Carbide Fullerenes

DOI: 10.1002/anie.201201325

The Long-Believed $Sc_2@C_{2v}(17)$-C_{84} is Actually $Sc_2C_2@C_{2v}(9)$-C_{82}: Unambiguous Structure Assignment and Chemical Functionalization**

Xing Lu, Koji Nakajima, Yuko Iiduka, Hidefumi Nikawa, Takahiro Tsuchiya, Naomi Mizorogi, Zdenek Slanina, Shigeru Nagase, and Takeshi Akasaka**

Endohedral metallofullerenes (EMFs), that is, fullerenes with metal atoms inside the cage cavities, have attracted great attention because of their fascinating properties and broad applications in materials science, photovoltaics, electronics, and biomedicine.[1] Great success has been achieved recently in preparing EMFs, and the types of encapsulated metal species are rather diverse.[1] In addition to such conventional EMFs containing one or two metal atoms,[2] novel EMFs incorporating a variety of metal compounds, including metal carbide ($M_2C_2/M_3C_2/M_4C_2$),[3] metal nitride (M_3N),[4] metal oxide ($M_2O/M_4O_2/M_4O_3$),[5] metal sulfide (M_2S),[6] and metal cyanide (Sc_3CN) clusters,[7] have been obtained and structurally characterized by single-crystal XRD.

Among these species, carbide cluster metallofullerenes (CCMFs) are unique because encapsulation of two carbon atoms inside the cage instead of incorporation in the cage framework makes structural identification of CCMFs fairly difficult.[3] Therefore, several CCMFs were assigned incorrectly as conventional EMFs in previous reports. For example, $Sc_3@C_{3v}(7)$-C_{82}[8] which had been regarded as the sole example of trimetallic EMFs for many years, was revealed to be $Sc_3C_2@I_h(7)$-C_{80}.[3b] Moreover, the previously proposed $Sc_2@C_s(10)$-C_{84} and $Sc_2@D_{2d}(23)$-C_{84}[9] were both identified as carbide species, namely, $Sc_2C_2@C_s(6)$-C_{82}[3g] and $Sc_2C_2@C_{3v}(8)$-C_{82},[3c] respectively. Of the two isolated Sc_2C_{82} isomers,[10] one was identified as $Sc_2C_2@C_{2v}(5)$-C_{80},[3f] whereas the other was proved to be a conventional species, namely, $Sc_2@C_{3v}(8)$-C_{82}.[2b] Thus, the situation with Sc EMFs is complicated and their structural identification is quite intractable.

Herein we present unambiguous experimental results showing that the long-believed $Sc_2@C_{2v}(17)$-C_{84}[9] is also a CCMF species, that is, $Sc_2C_2@C_{2v}(9)$-C_{82}. Moreover, its chemical properties were investigated for the first time by performing a 1,3-dipolar reaction.

The molecular structure of $Sc_2C_2@C_{2v}(9)$-C_{82} was firmly established by performing NMR spectroscopy on 15% ^{13}C-enriched samples, which ensures the detection of every possible signal, especially that from the internal carbide cluster.[3] Figure 1 shows the two-dimensional INADEQUATE NMR spectrum of the endohedral fullerene. It consists of 24 signals in the aromatic region, among which 17 have full intensity and 7 half-intensity. This [17×4C, 7×2C] pattern points to the $C_{2v}(9)$-C_{82} cage, instead of any of the 24 C_{84} isomers obeying the isolated-pentagon rule.[11] Furthermore, the signal of the internal Sc_2C_2 cluster is readily observed at 242.7 ppm (Supporting Information), and unambiguously confirms the assignment of the C_{82} cage. This value is similar to those observed in $Sc_2C_2@C_{2v}(5)$-C_{80} (231.5 ppm),[3f] $Sc_2C_2@C_{3v}(8)$-C_{82} (253.2 ppm),[3e] $Sc_2C_2@C_s(6)$-C_{82} (244.4 ppm),[3g] and $Sc_2C_2@D_{2d}(23)$-C_{84} (249.2 ppm),[3e] which all have the same Sc_2C_2 cluster. However, all of the above values are markedly different from that of the $[Sc_3C_2@I_h(7)\text{-}C_{80}]^-$ anion (328.3 ppm),[3e] which encapsulates an Sc_3C_2 cluster. Certainly such a difference is caused by the different compositions of the internal cluster (Sc_2C_2 vs. Sc_3C_2).

