Selective reduction of fullerene C_{60} by metals in neutral and alkaline media. Interaction of C_{60} with KOH

A. L. Litvinov,* D. V. Konarev, E. I. Yudanova, M. G. Kaplunov, and R. N. Lyubovskaya

Institute of Problems of Chemical Physics, Russian Academy of Sciences,
142432 Chernogolovka, Moscow Region, Russian Federation.
Fax: +7 (096) 515 3588. E-mail: litvin@cat.icp.ac.ru

The reduction of fullerene C_{60} by Zn and Mg in DMF was studied both in the presence and absence of KOH. Fullerene C_{60} was reduced in these systems to form the $C_{60}{}^{n-}$ (n = 1, 2, and 3) anions. The anions were detected by optical and ESR spectroscopies. It was found that Mg reduced C_{60} to the monoanion, Mg/KOH and Zn reduced C_{60} to the dianion, and Zn/KOH reduced C_{60} to the trianion. Like KCN, potassium hydroxide adds to fullerene upon interaction with C_{60} in DMF. The reaction of C_{60} with KOH in benzonitrile was accompanied by the generation of the fullerene monoanion. A possible mechanism of the formation of fullerene monoanions in the presence of KOH is discussed. The degradation of the $C_{60}{}^{n-}$ anions in air was studied.

Key words: fullerene C_{60}, $[C_{60}(OH)_x]^-$ anions; ESR spectroscopy, optical spectroscopy.

Studies of fullerene radical anion salts in both a solution and the solid state[1—5] are of great interest because compounds containing $C_{60}{}^{n-}$ exhibit interesting conducting and magnetic properties.[6—8] The $C_{60}{}^{n-}$ ($C_{70}{}^{n-}$) (n = 1—6) anions can be generated by electrochemical or chemical methods.[9—17] The reduction of fullerenes by Zn, Sn, or the Al—Ni melt was studied[13—15] in aqueous solutions of THF or DMSO in the presence of an alkali and also by the reaction of C_{60} with NaH, $NaBH_4$, and $Na_2S_2O_4$. Fullerene anions (especially in highest oxidation states) are unstable toward water and, hence, it is desirable to use anhydrous solvents in syntheses. It is known that C_{60} is selectively reduced in anhydrous DMF by thiols in the presence of alkaline metal carbonates[16] and by mercury in anhydrous THF in the presence of tetralakylammonium halides.[17]

In this work we studied the reduction of C_{60} by metals (Zn and Mg) to the $C_{60}{}^{n-}$ (n = 1—3) anions in anhydrous DMF, in neutral and alkaline media. The formation of the $C_{60}{}^{n-}$ anions was detected by optical and ESR spectroscopies. The data on the addition of KOH to C_{60} were obtained for the first time. This reaction in benzonitrile is accompanied by the generation of radical monoanions of fullerenes. A possible mechanism of their formation in the presence of KOH is discussed. The oxidation of the $C_{60}{}^{\bullet -}$ and $C_{60}{}^{\bullet 3-}$ radical anions, unlike the dianions, was found to afford products, which are characterized by narrow signals in the ESR spectra.

Experimental

Fullerene C_{60} with 99.5% purity was used. Dimethylformamide was dried with KOH and molecular sieves and then distilled over CaH_2 at reduced pressure in an argon atmosphere (prior to experiments). Benzonitrile (BN) was distilled over sodium in an argon atmosphere.

ESR spectra were recorded at 77 K on an SE/X 2544 radiospectrometer (Radiopan, Poznań, Poland) with a magnetic modulation frequency of 100 kHz, and an MSM101 nuclear magnetometer was used.

Optical spectra were recorded 1 h and 1 day after the beginning of the reaction using an SF-8 spectrophotometer at ~20 °C in the wavelength interval from 400 to 1600 nm. The measurements were carried out in an argon atmosphere.

Reactions were carried out in a sealed quartz 4-mL flask using a cell with a thickness of 0.5 cm and a volume of 1 mL.

The reaction mixture was degassed three times. Fullerene was reduced with vigorous stirring in an argon atmosphere at ~20 °C in mixtures of C_{60} (5 mg, 0.007 mmol) and a powdered metal (M = Zn, Mg), KOH, or M/KOH (M/KCN) in DMF (5 mL) during 20—60, 20—60, and 60 min, respectively, at molar ratios of 1 : 50, 1 : 50 : 50, and 1 : 50. The qualitative indications for the end of the reaction were the complete dissolution of fullerene and a change in the initial color of the solution.

