

Catalytic Hydroamination of Fullerene C₆₀ with Primary and Secondary Amines

U. M. Dzhemilev^a, A. G. Ibragimov^a, A. R. Tuktarov^a, V. A. D'yakonov^a,
M. Pudas^b, and U. Bergmann^b

^a Institute of Petroleum Chemistry and Catalysis, Russian Academy of Sciences,
pr. Oktyabrya 141, Ufa, 450075 Bashkortostan, Russia
e-mail: ink@anrb.ru

^b Microelectronics and Material Physics Laboratories, University of Oulu, EMPART Research Group of Infotech Oulu,
Linnanmaa P.O. Box 4500, Oulu, 90014 Finland

Received May 30, 2006

Abstract—Catalytic 1,2-hydroamination of fullerene C₆₀ with primary and secondary amines in the presence of Ti, Zr, and Hf complexes gave the corresponding alkyl-, aryl-, and hetarylaminodihydrofullerenes.

DOI: 10.1134/S1070428007030074

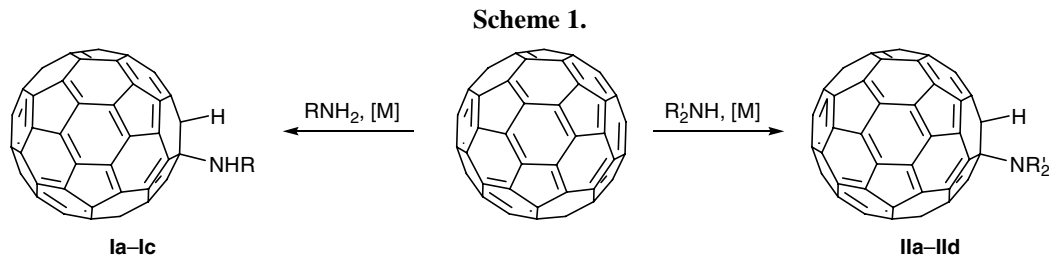
As shown in [1], excess methyl- and dimethylamines add to fullerene C₆₀ at 25°C to form complex mixtures of aminodihydrofullerenes. Butylamine reacts with fullerene C₆₀ at a ratio of 2:1 only in boiling toluene (reaction time 30 h) [1]. Reactions of primary and secondary amines with C₆₀ were reported [2–4] to occur only on heating. Likewise, fullerene C₆₀ takes up amino acids and dipeptides at elevated temperature [5–7]. Our interest in aminodihydro(C₆₀-I_h)[5,6]fullerenes originates from their application in medicine [8, 9] and as sorbents [10] and photosensitizers for generation of singlet oxygen [11].

In continuation of our studies on the development of procedures for selective functionalization of carbon clusters [12] and with a view to find an efficient preparative synthetic route to aminodihydrofullerenes, we made an attempt to accomplish catalytic hydroamination of C₆₀ with primary and secondary amines in the

presence of transition metal complexes (Fe, Co, Mn, Pd, Ti, Zr, Hf) that are widely used to catalyze transformations of unsaturated compounds. Prior to our study no data have been reported on catalytic methods of synthesis of aminodihydrofullerenes.

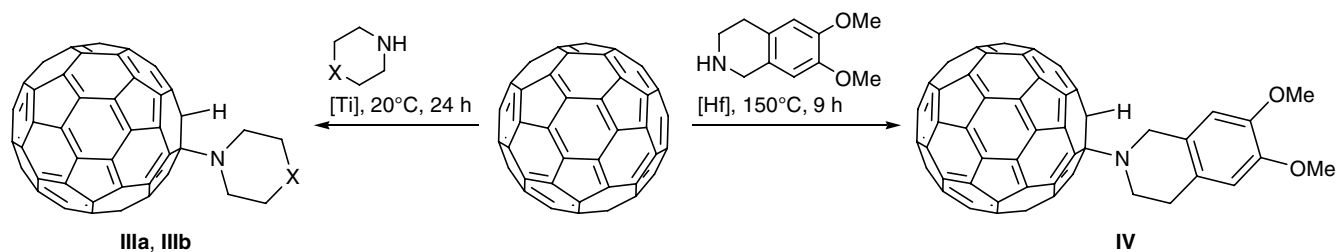
As primary and secondary amines we selected hexylamine, 2-aminobutan-1-ol, aniline, propane-1,2-diamine, *N*-(2-aminoethyl)ethane-1,2-diamine, diethyl-, diallyl-, dicyclohexyl-, and diphenylamines, piperidine, morpholine, and 6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline. In order to obtain the corresponding monoadducts with fullerene, the hydroamination was performed with equimolar amounts of the reactants.

