# Synthesis of $C_{60}$ -fused tetrahydrothiophene derivatives *via* nucleophilic cycloaddition of thiocyanates<sup>†</sup>

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Nucleophilic cycloaddition of thiocyanates 1a-e with  $C_{60}$  in the presence of

1,8-diazabicyclo[5.4.0]undec-7-ene afforded  $C_{60}$ -fused 2-iminotetrahydrothiophene derivatives **2a**–e and methanofullerenes **3a–d**. The product distributions were highly sensitive to the substrates employed. The 2-iminotetrahydrothiophene derivatives **2a**–e could be further manipulated by hydrolysis and acetylation to give 2-oxotetrahydrothiophene derivatives **4a–e** and 2-acetamidotetrahydrothiophene derivatives **5a–e**. A possible reaction mechanism for the formation of products **2a–e** and **3a–d** was proposed.

### Introduction

Since fullerenes became available in a macroscopic amount in 1990, various effective methods<sup>1</sup> have been developed to synthesize an impressive number of fullerene derivatives, which may find application in biology and material science.<sup>2</sup> Among them sulfur-containing fullerene derivatives demonstrate interesting electronic properties.<sup>3</sup> Fullerene diads and triads bearing oligothiophene/polythiophene<sup>4</sup> and tetrathiofulvalene/ $\pi$ extended tetrathiofulvalene5 have been intensively studied. Sulfur reagents such as sulfones,<sup>4b,6</sup> sultines,<sup>7</sup> stabilized sulfonium ylides,<sup>8</sup> α,β-unsaturated thiocarbonyl compounds,<sup>9</sup> o-thioquinone methide,10 a thiocarbonyl ylide,11 heterocyclic masked 1,3-dipoles 5-imino-1,2,4-thiadiazolidine-3-ones,12 disulfides,13 SO3,14 H2S15 and sulfur itself<sup>16</sup> have been employed in fullerene chemistry. Recently a new protocol for the synthesis of sulfur-containing dihydro-pyrrolo C<sub>60</sub> derivatives was reported by Elemes and coworkers,<sup>17</sup> utilizing the 1,3-dipolar cycloaddition reaction of C<sub>60</sub> with sulfide-bearing imines of glycine esters. We synthesized sulfurcontaining  $C_{60}$  derivatives by the reaction of  $C_{60}$  with CS<sub>2</sub> and amino acid ester hydrochlorides in the presence of triethylamine (Et<sub>3</sub>N).<sup>18</sup> Isothiocyanates generated in situ from amino acid ester hydrochlorides and CS<sub>2</sub> in the presence of Et<sub>3</sub>N were believed to undergo subsequent nucleophilic cycloaddition with C60. However, the reaction of thiocyanates with  $C_{60}$  has not been reported until now. In continuation of our interest in fullerene chemistry,<sup>18,19</sup> herein we disclose the nucleophilic cycloaddition of thiocyanates with C<sub>60</sub>, affording C<sub>60</sub>-fused 2-iminotetrahydrothiophene derivatives, and further transformations to other fullerene derivatives

### **Results and discussion**

Thiocyanates have been used in the synthesis of thiazole derivatives.<sup>20</sup> However, reactions employing the  $\alpha$ -carbon of these compounds as a nucleophilic site are really rare.<sup>21</sup> We thus investigated the feasibility of the nucleophilic attack of the  $\alpha$ -carbon of thiocyanates on C<sub>60</sub> under basic conditions.

We chose the reaction of  $C_{60}$  with 1-(4-methoxyphenyl)-2-thiocyanatoethanone (1a) as a model reaction to optimize the reaction conditions (Scheme 1).

