J|A|C|S
COMMUNICATIONS

High-Nuclearity Silver Clusters Templated by Carbonates Generated from Atmospheric Carbon Dioxide Fixation

Shu-Dan Bian, Jian-Hua Jia, and Quan-Ming Wang*

State Key Laboratory of Physical Chemistry of Solid Surfaces, Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen, 361005, P. R. China

Received November 8, 2008; E-mail: qmwang@xmu.edu.cn

Chemical fixation and activation of carbon dioxide by metal complexes have attracted continuing attention,[1] and the reactivity of the carbon dioxide[2] and its hydration products such as HCO_3^- and CO_3^{2-} are also of great interest.[3−10] The carbonate anion can function as a versatile bridging ligand showing a variety of flexible coordination modes. It has been reported that many metal complexes can be used for CO_2 fixation and transformation, including complexes containing metal centers such as Zn^{II}, Cu^{II}, Co^{II}, Ni^{II}, and oxovanadium(IV).[3−10] Although it is known that Ag_2O can be used as a starting material to prepare silver carbamato complexes,[11] there is no other report about CO_2 fixation by a silver(I) complex. On the other hand, silver(I) has a rich coordination chemistry with many halides and polyatomic anions, such as cyanide, phosphate, and even the acetylide dianion,[12] but no precedent of a structurally characterized carbonato-coordinated silver complex has been reported so far.

Silver alkynyls can be used as versatile precursors for the synthesis of high-nuclearity silver clusters, and the anion-templated synthetic appoach[13] has been employed in the preparation of novel cage complexes with spherical anions such as $[Ag_{14}(C\equiv CBu^t)_{12}X]^+$ (X = F, Cl, Br)[12a] and $[Ag_{19}(C\equiv CBu^t)_{11}(CF_3CO_2)_7Cl]$.[14a] In the course of our research on the assembly of silver alkynyl clusters,[14] our synthetic attempt under basic conditions led accidentally to the isolation of two novel high-nuclearity silver cages each encapsulating a carbonate ion, namely $[Ag_{17}(Bu^tC\equiv C)_{14}(CO_3^{2-})]OTf$ (**1**) and $[Ag_{19}(Bu^tC\equiv C)_{16}(CO_3^{2-})]BF_4\cdot MeOH$ (**2**·MeOH). Herein, we report the first examples of silver clusters prepared from the templation of carbonate that is generated from atmospheric CO_2 fixation.

The reaction of $Bu^tC\equiv CAg$ with AgOTf in methanol solution in the presence of tetramethylethylenediamine (TMEDA) in air led to the isolation of **1** as colorless crystals in *ca.* 73% yield. An IR vibration band at 2028 cm^{-1} confirmed the presence of the C≡C group in **1**, and the bands at 1123 and 1083 cm^{-1} are assigned to the triflate anion. Single crystal X-ray structural analysis[15] revealed that the cationic part of **1** is a large cluster consisting of 17 silver atoms bridged by 14 alkynyl ligands with an enclosed carbonate ion (Figure 1). The shape of the skeleton of **1** is like an antique clock which has m symmetry with a mirror passing through Ag1, Ag5, Ag6, Ag9, Ag10, and the carbonate. The CO_3^{2-} ion acts as a template for the formation of this novel silver cluster, with Ag−O bond distances varying from 2.39 to 2.75 Å for O1 and from 2.41 to 2.71 Å for O2. There are only weak interactions between O3 and silver atoms with the shortest Ag3−O3 distance being 2.84 Å. This is quite different from other cases in which the carbonate is evenly coordinated to three metal centers. Each $Bu^tC\equiv C$ ligand adopts the μ_3 bridging mode to link three silver atoms, and a total of 14 of them are coordinated to silver atoms peripherally to hold the cluster together. Triflate counterions sit in the intervening space between cationic clusters to balance the charge.

