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Stabilization of a Reactive Polynuclear Silver Carbide Cluster through the Encapsulation within a Supramolecular Cage

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Supporting Information

ABSTRACT: We report herein the synthesis of a new metal cluster-encapsulated supramolecular capsule, $[(C\equiv C)@Ag_{5-6}@(\mathbf{Py6})_2](CF_3SO_3)_{3-4}$ (**3**, **Py6** = azacalix[6]pyridine), by use of a bowl-shaped macrocyclic ligand **Py6**. The multinuclear silver carbide cluster aggregate in **3** is encapsulated by two **Py6** ligands through both metal−ligand coordination and cation−π interactions, spotlighting a new synthetic strategy for supramolecular capsules.

Supramolecular capsules spontaneously assembled from molecular building blocks have long captivated chemists due to their abilities to encapsulate guest molecules,[1] to serve as molecular flasks for chemical reactions,[2] and to stabilize reactive intermediates and unstable species.[3] The appealing aspect of supramolecular capsules to stabilize labile species, such as white phosphorus,[3g] can be mostly ascribed to their confined inner cavities, which restrain the conformation or configuration change of guest molecules and prevent the interactions and reactions between entrapped guests and outside reactants.[3j] In this regard, a polynuclear metal cluster, a highly reactive species in a multimetallic assembly, could possibly be embedded in a supramolecular capsule.[4] Such encapsulation may afford a viable means to permit control over the coordination environments of individual metal atoms and facilitate the rational design of new clusters. In addition, encapsulation of metal clusters inside an isolated cavity, for example, metal oxide and nitride clusters in endohedral metallofullerenes, may produce novel functional materials that own unique physical properties different from their bulk phase.[5]

However, several factors limit the chemical accessibility of metal cluster-encapsulated supramolecular capsules. First, metal atoms of cluster aggregates hold potential to coordinate to the organic building blocks of capsules, often leading to the disassembly of the supramolecular capsule structures. Second, from the thermodynamic viewpoint it is difficult to implement a multinuclear assembly within a constrained space by incorporating a number of metal ions and anions together merely based on weak intermolecular interactions, such as the hydrophobic effect in some previously reported examples.[6] We herein report the synthesis of a supramolecular capsule that encapsulates a silver carbide cluster through both metal−ligand coordination and cation−π interactions. Three metallosupramolecular complexes, namely $[(CF_3SO_3)_{1.5}Ag_{3.5}(^tBuC\equiv C)(\mathbf{Py6})(CH_3OH)_{0.5}](CF_3SO_3)\cdot(H_2O)_{0.5}$ (**1**), $[(CF_3SO_3)_4Ag_8(C\equiv C{-}C\equiv C)(\mathbf{Py6})_2](CF_3SO_3)_2$ (**2**), and $\{[Ag_5(C\equiv C)(\mathbf{Py6})_2](CF_3SO_3)_3\}_{0.7}\{[Ag_6(C\equiv C)(\mathbf{Py6})_2]\ (CF_3SO_3)_4\}_{0.3}$ (**3**) (**Py6** = azacalix[6]pyridine),[7] are structurally characterized by X-ray crystallography, electrospray ionization mass spectroscopy (ESI-MS), and ^1H NMR spectroscopy.[8] *Warning! Silver carbides are highly explosive in the dry state when subjected to heating or mechanical shock.* These supramolecular capsules can serve as a new class of container molecules for the storage of unstable silver carbide clusters.

