Supramolecular Chemistry

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# Highly Regioselective Addition of Adamantylidene Carbene to Yb@$C_{2v}$(3)-$C_{80}$ to Afford the First Derivative of Divalent Metallofullerenes**

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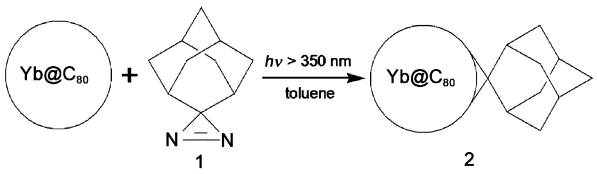
Endohedral metallofullerenes (EMFs), a new family of metal–carbon hybrid molecules formed by encapsulation of metallic species inside fullerene cages, have attracted a great deal of attention because of their unique structures, fascinating properties, and potential applications in such fields as materials science, photovoltaics, nanoelectronics, and biomedicine.[1] During the past two decades, many examples of EMFs encapsulating a wide range of metallic species have been successfully synthesized and characterized. The results showed that not only pure metals,[2] but also some otherwise unstable metallic species, such as a cluster of 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 even metal cyanide ($M_3CN$)[7] can also be encapsulated inside fullerene cages, thereby forming stable cluster-EMFs.

One of the most intriguing features of EMFs is intramolecular electron transfer from the entrapped metallic species to the surrounding cage. For elucidating metal–cage interactions, the most suitable prototypes of EMFs are those compounds containing only one metal ion (mono-EMFs).[2a] Mono-EMFs are classified into two categories according to the number of transferred electrons: divalent EMFs and trivalent EMFs.[8] They show distinct differences in terms of both their molecular structures and inherent properties. In particular, the yield of divalent EMFs is much lower than that of the trivalent ones, which has resulted in divalent EMFs having rarely been explored. In particular, no report on the chemical properties of divalent EMFs is available, while the many recent investigations on trivalent EMFs have afforded many meaningful results related to the templating effect of the internal metal ion on the chemical properties of the cage carbon atoms.[9]

Herein, we present our first attempt to functionalize a divalent metallofullerene by performing an electrophilic cycloaddition reaction of 2-adamantane-2,3-[3*H*]-diazirine ($AdN_2$, **1**; Scheme 1) with Yb@$C_{2v}$(3)-$C_{80}$, which is a typical divalent EMF with a clearly elucidated molecular structure.[10] Fortunately, but surprisingly, the reaction features very high regioselectivity and affords only one monoadduct isomer (**2**), which has been systematically characterized by using a series of experimental techniques.




***Scheme 1.*** Photochemical reaction of Yb@$C_{2v}$(3)-$C_{80}$ with **1**.

The reaction of Yb@$C_{2v}$(3)-$C_{80}$ and **1** (ca. 50 fold) was triggered by light. The progress of the reaction was tracked by HPLC (see Figure S1 in the Supporting Information). It was terminated when a small amount of bisadduct had formed. The sole monoadduct isomer Yb@$C_{2v}$(3)-$C_{80}$Ad (**2**) was finally isolated in a high yield of 95% based on the consumed Yb@$C_{2v}$(3)-$C_{80}$ (Figure 1). The purity of **2** was estimated to be higher than 99% by HPLC on several different columns (see Figure S2 in the Supporting Information).

A MALDI-TOF mass spectrometric study verified the successful attachment of the Ad moiety onto the fullerene cage (Figure 1, inset). The single signal observed at $m/z$ 1269 corresponds to a 1:1 adduct, and its isotropic distribution agrees well with the calculated pattern of Yb@$C_{2v}$(3)-$C_{80}$-($C_{10}H_{14}$) (see Figure S3 in the Supporting Information). The absence of any fragmentation signals reflects the high stability

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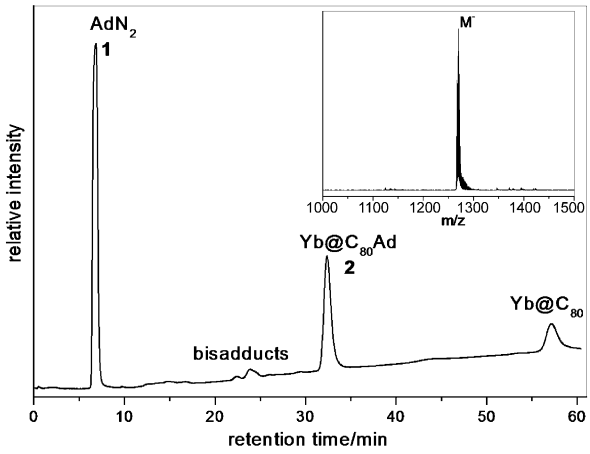


***Figure 1.*** HPLC separation of **2** from the reaction mixture on a Buckyprep column with a toluene flow rate of 10 mL min$^{-1}$. The inset shows the mass spectrum of **2** in a negative linear mode.

of the derivative, thus promising its potential application in photovoltaics and electronics.