After the end of the reaction, the solution was frozen and the ESR spectrum was recorded. In order to study the degradation of the fullerene anions, the solution was heated to ~20 °C and stirred in air for 2 min, after which it was frozen again, and the ESR spectrum was measured.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 11, pp. 1849—1853, November, 2002.

Table 1. Published (I) and obtained in the present work (II) data of optical and ESR spectroscopies for anions of fullerene C_{60}

Anion	Wave length/nm		*g* Factor (T = 77 K)	
	I [a]	II	I	II
$C_{60}^{\bullet -}$	1080, 1001, 936	1081, 1001, 939	1.9950, 2.0000 [b]	1.9967, 2.0000
C_{60}^{2-}	1332, 957, 844	1314, 951, 831	2.000, center of triplet spectrum[b]	2.0001, center of triplet spectrum
$C_{60}^{\bullet 3-}$	1378, 1002, 868, 796	1364, 987, 869, 777	2.002 [c]	2.0025
$C_{60}(OH)_x^-$	—	1080, 958, 838, 485	—	—
$C_{60}(CN)_x^-$	—	1074, 936, 843, 628	—	—
$C_{60}(OMe)_x^-$	1080, 920, 598, 536 [d]	—	—	—

[a] In a solution of BN.[12]

[b] See Ref. 10.

[c] See Ref. 11.

[d] See Ref. 19.

For measurements of optical spectra, solutions were prepared similarly; the concentration of C_{60} was 0.2 mg mL^{-1}.

Results and Discussion

The selective reduction of fullerenes in an anhydrous medium was based on the method[13] of C_{60} reduction by metals in an alkaline medium in a mixture of a polar solvent with water. The solvent DMF is capable of dissolving both KOH and fullerene anions. In a blank experiment with a solution of C_{60} in pure DMF in inert atmosphere, the optical and ESR spectra of the solution remained unchanged for 1 day.

The C_{60}^{n-} anions exhibit the characteristic ESR spectra and absorption bands (AB) in the visible and near-IR regions. The positions of these bands depend slightly on the nature of the solvent or counterion.[2,12,18] The study of the optical and ESR spectra of solutions of C_{60} during the reaction allows the unambiguous determination of formation of different fullerene anions.

Reduction of fullerene C_{60} with magnesium. The addition of Mg to a solution of C_{60} in DMF results in the reduction of fullerene to form the $C_{60}^{\bullet -}$ radical monoanion, whose spectrum contains intense AB at 1081, 1001, and 939 nm (Table 1). The ESR spectra of these solutions (Fig. 1, *a*) contain two superimposing signals characteristic of frozen solutions of the $C_{60}^{\bullet -}$ monoanions (g_1 = 1.9967, $\Delta H_{pp1} \approx 5$ G) and the products of C_{60} oxidation (g_2 = 2.0000, $\Delta H_{pp2} \approx 1.5$ G).[10,11] The lines corresponding to different *g* factors (g_1 and g_2) have different widths and are saturated in different manners, *i.e.*, these signals refer to independent spins. On exposure to air oxygen, the intensity of the narrow signal with g_2 at first (15—20 min) increases (Fig. 1, *b*) and then (during 40—60 min) decreases to the complete disappearance of the signal, while the intensity of the broad line with g_2 immediately decreases and disappears completely in 40—60 min.

Reduction of fullerene C_{60} by zinc. Zinc, unlike Mg, reduces fullerene to the C_{60}^{2-} dianion, whose optical spectrum contains AB at 1314, 951, and 831 nm (see Table 1). The ESR spectrum (Fig. 2, *a*) coincides with the previously[9—11] observed spectra of the C_{60}^{2-} anions. The lateral components are spaced at a distance of 12 G. Such a pattern corresponds, most likely, to the temperature-

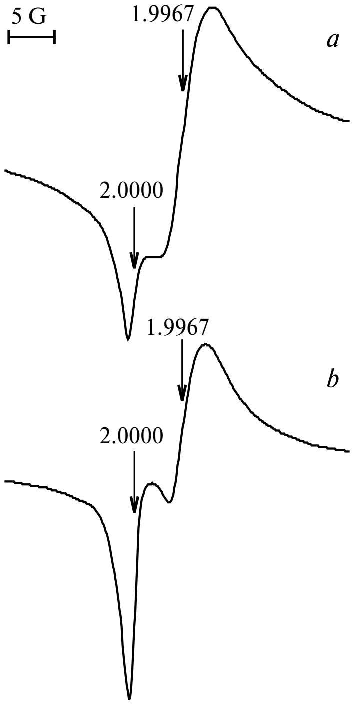

Fig. 1. ESR spectra of a frozen solution of the $C_{60}^{\bullet -}$ radical monoanion (C_{60} with KOH in BN) before (*a*) and after storage in the air for 20 min (*b*).