The reaction of 2-aminobutan-1-ol with C₆₀ in the presence of Cp₂MCl₂ as catalyst (20 mol %; M = Ti, Zr, Hf; toluene, 20°C, 48 h) gave 1-(2-hydroxybutylamino)-1,9-dihydro(C₆₀-I_h)[5,6]fullerene (**1a**) whose yield exceeded 90% (Scheme 1). No reaction occurred



[M] = Cp₂ZrCl₂, Cp₂TiCl₂, Cp₂HfCl₂; R = MeCH₂CH(OH)CH₂ (**a**), C₆H₁₃ (**b**), Ph (**c**);
R' = Et (**a**), CH₂=CHCH₂ (**b**), *cyclo*-C₆H₁₁ (**c**), Ph (**d**).

Scheme 2.



in the presence of complexes and salts derived from other transition metals [Ni(acac)₂, Pd(acac)₂, Fe(acac)₃, TiCl₄, Cp₂Fe, MnCl₂, CoCl₂, FeCl₃, ZrCl₄] or in the absence of a catalyst. When the amount of Cp₂MCl₂ (M = Ti, Zr, Hf) was smaller than 20 mol %, the yield of **Ia** decreased.

Compound **Ia** displayed in the UV spectrum an absorption maximum at λ 253 nm, which is consistent with the known data for aminodihydrofullerene derivatives [1, 13]. In the ¹³C NMR spectrum of **Ia**, sp³-hybridized carbon atoms in the fullerene sphere resonate at δ_C 61.11 and 74.43 ppm, and signals in the region δ_C 128–152 ppm correspond to fullerene sp²-carbon atoms. The MALDI TOF mass spectrum of adduct **Ia** contained the molecular ion peak with m/z 809 [M]⁺, which indicated addition of one amine molecule to C₆₀.

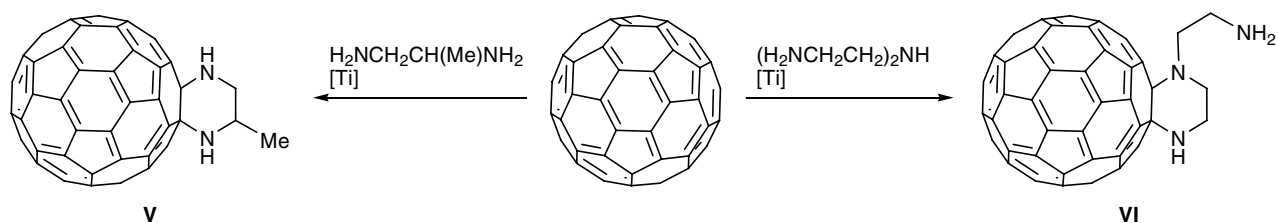
Under the above conditions (20 mol % of Cp₂TiCl₂, 20°C, 48 h), hydroamination of C₆₀ with hexyl-, diethyl-, diallyl-, and dicyclohexylamines resulted in the formation of 90–95% of compounds **Ib** and **IIa–IIc** (Scheme 1). The optimal conditions for the hydroamination of C₆₀ with aromatic amines, such as aniline and diphenylamine, were as follows: 20 mol % of Cp₂HfCl₂, 150°C, 9 h; these conditions ensured aminodihydrofullerenes **Ic** and **IId** to be obtained in ~80 and ~75% yield, respectively. In the presence of Cp₂TiCl₂ or Cp₂ZrCl₂ (20 mol %) instead of Cp₂HfCl₂, other conditions being equal (150°C, 9 h), the yield of **Ic** and **IId** fell down to ~40%.

