Fine tuning of the orifice size of an open-cage fullerene by placing selenium in the rim: insertion/release of molecular hydrogen†

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A newly synthesized open-cage fullerene containing selenium in the rim of the 13-membered-ring orifice allows milder conditions for hydrogen insertion, and the rate for hydrogen release is *ca.* three times faster than its sulfur analogue.

Open-cage fullerenes are one of the current synthetic targets besides the well developed closed-cage functionalization chemistry.[1] The ultimate objectives for making an orifice in the fullerene cage are the replacement of conventional methods for the creation of novel endohedral fullerenes and the elucidation of their properties.[2] To date, various open-cage fullerenes have been synthesized by controlled bond scissions of fullerene skeletons and have been shown to be able to encapsulate a small atom or molecule.[3] Such a molecular surgery approach has enabled us to synthesize $H_2@C_{60}$ by complete restoration of the cage structure.[3i,3k]

Because the orifice size is an important factor in the insertion of chemical species into an open-cage fullerene, we now focus our attention on tuning the orifice size by replacing sulfur with a larger element without changing the number of atoms in the rim. This will be followed by our previous method for orifice-size reduction, retaining the encapsulated species.[3h,3j]

In our previous approach, a key step to generate a sufficiently large opening in the fullerene framework is the insertion of a sulfur atom into the rim of the 12-membered-ring open-cage compound **1**. This was achieved with the help of a typical π-electron donor, tetrakis(dimethylamino)ethylene (TDAE),[4] as an activator, in the presence of added crystalline elemental sulfur (S_8) as the source of the sulfur atom, to give open-cage compound **2** with a 13-membered-ring orifice. Because of this ring enlargement, the energy barrier for hydrogen insertion was substantially lowered. In the present paper, we report the synthesis of a new open-cage fullerene **3**, containing a higher member of the group 16 elements, selenium, and we reveal the behavior of **3** when encapsulating and releasing molecular hydrogen.
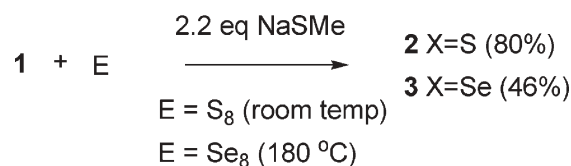
For the synthesis of **3**, application of the procedure used for the synthesis of **2**, simply replacing sulfur with selenium in the presence of TDAE, was not successful. Furthermore, considering the
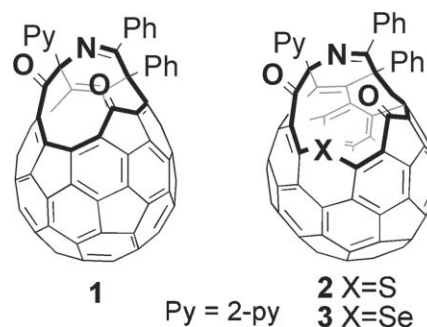
commercial non-availability of TDAE,[4] it was necessary to explore another reagent to activate precursor **1**. We found that sodium alkanethiolate,[5] which has been used as a convenient reagent to generate the dianion of C_{60}, is highly effective for this purpose and can incorporate sulfur in the rim of the orifice of **1** efficiently (Scheme 1). While heating at 180 °C was necessary for the reaction with TDAE, the reaction can be performed at room temperature with addition of 2.2 equivalents of 90% technical grade sodium 2-methyl-2-propanethiolate or isopropanethiolate, or 95% sodium methanethiolate, in dry benzonitrile under anaerobic conditions. With any of these thiolates, the reaction proceeded smoothly within 3 h to give **2** in a yield comparable to that obtained using TDAE. The reaction can be upgraded to a 3 g scale of **1**.

We then attempted to incorporate selenium (10 equivalents) in place of sulfur under similar conditions. Although the reaction did not take place at room temperature, heating at 180 °C in dry 1,2-dichlorobenzene (ODCB), using 95% sodium methanethiolate as the reducing agent, afforded the desired product **3** as an orange-brown powder in 46% yield after purification (53% based on consumed **1**).[6,7] Prolonged reaction time (>4 h) did not improve the yield.