Our study was initiated with the synthesis and structural characterization of $[(CF_3SO_3)_{1.5}Ag_{3.5}(^tBuC\equiv C)(\mathbf{Py6})(CH_3OH)_{0.5}](CF_3SO_3)\cdot(H_2O)_{0.5}$ (**1**). The reaction between a suspension of $[^tBuC\equiv CAg]_n$[9] and silver triflate and the neutral polydentate macrocyclic ligand **Py6** in a CH_2Cl_2/CH_3OH solution resulted in a pale-yellow solution of complex **1**. Light-yellow crystals were subsequently deposited by the diffusion of diethyl ether into the solution. X-ray crystallographic analysis revealed that complex **1** comprises two triflate groups and a discrete trinuclear silver aggregate which is coordinated by a **Py6** ligand. A $[Ag(CF_3SO_3)(CH_3OH)]$ unit with a half site occupancy ratio binds with the **Py6** ligand through the Ag4−N3 bond, as shown in Figure 1. The trigonal silver aggregate held together by a *tert*-butylacetylide group is located at the center of the **Py6** macrocycle and is coordinated by three alternate pyridyl nitrogen atoms (N1, N5, and N9). The remaining three pyridine rings (**II**, **IV**, and **VI**) laterally encompass the Ag_3 aggregate by η^1 or η^2 silver−aromatic π interactions. The Ag−C distances of the π interactions are in the range of 2.67−3.05 Å, being well below the sum of the van der Waals radii of the silver atom (1.72 Å) and the carbon atom (1.70 Å).[10] This is comparable with the reported coordination-driven self-assembled square of 4-ethynylpyridine that binds to several silver atom guests via the silver−acetylene π interactions.[11] The **Py6** ligand in **1** exhibits a quasi-C_{3v} bowl-shaped conformation with three coplanar coordinative pyridine rings (**I**, **III**, and **V**) as a basal plane, while the lateral pyridine rings (**II**, **IV**, and **VI**) form an average dihedral angle of 55.8° with the basal plane. The radius of the inner coordination environment of **Py6** in **1** is approximately 4.06 Å, shorter than the sum of the average bond lengths of Ag−C (2.1−2.3 Å) and Ag−N (2.2−2.3 Å). Therefore, the Ag_3 aggregate is located about 0.57 Å out of the basal plane. According to the bowl-shaped conformation of the **Py6** ligand, the Ag_3 aggregate is remarkably situated on the concave surface of **Py6**. In contrast to the reported single metal atom *endo* coordination complexes

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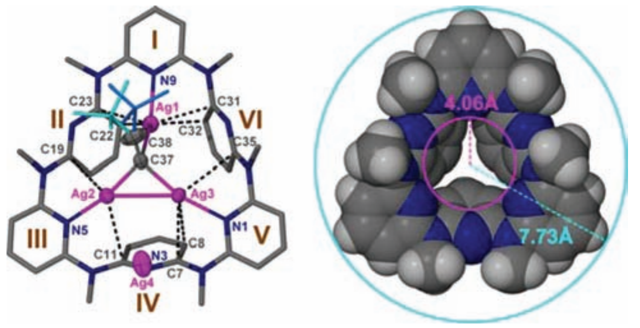

Figure 1. (left) Crystal structure of complex $[(CF_3SO_3)_{1.5}Ag_{3.5}({}^tBuC{\equiv}C)(\mathbf{Py6})(CH_3OH)_{0.5}](CF_3SO_3)\cdot(H_2O)_{0.5}$ (**1**) with partial atom labeling (50% thermal ellipsoids for the $C{\equiv}C$ acetylide unit and four silver atoms). Hydrogen atoms and other groups are omitted for clarity. The *tert*-butyl group is disordered at two positions that are highlighted in cyan and blue colors. Selected bond lengths and distances (Å): C37−C38 1.215(10); C37−Ag1 2.231(6); C37−Ag2 2.126(6); C37−Ag3 2.109(6); C38−Ag1 2.372(7); Ag1−N9 2.264(5); Ag2−N5 2.212(5); Ag3−N1 2.227(5); Ag4−N3 2.325(5); Ag2···Ag3 3.019(1). Ag−C distances for the silver−aromatic π interactions (Å): Ag1−C22 2.668; Ag1−C23 2.758; Ag1−C31 2.732; Ag1−C32 2.772; Ag2−C19 3.053; Ag2−C11 2.977; Ag3−C7 2.894; Ag3−C8 3.031; Ag3−C35 3.035. (right) Space-filling model of the **Py6** ligand in **1**. Color scheme for atoms: C, black; H, gray; N, blue.

of curved ligands, such as calixarene,[12] cyclotriveratrylene (CTV),[13] corannulene,[14] and sumanene,[15] **1** represents the first concave-bound metal cluster complex.