Heterocyclic amines, namely piperidine, morpholine, and 6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline, reacted with an equimolar amount of C₆₀ in the presence of Cp₂MCl₂ (M = Ti, Zr, Hf) to produce the corresponding 1-substituted 1,9-dihydro(C₆₀-I_h)-[5,6]fullerenes **IIIa**, **IIIb**, and **IV** in 75–90% yield (Scheme 2). Hydroamination of C₆₀ with excess piperidine or morpholine without a catalyst led to the formation of a complex mixture of aminofullerenes [9, 14].

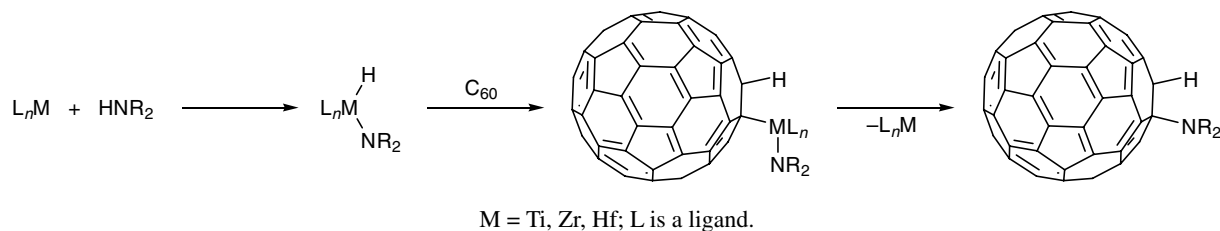
Unlike monoamines, Cp₂TiCl₂-catalyzed addition of 1,2-diamines [propane-1,2-diamine and *N*-(2-aminoethyl)ethane-1,2-diamine] to C₆₀ (20 mol % of the catalyst, 20°C, 48 h) afforded ~90% of piperazine derivatives **V** and **VI** (Scheme 3). As in the above cases, no reaction occurred without a catalyst (20°C, 48 h). Presumably, the cycloamination process is accompanied by oxidative deprotonation [15], which favors formation of piperazinofullerenes **V** and **VI** having no hydrogen atoms on the fullerene sphere.

According to the data of [16–19], noncatalytic addition of primary and secondary aliphatic amines to electron-deficient fullerene C₆₀ involves initial electron transfer from the nucleophile to give radical ion pair, and the subsequent proton transfer from the nitrogen atom to 6,6-carbon atom of fullerene leads to 1,2-hydroamination products. Presumably, catalytic addition of primary and secondary amines to C₆₀ follows a scheme analogous to that proposed previously for hydroamination of 1,3-dienes [20] and olefins [21] in the presence of transition metal complexes (Scheme 4).

Scheme 3.



Scheme 4.



The developed procedure for catalytic addition of primary and secondary amines to C₆₀ ensures preparation of various amino-substituted dihydrofullerenes with high yield and selectivity, thus opening wide prospects in using these compounds in practice.

EXPERIMENTAL

Commercial (C₆₀-I_h)[5,6]fullerene with a purity of 99.5% (Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences) was used. Toluene was dried over metallic sodium and was distilled just before use. The reaction mixtures were analyzed by gel-permeating liquid chromatography on an Altex-330 chromatograph (USA) equipped with an UV detector (λ 313 nm) and a 250×8-mm metal column packed with PL gel 100 Å (grain size 5 μ m); eluent toluene, flow rate 0.2 ml/min; components were separated at room temperature. The IR spectra were recorded in KBr on a Specord 75IR spectrometer. The UV spectra were measured from solutions in chloroform on Specord M-40 and Specord M-80 spectrophotometers. The ¹H and ¹³C NMR spectra were obtained on JEOL FX-90Q (90 and 22.5 MHz, respectively) and Bruker AM-300 (300.13 and 75.46 MHz, respectively) spectrometers using CDCl₃ or CS₂ as solvent. The mass spectra were run on a MALDI Voyager-D STR TOF instrument.

