Electrochemical Properties of (η^5-C₅Me₅)–Rhodium and –Iridium Complexes Containing Bis(pyrazolyl)alkane Ligands

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Abstract

The electrochemical properties of rhodium(III) **1**-**3** and iridium(III) **4**-**6** complexes containing bis(pyrazolyl)alkane ligands [MCp*Cl(R₂C(3,5-R'₂pz)₂)]X (M = Rh (**1**) or Ir (**4**), R = R' = H, X = Cl; M = Rh (**2**) or Ir (**5**), R = H, R' = Me, X = Cl; M = Rh (**3**) or Ir (**6**), R = Me, R' = H, X = OTf; pz = pyrazolyl; Cp* =η^5-C₅Me₅) were investigated by cyclic voltammetry and controlled potential electrolysis. They exhibit two sequential irreversible reductions assigned to the $M^{III} \to M^{II}$ and $M^{II} \to M^{I}$ reductions, which are dependent on the methylation of the bis(pyrazolyl)alkane ligands.

Introduction

Poly(pyrazolyl)borates and their metal complexes are widely studied and applied in several areas of chemistry [1,2]. We have been interested [3-10] in the coordination chemistry of their much less studied carbon analogues, the poly(pyrazolyl)alkane-type scorpionates, as well as on the synthesis of new derivatives [11-13] either by substitution at the pyrazolyl rings or functionalization of the apical carbon, which can play a critical role for the modification of their properties.

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The knowledge that Rh(I) [14] and Ir(I) [15] compounds containing dihydro(pyrazolyl)methane [$H_2C(3,5-R_2pz)_2$, (R = H or Me; pz = pyrazolyl)] ligands exhibit interesting applications namely in catalysis, prompted us [9] to undertake a systematic study of the reactions between [$MCp^*Cl(\mu-Cl)]_2$ dimers (M = Rh or Ir; $Cp^* = \eta^5-C_5Me_5$) and bis(pyrazolyl)alkanes $R_2C(pz^{R'2})_2$ (R, R' = H or Me). Rhodium(III) and iridium(III) complexes of general formula [$MCp^*Cl(R_2C(3,5-R'_2pz)_2)]X$ (M = Rh or Ir; R, R' = H or Me; X = Cl or OTf) have been prepared (Fig. 1). Herein we report their electrochemical properties using cyclic voltammetry (CV) and controlled potential electrolysis (CPE) techniques.
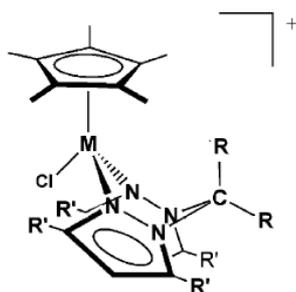
Figure 1. Bis(pyrazolyl)alkane rhodium(III) and iridium(III) complexes **1 – 6**, [$MCp^*Cl(R_2C(3,5-R'_2pz)_2)]X$ (M = Rh (**1**) or Ir (**4**), R = R' = H, X = Cl; M = Rh (**2**) or Ir (**5**), R = H, R' = Me, X = Cl; M = Rh (**3**) or Ir (**6**), R = Me, R' = H, X = OTf; pz = pyrazolyl; $Cp^* = \eta^5-C_5Me_5$).


Experimental

The electrochemical experiments were performed on an EG&G PAR 273A potentiostat/galvanostat connected to a personal computer through a GPIB interface. Cyclic voltammograms were obtained in 0.2 M [$^nBu_4N$][BF_4]/CH_2Cl_2, at a platinum disc-working electrode (d = 0.5 mm) and at 25 ºC. Controlled-potential electrolyses were carried out in electrolyte solutions with the above-mentioned composition, in a three-electrode H-type cell. The compartments were separated by a sintered glass frit and equipped with platinum gauze working and counter electrodes. For both CV and CPE experiments, a Luggin capillary connected to a silver wire pseudo-reference electrode was used to control the working electrode potential, and a Pt wire was employed as the counter-electrode for the CV cell. The CPE experiments were monitored regularly by cyclic voltammetry, thus assuring no significant potential drift occurred along the electrolyses. The redox potentials of the complexes were measured by CV in the presence of ferrocene as the internal standard, and their values are quoted relative to the SCE by using the [$Fe(\eta^5-C_5H_5)_2$]$^{0/+}$ redox couple ($E_{1/2}^{ox}$ = 0.525 V *vs.* SCE) [21,22].