To determine the addition pattern in **2** unambiguously, single crystallization was performed using an interfacial diffusion method. Black single crystals of **2** were obtained, thereby finally enabling an accurate X-ray elucidation of its molecular structure.[11]

The asymmetric crystallographic unit contains two molecules of **2**: one cage is fully ordered, but the other features two cage orientations that are enantiomers. Hexane and $CS_2$ molecules are intercalated in the cell cavities. Multiple metal positions are found in the cages, thus indicating a dynamic motion of the internal metal ion. Figure 2 shows the X-ray structure of **2** with the fully ordered cage and the major metal site (Yb1a, 0.43 occupancy). The Ad group adds to a [5,6]-bond junction at the most curved part of the cage. The distance between the two carbon atoms at the sites of addition (2.063 Å) confirms an open-cage structure. An earlier crystallographic study of Yb@$C_{80}$ cocrystallized with nickel porphyrin established that the $Yb^{2+}$ cation is localized under a hexagonal ring away from the twofold axis of the $C_{80}$ cage.[10b] The multiple metal positions found in **2** verify that the Ad addition has markedly changed the metal location. A detailed examination of the X-ray structure of **2** reveals that the fixed metal ion in underivatized Yb@$C_{80}$ has been spread into three different areas, with most metal sites being trapped inside the cavity produced by bond breaking on addition of Ad (see Figure S4 in the Supporting Information). This fact demonstrates that exohedral modification is a practical strategy to alter the motional behavior of the untouchable metal ions in EMFs. Several successful examples related to the positional control of the multiple metal ions in di-EMFs and cluster-EMFs have been reported,[1b] but for mono-EMFs, only the $La^{3+}$ ion in La@$C_{74}$ has been found to be sensitive to the addition positions of the substituent.[12] This study further corroborates that the position/motion of a divalent ion (e.g. $Yb^{2+}$) is also controllable through chemical modification.

The electrophilic adamantylidene carbene (**1**) has shown great success in differentiating the reactivity of cage carbon atoms of EMFs. A thorough examination of the Ad derivatives of trivalent EMFs M@$C_{82}$ (M = Sc, Y, La, Ce, Gd)[13] and $M_2$@$C_{2n}$ (M = La, Ce; $2n$ = 72, 78, 80)[14] confirms that the negative charges transferred from the internal trivalent metal ion(s) are more prominent than the local strains for mediating the reactivity of cage carbon atoms toward **1**. However, for Yb@$C_{2v}$(3)-$C_{80}$, which contains a divalent metal ion, the reactivity is mainly driven by release of the local strain on the cage carbon atoms at the site of addition. These carbon atoms, however, have lower charge densities than those carbon atoms near the $Yb^{2+}$ ion (see Figure S5 in the Supporting Information). It is, therefore, concluded tentatively that the chemical properties of divalent EMFs more resemble those of empty fullerenes, which all have closed-shell electronic structures, while they differ greatly from those of open-shell trivalent EMFs such as M@$C_{82}$ (M = Sc, Y, La, Ce, Gd, etc.).

The electronic properties of Yb@$C_{2v}$(3)-$C_{80}$ are little altered upon carbene addition. As Figure 3 shows, the absorption spectrum of **2** closely resembles that of underivatized Yb@$C_{2v}$(3)-$C_{80}$. Each shows two or three distinct absorption peaks in the visible region and a broad near-infrared band, but the corresponding absorptions of **2** are generally red-shifted by 5–15 nm. The onsets of both compounds are observed at 1460 nm, which corresponds to a relatively small optical bandgap (ca. 0.85 eV).

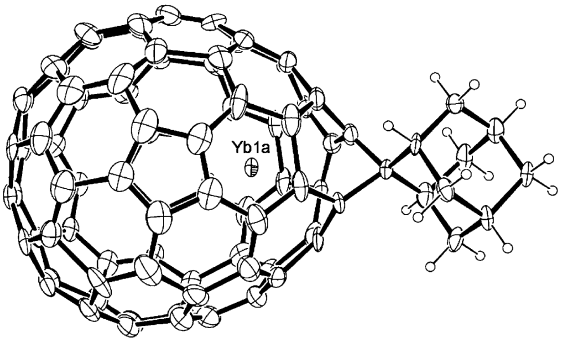


***Figure 2.*** Ortep drawing of **2** showing thermal ellipsoids at the 30% probability level. Solvent molecules and minor metal sites are omitted for clarity.