Addition of primary and secondary amines to fullerene C₆₀. A glass reactor or a 17-ml metal finger-like high-pressure reactor was charged with a freshly prepared solution of 0.01 mmol of C₆₀ in 10 ml of toluene, 0.0105 mmol of the corresponding amine, and 0.002 mmol of Cp₂MCl₂ catalyst (M = Ti, Zr, Hf), and the mixture was stirred for 9–48 h at 20–150°C. Products I–VI were separated from unreacted fullerene by column chromatography on silica gel L (100–250 μ m) using hexane–chloroform (6:1) as eluent.

1-(1,9-Dihydro(C₆₀-I_h)[5,6]fulleren-1-ylamino)-butan-2-ol (Ia). IR spectrum, ν , cm⁻¹: 520, 720, 1030, 1150, 1260, 1380, 1460, 3330–3380. UV spectrum:

λ_{\max} 253 nm. ¹H NMR spectrum, δ , ppm: 1.06 t (3H, CH₃), 1.16–1.36 m (2H, CH₂), 1.58 s (1H, C₆₀H), 2.59–2.70 m (1H, CH), 3.34 t (2H, CH₂), 4.16 d (1H, NH), 4.16 t (1H, OH). ¹³C NMR spectrum, δ_C , ppm: 12.85, 26.85, 56.35, 56.74, 61.11, 74.43, 128–152. Mass spectrum, m/z (I_{rel} , %): 809 [M]⁺ (3), 808 [M – H]⁺ (4), 736 [C₆₀NH₂]⁺ (38), 762 [C₆₀NHCHCH₂]⁺ (6), 720 [C₆₀]⁺ (89), 721 [C₆₀ + H]⁺ (100), 722 [C₆₀ + 2H]⁺ (62).

N-(1,9-Dihydro(C₆₀-I_h)[5,6]fulleren-1-yl)hexan-1-amine (Ib). IR spectrum, ν , cm⁻¹: 530, 580, 750, 1020, 1150, 1260, 1480, 3340–3380. UV spectrum: λ_{\max} 257 nm. ¹H NMR spectrum, δ , ppm: 0.84 t (3H, CH₃), 1.03–1.12 m (4H, CH₂), 1.24–1.30 m (4H, CH₂), 1.59 s (1H, C₆₀H), 2.72 t (2H, CH₂), 7.28 t (1H, NH). ¹³C NMR spectrum, δ_C , ppm: 14.19, 22.78, 29.78, 31.51, 33.36, 46.23, 54.73, 74.46, 130–153.

N-(1,9-Dihydro(C₆₀-I_h)[5,6]fulleren-1-yl)aniline (Ic). IR spectrum, ν , cm⁻¹: 520, 730, 1380, 1470, 2840, 2910, 3350. UV spectrum: λ_{\max} 253 nm. ¹H NMR spectrum, δ , ppm: 1.56 s (1H, C₆₀H), 6.71 d (2H, H_{arom}), 6.83 t (1H, H_{arom}), 7.02 t (2H, H_{arom}), 8.27 s (1H, NH). ¹³C NMR spectrum, δ_C , ppm: 56.29, 73.68, 115.09, 120.99, 129.06, 147.43, 128–157.

N-(1,9-Dihydro(C₆₀-I_h)[5,6]fulleren-1-yl)-N-ethylethanamine (IIa). IR spectrum, ν , cm⁻¹: 530, 720, 1160, 1270, 1380, 1470. UV spectrum (CHCl₃): λ_{\max} 254 nm. ¹H NMR spectrum, δ , ppm: 1.06 t (6H, CH₃), 1.58 s (1H, C₆₀H), 2.51 q (4H, CH₂). ¹³C NMR spectrum, δ_C , ppm: 12.69, 45.02, 56.35, 74.63, 137–157.

