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Unexpected Formation of a $Sc_3C_2@C_{80}$ Bisfulleroid Derivative

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Supporting Information

ABSTRACT: The reaction of tetrazine **1** with $Sc_3C_2@C_{80}$ exclusively affords the open-cage derivative **2** instead of the expected C_2-inserted derivative **3** bearing a four-membered ring, as previously obtained for C_{60}. The structure of **2** has been firmly established by NMR spectroscopy and theoretical calculations. EPR spectroscopy shows that a single Sc atom of the Sc_3C_2 cluster gets located within the bulge created by the bridging addend, which is a first step toward release of the internal metal atoms.

The chemical derivatization of fullerenes has largely taken advantage of their spherical structures and rich electronic properties. From the exohedral point of view, the strained nature of the sp^2-hybridized cage carbons allows them to undergo a wide variety of chemical transformations, resulting, among others, in useful materials for electronic, photovoltaic, or biological applications.[1] From the endohedral point of view, the subnanosized interior of fullerenes is capable of hosting various atoms or small molecules and even otherwise unstable species, affording a large family of endohedral fullerene complexes.[2] When metallic clusters are encapsulated, multielectron transfer from the internal metal atoms to the cage occurs, imparting fantastic physicochemical properties to the endohedral metallofullerenes (EMFs).[2]

The framework or topological modification of fullerenes can be considered a third aspect of their rich chemistry that derives from single or multiple bond-rearrangement processes of exohedral addition products. Since fullerenes are generally obtained as topogically restricted cages made up of five- and six-membered ring combinations [according to the "isolated pentagon rule" (IPR)], the generation of smaller or larger rings within fullerene cages has become an exciting target of research.

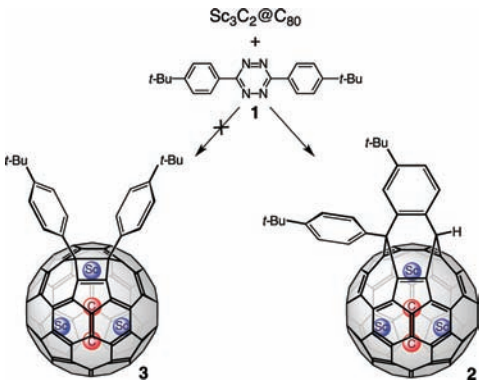
Azafullerene $C_{59}N$ was the first discovered heterofullerene prepared by this approach.[3] Its synthesis results from a striking rearrangement sequence involving an 11-membered ring-scission intermediate.[3] Since then, a number of interesting transformations of C_{60} adducts have succeeded in introducing four- to seven-membered rings within the fullerene framework.[3,4]

Importantly, the "molecular surgery" concept, which uses a rational synthetic approach to open fullerene cages by exploiting the ring-expansion method, has permitted the creation of orifices large enough to enable the introduction of atoms (He, Ne) or small molecules (H_2, H_2O, NH_3 or CH_4) into the cage[5] as well as the ability to reclose the opened cage to its original framework, encaging the entrapped species.[6]

EMFs are now easily available through carbon evaporation methods.[2] They encapsulate metal clusters that would otherwise not exist without the steric and electronic protection of the fullerene cage. It seemed intriguing to determine whether opening an orifice within the cage of an EMF could let one or more metal atoms "leak" out of the cage. This process would be the reverse of the incorporation approach and would present an interesting approach for producing empty or partially occupied large fullerene cages otherwise not available through carbon evaporation methods. Such molecules would be both interesting in structure and promising for practical uses, not only because EMFs can be obtained in high yields when they encapsulate rare-earth metals but also because the latter metals are the basis of many magnetic, optical, electronic, and catalytic applications.[7]

In this context, we report our first results of attempts to open the cage of an EMF through the reaction between a substituted tetrazine, **1**, and $Sc_3C_2@C_{80}$ (Scheme 1). This reagent was previously shown by Rubin and co-workers to insert a C_2 unit into the framework of C_{60}, resulting in a stable C_{62} derivative incorporating a four-membered ring as part of the cage.[4a]

Scheme 1. Reaction of Tetrazine 1 with $Sc_3C_2@C_{80}$ Giving Bisfulleroid 2 Instead of the Expected Four-Membered Ring Product 3



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However, our results revealed that addition of **1** to $Sc_3C_2@C_{80}$ does not form the expected C_2-inserted adduct **3** but affords instead the unprecedented EMF derivative **2** having a bisfulleroid structure containing a doubly bridged 14-membered ring. The structure of bisfulleroid **2** has been unequivocally established through extensive experimental and theoretical NMR characterization.

