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# Metallocenyl-Containing and Unsaturated Fulleropyrrolidine Derivatives: Synthesis and Hydrogenation

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**Abstract**—The possibility of Pd/C-catalyzed hydrogenation of ferrocenyl, cymantrenyl, and ruthenocenyl derivatives of *N*-methyl-2-(3-chlorovinyl)fulleropyrrolidine and *N*-methyl-2-(2-styryl)fulleropyrrolidine with hydrogen was elucidated. A new compound, *N*-methyl-2-(3-chlorovinyl-3-ruthenocenyl)fulleropyrrolidine, was synthesized.

*Keywords:* fulleropyrrolidine, metallocene, hydrogenation, hydrogenolysis

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## INTRODUCTION

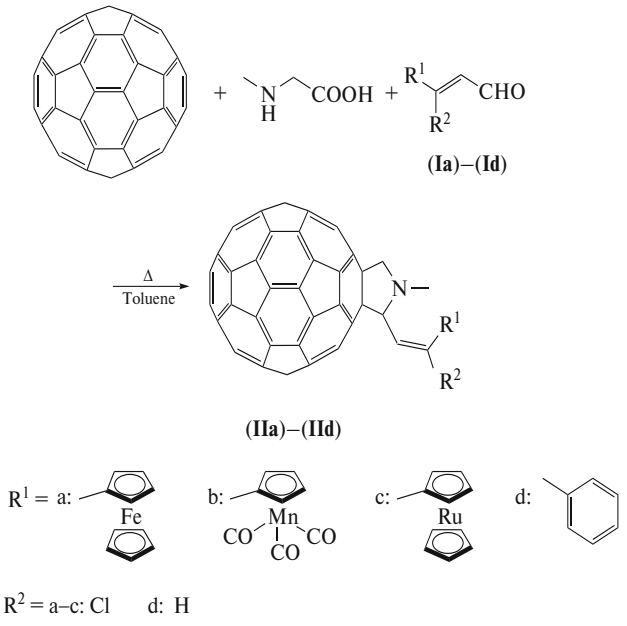
Fullerene functionalization is the subject of a large body of publications, as this is a newly emerging and actively developing research area. Among known methods for fullerene C60 modification, worth noting are cycloaddition reactions, which represent the key route to heterocyclic fullerene derivatives. The best known synthesis of fulleropyrrolidines is the Prato reaction, which consists in the addition of azomethine ylide, formed from an aldehyde and an amino acid, to a fullerene double bond [1–3].

A number of compounds containing metallocenyl and fullerene moieties have been reported. Among them are derivatives of ferrocene [4, 5], ruthenocene [6], cyclopentadienylmanganese tricarbonyl (cymantrene), cyclopentadienylrhenium tricarbonyl [7–9], and some other substituted metallocenes [10, 11]. The molecules containing both fullerene and metallocenyl moieties are of particular interest for their electrophysical and optical properties. The chemical reactivity of these compounds caused by the presence of multiple bonds and the metal in the molecule are equally important.

This study deals with the possibility of hydrogenation of chlorovinylmetallocene (ferrocene, cymantrene, and ruthenocene) fulleropyrrolidine derivatives under various conditions.

## RESULTS AND DISCUSSION

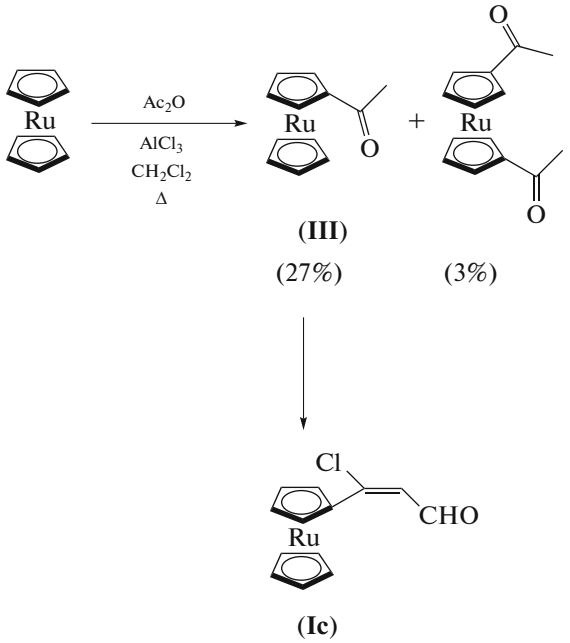
*N*-Methyl-2-(3-chlorovinyl-3-ferrocenyl)fulleropyrrolidine **(IIa)** and *N*-methyl-2-(3-chlorovinyl-3-cymantrenyl)fulleropyrrolidine **(IIb)** were prepared and characterized previously [7]. We extended this series of metallocene derivatives by synthesizing a new compound, *N*-methyl-2-(3-chlorovinyl-3-ruthenocenyl)fulleropyrrolidine **(IIc)**, by the Prato reaction (Scheme 1).




