The 1,4-diazabutadiene/1,2-enediamido non-innocent ligand system in the formation of iridaheteroaromatic compounds: Spectroelectrochemistry and electronic structure

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ARTICLE INFO

ABSTRACT

Oxidation of the unambiguously characterized iridium(III)-enediamido complex IrCp*(RNCHCHNR), R = 2,6-dimethylphenyl, with six cyclically arranged π electrons was investigated using EPR and UV–vis spectroelectrochemistry. In contrast to a corresponding iminocatecholato system reported recently by Rauchfuss et al. [27] the two one-electron oxidation steps are not completely reversible, depending on the solvent. We attribute the electrochemical behavior observed in weakly coordinating dichloromethane and propylene carbonate solvents to an enhanced propensity for ligand addition: while neutral IrCp*(RNCHCHNR) remains coordinatively unsaturated with the strongly σ and π donating enediamido(2−) ligand mitigating the electron deficit, the oxidation to the less donating radical anion ligand (RNCHCHNR)[·-] or even to neutral 1,4-diazabutadiene is considered to induce a strong tendency for quasi-hexacoordination in [IrCp*(L)(RNCHCHNR)], L = solvent, halide, substrate. The presence of excess chloride thus leads to formation of the precursor complex ion [IrCp*ClRNCHCHNR)][+] after oxidation. EPR spectroscopy of the one-electron oxidation intermediate [IrCp*(RNCHCHNR)][+] was successful only for a frozen solution in propylene carbonate/0.1 M Bu_4NPF_6 which revealed an axial signal with sizeable g anisotropy. DFT calculation results for [IrCp*(RNCHCHNR)][n], n = 0, +, 2+ confirm the available structural and spectroelectrochemical data (UV–vis, EPR).

1. Introduction

The two-electron reductive elimination of chloride from complexes [IrCp*Cl(E–E)][+] where E–E is a bidentate ligand has been described and analyzed [1–3] for mononuclear [4–14], for homodinuclear [15–18] and for heterodinuclear systems [19,20]. The resulting compounds [IrCp*(E–E)] [11,6,21], mixed-valent intermediates [Cp*Ir(μ-(E–E))IrCp*][+] [16] and dinuclear complexes [Cp*Ir(μ-(E–E))IrCp*] [15–18] were identified and investigated by various methods including EPR, UV–vis-NIR spectroelectrochemistry, resonance Raman spectroscopy, fast scan cyclovoltammetry, and DFT methodology [1,2,6,22–24]. The catalysis potential of such complexes, mainly of the prototypical E–E = bpy = 2,2′-bipyridine system, has been studied with emphasis on hydride activation and photoreactivity [4,5,13,14,25].

Mononuclear compounds with E–E = 1,4-diazabutadiene were among the investigated examples [11,21,23,26], however, a detailed (spectro)electrochemical analysis and an electronic description of intermediates were lacking. Following a recent report on the redox-switched dissociative oxidation of H_2 by the semiquinone form **3**[+] of the analogue with E–E = N-(2-trifluoromethylphenyl)-4,6-di-*tert*-butyl-iminobenzosemiquinone [27] we have undertaken experimental and theoretical studies in order to obtain a clearer insight into the structurally characterized [21] systems **1** and **2** (Scheme 1).

1,4-Diazabutadienes [28–30] are among the most conspicuous non-innocent ligands [31–33], being able to coordinate also as 1,2-enediamido(2−) ligands [21,34–38] or as radical anion complex intermediates (RNCHCHNR)[·-] [29,33,39–45].
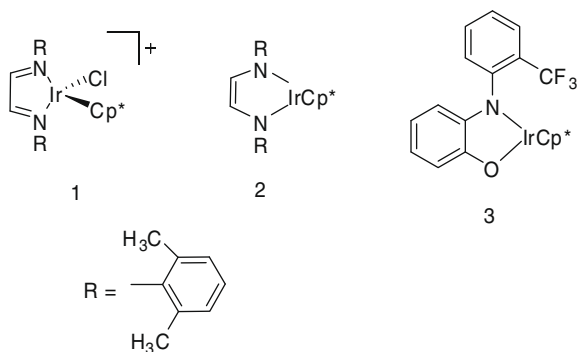
We also undertook the presented investigation because of the reawakened interest in metallaaromaticity [46–49], especially involving iridium [50,51]. Compound **2** may be described as iridaheteroaromatic [21,50], and related osmaheteroaromatic analogues have also been reported [11].