The reaction between $Sc_3C_2@C_{80}$ and a large excess of tetrazine **1** proceeded smoothly in ODCB at 180 °C, although it was much slower than the corresponding reaction between **1** and C_{60},[4a] necessitating 60 h of reaction time. The reaction was monitored by HPLC, and the profiles are shown in Figure 1a. After 60 h, when more than 60% of the starting $Sc_3C_2@C_{80}$ had been consumed, the reaction was terminated, and the product was separated from the reaction mixture by preparative HPLC in ~50% yield. The MALDI–TOF mass spectrum (Figure 1b) displays a single peak at *m*/*z* 1409, which could easily be ascribed to $Sc_3C_2@C_{80}(C_{22}H_{26})$, and the observed isotopic distribution agreed perfectly with the theoretical one. The lack of any fragmentation is indicative of the high stability of the adduct. Unfortunately, at this stage it was not possible to determine whether **2**, **3**, or another isomer was formed, since they have the same molecular formula.

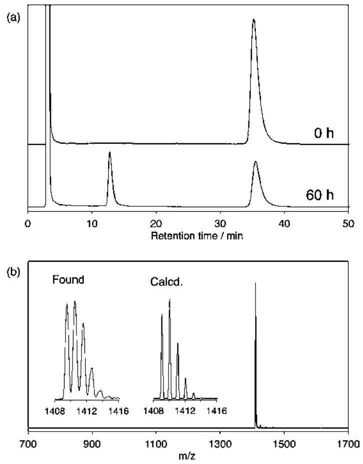
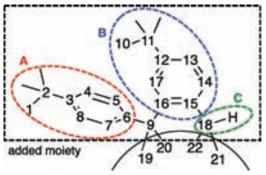


Figure 1. (a) HPLC traces of the reaction between $Sc_3C_2@C_{80}$ and **1**. (b) MALDI–TOF spectrum of isolated **2**.

To get structural information on the derivative, several NMR methods were used. However, the paramagnetic characteristics of **2** prevented direct NMR analysis. Thus, chemical reduction with pyridine in presence of $Bu_4N^+ClO_4^-$ was first performed to obtain the corresponding anion,[8] allowing several NMR measurements to be performed. The respective ^1H NMR and ^{13}C NMR spectra of $\mathbf{2}^-$ are shown in Figures S2 and S3,[9] and typical values are summarized in Table 1. The ^1H NMR spectrum of $\mathbf{2}^-$ displays 10 peaks that belong to the added moiety, while the ^{13}C NMR spectrum has 80 signals for the C_{80} cage, indicating that the adduct has C_1 symmetry. The signal of the encaged C_2 unit was not observed (a ^{13}C-enriched sample was not prepared). The lack of symmetry was surprising because the expected four-membered-ring derivative **3** would have been C_s-symmetric if the addition took place at the expected [5,6] bond. Moreover, the ^1H signals from the addend in **3** would have appeared as only three sets of peaks.

Table 1. Selected NMR Data Proving the Addend Structure of 2



δ (ppm)			
atom	^{13}C	$^1H^a$	HMBC ^1H–^{13}C
1	31.60	1.35 (s, 9H)	C-1, C-2, C-3
2	35.53		
3	151.62		
4	126.48	7.58 (dd, 8.7, 2.0, 1H)	C-2, C-6, C-8
5	129.20	8.03 (m, 1H)	C-3, C-7, C-9
6	142.25		
7	131.02	7.93 (m, 1H)	C-3, C-5, C-9
8	124.73	7.56 (dd, 8.7, 2.0, 1H)	C-2, C-4, C-6
9	54.82		
10	31.47	1.28 (s, 9H)	C-10, C-11, C-12
11	35.21		
12	152.42		
13	126.77	7.72 (d, 7.7, 2.0, 1H)	C-11, C-17, C-15
14	129.61	8.05 (d, 7.7, 1H)	C-12, C-16, C-18
15	132.51		
16	140.02		
17	127.24	7.34 (d, 2.0, 1H)	C-9, C-11, C-13, C-15
18	42.30	6.21 (s, 1H)	

[a] The peak multiplicity, coupling constant(s) (*J*, in Hz), and integral are given in parentheses.

