

Cycloaddition of Tertiary Amines to Fullerene C₆₀, Catalyzed by Ti, Zr, and Hf Complexes

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Abstract—Cycloaddition of various tertiary amines to fullerene C₆₀ in the presence of Cp₂MCl₂ complexes (M = Ti, Zr, Hf) in toluene at 20–150°C in 3–48 h leads to the formation of pyrrolofullerenes in high yields.

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The most widely used method for the synthesis of fused tetrahydropyrrolofullerenes is based on 1,3-dipolar cycloaddition of azomethine ylides to C₆₀ (Prato reaction) [1, 2]. In 1995, Lawson et al. [3] reported on the synthesis of pyrrolofullerenes by photochemical addition of tertiary amines to C₆₀, and this reaction was further developed by some authors [4–8]. Interest in pyrrolidines fused to a fullerene sphere originates from application of these compounds in medicine [9–11], electronics, and nonlinear optics [12] and as organic ferromagnetics [13–15], photosensitizers for generation of singlet oxygen [16], and solar energy transducers [17, 18]. The scope of application of pyrrolofullerenes was discussed in detail in [19, 20].

Taking into account that known procedures for the preparation of pyrrolofullerenes are not free from some limitations related to the necessity of using initial reactants with a definite structure to generate azomethine ylides under the Prato reaction conditions and that the yields of the target products in photochemical reactions are relatively poor, we made an attempt to effect catalytic cycloaddition of tertiary amines to C₆₀ in the presence of metal complexes. Prior to our studies, no data on catalytic methods of synthesis of pyrrolofullerenes were reported.

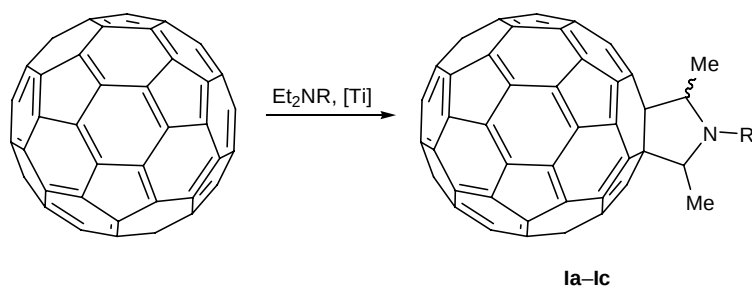
As catalysts we tried a number of salts and complexes of such transition metals as Fe, Co, Mn, Pd, Ti, Zr, and Hf, which are widely used in catalytic reactions. With a view to obtain the corresponding monoadducts of C₆₀ to tertiary amines, the reactions were

carried out with equimolar amounts of the reactants under specially developed optimal conditions.

In the reaction of triethylamine with C₆₀ in the presence of 20 mol % of Cp₂TiCl₂ (toluene, ~20°C, 48 h) we isolated 1'-ethyl-2',5'-dimethyltetrahydropyrrolo[3',4':1,9](C₆₀-I_h)[5,6]fullerene (**1a**) in ~90% yield (Scheme 1). The same yield of **1a** was reached in 3 h when the reaction was performed at 60°C. Analogous results were obtained in the presence of Cp₂ZrCl₂ and Cp₂HfCl₂ as catalyst: the yield of **1a** was larger than 90%. No reaction occurred when complexes or salts of other transition metals were used as catalyst [Ni(acac)₂, Pd(acac)₂, Fe(acac)₃, TiCl₄, Cp₂Fe, MnCl₂, CoCl₂, FeCl₃, ZrCl₄] or in the absence of catalyst.

Compound **1a** was isolated by column chromatography on silica gel (hexane–chloroform, 6:1). Its UV spectrum contains an absorption maximum at λ 429 nm, which is typical of closed [6,6]-monoadducts [21, 22]. In the ¹³C NMR spectrum of **1a**, sp³-hybridized carbon atoms of the fullerene polyhedron resonate at δ_C 75.06 ppm, pyrrolidine CH carbon signals appear at δ_C 63.25 ppm, and methyl carbon atoms give a signal at δ_C 15.20 ppm; these data are consistent with those given in [3] for 1'-ethyl-*trans*-2',5'-dimethyltetrahydropyrrolo[3',4':1,9](C₆₀-I_h)[5,6]fullerene. Signals in the δ_C range from 128.00 to 156.93 ppm belong to sp²-carbon atoms of the fullerene fragment. The mass spectrum (MALDI TOF, see figure) of **1a** contains a strong peak at *m/z* 819 which corresponds to the molecular ion [M]⁺ derived

Scheme 1.