2. Results and discussion

2.1. Characterization

Compounds **1** and **2** were prepared according to the described procedure [21], using tetrahydridoborate for conversion. The

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Scheme 1.

Fig. 2. Simulated UV–vis absorption spectra of IrCp*(RNCHCHNR), **2**, and of its one-electron oxidation product from TD-DFT calculations. Full and dashed lines represent simulated spectra of **2** and **2**⁺, respectively.

confirmed (*vide infra*) reduction of the ligand instead of the metal through the hydride reagent may involve an intraligand electron transfer because the primary hydride attack is believed to occur at the Ir–Cl site of the precursor **1** [26].

UV–vis-spectroelectrochemical monitoring of the reduction of the precursor shows a clean conversion of **1** to **2** with its characteristic intense band at 430 nm (Fig. 1). A similar intense feature was observed for **3** at 449 nm [27].

TD-DFT calculations for **2** confirm the characteristic features of the experimental spectrum and support [23] a HOMO–LUMO transition assignment for the 430 nm absorption with a ligand-centered HOMO and more metal-centered LUMO (ligand-to-metal charge transfer, LMCT; Figs. 2 and 3, Table 1). The precursor **1**, on the other hand, displays weak long-wavelength LLCT transitions [23].

DFT calculations for **2** (Table 2, Table S1) agree with the previous description of a Cp-containing model [21,23] suggesting a C=C double bond and C–N single bonds in the five-membered chelate ring with rather short N–Ir distances. Table 2 with representative examples of compounds involving unreduced, singly reduced and doubly reduced 1,4-diazabutadiene components confirm this assignment [35]. It is noteworthy that the "Arduengo carbene" as prototypical N-heterocyclic carbene (NHC) displays a similar CC and CN bond length sequence [52] as compound **2** (which is unusual in that it contains a late transition metal associated with an enediamido(2−) ligand). All other reported enediamido chelates involve either early transition metals [36], specially zirconium [53], hafnium [54], tantalum [55], or chromium [56,57], or main group element atoms [34,38,58–62].
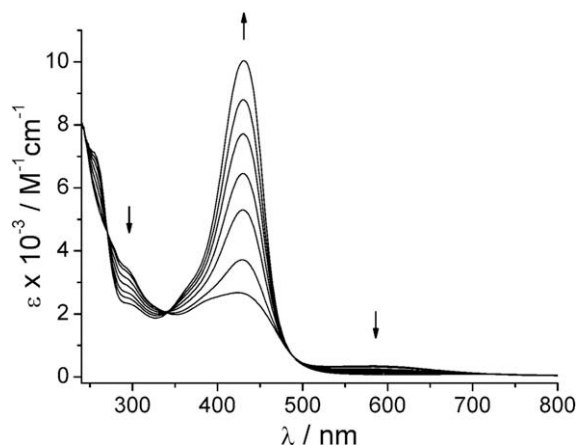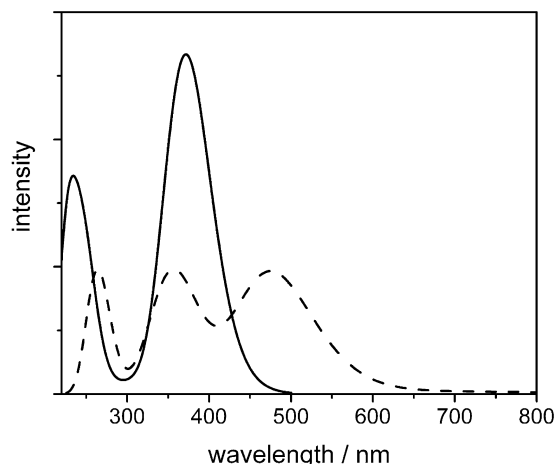

Fig. 1. UV–vis-spectroelectrochemical reduction of **1**(PF₆) to **2** in CH₂Cl₂/0.1 M Bu₄NPF₆.