To gain information about the chemical properties of the newly assigned $Sc_2C_2@C_{2v}(9)$-C_{82}, a 1,3-dipolar reaction with 3-triphenylmethyl-5-oxazolidinone (**1**) was performed. Under refluxing conditions, decarboxylation of **1** gave rise to the corresponding 1,3-dipolar reagent, ylide $(CH_2)_2NCPh_3$, which reacted in situ with the endofullerene to form pyrrolidino derivatives.

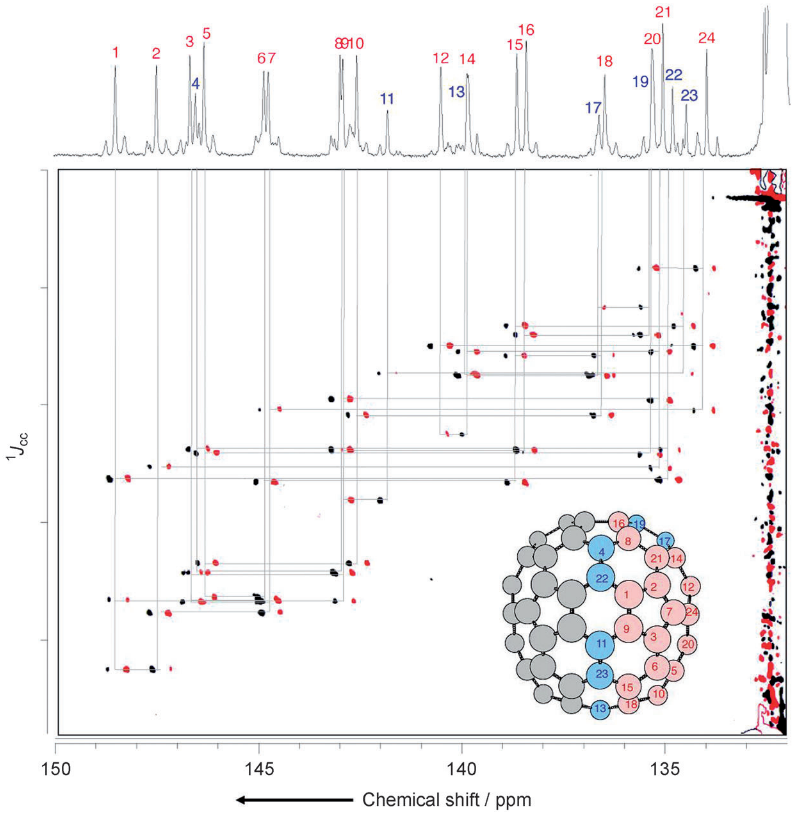
The corresponding HPLC profiles probed at different reaction times are shown in Figure 2. In addition to the peak of starting $Sc_2C_2@C_{2v}(9)$-C_{82} at 35.9 min, new peaks appeared at 15–20 min after refluxing for 1 h, which all correspond to mono-adduct isomers **2** according to MALDI-TOF mass-spectrometric data. The reaction was terminated after 6 h when a small amount of multiple adducts emerged. Finally, three monoadduct isomers, **2a**, **2b**, and **2c**, were isolated in a relative ratio of 2:1.5:1.

---

[*] Prof. Dr. X. Lu
Huazhong University of Science and Technology (HUST) (China)
Prof. Dr. X. Lu, K. Nakajima, Dr. Y. Iiduka, Dr. H. Nikawa,
Dr. T. Tsuchiya, Dr. N. Mizorogi, Dr. Z. Slanina, Prof. Dr. T. Akasaka
Life Science Center for Tsukuba Advanced Research Alliance,
University of Tsukuba
Tennodai 1-1-1, Tsukuba, Ibaraki 305-8577 (Japan)
E-mail: akasaka@tara.tsukuba.ac.jp
Prof. Dr. S. Nagase
Department of Theoretical and Computational Molecular Science,
Institute for Molecular Science
Okazaki, Aichi 444-8585 (Japan)
E-mail: nagase@ims.ac.jp

[**] This work is supported in part by a Grant-in-Aid for Scientific Research on Innovative Areas (No. 20108001, "pi-Space"), a Grant-in-Aid for Scientific Research (A) (No. 20245006), The Next Generation Super Computing Project (Nanoscience), Nanotechnology Support Project, Grants-in-Aid for Scientific Research on Priority Area (Nos. 20036008, 20038007), and Specially Promoted Area (No. 22000009) from MEXT of Japan, and The Strategic Japanese-Spanish Cooperative Program funded by JST and MICINN. Generous support from The National Thousand Talents Program, The National Natural Science Foundation of China (No. 21171061), and HUST to X. L. is gratefully acknowledged.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201201325.



