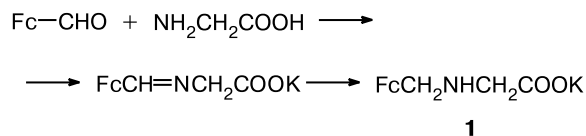


New modification of the Prato reaction applied to the synthesis of *N*-ferrocenylmethylpyrrolidino[60]fullerene

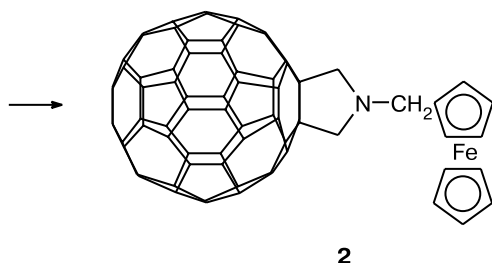
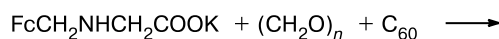
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The cycloaddition of the intermediate formed from aldehydes and *N*-substituted glycines is a widely used method for modification of the fullerene cage.^{1,2} The intermediate formed upon the abstraction of CO₂ has a zwitter-ion structure with a negative charge on the former α -carbon atom of the amino acid. One could suggest that preliminary formation of a negative charge on the carbon atom of the carboxy group in the salt of *N*-substituted amino acid would be favorable for the formation of the zwitter-ion intermediate.



In view of the general strategy of the research into fullerene-metalloocene molecules with various structures, it was of interest to introduce *N*-ferrocenylmethylglycine (**1**) into the Prato reaction. We prepared this compound as the potassium salt using our solid-state procedure³ and successfully carried out the reaction, which gave *N*-ferrocenylmethylpyrrolidino[60]fullerene (**2**) containing ferrocenyl and fullerene fragments separated by a triatomic saturated spacer.



A mixture of ferrocenylcarboxaldehyde (2 g, 9.2 mmol), glycine (0.69 g, 9.2 mmol), and K₂CO₃ (2.5 g, 18.4 mmol) was placed in a ball mill and mixed for 5 min. The resulting powder was placed in a round-bottom flask and heated on an oil bath for 5 h at 60°C, the mixture being stirred at intervals by a glass rod. Then MeOH (5×20 mL) was added. The methanol solution was

placed in an autoclave (0.25 L), hydrogenated (2 g, 5% Pd/C, 6 h, 20 atm, 50 °C), cooled, and filtered. The solvent was evaporated and the residue was dissolved in water and washed with Et₂O (3×50 mL). The aqueous layer was diluted with 100 mL of PrⁱOH and the solvent was evaporated (the procedure of PrⁱOH evaporation was repeated twice). Product **1** was crystallized from a PrⁱOH–water mixture. Compound **1** (as the carbonate) was obtained in a yield of 1.75 g (61%).

Found (%): C, 45.38; H, 4.61; N, 3.64. C₁₃H₁₄FeKNO₂ • H₂CO₃. Calculated (%): C, 45.05; H, 4.32; N, 3.75. ¹H NMR (CD₃OD), δ : 3.43 (m, 2 H, CH₂); 3.87 (m, 2 H, CH₂); 4.37 (m, 7 H, C₅H₅ + C₅H₄); 4.49 (m, 2 H, C₅H₄).

A mixture of the potassium salt of *N*-ferrocenylmethylglycine (106 mg, 0.4173 mmol), paraformaldehyde (41.7 mg, 1.39 mmol), and C₆₀ (100 mg, 0.139 mmol) was refluxed in 200 mL of toluene for 5 h in an argon flow with stirring by a magnetic stirrer. During the reaction, the precipitate of the K salt dissolved and the solution color changed from violet to red. The reaction mixture was concentrated to dryness. The product was purified by column chromatography. The unreacted C₆₀ was eluted by a toluene–light petroleum mixture, and *N*-ferrocenylmethylpyrrolidino[60]fullerene (**2**), by toluene. R_f 0.25 (toluene–light petroleum, 1 : 1). The isolated yield of product **2** was 60 mg (58%).

¹H NMR (CDCl₃), δ : 4.15 (s, 2 H, CH₂); 4.24 (m, 5 H, C₅H₅); 4.26 (m, 2 H, C₅H₄); 4.38 (s, 4 H, CH₂); 4.46 (m, 2 H, C₅H₄). The ¹³C NMR spectrum could not be recorded due to the poor solubility of **2**.

Electrochemical study of compound **2** was carried out using a PI-50-1 potentiostat in an *o*-dichlorobenzene solution at a glass carbon electrode. A 0.2 M solution of Bu₄NBF₄ was used as the supporting electrolyte.

The electrochemical study of *N*-ferrocenylmethylpyrrolidino[60]fullerene (**2**) showed that compound **2** was much less prone to be reduced than C₆₀. The reduction potentials of C₆₀ are –0.56, –1.00, –1.45, and –2.0 V, while those of **2** are –0.65, –1.02, and –1.55 V under the same conditions. The presence of the fullerene fragment has virtually no influence on the oxidation potential of the product. The oxidation potential of compound **2** is 0.75 V (vs. SCE); under the same conditions, the oxidation potential of dimethylaminomethylferrocene and ferrocene is 0.76 V.

This version of the reaction may prove useful when the synthesis of *N*-substituted amino acid passes through

a salt (the isolation of the free acid can be bypassed) and also in those cases where the carboxylic acid is stable only as a salt.

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