[Ti] = Cp₂TiCl₂; R = Et (**a**), CH₂=CHCH₂ (**b**), CH₂=CH(CH₂)₃CH=CHCH₂ (**c**).

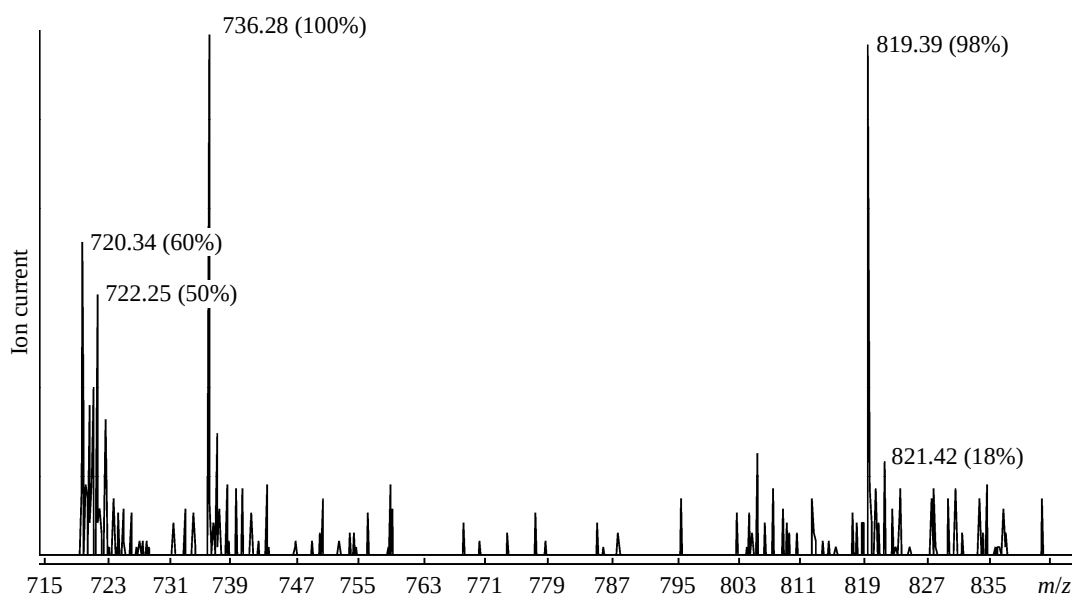
from monocycloadduct having no hydrogen atoms in the fullerene moiety. Photochemical addition of triethylamine to C₆₀ gives ~55% of cycloadduct **Ia** [3, 7].

We then tried to involve in the same reaction *N,N*-diethylprop-2-en-1-amine and *N,N*-diethylocta-2,7-dien-1-amine. These amines reacted with C₆₀ in the presence of Cp₂TiCl₂ to give 75–80% of the corresponding pyrrolofullerenes **Ib** and **Ic**. Here, as in the reaction with triethylamine, the pyrrolidine fragment is built up via successive addition of the α-carbon atoms in the ethyl groups of tertiary amines to the 6,6-double bond of C₆₀ through formation of radical ion pairs due to one-electron transfer. Compounds **Ib** and **Ic** were isolated by column chromatography, and their structure was determined by spectral methods (including mass spectrometry).