2.2. Electrochemistry

The electrochemical behavior of [IrCp*(RNCHCHNR)] was investigated in dichloromethane and propylene carbonate, in the presence of 0.1 M Bu₄NClO₄ or Bu₄NPF₆ as supporting electrolyte. A reversible one-electron oxidation was detected at −0.34 V (in dichloromethane) or −0.30 V (in propylene carbonate) versus FeCp₂⁺/⁰ by polarography and cyclic voltammetry; the half-wave potentials were found to be independent on the electrolyte used (Bu₄NClO₄ versus Bu₄NPF₆). This one-electron transfer contrasts with the two-electron step reported previously [21] in the well coordinating solvent acetonitrile. The log-plot analysis of the polarographic wave (plot $\log[(i_d-i)/i]$ versus potential) exhibits a linear dependence (Fig. S1) with a reciprocal slope $(1/S)$ of 53 mV, i.e. near the theoretical value of 59 mV for a one-electron reversible process at 298 K [63]. The one-electron consumption was confirmed by coulometry. Fig. 4 depicts the polarographic monitoring of the coulometric experiment and shows the transition of the original anodic oxidation wave into a reversible anodic–cathodic wave after passing 0.5 F/mol charge, and finally into a cathodic wave after the oxidation by 1 F/mol.

The more positive second oxidation wave which is depicted also in Fig. 3 and which corresponds to further oxidation of the one-electron oxidation product [IrCp*(RNCHCHNR)]⁺ is irreversible in cyclic voltammetry (Fig. 5). Its potential depends strongly on the experimental conditions, e.g. on solvent and electrolyte, on the material of the electrode, and on the electrochemical time-constant parameters. For instance, the polarographic half-wave potentials are +0.04, +0.24, and +0.09 V versus FeCp₂⁺/⁰ in dichloromethane/Bu₄NClO₄, dichloromethane/Bu₄NPF₆ and propylene carbonate/Bu₄NClO₄, respectively.

We ascribe this behavior to a fast follow-up reaction (cf. the Section 2.3) of the highly electron deficient and thus reactive two-electron oxidized species [IrCp*(RNCHCHNR)]²⁺, formed at the electrode in the second wave. The disintegration of the two-electron oxidation product can be avoided in the presence of a well coordinating ligand such as chloride. Figs. 6 and 7 compare the electrochemical responses in the absence and in the presence of excess Et₄NCl. The wave on the rotating disk electrode is increased to double intensity on addition of chloride, thus indicating the simultaneous uptake of the first and the second electron in one electrochemical step.

The anodic signal in cyclic voltammetry is also increased and shifted negatively, the counter-peak disappears, and at more neg-
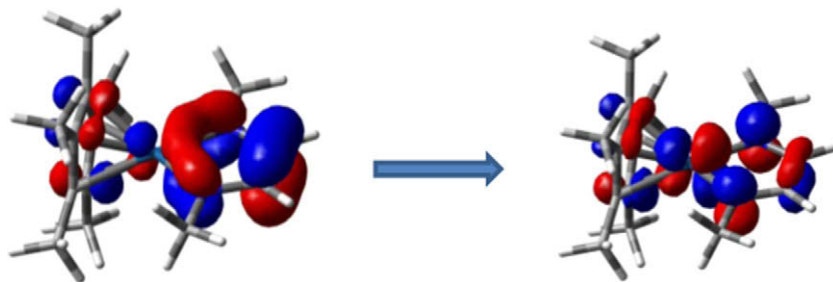
Fig. 3. Representation of HOMO-to-LUMO transition for the intense band in the visible of IrCp*(RNCHCHNR) from TD-DFT calculations (R replaced by CH_3 for simplicity).

Table 1

TD-DFT (PBE0/CPCM-CH_2Cl_2) calculated lowest singlet excitation energies (eV) for [IrCp*(RNCHCHNR)]^n with oscillator strengths larger than 0.005. MOs involved in excitations are depicted in Figs. S6 and S7.