By using triethylamine, pyridine, 4-dimethylaminopyridine (DMAP) or triethylenediamine (DABCO) as a base, the reaction afforded products 2a and 3a (Scheme 1) in very low yields with over 90% recovered C<sub>60</sub> (entries 1-4, Table 1). To our delight, the reaction proceeded rapidly to give products 2a and 3a in 65% total yield in 10 min when 1 equiv. of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was used. Product 3a was obtained as the major product with a yield of 44%, being more than twice that (21%) of product 2a (entry 5, Table 1). The structures of products 2a and 3a were assigned as a C<sub>60</sub>-fused 2-iminotetrahydrothiophene derivative and a methanofullerene derivative, respectively (vide infra). Reducing the amount of DBU to 0.5 equiv., the total yield of the two products was almost the same with little change in the product distribution (entry 6, Table 1). Interestingly, further reducing the quantity of DBU to 0.2 equiv. led to the preferred formation of adduct 2a (entry 7, Table 1). The product ratio of adduct 2a vs. adduct 3a increased to nearly 3:1 when 0.1 equiv. of DBU was employed (entry 8, Table 1). Nevertheless, an unsatisfactory result was obtained in terms of total yield and reaction time when 0.05 equiv. of DBU was applied (entry 9, Table 1). The above data demonstrated that the major product (adduct 2a vs. adduct 3a) could be altered by adjusting the amount of DBU used.

Being interested in the product type of adduct 2a, we extended the reaction shown in Scheme 1 by replacing substrate 1a with various types of thiocyanate and using the appropriate amount of DBU. Other 1-aryl-2-thiocyanatoethanones (1b and 1c), thiocyanatoacetate (1d) and thiocyanatomalonate (1e) were explored for their reactions with  $C_{60}$  in the presence of DBU. It was found that the reaction of  $C_{60}$  with thiocyanates 1b-e gave

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<sup>&</sup>lt;sup>†</sup> Electronic supplementary information (ESI) available: Spectral data of products **2a–e**, **3c**, **4a–e** and **5a–e**, and NMR spectra of representative products **2a**, **3c**, **4a** and **5a**. For ESI see DOI: 10.1039/b807394e



Table 1 Product yields and recovered  $C_{60}$  for the reaction of  $C_{60}$  with 1a under different reaction conditions <sup>a</sup>

Entry	Base	Equiv. of base	Time	Yield of 2a <sup>b</sup>	Yield of 3a <sup>b</sup>	Recovered C <sub>60</sub>
1	Et₃N	1	24 h	2%	3%	91%
2	Pyridine	1	24 h	2%	2%	94%
3	<b>D</b> MAP	1	24 h	2%	3%	90%
4	DABCO	1	24 h	2%	3%	91%
5	DBU	1	10 min	21%	44%	19%
6	DBU	0.5	1 h	25%	39%	17%
7	DBU	0.2	4 h	34%	21%	25%
8	DBU	0.1	4 h	31%	11%	49%
9	DBU	0.05	12 h	13%	4%	74%

both tetrahydrothiophene derivatives **2b–e** and methanofullerene derivatives **3b–d** except for **1e**, which afforded **2e** exclusively (Scheme 2).



The yields of products **2a–e** and **3a–d**, along with recovered C<sub>60</sub>, for the reaction of C<sub>60</sub> with thiocyanates **1a–e** are listed in Table 2. As seen from Table 2, when  $\mathbf{R} = \mathbf{H}$  and  $\mathbf{R}' = \mathbf{Ar}$ , the yields of products **2a–c** were more than 30%, while the yields of products **3a–c** were less than 12%, and the electronic properties of the substituent on the phenyl ring of the  $\mathbf{R}'$  group had little effect on the product yields. However, when  $\mathbf{R} = \mathbf{H}$  and  $\mathbf{R}' = CO_2C(CH_3)_3$ (**1d**), product **2d** was obtained in a lower yield (13%), while the Bingel-type adduct **3d** was isolated in a slightly higher yield (18%). To our surprise, when diethyl 2-thiocyanatomalonate (**1e**)

Table 2The yields of products 2a-e and 3a-d for the reaction of  $C_{60}$  with1a-e in the presence of DBU at room temperature<sup>a</sup>

Substrate	Time (h)	Yield of 2 <sup>b</sup>	Yield of $3^b$	Recovered C <sub>60</sub>
1a	4	31%	11%	49%
1b	4	31%	11%	47%
1c	4	30%	12%	50%
1d <sup>c</sup>	12	13%	18%	60%
$1e^d$	12	32%	0	64%

<sup>*a*</sup> Unless specified, the molar ratio of  $C_{60}$ : **1** : DBU = 1 : 2 : 0.1. <sup>*b*</sup> Isolated yield. <sup>*c*</sup> Molar ratio of  $C_{60}$ : **1d** : DBU = 1 : 2 : 0.2. <sup>*d*</sup> Molar ratio of  $C_{60}$  : **1e** : DBU = 1 : 2 : 1.

was employed, tetrahydrothiophene derivative 2e was obtained selectively.