With a view to extend the scope of application of catalytic cycloaddition of tertiary amines to fullerene C₆₀, as well as to synthesize pyrrolofullerenes with

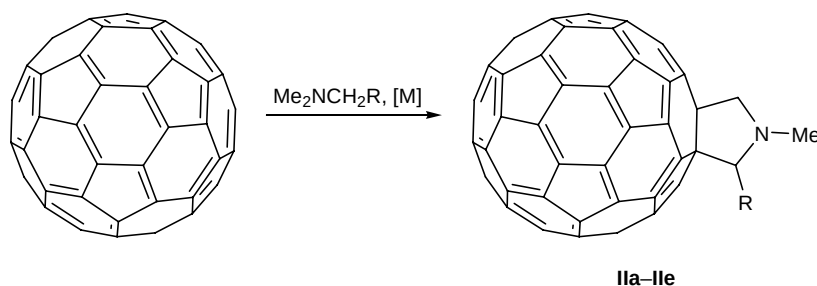
more complex structures, we examined reactions of C₆₀ with *N,N,N',N'*-tetramethylmethanediamine, 1-(*N,N*-dimethylaminomethyl)-1,2,4-triazole, 2-(*N,N*-dimethylaminomethyl)-1,2,3-benzotriazole, 2-(*N,N*-dimethylaminomethyl)phenol, and 2-(*N,N*-dimethylaminomethyl)-3,5-di-*tert*-butylphenol. The reactions were carried out in the presence of 20 mol % of Cp₂TiCl₂ at 150°C (reaction time 3 h), and the products were [6,6]-cycloadducts **Ila–Ile** (yield 65–80%; Scheme 2).

While discussing the mechanism of catalytic action of transition metal complexes on the cycloaddition of tertiary amines to fullerenes, we took into account the data reported in [23–26], according to which strongly nucleophilic primary and secondary aliphatic amines readily add to electron-deficient carbon atoms in C₆₀ molecule. Initial one-electron transfer from amine to C₆₀ is followed by recombination of the resulting amine radical cation and fullerene readical anion. In



MALDI-TOF mass spectrum of compound **Ia**.

Scheme 2.



R = 1*H*-1,2,4-triazol-1-yl (**a**), 1*H*-1,2,3-benzotriazol-1-yl (**b**), Me₂N (**c**), 2-HOC₆H₄ (**d**), 3,5-(*t*-Bu)₂-4-HOC₆H₂ (**e**).

the final step, hydrogen atom is transferred from the nitrogen to 6,6-carbon atom of fullerene to give addition product. Unlike primary and secondary amines, tertiary amines lacking active N–H bond are incapable of adding to C₆₀ under usual conditions; however, electron transfer from the tertiary nitrogen atom to C₆₀ gives rise to radical ion pairs C₆₀^{•−}NR₃^{•+} [27]. Presumably, metallocene dichloride catalysts not only facilitate one-electron transfer [28] from tertiary amine to C₆₀ with formation of radical ion pairs but also activate C–H bond in the amine and participate in hydrogen transfer from the α -carbon atom of the amine to the 6,6-carbon atom of fullerene, leading to the formation of neutral adduct. Hydrogen transfer from the second α -carbon atom of tertiary amine along the above scheme results in closure of pyrrolidine ring. Hydrogen atoms directly linked to fullerene carbon atoms are likely to undergo oxidative elimination [29–32] or are transferred to another fullerene molecule [4]. The latter assumption is supported by the presence in the mass spectra of peaks corresponding to the molecular ions C₆₀H₂, [M_(I) + 2H]⁺, and [M_(II) + 2H]⁺.

Thus the proposed procedure for catalytic cycloaddition of tertiary amines to fullerene C₆₀ in the presence of Ti, Zr, and Hf complexes ensures preparation of the target products with high yield and selectivity, which opens some prospects in the application of pyrrolfullerenes in practice.

EXPERIMENTAL

Commercially available (C₆₀-I_h)[5,6]fullerene of 99.5% purity (Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, Nizhnii Novgorod, Russia) was used. Toluene was distilled over metallic sodium just before use. Reaction mixtures were analyzed by gel-permeating liquid chromatography at room temperature on an Altex Model 330 instrument (USA) equipped with an UV detector

(λ 313 nm) and a 250×8-mm metallic column packed with PL gel 100 Å (grain size 5 μ m); eluent toluene, flow rate 0.2 ml/min. The IR spectra were recorded in KBr on a Specord 75IR spectrometer (Carl Zeiss Jena). The UV spectra were measured on Specord M-40 and Specord M-80 spectrophotometers. The ¹H and ¹³C NMR spectra were obtained on a Jeol FX 90Q instrument at 90 and 22.5 MHz, respectively, using CDCl₃–CS₂ (1:1) as solvent. The mass spectra (positive ion monitoring) were run on a Maldi Voyager-D STR TOF mass spectrometer.