Interatomic connection

1 - 2
1 - 9
1 - 22
2 - 7
2 - 21
3 - 6
3 - 7
3 - 9
4 - 8
4 - 22
5 - 6
5 - 10
5 - 20
6 - 15
7 - 24
8 - 16
8 - 21
9 - 11
10 - 18
11 - 23
12 - 14
12 - 24
13 - 18
14 - 17
14 - 21
15 - 18
15 - 23
16 - 19
17 - 19
20 - 24

Figure 1. 2D INADEQUATE NMR spectrum of 15% ^{13}C-enriched $Sc_2C_2@C_{2v}(9)$-C_{82}. The inset illustrates the $C_{2v}(9)$-C_{82} cage with all 24 nonequivalent cage carbon atoms labeled in accordance with the NMR spectrum. Bond connections are summarized on the right.

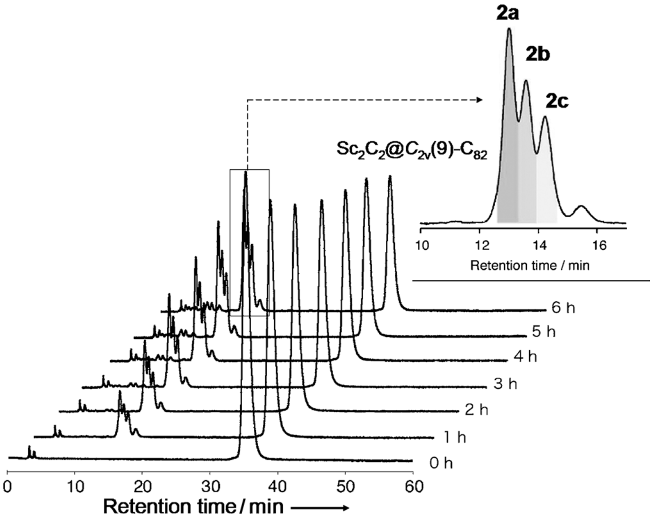


Figure 2. HPLC profile of the reaction mixture of $Sc_2C_2@C_{2v}(9)$-C_{82} and **1**.

High-quality single crystals of **2a** were obtained and its molecular structure containing an Sc_2C_2 cluster was firmly established by X-ray crystallography.[12] Figure 3 shows the X-ray structure of the major enantiomer of **2a**. Plots of other enantiomers are portrayed in the Supporting Information. The fullerene adopts the $C_{2v}(9)$-C_{82} cage and encapsulates an Sc_2C_2 cluster. The pyrrolidino addend adds to a [5,6]-bond junction involving C15 and C18 (see Figure 1), which is very close and nearly parallel to one of the mirror planes of the C_{2v}-symmetric cage. The distance between the two cage carbon atoms at the addition sites of 1.609(4) Å confirms a closed-cage structure. The Sc_2C_2 cluster is bent to resemble a butterfly. The Sc-C_2-Sc dihedral angle of about 120° reflects strong torsion within the cluster. The C−C bond length in Sc_2C_2 of 1.184(17) Å represents a typical $C\equiv C$ bond. The Sc−C distances within the cluster range from 2.177(7) to 2.496(8) Å, which are comparable to the values of the closest Sc–cage contacts (2.127(4)–2.203(4) Å), that is, the metal atoms are balanced between the surrounding cage and the central C_2 unit to attain the bent structure.

