Fullerenes

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Carbon Monoxide Inside an Open-Cage Fullerene**

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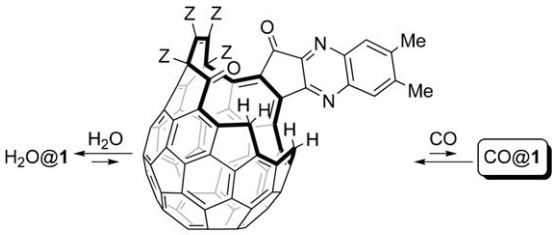

Scheme 1. Open-cage fullerene **1** and its reactivity towards CO and H_2O.

The chemistry of fullerenes that encapsulate molecules or atoms (endohedral fullerenes) has developed extensively in the last decade. A high-pressure, high-temperature method has made it feasible to insert atoms and some small molecules into fullerene cages.[1] However, the yield of the incorporated product obtained by this method is very low. In an attempt to prepare endohedral fullerenes in higher quantities, carbon–carbon bonds of fullerene cages have been cleaved by organic reactions.[2–4] The resulting product, a so-called open-cage fullerene, has an opening that is large enough to insert an atom or a molecule into the cavity of the fullerene.[5–9] Unlike complete endohedral fullerenes, these derivatives can hold and release substrates in a reversible manner. This property offers sensing and storage materials as potential applications.[10] Furthermore, an open moiety can be restored to an intact cage with the inserted chemical species inside. Indeed, pure endohedral $H_2@C_{60}$ was recently synthesized from C_{60} by using this strategy.[6b]

The narrow orifices of previously obtained open-cage derivatives restricted the molecules that could be inserted to helium and hydrogen.[5–8] Recently, we constructed a wide opening on C_{60} by successive cage scissions.[9] The orifice of **1** (Scheme 1) is the largest known to date for a fullerene, and **1** spontaneously encapsulates one water molecule to form $H_2O@$**1**.[9a] This result shows that it is possible for atoms or molecules larger than H_2 or He to enter the fullerene cage. Herein, we describe the formation, characterization, and properties of an endohedral carbon monoxide complex, CO@**1**. Although several theoretical studies have been carried out on $CO@C_{60}$,[11,12] the formation of this complex was confirmed only by mass spectrometry.[13]

Carbon monoxide was introduced into **1** by heating a mixture of $H_2O@$**1** and **1** dissolved in 1,1,2,2-tetrachloroethane (TCE) under 9.0 MPa of CO. The signal at $\delta = -11.4$ ppm, characteristic of $H_2O@$**1**, disappeared in the ^{1}H NMR spectrum of the reaction mixture,[9a] and the fraction of CO@**1** in the final product reached 84% (see below). By a similar method, ^{13}CO@**1** was prepared under 3.3 MPa of ^{13}CO (^{13}C content: 99%); the fraction of ^{13}CO@**1** at the end of the process was 59%. The reaction even proceeded under ambient pressure of CO; however, the final mixture yielded only 20% CO@**1**. For a higher incorporation of CO, it is necessary to carry out the reaction in solution; when the reaction mixture was pressurized as a solid, the conversion into CO@**1** was only 52% even at 9.0 MPa and 150 °C. This low yield may arise from the difficulty in releasing the water molecule of $H_2O@$**1** in the solid state.[9a] Alternatively, CO and/or H_2O might not be able to diffuse through solid **1**.

The product was identified as CO@**1** by electrospray mass spectrometry (ES-MS), ^{1}H NMR, ^{13}C NMR, and IR spectroscopy. In the ES mass spectrum of the product, a series of parent ion peaks was observed around m/z 1200. These peaks correspond to the presence of varying numbers of ^{13}C atoms (Figure 1a). For ^{13}CO@**1**, the series of parent ion peaks shifts to m/z 1201 (Figure 1b). Figure 1c shows the spectrum of the starting material with peaks centered at m/z 1172, which correspond to **1** (peaks corresponding to $H_2O@$**1** were not detected by ES-MS).[9a] It is apparent that the addition of CO causes a decrease in the intensity of the peaks at m/z 1172 and an increase of those at m/z 1200 or 1201. These results are consistent with the formation of the 1:1 complex of CO and **1**.