General procedure for the addition of tertiary amines to fullerene C₆₀. A 17-ml glass reactor or a metal finger-like high-pressure reactor was charged with 0.01 mmol of fullerene C₆₀, 10 ml of toluene, 0.0105 mmol of the corresponding tertiary amine, and 0.002 mmol of Cp₂MCl₂ (M = Ti, Zr, Hf), and the mixture was stirred for 3–48 h at 20–150°C. Compounds **I** and **II** were separated from unreacted C₆₀ by column chromatography on silica gel L (100–250 μ m) using hexane–chloroform (6:1) as eluent. Compound **I**e was identified by comparison with a sample prepared as described in [33].

1'-Ethyl-2',5'-dimethyltetrahydropyrrolo-[3',4':1,9](C₆₀-I_h)[5,6]fullerene (Ia**).** IR spectrum, ν , cm^{−1}: 530, 730, 1100, 1170, 1270, 1380, 1420, 1480, 2850, 2920. UV spectrum (CHCl₃): $\lambda_{\max}$ 429 nm. ¹H NMR spectrum, δ , ppm: 1.45 t (3H, CH₃), 1.81 d (6H, CH₃), 2.63 q (H_A, CH₂), 3.26 q (H_B, CH₂), 4.58 q (2H, CH). ¹³C NMR spectrum, δ_C , ppm: 14.27, 15.20, 46.04, 63.25, 75.06, 128.00–156.93. Mass spectrum, m/z (*I*_{rel}, %): 821 [M + 2H]⁺ (17), 819 [M]⁺ (98), 722 [C₆₀H₂]⁺ (50), 721 [C₆₀H]⁺ (33), 720 [C₆₀]⁺ (60).

2',5'-Dimethyl-1'-(prop-2-en-1-yl)tetrahydropyrrolo[3',4':1,9](C₆₀-I_h)[5,6]fullerene (Ib**).** IR spectrum, ν , cm^{−1}: 520, 730, 1100, 1260, 1390, 1460, 1650, 2900, 2950. UV spectrum (CHCl₃), $\lambda_{\max}$, nm: 258, 329, 430. ¹H NMR spectrum, δ , ppm: 1.81 d (6H, CH₃),

4.68 q (2H, CH), 3.36 d (2H, CH₂), 5.32–5.40 m (1H, CH), 5.38 d (2H, CH₂). ¹³C NMR spectrum, δ_C, ppm: 15.30, 61.02, 64.17, 75.37, 116.08, 137.86, 123.86–156.65. Mass spectrum, *m/z* (*I*_{rel}, %): 831 [*M*]⁺ (0.4), 733 [C₆₀CH]⁺ (15), 722 [C₆₀H₂]⁺ (70), 721 [C₆₀H]⁺ (100), 720 [C₆₀]⁺ (90).

2',5'-Dimethyl-1'-(octa-2,7-dien-1-yl)tetrahydropyrrolo[3',4':1,9](C₆₀-I_h)[5,6]fullerene (Ic). IR spectrum, ν, cm⁻¹: 520, 740, 1100, 1160, 1270, 1460, 1640, 2900, 2950. UV spectrum (CHCl₃), λ_{max}, nm: 258, 329, 404, 428. ¹H NMR spectrum, δ, ppm: 1.81 d (6H, CH₃), 4.58 q (2H, CH), 3.36 d (2H, CH₂), 5.32–5.40 m (3H, CH), 1.42 t (2H, CH₂), 1.95–2.07 m (4H, CH₂), 5.38 d (2H, CH₂). ¹³C NMR spectrum, δ_C, ppm: 15.04, 26.45, 31.60, 31.65, 51.10, 67.14, 75.20, 116.10, 129.14, 133.35, 137.73, 123.86–156.65. Mass spectrum, *m/z* (*I*_{rel}, %): 899 [*M*]⁺ (0.4), 858 [*M* – C₃H₅]⁺ (2.5), 722 [C₆₀H₂]⁺ (40), 720 [C₆₀]⁺ (100).