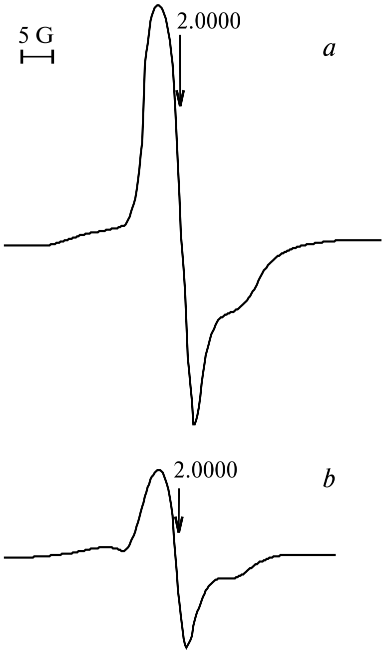

Fig. 2. ESR spectra of a frozen solution of the C_{60}^{2-} dianion (C_{60} with Mg/KOH in DMF) before (*a*) and after storage in air for 20 min (*b*).

populated triplet state of C_{60}^{2-}. The central part of the spectrum appears as an asymmetric line, which also corresponds to a triplet with an almost zero coupling.[9] The intensity of the signal decreases on exposure to air but the spectrum shape remains unchanged (Fig. 2, *b*), and the ESR signal disappears completely in 30—40 min.

Reduction of fullerene C_{60} by magnesium in the presence of KOH. The addition of KOH to the C_{60}—Mg system in DMF results in the reduction of fullerene to the C_{60}^{2-} dianion. At first the $C_{60}^{\bullet -}$ radical anion and then the C_{60}^{2-} dianion are formed. The solution turns red within 20 min, and signals characteristic of the $C_{60}^{\bullet -}$ radical anion appear in the optical and ESR spectra. After 1 h, the color of the solution changes for red-brown, and only the AB characteristic of the C_{60}^{2-} dianion are observed in the optical spectrum. The ESR signal also corresponds to the C_{60}^{2-} dianion. Then the optical and ESR spectra remain unchanged for 1 day. Thus, C_{60}^{2-} is selectively formed in a solution for 1 h, and reduction does not occur further.

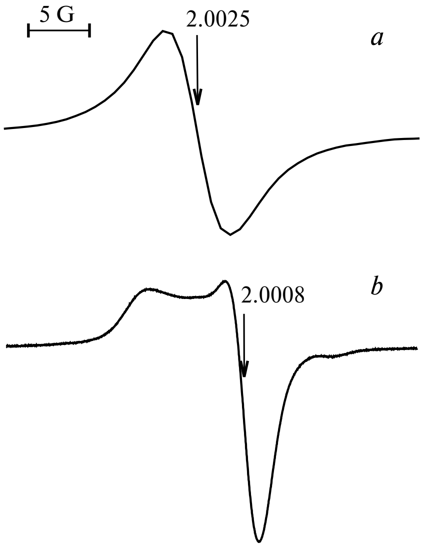

Fig. 3. ESR spectra of a frozen solution of the $C_{60}^{\bullet 3-}$ radical trianion (C_{60} with Zn/KOH in DMF) before (*a*) and after storage in air for 20 min (*b*).

Reduction of fullerene C_{60} by zinc in the presence of KOH. In the presence of Zn and KOH in DMF, fullerene is reduced to the $C_{60}^{\bullet 3-}$ radical trianion, whose optical spectrum exhibits new AB at 1364, 987, 869, and 777 nm, which are characteristic of $C_{60}^{\bullet 3-}$ (see Table 1). The ESR spectrum appears as a singlet with the *g* factor equal to 2.0025 and $\Delta H = 4.5$ G (Fig. 3, *a*). The oxidation of the $C_{60}^{\bullet 3-}$ radical trianion is accompanied by the appearance of a narrow ESR signal with $g = 2.0008$ and $\Delta H = 1.8$ G (Fig. 3, *b*), like in the case of oxidation of the $C_{60}^{\bullet -}$ monoanion.