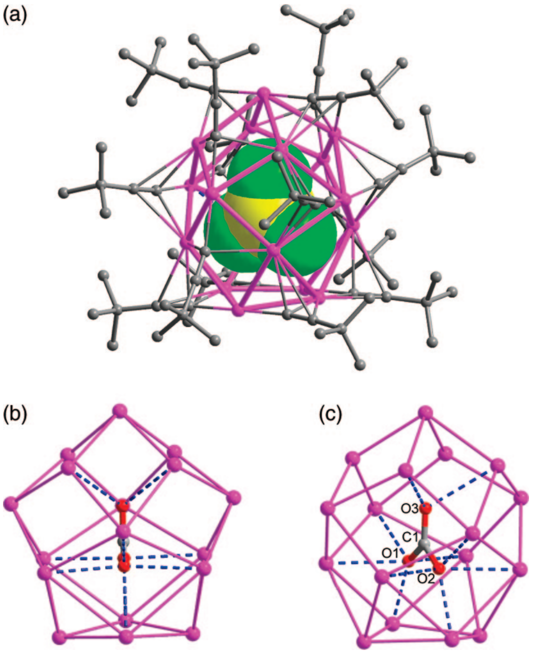

Figure 1. (a) Molecular structure of the cationic part of $[Ag_{17}(Bu^tC\equiv C)_{14}(CO_3^{2-})]OTf$ (**1**). The encapsulated carbonate ion is shown in space-filling mode. (b) The antique-clock shape of the cluster viewed along the mirror plane. (c) The core structure illustrating the silver−carbonate interaction.

Interestingly, it is found that the counterion affects the nuclearity of the cluster formed, probably due to the packing effect. When $AgBF_4$ was used instead of AgOTf in the same preparative procedure, a higher nuclearity silver cluster **2** was isolated in 18.32% yield ($CO_3^{2-}@Ag_{17}$ in **1** vs $CO_3^{2-}@Ag_{19}$ in **2**). IR vibration bands at 2030 and 1083 cm^{-1} revealed the presence of the C≡C group and BF_4^-. Structural determination indicated that the cation of **2** is a nonadecanuclear silver cluster (Figure 2).[16] The shape of this silver cluster is not so regular, but it could be roughly described as a flying saucer with nine silver atoms and a carbonate constructing the equatorial rim, and two groups of five silver atoms each acting as the upper and lower rim, respectively. The carbonate template inside this Ag_{19} cluster is similar to that in **1**, with Ag−O distances falling in the range 2.55−2.81 Å for O1, 2.45−2.84 Å for O2, and 2.56−2.86 Å for O3. The cage is consolidated by 16 peripheral alkynyl ligands adopting the μ_3 bridging mode.

EPR spectroscopy was used to confirm that no redox process occurred. Both **1** and **2** are EPR silent at 100 K (Figure S1), which indicates that all the silver atoms have a +1 oxidation state.

Deliberately adding potassium carbonate in the preparation of **2** significantly improved the yield from 18.3% to 88.4%, providing indirect proof that the enclosed carbonate species originates from hydration of atmospheric CO_2 to give H_2CO_3, which in turn

10.1021/ja8087696 CCC: $40.75

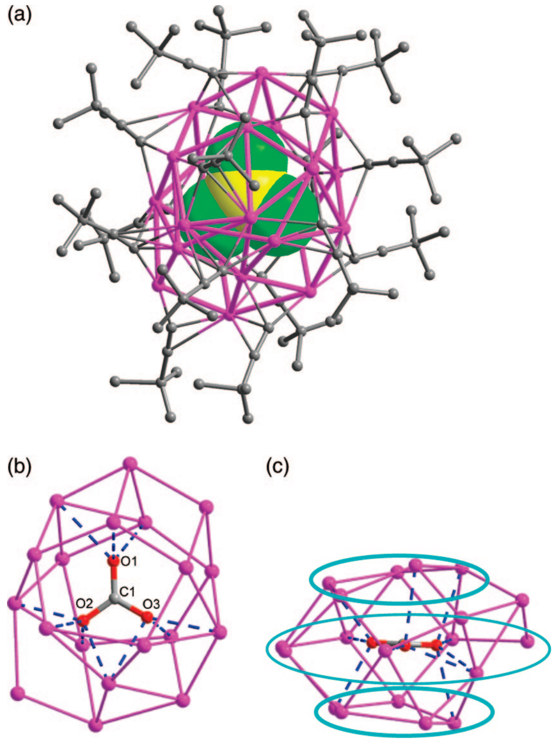

Figure 2. (a) Molecular structure of the cationic part of [$Ag_{19}(Bu^tC{\equiv}C)_{16}(CO_3^{2-})]BF_4$ (**2**). The encapsulated carbonate ion is shown in space-filling mode. (b) Top view: the core structure illustrating the silver−carbonate interaction; (c) side view: the flying saucer shape.