Results and discussion

The redox properties of bis(pyrazolyl)alkane rhodium(III) and iridium(III) compounds $[MCp*Cl(R_2C(3,5-R'_2pz)_2)]X$ (M = Rh (**1**) or Ir (**4**), R = R' = H, X = Cl; M = Rh (**2**) or Ir (**5**), R = H, R' = Me, X = Cl; M = Rh (**3**) or Ir (**6**), R = Me, R' = H, X = OTf) have been investigated by cyclic voltammetry, at a Pt electrode, in a 0.2 M $[^nBu_4N][BF_4]/CH_2Cl_2$ solution, at 25 °C. They exhibit (Fig. 2 for complex **3**) two single-electron irreversible reduction waves, assigned to the $M^{III} \to M^{II}$ (wave I) and $M^{II} \to M^{I}$ (wave II) (M = Rh or Ir) reductions, at the reduction peak potential values given in Table 1 ($^I E_p^{red}$ in the range from -0.88 to -1.28 V *vs*. SCE, and $^{II} E_p^{red}$ between -1.27 and -1.80 V *vs*. SCE).

The occurrence of a single-electron reduction per M^{III} (or M^{II}) atom has been confirmed by exhaustive controlled potential electrolysis (CPE) at a potential slightly cathodic to that of the peak potentials of wave I (or II). CPE at any of the reduction waves corresponds to a charge consumption of 1 F/mole of complex.

In addition, compounds **1**, **2**, **4** and **5** exhibit a single-electron (CPE) irreversible oxidation wave, at E_p^{ox} *ca*. 1.1 V *vs*. SCE, corresponding to the oxidation of the Cl^- counter-ion. No other oxidation wave has been detected, for any of the complexes, by a first anodic sweep without a previous reduction scan, indicating that neither a metal centred nor a ligand-centred oxidation are observed.
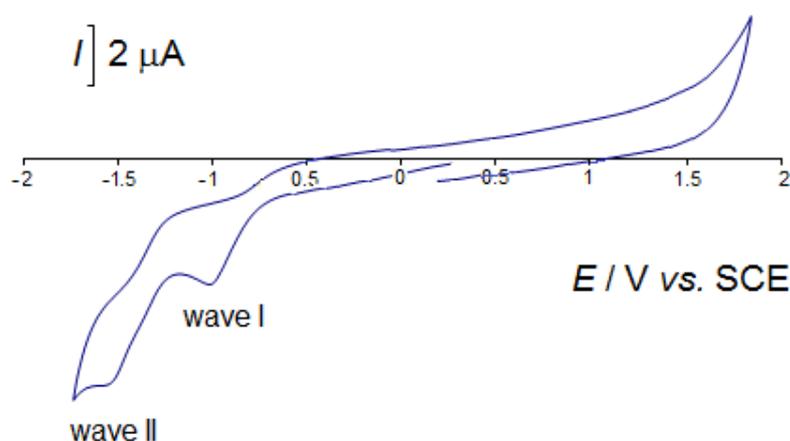
Figure 2. Cyclic voltammogram of $[RhCp*Cl(Me_2C(pz)_2)](OTf)$ (**3**) in a 0.2 M $[Bu_4N][BF_4]/CH_2Cl_2$ solution, at a Pt disc working electrode ($d = 0.5$ mm), run at a scan rate of 200 mVs^{-1}.

