

Direct Arc-Discharge Assisted Synthesis of $C_{60}H_2(C_3H_5N)$: A cis-1-Pyrrolino C₆₀ Fullerene Hydride with Unusual Redox Properties

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By direct arc synthesis of $C_{60}H_2(C_3H_5N)$ using a modified Krätschmer-Huffman method, it is demonstrated for the first time that exohedral fullerenes with large side groups can be formed under the arc and reactive gas atmosphere conditions. The thus formed novel pyrrolino fullerene hydride was comprehensively characterized by UV-vis, infrared (IR), Raman and nuclear magnetic resonance (NMR) and studied by means of electrochemistry and in situ electron spin resonance/ visible-near infrared (ESR/Vis-NIR) spectroelectrochemistry. The detailed NMR and absorption spectroscopic studies show $C_{60}H_2(C_3H_5N)$ as the fullerene hydride with a pyrrolino ring attached on the vicinal position of two hydrogen atoms. This first cycloaddition adduct of $C_{60}H_2$ gives rise to an unusual reversible dimerization of its anion radicals and a loss of cage hydrogen atoms at the third electron transfer. The spectroelectrochemical study confirms the formation of a $[C_{60}H_2(C_3H_5N)]^{-1}$ radical and the diamagnetic state of $[C_{60}H_2(C_3H_5N)]^{2-}$. This study reveals a unique function of a carbide structure like Al_4C_3 and the presence of a reactive gas atmosphere with NH_3 in the formation of such an exohedral pyrrolino structure $C_{60}H_2(C_3H_5N)$.

Introduction

Various synthesis methods have been developed for the preparative access to spherical cage carbon molecules like fullerenes constructed from 12 pentagons and a large number of hexagons.¹ Among them, the Krätschmer-Huffman method is most commonly used to prepare empty cage and endohedral fullerenes.^{2,3} Fullerenes, including endohedral fullerenes and unconventional fullerenes, have been extensively grown in their number and variety.4-11 Recently, a modified Krätschmer-Huffman method, in which a reactive gas and chemicals are introduced to the arc discharging process, was developed to produce novel endohedral fullerene structures. In the

- (1) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. Nature 1985, 318, 162-163.
- (2) Krätschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. Nature 1990, 347, 354-358.
- (3) Hirsch, A.; Brettreich, M. Fullerenes: Chemistry and Reactions; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2005.
- (4) Yang, S. F.; Dunsch, L. Endohedral Fullerenes. In Encyclopedia of Nanoscience and Nanotechnology; Nalwa, H. S., Ed.; American Scientific Publishers: Stevenson Ranch, CA, 2008.
- (5) Akasaka, T.; Nagase, S. Endofullerenes: A New Family of Carbon Clusters; Kluwer: Dordrecht, The Netherlands, 2002.
- (6) Dunsch, L.; Krause, M.; Noack, J.; Georgi, P. J. Phys. Chem. Solids 2004, 65, 309-315.
- Dunsch, L.; Yang, S. *Small* **2007**, *3*, 1298–1320. Wang, C. R.; Kai, T.; Tomiyama, T.; Yoshida, T.; Kobayashi, Y.; (8)Nishibori, E.; Takata, M.; Sakata, M.; Shinohara, H. Nature 2000, 408, 426-427
- 9) Chen, N.; Wang, C. R. J. Phys. Chem. B 2006, 110, 13322-13324.
- (10) Martin, N. *Chem. Commun.* **2006**, 2093–2104.
 (11) Martin, N.; Altable, M.; Filippone, S.; Martin-Domenech, A.
- Synlett 2007, 3077-3095.

synthesis of trimetallic nitride fullerenes, nitrogen, ammonia, and some other nitrogen containing chemicals like $Ca(CN)_2$ were utilized as the source of nitrogen atoms.¹²⁻²⁰ Through the use of methane in the reactive gas atmosphere method, the formation of new fullerene cages like $C_{64}H_4$ was demonstrated.²¹ The arc discharge applying a reactive gas was extended to non-isolated pentagon rule (IPR) structures like C_{50} and two I_h -symmetry-breaking C_{60} isomers using chlorine as a reactive gas to the burning process.^{22,23}