The ESI-MS analysis of the methanol solution of **1** showed an isotopically well-resolved peak at m/z = 1189.06 corresponding to the $[(CF_3SO_3)Ag_3({}^tBuC{\equiv}C)(\mathbf{Py6})]^+$ species (Figure S1, Supporting Information). The ^1H NMR spectrum of **1** exhibited two sets of resonances at 8.13/7.62 and 7.17/6.74 ppm for the γ- and β-protons of coordinated and free pyridine rings of **Py6**, respectively (Figure S3, Supporting Information). These observations indicate that the dominant species in the solution of **1** is $[(CF_3SO_3)_2Ag_3({}^tBuC{\equiv}C)(\mathbf{Py6})]$ and that the partially occupied $[Ag(CF_3SO_3)(CH_3OH)]$ unit is incorporated in the process of crystallization.

The shell-like conformation of the $Ag_3{\subset}\mathbf{Py6}$ component ($\subset$ represents encirclement) in **1** made us envision that the employment of a ditopic anionic ligand instead of ${}^tBuC{\equiv}C^-$ may possibly integrate two shells into a discrete supramolecule. The use of the silver 1,3-butadiynediide (Ag_2C_4)[16] in a synthetic procedure similar to complex **1** led to the formation of a new cluster complex $[(CF_3SO_3)_4Ag_8(C{\equiv}C{-}C{\equiv}C)(\mathbf{Py6})_2](CF_3SO_3)_2$ (**2**). Complex **2** crystallizes in the monoclinic space group $C2/c$, and a C_2 axis passes through the center of the tetracarbon chain (Figure 2a). At the two ends of the C_4^{2-}, each acetylide moiety is joined to a trinuclear silver aggregate. Each Ag_3 aggregate is encircled by a **Py6** ligand through the Ag−N coordination and silver-aromatic π interactions (Figure 2b), which is similar to **1**. The two C_2-related **Py6** ligands in **2** are arranged in an eclipsed face-to-face fashion with a dihedral angle of 23° (Figure 3). Furthermore, such two $Ag_3{\subset}\mathbf{Py6}$ fragments are bridged by the tetracarbon chain to produce a clam-like structure. The open side (9.07 Å) of this structure accommodates a $[Ag_2(CF_3SO_3)_4]$ unit, while the other side (3.80 Å) is sealed by the C−H···π interactions between a bridging N-Me group and a pyridine ring (C−H···$Py_{Centroid}$ = 3.11 Å). This clam-like assembly formulated as $[(CF_3SO_3)_4Ag_8(C{\equiv}C{-}C{\equiv}C)(\mathbf{Py6})_2]^{2+}$ has a nanosized dimension of 1.34 ×1.74 nm.