The addition pattern in **2a** is readily explainable by frontier molecular orbital theory, because 1,3-dipolar cycloaddition of azomethine ylides to alkenes obeys Woodward–Hoffmann rules. Our calculations reveal that the LUMO of the $(CH_2)_2NCPh_3$ ylide lies at -3.89 eV, which perfectly matches the HOMO level of $Sc_2C_2@C_{2v}(9)$-C_{82} (-3.63 eV). Thus, the ylide tends to selectively attack the regions on the cage where the LUMO is mainly localized. Indeed, as Figure 4 clearly shows, the addition positions in **2a** have the largest orbital coefficients of the LUMO and accordingly are most reactive toward **1**. Hence, the addition sites in **2b** and **2c** are also predictable by considering large orbital coefficients of adjacent cage carbon atoms. As shown in Figure S12 (Supporting Information), the

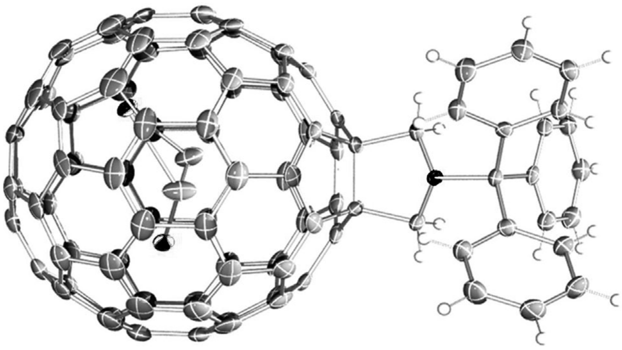


Figure 3. ORTEP of the major enantiomer of **2a** with 50% thermal contours. Solvent molecules are omitted for clarity.

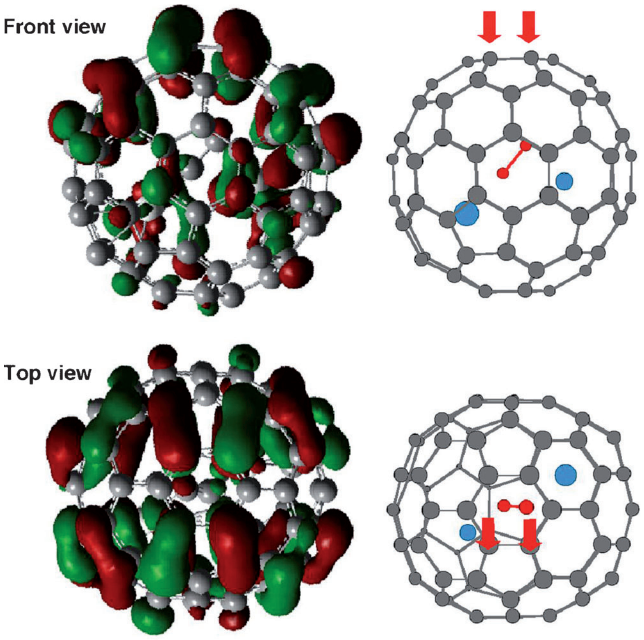


Figure 4. Perspective views of the LUMO distribution and corresponding schematic structures of $Sc_2C_2@C_{2v}(9)\text{-}C_{82}$. Arrows indicate the addition site in **2a**.

addition sites in **2b** and **2c** most probably involve two different [6,6]-bond junctions on the cage.

Chemical modification of $Sc_2C_2@C_{2v}(9)\text{-}C_{82}$ significantly altered its electrochemical properties. Table 1 lists the redox potentials of $Sc_2C_2@C_{2v}(9)\text{-}C_{82}$ and **2a**–**2c**. Although the corresponding redox potentials of **2a**–**2c** are not uniform, their electrochemical bandgaps (1.40 V for **2a**, 1.23 V for **2b**, and 1.19 V for **2c**) are all larger than that of pristine $Sc_2C_2@C_{2v}(9)\text{-}C_{82}$ (0.99 V), that is, the derivatives are more stable. This is particularly important because most perspective applications of EMFs require high stability of the materials.

Table 1: Redox potentials[a] [V] of $Sc_2C_2@C_{2v}(9)\text{-}C_{82}$ and **2a**–**2c**.

Compound	${}^{ox}E_2$	${}^{ox}E_1$	${}^{red}E_1$	${}^{red}E_2$
$Sc_2C_2@C_{2v}(9)\text{-}C_{82}$	0.67	0.25	−0.74	−0.96
2a	0.70[b]	0.27	−1.13[b]	−1.56[b]
2b	0.73[b]	0.39	−0.84	−1.19
2c	0.51[b]	0.12	−1.07[b]	−1.62[b]

[a] Half-wave potentials versus Fc/Fc^+ on a Pt working electrode in 1,2-dichlorobenzene unless otherwise noted. [b] Irreversible; values from differential pulse voltammetry.