- (12) Stevenson, S.; Fowler, P. W.; Heine, T.; Duchamp, J. C.; Rice, G.; Glass, T.; Harich, K.; Hajdu, E.; Bible, R.; Dorn, H. C. Nature 2000, 408, 427-428.
- (13) Iezzi, E. B.; Duchamp, J. C.; Fletcher, K. R.; Glass, T. E.; Dorn, H. C. Nano Lett. 2002, 2, 1187-1190.
- (14) Zuo, T.; Walker, K.; Olmstead, M. M.; Melin, F.; Holloway, B. C.; Echegoyen, L.; Dorn, H. C.; Chaur, M. N.; Chancellor, C. J.; Beavers, C. M.; Balch, A. L.; Athans, A. J. Chem. Commun. 2008, 1067-1069.
- (15) Yang, S. F.; Troyanov, S. I.; Popov, A. A.; Krause, M.; Dunsch, L. J. Am. Chem. Soc. 2006, 128, 16733-16739.
- (16) Yang, S. F.; Popov, A. A.; Dunsch, L. Angew. Chem., Int. Ed. 2008, 47, 8196-8200.
- (17) Yang, S. F.; Popov, A. A.; Dunsch, L. Chem. Commun. 2008, 2885-2887.
- (18) Popov, A. A.; Dunsch, L. J. Am. Chem. Soc. 2007, 129, 11835-11849. (19) Pradeep, T.; Vijayakrishnan, V.; Santra, A. K.; Rao, C. N. R.
- J. Phys. Chem. 1991, 95, 10564-10565. (20) Hummelen, J. C.; Knight, B.; Pavlovich, J.; Gonzalez, R.; Wudl, F.
- Science 1995, 269, 1554-1556.
- (21) Wang, C. R.; Shi, Z. Q.; Wan, L. J.; Lu, X.; Dunsch, L.; Shu, C. Y.; (11) Wang, C. Ri, Shi, Z. Q., Wan, Z. Y., Ed, Y., Darbin, Z., Shiq, C. Li, Tang, Y. L.; Shinohara, H. J. Am. Chem. Soc. 2006, 128, 6605–6610.
 (22) Tan, Y. Z.; Liao, Z. J.; Qian, Z. Z.; Chen, R. T.; Wu, X.; Liang, H.;
- Han, X.; Zhu, F.; Zhou, S. J.; Zheng, Z.; Lu, X.; Xie, S. Y.; Huang, R. B.; Zheng, L. S. Nat. Mater. 2008, 7, 790-794.
- Han, X.; Zhou, S. J.; Tan, Y. Z.; Wu, X.; Gao, F.; Liao, Z. J.; Huang, R. B.; Feng, Y. Q.; Lu, X.; Xie, S. Y.; Zheng, L. S. *Angew*. (23)Chem., Int. Ed. 2008, 47, 5340-5343.

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Figure 1. (a) Chromatogram of as-prepared fullerene extract (obtained on a 20 mm × 250 mm Buckyprep column with $\lambda = 320$ nm, a flow rate of 10 mL/min, and toluene as the eluent at 25 °C). (b) Chromatogram of the isolated fraction by the second-step recycling HPLC (obtained on a 10 mm × 250 mm Buckyprep column with $\lambda = 320$ nm, a flow rate of 1.6 mL/min, and toluene as the eluent at 25 °C). Inset: chromatogram of purified C₆₀H₂(C₃H₅N) (obtained on two 4.6 mm × 250 mm Buckyprep columns in row with detection at $\lambda = 320$ nm, a flow rate of 1.6 mL/min, and toluene as the eluent at 25 °C).

Extending our strategy of the reactive gas atmosphere, we tried to combine the application of a reactive gas (in our case ammonia as a nitrogen and hydrogen source) under the influence of a special carbide structure like Al_4C_3 (to form intermediate hydrocarbons for the fullerene formation). Besides the formation of non-IPR fullerenes stabilized with single atoms like hydrogen or chlorine, no reports on the formation of exohedral fullerene derivatives formed during the Krätschmer-Huffman has ever been reported. Herein we report the synthesis and structural characterization of the first organic C₆₀ derivative which is obtained directly from the arc burning process. The synthesis of the new $C_{60}H_2(C_3H_5N)$ not only provides a novel structure of an organic derivative of fullerene hydride but, more importantly, opens new routes of the reactive gas atmosphere concept in the arc burning and potential catalytic use of Al_4C_3 for the future production of novel fullerenes.

Experimental Section

Synthesis. Fullerene soot was prepared by a modified Krätschmer–Huffman arc-burning known as "reactive gas atmosphere".⁶ A mixture of aluminum carbide and graphite powder was pressed into the hole of graphite-rods in a molar Al/C ratio of 1:15. As the source of nitrogen, 20 Torr of NH₃ was added to reactor at the atmosphere of 200 Torr He. The fullerene soot was pre-extracted by acetone and further Soxhlet-extracted with CS₂ for 20 h. The isolation of the fullerenes from the as-prepared fullerene mixture (Figure 1a) was accomplished by a two-step high-pressure liquid chromatography (HPLC) separation. In the first-step of HPLC (Abimed Gilson 1038), $C_{60}H_2(C_3H_5N)$ was eluted on a Buckyprep column along with C_{60} oxide, which was subsequently removed by the recycling HPLC (Sunchrom, Germany) step on the Buckyprep column.

