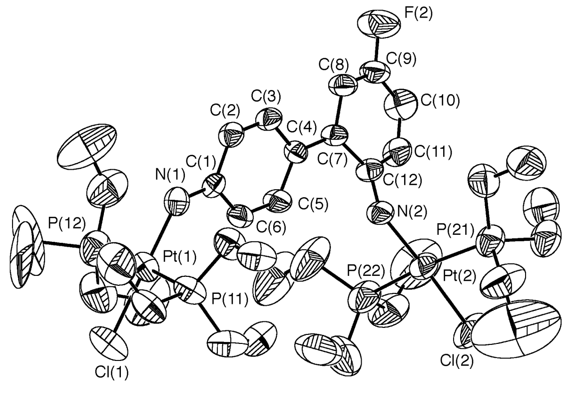

Fig. 2 Ortep drawing of **3** (the anions, BF_4, and H atoms are omited for clarity). Selected bond lengths (Å): Pt(1)–N(1) 1.973(11), N(1)–C(1) 1.300(13), C(1)–C(2) 1.460(16), C(2)–C(3) 1.333(15), C(3)–C(4) 1.453(15), C(4)–C(5) 1.426(15), C(5)–C(6) 1.301(15), C(1)–C(6) 1.436(15), C(4)–C(7) 1.387(15), C(7)–C(8) 1.412(15), C(8)–C(9) 1.332(16), C(9)–C(10) 1.389(18), C(10)–C(11) 1.315(16), C(11)–C(12) 1.439(16), C(7)–C(12) 1.509(15), N(2)–C(12) 1.288(13), N(2)–Pt(2) 2.011(9).

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Notes and references

† *CV studies*: solutions (CH_2Cl_2) 5 × 10^{-4} mol dm^{-3} in complex and 0.1 mol dm^{-3} in $(NBu_4)PF_6$; the w.e. was a platinum bead, the a.e. a platinum wire, and the reference an aqueous s.c.e. $FeCp_2$ was used as standard.

‡ **2**: To a mixture of **1** (0.107 g, 0.18 mmol) and Na_2CO_3 (0.115 g, 1.08 mmol) in freshly distilled acetone (12 ml) was added dropwise a solution of $AgBF_4$ (0.054 g, 0.28 mmol) in acetone (10 ml). The suspension turned green and a Ag mirror was formed. It was stirred for 15 min and then evaporated to dryness. The residue was extracted with CH_2Cl_2, filtered, and the filtrate evaporated to dryness. The residue was triturated with n-hexane (2 ml) to give a dark green solid (0.091 g, 82% yield). Anal. Calcd for $C_{36}H_{68}BCl_2F_6N_2P_4Pt_2$: C, 34.90; H, 5.53; N, 2.26. Found: C, 35.23; H, 5.20; N, 2.23%.

3: To a mixture of **1** (0.156 g, 0.27 mmol) and Na_2CO_3 (0.143 g, 1.35 mmol) in freshly distilled acetona (8 ml) at −80 °C was slowly added a precooled solution of $AgBF_4$ (0.066 g, 0.34 mmol) in acetone (3 ml). The suspension turned dark blue and after 1 h at −80 °C it was filtered, and the filtrate evaporated to dryness. The residue was triturated with Et_2O to give a dark blue solid (0.116 g, 66% yield). Anal. Calcd for $C_{36}H_{69}B_2Cl_2F_9N_2P_4Pt_2$: C, 33.06; H, 5.32; N, 2.14. Found: C, 32.42; H, 4.91; N, 2.13%; NMR ($CDCl_3$, δ): $^{31}P\{^1H\}$ (121.4 MHz), 15.9 (s, $^2J_{Pt-P}$ = 2367 Hz), 15.7 (s, $^2J_{Pt-P}$ = 2367 Hz); ^1H (300.13 MHz), 10.8 (b, 1H, NH), 10.6 (b, 1H, NH), 7.75 (m, 2H), 7.6 (m, 2H), 7.15 (m, 3H), 1.95 (m, 6H, CH_2), 1.87 (m, 6H, CH_2), 1.75 (m, 12H, CH_2), 1.2 (m, CH_3, 36H); ^{19}F (282 MHz), −104 (s, 1F).

§ *Crystal data*: $C_{36}H_{69}B_2Cl_2F_9N_2P_4Pt_2$, M = 1307.51, monoclinic, a = 16.155(5), b = 14.825(4), c = 22.220(6) Å; $\alpha = \gamma = 90°$, β = 100.537(7)°, V = 5232(3) Å^3, T = 293 K, space group $P2(1)/n$, Z = 4, μ(Mo-K$_\alpha$) = 5.625 mm^{-1}, 24649 reflections measured, 6385 unique (R_{int} = 0.0684) which were used in all calculations. Final R values were $R1$ = 0.0471 and $wR2$ = 0.1010 (for $F^2 > 2\sigma(F^2)$). CCDC 172144. See http://www.rsc.org/suppdata/cc/b1/b110909j/ for crystallographic files in .cif format.

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