N-Allyl-N-(1,9-dihydro(C₆₀-I_h)[5,6]fulleren-1-yl)-prop-2-en-1-amine (IIb). IR spectrum, ν , cm⁻¹: 520, 720, 1180, 1370, 1430, 1640, 3080. UV spectrum: λ_{\max} 255 nm. ¹H NMR spectrum, δ , ppm: 1.56 s (1H, C₆₀H), 3.36 d (4H, CH₂), 5.23 d (4H, CH₂), 5.52–5.65 m (2H, CH). ¹³C NMR spectrum, δ_C , ppm: 56.42, 58.73, 74.85, 116.53, 133.04, 135–143.

N-Cyclohexyl-N-(1,9-dihydro(C₆₀-I_h)[5,6]fulleren-1-yl)cyclohexanamine (IIc). IR spectrum, ν , cm⁻¹:

520, 720, 1340, 1400, 1485. UV spectrum: λ_{\max} 258 nm. ^1H NMR spectrum, δ , ppm: 1.20–1.30 m (12H, CH_2), 1.53 q (8H, CH_2), 1.59 s (1H, C_{60}H), 3.05–3.13 m (2H, CH). ^{13}C NMR spectrum, δ_{C} , ppm: 22.89, 32.71, 56.55, 61.25, 74.46, 137–156. Mass spectrum, m/z (I_{rel} , %): 901 $[M]^+$ (1), 734 $[\text{C}_{60}\text{H}]^+$ (3), 735 $[\text{C}_{60}\text{NH}]^+$ (1.7), 736 $[\text{C}_{60}\text{NH}_2]^+$ (5), 720 $[\text{C}_{60}]^+$ (91), 721 $[\text{C}_{60} + \text{H}]^+$ (100), 722 $[\text{C}_{60} + 2\text{H}]^+$ (62).

***N*-(1,9-Dihydro($\text{C}_{60}\text{-I}_h$)[5,6]fulleren-1-yl)-*N*-phenylaniline (IIId).** IR spectrum, ν , cm^{-1} : 520, 730, 1380, 1460, 2840, 2910. UV spectrum: λ_{\max} 258 nm. ^1H NMR spectrum, δ , ppm: 1.59 s (1H, C_{60}H), 6.85 d (4H, H_{arom}), 6.95 t (2H, H_{arom}), 7.30 t (4H, H_{arom}). ^{13}C NMR spectrum, δ_{C} , ppm: 56.42, 74.10, 117.86, 121.09, 129.39, 154.20, 130–161. Mass spectrum, m/z (I_{rel} , %): 831 $[M]^+$ (2.5), 887 $[M - 2\text{H}]^+$ (5), 736 $[\text{C}_{60}\text{NH} + \text{H}]^+$ (30), 737 $[\text{C}_{60}\text{NH} + 2\text{H}]^+$ (36), 720 $[\text{C}_{60}]^+$ (94), 721 $[\text{C}_{60} + \text{H}]^+$ (100), 722 $[\text{C}_{60} + 2\text{H}]^+$ (84).

***N*-(1,9-Dihydro($\text{C}_{60}\text{-I}_h$)[5,6]fulleren-1-yl)piperidine (IIIa).** IR spectrum, ν , cm^{-1} : 520, 760, 1380, 1470. UV spectrum: λ_{\max} 257 nm. ^1H NMR spectrum, δ , ppm: 1.42–1.53 m (4H, CH_2), 1.58 s (1H, C_{60}H), 2.61 t (2H, CH_2). ^{13}C NMR spectrum, δ_{C} , ppm: 25.39, 25.97, 51.70, 56.42, 74.62, 128–133. Mass spectrum, m/z (I_{rel} , %): 805 $[M]^+$ (6.8), 720 $[\text{C}_{60}]^+$ (100), 721 $[\text{C}_{60} + \text{H}]^+$ (80).