n	State	Main contributing excitations (%)	Calculated transition energy[a] eV (nm)	Calculated oscillation strength	Expected absorption maximum (nm)	Molar extinction coefficient (M^{-1} cm^{-1})
0	b^{1}A	99 (HOMO → LUMO)	3.32 (373)	0.270	430	10000
0	c^{1}A	96 (HOMO−1 → LUMO)	3.38 (366)	0.025	365	sh
0	d^{1}A	79 (HOMO−2 → LUMO+1)	4.82 (257)	0.038	255	sh
0	e^{1}A	57 (HOMO−4 → LUMO+1)	5.04 (245)	0.071		
1	b^{2}A	96 (αHOMO → αLUMO)	2.60 (476)	0.101	539	1300
1	c^{2}A	85 (βHOMO−6 → βLUMO)	3.39 (366)	0.073	390	sh
1	d^{2}A	29 (αHOMO−6 → αHOMO)	3.64 (341)	0.045	340	sh
		37 (βHOMO−7 → βHOMO)				
1	e^{2}A	Mixed	4.68 (265)	0.070	296	6400
1	f^{2}A	Mixed	4.72 (262)	0.013		

[a] Wavelength in parenthesis.

Table 2

Intra-ring bond lengths in compounds cyclo-EX$_n$(RNCHCHNR).

R[a]	EX$_n$	d_{CC}	d_{CN}	References
Dipp	–	1.445(5)	1.234(3)	[11]
tert-Bu	ZnMe$_2$	1.48(1)	1.25(1)	[33]
Dmp	[IrClCp*]$^+$	1.482(15)	1.280(10)	[21]
Dipp	[IrClCp*]$^+$	1.430(15)	1.293(14)	[11]
Dmp	[OsCl(C_6Me_6)]$^+$	1.429(15)	1.300(8)	[11]
Cy	PtMe$_4$	1.440(9)	1.292(7)	[42]
Dipp	S^{2+}	1.407(10)	1.31(1)	[58]
Dipp	[GaI$_2$]$^+$	1.406(2)	1.3386(15)	[40]
Dipp	Ga^{3+}	1.402(3)	1.337(2)	[40]
		1.331(4)	1.413(2)	
Mes	Sn^{2+}	1.356(6)	1.378(5)	[59]
tert-Bu	Si^{2+}	1.347(21)	1.400(9)	[60]
tert-Bu	[SbCl]$^{2+}$	1.346(6)	1.399(6)	[61]
Dipp	P^{3+}	1.342(9)	1.371(6)	[62]
Dipp	[Cr$_2$]$^{4+}$	1.350(5)	1.368(3)	[56,57]
Ad	C^{2+}	1.338(3)	1.382(2)	[52]
Dmp	[IrCp*]$^{2+}$	1.334(15)	1.366(14)	[21]
			1.379(13)	
Dmp	[IrCp*]$^{2+}$	1.363 (calc.)	1.361 (calc.)	this work

[a] Dipp = 2,6-diisopropylphenyl; Dmp = 2,6-dimethylphenyl; Cy = cyclohexyl; Mes = Mesityl (2,4,6-trimethylphenyl); Ad = 1-adamantyl.

Fig. 4. Controlled potential coulometry with polarographic monitoring. 1.29 mM [IrCp*(RNCHCHNR)] in CH_2Cl_2/0.1 M Bu$_4$NClO$_4$ before electrolysis (full line) and after electrolysis at −0.15 V on passing 0.5 F/mol (dashed line) and 1.0 F/mol (dotted line).

ative potentials a new signal arises which is ascribed to the back reduction of the now formed chloride-containing complex [IrCp*Cl(RNCHCHNR)]$^+$ [21]. These observations support an ECE oxidation mechanism, involving chloride addition after the first electron transfer and consequent oxidation of [IrCp*Cl/RNCHCHNR)] to [IrCp*Cl(RNCHCHNR)]$^+$ at less positive potential.

2.3. Spectroelectrochemistry

The reversible transition between [IrCp*(RNCHCHNR)] and [IrCp*(RNCHCHNR)]$^+$ can be observed UV–vis spectroelectrochem-

ically using an optically transparent thin-layer electrolytic (OTTLE) cell [64]. The spectral response in the OTTLE cell during oxidation at the potential of the first wave (Fig. 8) shows a decrease of the typical intensive ligand-to-metal charge transfer band [21] of [IrCp*(RNCHCHNR)] (at 430 nm in propylene carbonate) and the appearance of new bands at 296 and 539 nm. On the back reduction the original spectrum is restored to >95%.

