Facile and potent synthesis of carbon bridged fullerene dimers ($HC_{60}–CR_2–C_{60}H$ type)†

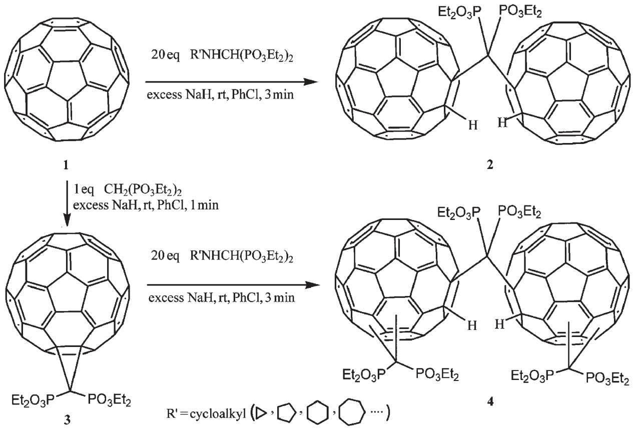
Juan-Juan Yin,[a] Yu-Guo Li,[a] Bin Li,[a] Wen-Xin Li,*[a] Li-Mei Jin,[b] Jin-Ming Zhou[b] and Qing-Yun Chen*[b]

Received (in Cambridge, UK) 27th January 2005, Accepted 19th April 2005
First published as an Advance Article on the web 3rd May 2005
DOI: 10.1039/b501390a

Novel carbon bridged fullerene dimers ($HC_{60}–CR_2–C_{60}H$ type) are obtained in high yield by the reaction of aminomethylenebis(phosphonate) anions with [60]fullerene.

The preparation and characterization of fullerene dimers and polymers have been attracting great interest in the field of fullerene chemistry.[1] The C_{60} dimers $C_{121}H_2$,[2] $C_{120}O$[2–5] and $C_{120}O_2$[5] have been reported, in which the two C_{60} molecules are linked by, respectively, a cyclopentane ring, a furan group and a cyclobutane ring plus two oxygen bridges, while the C_{60} dimer $C_{120}Si(Ph)_2$,[6] connected by a silicon bridge and a single bond, has also been synthesized by the high-speed vibration milling (HSVM) technique. The simplest [2 + 2] structural fullerene dimer, C_{120},[7] and the C_{60}/C_{70} cross dimer, C_{130},[8] as well as five isomers of C_{140},[9] have been prepared by Murata and Shinohara. To date, on the other hand, among the C_{60} dimers in which the two C_{60} molecules are connected by a single carbon atom and not containing a direct fullerene–fullerene bond,[10–14] there has been only one type of structure ($C_{2m} > C < C_{2n}$ type, $m = n$ or $m \neq n$),[15–18] but a single carbon atom carrying two large C_{60} cages and no ring unit between the bridge carbon atom and fullerenes ($HC_{60}–CR_2–C_{60}H$ type, $R = PO_3Et_2$) has not so far been isolated and characterized.

We herein report a facile method for synthesizing novel $HC_{60}–CR_2–C_{60}H$ type organophosphorus fullerene dimers (**2** and **4**‡) according to Scheme 1, by using substituted aminomethylenebis(phosphonate)s [$R'NHCH(PO_3Et_2)_2$, R′ = cycloalkyl][19] which are easily available.



Scheme 1

The dimerization reaction was finished within only 3 minutes and the product was easily purified by flash chromatography. For the synthesis of **2**, an example is given to illustrate the general procedure. A mixture of C_{60} (20 mg, 0.028 mmol), 20 equivalents of cyclo-$C_6H_{11}NHCH(PO_3Et_2)_2$ (214 mg, 0.556 mmol) and excess NaH (13 mg, 0.542 mmol) in dry chlorobenzene (5 ml) was stirred at room temperature for 3 minutes, followed by flash column chromatography eluting with chlorobenzene–acetone (100:0.6), and afforded product **2** (16.4 mg, 68%) instead of the anticipated product, $HC_{60}\ NR'CH(PO_3Et_2)_2$. The new dimer **2** is very stable in air in spite of its high steric hindrance effect, but under severe conditions (*i.e.* refluxing in concentrated HCl or TFA), it dissociates to C_{60}.[20]