In the ^{1}H NMR spectrum of CO@**1**, signals associated with H_2O were absent and resonances of methylene protons along the orifice of CO@**1** showed upfield shifts with respect to those of $H_2O@$**1**. As shown in Figure 2a, two out of the four methylene-proton signals were observed at $\delta = 3.38$ and 2.86 ppm ($J = 20$ and 19 Hz, respectively, each 1H). The corresponding chemical shifts of $H_2O@$**1** were $\delta = 3.50$ and 2.99 ppm, respectively (Figure 2b). The spectrum of empty **1** showed signals similar to those of $H_2O@$**1** (Figure 2c). Thus, the fraction of CO@**1** present can be estimated by comparing

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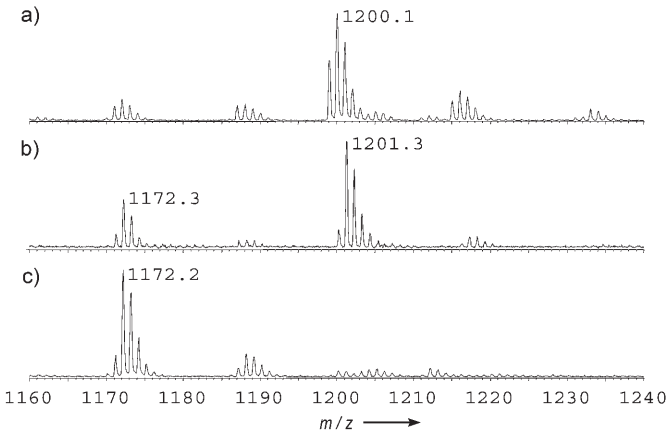

Figure 1. ES mass spectra (negative mode) of a) CO@**1**, b) ^{13}CO@**1**, and c) **1**. Ion peaks of $[M+16]^-$ and $[M+32]^-$ result from oxidation of the samples during measurement (e.g., m/z 1188 and 1216). These peaks are commonly observed in the spectra of fullerene derivatives.

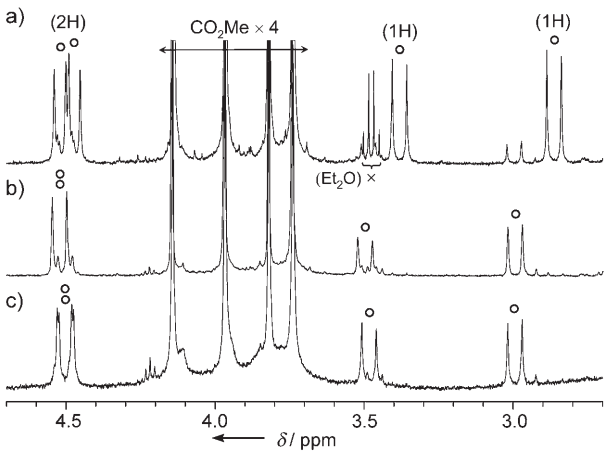

Figure 2. Segments of the ^{1}H NMR spectra (methylene- and methoxy-proton regions) of: a) CO@**1**; b) H_2O@**1**; c) empty **1** (measured in the presence of P_2O_5) in $CDCl_3$.

the ratio of integral values of these signals of CO@**1** with those of H_2O@**1** and **1**.

In the ^{13}C NMR spectrum of CO@**1**, one sharp signal characteristic of CO was observed at $\delta = 174.3$ ppm in $[D_2]$TCE ($\delta = 174.6$ ppm in $CDCl_3$) together with the signals of **1** (Figure 3a). For comparison, the resonance of CO in $CDCl_3$ is 184.6 ppm.[14] The calculated chemical shifts (GIAO-B3LYP/6-31G*) of CO inside **1** and free CO are $\delta =$ 172.3 ppm (average of the three rotational isomers CO@**1**-A, CO@**1**-B, and CO@**1**-C shown in Figure 5; Table 1) and $\delta = 181.3$ ppm, respectively.[15] These results agree well with the observed spectra. Furthermore, atoms and molecules inside fullerenes are known to show upfield shifts because of the magnetic shielding by the fullerene cage.[5–8,16] Thus, the observed upfield shift is clear evidence of the endohedral structure of CO@**1**. In a variable-temperature ^{13}C NMR study of ^{13}CO@**1** in CD_2Cl_2, the CO signal showed slight broadening at −90 °C, which suggests that the encapsulated CO rotates rapidly on the NMR time scale.