The structures of products 2a-e were fully established by their MS, <sup>1</sup>H NMR, <sup>13</sup>C NMR, FT-IR and UV-vis spectral data. It should be noted that the very low solubility of 2c precluded its <sup>13</sup>C NMR measurement. The ESI mass spectra of 2a-e showed the correct molecular ion peaks. The <sup>1</sup>H NMR spectra of 2ae displayed a broad singlet at 10.54-11.33 ppm for the =NH group. In the <sup>13</sup>C NMR spectra of 2a, 2b, 2d and 2e, the imine carbon and the two  $sp^3$ -carbons of the C<sub>60</sub> cage appeared at 173.12-178.52 ppm, 76.60-79.91 ppm and 69.74-71.94 ppm, respectively. More than forty-nine peaks for 2a, 2b and 2d and twenty-nine peaks for 2e were observed in the range 153.46-132.01 ppm, consistent with the  $C_1$  (2a, 2b and 2d) and  $C_s$  (2e) symmetry of their molecular structures. The IR spectra of 2a-e showed absorptions at 3272-3278 cm<sup>-1</sup> and 1622-1626 cm<sup>-1</sup> due to the C=NH group. The UV-vis spectra of 2a-e exhibited a peak at 428-429 nm, which is a diagnostic absorption for a cycloadduct of C<sub>60</sub> at the [6,6]-junction.

Products **3a**, **3b** and **3d** are known compounds, and their identities were confirmed by comparison of their spectral data with those reported in the literature.<sup>8a</sup> Product **3c** was fully characterized by its MS, <sup>1</sup>H NMR, <sup>13</sup>C NMR, FT-IR and UV–vis spectral data. The MS (+ESI) of **3c** showed its molecular ion peak at m/z 872. Its <sup>1</sup>H NMR spectrum exhibited a singlet at 5.54 ppm for the methine proton and two doublets at 8.37 and 7.62 ppm for the aromatic protons. In the <sup>13</sup>C NMR spectrum of **3c**, the peaks at 187.49 and 43.75 ppm were assigned to the carbonyl carbon and methine carbon, the two *sp*<sup>3</sup>-carbons of the C<sub>60</sub> cage appeared at 71.89 ppm, and twenty-eight peaks including overlapped ones were observed in the range 147.57–129.52 ppm due to the fifty-eight *sp*<sup>2</sup>-carbons of the C<sub>60</sub> skeleton and six aromatic carbons, consistent with the C<sub>s</sub> symmetry of its molecular structure.

Just as the C=S bond of the thioamide moiety in our previously synthesized fullerene derivative was moisture sensitive,<sup>18</sup> the C=N bond of the thioimidate unit in products 2a-e was prone to

hydrolysis.  $C_{60}$ -fused 2-iminotetrahydrothiophene derivatives **2ae** could be converted to  $C_{60}$ -fused 2-oxotetrahydrothiophene derivatives **4a**-**e** in excellent yields in a mixture of CS<sub>2</sub>-THF-H<sub>2</sub>O in the presence of *p*-toluenesulfonic acid (PTSA) at room temperature (Scheme 3). The isolated yields for products **4a**, **4b**, **4c**, **4d** and **4e** were 98%, 95%, 96%, 92% and 93%, respectively.