Single-crystal X-ray diffraction is certainly the most reliable method to get structural information,[10] but numerous attempts to obtain suitable single crystals of derivative **2** were unproductive; although a few good-looking single crystals were obtained, the diffraction patterns they provided did not allow any structural determination. The reasons for this are not completely clear, but it is likely that the *tert*-butyl groups introduce too much disorder in the crystal. As a result, we turned to a combination of theoretical and experimental NMR characterization, which in the end provided strong confirmation of the molecular structure of **2**. As shown in Table 1, additional NMR experiments were performed. The DEPT 135 measurement (Figure S4b)[9] clearly showed the presence of seven types of CH sp^2 carbons, one CH sp^3 carbon, and two CH_3 carbons, while the HSQC and COSY spectra allowed easy assignment of the C_6H_4-*t*-Bu (part A, red circle), C_6H_3-*t*-Bu (part B, blue circle), and sp^3 C–H (part C, green circle) substructures (Table 1). The last substructure is characteristic of a hydrogen directly bonded to an sp^3 carbon of the fullerene cage.[11] Furthermore, connections among these partial structures were reasonably established from the correlations observed in the HMBC experiment. For instance, bonding between C6, C9, and C16 was established from correlations between C9 and H5, H7, and H17, while a correlation between C18 and H14 indicated that C15 is attached to the bond at C18 (Figure S7).[9] On the basis of these results, the structure of the added moiety can be firmly established.

Although the addend structure was determined by NMR spectroscopy, the exact addition location of the addend was still not clear from these experimental NMR data. The I_h-C_{80} cage has two different types of bonds, those at [5,6] junctions and those at [6,6] junctions. Cycloaddition to a [5,6] junction would give rise to only a single isomer, defined as a [5,6]

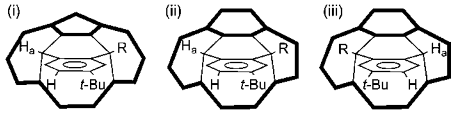
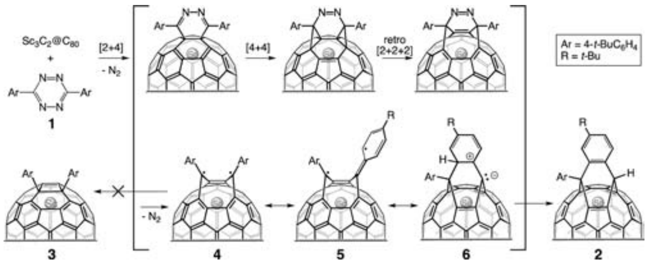


Figure 2. Possible addition patterns in **2**: (**i**) [5,6] adduct; (**ii**) [6,6] adduct with H18 over a cage hexagon; (**iii**) [6,6] adduct with H18 over a cage pentagon.

adduct (isomer **i** in Figure 2), while addition to a [6,6] junction should afford two isomers, with the methine hydrogen H18 (linked to C18) lying above either a seven-membered ring (isomer **ii**) or a six-membered ring (isomer **iii**). To help distinguish these three isomers and determine the addition position, the ^{1}H and ^{13}C NMR spectra of isomers **i**−**iii** were calculated[9] using the B3LYP functional[12] and the 3-21G∼LA (LA = LANL2DZ), 6-31G*∼LA, and 6-31G*∼SDD combined basis sets[13] as implemented in Gaussian 09,[14] and the results are shown in Figures S9 and S10.[9] Comparison with the experimental data easily rules out isomer **iii** (Figure 2) because the calculated signal of H18 is strongly shielded relative to its observed chemical shift. Although the calculated ^{1}H NMR spectra of isomers **i** and **ii** are rather similar, and both are consistent with the observed spectrum of $\mathbf{2}^-$, their ^{13}C NMR spectra are different enough to allow the final assignment (Figure S10).[9] From a comparison with the experimental ^{13}C NMR spectrum of $\mathbf{2}^-$, it is evident that the calculated pattern of isomer **i** is more consistent with the experimental result than that of isomer **ii**, especially for the signals of the four cage carbons connected with the addend (C19, C20, C21, and C22 in the Table 1 scheme). Accordingly, we conclude that $\mathbf{2}^-$ is the [5,6] adduct of $Sc_3C_2@C_{80}$ corresponding to isomer **i** in Figure 2. The [5,6] addition pattern is also supported by our experimental results, since only a single isomer was obtained. If the addition had taken place at a [6,6] bond, both **ii** and **iii** would have been formed, since there is no significant steric difference between the diradical intermediates of type **4** shown in the mechanism of this reaction (see Scheme 2). Furthermore, this is also consistent with previous reports showing that [4 + 2] cycloaddition to $Sc_3N@C_{80}$, which has the same I_h-C_{80} cage, exclusively affords the [5,6] adduct.[15]

