Endohedral Fullerenes

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Observation of ^{13}C NMR Chemical Shifts of Metal Carbides Encapsulated in Fullerenes: $Sc_2C_2@C_{82}$, $Sc_2C_2@C_{84}$, and $Sc_3C_2@C_{80}$**

Yuko Yamazaki, Koji Nakajima, Takatsugu Wakahara, Tsuchiya Tsuchiya, Midori O. Ishitsuka, Yutaka Maeda, Takeshi Akasaka, Markus Waelchli, Naomi Mizorogi, and Shigeru Nagase**

Endohedral metallofullerenes have attracted special interest as promising spherical molecules for material and catalytic applications, because of their unique properties that are not expected from empty fullerenes.[1–3] The successful isolation and purification of endohedral metallofullerenes in macroscopic quantities have made it possible to investigate the structures as well as the electronic properties and reactivities through a close interplay between theory and experiment. Since the first isolation and characterization of a metal carbide encapsulated metallofullerene ($Sc_2C_2@C_{84}$) by MEM (maximum entropy method)/Rietveld analysis of synchrotron powder diffraction data,[4] much attention has been paid to encapsulation of metal carbides. Recently, we found by ^{13}C NMR spectroscopy and X-ray single-crystal structure analyses that Sc_3C_{82} and Sc_2C_{84} have the structures $Sc_3C_2@C_{80}(I_h)$[5] and $Sc_2C_2@C_{82}(C_{3v})$,[6,7] encapsulating metal carbides, although it had long been believed from the MEM/Rietveld analyses that they have the conventional structures $Sc_3@C_{82}$[8] and $Sc_2@C_{84}$[9], respectively. The encapsulation of metal carbides has been confirmed by the recent improved MEM/Rietveld analyses of $Y_2C_2@C_{82}(C_{3v})$[10] as well as $Sc_2C_2@C_{82}(C_{3v})$[11] and $Sc_3C_2@C_{80}(I_h)$.[12] However, attempts to detect the ^{13}C NMR chemical shifts of the C_2 units of metal carbides encapsulated in the fullerenes have not been yet successful.[13,14] This unsuccessful detection has been explained in term of the spin-rotation interaction, because the C_2 unit may rotate rapidly inside carbon cages. It is an important task to observe the ^{13}C NMR chemical shift of the C_2 unit in an attempt to provide insight into its electronic and magnetic properties.

We present herein the first detection of the ^{13}C NMR chemical shifts of the C_2 unit in $Sc_2C_2@C_{82}(C_{3v})$, $Sc_2C_2@C_{84}(D_{2d})$, and $[Sc_3C_2@C_{80}(I_h)]^-$ by using ^{13}C-enriched samples. We also successfully assigned all ^{13}C NMR chemical shifts of the cage carbon atoms for the three compounds by 2D INADEQUATE (incredible natural abundance double quantum transfer experiment) NMR measurements.

The ^{13}C NMR spectrum of $Sc_2C_2@C_{82}(C_{3v})$ (Figure 1 a) shows 17 chemical shifts of the C_{82} cage at $\delta = 134.6$–151.9 ppm, as reported previously.[6] To map the bond connectivity in the carbon cage and assign the ^{13}C NMR chemical shifts, a 2D INADEQUATE NMR measurement[15] of ^{13}C-enriched $Sc_2C_2@C_{82}(C_{3v})$ was performed (Figure 2). Bonded carbon atoms share a double quantum frequency in the vertical dimension, and each peak appears at the respective chemical shifts in the horizontal dimension. For the $C_{82}(C_{3v})$ cage, a total of 19 cross-peaks should be observed. As shown in Figure 2 b, all the cross-peaks were observed and