2a, 4a: R = H, R' = 4 -CH<sub>3</sub>OPhCO; 2b, 4b: R = H, R' = PhCO; 2c, 4c: R = H, R' = 4 -CIPhCO; 2d, 4d: R = H, R' =  $CO_2C(CH_3)_3$ 2e, 4e: R = R' =  $CO_2C_2H_5$ 

#### Scheme 3

To demonstrate the utilization of 2-iminotetrahydrothiophene derivatives  $2\mathbf{a}-\mathbf{e}$ , the acetylation of the imine group was successfully exploited to generate C<sub>60</sub>-fused 2-acetamidotetrahydrothiophene derivatives  $5\mathbf{a}-\mathbf{e}$  by the reaction of  $2\mathbf{a}-\mathbf{e}$  with acetyl chloride in the presence of pyridine (Scheme 4). The isolated yields for products  $5\mathbf{a}$ ,  $5\mathbf{b}$ ,  $5\mathbf{c}$ ,  $5\mathbf{d}$  and  $5\mathbf{e}$  were 94%, 95%, 95%, 92% and 92%, respectively.



**2c**, **5c**: R = H, R' = 4 -CIPhCO; **2d**, **5d**: R = H,  $R' = CO_2C(CH_3)_3$ **2e**, **5e**:  $R = R' = CO_2C_2H_5$ 



The solubility of the resulting hydrolyzed products  $4\mathbf{a}-\mathbf{e}$  and N-acetylated products  $5\mathbf{a}-\mathbf{e}$  in CS<sub>2</sub> and CDCl<sub>3</sub> was improved dramatically over that of adducts  $2\mathbf{a}-\mathbf{e}$ , facilitating their NMR measurements.

Compounds 4a-e and 5a-e were also fully characterized by their MS, <sup>1</sup>H NMR, <sup>13</sup>C NMR, FT-IR and UV-vis spectral data. Compared with compounds 2a-e, products 4a-e and 5a-e lacked the absorptions at 3272-3278 cm<sup>-1</sup> in their IR spectra and the broad singlet in their <sup>1</sup>H NMR spectra for the =NH group. A new peak at 2.52–2.55 ppm for the methyl group was observed in the <sup>1</sup>H NMR spectra of 5a-e. In the <sup>13</sup>C NMR spectra of 4a-e, the carbonyl carbon derived from the hydrolysis of the C=NH group appeared at 191.72–194.60 ppm. In the <sup>13</sup>C NMR spectra of **5a–e**, besides the corresponding peaks of 2a-e, new peaks were found at 182.09–185.00 ppm and 24.80–25.95 ppm due to the acetyl group. It is interesting to note that the chemical shift difference of the two sp<sup>3</sup>-carbons of the  $C_{60}$  cage in compounds 4a-e (67.14-69.77 and 79.53–83.27 ppm) and **5a–e** (68.65–71.04 and 79.01–82.31 ppm) increased to 11.72–13.50 ppm and 10.06–11.27 ppm, respectively, from 6.64-8.08 ppm for products 2a-e, due to the downfield shift

of the low-field  $sp^3$ -carbon and the upfield shift of the high-field  $sp^3$ -carbon of the C<sub>60</sub> skeleton.

A possible reaction mechanism for the formation of products **2a–e** and **3a–d** is shown in Scheme 5. The deprotonation of thiocyanate **1** by DBU generates carbanion **6**, which attacks  $C_{60}$  to yield intermediate **7**. The resulting fullerenyl anion **7** could go through two pathways: in path a, the fullerenyl carbanion attacks the C=N bond of the SCN group to afford the five-membered heterocyclic anion **8**, which is then protonated to give the final product **2**; in path b, intramolecular nucleophilic addition of the fullerenyl carbanion to the carbon connected with the SCN group affords the Bingel-type adduct **3**, accompanied by extrusion of the SCN<sup>-</sup> anion.



### Conclusions

A novel procedure for the synthesis of tetrahydrothiophenefused fullerene derivatives through nucleophilic cycloaddition of thiocyanates with  $C_{60}$  has been established for the first time. The current protocol provides easy access to tetrahydrothiophenefused fullerene derivatives that may be of biological importance, and are difficult to synthesize by other methods.

