

Synthesis and electrochemistry of 2-polymethylmetallocenyl-substituted pyrrolidino[60]fullerenes

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The synthesis and voltammetric investigation of pyrrolidino[60]fullerenes bearing the polymethylated metallocenyl groups (Me₄C₄)Co(C₅H₄) and (Me₅C₅)Ru(C₅H₄) in the 2-position of the heterocyclic ring are reported.

Fullerenes have a great capacity to act as strong electron acceptors. Theoretically, C₆₀ is able to accept up to 12 electrons, even if electrochemistry proved experimentally its ability to accept reversibly 6 electrons.¹ A modern synthetic goal in fullerene chemistry is the design of molecules that couple this acceptor molecule with electron donor fragments, in particular, organometallic fragments.² The aim is to increase further the intramolecular electronic mobility in order to afford innovative physical properties. In this connection, metalloporphyrins and ferrocenes are typical redox active fragments, which are frequently conjugated to fullerenes.^{3,4}

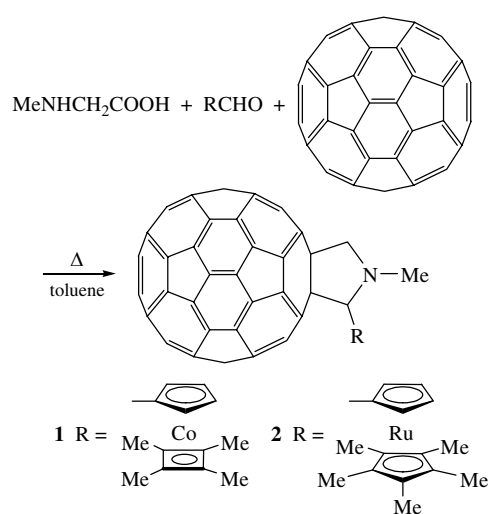
A useful synthetic strategy for the functionalization of fullerenes is the three-component [3 + 2] cycloaddition of a dipolar intermediate arising from the reaction of an aldehyde with N-substituted α -amino acids or the Prato reaction.⁵

Here, we describe the synthesis and cyclic voltammetric behaviour of pyrrolidino[60]fullerenes **1** and **2** bearing (in the 2-position of the heterocyclic ring) the uncommon polymethylated metallocenyl groups Cb*Co(C₅H₄) (Cb* = C₄Me₄) and Cp*Ru(C₅H₄) (Cp* = C₅Me₅), respectively (Scheme 1).[†]

As illustrated in Figure 1, complex **1** displays two chemically reversible one-electron reductions, which are conceivably centred on the fullerene moiety, and a partially chemically reversible one-electron oxidation, which is likely centred on the Cb*Co(C₅H₄) fragment. Further ill-defined reductions (not shown in Figure 1) are also present at more negative potential values, which could arise from the overlapping of fullerene- and Co(I)-centred reductions. A similar redox pattern is exhibited by complex **2**.

[†] A mixture of 40 mg of aldehyde Cb*Co(C₅H₄CHO)⁶ (0.153 mmol), 24.5 mg of *N*-methylglycine (0.275 mmol) and 100 mg of C₆₀ (0.139 mmol) in toluene (150 ml) was refluxed under argon during 8 h. The solvent was evaporated, and the residue was chromatographed on SiO₂ [eluent: hexane–toluene (1:1)] to give 46 mg of C₆₀ and 27 mg of product **1**. Yield on the reacted fullerene is 34.6%. ¹H NMR (CDCl₃) δ : 1.7 (s, 12H, Me), 3.23 (s, 3H, N–Me), 4.2–4.23 (d, 1H, CH₂), 4.4–4.5 (m, 2H, Cp), 4.7–4.8 (m, 2H, Cp), 4.9–4.92 (d, 1H, CH₂), 5.05 (s, 1H, CH). Found (%): C, 86.43; H, 2.29; Co, 5.75. Calc. for C₇₆H₂₂CoN (%): C, 90.56; H, 2.20; Co, 5.85.