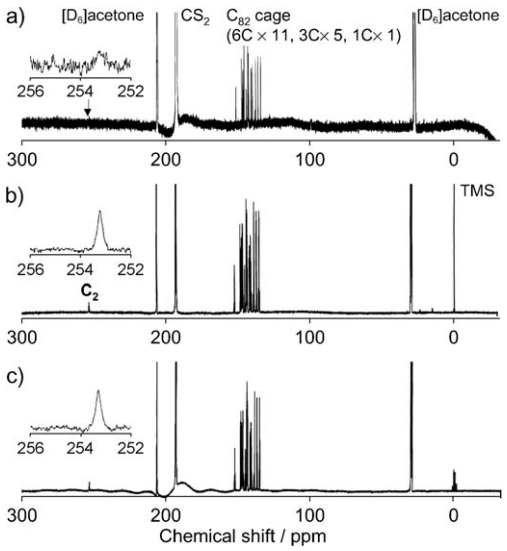

Figure 1. ^{13}C NMR (125 MHz) spectra of a) $Sc_2C_2@C_{82}(C_{3v})$ in proton-decoupled mode (CS_2, 298 K) and ^{13}C-enriched $Sc_2C_2@C_{82}(C_{3v})$ in b) proton-decoupled (CS_2, 298 K) and c) proton-coupled modes. A capillary tube containing [D_6]acetone was used as an internal lock.

[*] Dr. Y. Yamazaki, K. Nakajima, Dr. T. Wakahara, Dr. T. Tsuchiya, Dr. M. O. Ishitsuka, Prof. Dr. T. Akasaka
Center for Tsukuba Advanced Research Alliance, University of Tsukuba, Tsukuba, Ibaraki 305-8577 (Japan)
Fax: (+81) 29-853-6409
E-mail: akasaka@tara.tsukuba.ac.jp
Homepage: http://www.tara.tsukuba.ac.jp/~akasaka-lab/
Dr. N. Mizorogi, Prof. Dr. S. Nagase
Department of Theoretical and Computational Molecular Science, Institute for Molecular Science, Okazaki, Aichi 444-8585 (Japan)
Fax: (+81) 56-453-4660
E-mail: nagase@ims.ac.jp
Dr. Y. Maeda
Department of Chemistry, Tokyo Gakugei University, Koganei, Tokyo 184-8501 (Japan)
Dr. M. Waelchli
Bruker Biospin, Co. Ltd., Tsukuba, Ibaraki 305-0051 (Japan)

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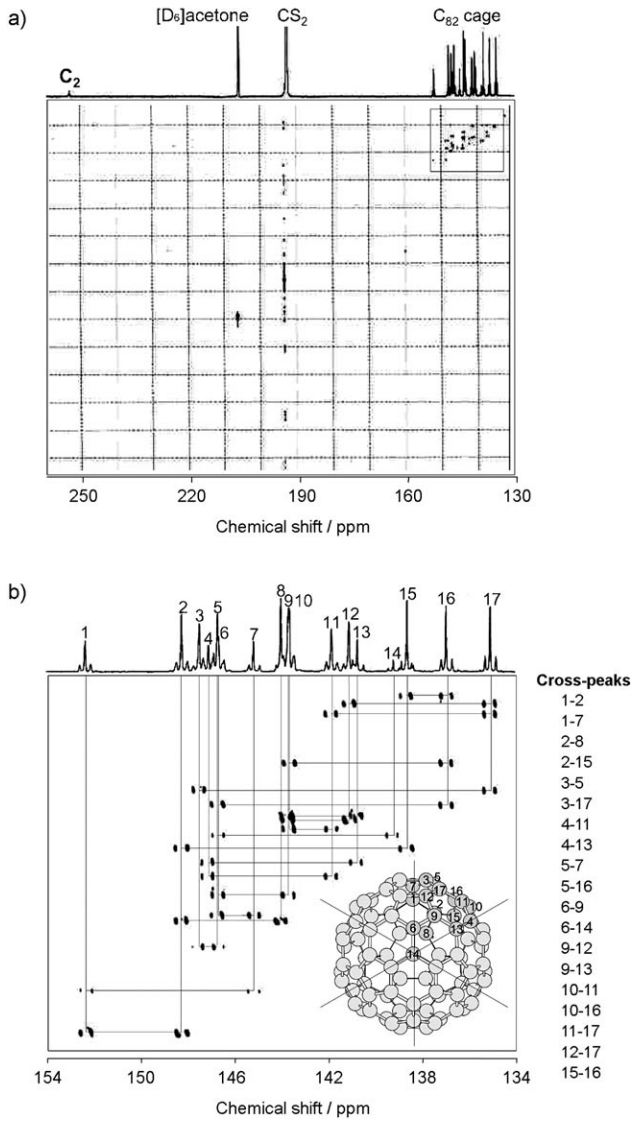