The study of the ESR spectra during the degradation of the $C_{60}^{\bullet -}$ and $C_{60}^{\bullet 3-}$ radical anions in air showed that the intensity of the broad signal ($g_1 = 1.9967$ for $C_{60}^{\bullet -}$ and $g = 2.0025$ for $C_{60}^{\bullet 3-}$) decreased with oxidation; simultaneously a narrow signal appeared ($g_2 = 2.0000$) and its intensity increased. The narrow ESR signal is likely attributed to the formation of oxidation products, such as the air-unstable radical anion $C_{60}O_2^{\bullet -}$. It has previously[20] been mentioned that the oxidation of the $C_{60}^{\bullet -}$ radical anions in air affords the pure fullerene. Probably, this is related to the disappearance of the ESR signal upon a prolonged storage of the solutions in air. No new signals appear upon the oxidation of the C_{60}^{2-} dianions.

The reduction of C_{60} by zinc in DMF to the the dianions agree with the redox potentials of Zn and C_{60} ($E(\mathrm{Zn/Zn^{2+}}) = -0.76$ V,[21] $E(C_{60}^{\bullet -}/C_{60}^{2-}) = -0.72$ V in DMF).[21] In the presence of KOH, zinc reduces C_{60} to the trianion because the redox potential of the reaction $\mathrm{Zn} + 4\ \mathrm{OH}^- \rightarrow \mathrm{ZnO_2}^{2-} + 2\ \mathrm{H_2O} + 2\ \mathrm{e}$ in DMF is -1.215 V, which can be sufficient to reduce C_{60} to the trianion ($E(C_{60}^{2-}/C_{60}^{\bullet 3-}) = -1.31$ V).[22] In a less polar solvent, for example, benzonitrile, the Zn and Mg metals do not reduce fullerene C_{60}. It is of interest that Mg, which has a more negative reduction potential than Zn,[22] reduces C_{60} only to the monoanions in DMF in a neutral medium, whereas in an alkaline medium C_{60} is reduced to the dianions.

Thus, fullerene C_{60} in DMF is reduced by the metals in both neutral and alkaline media (Table 2), whereas Mg reduces C_{60} only to the $C_{60}^{\bullet -}$ radical monoanion. The

Table 2. Formation of fullerene anions by the interaction of C_{60} with various systems in DMF

System	$C_{60}{}^{\bullet -}$	$C_{60}{}^{2-}$	$C_{60}{}^{\bullet 3-}$	$C_{60}(OH)_x{}^-$ ($C_{60}(CN)_x{}^-$)
Mg	+	—	—	—
Mg/KOH	—	+	—	—
Zn	—	+	—	—
Zn/KOH	—	—	+	—
KOH (KCN)	o	—	—	+
KOH in BN	+	—	—	—

Note. The following designations were used: + is anion formation, and o is the formation of an anion as an admixture.

use of Mg/KOH or Zn and Zn/KOH in DMF as reducing agents allows the selective generation of the fullerene dianions and trianions, respectively.

Interaction of fullerene C_{60} with KOH (KCN). The addition of KOH to a solution of fullerene C_{60} in DMF produces new AB at 1080, 958, and 838 nm (see Table 1). The weak AB at 1080 nm can be attributed to the formation of the $C_{60}{}^{\bullet -}$ monoanion. However, the most intense AB at 958 nm does not correspond to the $C_{60}{}^{\bullet -}$ monoanion.

It has previously[23] been shown that the optical spectra of solutions of fullerene C_{60} in the presence of KCN contain the AB in the near-IR region with a maximum at 936 nm. This band is attributed to the $C_{60}(CN)_x{}^{\bullet -}$ cyanofullerene anions. The $C_{60}OMe^-$ methoxyfullerene anion in benzonitrile is also characterized[12] by the AB at 920 nm. In order to assign the AB, we studied the optical spectra of solutions of mixtures of fullerene C_{60} with KOH and with KCN in both DMF and BN.

The addition of KCN to a solution of fullerene C_{60} in DMF produces a green solution, whose optical spectrum contains AB at 1074, 936, and 843 nm (see Table 1). The AB at 936 nm is most intense.

It is of interest that in less polar BN, in the presence of KOH, fullerene forms solutions, whose absorption spectra exhibit AB with maxima at 1080, 1001, and 939 nm, which are characteristic of the $C_{60}{}^{\bullet -}$ monoanion. At the same time, the addition of KCN to a solution of C_{60} in BN does not initiate remarkable changes in the optical spectra.