Instrumentation. Mass spectra were measured by laser desorption-time-of-flight (LD-TOF) mass spectrometric (MS) analysis running in both the positive and negative ion mode (Biflex III, Bruker, Germany). Various chemicals, including 9-nitroanthracene, 1,8,9-anthracenetriol, and 3-indolylacrylicacid, were utilized as matrix for comparison.

Electron spectroscopy for chemical analysis (ESCA) was performed using a PHI 5600 CI (Physical Electronics) analyzer with the following standard parameters: Mg-K X-rays, nonmonochromatized, 350 W. Freshly cleaved highly oriented pyrolytic graphite (HOPG, basal plane) with dimensions of 10 mm \times 10 mm was used as the substrate for fullerene deposition.

Nuclear magnetic resonance (NMR) spectra were obtained on a Bruker Avance II 500 MHz spectrometer equipped with a standard 5 mm broadband observe (BBO) probe using the software package TopSpin 2.1 for acquisition and spectra analysis. The fullerene compound studied was dissolved in CS_2 and measured within a thin wall 5 mm tube. Acetone- d_6 in a coaxial tube was used as an internal lock. The spectra were referenced to the solvent signal. The spectra were acquired with acquisition times of 4 s using repetition times (D1) of 2 s for ¹H spectra. For ¹³C spectra, D1 of 8 s and proton broadband decoupling were used. For the 2D experiments, standard pulse sequences within the software package were used with adjusting repetition delays to the investigated coupling constants.

For Fourier transform infrared (FTIR) and Raman measurements, approximately 100 μ g of C₆₀H₂(C₃H₅N) was dropcoated on copper disks. The residual toluene was removed by heating the polycrystalline films in a vacuum of 2 × 10⁻⁶ mbar at 235 °C for 3 h. The FTIR spectra were recorded at room temperature in reflection mode by an IFS 66v spectrometer (Bruker, Germany) with a resolution of 2 cm⁻¹. Raman spectra were recorded on the FT-Raman spectrometer RFS 100 (Bruker, Germany) with the 1064 nm excitation wavelength of the Nd: YAG laser and a resolution of 4 cm⁻¹.

Cyclic voltammetry as well as square wave voltammetry experiments were performed with a PAR 273 potentiostat (EG&G) at room temperature in a glovebox. A three-electrode system with platinum (Pt) working and counter electrodes and a silver (Ag) wire pseudoreference electrode was used. The solutions of fullerene sample in toluene were dried, transported to a glovebox, and immediately dissolved in *o*-dichlorobenzene (*o*-DCB, anhydrous, 99%, Aldrich; $2 \times$ vacuum distilled before use). The supporting electrolyte, tetrabutylammoniumtetrafluoroborate (TBABF₄, electrochemical grade, Fluka), was dried under reduced pressure at 340 K for 24 h and stored in a glovebox prior to use. The concentration of TBABF₄ in *o*-DCB solutions was 0.2 mol/L. Ferrocene (Fc) was added as the internal standard for the final voltammetric cycle, and all potentials are referred to the Fc/Fc⁺ couple.

The ESR spectra were recorded by an EMX X-band ESR spectrometer (Bruker, Germany) and the optical spectra by an UV/vis/NIR spectrometer system TIDAS (J&M, Aalen, Germany).

A potentiostat PG 285 (HEKA, Lambrecht, Germany) was used for potential control in spectroelectrochemical experiments.

Calculations. DFT calculations were performed using PBE functional and TZ2P-quality basis with a $\{6,3,2\}/(11s,6p,2d)$ contraction scheme for C and N atoms and a $\{3,1\}/(5s,1p)$ scheme for the H atom as implemented in the PRIRODA package.²⁴

Results and Discussion

Isolation. The HPLC profile of the as-prepared fullerene mixture is demonstrated in Figure 1a. The retention time of $C_{60}H_2(C_3H_5N)$ on the Buckyprep column is inbetween that of C_{60} and C_{70} . In the raw extraction, relative product yield of $C_{60}H_2(C_3H_5N)$ to C_{60} was estimated to be 1:5. Figure 1b presents the further separation with recycling HPLC, while HPLC analysis underlines the purity of the isolated $C_{60}H_2(C_3H_5N)$ (Figure 1b, inset). After the two-step HPLC separation, 10 mg of purified product were obtained. $C_{60}H_2(C_3H_5N)$ can be dissolved in toluene and carbon disulfide. The purified sample shows a reddish-brown color in toluene which is different from that of C_{70} and C_{60} .