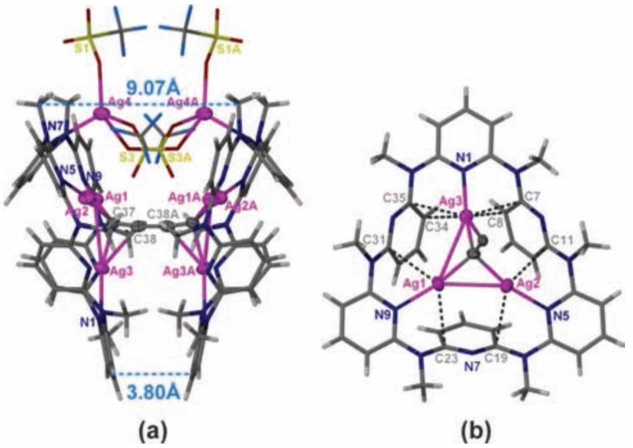

Figure 2. (a) Crystal structure of complex $[(CF_3SO_3)_4Ag_8(C{\equiv}C{-}C{\equiv}C)(\mathbf{Py6})_2](CF_3SO_3)_2$ (**2**) with partial atom labeling (50% thermal ellipsoids for the central $Ag_3C{\equiv}C{-}C{\equiv}CAg_3$ unit). Other triflate groups are omitted for clarity. The silver atom Ag3 is disordered at two positions, and only one position is shown here. Symmetry code: A $-x$, y, $1/2 - z$. Selected bond lengths and distances (Å): C37−C38 1.217(19); C38−C38A 1.40(3); C37−Ag1 2.107(13); C37−Ag2 2.152(13); C37−Ag3 2.076(19); C38−Ag3 2.57(3); Ag1−N9 2.211(11); Ag2−N5 2.221(11); Ag3−N1 2.224(16); Ag4−N7 2.340(12); Ag···Ag 3.066(2)−3.342(9). (b) Coordination environment of the central Ag_3 aggregate in **2**. Ag−C distances for the silver−aromatic π interactions (Å): Ag1−C23 2.972; Ag1−C31 2.973; Ag2−C11 2.934; Ag2−C19 2.928; Ag3−C7 2.766; Ag3−C8 2.838; Ag3−C34 2.932; Ag3−C35 2.839.

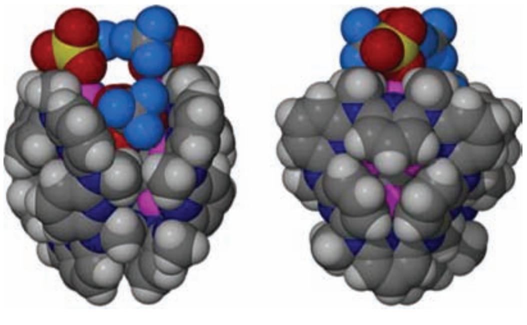

Figure 3. Clam-like structure in **2** shown in space-filling model: 0° (left) and 90° (right) view. Color scheme for atoms: Ag, purple; C, black; H, gray; O, red; N, blue; F, cyan.

The ESI mass spectrum of **2** revealed two peaks at m/z = 2414.93 and 1132.99 corresponding to the $[(CF_3SO_3)_3Ag_6(C{\equiv}C{-}C{\equiv}C)(\mathbf{Py6})_2]^+$ and $[(CF_3SO_3)_2Ag_6(C{\equiv}C{-}C{\equiv}C)(\mathbf{Py6})_2]^{2+}$ species, respectively (Figure S1, Supporting Information). This indicates the dominant species in the solution of **2** does not include the $[Ag_2(CF_3SO_3)_2]$ unit at the open side of the clam structure. This was also substantiated by the NMR studies. The ^1H NMR spectrum of **2** at 298 K showed several broad peaks in the ranges of 7.62−8.14 and 6.66−7.18 ppm, corresponding to the pyridyl γ- and β-proton signals of the **Py6** ligand, respectively (Figure S4, Supporting Information). As the temperature rises from 298 to 323 K, the broad signals merge into two sharp peaks at 7.86 and 6.82 ppm. In contrast, these peaks are gradually split into several singlet and doublet peaks upon the temperature decreasing from 298 to 193 K, suggesting that there is a possible equilibrium between fluxional conformations of **Py6** in the solution of **2**.

Ag_2C_2 was applied in the ensuing study for the sake of shortening the carbon chain of C_4^{2-}. Along with the shrinkage, the two separate trigonal silver aggregates at two terminals of the C_4^{2-} in **2** approach each other, finally resulting in the formation of a closed silver cage in **3** with a C_2^{2-} anion trapped inside (Figure 4a). Based on the crystal refinement, the closed silver carbide cluster in **3** can be resolved as two disordered parts, $C_2@Ag_5$ and $C_2@Ag_6$ (@ means encapsulation). Four silver atoms (Ag1, Ag2, Ag3, and Ag4) share their positions in both two cluster aggregates, and the interatomic distances among them lie in the range of 3.186(2)−3.361(2) Å, being shorter than the characteristic argentophilic contact of 3.4 Å.[17] The remaining three silver atoms (Ag5 and the Ag5A−Ag5B pair) are disordered with a refined site-occupancy ratio of 0.70 and 0.30, respectively. Thus, the formula of complex **3** can be expressed as $\{[Ag_5(C{\equiv}C)(\mathbf{Py6})_2](CF_3SO_3)_3\}_{0.7}\{[Ag_6(C{\equiv}C)(\mathbf{Py6})_2](CF_3SO_3)_4\}_{0.3}$, in which five independent triflate groups with partial site-occupancies are involved. In contrast to a series of previously reported $C_2@Ag_n$ (n = 6−10) clusters,[18] the present trigonal bipyramidal $C_2@Ag_5$ aggregate is observed for the first time. This $C_2@Ag_{5-6}$ silver carbide cluster in **3** is encapsulated by two bowl-shaped **Py6** ligands through the Ag−N coordination and the silver−aromatic π interactions as found in complexes **1** and **2** (Figure S2, Supporting Information). Distinct from the eclipsed face-to-face arrangement of two **Py6** ligands in **2**, the two **Py6** in **3** are parallel but staggered at an angle of 37°. In this way, the two **Py6** macrocycles are associated through multiple C−H···π and C−H···N interactions. The closed cluster-encaged capsule structure in **3** is reminiscent of the well-known endohedral metallofullerenes.[5] Crystalline **3** has very poor solubility which obstructs its further NMR study. However, in its ESI mass spectrum, an isotopically well-resolved peak at m/z = 993.08 corresponding to the $C_2@Ag_5$ binding species $\{[(C{\equiv}C)@Ag_5@(\mathbf{Py6})_2](CF_3SO_3)\}^{2+}$ was unambiguously observed (Figure S1, Supporting Information). The absence of peaks for the $C_2@Ag_6$ related species is mostly attributed to its relatively low abundance.