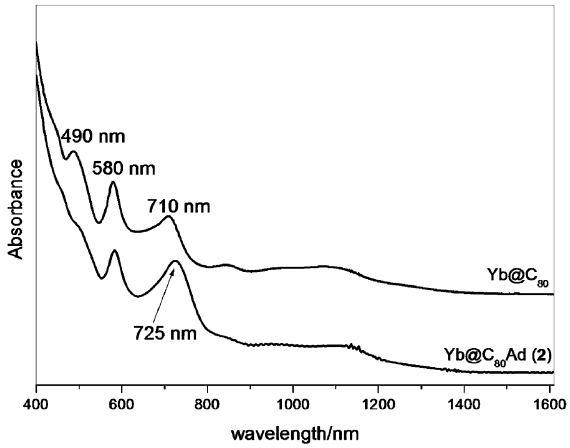


***Figure 3.*** Vis/NIR spectra of Yb@$C_{2v}$(3)-$C_{80}$ and **2**.

Figure 4 shows the cyclic voltammograms of Yb@$C_{2v}$(3)-$C_{80}$ and **2**. The parent sample exhibits one reversible oxidation step and four reduction processes, while the derivative shows two oxidation steps, which are irreversible, and four reversible

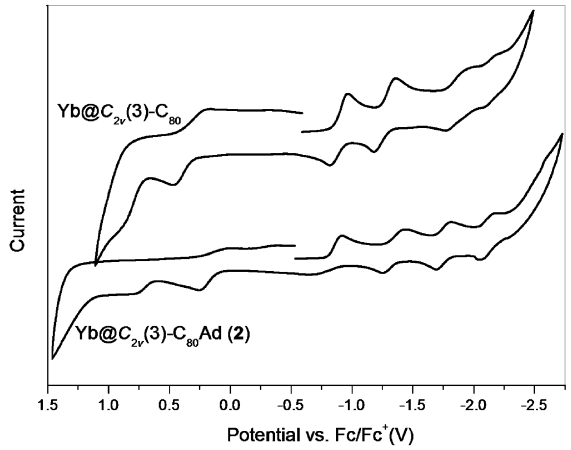


***Figure 4.*** Cyclic voltammograms of Yb@$C_{2v}$(3)-$C_{80}$ and **2**.

reduction processes. As compared with the redox properties of Yb@$C_{2v}$(3)-$C_{80}$, the third and the fourth reductions of **2** are more reversible, although the reversibility of its oxidation processes is completely lost. These changes may be related to the different dynamic behaviors of the metal ion in Yb@$C_{2v}$(3)-$C_{80}$ and **2**.[15] In addition, most of the redox potentials of **2** are shifted cathodically by 0.1–0.2 V compared with the corresponding values of Yb@$C_{2v}$(3)-$C_{80}$ (Table 1), thus confirming the electron-donating ability of Ad.

***Table 1:*** Redox potentials[a] (V versus Fc/Fc$^+$) of Yb@$C_{2v}$(3)-$C_{80}$ and **2**.

| Compound | $^{ox}E_2$ | $^{ox}E_1$ | $^{red}E_1$ | $^{red}E_2$ | $^{red}E_3$ | $^{red}E_4$ |
|---|---|---|---|---|---|---|
| Yb@$C_{2v}$(3)-$C_{80}$[c] | 0.78[b] | 0.34 | −0.89 | −1.27 | −1.87 | −2.13 |
| **2** | 0.66[b] | 0.13 | −0.81 | −1.34 | −1.76 | −2.13 |

[a] Half-wave potentials on a Pt working electrode in 1,2-dichlorobenzene containing 0.1 M ($n$Bu$_4$)NPF$_6$. [b] Irreversible; differential pulse voltammetry (DPV) values. [c] Ref. [10a]. Fc/Fc$^+$ = ferrocene/ferrecenium couple.

In conclusion, we have accomplished the first exohedral functionalization of a divalent metallofullerene by performing a regioselective cycloaddition reaction of adamantylidene carbene (**1**) to Yb@$C_{2v}$(3)-$C_{80}$, which afforded only one monoadduct isomer (**2**). X-ray crystallographic analyses of **2** confirm a [5,6]-open structure, and multiple positions of the single $Yb^{2+}$ ion have been identified. Our results suggest that the chemical reactivity of divalent EMFs differs greatly from that of the trivalent analogues, but that it is similar to that of empty fullerenes, with novel metal–cage interactions evident in divalent EMFs. Our study has shed new light on the chemical behaviors of divalent EMFs and will certainly stimulate more concerns on these less-explored species, finally making these low-yielding materials truly useful.