Figure 2. a) INADEQUATE NMR (125 MHz) spectrum of ^{13}C-enriched $Sc_2C_2@C_{82}(C_{3v})$ in CS_2 at 298 K and b) the expanded spectrum between $\delta = 134$ and 154 ppm. A capillary tube containing [D_6]acetone was used as an internal lock. [Cr(acac)$_3$] was used as a relaxation reagent.

the ^{13}C NMR chemical shifts of the C_{82} cage were completely assigned, as recently done for $[La@C_{82}]^-$[16] and $[Ce@C_{82}]^-$.[17]

We now focus on the chemical shift at $\delta = 253.2$ ppm observed for the ^{13}C-enriched sample of $Sc_2C_2@C_{82}(C_{3v})$. As Figure 1 b,c shows, the peak was observed in both proton-decoupled and proton-coupled modes, which indicates that it originates from a quaternary carbon atom. An INVGATE (inverse-gated decoupling) sequence was used for quantitative ^{13}C NMR spectral analysis. As is apparent from Table 1, the chemical shift at $\delta = 253.2$ ppm originates from two carbon atoms. No cross-peak was observed for the chemical shift at $\delta = 253.2$ ppm (Figure 2 a), but cross-peaks were observed for those of the C_{82} cage carbon atoms. This result indicates that the two carbon atoms responsible for the chemical shifts at $\delta = 253.2$ ppm have no bonding with cage carbons. The ^{13}C NMR chemical shifts of $Sc_2C_2@C_{82}(C_{3v})$ were calculated at the B3LYP-GIAO level.[18] For the most stable

Table 1: ^{13}C NMR signals for $Sc_2C_2@C_{82}(C_{3v})$ and their integration.

Signal	Integral	Signal	Integral	Signal	Integral
C_2	2.04 (2C)	5, 6	9.04 (9C)	14	1.17 (1C)
1	3.00 (3C)	7	3.29 (3C)	15	6.53 (6C)
2	6.32 (6C)	8–10	18.37 (18C)	16	6.02 (6C)
3	6.36 (6C)	11	6.26 (6C)	17	6.40 (6C)
4	3.34 (3C)	12, 13	9.42 (9C)		

optimized structure, two slightly different chemical shifts were calculated for the C_2 unit, because the optimized structure has C_1 symmetry (Figure 3 a). The calculated chemical shifts at $\delta = 276.3$ (C_a) and 277.2 ppm (C_b) (Figure 3 b) agree reasonably well with the experimental value at

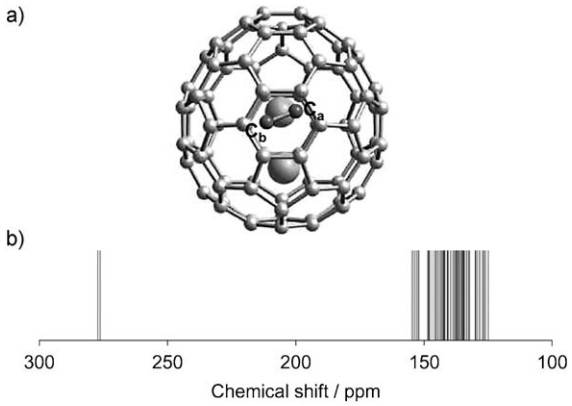

Figure 3. a) Optimized structure of $Sc_2C_2@C_{82}(C_{3v})$ and b) its calculated chemical shifts.