**Scheme 1.**

The starting aldehyde (2-chloro-2-ruthenocenylacrolein, **Ic**) was prepared by a known method [12] from monoacetylruthenocene **(III)**, which was synthesized by a procedure we modified. According to a known procedure [13], acetic anhydride acylation was carried out using a twofold excess of ruthenocene, the yield of **III** being 14% with no side products. Because of low yield of the monosubstituted product, we attempted the use of equivalent amounts of reactants

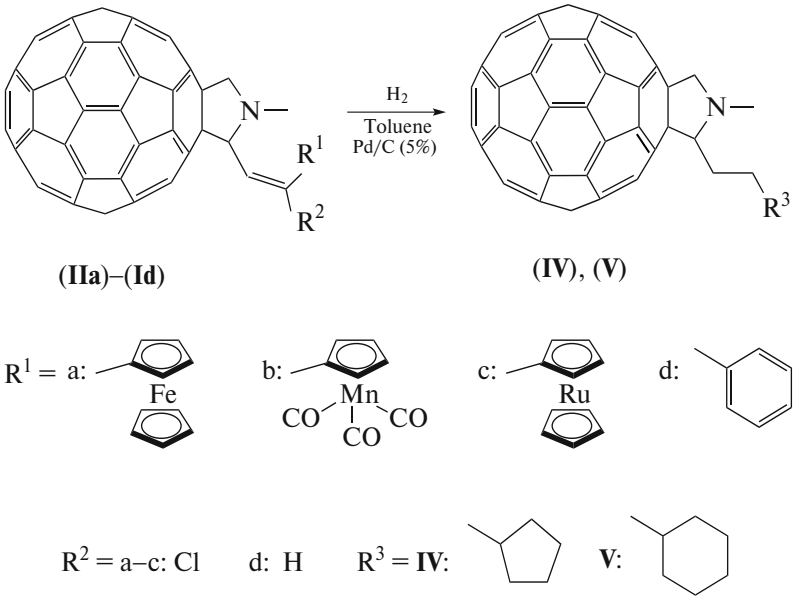
and twice longer reaction time. This gave a mixture of mono- and diacetylruthenocenes in 9 : 1 ratio. The yield of **III** was 27%, which was almost twice higher than that in the previous case (Scheme 2).




**Scheme 2.**

Compound **IIc** was obtained in 12% yield and identified by $^1$H and $^{13}$C NMR spectra. The $^1$H NMR spectrum exhibits signals for pyrrolidine ring protons (one singlet due to the *N*-methyl group (2.89 ppm) and three doublets (4.17, 4.84, 5.07 ppm)), a doublet for the vinyl proton (6.44 ppm), and proton signals for unsubstituted (4.38 ppm) and substituted (4.61, 4.65, 4.92, and 5.02 ppm) Cp rings of the metallocenyl moiety. It is noteworthy that in the spectrum of **IIc**, the pyrrolidine proton signal is shifted upfield relative to the proton signals for free cyclopentadienyl ring; this shift is not observed for other derivatives. The $^{13}$C NMR spectrum shows carbon signals for the *N*-methyl group (40.2 ppm), pyrrolidine (69.0, 70.1 ppm) and ruthenocene (72.0) moieties, the vinyl group (71.5 ppm), and fullerene (120.7–147.4 ppm).

In order to study the effect of fullerene and metallocenyl moieties on the chemical reactivity of compounds **IIa**–**IIc**, we subjected the compounds to hydrogenation. According to [14], ferrocene derivatives containing an additional conjugated double bond are reduced with hydrogen to cyclopentane derivatives; the free double bond is the first to be reduced, followed by reduction of the cyclopentadienyl ring. We assumed that hydrogenation of chlorovinylmetallocenes incorporated in fulleropyrrolidine molecules would occur in a similar way to give *N*-methyl-2-[(β-cyclopentyl)ethyl]fulleropyrrolidine (**IV**) (Scheme 3).




**Scheme 3.**

Unfortunately, we were unable to isolate compound **IV** in a pure state by column chromatography. However, the presence of this product in the reaction mixture and the product to substrate ratio were determined from the $^1$H NMR and MALDI-TOF mass spectra.