Thus, the anions of substituted fullerenes are characterized by AB with maxima at 920—940 nm. Like KCN, KOH can likely add to C_{60} in a solution of DMF to form the $C_{60}(OH)_x{}^-$ hydroxyfullerene anions, whose optical spectrum contains a new intense AB at 958 nm. The presence of the weak AB corresponding to the $C_{60}{}^{\bullet -}$ monoanion indicates that the latter is formed in minor amounts. By contrast, the near-IR part of the spectrum of the reaction product formed in BN under similar conditions contains only the AB of the $C_{60}{}^{\bullet -}$ monoanion and the AB of hydroxyfullerene are absent (see Table 2).

The formation of the hydroxyfullerene anions can be attributed to a high hydrophilicity of the double [6-6]-bonds in the fullerene molecule to which nucleophilic and radical species add readily.[24—26] The interaction of fullerene C_{60} with nucleophiles (CN^-, OMe^-) generates[19,23] the corresponding anions ($C_{60}CN^-$, $C_{60}OMe^-$).

The formation of fullerene monoanions is a specific feature of addition reactions, although nucleophiles themselves do not possess donating properties sufficient for the reduction of C_{60}. For example, in BN fullerene reacts with the OMe^- anion to form the $[C_{60}(OMe)_2]$ adduct and $C_{60}{}^{\bullet -}$ radical anion.[19]

$$3\,C_{60} + 2\,OMe^- = 2\,C_{60}{}^{\bullet -} + [C_{60}(OMe)_2]$$

In our case, an analogous reaction probably occurs. In the first stage, the OH^- anion adds to fullerene to form the $[C_{60}OH]^-$ anion. The $[C_{60}OH]^-$ anion is likely a stronger donor than the $C_{60}{}^{\bullet -}$ radical anion due to the violation of delocalization of π-electrons and can reduce fullerene to the radical anion.

The difference in the $C_{60}{}^{\bullet -}/[C_{60}OH]^-$ ratio in DMF ($C_{60}{}^{\bullet -}$ is the by-product) and in BN ($C_{60}{}^{\bullet -}$ is the main product) is related, most likely, to the difference in the redox potentials of $[C_{60}OH]^-$ and $C_{60}{}^{\bullet -}$ in these solvents. When the difference between these potentials increases, almost all hydroxyfullerene anions that formed immediately reduce fullerene to the $C_{60}{}^{\bullet -}$ monoanion. In this case, only the AB of the $C_{60}{}^{\bullet -}$ monoanion is observed in the optical spectrum in the near-IR region, which was found in solutions of BN.

Hydroxyfullerene anions are not formed in an alkaline medium in solutions of C_{60} in DMF in the presence of the metals. Probably, this is related to the fact that fullerene is reduced by the metals much more rapidly than the addition of KOH occurs.

Thus, fullerene C_{60} is reduced in DMF by Zn and Mg in neutral and alkaline media to form the $C_{60}{}^{n-}$ anions (n = 1, 2, and 3). Selective fullerene reduction can be used for the preparative synthesis of salts containing fullerene anions. Potassium hydroxide, like KCN, can add to fullerene C_{60}. Fullerene monoanions are generated in the presence of KOH likely due to the formation of the hydroxyfullerene radical anion, which reduces fullerene to the radical anion. The oxidation of the $C_{60}{}^{\bullet -}$ and $C_{60}{}^{\bullet 3-}$ radical anions results in the appearance of new narrow ESR signals attributed to unstable paramagnetic intermediates ($C_{60}O_2{}^{\bullet -}$), whose decomposition results in the disappearance of the ESR signals.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 00-03-

32577a) and the Russian State Program "Fullerenes and Atomic Clusters."