Oxidation of **2** in dichloromethane/0.1 M Bu$_4$NPF$_6$ proceeds also reversibly, however, prolonged spectroelectrochemical electrolysis indicates lower stability of the oxidized species **2**$^+$. This first oxidation would run parallel to the observation made for system **3**$^{n+}$. In fact, the UV–vis-spectroelectrochemical monitoring (Fig. S3) reveals band systems for **2**$^+$ at 294, 357, 408sh, 546 nm whereas **3**$^+$

Fig. 5. Cyclic voltammetry of [IrCp*(RNCHCHNR)] in CH$_2$Cl$_2$/0.1 M Bu$_4$NClO$_4$ at a glassy carbon electrode, scan rate 200 mV/s.

Fig. 7. Cyclic voltammogram of [IrCp*(RNCHCHNR)] in propylene carbonate/0.1 M Bu$_4$PF$_6$ (full line) and after addition of a ten-fold excess of Et$_4$NCl (dashed line); glassy carbon electrode, scan rate 200 mV/s.

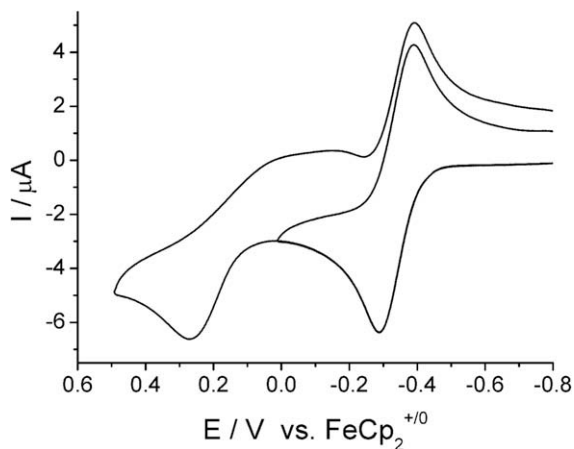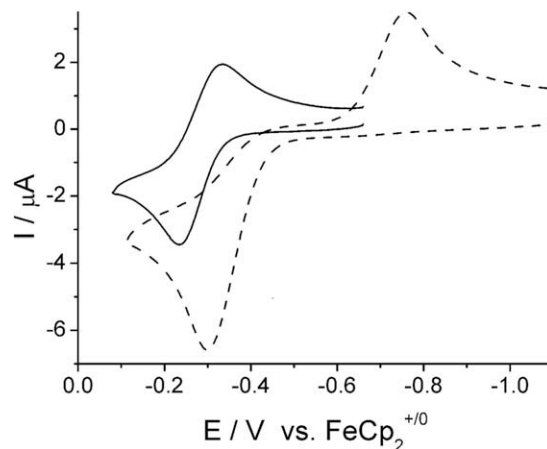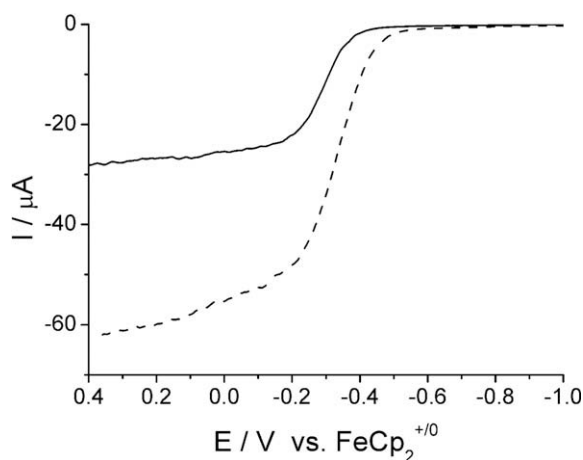**Fig. 6.** Linear scan voltammetry of [IrCp*(RNCHCHNR)] on a glassy carbon rotating disc electrode in propylene carbonate/0.1 M Bu$_4$PF$_6$ (full line) and after addition of a ten-fold excess of Et$_4$NCl (dashed line); scan rate 30 mV/s.