Structure Determination. To exclude the influence of different matrices, matrix-assisted laser desorption ionization mass spectrometric (MALDI-MS) studies of the sample were carried out with three kinds of matrix. All the spectra show a similar multipeaks pattern featured by a strong peak at 720 followed by 734, 755, 777. Among all the matrices taken into account, 9-nitroanthracene was proved to have the best performance (Figure 2). The C_{60} fragment was observed under different ionization conditions, suggesting that the isolated structure is based on a C_{60} cage and exohedrally derivatized. Besides, a peak at 777 m/e as the most intensive peak is found which could be assigned as the molecular ion peak. This result was also verified by electrospray ionization-mass spectrometry (ESI-MS, see the Supporting Information). ESCA measurements of this compound indicated that, besides carbon and hydrogen, nitrogen is also present in the molecular structure. Taking carbon, nitrogen, and hydrogen into account as the elements in this compound, the composition of this compound can be described as $C_{60}C_{3}H_{7}N.$

In depth NMR spectroscopic analysis was performed to reveal the molecular structure of the isolated compound. Figure 3a shows a 500 MHz ¹H NMR spectrum of $C_{60}C_3H_7N$ in CS₂ solution at room temperature. A total of four signals with chemical shifts of 1.82, 3.45, 5.36, and 5.41 ppm were observed in the spectrum. The signal at 1.82 ppm is a singlet with a relative intensity of 3 assigned to the methyl group. The second signal, assigned to the CH₂ group, has a relative intensity of two and shows two different couplings with one constant of 52 Hz for a two bond distance and another smaller coupling with 18 Hz over more than three bonds. The third and fourth signals



Figure 2. Negative-ion matrix-assisted laser desorption ionization-mass spectrometry (MALDI-MS) of $C_{60}H_2(C_3H_5N)$ with 9-nitroanthracene as a matrix.

from the two C-H groups have a coupling constant of 18 Hz and a relative intensity of 1 for each signal.

The ¹³C spectrum (Figure 3b,c) which is divided into two different parts, give 6 carbon signals in the range of sp³ carbons. Besides four carbon signals with an attached proton, two other signals with lower intensity are found. In the range of sp² carbon signals (130–150 ppm), 48 lines with intensity 1 and 4 lines with intensity 2 are attributed to the 56 fullerene cage sp² carbons. The cage symmetry cannot be determined because of the high number of signals. One additional carbon signal is shifted to lower field at 170.9 ppm which can be ascribed to the electron withdrawing effect of the nitrogen in the C=N group.

The H,H-COSY experiment confirms the attribution of the two C–H signals to one single C–C bond. One C–H line (at 5.41 ppm) of the coupling to the CH₂ group is weaker, which indicates that this C–H group is more distant to the side ring than the other one. A weak signal for the interaction of the CH₂ and the CH₃ group points to a spatially close position in the ring structure but with a longer distance (more than 3 bonds).

Figure 4a presents a heteronuclear multiple quantum coherence (HMQC) experiment confirming the direct coupling of the sp³ carbons to their attached protons. The signal at 20.1 ppm can be attributed to the methyl group whereas that at 62.9 ppm is attributed to the CH₂ group and those at 61.0 and 56.9 ppm are assigned to the two CH groups.

The cross signals to some carbon signals in the sp² range presented in the heteronuclear multiple bond correlation (HMBC) experiment (see Figure 4b) confirm that all protons are attached to the fullerene structure. A cross signal of the CH₃ group to the CH₂ group as well as cross signals from both to the C=N group prove the spatial closeness of these groups in the exohedrally attached ring system. The assignment of the two small sp³ carbons is possible by a weak cross signal related to one CH group and the CH₂ group while the others are not coupled because of the longer distance. Furthermore no cross signal of the CH₃ group to the second sp³ carbon is observed.

On the basis of the detailed NMR analysis, we propose the structure of $C_{60}H_2(C_3H_5N)$ given in Figure 5 (inset)

 ^{(24) (}a) Perdew, J. P.; Burke, K.; Ernzerhof, M. Phys. Rev. Lett. 1996, 77, 3865–3868. (b) Laikov, D. N. Chem. Phys. Lett. 1997, 281, 151– 156. (c) Laikov, D. N.; Ustynyuk, Y. A. Russ. Chem. Bull., Int. Ed. 2004, 54, 820–826.