The structure of **2** was determined by MS, DEPT, HMBC, UV, FT-IR, $^{31}P\{^1H\}$ and ^{13}C NMR spectroscopy as well as elemental analysis. The positive-ion mode Fourier-transform MALDI-MS spectra showed the molecular ion peak of $C_{121}(PO_3Et_2)_2$ at *m/z* 1728 (intensity 12.0%) (plus isotopic peaks) and a series of peaks for $C_{121}(PO_3Et_2)_2 \pm C_{2n}$, ion clusters of higher fullerenes presumably generated by the carbon recombination of fragments under the MS experiment conditions.[7,21] The ^{13}C NMR and DEPT spectrum (in ODCB-d_4) located a set of CH_3 peaks at 17.557 ppm (OCH_2CH_3) ($^3J_{C–P} = 3.15$ Hz), a set of CH_2 peaks at 66.241 ppm (OCH_2CH_3) ($^2J_{C–P} = 4.35$ Hz), a set of CH peaks at 57.453 ppm (two equivalent sp^3C of C_{60}) and two sets of quaternary carbon peaks at 66.241 and 67.426 ppm [$C(PO_3Et_2)_2$ and two equivalent sp^3 C of C_{60}]. The ^{13}C NMR (in $CDCl_3$) exhibited 36 signals for the sp^2 carbons of the two C_{60} cages ranging from 128.99 to 162.44 ppm, some sp^2 carbons signals of **2** split by the long range coupling of the phosphorus; the $^{31}P\{^1H\}$ and ^{13}C NMR spectrum indicate that **2** has C_{2v} symmetry.

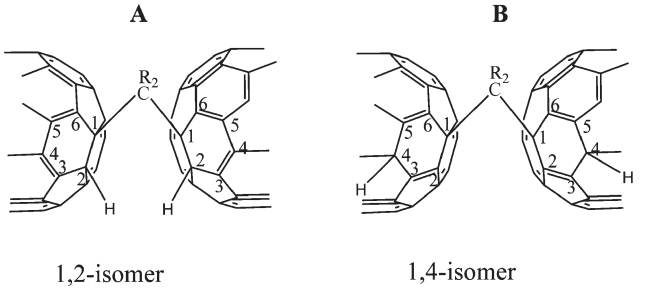


Fig. 1 Two possible isomers of **2**.

---

† Electronic supplementary information (ESI) available: AFM preparation and imaging and spectroscopic data for dimers **2** and **4**. See http://www.rsc.org/suppdata/cc/b5/b501390a/

*yinjj@mail.sioc.ac.cn (Wen-Xin Li)
Chenqy@mail.sioc.ac.cn (Qing-Yun Chen)

There are two possible isomers of **2** as shown in Fig. 1. The possibility of B can be eliminated by the HMBC [(^1H-detected) heteronuclear multiple-bond correlation] spectroscopic method[11] as shown in Fig. 2. It was shown that the two proton resonance (directly linked to C_{60}) at 7.35 ppm correlates to the quaternary carbon (67.426 ppm, bonded to the two phosphorus atoms). For the structure of B, the two proton resonance at 7.35 ppm and the quaternary carbon at 67.426 ppm should have no or weak correlation signal. Furthermore, the UV-absorption spectrum has an absorption peak at 434 nm demonstrating a characteristic feature of the 1,2-isomer structure.[22] Unexpectedly, under similar conditions, $CH_2(PO_3Et_2)_2$ reacted with C_{60} to afford mono-adduct **3**[23–25] within 1 minute in high yield but no dimer product **2** was detected; the reaction of $CHBr(PO_3Et_2)_2$ and C_{60} also afforded product **3**,[26] therefore, the amino groups RNH play an important role in the preparation of the dimer **2**. For various cycloalkyl aminomethylenebis(phosphonate)s, the dimer products were also obtained. Notably, the dimerization of **1** can be partially suppressed and the formation of **3** can be completely inhibited in the presence of 30 mol% of hydroquinone respectively.