undergoes deprotonation in basic conditions (TMEDA used). However, the yield of **2** could not be improved by running the experiment in a CO_2 rich atmosphere. There possibly exists a competition between the templation of fluoride and carbonate, which lowers the yield of **2**. It is known that decomposition of the BF_4^- anion to F^- could occur in the presence of heavy metals, and Rais et al. have reported the formation of $[Ag_{14}(C{\equiv}CBu^t)_{12}F]^+$ with BF_4^- as the source of F^-.[17]

Due to the overlap of vibration bands of carbonate and C−H in the range of ~1400 cm^{-1}, the presence of carbonate was not unambiguously confirmed by IR. Precipitation was observed when the complexes were dissolved in solvents such as MeCN and MeOH, which suggest the clusters do not maintain their solid state structure in solution. Finally, the presence of the carbonate ligand was confirmed by the solid-state ^{13}C NMR spretra (Figure S2). The peaks at 158.7 ppm for **1** and 159.9 ppm for **2** are assigned to the carbonate anion encapsulated in the silver cage.

TMEDA proved to be vital for the formation of the cage compounds, although it was not incorporated in the final products. As a base, TMEDA favors the transformation of CO_2 to CO_3^{2-} via hydration (wet solvents used), and the CO_3^{2-} thus formed then functions as a template for the formation of **1** and **2**. Reacting AgC_2Bu^t with $AgBF_4$ (or $AgCF_3CO_2$) in the absence of TMEDA led to the formation of one-dimensional structures without involvement of the anion-template effect.[14b,18] A noted exception was that a rhombohedral structure $[Ag_{14}(C{\equiv}CBut)_{12}](BF_4)_2$ could be obtained without a halide template.[19] In addition, attempts to run the reactions in the absence of CO_2 could not lead to the isolation of **1** or **2**. It is noteworthy that complexes **1** and **2** could also be prepared by using tetrametyldiaminobutane in place of TMEDA.

In summary, novel silver cages templated by the carbonate ion generated from the fixation of atmospheric CO_2 have been isolated, demonstrating that silver alkynyls are exemplary systems for the study of the anion-templating effect. Further work on polyatomic anion template is underway.

Acknowledgment. Dedicated to Prof. Xin-Tao Wu on the occasion of his 70th birthday. We acknowledge financial support by the Natural Science Foundation of China (20771091 and 20721001), the 973 Program (2007CB815301), and the Ministry of Education (NCET-06-0563). We are indebted to Prof. Y. Yang and Dr. X.-K. Huang for performing the solid state ^{13}C NMR measurements.