## *Experimental Section*

Experimental details are presented in the Supporting Information.

Black crystals of **2** were obtained by layering hexane over a saturated $CS_2$ solution of **2** for a period of two weeks. X-ray data were collected at 90 K on an AXS SMART machine (Bruker Analytik, Germany) equipped with an APEX II CCD camera. The structure was solved with a direct method and was refined using SHLEX 97.[16] CCDC 913852 (**2**) 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.

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[1] For recent reviews, see a) M. N. Chaur, F. Melin, A. L. Ortiz, L. Echegoyen, *Angew. Chem.* **2009**, *121*, 7650 – 7675; *Angew. Chem. Int. Ed.* **2009**, *48*, 7514 – 7538; b) M. Yamada, T. Akasaka, S. Nagase, *Acc. Chem. Res.* **2010**, *43*, 92 – 102; c) A. Rodríguez-Fortea, A. L. Balch, J. M. Poblet, *Chem. Soc. Rev.* **2011**, *40*, 3551 – 3563; d) X. Lu, L. Feng, T. Akasaka, S. Nagase, *Chem. Soc. Rev.* **2012**, *41*, 7723 – 7760; e) D. M. Rivera-Nazario, J. R. Pinzón, S. Stevenson, L. Echegoyen, *J. Phys. Org. Chem.* **2012**, DOI: 10.1002/poc.3009.

[2] a) H. Yang, H. X. Jin, B. Hong, Z. Y. Liu, C. M. Beavers, H. Y. Zhen, Z. M. Wang, B. Q. Mercado, M. M. Olmstead, A. L. Balch, *J. Am. Chem. Soc.* **2011**, *133*, 16911 – 16919; b) H. X. Jin, H. Yang, M. L. Yu, Z. Y. Liu, C. M. Beavers, M. H. Olmstead, A. L. Balch, *J. Am. Chem. Soc.* **2012**, *134*, 10933 – 10941.

[3] a) C. 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, 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; c) T. Wang, N. Chen, J. Xiang, B. Li, J. Wu, W. Xu, L. Jiang, K. Tan, C. Shu, X. Lu, C. Wang, *J. Am. Chem. Soc.* **2009**, *131*, 16646 – 16647.

[4] S. Stevenson, G. Rice, T. Glass, K. Harich, F. Cromer, M. R. Jordan, J. Craft, E. Hadju, R. Bible, M. M. Olmstead, K. Maitra, A. J. Fisher, A. L. Balch, H. C. Dorn, *Nature* **1999**, *401*, 55 – 57.

[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, M. A. Stuart, M. A. Mackey, J. E. Pickens, B. S. Confait, S. Stevenson, M. L. Easterling, R. Valencia, A. Rodriguez-Fortea, J. M. Poblet, M. M. Olmstead, A. L. Balch, *J. Am. Chem. Soc.* **2010**, *132*, 12098 – 12105.

[6] a) 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; b) N. Chen, C. M. Beavers, M. Mulet-Gas, A. Rodriguez-Fortea, E. Munoz, Y. Y. Li, M. H. Olmstead, A. L. Balch, J. M. Poblet, L. Echegoyen, *J. Am. Chem. Soc.* **2012**, *134*, 7851 – 7860.

[7] a) T. S. Wang, L. Feng, J. Y. Wu, W. Xu, J. F. Xiang, K. Tan, Y. H. Ma, J. P. Zheng, L. Jiang, X. Lu, C. Y. Shu, C. R. Wang, *J. Am. Chem. Soc.* **2010**, *132*, 16362 – 16364.

[8] H. J. Huang, S. H. Yang, *J. Phys. Chem. B* **1998**, *102*, 10196 – 10200.

[9] a) X. Lu, T. Akasaka, S. Nagase, *Chem. Commun.* **2011**, *47*, 5942 – 5957; b) Y. Maeda, T. Tsuchiya, X. Lu, Y. Takano, T. Akasaka, S. Nagase, *Nanoscale* **2011**, *3*, 2421 – 2429.

  

[10] a) X. Lu, Z. Slanina, T. Akasaka, T. Tsuchiya, N. Mizorogi, S. Nagase, *J. Am. Chem. Soc.* **2010**, *132*, 5896 – 5905; b) X. Lu, Y. Lian, C. M. Beavers, N. Mizorogi, Z. Slanina, S. Nagase, T. Akasaka, *J. Am. Chem. Soc.* **2011**, *133*, 10772 – 10775.