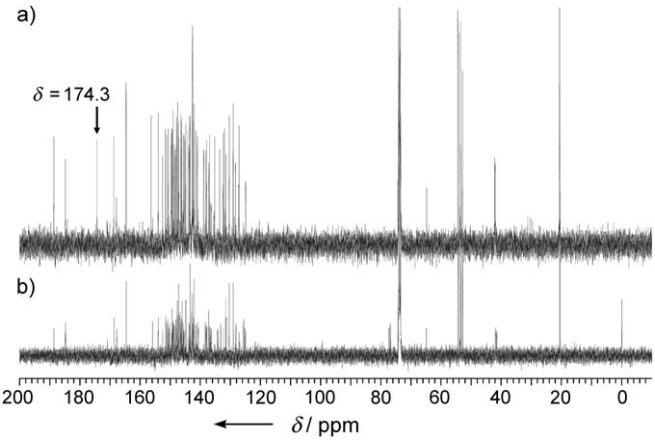

Figure 3. ^{13}C NMR spectra of: a) CO@**1**; b) H_2O@**1** + **1** in $[D_2]$TCE (308 K).

Table 1: Calculated chemical shifts and relative energies of CO@**1** (B3LYP/6-31G*).

Complex	δ(CO) [ppm]	E [kcal mol^{-1}][a]
CO@**1**-A	174.88	+2.7
CO@**1**-B	170.99	+3.8
CO@**1**-C	171.16	+8.1
H_2O@**1**	–	−2.4
CO@C_{60}	–	+8.4[11c]
H_2O@C_{60}	–	−1.5

[a] $E = E$(X@**1**) − [E(X) + E(**1**)], in which E(X@**1**) is the total energy of the complex, and E(X) and E(**1**) are the energies of guest molecule and cage, respectively.

In the IR spectrum of CO@**1**, two CO absorption bands are observed at $\nu = 2125$ and 2112 cm^{-1} (Figure 4), which

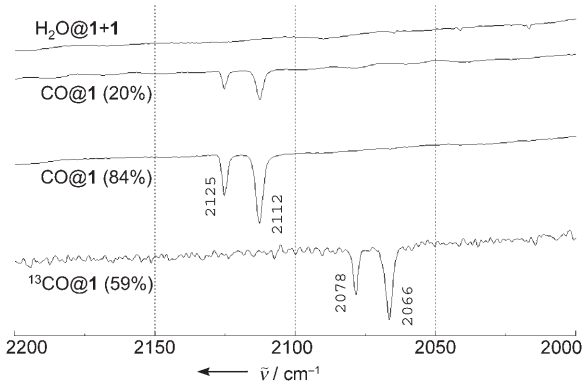

Figure 4. IR spectra of H_2O@**1** + **1**, CO@**1**, and ^{13}CO@**1** (KBr).

differ by −18 and −31 cm^{-1}, respectively, from the CO gas frequency (2143 cm^{-1}). For ^{13}CO@**1**, the corresponding absorptions exhibit clear shifts to lower frequencies ($\tilde{\nu} =$ 2078 and 2066 cm^{-1}; Figure 4), with a uniform ratio of ^{13}CO/^{12}CO ≈ 0.978. This ratio is slightly larger than that calculated for the ^{13}C/^{12}C isotope shift (0.961).[17]

In a related study, carbon monoxide absorbed on the exohedral surface of C_{60} showed two similar absorptions at