$\delta = 253.2$ ppm. These results show that the chemical shift at $\delta = 253.2$ ppm is due to the C_2 unit in $Sc_2C_2@C_{82}(C_{3v})$. It should be emphasized that ^{13}C NMR measurement of $Sc_2C_2@C_{82}(C_{3v})$ performed without ^{13}C-enrichment does not show a clear chemical shift for the C_2 unit because of the low signal-to-noise ratio (see Figure 1 a).

The carbon–carbon bond lengths of the C_2 unit in $Sc_2C_2@C_{82}(C_{3v})$ and its adamantylidene adduct are 1.273 Å and 1.107(6) Å, respectively, corresponding to a triple bond distance, as shown by theoretical calculations[7] and X-ray single-crystal structure analysis.[7] Theoretical studies reveal that the electronic structure of $Sc_2C_2@C_{82}(C_{3v})$ is formally described as $Sc_2^{6+}C_2^{2-}C_{82}^{4-}$.[7]

The chemical shift of the C_2 unit in $Sc_2C_2@C_{82}(C_{3v})$ ($\delta =$ 253.2 ppm) is observed at a much lower field than that of acetylene ($\delta = 71.6$ ppm).[19] The scandium acetylide compound $Cp^*_2ScC{\equiv}CScCp^*_2$ ($Cp^* =$ pentamethylcyclopentadienyl) shows a ^{13}C NMR chemical shift for the acetylenic carbon atom at a relatively low field ($\delta = 179.4$ ppm).[20] The positive charge of the Sc atom may be the reason for these observed downfield chemical shifts. The solid-state ^{13}C NMR measurement of lithium acetylide (Li_2C_2) also gives a low field chemical shift at $\delta = 195 \pm 10$ ppm.[21] The geometry of the metal cation relative to the acetylide dianion may influence the chemical shift. As supported by these data, it is not surprising that the chemical shift of the C_2 unit in

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$Sc_2C_2@C_{82}(C_{3v})$ appears at a low field because of the dianion character of the C_2 unit.

The dynamic behavior of the C_2 unit should be reflected in the ^{13}C NMR line width. The line width for the C_2 unit (30 Hz) is five times broader than those for cage carbon atoms (e.g., C1: 6.2 Hz) at 298 K. We carried out the variable-temperature ^{13}C NMR measurements of $Sc_2C_2@C_{82}(C_{3v})$. Interestingly, broadening of the ^{13}C NMR line width for the C_2 unit was observed with increasing temperature from 253 to 303 K owing to spin-rotation relaxation, as found for the ^{139}La NMR spectra of $La_2@C_{80}$,[22] suggesting that the C_2 unit rotates inside the C_{82} cage (Figure 4). In contrast, such line-width broadening was not observed for the C_{82} cage carbon atoms with increasing temperature.

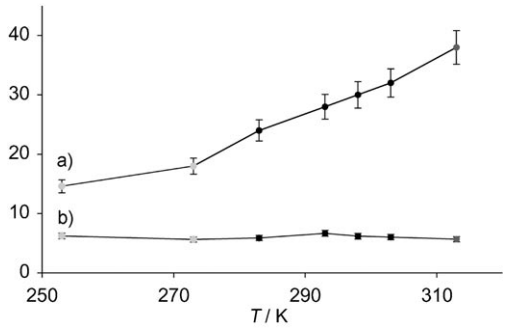

Figure 4. Line widths of the ^{13}C NMR chemical shifts of a) the C_2 unit and b) the C1 carbon in the C_{82} cage for ^{13}C-enriched $Sc_2C_2@C_{82}(C_{3v})$ as a function of temperature. Dark gray (150 MHz in [D_4]-*o*-dichlorobenzene), black (125 MHz in CS_2), and light gray (150 MHz in CS_2).