While studying hydrogenation of metallocenyl-containing chlorovinyl-fulleropyrrolidines, we found

**Table 1.** Results of hydrogenation of **IIa**–**IId** under various conditions

| Substrate | Reaction time, h | Addition of $CF_3C(O)OH$ | The ratio **IIx** : **IV** (**V**) ($x$ = a–d) |
|---|---|---|---|
| **IIa** | 2 | | 2 : 3 |
| **IIb** | 6.5 | | |
| **IIb** | 6.5 | + | 2.5 : 1 |
| **IIc** | 8 | | |
| **IIc** | 10.5 | | |
| **IIc** | 10.5 | + | 1 : 5 |
| **IId** | 6.5 | | |
| **IId** | 6.5 | + | |

that hydrogenation in the $CF_3C(O)OH$ medium results in destruction of compound **IIa**, whereas conduction of the reaction in toluene in the presence of the Pd/C catalyst affords a mixture of compounds **IIa** and **IV** in 2 : 3 ratio, respectively. This conclusion was derived from analysis of the $^1$H NMR spectrum. Apart from signals for the protons of the starting compound **IIa**, the spectrum exhibits proton signals for hydrogenolysis product **IV**, that is, multiplets corresponding to the cyclopentyl (0.55 ppm) and ethyl (0.97 ppm) protons, a singlet for the *N*-methyl protons (2.84 ppm) shifted upfield relative to the analogous signal for the substrate (2.91 ppm) [7], and signals for pyrrolidine protons (4.23, 4.96, 5.02 ppm). A molecular ion of mass 874 corresponding to hydrogenolysis product **IV** is observed in the MALDI-TOF mass spectrum. In order to increase the yield of product **IV**, we carried out the reaction at 50°C; however, the pyrrolidine moiety of the starting fulleropyrrolidine decomposed, as indicated by the absence of signals for the pyrrolidine protons of the starting compound and the presence of high-field signals due to aliphatic protons in the $^1$H NMR spectrum.

In the case of similar reactions with compounds **IIb** and **IIc**, we did not observe the formation of hydrogenation products at either the double bond or the cyclopentadienyl ring. Meanwhile, hydrogenation of these compounds in the presence of several drops of $CF_3C(O)OH$ gives rise to *N*-methyl-2-[(β-cyclopentyl)ethyl]fulleropyrrolidine. For comparison, we also carried out hydrogenation of *N*-methyl-2-(2-styryl)fulleropyrrolidine (**IId**) obtained by a reported procedure [9]. The results of hydrogenation of **IIa**–**IId** under various conditions are summarized in Table 1. Compound **IId** does not convert into the product **V** under the hydrogenation condition selected.

We observed an interesting result, in particular, two substituents with similar properties, ruthenocene and ferrocene, behave in different ways in the hydrogenation. The ferrocenyl substituent is partially reduced in toluene, but degrades in $CF_3C(O)OH$, whereas the ruthenocenyl moiety is successfully hydrogenated in the presence of $CF_3(O)OH$. The presence of the cymantrenyl moiety in the molecule also facilitates the reduction with addition of $CF_3C(O)OH$. The styryl group is fully inert under the same conditions. Thus, the metallocenyl group contained in these molecules has a crucial effect for hydrogenation.

## EXPERIMENTAL

The reactions were carried out using fullerene $C_{60}$ of 99.9% purity produced at the Razuvaev Institute of Organometallic Chemistry. 3-Chloro-3-ferrocenylacrolein, 3-chloro-3-cymantrenylacrolein, and compounds **IIa** and **IIb** were prepared by the procedure reported in [7]. Compound **IId** was obtained by the procedure reported in [9].

The $^1$H and $^{13}$C NMR spectra were measured on a Bruker 400 HX spectrometer (in $CDCl_3$, TMS as the internal standard). The positive ion MALDI mass spectra were measured on a Bruker Autoflex III instrument with a nitrogen laser at λ = 337 nm.

**Synthesis of IIc.** Compound **Ic** (0.144 g, 0.45 mmol) and sarcosine (0.08 g, 0.9 mmol) were added in an argon flow to a solution of $C_{60}$ (0.216 g, 0.3 mmol) in toluene (250 mL). The reaction mixture was refluxed for 11.5 h, concentrated, and chromatographed in a toluene–hexane mixture (1 : 1). The yield of **IIc** was 37.4 mg (12%).

$^1$H NMR ($CDCl_3$, δ, ppm; *J*): 2.89 (s, 3H, N–$CH_3$); 4.17 (d, 1H, $CH_2$-pyrrolidine; $J$ = 9.0 Hz); 4.38 (s, 5H, Cp); 4.61 (m, 1H, Cp); 4.65 (m, 1H, Cp); 4.84 (d, 1H, CH-pyrrolidine, $J$ = 9.0 Hz); 4.92 (m, 1H, Cp); 5.01 (m, 1H, Cp); 5.07 (d, 1H, $CH_2$-pyrrolidine, $J$ = 9.0); 6.44 (d, 1H, CCl=CH, $J$ = 9.0 Hz). $^{13}$C NMR ($CDCl_3$; δ, ppm): 40.2 (N–$CH_3$); 69.0 (C); 70.1 ($CH_2$); 71.5 (CH=CCl); 72.0 (Cp); 120.7–147.4 ($C_{60}$). MALDI-TOF MS, *m/z*: 1067 $[M-H]^+$.