***N*-(1,9-Dihydro($\text{C}_{60}\text{-I}_h$)[5,6]fulleren-1-yl)morpholine (IIIb).** IR spectrum, ν , cm^{-1} : 520, 720, 1120, 1140, 1380, 1420. UV spectrum: λ_{\max} 258 nm. ^1H NMR spectrum, δ , ppm: 1.41 s (1H, C_{60}H), 3.05 t (4H, CH_2), 3.62 t (4H, CH_2). ^{13}C NMR spectrum, δ_{C} , ppm: 45.09, 56.42, 70.22, 74.03, 137–161. Mass spectrum, m/z (I_{rel} , %): 807 $[M]^+$ (15), 734 $[\text{C}_{60}\text{H}]^+$ (16), 735 $[\text{C}_{60}\text{NH}]^+$ (37), 720 $[\text{C}_{60}]^+$ (100), 721 $[\text{C}_{60} + \text{H}]^+$ (83), 722 $[\text{C}_{60} + 2\text{H}]^+$ (67).

2-(1,9-Dihydro($\text{C}_{60}\text{-I}_h$)[5,6]fulleren-1-yl)-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (IV). IR spectrum, ν , cm^{-1} : 520, 760, 790, 1020, 1100, 1260, 1380, 1470, 2840, 2910. UV spectrum: λ_{\max} 257 nm. ^1H NMR spectrum, δ , ppm: 1.42 s (1H, C_{60}H), 2.70 t (2H, CH_2), 3.05 t (2H, CH_2), 3.79 s (6H, CH_3), 3.90 s (2H, CH_2), 6.62 s (2H, CH). ^{13}C NMR spectrum, δ_{C} , ppm: 30.76, 43.04, 49.52, 56.26, 56.42, 74.56, 109.69, 112.10, 126.49, 132.03, 147.20, 135–159. Mass spectrum, m/z (I_{rel} , %): 913 $[M]^+$ (10), 735 $[\text{C}_{60}\text{NH}]^+$ (12), 777 $[\text{C}_{60}\text{NHCH}_2\text{CH}_2\text{CH}_2]^+$ (11), 851 $[M - 2\text{OCH}_3]^+$ (13.5), 883 $[M - 2\text{CH}_3]^+$ (9), 720 $[\text{C}_{60}]^+$ (100), 721 $[\text{C}_{60} + \text{H}]^+$ (80).

5'-Methyl-1',4',5',6'-tetrahydropyrazino[2',3':1,9]($\text{C}_{60}\text{-I}_h$)[5,6]fullerene (V). IR spectrum, ν , cm^{-1} : 530, 720, 1030, 1150, 1380, 1400, 1460, 3320–3370. UV spectrum: λ_{\max} 428 nm. ^1H NMR spectrum, δ , ppm: 1.01 d (3H, CH_3), 2.26 d (2H, NH), 2.96 t (2H, CH_2), 3.38–3.46 m (1H, CH). ^{13}C NMR spectrum, δ_{C} , ppm: 16.37, 54.50, 56.29, 83.15, 132–164. Mass spectrum, m/z (I_{rel} , %): 792 $[M]^+$ (21), 777 $[M - \text{CH}_3]^+$ (16), 720 $[\text{C}_{60}]^+$ (100), 721 $[\text{C}_{60} + \text{H}]^+$ (97), 722 $[\text{C}_{60} + 2\text{H}]^+$ (56).

2-(1',4',5',6'-Tetrahydropyrazino[2',3':1,9]($\text{C}_{60}\text{-I}_h$)[5,6]fulleren-1-yl)ethanamine (VI). IR spectrum, ν , cm^{-1} : 520, 720, 1040, 1380, 1470, 2850, 2910, 3340, 3400. UV spectrum: λ_{\max} 428 nm. ^1H NMR spectrum, δ , ppm: 1.80 t (3H, NH, NH_2), 2.32 t (2H, CH_2), 2.65–2.78 m (2H, CH_2), 3.46 q (2H, CH_2), 4.58 t (2H, CH_2). ^{13}C NMR spectrum, δ_{C} , ppm: 42.71, 45.35, 54.53, 56.32, 84.58, 85.63, 137–160.