Scheme 2. Plausible Mechanism for the Formation of 2



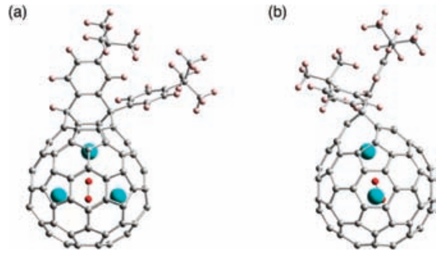


Figure 3. Optimized structure of **2**: (a) front view; (b) side view.

The molecular structure of **2**, calculated at the B3LYP level (Figure 3), shows that the addition of **1** to the highly symmetric I_h-C_{80} cage has considerably expanded the inner space of the C_{80} framework. This asymmetric cage expansion allows a Sc atom of the Sc_3C_2 cluster to become trapped within the bisfulleroid "bulge". The two other Sc atoms are positioned in such a way that they form a regular triangle with the first Sc, and all are coplanar with the endohedral C_2 unit. Because of the asymmetry of the addend, the whole molecule has C_1 symmetry, which is consistent with the NMR results.

Scheme 2 portrays the most plausible reaction pathway to generate structure **2** by the reaction between $Sc_3C_2@C_{80}$ and tetrazine **1**. The first two steps are [4 + 4] and retro-[2 + 2 + 2] cycloadditions identical to those in the reaction between C_{60} and substituted tetrazines.[4a] However, while the reaction with C_{60} proceeds via a doubly "benzylic" biradical intermediate that collapses to the corresponding C_{62} derivative incorporating a four-membered ring as part of the fullerene framework,[4a] the larger cage of $Sc_3C_2@C_{80}$ does not seem to favor the corresponding four-membered ring structure. This is due to the lower degree of pyramidalization of the carbons of fullerene cages larger than C_{60}.[16] This statement is corroborated by the DFT calculations, which shows that $Sc_3C_2@C_{80}$ derivative **3** cannot keep its four-membered ring intact. During calculations on a simplified species in which the *t*-Bu groups of **3** were replaced by H's (Figure S11), the C−C bond connecting the two benzylic carbons within the four-membered ring extends, releasing strain (the resulting interatomic distance is 1.772, 1.764, and 1.761 Å with the 3-21G∼LA, 6-31G*∼LA, and 6-31G*∼SDD basis sets, respectively).[9,17] Still, one could consider this C−C bond as a weak single bond, as its Wiberg bond index[13f] at the 6-31G*∼SDD level is 0.839. In contrast, the indices for the adjacent three bonds originating from the two benzylic carbons are 0.981, 0.966, and 0.962.

However, as shown in Scheme 2, one of the benzylic radicals of intermediate **4** recombines with the other radical through its hexadienyl radical resonance structure **5**, forming a very stable six-membered ring within bisfulleroid **2** after 1,3-hydrogen migration from intermediate **6**.

The Sc_3C_2 cluster orientation suggested by the calculations was also confirmed by EPR studies. Figure 4 depicts the experimental and simulated EPR spectra of **2**. Two sets of hyperfine coupling constants (hfcc's) can be distinguished at 6.73 G (one nucleus) and 4.00 G (two nuclei), suggesting two nonequivalent types of Sc nuclei in a 1:2 ratio. Since pristine $Sc_3C_2@C_{80}$ displays a pattern consisting of 22 lines (hfcc = 6.51, g = 1.9985) with three equivalent Sc nuclei,[18] the EPR pattern of **2** confirms that one Sc atom is trapped inside the bulge provided by the addend while the other two Sc atoms are rotating along the long axis of the cage. Similar observations have been reported for other $Sc_3C_2@C_{80}$ derivatives, such as the carbene adduct $Sc_3C_2@C_{80}$(Ad) (Ad = adamantylidene) (7.39, 1.99 G)[8] and the Prato adduct $Sc_3C_2@C_{80}$ fulleropyrrolidine (8.602, 4.822 G),[19] but the hfcc's of these systems differ greatly. These results provide an effective and versatile way to alter the spin properties of paramagnetic metal−carbon systems, making them particularly promising components of high-density memories and quantum-computing systems.