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$\tilde{\nu} = 2135$ and $2128\ cm^{-1}$ (at 77 K) arising from CO at the octahedral and tetrahedral sites, respectively, in the crystal lattice.[18] For comparison, carbon monoxide inside single-walled carbon nanotubes absorbs at $\tilde{\nu} = 2135\ cm^{-1}$.[19] The similar but larger shifts of CO@**1** indicate an enhanced interaction between CO and the fullerene cage with respect to that of the exohedral compound. This greater interaction might be due to the shorter distance between the trapped CO and the narrow C_{60} cage. As shown in Figure 4, the intensity ratio of the absorption at $\nu = 2125\ cm^{-1}$ versus that at $\nu = 2112\ cm^{-1}$ is approximately 35:65, independent of the fraction of CO@**1** present. This case contrasts with that of exohedral CO absorptions, in which the ratio is known to be dependent on the equilibrium pressure of CO.[18a] The presence of two absorption bands indicates that there are two distinct orientations for the trapped CO on the IR time scale (picoseconds) whereas there must be rapid interchange between these states on the NMR time scale (milli- to microseconds) to account for the single resonance in the ^{13}C NMR spectrum. In the UV/Vis spectrum, no detectable change was observed between CO@**1** and H_2O@**1** + **1**.

Carbon monoxide absorbed on the exohedral surface of C_{60} is known to disappear under reduced pressure, even at 77 K.[18a] In contrast, CO@**1** was relatively stable under reduced pressure even at ambient temperature. However, it gradually reverts to a mixture of **1** and H_2O@**1** both in solution and in the solid state. A ^1H NMR study on the escape of CO was carried out at 40 °C by using a solution of 2.2 μmol CO@**1** in 0.6 mL $CDCl_3$. In the presence of 9.3 μmol H_2O (ca. 4.2 equiv relative to CO@**1**, analyzed by Karl Fischer titration), the fraction of CO@**1** decreased from 88 to 68, 37, and 7 % after 4, 16, and 48 h, respectively. This escape of CO is in contrast to the spontaneous formation of H_2O@**1**, which suggests that H_2O is bound inside the cage more tightly.

To evaluate the rotation of CO in CO@**1**, six rotational isomers were geometrically optimized at the B3LYP/3-21G level.[15] The two lowest-energy geometries and one less-stable geometry were further optimized at the B3LYP/6-31G* level (Figure 5 and Table 1). In the conformation of lowest energy (CO@**1**-A), the CO molecule is aligned towards the opening with the C atom towards the opening. The conformation with the O atom towards the opening (CO@**1**-B) is higher in energy by 1.1 kcal mol^{-1}. Conformations with the CO perpendicular to the opening are even higher in energy but only by about 5.4 kcal mol^{-1} (CO@**1**-C). These results support that CO may rotate rapidly on the NMR time scale but not on the IR time scale, thus giving rise to two or possibly more IR bands. Calculated energies of CO@**1** relative to (CO + **1**) are in the range from +2.7 to +8.1 kcal mol^{-1} (Table 1).[20] The corresponding energy for H_2O@**1** is −2.4 kcal mol^{-1}. The same trend has been reported for CO@C_{60} and H_2O@C_{60} (Table 1).[11c,d] These results suggest that the encapsulation of CO is energetically less favorable than that of H_2O, which is in agreement with the observed instability of CO@**1**.

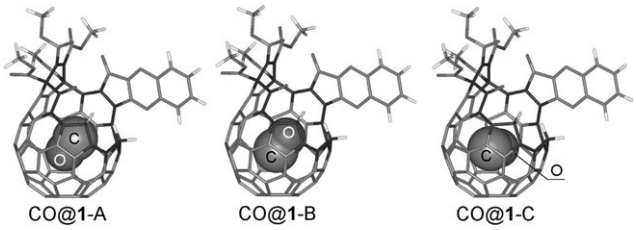

Figure 5. Optimized structures of the rotational isomers of CO@**1** (B3LYP/6-31G*). Carbon monoxide molecules in **1** are shown by the space-filling model.

In summary, we report the formation of an endohedral CO complex of a chemically modified fullerene derivative. The presence of carbon monoxide inside the fullerene cage was confirmed by ES-MS, ^{13}C NMR and IR spectroscopy. Gradual leakage of the CO from CO@**1** contrasts with the spontaneous formation of H_2O@**1**, which suggests that water binds more strongly than CO within **1**. Further investigations are now in progress to construct a library of endohedral complexes of open-cage fullerenes.