^{13}C NMR spectra of ^{13}C-enriched $Sc_2C_2@C_{84}(D_{2d})$ were measured over a considerably wide range. The chemical shift of the C_2 unit was observed at $\delta = 249.2$ ppm in both proton-decoupled and proton-coupled modes (see Figure S1 in the Supporting Information). The chemical shift at $\delta = 249.2$ ppm is not clearly observed without ^{13}C-enrichment (Figure S1). The value of $\delta = 249.2$ ppm is close to that of $\delta = 253.2$ ppm for $Sc_2C_2@C_{82}(C_{3v})$, which suggests that the magnetic environment around the Sc_2C_2 unit of $Sc_2C_2@C_{84}(D_{2d})$ is similar to that of $Sc_2C_2@C_{82}(C_{3v})$. It has been reported that the ^{13}C NMR chemical shift of the C_2 unit for $Sc_2C_2@C_{84}(D_{2d})$ is $\delta =$ 91.99 ppm.[4b] However, the reported signal at $\delta = 91.99$ ppm is ascribed to an impurity, as no important chemical shift is observed in that region by the present ^{13}C-enriched NMR study.

We also mapped the bond connectivity in the carbon cage of $Sc_2C_2@C_{84}(D_{2d})$ and assigned the ^{13}C NMR chemical shifts by 2D INADEQUATE NMR measurement (Figure S2 in the Supporting Information).[23] For $C_{84}(D_{2d})$, a total of 13 cross-peaks should be observed. Eleven cross-peaks were observed, and ^{13}C NMR chemical shifts of the C_{84} cage were assigned fully (Figure S2). The cross-peak between C1 and C2 was not observed, because C1 and C2 show almost identical ^{13}C NMR chemical shifts. For the same reason, the cross-peak between C3 and C4 was also not observed.

Since $Sc_3C_2@C_{80}(I_h)$ is paramagnetic, ^{13}C NMR spectra of the $[Sc_3C_2@C_{80}(I_h)]^-$ anion were measured with the ^{13}C-enriched sample. The ^{13}C-enriched anion was prepared chemically with pyridine, as described previously.[5] The chemical shift of the C_2 unit was observed at $\delta = 328.3$ ppm in both proton-decoupled and proton-coupled modes (Figure S3 in the Supporting Information). The line width for the C_2 unit (108 Hz) is three or more times broader than that of $Sc_2C_2@C_{82}(C_{3v})$ (30 Hz) at 298 K. As in the cases of $Sc_2C_2@C_{82}(C_{3v})$ and $Sc_2C_2@C_{84}(D_{2d})$, the ^{13}C NMR spectrum of $[Sc_3C_2@C_{80}(I_h)]^-$ measured without ^{13}C-enrichment (Figure S3) shows no clear chemical shift for the C_2 unit because of the low signal-to-noise ratio.

The 2D INADEQUATE spectrum of the ^{13}C-enriched $[Sc_3C_2@C_{80}(I_h)]^-$ sample shows a cross-peak between the two chemical shifts of the $C_{80}(I_h)$ cage (Figure S4 in the Supporting Information). Moreover, the chemical shift of the C_2 unit has no cross-peak with the two chemical shifts of the $C_{80}(I_h)$ cage, as in the case of $Sc_2C_2@C_{82}(C_{3v})$ (Figure S4). This result confirms that the C_2 unit is also separated from the fullerene cage.

Two chemical shifts at $\delta = 267.0$ (C_a) and 365.7 ppm (C_b) were calculated at the B3LYP-GIAO level[18] for the C_2 unit of $[Sc_3C_2@C_{80}(I_h)]^-$ by using the most stable optimized structure (C_s symmetry) (Figure S5 in the Supporting Information).[5] The observed chemical shift of the C_2 unit at $\delta = 328.3$ ppm shows the average of the two calculated values because of the rotation of the C_2 unit within the C_{80} cage.