The striking results obtained with C_{60} and $R'NHCH(PO_3Et_2)_2$ led us to examine the reaction of **3** with aminomethylenebis(phosphonate), under the same condition as shown in Scheme 1. The dimer **4**, indeed, was obtained, and its structure was characterized by ordinary spectroscopy and 2D NMR. But the exact position of cyclopropane rings cannot be assigned.

To confirm the structural assignment, we performed a direct observation of **2** using atomic force microscopy (AFM) as shown in Fig. 3. Before the AFM experiment, the dimer **2** was dispersed in dilute ethanol and irradiated by ultrasonic waves for several hours in order to guarantee the grain in the image was a single molecule. The AFM images of **2** deposited on a freshly cleaved mica surface show a dumbbell shape with an average height of 1.360 ± 0.056 nm [low (0.690 ~ 0.911 nm) and high (1.201 ~ 1.404 nm)] which is very consistent with the molecular size of **2** estimated by a preliminary molecular geometry calculation [the molecular size ranges from 6.915 Å to 16.910 Å as shown in Fig. 3(c)].

Because the reaction can be inhibited by the presence of hydroquinone, the formation of **2** and **3**, thus, might not be rationalized simply in terms of anionic addition reactions onto C_{60}, *i.e.*, a radical mechanism should be involved in the reaction.

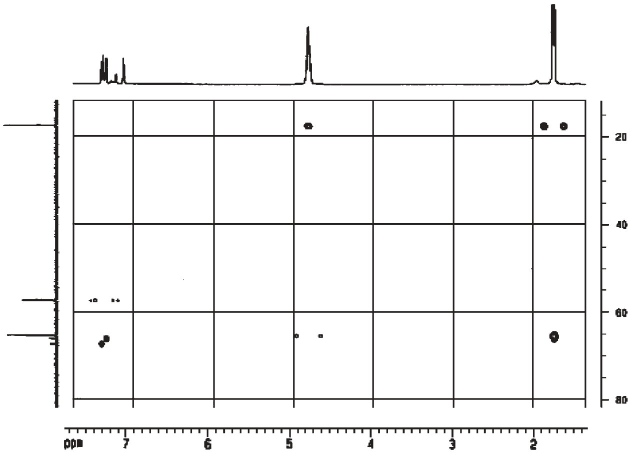


Fig. 2 HMBC spectrum of fullerene dimer **2** in ODCB-d_4, (sp^3 carbon range of ^{13}C NMR spectrum, 100 MHz).

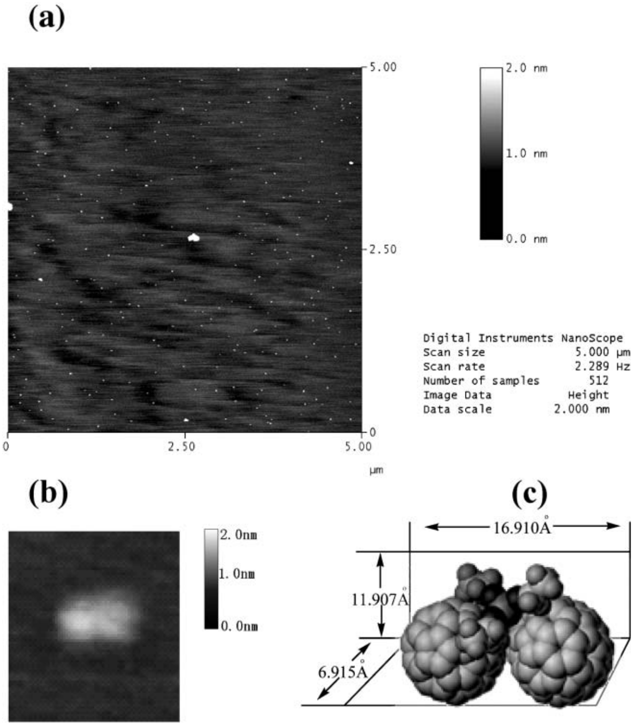


Fig. 3 Tapping-mode AFM height images of **2** after treatment with dilute ethanol followed by drying with a stream of air on mica substrate; (a) 5 µm × 5 µm AFM image of **2**; (b) a single molecule of **2**; (c) molecular geometry of **2**, which was constructed using the SYBYL program,[27] then the model was charged with MMFF94[28] atomic charge and optimized using MMFF94 force field.