Similarly, 45.7 mg (0.153 mmol) of aldehyde Cp*Ru(C₅H₄CHO)⁷ after 10 h gave 34.0 mg of **2** (44.2%). ¹H NMR (CDCl₃) δ : 2.03 (s, 15H, Me), 3.28 (s, 3H, N–Me), 3.98 (m, 1H, Cp), 4.11 (m, 1H, Cp), 4.14–4.17 (d, 1H, CH₂), 4.47 (m, 1H, Cp), 4.52 (s, 1H, CH), 4.52 (m, 1H, Cp), 4.88–4.91 (d, 1H, CH₂). ¹³C NMR (CDCl₃) δ : 12.19 (Cp–Me), 41.59 (N–Me), 68.32 (CH–C), 70.08, 71.15, 73.36, 73.53 (Cp), 70.76 (CH₂), 77.11 (CH), 85.36 (Cp*), 135.77–147.90 (C₆₀).



Scheme 1

The formal electrode potentials for the above processes are compiled in Table 1 together with those pertinent to either the free building components or ferrocenyl analogue **3**.⁵

The shift of the fullerene centred reductions towards negative potential values by about 0.15–0.20 V with respect to free fullerene indicates that the actual metal fragments exert an electron-donating effect towards the C₆₀ cage apparently greater than that exerted by the ferrocenyl fragment in similar complex (note, however, the different solvent).

The oxidation of complex **2** occurs irreversibly with the transfer of two electrons as typical of ruthenocenes. A shift

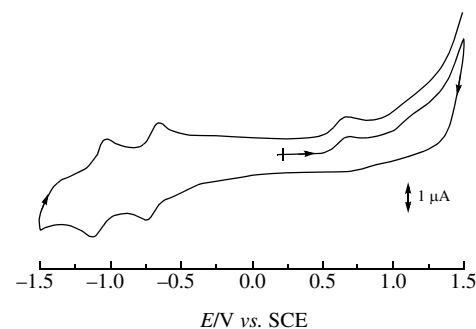


Figure 1 Cyclic voltammogram recorded at a platinum electrode in *o*-C₆H₄Cl₂ solution of **1** (0.8 × 10^{−3} mol dm^{−3}). [NBu₄][ClO₄] (0.1 mol dm^{−3}) supporting electrolyte. Scan rate: 0.2 V s^{−1}.

Table 1 Formal electrode potentials (V, vs. SCE) and peak-to-peak separation (mV) for the redox change exhibited by the derivatised pyrrolidino-[60]fullerenes. Values in parentheses are referred to the $\text{FcCp}_2^0/\text{FcCp}_2^+$ couple. Error is within 5 mV.

Complex	Ox			Red			Solvent
	$E^{0'}$	ΔE_p^a	$E^{0'}(1^{\text{st}})$	ΔE_p^a	$E^{0'}(2^{\text{nd}})$	ΔE_p^a	
1	+0.63 (+0.06)	80	−0.70 (−1.27)	73	−1.07 (−1.64)	90	<i>o</i> -C ₆ H ₄ Cl ₂
2	+0.85 (+0.24)	—	−0.85 (−1.46)	180	−1.23 (−1.84)	200	<i>o</i> -C ₆ H ₄ Cl ₂
3	— ^b	—	(−1.13)	—	(−1.52)	—	Toluene/ MeCN
C ₆₀	—	—	−0.52 (−1.09)	120	−0.91 (−1.48)	110	<i>o</i> -C ₆ H ₄ Cl ₂
Cb*CoCp	+0.65 (+0.08)	200	—	—	—	—	<i>o</i> -C ₆ H ₄ Cl ₂
Cp*RuCp	+0.54 ^c	—	—	—	—	—	CH ₂ Cl ₂
FeCp ₂ ⁰	+0.57	387	—	—	—	—	<i>o</i> -C ₆ H ₄ Cl ₂

^aMeasured at 0.2 V s^{−1}. ^bOxidation process almost coincident with that of free ferrocene. ^cFrom ref. 8.

by about 300 mV to the positive area of potentials comparing to Cp*RuCp confirms the acceptor character of the fullerene fragment. Surprisingly, there is no change in the oxidative potential of **1** comparing to Cb*CoCp as if there is no electron shift from the cobalt complex to fullerene.

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