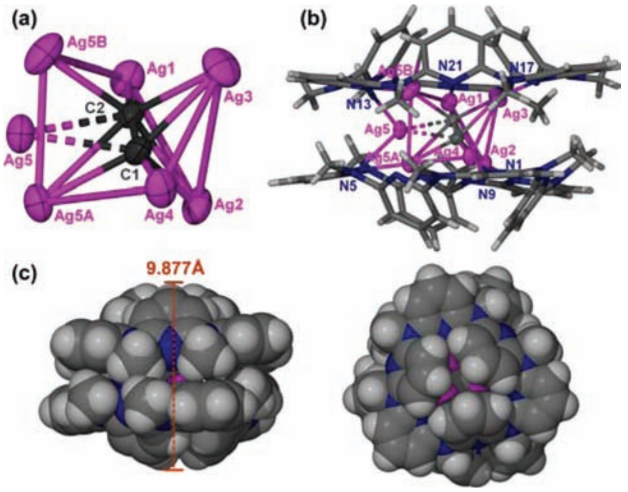

Figure 4. (a) Two silver−acetylide cluster aggregates $C_2@Ag_5$ and $C_2@Ag_6$ in complex $\{[Ag_5(C{\equiv}C)(\mathbf{Py6})_2](CF_3SO_3)_3\}_{0.7}\{[Ag_6(C{\equiv}C)(\mathbf{Py6})_2](CF_3SO_3)_4\}_{0.3}$ (**3**) with partial atom labeling (50% thermal ellipsoids). Selected bond lengths and distances (Å): C1−C2 1.212(16); C1−Ag2 2.310(11); C1−Ag3 2.377(12); C1−Ag4 2.072(12); C1−Ag5 2.387(11); C1−Ag5A 2.276(12); C2−Ag1 2.077(12); C2−Ag2 2.383(10); C2−Ag3 2.335(11); C2−Ag5 2.373(11); C2−Ag5B 2.247(10); Ag···Ag 3.012(5)−3.361(2). (b) Supramolecular capsule in **3** with the encapsulation of a silver carbide cluster by two **Py6** ligands. Other triflate groups are omitted for clarity. (c) The closed capsule structure in **3** shown in space-filling model (side and top view). Color scheme for atoms: Ag, purple; C, black; H, gray; N, blue.