In summary, we present here a facile method for synthesizing two novel organophosphorus C_{60} dimers in high yield, the first well-characterized fullerene dimers linked by a single carbon atom and no ring structure between the bridge carbon and fullerenes. The molecule was observed clearly using AFM.

Juan-Juan Yin,[a] Yu-Guo Li,[a] Bin Li,[a] Wen-Xin Li,*[a] Li-Mei Jin,[b] Jin-Ming Zhou[b] and Qing-Yun Chen*[b]
[a]*Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201800, China. E-mail: yinjj@mail.sioc.ac.cn*
[b]*Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Lu, 200032, China. E-mail: Chenqy@mail.sioc.ac.cn*

Notes and references

‡ **Synthesis of 2.** To a solution of C_{60} (100 mg, 0.139 mmol) and $C_7H_{13}NHCH(PO_3Et_2)_2$ (1110 mg, 2.78 mmol) in dry chlorobenzene (20 ml) at room temperature was added NaH (1 g) to give a deep green solution and volatile materials immediately. After 3 minutes, the reaction mixture was poured onto a silica gel column, and eluted with chlorobenzene–acetone (10:1) for the preliminary separation; a dark-amber band containing mainly the C_{60} dimer **2** (82.7 mg, 69%) was collected. Further separation was achieved with a chlorobenzene–acetone (100:0.6) mixture on a silica gel column. For $C_6H_{11}NHCH(PO_3Et_2)_2$ 1070 mg, $C_5H_9NHCH(PO_3Et_2)_2$ 1032 mg, $C_4H_7NHCH(PO_3Et_2)_2$ 993 mg, the yield of **2** was 68%, 60% and 61% respectively. ^1H NMR (300 MHz, $CDCl_3$) δ 1.72 (t, 12H, J = 7.2 Hz, OCH_2CH_3), 4.77 (m, 8H, OCH_2CH_3), 7.35 (s, 2H, C_{60}–H); ^{31}P NMR (160 MHz, $CDCl_3$) δ 21.33; ^{13}C NMR (75 MHz, ODCB-d_4) δ 17.52 (d, $^3J_{P–C}$ = 3.15 Hz, OCH_2CH_3), 57.45 (sp^3 C of C_{60}, bonded to hydrogen), 65.46 (d, $^2J_{P–C}$ = 4.35 Hz, OCH_2CH_3), 66.24 (sp^3 C

of C_{60}, bonded to the carbon bridge), 67.43 (the bridge carbon bonded to the two phosphorus atoms), 133.28, 133.45, 133.80, 134.74, 136.04, 136.06, 136.83, 136.87, 140.78, 140.96, 142.01, 142.11, 142.13, 142.18, 142.42, 142.50, 142.56, 143.03, 143.12, 143.71, 144.88, 145.16, 145.87, 145.93, 146.01, 146.03, 146.35, 146.73, 146.79, 146.86, 146.93, 147.56, 147.68, 147.75, 148.36, 148.37, 150.24, 150.34, 152.66, 152.71; UV-Vis λ_{max}/nm (CH_2Cl_2) 228, 255, 324, 434; IR ν/cm^{-1} (KBr) 2927, 2900, 2327, 1427, 1387, 1360, 1250, 1183, 1039, 1016, 972, 959, 801, 631, 572, 547, 525; HPLC: 98.3% pure, T_R = 33.5 min; MS (MALDI) *m*/*z*: 1728. Anal. calcd for $C_{129}H_{22}P_2O_6{\cdot}3H_2O$: C, 86.97; H, 1.57; N, 0; P, 3.48%. Found: C, 86.93; H, 1.45; N, 0; P, 3.62%.