In summary, the erroneously assigned $Sc_2@C_{2v}(17)\text{-}C_{84}$ is identified as new carbide cluster metallofullerene $Sc_2C_2@C_{2v}(9)\text{-}C_{82}$. Moreover, this newly assigned $Sc_2C_2@C_{2v}(9)\text{-}C_{82}$ was allowed to undergo a 1,3-dipolar reaction, affording three monoadduct isomers. X-ray data of the most abundant adduct **2a** confirm a [5,6]-closed structure, while the two minor adducts (**2b** and **2c**) are seemingly [6,6] isomers. Theoretical considerations reveal that the addition is driven by HOMO/LUMO matching between the endohedral fullerene and the ylide. The adducts are more stable than the pristine EMFs and potentially more useful in future applications. Our results have clarified the uncertain structure of the long-believed $Sc_2@C_{2v}(17)\text{-}C_{84}$, and provided information about the chemical properties of these less explored CCMFs, which will certainly stimulate more interest in the nature and intrinsic properties of EMFs. Finally, because all isolated Sc_2C_{84} isomers have now been identified as CCMF species, earlier results relating to "$Sc_2@C_{84}$" should be reconsidered.[13]

Experimental Section

Experimental details are presented in the Supporting Information.

Black crystals of **2a** were obtained by layering hexane over a nearly saturated toluene solution at 253 K. X-ray data were collected at 100 K with an AXS SMART APEX II machine (Bruker Analytik, Germany) equipped with a CCD camera. The structure was solved by a direct method and refined by using SHELX-97.[14] CCDC 865917 (**2a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Calculations were conducted with the Gaussian 03 program package.[15] Geometries were optimized at the B3LYP level[16] with the effective core potential (ECP) and (5s5p5d)/[4s4p3d] basis set for Sc[17] and the split-valence d-polarized 6-31G(d) basis set for C.[18]

Received: February 17, 2012

Keywords: carbides · cluster compounds · fullerenes · scandium · structure elucidation

---

[1] For representative reviews, see a) T. Akasaka, F. Wudl, S. Nagase, *Chemistry of Nanocarbons*, Wiley-Blackwell, London, **2010**; b) L. Dunsch, S. F. Yang, *Small* **2007**, *3*, 1298–1320; c) M. N. Chaur, F. Melin, A. L. Ortiz, L. Echegoyen, *Angew. Chem.* **2009**, *121*, 7650–7675; *Angew. Chem. Int. Ed.* **2009**, *48*, 7514–7538; d) M. Yamada, T. Akasaka, S. Nagase, *Acc. Chem. Res.* **2010**, *43*, 92–102; e) A. Rodríguez-Fortea, A. L. Balch, J. M. Poblet, *Chem. Soc. Rev.* **2011**, *40*, 3551–3563; f) X. Lu, T. Akasaka, S. Nagase, *Chem. Commun.* **2011**, *47*, 5942–5957.

[2] a) T. Akasaka, S. Nagase, K. Kobayashi, M. Walchli, 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; b) H. Kurihara, X. Lu, Y. Iiduka, N. Mizorogi, Z. Slanina, T. Tsuchiya, S. Nagase, T. Akasaka, *Chem. Commun.* **2012**, *48*, 1290–1292.

[3] 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) Y. Iiduka, et al., *J. Am. Chem. Soc.* **2005**, *127*, 12500–12501; c) Y. Iiduka, T. Wakahara, K. Nakajima, T. Tsuchiya, T. Nakahodo, Y. Maeda, T. Akasaka, N. Mizorogi, S. Nagase, *Chem. Commun.* **2006**, 2057–2059; d) Y. Iiduka, et al., *Angew. Chem.* **2007**, *119*, 5658–5660; *Angew. Chem. Int. Ed.* **2007**, *46*, 5562–5564; e) Y. Yamazaki, K. Nakajima, T. Wakahara, T. Tsuchiya, M. O. Ishitsuka, Y. Maeda, T. Akasaka, M. Waelchli, N. Mizorogi, S. Nagase, *Angew. Chem.* **2008**, *120*, 8023–8026; *Angew. Chem. Int. Ed.* **2008**, *47*, 7905–7908; f) H. Kurihara, X. Lu, Y. Iiduka, N. Mizorogi, Z. Slanina, T. Tsuchiya, T. Akasaka,

S. Nagase, *J. Am. Chem. Soc.* **2011**, *133*, 2382–2385; g) X. Lu, K. Nakajima, Y. Iiduka, H. Nikawa, N. Mizorogi, Z. Slanina, T. Tsuchiya, S. Nagase, T. Akasaka, *J. Am. Chem. Soc.* **2011**, *133*, 19553–19558; h) H. Kurihara, X. Lu, Y. Iiduka, H. Nikawa, M. Hachiya, N. Mizorogi, Z. Slanina, T. Tsuchiya, S. Nagase, T. Akasaka, *Inorg. Chem.* **2012**, *51*, 746–750.