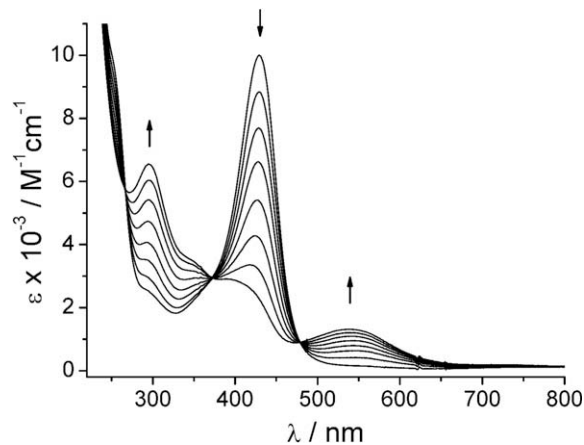**Fig. 8.** UV–vis spectroelectrochemical response during the oxidation of [IrCp*(RNCHCHNR)] to [IrCp*(RNCHCHNR)]$^+$ in propylene carbonate/0.1 M Bu$_4$PF$_6$.

was described [27] (also in CH$_2$Cl$_2$) with bands at 298sh, 351, 466, 567sh. TD-DFT calculations produce allowed transitions for **2**$^+$ at 476, 366, 341, and around 260 nm (Table 1). Shifts of transitions to longer wavelengths and the intensity variations in comparison with the non-oxidized species are well reproduced by the calculations (Fig. 2).

In contrast, the spectroelectrochemical oxidation at the second wave with an attempt to observe the two-electron oxidation product [IrCp*(RNCHCHNR)]$^{2+}$ failed due to the instability of the dication; a back scan does not restore the original spectrum at all. However, the addition of tetraethylammonium chloride to a solution of electrochemically generated [IrCp*(RNCHCHNR)]$^+$ (Fig. S2) produces a mixture of the chloride-containing two-electron oxidized complex [IrClCp*(RNCHCHNR)]$^+$ and the original compound [IrCp*(RNCHCHNR)] by a disproportionation reaction.

The (spectro)electrochemical one-electron oxidation of **2** proceeds cleanly in propylene carbonate/0.1 M Bu$_4$NPF$_6$, however, it was not possible to observe an EPR signal in fluid solution at 295 or 233 K. Only at 110 K in frozen propylene carbonate solution an axial signal was observed at $g_{1,2}$ = 2.064 and g_3 = 1.981 (Fig. 9) which yields g_{av} = 2.036. This result for **2**$^+$ is confirmed by DFT calculations (calc.: g_{11} = 2.070, g_{22} = 2.036, g_{33} = 1.993, g_{iso} = 2.033) and is similar to the one observed for **3**$^+$ [27] which showed a more

rhombic pattern due to lower symmetry and an apparent ^{14}N hyperfine splitting (triplet) for 1 N atom at g_3. The EPR silence of **2**$^+$ at higher temperatures is remarkable since the DFT calculations show a spin density centered largely (70%) on the DAB ligand (Fig. S4) and DAB radical complexes have been easily observed at room temperature [29,33,39–43,65,66]. The obviously rapid relaxation for **2**$^+$, the deviation of g(average) = 2.036 from the free electron value of 2.0023 and the sizable splitting into well separated g components (g anisotropy $g_1 - g_3$ = 0.083) in the immobilized state are unusual for a radical anion complex [67] but are attributed to the interaction of the radical ligand with a heavy transition metal with a high spin-orbit coupling constant of about 3000 cm^{-1} [68].

A formally comparable paramagnetic system to **2**$^+$ is the organoplatinum(IV) species [(CyNCHCHNCy)Pt(CH$_3$)$_4$]$^{\cdot-}$, Cy = cyclohexyl [42]. While it also involves a 5d^6 configured organometal bound to a 1,4-diazabutadiene radical anion, the much smaller g anisotropy ($g_{1,2}$ = 2.003, g_3 = 1.9776, $g_1 - g_3$ = 0.0254) indicates that **2**$^+$ is distinguished by a larger metal/radical interaction. In resonance structure description this implies a noticeable contribution from metal centered spin forms such as [Ir^{IV}Cp*(RNCHCHNR^{2-})]$^+$ in addition to as [Ir^{III}Cp*(RNCHCHNR$^{\cdot-}$)]$^+$. The axial symmetry of the g tensor for **2**$^+$ reflects the symmetry of the ion (in contrast to **3**$^+$) and the possible role of the [Ir^{IV}Cp*(RNCHCHNR^{2-})]$^+$ form; a d^5 configuration is expected to have $g_{1,2}$ > 2 and g_3 < 3.