In conclusion, our first attempt to synthesize a C_2-inserted derivative of $Sc_3C_2@C_{80}$ provided instead the surprising bisfulleroid

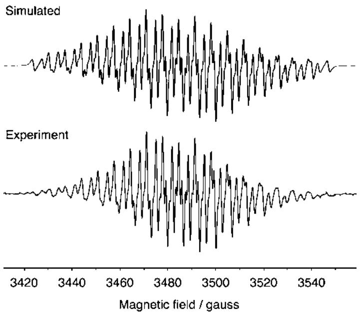


Figure 4. Experimental and simulated EPR spectra of **2**.

derivative **2** having a significant protruding addend that traps one of the Sc atoms. NMR experiments and DFT calculations have firmly established the molecular structure of **2**. EPR spectroscopy confirmed that one Sc atom of the Sc_3C_2 cluster is trapped inside the bulge, leaving the other two Sc atoms able to rotate around the cage. Future work will investigate the use of other cage expansion methods[5,6] to form an orifice within the framework of EMFs and, if possible, accomplish the release of the metal cluster.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Complete ref 14, experimental details, HPLC profiles, observed and calculated NMR spectra of 2^-, and the optimized structure of **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Hirsch, A. *The Chemistry of the Fullerenes*; Wiley-VCH, Weinheim, Germany, 2005.

(2) *Endofullerenes: A New Family of Carbon Clusters*; Akasaka, T., Nagase, S., Eds.; Kluwer: Dordrecht, The Netherlands, 2002.

(3) (a) Hummelen, J. C.; Knight, B.; Pavlovich, J.; González, R.; Wudl, F. *Science* **1995**, *269*, 1554. (b) Nuber, B.; Hirsch, A. *Chem. Commun.* **1996**, 1421. (c) Vostrowsky, O.; Hirsch, A. *Chem. Rev.* **2006**, *106*, 5191.

(4) (a) Qian, W.; Chuang, S.-C.; Amador, R. B.; Jarrosson, T.; Sander, M.; Pieniazek, S.; Khan, S. I.; Rubin, Y. *J. Am. Chem. Soc.* **2003**, *125*, 2066. (b) Ioffe, I.; Chen, C.; Yang, S.; Sidorov, L.; Kemnitz, E.; Troyanov, S. *Angew. Chem., Int. Ed.* **2010**, *49*, 4784.

(5) (a) Rubin, Y.; Jarrosson, T.; Wang, G.-W.; Bartberger, M. D.; Schick, G.; Saunders, M.; Cross, R. J.; Houk, K. N. *Angew. Chem., Int. Ed.* **2001**, *40*, 1543. (b) Murata, M.; Murata, Y.; Komatsu, K. *Chem. Commun.* **2008**, 6083. (c) Murata, Y.; Murata, M.; Komatsu, K. *J. Am. Chem. Soc.* **2003**, *125*, 7152. (d) Murata, Y.; Murata, M.; Komatsu, K. *Chem.—Eur. J.* **2003**, *9*, 1600. (e) Yu, Y.; Xie, X.; Zhang, T.; Liu, S.; Shao, Y.; Gan, L.; Li, Y. *J. Org. Chem.* **2011**, *76*, 10148. (f) Iwamatsu, S.; Uozaki, T.; Kobayashi, K.; Re, S.; Nagase, S.; Murata, S. *J. Am. Chem. Soc.* **2004**, *126*, 2668. (g) Whitener, K. E. Jr.; Frunzi, M.; Iwamatsu, S.; Murata, S. R.; Cross, J.; Saunders, M. *J. Am. Chem. Soc.* **2008**, *130*, 13996. (h) Gan, L.; Yang, D.; Zhang, Q.; Huang, H. *Adv. Mater.* **2010**, *22*, 1498. (i) Vougioukalakis, G. C.; Roubelakis, M. M.; Orfanopoulos, M. *Chem. Soc. Rev.* **2010**, *39*, 817.

(6) (a) Komatsu, K.; Murata, M.; Murata, Y. *Science* **2005**, *307*, 238. (b) Kurotobi, K.; Murata, Y. *Science* **2011**, *333*, 613.