The identification of compound **3** was made using its spectral data and X-ray crystallography.[8]† The MALDI-TOF mass spectrum showed a molecular ion peak, with an isotope distribution pattern, of $C_{80}H_{14}N_2O_2Se$ (*m/z* 1114). The ^{1}H NMR, ^{13}C NMR, IR, and UV-vis spectra showed close resemblance to those of **2**, suggesting similarity in electronic properties.[9]

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† Electronic supplementary information (ESI) available: Experimental procedures and spectral data of all new compounds. See DOI: 10.1039/b616478a
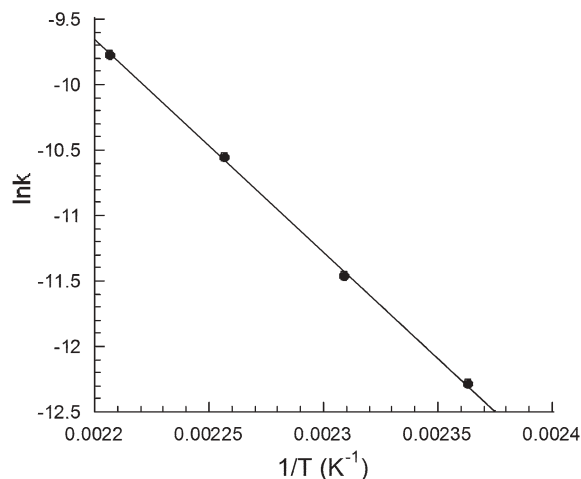
Scheme 1 Synthesis of compounds **2** and **3**.
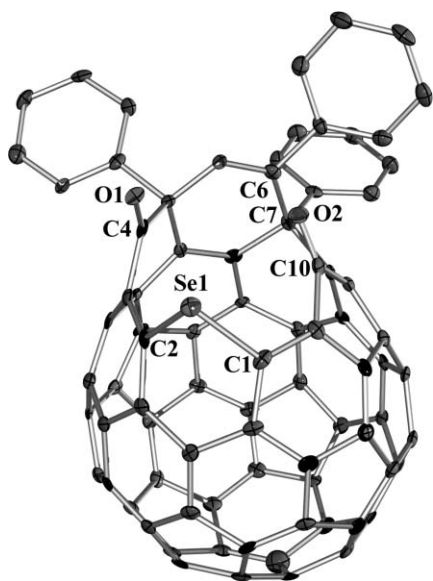
Fig. 1 X-Ray crystal structure of compound **3** drawn at the 50% probability level.
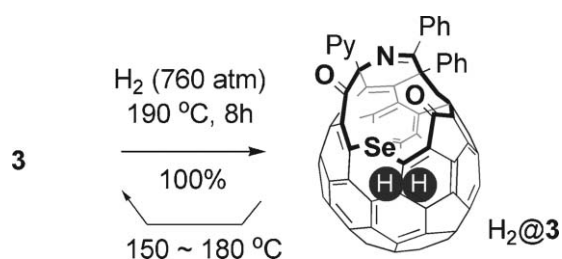
Scheme 2 Insertion/release of H₂ into **3** and from H₂@**3**.

Fig. 2 An Arrhenius plot of the kinetic results of hydrogen release from H₂@**3**.

The molecular structure of **3** is shown in Fig. 1. As expected, the two $C(sp^2)$–Se bonds (1.909(4) for C1–Se1 and 1.921(4) Å for C2–Se1) are longer than the corresponding $C(sp^2)$–S bonds in **2** (1.754(3) and 1.780(3) Å),[3g] but the bond angle C1–Se1–C2 (87.87(16)°) is smaller than the corresponding angle in **2** (92.18(12)°).[3g] As a result, the orifice size of **3** is now slightly larger than that of **2**, as shown by the lengths of the longest axis C7···Se1 (5.718(4) Å) (5.643(3) Å for **2**) and the shortest axis C4···C10 (3.877(5) Å) (3.753(3) Å for **2**) across the opening, i.e. the distance between these two carbonyl carbons is 0.124 Å longer in **3**. These observed bond distances and angles are in good agreement with their structures optimized at the B3LYP/3-21G level of theory.

Then we were able to achieve 100% encapsulation of H₂ within **3** under slightly milder conditions (Scheme 2) than for **2**, i.e., under a slightly lower pressure (760 atm) and at a lower temperature (190 °C) (800 atm and 200 °C for **2**).[10] The ^{1}H NMR signal of H₂ incorporated in **3** appears at −7.10 ppm (ODCB-d_4), with the

integrated peak area corresponding to 2H, which is 0.15 ppm downfield shifted as compared with that of H₂@**2** (−7.25 ppm).[10]

For a more detailed examination of the influence of orifice-size change, the energy barrier for the hydrogen passage through the orifice was determined by studying the kinetics of the release of encapsulated hydrogen from H₂@**3**. The rate of the release followed first-order kinetics with rate constants (k_1 in s^{-1}) of $4.63 \pm 0.27 \times 10^{-6}$ at 150 °C, $1.05 \pm 0.004 \times 10^{-5}$ at 160 °C, $2.62 \pm 0.04 \times 10^{-5}$ at 170 °C, and $7.07 \pm 0.48 \times 10^{-5}$ at 180 °C. These values are nearly three times larger than those for H₂@**2**,[10] as expected from the orifice-size enlargement.