Experimental Section

CO@**1**: Compound **1** (50 mg) and TCE (10 mL) were loaded into a 50-mL stainless-steel autoclave equipped with an inner glass tube. The reaction vessel was flushed with carbon monoxide three times, charged to 7.5 MPa of CO, and heated at 100 °C for 20 h (the pressure reached 9.0 MPa). After the reaction mixture was allowed to cool, the pressure was released and the solvent was removed in vacuo. The resulting product was centrifuged with Et_2O, and dried in vacuo to give CO@**1** (52 mg, quantitative) as a reddish brown powder. The fraction of CO@**1** present was estimated to be 84 % by ^1H NMR spectroscopy. ^1H NMR ($CDCl_3$): $\delta = 8.19$ (s, 1 H), 8.03 (s, 1 H), 4.51 (d, $J = 20$ Hz, 1 H), 4.48 (d, $J = 19$ Hz, 1 H), 4.14 (s, 3 H), 3.96 (s, 3 H), 3.82 (s, 3 H), 3.74 (s, 3 H), 3.38 (d, $J = 20$ Hz, 1 H), 2.86 (d, $J = 19$ Hz, 1 H), 2.61 (s, 3 H), 2.59 ppm (s, 3 H); ^{13}C NMR ([D_2]TCE, 308 K): $\delta = 174.30$ ppm (CO). Full data are given in the Supporting Information; IR (KBr): $\tilde{\nu} = 2125$, $2112\ cm^{-1}$; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 313 (72000), 351 (68000) nm; ES-MS (negative mode): m/z 1200 $[M]^-$ (100), 1172.

^{13}CO@**1**: Compound **1** (16 mg) and TCE (4 mL) were loaded into a 10-mL stainless-steel autoclave. The reaction vessel was immersed in a dewar of liquid nitrogen and evacuated. A ^{13}CO lecture bottle was connected to the reaction vessel, and approximately 0.9 L of ^{13}CO was condensed into the container. The cooling bath was removed, and the reaction vessel was heated to 100 °C and maintained at that temperature for 20 h (the pressure reached 3.3 MPa). The reaction mixture was allowed to cool, the pressure was released, and the solvent was removed under reduced pressure to give ^{13}CO@**1**. The fraction of ^{13}CO@**1** was estimated to be 59 % by ^1H NMR spectroscopy. ^{13}C NMR (CD_2Cl_2): $\delta = 174.92$; IR (KBr): $\tilde{\nu} = 2078$, $2066\ cm^{-1}$; ES-MS (negative mode): m/z 1201 $[M]^-$ (100), 1172.

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[1] "Putting nonmetals into fullerenes": M. Saunders, R. J. Cross in *Endofullerenes: A New Family of Carbon Clusters* (Eds.: T. Akasaka, S. Nagase), Kluwer Academic Publisher, Dordrecht, **2002**, pp. 1–11.
[2] Y. Rubin, *Top. Curr. Chem.* **1999**, *199*, 67–91.
[3] A. Hirsch, M. Brettreich, *Fullerenes: Chemistry and Reactions*, Wiley-VCH, Weinheim, **2005**, pp. 345–358.