[11] Crystal data of a black plate of $2[Yb@C_{80}(C_{10}H_{14})]\cdot 0.5(C_6H_{14})\cdot 3.5(CS_2)$: $C_{186.5}H_{35}S_7Yb_2$, $M_r = 2845.65$, $0.25 \times 0.14 \times 0.08$ mm, orthorhombic, space group *Fdd2*, $a = 34.1583(8)$, $b = 56.0562(11)$, $c = 21.4247(5)$ Å, $V = 41023.7(16)$ Å$^3$, $Z = 16$, $\rho_{calcd} = 1.843$ g cm$^{-3}$, $\mu(\text{Mo}K\alpha) = 2.032$ mm$^{-1}$, $\theta = 0.73$–$27.48°$; $T = 90$ K; $R_1 = 0.1868$, $wR_2 = 0.4093$ for all data; $R_1 = 0.1463$, $wR_2 = 0.3774$ for 23185 reflections ($I > 2.0\sigma(I)$) with 2588 parameters. Maximum residual electron density 1.755 e Å$^{-3}$.

[12] X. Lu, H. Nikawa, K. Kikuchi, N. Mizorogi, Z. Slanina, T. Tsuchiya, T. Akasaka, S. Nagase, *Angew. Chem.* **2011**, *123*, 6480 – 6483; *Angew. Chem. Int. Ed.* **2011**, *50*, 6356 – 6359.

[13] a) Y. Maeda, Y. Matsunaga, T. Wakahara, S. Takahashi, T. Tsuchiya, M. O. Ishitsuka, T. Hasegawa, T. Akasaka, M. T. H. Liu, K. Kokura, E. Horn, K. Yoza, T. Kato, S. Okubo, K. Kobayashi, S. Nagase, K. Yamamoto, *J. Am. Chem. Soc.* **2004**, *126*, 6858 – 6859; b) T. Akasaka, T. Kono, Y. Takematsu, H. Nikawa, T. Nakahodo, T. Wakahara, M. O. Ishitsuka, T. Tsuchiya, Y. Maeda, M. T. H. Liu, K. Yoza, T. Kato, K. Yamamoto, N. Mizorogi, Z. Slanina, S. Nagase, *J. Am. Chem. Soc.* **2008**, *130*, 12840 – 12841; c) Y. Takano, M. Aoyagi, M. Yamada, H. Nikawa, Z. Slanina, N. Mizorogi, M. O. Ishitsuka, T. Tsuchiya, Y. Maeda, T. Akasaka, T. Kato, S. Nagase, *J. Am. Chem. Soc.* **2009**, *131*, 9340 – 9346; d) X. Lu, H. Nikawa, L. Feng, T. Tsuchiya, Y. Maeda, T. Akasaka, N. Mizorogi, Z. Slanina, S. Nagase, *J. Am. Chem. Soc.* **2009**, *131*, 12066 – 12067; e) M. Hachiya, H. Nikawa, N. Mizorogi, T. Tsuchiya, X. Lu, T. Akasaka, *J. Am. Chem. Soc.* **2012**, *134*, 15550 – 15555.

[14] a) X. Lu, H. Nikawa, T. Nakahodo, T. Tsuchiya, M. O. Ishitsuka, Y. Maeda, T. Akasaka, M. Toki, H. Sawa, Z. Slanina, N. Mizorogi, S. Nagase, *J. Am. Chem. Soc.* **2008**, *130*, 9129 – 9136; b) B. Cao, H. Nikawa, T. Nakahodo, T. Tsuchiya, Y. Maeda, T. Akasaka, H. Sawa, Z. Slanina, N. Mizorogi, S. Nagase, *J. Am. Chem. Soc.* **2008**, *130*, 983 – 989; c) M. Yamada, C. Someya, T. Wakahara, T. Tsuchiya, Y. Maeda, T. Akasaka, K. Yoza, E. Horn, M. T. H. Liu, N. Mizorogi, S. Nagase, *J. Am. Chem. Soc.* **2008**, *130*, 1171 – 1176.

[15] a) C. M. Cardona, B. Elliott, L. Echegoyen, *J. Am. Chem. Soc.* **2006**, *128*, 6480 – 6485; b) A. A. Popov, N. B. Shustova, A. L. Svitova, M. A. Mackey, C. E. Coumbe, J. P. Phillips, S. Stevenson, S. H. Strauss, O. V. Boltalina, L. Dunsch, *Chem. Eur. J.* **2010**, *16*, 4721 – 4724.

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

  