The values of the $M^{III} \to M^{II}$ (wave I) and $M^{II} \to M^{I}$ (wave II) reduction potentials of **1** - **3** and **4** - **6** reflect the electron-donor character of their ligands as follows. Methylation at the apical carbon (R = Me) of the dihydrobis(pyrazolyl)methane ligand results in a measurable (*ca*. 0.3 V) cathodic shift of the potential, in accord with the better electron-donor character of the $Me_2C(pz)_2$ ligand in comparison with $H_2C(pz)_2$. An even more pronounced effect (cathodic shift of *ca*. 0.4 - 0.5 V) is observed if the hydrogen replacement by methyl occurs at the pyrazolyl rings (R' = Me) of the

dihydrobis(pyrazolyl)methane ligand. This is consistent with the shorter distance of the latter electron-donor groups to the metal compared with the previous case when they are bound to the apical carbon. However, any analysis has to be taken rather cautiously in view of the irreversible character of the oxidation waves.

Table 1. Cyclic voltammetric data[a] for complexes $[Cp*MCl(R_2C(3,5-R'_2pz)_2)]^+$ (M = Rh or Ir; R, R' = H or Me) **1** - **6**.

Complex	CATHODIC WAVES		ANODIC WAVE[b]
	$^{I}E_p^{red}$	$^{II}E_p^{red}$	E_p^{ox}
$[RhCp*Cl(H_2C(pz)_2)]Cl$ (**1**)	-0.88	-1.27	1.13
$[RhCp*Cl(H_2C(3,5-Me_2pz)_2)]Cl$ (**2**)	-1.26	-1.76	1.16
$[RhCp*Cl(Me_2C(pz)_2)](OTf)$ (**3**)	-1.06	-1.58	—
$[IrCp*Cl(H_2C(pz)_2)]Cl$ (**4**)	-0.90	-1.31	1.12
$[IrCp*Cl(H_2C(3,5-Me_2pz)_2)]Cl$ (**5**)	-1.28	-1.80	1.12
$[IrCp*Cl(Me_2C(pz)_2)](OTf)$ (**6**)	-1.11	-1.63	—[c]

[a] Potential values in Volt ± 0.02 *vs.* SCE, in a 0.2 M $[Bu_4N][BF_4]/CH_2Cl_2$ solution, at a Pt disc working electrode determined by using the $[Fe(\eta^5-C_5H_5)_2]^{0/+}$ redox couple ($E_{1/2}^{ox}$ = 0.525 V *vs.* SCE) as internal standard at a scan rate of 200 mVs^{-1}.
[b] Irreversible oxidation wave corresponding to the oxidation of the Cl$^-$ counter-ion.
[c] An anodic wave at E_p^{ox} = 0.60 V is generated upon scan reversal following the second reduction wave.

This study could provide an opportunity to estimate the E_L ligand parameter for the new bis(pyrazolyl)alkane ligands (although with the above limitation) by applying the Lever equation (1) [16,17], which relates linearly the redox potential (*E* in V *vs.* the standard hydrogen electrode (SHE)) of an octahedral complex with the sum (ΣE_L) of the E_L ligand parameters for all the ligands (2-electron donors, assuming additive contributions), and assuming that equation (1), valid for half-sandwich arene-type complexes [8,18-20], is also valid for half-sandwich Cp-type complexes.

$$E = S_M (\Sigma E_L) + I_M / V \ vs. \ NHE \qquad (1)$$

However, the slope (S_M) and the intercept (I_M), which are dependent upon the metal, redox couple, spin state and stereochemistry [16,17], are not know for the present redox couples and therefore the determination of the E_L ligand parameter was precluded.

Conclusions
This electrochemical study has allowed to determine the redox potentials of bis(pyrazolyl)alkane rhodium(III) and iridium(III) compounds bearing the Cp* ligand. Moreover, it allowed to compare the electron-donor characters of different methylated bis(pyrazolyl)alkane ligands, although one should be rather cautious due to the irreversibility of the reduction waves. The quantification of

that effect by the Lever formalism (by using equation 1) was not possible since the S_M and I_M values for the present redox couples are not known.

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