**Synthesis of III**. $AlCl_3$ (1.49 g, 11.2 mmol) was added to a solution of ruthenocene (1.16 g, 5 mmol) in

$CH_2Cl_2$ (100 mL), the mixture was brought to boiling, and a solution of acetic anhydride (0.42 mL, 4.42 mmol) in $CH_2Cl_2$ (25 mL) was added dropwise during 1 h. After the addition of acetic anhydride, the mixture was refluxed for 2 h. The yield of **III** was 0.3257 g (27%).

$^1$H NMR ($CDCl_3$; δ, ppm): 2.29 (s, 3H, $-COCH_3$); 4.59 (s, 5H, Cp); 4.78 (m, 2H, Cp); 5.09 (m, 2H, Cp).

**General procedure for hydrogenation of compounds IIa–IId.** Compound (**IIa–IId**) (20 mg) was placed into an autoclave and dissolved in toluene (2 mL); the Pd/C catalyst (5%) and $CF_3C(O)OH$ (2 drops) were added (alternatively, no acid was added). The autoclave was filled with hydrogen (up to hydrogen pressure of 11 atm) and stirred at room temperature for 2–10.5 h. The reaction mixture was filtered to remove the catalyst, washed, and concentrated. The degree of hydrogenolysis was determined from the $^1$H NMR spectra.

MALDI-TOF mass spectrum of **IIa**, *m/z*: 1022 $[M-H]^+$.

$^1$H NMR spectrum of **IV** ($CDCl_3$; δ, ppm): 0.55 (m, 9H, cyclopentane); 0.97 (m, 4H, $CH_2-CH_2$); 2.84 (s, 3H, $N-CH_3$); 4.23 (d, 1H, pyrrolidine); 4.96 (s, 1H, pyrrolidine); 5.02 (d, 1H, pyrrolidine). MALDI-TOF MS, *m/z*: 874 $[M-H]^+$.

The NMR studies were carried out at the Center of Investigations of Molecular Structure of the Nesmeyanov Institute of Organoelement Compounds.

## REFERENCES

1. Prato, M. and Maggini, M., *Chem. Res.*, 1998, vol. 31, p. 519.
2. Maggini, M. and Scorrano, G.J., *J. Am. Chem. Soc.*, 1993, vol. 115, p. 9798.
3. Guldi, D.M., Maggini, M., Scorrano, G., and Prato, M., *J. Am. Chem. Soc.*, 1997, vol. 119, p. 974.
4. Kharisov, B.I., Kharissova, O.V., and Gomez, M.J., *Ind. Eng. Chem. Res.*, 2009, vol. 48, p. 545.
5. Guldi, D.M., Maggini, M., Scorrano, G., and Prato, M., *J. Am. Chem. Soc.*, 1997, vol. 199, p. 974.
6. Oviedo, J.J., de la Cruz, P. Garin, J., et al., *Tetrahedron Lett.*, 2005, vol. 45, p. 4781.
7. Abramova, N.V., Ginzburg, A.G., and Sokolov, V.I., *Russ. Chem. Bull.,* 2010, vol. 59, p. 1964.
8. Abramova, N.V., Ginzburg, A.G., Peregudov, A.S., et al., *Russ. Chem. Bull.*, 2008, vol. 57, p. 1967.
9. Abramova, N.V., Peregudova, S.M., Emel'yanova, A.O., et al., *Russ. Chem. Bull. Int. Ed.*, 2007, vol. 56, p. 361.
10. Sokolov, V.I., Bashilov, V.V., and Dolgushin, F.M., *Tetrahedron Lett.*, 2009, vol. 50, p. 5347.
11. Sokolov, V.I., Abramova, N.V., Mutseneck, E.V., et al., *Mendeleev Commun.*, 2007, vol. 17, p. 202.
12. Hofer, O. and Schlogl, K., *J. Organomet. Chem.*, 1968, vol. 13, p. 443.
13. Rausch, M.D., Fischer, E.O., and Grubert, H., *J. Am. Chem. Soc.*, 1960, vol. 82, p. 76.
14. Sokolov, V.I., Troitskaya, L.L., Khrushcheva, N.S., and Reutov, O.A., *J. Organomet. Chem.*, 1989, vol. 378, p. 227.

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