The absence of an EPR signal after electrolytic oxidation of **2** in CH$_2$Cl$_2$/0.1 M Bu$_4$NPF$_6$ even at low temperatures confirms the suspected addition reactivity of **2**$^+$ under those conditions.

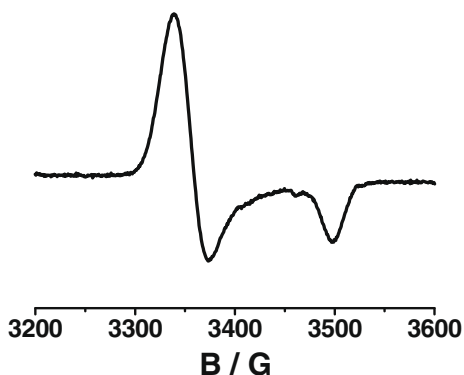**Fig. 9.** EPR spectrum, recorded at 110 K, from the oxidation of [IrCp*(RNCHCHNR)] to [IrCp*(RNCHCHNR)]⁺ in propylene carbonate/0.1 M Bu₄PF₆.

The formation of two-electron oxidized **3**$^{2+}$ [27] as opposed to the unstable **2**$^{2+}$ (Scheme 2) may be attributed to the lower basicity of the DAB system and to steric shielding. It is known from rhenium [69], chromium [70], and rhodium chemistry [71] involving σ and π donating catecholate ligands that coordinative unsaturation may result from the compensation of electron deficiency at the metal through the donor ligands. Enediamido(2−) is certainly a highly electron rich π system [72] comparable to catecholate. On oxidation, however, that electron donating capacity will diminish considerably, rendering the metal susceptible to coordination of a donor, either a solvent molecule or electrolyte component (e.g. halide) or a substrate, even as weak as H₂ [27]. We therefore assume that, in contrast to the propylene carbonate solution, the dichloromethane electrolyte solution reacts slowly after one-electron oxidation to yield a halide containing product. Indirect evidence for this assumption comes from the absorption band at 546 nm which is shifted in comparison to the analogous band of **2**⁺ in propylene carbonate (539 nm), obviously due to overlapping with the longer-wavelength (583 nm) band of the chloride-containing precursor. On the other hand, the maximum at 294 nm in dichloromethane is close to that in propylene carbonate (Figs. 1 and 8 and S3).
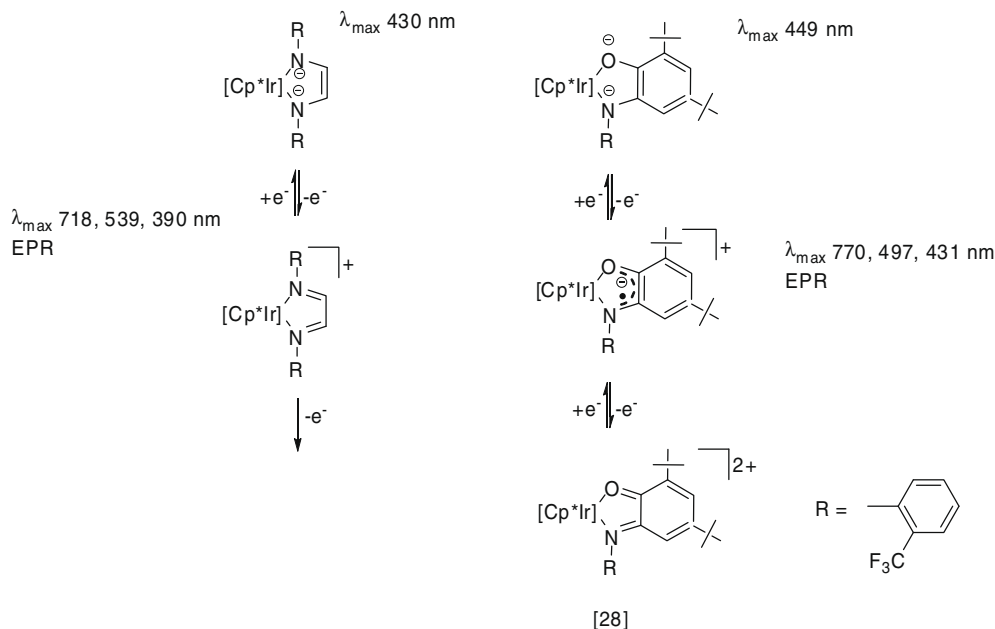
2.4. Concluding remarks