#### Experimental

# Procedure for the synthesis of compounds 2a-e and 3a-d by the reaction of $C_{60}$ with thiocyanates 1a-e

A mixture of  $C_{60}$  (36.0 mg, 0.05 mmol), thiocyanate **1a** (**1b**, **1c**, **1d**, or **1e**) and DBU in the desired amounts was dissolved in toluene (25 mL) and stirred at room temperature. The reaction was monitored by TLC and stopped at the designated time. After evaporation of the toluene, the residue was separated on a silica gel column with CS<sub>2</sub>, then CS<sub>2</sub>–ethyl acetate as the eluent, to give unreacted  $C_{60}$ , product **2a** (**2b**, **2c**, **2d**, or **2e**) and product **3a**<sup>8a</sup> (**3b**<sup>8a</sup>, **3c**, or **3d**<sup>8a</sup>), respectively. The yields, along with the recovered  $C_{60}$ , are listed in Table 2.

## Preparation of compounds 4a–e by the hydrolysis of compounds 2a-e

Compound **2a** (or **2b–e**, 0.02 mmol) was added to a mixture of  $CS_2$ -THF–H<sub>2</sub>O (15 mL, 10 : 1 : 0.1) and *p*-toluenesulfonic acid

(0.04 mmol) and the reaction mixture was vigorously stirred at room temperature for 12 h. After evaporation of the solvent, the residue was separated on a silica gel column with CS–ethyl acetate as the eluent to give product 4a (or 4b-e).

# Preparation of compounds 5a-e by the acetylation of compounds 2a-e

A mixture of **2a** (or **2b–e**, 0.02 mmol) and pyridine (0.08 mmol) was dissolved in  $CS_2$  (15 mL), then to the solution was added acetyl chloride (0.08 mmol) and the reaction was stirred at room temperature for 1 h. After evaporation of excess  $CS_2$ , the residue was separated on a silica gel column with  $CS_2$ –ethyl acetate as the eluent to give product **5a** (or **5b–e**).

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#### Notes and references

- For reviews, see: (a) R. Taylor and D. R. M. Walton, *Nature*, 1993, 363, 685; (b) A. Hirsch, *Synthesis*, 1995, 895; (c) F. Diederich and C. Thilgen, *Science*, 1996, 271, 317; (d) A. Hirsch, *Top. Curr. Chem.*, 1999, 199, 1; (e) F. Diederich and C. Thilgen, *Top. Curr. Chem.*, 1999, 199, 135; (f) M. A. Yurovskaya and I. V. Trushkov, *Russ. Chem. Bull.*, 2002, 51, 367.
- 2 (a) M. Prato, *Top. Curr. Chem.*, 1999, 199, 173; (b) F. Diederich and M. Gómez-López, *Chem. Soc. Rev.*, 1999, 28, 263; (c) E. Nakamura and H. Isobe, *Acc. Chem. Res.*, 2003, 36, 807; (d) D. M. Guldi, F. Zerbetto, V. Georgakilas and M. Prato, *Acc. Chem. Res.*, 2005, 38, 38.
- 3 L. Sánchez, M. A. Herranz and N. Martín, J. Mater. Chem., 2005, 15, 1409.
- 4 (a) T. Benincori, E. Brenna, F. Sannicoló, L. Trimarco, G. Zotti and P. Sozzani, Angew. Chem., Int. Ed. Engl., 1996, 35, 648; (b) F. Effenberger and G. Grube, Synthesis, 1998, 1372; (c) A. Cravino, G. Zerza, M. Maggini, S. Bucella, M. Svensson, M. R. Andersson, H. Neugebauer and N. S. Sariciftci, Chem. Commun., 2000, 2487; (d) P. A. van Hal, J. Knol, B. M. W. Langeveld-Voss, S. C. J. Meskers, J. C. Hummelen and R. A. J. Janssen, J. Phys. Chem. A, 2000, 104, 5974; (e) E. H. A. Beckers, P. A. van Hal, A. Dhanabalan, S. C. J. Meskers, J. Knol, J. C. Hummelen and R. A. J. Janssen, J. Phys. Chem. A, 2003, 107, 6218; (f) N. Negishi, K. Yamada, K. Takimiya, Y. Aso, T. Otsubo and Y. Harima, Chem. Lett., 2003, 32, 404; (g) Y. Murata, M. Suzuki and K. Komatsu, Org. Biomol. Chem., 2003, 1, 2624; (h) E. H. A. Beckers, P. A. van Hal, A. Dhanabalan, S. C. J. Meskers, J. Knol, J. C. Hummelen and R. A. J. Janssen, J. Phys. Chem. A, 2003, 107, 6218; (i) B. Jousselme, P. Blanchard, E. Levillain, R. Bettignies and J. Roncali, Macromolecules, 2003, 36, 3020; (j) K. Yamanaka, M. Fujitsuka, Y. Araki, O. Ito, T. Aoshima, T. Fukushima and T. Miyashi, J. Phys. Chem. A, 2004, 108, 250; (k) D. M. Guldi, C. Luo, A. Swartz, R. Gómez, J. L. Segura and N. Martín, J. Phys. Chem. A, 2004, 108, 455; (1) T. Yamazaki, Y. Murata, K. Komatsu, K. Furukawa, M. Morita, N. Maruyama, T. Yamao and S. Fujita, Org. Lett., 2004, 6, 4865; (m) N. Negishi, K. Takimiya, T. Otsubo, Y. Harima and Y. Aso, Chem. Lett., 2004, 33, 654; (n) H. Kanato, K. Takimiya, T. Otsubo, Y. Aso, T. Nakamura, Y. Araki and O. Ito, J. Org. Chem., 2004, 69, 7183; (o) M. Narutaki, K. Takimiya, T. Otsubo, Y. Harima, H. Zhang, Y. Araki and O. Ito, J. Org. Chem., 2006, 71, 1761; (p) T. Nakamura, H. Kanato, Y. Araki, O. Ito, K. Takimiya, T. Otsubo and Y. Aso, J. Phys. Chem. A, 2006, 110, 3471; (q) Z. Tan, J. Hou, Y. He, E. Zhou, C. Yang and Y. Li, Macromolecules, 2007, 40, 1868; (r) T. Nakamura, Y. Araki, O. Ito, K. Takimiya and T. Otsubo, J. Phys. Chem. A, 2008, 112, 1125.
- 5 (a) N. Martín, L. Sánchez, C. Seoane, R. Andreu, J. Garín and J. Orduna, *Tetrahedron Lett.*, 1996, **37**, 5979; (b) M. Prato, M. Maggini,