Synthesis of 3. To a solution of C_{60} (100 mg, 0.139 mmol) and tetraethyl methylenediphosphonate [$CH_2(PO_3Et_2)_2$] (35 µl, 0.139 mmol) in dry chlorobenzene (20 ml) at room temperature was added NaH (1 g). After 1 minute, the reaction mixture was poured onto a silica gel column, and eluted with chlorobenzene–acetone (20:1); the second dark-amber band containing mainly the product **3** was collected (58.4 mg, 42%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.53 (t, 12H, J = 7.2 Hz, OCH_2CH_3), 4.47 (m, 8H, OCH_2CH_3); ^{31}P NMR (160 MHz, $CDCl_3$) δ 14.89 (m, 1P); ^{13}C NMR (75 MHz, ODCB-d_4) δ 16.60 (t, $^3J_{P–C}$ = 2.98 Hz, OCH_2CH_3), 63.90 (t, $^2J_{P–C}$ = 3.15 Hz, OCH_2CH_3), 140.36, 140.99, 142.26, 142.37, 142.94, 143.03, 143.09, 144.08, 144.67, 144.72, 144.91, 144.97, 145.09, 145.19, 145.35, 146.03, 146.09, 146.16; UV-Vis λ_{max}/nm (CH_2Cl_2) 228, 255, 324, 434; MALDI-TOF *m*/*z*: 1029 $[M + Na]^+$. The spectroscopic data is identical to previously reported spectra for this compound in ref. 23.

Synthesis of 4. To a solution of **3** (100 mg, 0.099 mmol) and $C_6H_{11}RNHCH(PO_3Et_2)_2$ (766 mg, 1.988 mmol) in dry chlorobenzene (20 ml) at room temperature was added NaH (1 g) to give a dark brown solution and volatile materials immediately. After 3 minutes, the reaction mixture was poured onto a silica gel column, and eluted with (20:1) for the preliminary separation; a dark-amber band containing mainly **4** was collected (58 mg, 50.7%). Further separation was achieved with a CH_2Cl_2/CH_3OH (100:1) mixture on a silica gel column [for $C_7H_{13}NHCH(PO_3Et_2)_2$ 794 mg, 52 mg **4** was obtained with a yield of 45.5%]. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.36 (t, J = 7.0 Hz, 12H), 1.44 (t, J = 7.0 Hz, 12H), 1.57 (t, J = 7.0 Hz, 12H), 4.24 (m, 8H), 4.36 (m, 8H), 4.60 (m, 8H), 6.67 (s, 1H, C_{60}–H), 6.76 (s, 1H, C_{60}–H); ^{31}P NMR (160 MHz, $CDCl_3$) δ 14.63 (m, 4P), 22.05 (m, 2P); ^{13}C NMR (125 MHz, $CDCl_3$) δ 16.43 (d × 2, overlapping, OCH_2CH_3), 16.76 (d, $^3J_{P–C}$ = 5.4 Hz, OCH_2CH_3), 29.70, 34.20, 55.571 (two sp^3 C of C_{60}, bonded to hydrogen, overlapping), 63.54 (d, $^2J_{P–C}$ = 6.2 Hz, OCH_2CH_3), 63.74 (d, $^2J_{P–C}$ = 6.2 Hz, OCH_2CH_3), 64.71, 64.99 (d, $^2J_{P–C}$ = 7.5 Hz, OCH_2CH_3), 66.05, 66.75, 137.35, 137.37, 139.23, 139.24, 140.76, 140.81, 141.90, 142.12, 143.07, 143.14, 143.99, 144.07, 144.26, 144.47, 144.58, 144.61, 144.65, 144.70, 144.91, 145.35, 145.61, 145.75, 145.77, 146.11, 146.66, 146.75, 147.38, 147.41, 147.64, 147.66, 147.76, 148.02, 148.50, 149.08, 155.00, 155.05; UV-Vis λ_{max}/nm (CH_2Cl_2) 228, 255, 324, 434; HPLC (C18 column): 97.3% pure, T_R = 95 min; MALDI *m*/*z*: 2300.3 [M^+], HRMS (MALDI) *m*/*z* calcd for $C_{147}H_{63}P_6O_{18}$ (MH^+) 2301.24347, found 2301.2360.