The authors thank L.M. Khalilov for his help in discussing the NMR data. This study was performed under financial support by the Russian Foundation for Basic Research (project no. 05-03-32367) and by the Ministry of Science and Education of the Russian Federation (project no. NSh-7470.2006.3).

REFERENCES

- Seshadri, R., Govindaraj, A., Nagarajan, R., Pradeep, T., and Rao, C.N.R., *Tetrahedron Lett.*, 1992, vol. 33, p. 2069.
- Isobe, H., Tomita, N., and Nakamura, E., *Org. Lett.*, 2000, vol. 2, p. 3663.
- Balch, A.L., Ginwalla, A.S., Olmstead, M.M., and Herbstirmer, R., *Tetrahedron*, 1996, vol. 52, p. 5021.
- Kampe, K.-D., Egger, N., and Vogel, M., *Angew. Chem., Int. Ed. Engl.*, 1993, vol. 32, p. 1174.
- Gan, L.B., Luo, C.P., Xu, L.B., Zhou, D.J., and Huang, C.H., *Symposium Fullerenes*, Santa Barbara, 1993.
- Romanova, V.S., Tsyryapkin, V.A., Lyakhovetskii, Yu.I., Parnes, Z.N., and Vol'pin, M.E., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 1994, p. 1154.
- Vol'pin, M.E., Parnes, Z.N., and Romanova, V.S., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 1998, p. 1050.
- Skiebe, A., Hirsch, A., Klobs, H., and Gotschy, B., *Chem. Phys. Lett.*, 1994, vol. 220, p. 138.
- Hirsch, A., Li, Q., and Wudl, F., *Angew. Chem., Int. Ed. Engl.*, 1991, vol. 30, p. 1309.
- Gumanov, L.L., Volkov, G.A., Shastin, A.V., and Korsunskii, B.L., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 1996, p. 814.

11. Wudl, F., Hirsch, A., Khemani, K.C., Suzuki, T., Allemand, P.-M., Koch, A., Eckert, H., Srdanov, H.G., and Webb, H.M., *Fullerenes: Synthesis, Properties, and Chemistry of Large Carbon Clusters*, Hammond, G.S. and Kuck, V.J., Eds., Washington DC: Am. Chem. Soc., 1992, ACS Symp. Ser. vol. 481, p. 161.
12. Dzhemilev, U.M., Ibragimov, A.G., Pudas, M., D'yakov, V.A., and Tuktarov, A.R., *Russ. J. Org. Chem.*, 2007, vol. 43, p. 370.
13. Inoue, M., Machi, L., Brown, F., Inoue, M.B., and Fernando, Q., *J. Mol. Struct.*, 1995, vol. 345, p. 113.
14. Schick, G., Kampe, K.-D., and Hirsch, A., *J. Chem. Soc., Chem. Commun.*, 1995, p. 2023.
15. Maggini, M., Scorrano, G., Bianco, A., Toniolo, C., and Prato, M., *Tetrahedron Lett.*, 1995, vol. 36, p. 2845.
16. Liou, K.-F. and Cheng, C.-H., *Chem. Commun.*, 1996, p. 1423.
17. Wu, S.-H., Sun, W.-Q., Zhang, D.-W., Shu, L.-H., Wu, H.-M., Xu, J.-F., and Lao, X.-F., *J. Chem. Soc., Perkin Trans. 1*, 1998, p. 1733.
18. Lawson, G.E., Kitaygorodskiy, A., Ma, B., Bunker, C.E., and Sun, Y.-P., *J. Chem. Soc., Chem. Commun.*, 1995, p. 2225.
19. Wu, S.-H., Zhang, D.-W., Wang, G.-W., Shu, L.-H., Wu, H.-M., Xu, J.-F., and Lao, X.-F., *Synth. Commun.*, 1997, vol. 27, p. 2289.
20. Dzhemilev, U.M., Yakupova, A.Z., and Tolstikov, G.A., *Izv. Akad. Nauk SSSR, Ser. Khim*, 1978, p. 1068.
21. Muller, T.E. and Beller, M., *Chem. Rev.*, 1998, vol. 98, p. 675.