C. Giacometti, G. Scorrano, G. Sandonà and G. Farnia, Tetrahedron, 1996, 52, 5221; (c) N. Martín, I. Pérez, L. Sánchez and C. Seoane, J. Org. Chem., 1997, 62, 5690; (d) S. Ravaine, P. Delhaès, P. Leriche and M. Sallé, Synth. Met., 1997, 87, 93; (e) C. Boulle, J. M. Rabreau, P. Hudhomme, M. Cariou, M. Jubault, A. Gorgues, J. Orduna and J. Garín, Tetrahedron Lett., 1997, 38, 3909; (f) J. Llacay, J. Veciana, J. Vidal-Gancedo, J. L. Bourdelande, R. González-Moreno and C. Rovira, J. Org. Chem., 1998, 63, 5201; (g) A. Herranz and N. Martín, Org. Lett., 1999, 1, 2005; (h) N. Martín, L. Sánchez and D. M. Guldi, Chem. Commun., 2000, 113; (i) N. Martín, L. Sánchez, M. A. Herranz and D. M. Guldi, J. Phys. Chem. A, 2000, 104, 4648; (j) D. M. Guldi, S. González, N. Martín, A. Antón, J. Garín and J. Orduna, J. Org. Chem., 2000, 65, 1978; (k) J. L. Segura, E. M. Priego, N. Martín, C. Luo and D. M. Guldi, Org. Lett., 2000, 2, 4021; (1) S.-G. Liu, D. Kreher, P. Hudhomme, E. Levillain, M. Cariou, J. Delaunay, A. Gorgues, J. Vidal-Gancedo, J. Veciana and C. Rovira, Tetrahedron Lett., 2001, 42, 3717; (m) J. L. Segura, E. M. Priego, N. Martín, C. Luo and D. M. Guldi, Org. Lett., 2002, 2, 4021; (n) S. González, N. Martín and D. M. Guldi, J. Org. Chem., 2003, 68, 779; (o) S. González, N. Martín, A. Swartz and D. M. Guldi, Org. Lett., 2003, 5, 557; (p) M. C. Díaz, M. A. Herranz, B. M. Illescas, N. Martín, N. Godbert, M. R. Bryce, C. Luo, A. Swartz, G. Anderson and D. M. Guldi, J. Org. Chem., 2003, 68, 7711; (q) A. D. Darwish, A. G. Avent, O. V. Boltalina, I. Goldt, I. Kuvytchko, T. Da Ros, J. M. Street and R. Taylor, Chem.-Eur. J., 2003, 9, 2008; (r) F. Oswald, S. Chopin, P. de la Cruz, J. Orduna, J. Garin, A. S. D. Sandanayaka, Y. Araki, O. Ito, J. L. Delgado, J. Cousseau and F. Langa, New J. Chem., 2007, 31, 230; (s) S. Saha, A. H. Flood, J. F. Stoddart, S. Impellizzeri, S. Silvi, M. Venturi and A. Credi, J. Am. Chem. Soc., 2007, 129, 12159; (t) B. M. Illescas, J. Santos, M. C. Diaz, N. Martín, C. M. Atienza and D. M. Guldi, Eur. J. Org. Chem., 2007, 5027