Figure 3. (a) ¹H NMR spectrum of $C_{60}H_2(C_3H_5N)$; "s" denotes deuterated solvent signal (acetone as internal lock), "i" denotes impurities; (b, c) ¹³C NMR spectrum of $C_{60}H_2(C_3H_5N)$; (a) sp²-carbon range and (b) range of sp³-carbons.

featuring $C_{60}H_2$ with an additional ring system attached to the cage. This conjecture can be further confirmed by other spectroscopic techniques. Figure 5 also shows the electronic absorption spectrum of $C_{60}H_2(C_3H_5N)$, which is characterized by a strong absorption at 314 nm as well as some lower intensity transitions in the visible part of the spectrum. An absorption peak at 435 nm as well as shoulders up to 700 nm closely resemble the absorption spectrum of the recently isolated cis-1 bicyclic-fused pyrrolidinofullerene, $C_{60}H(C_4H_8NO)$.²⁵ It is known that absorption spectra of the fullerene derivatives in the visible range are determined by the $\pi - \pi^*$ transitions and by the addition pattern, while the nature of the addends (if they are not chromophores) appears to be without any influence. That is, compounds with the same π -system show very similar absorption spectra. With this respect, the close similarity of the spectrum of C₆₀H₂-(C₃H₅N) and C₆₀H(C₄H₈NO) indicates that in C₆₀H₂- (C_3H_5N) , just like in $C_{60}H(C_4H_8NO)$, two neighboring double bonds of the parent fullerene are transformed into a single bond by the addition, while the rest of the C_{60} fullerene core remains intact.²⁶ This suggestion agrees well with the structural conjecture of $C_{60}H_2(C_3H_5N)$ based on the NMR analysis.

The FTIR spectrum of $C_{60}H_2(C_3H_5N)$ exhibits a complex pattern suggesting a low molecular symmetry of the compound (Figure 6a). At the same time, main features of the cage vibrations are preserved, pointing to the fullerene core being largely preserved. A strong band observed at 1655 cm^{-1} can be readily assigned to the C=N stretching mode, which confirms the presence of the C=N bond in the heteroring attached to C₆₀ cage, as already proposed in NMR analysis. This is also consistent with the ESCA result on the presence of nitrogen. Two weak C-H stretching vibrations shown at 2914 and 2957 cm⁻¹ are similar to those of the $C_{60}H_2$, suggesting that there are two H atoms attached to the cage.²⁷ Raman spectrum of $C_{60}H_2(C_3H_5N)$ (Figure 6b) shows that the most prominent vibrations of the fullerene cage are preserved. Namely, the modes analogous to $A_g(1)$ and $A_g(2)$ modes of C_{60} are observed at 466 and 1461 cm⁻¹ (compare to 465 and 1465 cm⁻¹ in C_{60}), $H_g(8)$ -like vibration is found at 1568 cm⁻¹ (1567 cm⁻¹ in C_{60}), while $H_g(1)$ mode of

⁽²⁵⁾ Izquierdo, M.; Osuna, S.; Filippone, S.; Martín-Domenech, A.; Solà, M.; Martín, N. J. Org. Chem. 2009, 74, 6253.

^{(26) (}a) Kordatos, K.; Bosi, S.; Da Ros, T.; Zambon, A.; Lucchini, V.; Prato, M. J. Org. Chem. 2001, 66, 2802–2808. (b) Nakamura, Y.; Takano, N.; Nishimura, T.; Yashima, E.; Sato, M.; Kudo, T.; Nishimura, J. Org. Lett. 2001, 3, 1193–1196. (c) Martín, N.; Altable, M.; Filippone, S.; Martín-Domenech, A.; Güell, M.; Solà, M. Angew. Chem., Int. Ed. 2006, 45, 1439–1442.

⁽²⁷⁾ Henderson, C. C.; Cahill, P. A. Science 1993, 259, 1885-1887.



Figure 4. (a) Heteronuclear multiple quantum coherence (HMQC) spectrum of $C_{60}H_2(C_3H_5N)$; (b) heteronuclear multiple bond correlation (HMBC) spectrum of $C_{60}H_2(C_3H_5N)$.

 C_{60} (270 cm⁻¹) is split in the derivative, the two components being observed at 246 and 270 cm⁻¹. These data prove the C_{60} - I_h fullerene core in the synthesized structure as mostly preserved, in line with the other spectroscopic results.