We recently reported a similar C_{3v} conformation in azacalix[3]pyrimidine[3]pyridine,[19] wherein three electron-deficient pyrimidine rings are located on a basal plane and three pyridine rings form a dihedral angle of 60° with the basal plane. This affords a rationale for the bowl-shaped C_{3v} conformation of **Py6** in **1**−**3** since the coordination between three alternate pyridines and silver atoms would decrease the electron density of pyridine rings and thus differentiate the six pyridine rings of **Py6** into two kinds. The consistency of the $Ag_3{\subset}\mathbf{Py6}$ mode in **1**−**3** reflects a complementary relationship between silver aggregates and macrocyclic ligands and facilitates the construction of supramolecular capsules by the variation of central carbide anions. These results provide important fundamental knowledge on the construction of functional cluster-contained supramolecular materials by use of coordinative macrocyclic ligands. In addition, encapsulation of reactive and unstable metal clusters within organic hosts provides a promising practical means for their stabilization, thereby making their existing applications more feasible and potentiating some new applications. Further studies on the assembly of other labile metal clusters with these macrocycles and their variants are now in progress.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures and crystal structure determination details. ESI mass spectra of **1**−**3** and NMR spectra of **1** and **2**. X-ray crystallographic data for **1**−**3** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) (a) Conn, M. M.; Rebek, J. Jr. *Chem. Rev.* **1997**, *97*, 1647. (b) Caulder, D. L.; Raymond, K. N. *Acc. Chem. Res.* **1999**, *32*, 975. (c) Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853. (d) Hof, F.; Craig, S. L.; Nuckolls, C.; Rebek, J. Jr. *Angew. Chem., Int. Ed.* **2002**, *41*, 1488. (e) Mateos-Timoneda, M. A.; Crego-Calama, M.; Reinhoudt, D. N. *Chem. Soc. Rev.* **2004**, *33*, 363. (f) Fujita, M.; Tominaga, M.; Hori, A.; Therrien, B. *Acc. Chem. Res.* **2005**, *38*, 371. (g) Dalgarno, S. J.; Power, N. P.; Atwood, J. L. *Coord. Chem. Rev.*

2008, *252*, 825. (h) Jin, P.; Dalgarno, S. J.; Atwood, J. L. *Coord. Chem. Rev.* **2010**, *254*, 1760.

(2) (a) Kang, J.; Rebek, J. Jr. *Nature* **1997**, *385*, 50. (b) Merlau, M. L.; del Pilar Mejia, M.; Nguyen, S. T.; Hupp, J. T. *Angew. Chem., Int. Ed.* **2001**, *40*, 4239. (c) Leung, D. H.; Fiedler, D.; Bergman, R. G.; Raymond, K. N. *Angew. Chem., Int. Ed.* **2004**, *43*, 963. (d) Yoshizawa, M.; Tamura, M.; Fujita, M. *Science* **2006**, *312*, 251. (e) Leung, D. H.; Bergman, R. G.; Raymond, K. N. *J. Am. Chem. Soc.* **2007**, *129*, 2746. (f) Pluth, M. D.; Bergman, R. G.; Raymond, K. N. *Science* **2007**, *316*, 85. (g) Podkoscielny, D.; Gadde, S.; Kaifer, A. E. *J. Am. Chem. Soc.* **2009**, *131*, 12876. (h) Dube, H.; Ams, M. R.; Rebek, J. Jr. *J. Am. Chem. Soc.* **2010**, *132*, 9984. (i) Wiester, M. J.; Ulmann, P. A.; Mirkin, C. A. *Angew. Chem., Int. Ed.* **2010**, *49*, 2. (j) Meeuwissen, J.; Reek, J. N. H. *Nat. Chem.* **2010**, *2*, 615. (k) Breiner, B.; Clegg, J. K.; Nitschke, J. R. *Chem. Sci.* **2011**, *2*, 51.