1 A. Hirsch, *The Chemistry of the Fullerenes*, Thieme Medical Publishers, New York, 1994; J. L. Segura and N. Martin, *Chem. Soc. Rev.*, 2000, **29**, 13–25.
2 A. B. Smith, III, T. Hidetoshi, R. M. Strongin, G. T. Furst and W. J. Romanow, *J. Am. Chem. Soc.*, 1995, **117**, 9359.
3 A. Balch, D. A. Costa, W. R. Faweett and K. Winkler, *J. Phys. Chem.*, 1996, **100**, 4823.
4 P. Parimal, K. C. Kim, D. Y. Sun, P. D. W. Boyd and C. A. Reed, *J. Am. Chem. Soc.*, 2002, **124**, 4394.
5 K. Komatsu, G.-W. Wang, Y. Murata, T. Tanaka and K. Fujiwara, *J. Org. Chem.*, 1998, **63**, 9358.
6 K. Fujiwara and K. Komatsu, *Org. Lett.*, 2002, **4**, 1039.
7 G.-W. Wang, K. Komatsu, Y. Murata and M. Shiro, *Nature*, 1997, **387**, 583.
8 K. Komatsu, K. Fujiwara and Y. Murata, *Chem. Commun.*, 2000, 1583.
9 G. S. Forman, N. Tagmatarchis and H. Shinohara, *J. Am. Chem. Soc.*, 2002, **124**, 178.
10 S. Osawa, E. Osawa and M. Harada, *J. Org. Chem.*, 1996, **61**, 257.
11 T. Kusukawa and W. Ando, *J. Organomet. Chem.*, 1998, **561**, 109.
12 F. Y. Cheng, Y. Murata and K. Komatsu, *Org. Lett.*, 2002, **4**, 2541.
13 Y. Murata, F. Y. Cheng, T. Kitagawa and K. Komatsu, *J. Am. Chem. Soc.*, 2004, **126**, 8874.
14 G.-W. Wang, T. H. Zhang, X. Cheng and F. Wang, *Org. Biomol. Chem.*, 2004, **2**, 1160.
15 N. Dragoe, S. Tanibayashi, K. Nakahara, S. Nakao, H. Shimotani, L. Xiao, K. Kitazawa and Y. Achiba, *Chem. Commun.*, 1999, 85.
16 Y. H. Zhu, S. Bahnmueller, C. Chibun, K. Carpenter, N. S. Hosmane and J. A. Maguire, *Tetrahedron Lett.*, 2003, **44**, 5473.
17 H. Shimotani, N. Dragoe and K. Kitazawa, *J. Phys. Chem. A.*, 2001, **105**, 4980.
18 Y. L. Zhao, Z. L. Chen, H. Yuan, X. F. Gao, L. Qu, Z. F. Chai, G. M. Xing, S. Yoshimoto, E. Tsutsumi and K. Itaya, *J. Am. Chem. Soc.*, 2004, **126**, 11134.
19 M. Takeuchi, S. Sakamoto, M. Yoshida, T. Abe and Y. Isomura, *Chem. Pharm. Bull.*, 1993, **41**, 688.
20 Some fullerene dimers [C_{140}, $C_{120}Si(Ph)_2$] are sensitive to light or moisture (refs. 9 and 17).
21 L. Y. Chiang, R. B. Upassani and J. W. Swirezewski, *J. Am. Chem. Soc.*, 1992, **114**, 10154.
22 T. Akasaka, M. T. H. Liu, Y. Niino, Y. Maeda, T. Wakahara, M. Okamura, K. Kobayashi and S. Nagase, *J. Am. Chem. Soc.*, 2000, **122**, 7134.
23 F. Y. Cheng, X. L. Yang, C. H. Fan and H. S. Zhu, *Tetrahedron*, 2001, **57**, 7331.
24 F. Y. Cheng, X. L. Yang, H. S. Zhu and Y. L. Song, *Tetrahedron Lett.*, 2000, **41**, 3947.
25 Compound **3** was usually synthesized by the reaction of C_{60} with $CH_2(PO_3Et_2)_2$ in the presence of I_2 at 40 °C for 9 hours (refs. 23 and 24).
26 I. A. Nuretdinov, V. P. Gubskaya, N. I. Shishikina, G. M. Fazleeva, L. Sh. Berezhnaya, I. P. Karaseva, F. G. Sibgatullina and V. V. Zverev, *Izv. Akad. Nauk, Ser. Khim.*, 2002, **51**, 317.
27 *SYBYL® 6.9*, Tripos Inc., 1699 South Hanley Rd., St. Louis, MO, 63144, USA.
28 T. A. Halgren, *J. Am. Chem. Soc.*, 1990, **112**, 4710.