Voltammetric Studies. The cyclic voltammogram of $C_{60}H_2(C_3H_5N)$ (Figure 7) in *o*-DCB or in *o*-DCB/toluene

exhibits a quite different redox pattern as compared to C_{60} , although the first half-wave reduction potential for $C_{60}H_2(C_3H_5N)$ (-1.22 V vs Fc/Fc⁺) is shifted by only 0.1 V to more negative potentials as compared to C_{60} (-1.12 V vs Fc/Fc⁺). Four reduction steps of $C_{60}H_2(C_3H_5N)$ are detected in the potential window available, but no oxidation step is found at potentials up to 0.55 V vs Fc/Fc⁺.



Figure 5. UV-vis absorption spectra of $C_{60}H_2(C_3H_5N)$ (black line) and C_{60} (red line) in toluene and (inset) molecular structure of $C_{60}H_2(C_3H_5N)$.



Figure 6. FTIR (a) and FT-Raman (b) spectra of $C_{60}H_2(C_3H_5N)$; the inset shows FTIR spectrum in the range of CH stretching vibrations. The arrow labels the C=N vibration at 1655 cm⁻¹.

This redox behavior is quite similar to that of $C_{60}H_2$.²⁸ However voltammograms of C₆₀H₂(C₃H₅N) and C₆₀H₂ differ on the first reduction peak and its reoxidation counterpart. While the first two C₆₀H₂ reduction steps are reversible,^{28,29} a chemical follow-up reaction is evident for the first reduction of $C_{60}H_2(C_3H_5N)$. Besides the anodic counter peak, indicating a good stability of the $C_{60}H_2(C_3H_5N)^-$ anion radical, two further peaks arise below -1 V vs Fc/Fc⁺ (indicated by 1 and 2 in Figure 7b) as a consequence of a follow up reaction of the $C_{60}H_2$ - $(C_3H_5N)^-$ anion radical. If the potential is reversed at the beginning of the first reduction peak, no counterpeaks arise (red line in inset of Figure 8a). By addition of toluene to the *o*-DCB solution (v/v, 3/1), the reversibility of the first reduction peak decreases (Figure 7a). The decrease in intensity of two shifted counterpeaks points to their dependence on the anion concentration. Moreover, no significant change was observed in the shape and intensity of the voltammetric peaks during multiple potential cycling at the first electron transfer indicating a reversible redox process. On the basis of our experimental and recent literature data,³⁰ the new peaks observed at -0.78



Figure 7. (a) Cyclic voltammograms of $C_{60}H_2(C_3H_5N)$ in *o*-DCB/TBABF₄ solution (black line) and *o*-DCB/toluene solution (red line) at a scan rate of 0.1 V s⁻¹. (b) Cyclic voltammograms of $C_{60}H_2(C_3H_5N)$ in *o*-DCB/TBABF₄ solution at a scan rate of 0.1 (red line) and 1 V s⁻¹ (black line).

and -0.58 V vs Fc/Fc⁺ in the back scan can be attributed to the dimerization product of the anion radicals formed in a reversible reaction (Scheme 1). Because of the limited stability of these dimers and a chemical follow-up reaction in the reoxidation of the dimer, the height of the new voltammetric peaks depends on the scan rate. With an increasing scan rate, the dimeric dianion (AA²⁻) at -0.58 V vs Fc/Fc⁺ becomes visible and does not decompose to the parent anion radicals in the time scale of the voltammetric scan (Figure 7b). One additional chemical step (EC or CE) is involved in the reaction scheme, attributed to the decomposition of the dimer into the monomer units, which is scan rate dependent and results in the complex voltammetric response.

In cyclic square wave voltammetry of $C_{60}H_2(C_3H_5N)$ fullerene in 0.2 M TBABF₄/*o*-DCB solution, both the large stability of the anion radical and the formation of two follow-up products in the first reduction step were confirmed (Figure 8a).

At the first electron transfer (black line in Figure 8a), these two new peaks arise in the back scan (red line), but in the second electron transfer (blue line in Figure 8a), higher concentrations of dimers were found in the back scan (green line in Figure 8a). Because of the symproportionation reaction ($A^{2-} + A \rightleftharpoons 2A^{-}$), a larger extent of anion radicals and consequently also of dimers is formed close to the electrode.

⁽²⁸⁾ Guarr, T. F.; Meier, M. S.; Vance, V. K.; Clayton, M. J. Am. Chem. Soc. 1993, 115, 9862–9863.

⁽²⁹⁾ Boulas, P.; D'Souza, F.; Henderson, C. C.; Cahill, P. A.; Jone, M. T.; Kadish, K. M. *J. Phys. Chem.* **1993**, *97*, 13435–13437.
(30) Macias-Ruvalcaba, N. A.; Felton, G. A. N.; Evans, D. H. *J. Phys.*

⁽⁵⁰⁾ Macias-Ruvalcaba, N. A.; Felton, G. A. N.; Evans, D. H. J. Phys. Chem. C 2008, 113, 338–345.