(3) (a) Yoshizawa, M.; Kusukawa, T.; Fujita, M.; Sakamoto, S.; Yamaguchi, K. *J. Am. Chem. Soc.* **2001**, *123*, 10454. (b) Kawano, M.; Kobayashi, Y.; Ozeki, T.; Fujita, M. *J. Am. Chem. Soc.* **2006**, *128*, 6558. (c) Dong, V. M.; Fiedler, D.; Carl, B.; Bergman, R. G.; Raymond, K. N. *J. Am. Chem. Soc.* **2006**, *128*, 14464. (d) Kuil, M.; Soltner, T.; van Leeuwen, P. W. N. M.; Reek, J. N. H. *J. Am. Chem. Soc.* **2006**, *128*, 11344. (e) Flapper, J.; Reek, J. N. H. *Angew. Chem., Int. Ed.* **2007**, *46*, 8590. (f) Lee, S. J.; Cho, S.-H.; Mulfort, K. L.; Tiede, D. M.; Hupp, J. T.; Nguyen, S. T. *J. Am. Chem. Soc.* **2008**, *130*, 16828. (g) Mal, P.; Breiner, B.; Rissanen, K.; Nitschke, J. R. *Science* **2009**, *324*, 1697. (h) Sarmentero, M. A.; Fernandez, P. H.; Zuidema, E.; Bo, C.; Vidal, F. A.; Ballester, P. *Angew. Chem., Int. Ed.* **2010**, *49*, 7489. (i) Cavarzan, A.; Scarso, A.; Sgarbossa, P.; Strukul, G.; Reek, J. N. H. *J. Am. Chem. Soc.* **2011**, *133*, 2848. (j) Horiuchi, S.; Murase, T.; Fujita, M. *J. Am. Chem. Soc.* **2011**, *133*, 12445.

(4) (a) Leeland, J. W.; White, F. J.; Love, J. B. *J. Am. Chem. Soc.* **2011**, *133*, 7320. (b) Liu, Y.; Hu, C.; Comotti, A.; Ward, M. D. *Science* **2011**, *333*, 436.

(5) (a) Chaur, M. N.; Melin, F.; Ortiz, A. L.; Echegoyen, L. *Angew. Chem., Int. Ed.* **2009**, *48*, 7514. (b) Lu, X.; Akasaka, T.; Nagase, S. *Chem. Commun.* **2011**, *47*, 5942.

(6) Rebek, J. Jr. *Acc. Chem. Res.* **2009**, *42*, 1660.

(7) Zhang, E.-X.; Wang, D.-X.; Zheng, Q.-Y.; Wang, M.-X. *Org. Lett.* **2008**, *10*, 2565.

(8) See the Supporting Information for synthetic procedures, ESI-MS data, X-ray diffraction structural refinement details, and NMR data.

(9) (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. (b) Halbes-Letinois, U.; Weibel, J.-M.; Pale, P. *Chem. Soc. Rev.* **2007**, *36*, 759. (c) Mak, T. C. W.; Zhao, L. *Chem.—Asian J.* **2007**, *2*, 456.

(10) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

(11) Whiteford, J. A.; Lu, C. V.; Stang, P. J. *J. Am. Chem. Soc.* **1997**, *119*, 2524.

(12) (a) Wetherby, A. E.; Goeller, L. R.; DiPasquale, A. G.; Rheingold, A. L.; Weinert, C. S. *Inorg. Chem.* **2007**, *46*, 7579. (b) Dalgarno, S. J.; Claudio-Bosque, K. M.; Warren, J. E.; Glass, T. E.; Atwood, J. L. *Chem. Commun.* **2008**, 1410.

(13) Abrahams, B. F.; FitzGerald, N. J.; Hudson, T. A.; Robson, R.; Waters, T. *Angew. Chem., Int. Ed.* **2009**, *48*, 3129.

(14) Spisak, S. N.; Zabula, A. V.; Filatov, A. S.; Rogachev, A. Y.; Petrukhina, M. A. *Angew. Chem., Int. Ed.* **2011**, *50*, 8090.

(15) Sakane, H.; Amaya, T.; Moriuchi, T.; Hirao, T. *Angew. Chem., Int. Ed.* **2009**, *48*, 1640.

(16) Zhao, L.; Mak, T. C. W. *J. Am. Chem. Soc.* **2004**, *126*, 6852.

(17) (a) Jansen, M. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1098. (b) Pyykkö, P. *Chem. Rev.* **1997**, *97*, 597.

(18) (a) Mak, T. C. W.; Zhao, X.-L.; Wang, Q.-M.; Guo, G.-C. *Coord. Chem. Rev.* **2007**, *251*, 2311. (b) Bruce, M. I.; Low, P. J. *Adv. Organomet. Chem.* **2004**, *50*, 399.

(19) Wang, L.-X.; Zhao, L.; Wang, D.-X.; Wang, M.-X. *Chem. Commun.* **2011**, *47*, 9690.