References

1. C. Bossara, S. Rigaut, D. Astruc, M. H. Delville, G. Felix, A. Fevrier-Bouveir, J. Amiell, S. Flandrois, and P. Delxaes, *J. Chem. Soc.*, *Chem. Commun*., 1993, 333.
2. P. Bhyrappa, P. Paul, J. Stinchcombe, P. D. W. Boyd, and C. A. Reed, *J. Am. Chem. Soc.*, 1993, **115**, 11004.
3. C. Boulas, R. Subramanian, W. Kutner, M. T. Jones, and K. M. Kadish, *J. Electrochem. Soc.*, 1993, **140**, L130.
4. A. S. Lobach, N. F. Goldshleger, M. G. Kaplunov, and A. V. Kulikov, *Chem. Phys. Lett.*, 1995, **24**, 322.
5. S. P. Solodovnikov, *Izv. Akad. Nauk*, *Ser. Khim.*, 1996, 2256 [*Russ. Chem. Bull.*, 1996, **45**, 2141 (Engl. Transl.)].
6. M. J. Rosseinsky, *J. Mater. Chem.*, 1995, **5**, 1497.
7. P. W. Stephens, D. Cox, J. W. Lauher, L. Mihaly, J. B. Wiley, P.-M. Allemand, A. Hirsch, K. Holczer, Q. Li, J. D. Thompson, and F. Wudl, *Nature (London)*, 1992, **355**, 331.
8. D. V. Konarev and R. N. Lyubovskaya, *Usp. Khim.*, 1999, **68**, 23 [*Russ. Chem. Rev.*, 1999, **68** (Engl. Transl.)].
9. D. Dubois and K. M. Kadish, *J. Am. Chem. Soc.*, 1991, **113**, 4364.
10. M. Khaled, R. T. Carlin, P. C. Trulove, G. R. Eaton, and S. S. Eaton, *J. Am. Chem. Soc.*, 1994, **116**, 3465.
11. D. Dubois, M. T. Jones, and K. M. Kadish, *J. Am. Chem. Soc.*, 1992, **114**, 6446.
12. D. V. Konarev, N. V. Drichko, and A. Graja, *J. Chim. Phys.*, 1998, **95**, 2143.
13. M. F. Wu, X. W. Wei, L. Qi, and Z. Xu, *Tetrahedron Lett.*, 1996, **37**, 7409.
14. X. Wei, Z. Suo, K. Zhou, Z. Xu, W. Zhang, R. Wang, H. Shen, and X. Li, *J. Chem. Soc.*, *Perkin Trans. 2*, 1999, 121.
15. X. Wei, Z. Suo, K. Yin, and Z. Xu, *J. Organomet. Chem.*, 2000, **599**, 69; S. Takekuma, H. Takekuma, T. Matsumoto, and Z. Yoshida, *Tetrahedron Lett.*, 2000, **41**, 2929.
16. R. Sabramanian, P. Boulas, M. N. Vijayashree, F. D´Souza, M. T. Jones, and K. M. Kadish, *J. Chem. Soc.*, *Chem. Commun.*, 1994, 1847.
17. M. T. Jones, K. M. Kadish, R. Subramanian, P. Boulas, and M. N. Vijayashree, *Synth. Met.*, 1995, **70**, 1341.
18. C. A. Reed and R. D. Bolkskar, *Chem. Rev.*, 2000, **100**, 1075.
19. S. Fukuzumi, I. Nakanishi, J. Maruta, T. Yorisue, T. Suenobu, S. Itoh, R. Arakawa, and K. M. Kadish, *J. Am. Chem. Soc.*, 1998, **120**, 6673.
20. X. Wei, Z. Suo, G. Yin, and Z. Xu, *J. Organomet. Chem.*, 2000, **599**, 69.
21. Ch. K. Mann and K. K. Barnes, *Electrochemical Reactions in Nonaqueous Systems*, Marcel Dekker Inc., New York, 1970.
22. D. Dubois, G. Moninot, W. Kurner, M. T. Jones, and K. M. Kadish, *J. Phys. Chem.*, 1992, **96**, 7137.
23. M. Keshavarz, B. Knight, G. Srdanov, and F. Wudl, *J. Am. Chem. Soc.*, 1995, **117**, 11371.
24. M. E. Vol´pin, Z. N. Parnes, and V. S. Romanova, *Izv. Akad. Nauk*, *Ser. Khim.*, 1998, 1050 [*Russ. Chem. Bull.*, 1998, **47**, 1021 (Engl. Transl.)].
25. E. M. Belavtseva, E. V. Kichenko, V. S. Romanova, Z. N. Parnes, and M. E. Vol´pin, *Izv. Akad. Nauk*, *Ser. Khim.*, 1996, 876 [*Russ. Chem. Bull.*, 1996, **45**, 831 (Engl. Transl.)].
26. S. R. Wilson and Y. J. Wu, *J. Am. Chem. Soc.*, 1993, **115**, 10334.

Received October 8, 2001