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[4] T. Kitagawa, Y. Murata, K. Komatsu, *Fullerene Reactivity—Fullerene Cations and Open-Cage Fullerenes* in *Carbon-Rich Compounds: From Molecules to Materials* (Eds.: M. M. Haley, R. R. Tykwinski), Wiley-VCH, Weinheim, **2006**, pp. 383–420.
[5] Y. Rubin, T. Jarrosson, G.-W. Wang, M. D. Bartberger, K. N. Houk, G. Schick, M. Saunders, R. J. Cross, *Angew. Chem.* **2001**, *113*, 1591–1594; *Angew. Chem. Int. Ed.* **2001**, *40*, 1543–1546.
[6] a) Y. Murata, M. Murata, K. Komatsu, *J. Am. Chem. Soc.* **2003**, *125*, 7152–7153; b) K. Komatsu, M. Murata, Y. Murata, *Science* **2005**, *307*, 238–240.
[7] C. M. Stanisky, R. J. Cross, M. Saunders, M. Murata, Y. Murata, K. Komatsu, *J. Am. Chem. Soc.* **2005**, *127*, 299–302.
[8] S.-i. Iwamatsu, S. Murata, Y. Andoh, M. Minoura, K. Kobayashi, N. Mizorogi, S. Nagase, *J. Org. Chem.* **2005**, *70*, 4820–4825.
[9] a) S.-i. Iwamatsu, T. Uozaki, K. Kobayashi, R. Suyong, S. Nagase, S. Murata, *J. Am. Chem. Soc.* **2004**, *126*, 2668–2669; b) S.-i. Iwamatsu, S. Murata, *Synlett* **2005**, 2117–2129.
[10] a) P. Sozzani, S. Bracco, A. Comotti, L. Ferretti, R. Simonutti, *Angew. Chem.* **2005**, *117*, 1850–1854; *Angew. Chem. Int. Ed.* **2005**, *44*, 1816–1820; b) L. Dobrzañska, G. O. Lloyd, H. G. Raubenheimer, L. J. Barbour, *J. Am. Chem. Soc.* **2005**, *127*, 13134–13135; c) J. A. R. Navarro, E. Barea, J. M. Salas, N. Masciocchi, S. Galli, A. Sironi, C. O. Ania, J. B. Parra, *Inorg. Chem.* **2006**, *45*, 2397–2399.
[11] a) J. Cioslowski, *J. Am. Chem. Soc.* **1991**, *113*, 4139–4141; b) C. I. Williams, M. A. Whitehead, L. Pang, *J. Phys. Chem.* **1993**, *97*, 11652–11656; c) Y. H. Hu, E. Ruckenstein, *J. Chem. Phys.* **2005**, *123*, 144303; d) C. N. Ramachandran, N. Sathyamurthy, *Chem. Phys. Lett.* **2005**, *410*, 348–351.
[12] a) E. H. T. Olthof, A. van der Avoird, P. E. S. Wormer, *J. Chem. Phys.* **1996**, *104*, 832–847; b) J. Hernández-Rojas, A. Ruiz, J. Bretón, J. M. G. Llorente, *Int. J. Quantum Chem.* **1997**, *65*, 655–663.
[13] T. Peres, B. Cao, W. Cui, A. Khong, R. J. Cross, M. Saunders, C. Lifshiz, *Int. J. Mass Spectrom.* **2001**, *210/211*, 241–247.
[14] C. G. Kalodimos, I. P. Gerothanassis, R. Pierattelli, B. Ancian, *Inorg. Chem.* **1999**, *38*, 4283–4293.
[15] Two methyl groups on the quinoxaline moiety in **1** were replaced by two hydrogen atoms in the calculations. Gaussian 03 (Revision C.02): M. J. Frisch et al., see Supporting Information.
[16] a) M. Saunders, R. J. Cross, H. A. Jiménez-Vázquez, R. Shimshi, A. Khong, *Science* **1996**, *271*, 1693–1697; b) Z. Chen, R. B. King, *Chem. Rev.* **2005**, *105*, 3613–3642.
[17] C.-C. Chen, C. M. Lieber, *J. Am. Chem. Soc.* **1992**, *114*, 3141–3142.
[18] a) M. Folman, M. Fastow, Y. Kozirovski, *Langmuir* **1997**, *13*, 1118–1122; b) I. Holleman, G. von Helden, A. van der Avoird, G. Meijer, *J. Chem. Phys.* **1999**, *110*, 2129–2139.
[19] C. Matranga, B. Bockrath, *J. Phys. Chem. B* **2005**, *109*, 4853–4864.
[20] In contrast to the B3LYP results, single-point calculations at the MP2/6-31G(d) level on the optimized geometries of CO@**1** showed stabilizing energies ($E = -12$ to -16 kcal mol^{-1}). Density functional theory (DFT) calculations are known to underestimate the binding energies of the endohedral noble-gas complexes; see a) S. Patchkovskii, W. Thiel, *J. Chem. Phys.* **1997**, *106*, 1796–1799; b) M. Bühl, S. Patchkovskii, W. Thiel, *Chem. Phys. Lett.* **1997**, *275*, 14–18. Experimental verification of the binding energy for CO was not possible due to the contamination of **1** with H_2O@**1** (see reference [8]).

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