Figure 8. (a) Cyclic square wave voltammetry of $C_{60}H_2(C_3H_5N)$ in *o*-DCB/TBABF₄ solution (black and blue lines, forward scan; red and green lines, back scan; inset, cyclic voltammograms of $C_{60}H_2(C_3H_5N)$ in *o*-DCB/TBABF₄. (b) Cyclic square wave voltammetry of $C_{60}H_2(C_3H_5N)$ in *o*-DCB/TBABF₄ solution up to the 4th redox peak (black line, forward scan; red line, back scan).



Remarkable differences in cyclic voltammetry of C₆₀H₂(C₃H₅N) in comparison to other C₆₀ and C₆₀ derivatives were observed at the third electron transfer (Figure 8b). Interestingly, two further reduction peaks beyond the second redox peak were observed at quite different potentials. Their intensity is substantially smaller as compared to that of the first two redox peaks. However, the sum of heights of these two peaks gives almost the same peak height as observed for the first and the second reduction peak, respectively. Quantum chemical studies and a comparison with known literature data on the electrochemistry of hydrogenated fullerenes were used to explain this redox behavior. For $C_{60}H_2$, the products of the first two reduction steps are stable on the time scale of the experiment while the third and fourth steps result in a decomposition to give the parent C_{60} .²⁹ Therefore, two compounds, $C_{60}H_2(C_3H_5N)$ (Figure 5), and a dehydrogenation product, $C_{60}(C_3H_5N)$, were analyzed by density functional theory (DFT) at the PBE/ TZ2P level. The lowest unoccupied molecular orbital

(LUMO) levels of these two structures (-4.14 and -4.21 eV, respectively) differ by less than 0.1 eV. Hence, both structures do not give a difference in peak potentials and the first and second reduction step are detected at nearly the same potential.

However, the difference in LUMO + 1 levels (-3.88 and -4.14 eV in $C_{60}H_2(C_3H_5N)$ and $C_{60}(C_3H_5N)$, respectively) is much more apparent for the structure $C_{60}(C_3H_5N)$; the difference between the LUMO + 1 and LUMO is very small (0.07 eV). Therefore the gap between the second and the third reduction steps should be close to that in C_{60} . On the contrary, a much larger difference (0.24 eV) is found between the LUMO and LUMO + 1 level in the structure $C_{60}H_2(C_3H_5N)$, resulting in a significant cathodic shift of the third reduction as compared to C_{60} (i.e., the difference between the second and the third reduction should be larger). This large difference of about 680 mV between the second and third electron transfer was observed for cis-1 bicyclic-fused organofullerenes having H atoms attached at the fullerene cage close to the bicyclic addend.³¹ Therefore, we can ascribe the third peak to the $C_{60}(C_3H_5N)$ structure and the fourth one to the hydrogenated form $C_{60}H_2(C_3H_5N)$. The voltammetric behavior at the third and fourth reduction peak is therefore attributed to a hydrogen removal of the $C_{60}H_2(C_3H_5N)$ trianion. Consequently, the third and the fourth reduction correspond to the third electron transfer for two different structures, $C_{60}H_2(C_3H_5N)$ and $C_{60}(C_3H_5N)$.

Preparing a fresh o-DCB solution of C₆₀H₂(C₃H₅N) from the original toluene solution, square wave voltammetry of $C_{60}H_2(C_3H_5N)$ (Figure 9) gives a higher third peak than the fourth one in the first minutes after dissolution (Figure 9a, black line). After 5 h of storage, the intensity of the third peak is decreased resulting in a simultaneous increase of the fourth peak (Figure 9a, blue line). With the use of a CS_2 solution of $C_{60}H_2(C_3H_5N)$, SW voltammetry gives the same pattern as in the case of the toluene solution after 12 h of storage (Figure 9b). The difference in stability of the $C_{60}H_2(C_3H_5N)$ trianion in different solvents results in a variation of the ratio of the third and the fourth reduction peak. $C_{60}H_2(C_3H_5N)$ as a C₆₀H₂ based structure with a heteroring attached on the neighboring position of hydrogen is similar in its decomposition upon the electrochemical reactions as $C_{60}H_2$.²⁹