1'-Methyl-2'-(1*H*-1,2,4-triazol-1-yl)tetrahydropyrrolo[3',4':1,9](C₆₀-I_h)[5,6]fullerene (IIa). IR spectrum, ν, cm⁻¹: 530, 740, 1100, 1260, 1380, 1410, 1460, 1650, 2900, 2950. UV spectrum (CHCl₃), λ_{max}, nm: 258, 329, 428. ¹H NMR spectrum, δ, ppm: 3.56 s (2H, CH₂), 4.85 s (1H, CH), 2.25 s (3H, CH₃), 8.10–8.30 s (2H, CH=N). ¹³C NMR spectrum, δ_C, ppm: 45.87, 93.22, 73.16, 77.45, 67.5, 123.89–164.92. Mass spectrum, *m/z* (*I*_{rel}, %): 844 [*M*]⁺ (4), 776 [*M* – C₂H₂N₃]⁺ (7), 761 [C₆₀CH₂CHN]⁺ (8), 722 [C₆₀H₂]⁺ (30), 721 [C₆₀H]⁺ (65).

2'-(1*H*-1,2,3-Benzotriazol-1-yl)-1'-methyltetrahydropyrrolo[3',4':1,9](C₆₀-I_h)[5,6]fullerene (IIb). IR spectrum, ν, cm⁻¹: 520, 750, 1100, 1150, 1260, 1380, 1400, 1460, 2850, 2910. UV spectrum (CHCl₃), λ_{max}, nm: 278, 330, 403, 427. ¹H NMR spectrum, δ, ppm: 3.42 s (2H, CH₂), 4.83 s (1H, CH), 2.22 s (3H, CH₃), 6.3–7.5 m (4H, C₆H₄). ¹³C NMR spectrum, δ_C, ppm: 45.09, 92.51, 79.9, 72.31, 67.81, 111.15, 119.95, 121.64, 125.87–152.30. Mass spectrum, *m/z* (*I*_{rel}, %): 894 [*M*]⁺ (4), 778 [*M* – C₆H₄N₃]⁺ (30), 761 [C₆₀CH₂NCH]⁺ (5), 722 [C₆₀H₂]⁺ (70), 721 [C₆₀H]⁺ (100), 720 [C₆₀]⁺ (92).

***N,N*,1'-Trimethyltetrahydropyrrolo[3',4':1,9](C₆₀-I_h)[5,6]fulleren-2'-amine (IIc).** IR spectrum, ν, cm⁻¹: 520, 700, 730, 1100, 1260, 1460, 2870, 2900, 2950. UV spectrum (CHCl₃), λ_{max}, nm: 255, 301. ¹H NMR spectrum, δ, ppm: 3.46 s (2H, CH₂), 4.17 s (1H, CH), 2.24 s (3H, CH₃), 2.65 s (6H, CH₃). ¹³C NMR spectrum, δ_C, ppm: 42.95, 44.11, 44.11, 72.5, 74.95, 77.81, 92.45, 125.39–154.65.

2-{1'-Methyltetrahydropyrrolo[3',4':1,9](C₆₀-I_h)-[5,6]fulleren-2'-yl}phenol (IIId). IR spectrum, ν, cm⁻¹: 530, 770, 1100, 1260, 1380, 1460, 2860, 2920, 3650. UV spectrum (CHCl₃), λ_{max}, nm: 258, 329, 404, 427. ¹H NMR spectrum, δ, ppm: 3.56 s (2H, CH₂), 4.63 s (1H, CH), 2.17 s (3H, CH₃), 7.16–7.21 m (4H, H_{arom}). ¹³C NMR spectrum, δ_C, ppm: 45.05, 66.19, 71.43, 77.15, 79.90, 113.3, 119.3, 128.09–156.11. Mass spectrum, *m/z* (*I*_{rel}, %): 869 [*M*]⁺ (12), 776 [*M* – C₆H₅O]⁺ (6), 761 [C₆₀CH₂CHN]⁺ (6), 721 [C₆₀H]⁺ (9).

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