(7) (a) *Chemistry of Nanocarbons*; Akasaka, T., Wudl, F., Nagase, S., Eds.; Wiley: Chichester, U.K., 2010. (b) Dunsch, L.; Yang, S. *Small* **2007**, *3*, 1298. (c) Chaur, M. N.; Melin, F.; Ortiz, A. L.; Echegoyen, L. *Angew. Chem., Int. Ed.* **2009**, *48*, 7514. (d) Yamada, M.; Akasaka, T.; Nagase, S. *Acc. Chem. Res.* **2010**, *43*, 92. (e) Osuna, S.; Swart, M.; Solà, M. *Phys. Chem. Chem. Phys.* **2011**, *13*, 3585.

(8) Iiduka, Y.; Wakahara, T.; Nakahodo, T.; Tsuchiya, T.; Sakuraba, A.; Maeda, Y.; Akasaka, T.; Yoza, K.; Horn, E.; Kato, T.; Liu, M. T. H.; Mizorogi, N.; Kobayashi, K.; Nagase, S. *J. Am. Chem. Soc.* **2005**, *127*, 12500.

(9) See the Supporting Information.

(10) (a) Lu, X.; Nikawa, H.; Tsuchiya, T.; Akasaka, T.; Toki, M.; Sawa, H.; Mizorogi, N.; Nagase, S. *Angew. Chem., Int. Ed.* **2010**, *49*, 594. (b) Lu, X.; Nikawa, H.; Kikuchi, T.; Mizorogi, N.; Slanina, Z.; Tsuchiya, T.; Nagase, S.; Akasaka, T. *Angew. Chem., Int. Ed.* **2011**, *50*, 6356.

(11) (a) Fagan, P. J.; Krusic, P. J.; Evans, D. H.; Lerke, S. A.; Johnston, E. *J. Am. Chem. Soc.* **1992**, *114*, 9697. (b) Anderson, H. L.; Faust, R.; Rubin, Y.; Diederich, F. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1366. (c) Matsuo, Y.; Iwashita, A.; Abe, Y.; Li, C.-Z.; Matsuo, K.; Hashiguchi, M.; Nakamura, E. *J. Am. Chem. Soc.* **2008**, *130*, 15429.

(12) (a) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (c) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(13) (a) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939. (b) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299. (c) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; DeFrees, D. J.; Pople, J. A.; Gordon, M. S. *J. Chem. Phys.* **1982**, *77*, 3654. (d) Cao, X. Y.; Dolg, M. *THEOCHEM* **2002**, *581*, 139. (e) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650. (f) Wiberg, K. B. *Tetrahedron* **1968**, *24*, 1083. (g) Reed, A. E.; Weinstock, R. B.; Weinhold, F. J. *J. Chem. Phys.* **1985**, *83*, 735.

(14) Frisch, M. J. et al.; *Gaussian 09*, revision A.02; Gaussian, Inc.: Wallingford, CT, 2009.

(15) (a) Iezzi, E. B.; Duchamp, J. C.; Harich, K.; Glass, T. E.; Lee, H. M.; Olmstead, M. M.; Balch, A. L.; Dorn, H. C. *J. Am. Chem. Soc.* **2002**, *124*, 524. (b) Lee, H. M.; Olmstead, M. M.; Iezzi, E.; Duchamp, J. C.; Dorn, H. C.; Balch, A. L. *J. Am. Chem. Soc.* **2002**, *124*, 3494.

(16) Cyrański, M. K.; Howard, S. T.; Chodkiewicz, M. L. *Chem. Commun.* **2004**, 2458.

(17) For recent record C—C bond lengths in sterically crowded molecules and related background, see: Schreiner, P. R.; Chernish, L. V.; Gunchenko, P. A.; Tikhonchuk, E. Y.; Hausmann, H.; Serafin, M.; Schlecht, S.; Dahl, J. E. P.; Carlson, R. M. K.; Fokin, A. A. *Nature* **2011**, *477*, 308.

(18) Shinohara, H.; Inakuma, M.; Hayashi, N.; Sato, H.; Saito, Y.; Kato, T.; Bandow, S. *J. Phys. Chem.* **1994**, *98*, 8597.

(19) Wang, T.; Wu, J.; Xu, W.; Xiang, J.; Lu, X.; Li, B.; Jiang, L.; Shu, C.; Wang, C. *Angew. Chem., Int. Ed.* **2010**, *49*, 1786.