In Situ ESR UV-vis NIR Spectroelectrochemistry. The spectroelectrochemistry of $C_{60}H_2(C_3H_5N)$ points to the radical nature of the $C_{60}H_2(C_3H_5N)^-$ monoanion upon reduction. A sharp and intense ESR line ($\Delta B_{pp} = 0.17$ G) with a *g*-factor of 2.0014 (for $[C_{60}H_2]^-$ the *g* value is 2.000)²⁷ with some "sidebands" is observed during the voltammetric cycle (Figure 10). As for $[C_{60}H_2]^-$, no hyperfine coupling with two hydrogen atoms at the cage is observed. Such similar sharp and intense ESR signals were reported for the monoanions and monocations of the multiply derivatized C_{60} as well as for higher fullerenes (e.g C_{82} fullerene) with low symmetry. The "sidebands" observed

⁽³¹⁾ Izquierdo, M.; Osuna, S.; Filippone, S.; Martin-Domenech, A.; Sola, M.; Martin, N. J. Org. Chem. 2009, 74, 1480–1487.

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Figure 9. Square wave voltammetry of $C_{60}H_2(C_3H_5N)$ in *o*-DCB/TBABF₄ solution freshly prepared from its (a) original toluene solution (black line, fresh *o*-DCB solution; red line, measurement after 2 h; dark yellow line, measurement after 5 h) or from its (b) original CS₂ solution (blue line). For comparison of fresh solutions, voltammetry of the original toluene solution (black line) is also shown in part b. Scan rate, 75 mV s⁻¹; step height, 3 mV; pulse amplitude, 50 mV; pulse duration, 0.02 s; Ag-wire pseudoreference electrode; Pt-working electrode (performed in glovebox).



Figure 10. In situ ESR/UV–vis-NIR spectroelectrochemistry of $C_{60}H_2$ -(C_3H_5N): vis/NIR spectra collected in the first and second reduction step (-0.15 to -1.65 V vs Fc/Fc⁺, scan rate = 3 mV s⁻¹). In the inset, ESR spectra (measured at potentials of -0.85 V (red line) and at -1.35 V (black line) vs Fc/Fc⁺ and details of the ¹³C satellite pattern are given.

are assigned to ¹³C satellites. In situ ESR/vis-NIR spectroeletrochemical studies of the anion formed in the first reduction step of $C_{60}H_2(C_3H_5N)$ gives rise to a new optical band at 928 nm (Figure 10). The potential dependence of this band is well correlated with that of the ESR signal during the voltammetric cycle. Therefore the signal can be assigned to the $[C_{60}H_2(C_3H_5N)]^-$ monoanion. At more negative potentials, including the second reduction step, the intensity of the ESR signal of $[C_{60}H_2(C_3H_5N)]^-$ is decreased and no new ESR signal was observed, confirming the diamagnetic character of the dianion. During the back scan, the intensity of the ESR signal is increased after reoxidation of the dianion to the monoanion. A new absorption band at 850 nm occurred in the vis/NIR spectra in the second reduction step (Figure 10). This band can be assigned to the $[C_{60}H_2(C_3H_5N)]^{2-}$ dianion based on the correlation of their intensities with the charge transferred in the second reduction step. The ESR and UV-vis NIR spectroelectrochemistry results are consistent, confirming the paramagnetic state of the $[C_{60}H_2(C_3H_5N)]^-$ monoanion and the diamagnetic state of the $[C_{60}H_2(C_3H_5N)]^{2-1}$ dianion.

Conclusions

The first direct arc synthesis of $C_{60}H_2(C_3H_5N)$, a large exohedral structure of IPR C60, has been reported including the structural characterization. The unconventional redox behavior has been studied by electrochemistry and in situ spectroelectrochemistry. The NMR and absorption spectra confirmed the structure as a hydride fullerene with a pyrrolino ring attached on the vicinal position of two hydrogen atoms. $C_{60}H_2(C_3H_5N)$ is the first cycloaddition adduct of $C_{60}H_2$. This novel exohedral fullerene gives rise to a unique redox behavior indicated by a redox initiated dimerization. The spectroelectrochemical study confirms the paramagnetic state of the $[C_{60}H_2(C_3H_5N)]^$ anion and the diamagnetic state of the $[C_{60}H_2(C_3H_5N)]^2$ dianion. This study opens a new synthetic route to exohedral fullerenes via the reactive gas atmosphere concept including Al₄C₃ as a reaction agent to produce in situ hydrocarbons. The generation of $C_{60}H_2(C_3H_5N)$ by arc synthesis is a first step to a one step process in exohedral fullerene production.

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Supporting Information Available: ESI-MS analysis of $C_{60}H_2$ -(C_3H_5N) and a reaction scheme of the fullerene formation (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.