From a linear Arrhenius plot (Fig. 2, $r^2 = 0.999$), the activation energy for hydrogen release from H₂@**3** was calculated to be 32.4 ± 0.67 kcal mol^{-1}, which is 2.0 kcal mol^{-1} lower than that for H₂@**2**. Other activation parameters for hydrogen release from H₂@**3** at 25 °C are summarized in Table 1 together with those of H₂@**2**.[10] The more negative value for the activation entropy $\Delta S^{\ddagger}$ of H₂@**3** compared to H₂@**2** reveals that the hydrogen molecule of H₂@**3** in its ground state is less restricted in motion compared to that of H₂@**2**.

The activation energy of hydrogen release from H₂@**3** was calculated[11] as 28.2 kcal mol^{-1} (0.7 kcal mol^{-1} lower than that for H₂@**2**), supporting the experimental result. The energy barriers for H₂ insertion into **2** and **3** were calculated as 30.4 and 29.9 kcal mol^{-1}, respectively, also supporting the occurrence of 100% H₂ insertion into **3** at lower hydrogen pressure.

In summary, we have synthesized the first fullerene derivative that contains the element selenium in the cage. This new open-cage fullerene shows electronic properties similar to those of its sulfur analogue, but kinetic data of hydrogen release reveal that the orifice size can be finely tuned by substitution of an atom in the rim that is slightly large in size.

Table 1 Activation parameters for H₂ release from H₂@**2** and H₂@**3**

	$t_{1/2}{}^a$	$E_a{}^c$	A	$\Delta G^{\ddagger c}$	$\Delta H^{\ddagger c}$	$\Delta S^{\ddagger d}$
H₂@**2**^{b}	53.9 ± 0.56	34.2 ± 0.58	$10^{11.8} \pm 10^{0.3}$	35.6 ± 0.59	33.4 ± 0.59	-7.5 ± 1.3
H₂@**3**	18.3 ± 0.07	32.4 ± 0.67	$10^{11.3} \pm 10^{0.3}$	34.4 ± 0.66	31.5 ± 0.67	-9.6 ± 1.5

^{a} Half-life (h) at 160 °C. ^{b} Ref. 10. Error limits were re-examined in this study for consistency. ^{c} kcal mol^{-1}. ^{d} cal K^{-1} mol^{-1}.