We have recently synthesized the adamantylidene derivative $Sc_3C_2@C_{80}(I_h)$(Ad) and determined its structure by X-ray single-crystal analysis.[5] ^{13}C NMR spectra of $[Sc_3C_2@C_{80}(Ad)]^-$ were measured using the ^{13}C-enriched sample. Two chemical shifts are observed at $\delta = 257.2$ and 384.4 ppm for the C_2 unit in both proton-decoupled and proton-coupled modes, because the two carbon atoms are not equivalent, as shown by the X-ray crystal structures (Figure S6 in the Supporting Information). The two observed chemical shifts agree well with the calculated values of $\delta = 275.4$ (C_a) and 380.9 ppm (C_b) (for the C_a and C_b atoms, see Figure S7).

Experimental Section

15% ^{13}C-enriched samples of $Sc_2C_2@C_{82}(C_{3v})$, $Sc_2C_2@C_{84}(D_{2d})$, and $Sc_3C_2@C_{80}(I_h)$ were prepared by the reported method.[24] $[Sc_3C_2@C_{80}(I_h)]^-$ was prepared chemically, as described before.[5] [$Cr(acac)_3$] (acac = acetylacetonate) was used as a relaxation reagent for the 2D INADEQUATE and INVGATE NMR measurements of $Sc_2C_2@C_{82}(C_{3v})$ and $Sc_2C_2@C_{84}(D_{2d})$. The ^{13}C NMR spectra were measured at 125 and 150 MHz on a Bruker AVANCE-500 (with a CryoProbe system) and AVANCE-600 spectrometers. All calculations were performed with the Gaussian 03 program.[18] Geometries were optimized with the hybrid density functional theory at the B3LYP[25–27] level with the effective core potential[28] and the (5s5p5d)/[4s4p3d] basis set for Sc, and the 6-31G(d) basis set[29] for C and H. The ^{13}C NMR chemical shifts were calculated by the B3LYP-GIAO[30] method.

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[1] J. R. Heath, S. C. O'Brien, Y. Liu, R. F. Curl, H. W. Kroto, F. K. Title, R. E. Smalley, *J. Am. Chem. Soc.* **1985**, *107*, 7779 – 7780.

[2] Y. Chai, T. Guo, C. Jin, R. E. Haufler, L. P. F. Chibante, J. Fure, L. Wang, J. M. Alford, R. E. Smalley, *J. Phys. Chem.* **1991**, *95*, 7564 – 7568.

[3] *Endofullerenes: A New Family of Carbon Clusters* (Eds.: T. Akasaka, S. Nagase), Kluwer, Dordrecht, **2002**.

[4] a) C.-R. Wang, T. Kai, T. Tomiyama, T. Yoshida, Y. Kobayashi, E. Nishibori, M. Takata, M. Sakata, H. Shinohara, *Angew. Chem.* **2001**, *113*, 411 – 413; *Angew. Chem. Int. Ed.* **2001**, *40*, 397 – 399; b) The ^{13}C NMR chemical shift of the C_2 unit in $Sc_2C_2@C_{84}$ was observed at $\delta = 91.99$ ppm in Ref. [4a]. However, Wang has informed us that the chemical shift at $\delta = 91.99$ ppm is ascribed to an impurity.

[5] Y. Iiduka, T. Wakahara, T. Nakahodo, T. Tsuchiya, A. Sakuraba, Y. Maeda, T. Akasaka, K. Yoza, E. Horn, T. Kato, M. T. H. Liu, N. Mizorogi, K. Kobayashi, S. Nagase, *J. Am. Chem. Soc.* **2005**, *127*, 12500 – 12501.

[6] Y. Iiduka, T. Wakahara, K. Nakajima, T. Tsuchiya, T. Nakahodo, Y. Maeda, T. Akasaka, N. Mizorogi, S. Nagase, *Chem. Commun.* **2006**, 2057 – 2059.

[7] Y. Iiduka, T. Wakahara, K. Nakajima, T. Nakahodo, T. Tsuchiya, Y. Maeda, T. Akasaka, K. Yoza, M. T. H. Liu, N. Mizorogi, S. Nagase, *Angew. Chem.* **2007**, *119*, 5658 – 5660; *Angew. Chem. Int. Ed.* **2007**, *46*, 5562 – 5564.