- 6 (a) J. Llacay, M. Mas, E. Molins, J. Veciana, D. Powell and C. Rovira, *Chem. Commun.*, 1997, 659; (b) A. C. Tomé, R. F. Enes, J. A. S. Cavaleiro and J. Elguero, *Tetrahedron Lett.*, 1997, 38, 2557; (c) M. Ohno, N. Koide, H. Sato and S. Eguchi, *Tetrahedron*, 1997, 53, 9075; (d) A. C. Tomé, R. F. Enes, J. P. C. Tomé, J. Rocha, M. G. P. M. S. Neves, J. A. S. Cavaleiro and J. Elguero, *Tetrahedron*, 1998, 54, 11141; (e) F. P. Montforts and O. Kutzki, *Angew. Chem., Int. Ed.*, 2000, 39, 599; (f) H. Ishida, H. Asaji, T. Hida, K. Itoh and M. Ohno, *Tetrahedron Lett.*, 2000, 41, 2153; (g) A. Rieder and B. Kräutler, *J. Am. Chem. Soc.*, 2000, 122, 9050; (h) H. Ishida, K. Itoh, S. Ito, N. Ono and M. Ohno, *Synlett*, 2001, 2965; (i) N. Watanabe, N. Kihara, Y. Furusho, T. Takata, Y. Araki and O. Ito, *Angew. Chem., Int. Ed.*, 2003, 42, 681; (j) R. F. Enes, A. C. Tomé and J. A. S. Cavaleiro, *Tetrahedron*, 2005, 61, 1423; (k) H.-T. Yang, G.-W. Wang, Y. Xu and J.-C. Huang, *Tetrahedron Lett.*, 2006, 47, 4129.
- 7 (a) B. Illescas, N. Martín, C. Seoane, P. de la Cruz, F. Langa and F. Wudl, *Tetrahedron Lett.*, 1995, **36**, 8307; (b) B. M. Illescas, N. Martín, C. Seoane, E. Ortí, P. M. Viruela, R. Viruela and A. de la Hoz, *J. Org. Chem.*, 1997, **62**, 7585; (c) J.-H. Liu, A.-T. Wu, M.-H. Huang, C.-W. Wu and W.-S. Chung, *J. Org. Chem.*, 2000, **65**, 3395; (d) S. Kotha and A. K. Ghosh, *Tetrahedron Lett.*, 2004, **45**, 2931; (e) S. Kotha and A. K. Ghosh, *Tetrahedron*, 2004, **60**, 10833; (f) C.-C. Chi, I.-F. Pai and W.-S. Chung, *Tetrahedron*, 2004, **60**, 10869.
- 8 (a) Y. Wang, J. Cao, D. I. Schuster and S. R. Wilson, *Tetrahedron Lett.*, 1995, **36**, 6843; (b) B. Ma, C. E. Bunker, R. Guduru, X.-F. Zhang and Y.-P. Sun, *J. Phys. Chem. A*, 1997, **101**, 5626; (c) T. Tada, Y. Ishida and K. Saigo, *J. Org. Chem.*, 2006, **71**, 1633.
- 9 M. Ohno, S. Kojima and S. Eguchi, J. Chem. Soc., Chem. Commun., 1995, 565.
- 10 M. Ohno, S. Kojima, Y. Shirakawa and S. Eguchi, *Tetrahedron Lett.*, 1995, 36, 6899.
- 11 (a) H. Ishida and M. Ohno, *Tetrahedron Lett.*, 1999, 40, 1543; (b) H. Ishida, K. Itoh and M. Ohno, *Tetrahedron*, 2001, 57, 1737.
- 12 W. Duczek, F. Tittelbach, B. Costisella and H. J. Niclas, *Tetrahedron*, 1996, **52**, 8733.
- 13 (a) M. D. Westmeyer, C. P. Galloway and T. B. Rauchfuss, *Inorg. Chem.*, 1994, **33**, 4615; (b) M. D. Westmeyer, T. B. Rauchfuss and A. K. Verma, *Inorg. Chem.*, 1996, **35**, 7140; (c) Y. Takaguchi, Y. Katayose, Y. Yanagimoto, J. Motoyoshiya, H. Aoyama, T. Wakahara, Y. Maeda and T. Akasaka, *Chem. Lett.*, 2003, **32**, 1124.
- 14 (a) G. P. Miller, M. A. Buretea, M. M. Bernardo, C. S. Hsu and H. L. Fang, *J. Chem. Soc., Chem. Commun.*, 1994, 1549; (b) B.-H. Chen, J.-P. Huang, L. Y. Wang, J. Shiea, T.-L. Chen and L. Y. Chiang, *J. Chem. Soc., Perkin Trans.* 1, 1998, 1171.