Supporting Information Available: Detailed experimental procedures and cif files for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Palmer, D. A.; van Eldik, R. *Chem. Rev.* **1983**, *83*, 651–731. (b) Leitner, W. *Coord. Chem. Rev.* **1996**, *153*, 257–284. (c) Yin, X. L.; Moss, J. R. *Coord. Chem. Rev.* **1999**, *181*, 27–59. (d) Belli Dell'Amico, D.; Calderazzo, F.; Labella, L.; Marchetti, F.; Pampaloni, G. *Chem. Rev.* **2003**, *103*, 3857–3897.
(2) Gao, G. G.; Li, F. Y.; Xu, L.; Liu, X. Z.; Yang, Y. Y. *J. Am. Chem. Soc.* **2008**, *130*, 10838–10839.
(3) Kersting, B. *Angew. Chem., Int. Ed.* **2001**, *40*, 3988–3990.
(4) García-España, E.; Gaviña, P.; Latorre, J.; Soriano, C.; Verdejo, B. *J. Am. Chem. Soc.* **2004**, *126*, 5082–5083.
(5) Mukherjee, P.; Drew, M. G. B.; Estrader, M.; Ghosh, A. *Inorg. Chem.* **2008**, *47*, 7784–7791.
(6) Kong, L.-Y.; Zhang, Z.-H.; Zhu, H.-F.; Kawaguchi, H.; Okamura, T.; Doi, M.; Chu, Q.; Sun, W.-Y.; Ueyama, N. *Angew. Chem., Int. Ed.* **2005**, *44*, 4352–4355.
(7) Sarkar, B.; Liaw, B.-J.; Fang, C.-S.; Liu, C. W. *Inorg. Chem.* **2008**, *47*, 2777–2785.
(8) Graham, A.; Meier, S.; Parsons, S.; Winpenny, E. P. *Chem. Commun.* **2000**, *81*, 1–812.
(9) Chen, J.-M.; Wei, W.; Feng, X.-L.; Lu, T.-B. *Chem. Asian J.* **2007**, *2*, 710–719.
(10) (a) Schrodt, A.; Neubrand, A.; van Eldik, R. *Inorg. Chem.* **1997**, *36*, 4579–4584. (b) Mak, T. C. W.; Li, P.-J.; Zheng, C.-M.; Huang, K.-Y. *Chem. Commun.* **1986**, 1597–1598.
(11) Alessio, R.; Belli Dell'Amico, D.; Calderazzo, F.; Englert, U. *Gazz. Chim. Ital.* **1993**, *123*, 719.
(12) (a) Rais, D.; Yau, J.; Mingos, D. M. P.; Vilar, R.; White, A. J. P.; Williams, D. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 3464–3467. (b) Wang, Q.-M.; Mak, T. C. W. *Chem. Commun.* **2000**, 1435–1436. (c) Tong, M.-L.; Zheng, S.-L.; Chen, X.-M. *Chem.—Eur. J.* **2000**, *6*, 3729–3738. (d) Mak, T. C. W.; Zhao, X.-L.; Wang, Q.-M.; Guo, G.-C. *Coord. Chem. Rev.* **2007**, *251*, 2311–2333.
(13) (a) Vilar, R. *Angew. Chem., Int. Ed.* **2003**, *42*, 1460–1477. (b) Vilar, R. *Eur. J. Inorg. Chem.* **2008**, *35*, 7–367. (c) Beer, P. D.; Gale, P. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 486–516.
(14) (a) Chen, M.-L.; Xu, X.-F.; Cao, Z.-X.; Wang, Q.-M. *Inorg. Chem.* **2008**, *47*, 1877–1879. (b) Bian, S.-D.; Wang, Q.-M. *Chem. Commun.* **2008**, 5586.
(15) Crystal data for **1**, $C_{86}H_{126}O_6SF_3Ag_{17}$, $a = 13.8153(5)$ Å, $b = 26.2742(7)$ Å, $c = 14.8383(6)$ Å, $\beta = 108.159(4)°$, $V = 5117.8(3)$ Å^3, space group $P2_1/m$, $Z = 2$, $T = 173$ K, 31 617 reflections measured, 14 144 unique ($R_{int} = 0.0961$), final $R1 = 0.0452$, $wR2 = 0.0648$ for 4178 observed reflections [$I > 2\sigma(I)$].
(16) Crystal data for **2** · MeOH, $C_{98}H_{148}BO_4F_4Ag_{19}$, $a = 21.7271(4)$ Å, $b = 15.8981(2)$ Å, $c = 34.0433(5)$ Å, $\beta = 93.151(2)°$, $V = 11741.4(3)$ Å^3, space group $P2_1/c$, $Z = 4$, $T = 173$ K, 77 351 reflections measured, 31 322 unique ($R_{int} = 0.0662$), final $R1 = 0.0649$, $wR2 = 0.1309$ for 13 604 observed reflections [$I > 2\sigma(I)$].
(17) Rais, D.; Mingos, D. M. P.; Vilar, R.; White, A. J. P.; Williams, D. J. *J. Organomet. Chem.* **2002**, *652*, 87–93.
(18) Al-Farhan, K. A.; Ja'far, M. H.; Abu-Salah, O. M. *J. Organomet. Chem.* **1999**, *579*, 59–62.
(19) Abu-Salah, O. M.; Ja'far, M. H.; Al-Ohaly, A. R.; Al-Farhan, K. A.; Al-Enzi, H. S.; Dolomanov, O. V.; Howard, J. A. K. *Eur. J. Inorg. Chem.* **2006**, *235*, 3–2356.

JA8087696