[8] M. Takata, M. Nishibori, M. Sakata, M. Inakuma, E. Yamamoto, H. Shinohara, *Phys. Rev. Lett.* **1999**, *83*, 2214 – 2217.

[9] M. Takata, E. Nishibori, B. Umeda, M. Sakata, E. Yamamoto, H. Shinohara, *Phys. Rev. Lett.* **1997**, *78*, 3330 – 3333.

[10] E. Nishibori, S. Narioka, M. Takata, M. Sakata, T. Inoue, H. Shinohara, *ChemPhysChem* **2006**, *7*, 345 – 348.

[11] E. Nishibori, M. Ishihara, M. Takata, M. Sakata, Y. Ito, T. Inoue, H. Shinohara, *Chem. Phys. Lett.* **2006**, *433*, 120 – 124.

[12] E. Nishibori, I. Terauchi, M. Sakata, M. Takata, Y. Ito, T. Sugai, H. Shinohara, *J. Phys. Chem. B* **2006**, *110*, 19215 – 19219.

[13] T. Inoue, T. Tomiyama, T. Sugai, T. Okazaki, T. Suematsu, N. Fujii, H. Utsumi, K. Nojima, H. Shinohara, *J. Phys. Chem. B* **2004**, *108*, 7573 – 7579.

[14] T. Inoue, T. Tomiyama, T. Sugai, H. Shinohara, *Chem. Phys. Lett.* **2003**, *382*, 226 – 231.

[15] a) A. Bax, R. Freeman, *J. Magn. Reson.* **1980**, *41*, 507 – 511; b) A. Bax, R. Freeman, S. T. Kempsell, *J. Am. Chem. Soc.* **1980**, *102*, 4849 – 4851.

[16] T. Tsuchiya, T. Wakahara, Y. Maeda, T. Akasaka, M. Waelchli, T. Kato, H. Okubo, N. Mizorogi, K. Kobayashi, S. Nagase, *Angew. Chem.* **2005**, *117*, 3346 – 3349; *Angew. Chem. Int. Ed.* **2005**, *44*, 3282 – 3285.

[17] M. Yamada, T. Wakahara, Y. Lian, T. Tsuchiya, T. Akasaka, M. Waelchli, N. Mizorogi, S. Nagase, K. M. Kadish, *J. Am. Chem. Soc.* **2006**, *128*, 1400 – 1401.

[18] M. J. Frisch, et al., Gaussian 03, Revision C. 01, Gaussian Inc., Wallingford, CT, **2004**.

[19] T. T. Morrison, R. N. Boyd, *Organic Chemistry*, Allyn and Bacon, Boston, **1980**, pp. 250.

[20] M. St. Clair, W. P. Schaefer, J. E. Bercaw, *Organometallics* **1991**, *10*, 525 – 527.

[21] T. M. Duncan, *Inorg. Chem.* **1989**, *28*, 2663 – 2668.

[22] T. Akasaka, S. Nagase, K. Kobayashi, M. Waelchli, K. Yamamoto, H. Funasaka, M. Kako, T. Hoshino, T. Erata, *Angew. Chem.* **1997**, *109*, 1716 – 1719; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1643 – 1645.

[23] For $C_{84}(D_{2d})$, there are two D_{2d} isomers that satisfy the ^{13}C NMR spectrum, IPR isomer **23** and non-IPR isomer **28620**. Isomer **28620** can be excluded from the present INADEQUATE NMR spectral analysis.

[24] H. Shinohara, H. Sato, M. Ohkohchi, Y. Ando, T. Kodama, T. Shida, T. Kato, Y. Saito, *Nature* **1992**, *357*, 52 – 54.

[25] A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098 – 3100.

[26] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648 – 5652.

[27] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785 – 789.

[28] P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 299 – 310.

[29] W. J. Hehre, R. Ditchfield, J. A. Pople, *J. Chem. Phys.* **1972**, *56*, 2257 – 2261.

[30] K. Wolinski, J. F. Hilton, P. Pulay, *J. Am. Chem. Soc.* **1990**, *112*, 8251 – 8260.

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