- 15 A. D. Darwish, H. W. Kroto, R. Taylor and D. R. M. Walton, Fullerene Sci. Technol., 1993, 1, 571.
- 16 (a) S. Giesa, J. H. Gross, W. E. Hull, S. Lebedkin, A. Gromov, R. Gleiter and W. Krätschmer, *Chem. Commun.*, 1999, 465; (b) Y. Murata, M. Murata and K. Komatsu, *Chem.-Eur. J.*, 2003, 9, 1600.
- 17 (a) G. Naxakis, P. Sofou and Y. Elemes, *Fullerenes, Nanotubes, Carbon Nanostruct.*, 2004, **12**, 781; (b) E. Ioannou, A. Hirsch and Y. Elemes, *Tetrahedron*, 2007, **63**, 7070.
- 18 G.-W. Wang, J.-X. Li, Y.-J. Li and Y.-C. Liu, J. Org. Chem., 2006, 71, 680.
- 19 For our recent representative papers, see: (a) G.-W. Wang, X.-H. Zhang, H. Zhan, Q.-X. Guo and Y.-D. Wu, J. Org. Chem., 2003, 68,

6732; (b) Z.-X. Chen and G.-W. Wang, J. Org. Chem., 2005, **70**, 2380; (c) G.-W. Wang, F.-B. Li and T.-H. Zhang, Org. Lett., 2006, **8**, 1355; (d) G.-W. Wang, H.-T. Yang, P. Wu, C.-B. Miao, Y. Xu and F. Liu, J. Org. Chem., 2006, **71**, 4346; (e) G.-W. Wang, X.-P. Chen and X. Cheng, Chem.–Eur. J., 2006, **12**, 7246; (f) G.-W. Wang, F.-B. Li and Y. Xu, J. Org. Chem., 2007, **72**, 4474; (g) G.-W. Wang, F.-B. Li, Z.-X. Chen, B. Chen and Y. Xu, J. Org. Chem., 2007, **72**, 4479.

- 20 (a) J. Teller, H. Dehne, T. Zimmermann, G. W. Fischer and B. Olk, J. Prakt. Chem., 1990, 332, 453; (b) S. M. Sondhi, M. Johar and N. Singh, Indian J. Chem. Sect. B, 2004, 43, 162.
- 21 M. Kleist, P. Chume, H. Reinke, J. Teller and H. Dehne, *Phosphorus, Sulfur Silicon Relat. Elem.*, 1998, **139**, 123.