[4] a) S. Stevenson, et al., *Nature* **1999**, *401*, 55–57; b) T. M. Zuo, C. M. Beavers, J. C. Duchamp, A. Campbell, H. C. Dorn, M. M. Olmstead, A. L. Balch, *J. Am. Chem. Soc.* **2007**, *129*, 2035–2043; c) C. M. Beavers, M. N. Chaur, M. M. Olmstead, L. Echegoyen, A. L. Balch, *J. Am. Chem. Soc.* **2009**, *131*, 11519–11524.

[5] a) S. Stevenson, M. A. Mackey, M. A. Stuart, J. P. Phillips, M. L. Easterling, C. J. Chancellor, M. M. Olmstead, A. L. Balch, *J. Am. Chem. Soc.* **2008**, *130*, 11844–11845; b) B. Q. Mercado, et al., *J. Am. Chem. Soc.* **2010**, *132*, 12098–12105.

[6] B. Q. Mercado, N. Chen, A. Rodriguez-Fortea, M. A. Mackey, S. Stevenson, L. Echegoyen, J. M. Poblet, M. M. Olmstead, A. L. Balch, *J. Am. Chem. Soc.* **2011**, *133*, 6752–6760.

[7] T. S. Wang, et al., *J. Am. Chem. Soc.* **2010**, *132*, 16362–16364.

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

[9] M. Inakuma, E. Yamamoto, T. Kai, C. R. Wang, T. Tomiyama, H. Shinohara, T. J. S. Dennis, M. Hulman, M. Krause, H. Kuzmany, *J. Phys. Chem. B* **2000**, *104*, 5072–5077.

[10] C. R. Wang, M. Inakuma, H. Shinohara, *Chem. Phys. Lett.* **1999**, *300*, 379–384.

[11] P. W. Fowler, D. E. Manolopoulos, *An Atlas of Fullerenes*, Oxford Press, Clarendon, **1995**.

[12] Crystal data of a black plate of $Sc_2C_2@C_{82}(CH_2)_2NC(C_6H_5)_3 \cdot C_6H_{14} \cdot C_7H_8$: $C_{118}H_{41}NSc_2$, $M = 1562.44\ \mathrm{g\,mol^{1}}$; $0.30 \times 0.20 \times 0.05$ mm; monoclinic, $P21/n$; $a = 11.0575(14)$, $b = 21.477(3)$, $c = 27.282(3)$ Å; $V = 6438.5(14)$ Å^3; $Z = 4$; $\rho_{\mathrm{calcd}} = 1.612\ \mathrm{g\,cm^{-3}}$; $\mu(\mathrm{Mo_{K\alpha}}) = 0.283\ \mathrm{mm^{-1}}$; $\theta = 1.21$–$27.90°$; $T = 100$ K; $R_1 = 0.1373$, $wR_2 = 0.2414$ for all data; $R_1 = 0.0840$, $wR_2 = 0.2414$ for 8977 reflections ($I > 2.0\sigma(I)$) with 1398 parameters. Maximum residual electron density 1.215 e Å^{-3}.

[13] a) M. Krause, M. Hulman, H. Kuzmany, P. Kuran, L. Dunsch, T. J. S. Dennis, M. Inakuma, H. Shinohara, *J. Mol. Struct.* **2000**, *521*, 325–340; b) K. Suenaga, T. Okazaki, C. R. Wang, S. Bandow, H. Shinohara, S. Iijima, *Phys. Rev. Lett.* **2003**, *90*, 055506.

[14] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, *64*, 112–122.

[15] Gaussian03 (Revision C.01), M. J. Frisch, et al., Gaussian Inc., Wallingford, CT, **2004**.

[16] a) A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098–3100; b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785–789; c) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652.

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

[18] M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. DeFrees, J. A. Pople, *J. Chem. Phys.* **1982**, *77*, 3654–3665.