Refraining from a quantitative assessment of aromaticity of **2** because of the heterogeneity of the participating atoms we still note that the calculated MO description would allow for a cyclic conjugation of 6 π electrons involving a C=C double bond, two N lone pairs, and one (empty) dπ orbital on iridium(III). The strong π acceptor effect of [IrCp*]$^{2+}$ [73] has been recognized before, evident from the unprecedented cathodic shift for the reduction potential of the bpy complex [6]. It has been shown that the systems from Scheme 2 are offering chemical reactivity as a consequence of spectroscopically accessible electron transfer which may stimulate further research involving related, differently substituted electroactive ligands and also equivalent, electrochemically and spectroscopically related areneosmium species in replacement of cyclopentadienyliridium [1,11].

3. Experimental

3.1. Materials

Compounds **1** and **2** were obtained as described [21]. Dichloromethane (Fluka, puriss.p.a.) was boiled with LiAlH₄ and freshly distilled. Propylene carbonate (Aldrich, anhydrous 99.7%, Sure/Seal) was used as received. Supporting electrolytes (Fluka, puriss., electrochemical grade) were dried in vacuum, *n*-Bu₄NPF₆ at 110 °C, *n*-Bu₄NClO₄ at 40 °C (Caution: Explosion hazard).

3.2. Instrumentation

Polarography and cyclic voltammetry was carried out using a three-electrode configuration (dropping mercury or glassy carbon working electrode, Pt counter electrode, SCE reference) and a PAR 263A potentiostat and function generator. The rotating disk electrode was from Laboratorni pristroje, Prague. The ferrocene/ferrocenium (FeCp₂$^{+/0}$) or cobaltocenium/cobaltocene (CoCp₂$^{+/0}$) couples served as internal reference. The electrochemical vessel for coulometry was equipped with a side-arm for the counter electrode, separated by sintered glass, and a mercury pool was used as

Scheme 2.

working electrode for bulk electrolysis. UV–vis absorption spectra were recorded on J&M TIDAS and Agilent 8453 spectrophotometers. Spectroelectrochemistry was performed using an optically transparent thin-layer electrode (OTTLE) cell [64]. EPR experiments were carried out in a two-electrode tube [74] in an ESP 300 system (Bruker).

3.3. Quantum chemical calculations

The electronic structures of [IrCp*(RNCHCHNR)], R = 2,6-dimethylphenyl, and of its oxidized forms were calculated by density functional theory (DFT) methods using the GAUSSIAN 03 [75] and AMSTERDAM DENSITY FUNCTIONAL (ADF2008.01) [76] program packages.

G03/DFT calculations employed the Perdew, Burke, Ernzerhof [77] (PBE0) hybrid functional. The geometry of the cationic form was calculated by the UKS approach. Low-lying excitation energies were calculated by time-dependent DFT (TD-DFT) at the optimized geometry of the corresponding oxidation state. For H, C, and N atoms, either polarized triple-ζ basis sets 6-311G(d) [78] for geometry optimization and vibrational analysis, or cc-pvdz correlation consistent polarized valence double-ζ basis sets [79] (TD-DFT) were used, together with quasirelativistic effective core pseudopotentials and a corresponding optimized set of basis functions for Ir [80]. The solvent was described by the polarizable conductor calculation model (CPCM) [81] in TD-DFT calculations.

Within the ADF program Slater type orbital (STO) basis sets of triple-ζ quality with two polarization functions for Ir atoms and with one polarization function for C, N, and O atoms were employed. The inner shells were represented by the frozen core approximation (1s for C, N and O, and 1s-4d for Ir were kept frozen). Within ADF the functional including Becke's gradient correction to the local exchange expression in conjunction with Perdew's gradient correction to local density approximation (LDA) with VWN parametrisation of electron gas data was used (ADF/BP) [82]. The g tensor was obtained from a spin-nonpolarized wave function after incorporating the spin-orbit (SO) coupling by first-order perturbation theory from a ZORA Hamiltonian in the presence of a time-independent magnetic field [83].

Acknowledgment

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.11.042.

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