Notes and references

1 (*a*) F. Wudl, *Acc. Chem. Res.*, 1992, **25**, 157; (*b*) S. Anderson, H. L. Anderson and J. K. M. Sanders, *Acc. Chem. Res.*, 1993, **26**, 469; (*c*) L. Isaacs, R. F. Haldimann and F. Diederich, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 2339; (*d*) I. Lamparth, C. Maichle-Mössner and A. Hirsch, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1607; (*e*) F. Diederich and M. Gomez-Lopez, *Chem. Soc. Rev.*, 1999, **28**, 263; (*f*) F. Djojo, A. Hirsch and S. Grimme, *Eur. J. Org. Chem.*, 1999, 3027; (*g*) G. Rapenne, J. Crassous, A. Collet, L. Echegoyen and F. Diederich, *Chem. Commun.*, 1999, 1121; (*h*) F. Diederich and R. Kessinger, *Acc. Chem. Res.*, 1999, **32**, 537; (*i*) L. E. Echegoyen, F. D. Djojo, A. Hirsch and L. Echegoyen, *J. Org. Chem.*, 2000, **65**, 4994; (*j*) U. Reuther, T. Brandmüller, W. Donaubauer, F. Hampel and A. Hirsch, *Chem.–Eur. J.*, 2002, **8**, 2261; (*k*) S. Sergeyev and F. Diederich, *Angew. Chem., Int. Ed.*, 2004, **43**, 1738.
2 (*a*) M. Saunders, H. A. Jiménez-Vázquez, R. J. Cross, S. Mroczkowski, D. I. Freedberg and F. A. L. Anet, *Nature*, 1994, **367**, 256; (*b*) S. Kobayashi, S. Mori, S. Iida, H. Ando, T. Takenobu, Y. Taguchi, A. Fujiwara, A. Taninaka, H. Shinohara and Y. Iwasa, *J. Am. Chem. Soc.*, 2003, **125**, 8116; (*c*) *Endofullerenes: A New Family of Carbon Clusters*, ed. T. Akasaka and S. Nagase, Kluwer Academic Publishers, Dodrecht, The Netherlands, 2002.
3 (*a*) M.-J. Arce, A. L. Viado, Y.-Z. An, S. I. Khan and Y. Rubin, *J. Am. Chem. Soc.*, 1996, **118**, 3775; (*b*) Y. Rubin, *Chem.–Eur. J.*, 1997, **3**, 1009; (*c*) Y. Rubin, *Chimia*, 1998, **52**, 118; (*d*) Y. Rubin, *Top. Curr. Chem.*, 1999, **199**, 67; (*e*) G. Schick, T. Jarrosson and Y. Rubin, *Angew. Chem., Int. Ed.*, 1999, **38**, 2360; (*f*) Y. Rubin, T. Jarrosson, G.-W. Wang, M. D. Bartberger, K. N. Houk, G. Schick, M. Saunders and R. J. Cross, *Angew. Chem., Int. Ed.*, 2001, **40**, 1543; (*g*) J.-F. Nierengarten, *Angew. Chem., Int. Ed.*, 2001, **40**, 2973; (*h*) Y. Murata, M. Murata and K. Komatsu, *Chem.–Eur. J.*, 2003, **9**, 1600; (*i*) K. Komatsu, M. Murata and Y. Murata, *Science*, 2005, **307**, 238; (*j*) K. Komatsu and Y. Murata, *Chem. Lett.*, 2005, **34**, 886; (*k*) M. Murata, Y. Murata and K. Komatsu, *J. Am. Chem. Soc.*, 2006, **128**, 8024; (*l*) S. Iwamatsu, T. Uozaki, K. Kobayashi, S. Re, S. Nagase and S. Murata, *J. Am. Chem. Soc.*, 2004, **126**, 2668; (*m*) S. Iwamatsu, S. Murata, Y. Andoh, M. Minoura, K. Kobayashi, N. Mizorogi and S. Nagase, *J. Org. Chem.*, 2005, **70**, 4820; (*n*) S. Iwamatsu and S. Murata, *Synlett*, 2005, 2117; (*o*) S. Iwamatsu, C. M. Stanisky, R. J. Cross, M. Saunders, N. Mizorogi, S. Nagase and S. Murata, *Angew. Chem., Int. Ed.*, 2006, **45**, 5337.
4 TDAE became commercially unavailable in the middle of 2005. When it became available again in the summer of 2006, the price was more than 10 times higher than before (US$180 per 10 g, Aldrich, 2006).
5 (*a*) W.-D. Braschwitz, T. Otten, C. Rücker, H. Fritz and H. Prinzbach, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1348; (*b*) D. L. Mohler, K. P. C. Vollhardt and S. Wolff, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 1151; (*c*) E. Allard, L. Riviére, J. Delaunay, D. Dubois and J. Cousseau, *Tetrahedron Lett.*, 1999, **40**, 7223; (*d*) E. Allard, J. Delaunay, F. Cheng, J. Cousseau, J. Ordúna and J. Garín, *Org. Lett.*, 2001, **3**, 3503; (*e*) F. Cheng, Y. Murata and K. Komatsu, *Org. Lett.*, 2002, **4**, 2541.
6 Since the solubility of selenium is much lower than that of sulfur, it is necessary to preheat the mixture of **1** and the Se powder at 180 °C for 2 h before the reducing agent is added.
7 In addition to the desired **3**, the sulfur compound **2** was found in variable amounts in the isolated product when sodium *tert*-butanethiolate was used. The source of the sulfur is supposed to be elemental sulfur or residual Na_2S that is present as a contaminant in the 90% alkanethiolate, based on a control experiment. Using 95% methanethiolate gives much less contamination by compound **2**. For more details, see supplementary information†.
8 Crystallographic data of **3**: black needles, approximate dimensions 0.21 mm × 0.07 mm × 0.05 mm, $C_{80}H_{14}N_2O_2Se\cdot3CS_2$, $M = 1342.28$, monoclinic, space group $P2_1/c$, $Z = 4$, $a = 9.9575(7)$ Å, $b = 51.425(4)$ Å, $c = 10.1013(7)$ Å, $\beta = 99.7660(3)°$, $V = 5097.6(6)$ Å^3, $T = 100(2)$ K, $\mu = 1.049$ mm^{-1}, $R_{int} = 0.0615$, $R1 = 0.0509$, $wR2 = 0.0846$ ($I > 2\sigma(I)$), Gof = 1.012. CCDC 626966. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b616478a.
9 The Pauling electronegativity value of S is 2.58, while that for Se is 2.55.
10 Y. Murata, M. Murata and K. Komatsu, *J. Am. Chem. Soc.*, 2003, **125**, 7152.
11 The structures of compounds **2**, **3** and their hydrogen encapsulated molecules $H_2@2$ and $H_2@3$ were optimized at the B3LYP/3-21G level of theory using the Gaussian 03 program.[12] Transition state searches were performed at the same level of theory and single point energies were calculated at the B3LYP/6-31G** level.
12 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *GAUSSIAN 03 (Revision B.05)*, Gaussian, Inc., Wallingford, CT, 2004.