JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Communication
pubs.acs.org/JACS

Synthesis of Unstable Carbides Ag_2C_{2n} (n = 3, 4) and Characterization via Crystallographic Analysis of Their Double Salts with Silver(I) Trifluoroacetate

Sam C. K. Hau and Thomas C. W. Mak*

Department of Chemistry and Center of Novel Functional Molecules, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong SAR, People's Republic of China

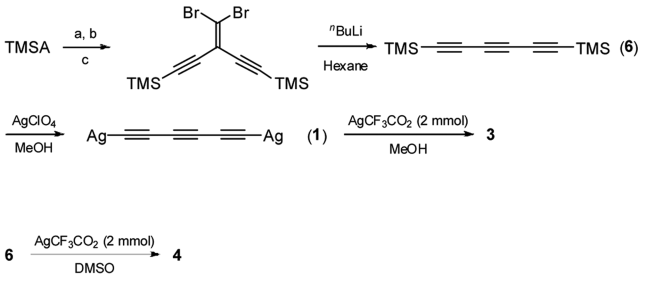
Supporting Information

ABSTRACT: Two new silver(I) carbides, Ag_2C_6 and Ag_2C_8, have been synthesized, and single-crystal X-ray analysis of their crystalline silver(I) trifluoroacetate complexes, $Ag_2C_6 \cdot 8AgCF_3CO_2 \cdot 6H_2O$, $4(Ag_2C_6) \cdot 16AgCF_3CO_2 \cdot 14.5DMSO$, and $2.5(Ag_2C_8) \cdot 10AgCF_3CO_2 \cdot 10DMSO$, provides detailed information on the influence of ligand disposition and orientation of the all-carbon anionic ligands in the construction of multidimensional supramolecular structures, which are consolidated by argentophilic and weak inter-/intramolecular interactions.

Over the past decade, transition metal complexes containing the linear M−C≡C−(C≡C)$_n$−C≡C−M (n = 1, 2) moiety, in which each terminal metal center (M = Re,[1a] Au,[1b] Fe,[1c] Ru,[2] Os,[3] Pt,[4]) is also coordinated by other ligands, have aroused much interest in view of their potential application as intriguing structure building blocks owing to their unique linear structural property.[1−4] Meanwhile, our group has conducted a systematic investigation on the synthesis and structural characterization of a series of Ag(I) multiple salts containing silver carbide, Ag_2C_{2n} (n = 1, 2), as a component, in which the all-carbon dianion ethynediide, C_2^{2-}, is generally capsulated inside a polyhedral Ag_m (m = 6−10) cage, whereas 1,3-butadiyne-1,4-diide, C_4^{2-}, exhibits variable coordination modes involving each terminal triple bond and a Ag_m (m = 3−5) basket.[5,6] Herein we report the first successful synthesis of their unstable higher homologues, silver(I) 1,3,5-hexatriyne-1,6-diide (Ag_2C_6, **1**) and silver(I) 1,3,5,7-octatetrayne-1,8-diide (Ag_2C_8, **2**), together with the crystal structures of three polymeric Ag(I) double salts, $Ag_2C_6 \cdot 8AgCF_3CO_2 \cdot 6H_2O$ (**3**),[7] $4(Ag_2C_6) \cdot 16AgCF_3CO_2 \cdot 14.5DMSO$ (**4**),[8] and $2.5(Ag_2C_8) \cdot 10AgCF_3CO_2 \cdot 10DMSO$ (**5**).[9]

Preparation of TMS−C≡C−C≡C−C≡C−TMS (**6**) according to literature procedures[10−12] involved two key reactions, Corey−Fuchs olefination[13] and carbene rearrangement reaction.[12,14] Reaction of **6** with $AgClO_4$ in a 1:2 molar ratio in MeOH at 23 °C for 30 min produced an orange precipitate containing Ag_2C_6 (**1**), which was filtered out and washed with deionized water (Scheme 1). [***Caution!*** *This crude orange Ag_2C_6 amorphous powder, being insoluble in polar or nonpolar solvents, is more explosive in the dry state than its lower homologues Ag_2C_2 and Ag_2C_4 and could only be stored in the wet form for 1−2 days in a refrigerator at −10 °C.* In addition, **1** gradually darkened in color, which indicated slow decomposition during storage. Attempts to measure its IR or Raman spectra were unsuccessful due to its instability to heat and mechanical shock.]

Scheme 1. Synthesis of Silver(I) Double Salts 3 and 4[a]



[a]Reagents and conditions: (a) ^{n}BuLi, (EtO)CHO, Et_2O, 0 °C; (b) PCC, CH_2Cl_2; (c) CBr_4, PPh_3, CH_2Cl_2.

Orange block-like crystals of the double salt $Ag_2C_6 \cdot 8AgCF_3CO_2 \cdot 6H_2O$ (**3**)[7] were obtained from the crystallization of crude **1** in a concentrated aqueous solution of $AgCF_3CO_2$ (Scheme 1). In the crystal structure of **3**, the C_6^{2-} ion is located at an inversion center, each terminal C atom being capsulated by a butterfly-shaped Ag_4 basket via the μ_4-$\eta^1,\eta^1,\eta^1,\eta^1$ mode (Figure 1a). Exterior silver atom Ag5 is attached to the Ag_4 aggregate through a pair of μ_3-η^1,η^2 trifluoroacetate groups (abbreviated as O1·O2 and O7·O8). The resulting barbell-like $[Ag_5C_6Ag_5]$ aggregate exhibits quasi-C_{2h} symmetry with a plane passing through atoms Ag3, Ag4, Ag5, Ag3A, Ag4A, and Ag5A (Figure 1b). The Ag···Ag distances within the Ag_4 aggregate lie in the range 2.833(14)−2.962(13) Å, suggesting the existence of significant argentophilic interactions.[15,16] Three independent aqua ligands are attached to the Ag atoms via different coordination modes (O1W coordinates to Ag3 and Ag4 via μ_2 mode, while both O2W and O3W attach to Ag5 via μ_1 mode).

As illustrated in Figure 2a, adjacent barbell units are interconnected by two pairs of symmetry-related trifluoroacetate groups (O3·O4 and O3A·O4A; O5·O6 and O5B·O6B) to produce an infinite silver−organic layer structure, which is further stabilized by additional H-bonding between trifluoroacetate groups and aqua ligand O1W (O1W···O4A, 2.825(12) Å; O1W···O6A, 2.836(12) Å).

Received: November 27, 2013

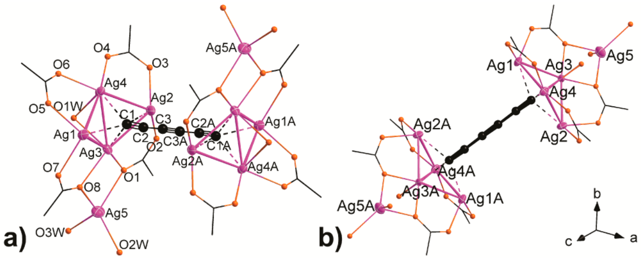


Figure 1. (a) Coordination environment of the Ag(I) atoms in double salt $Ag_2C_6\cdot 8AgCF_3CO_2\cdot 6H_2O$ (**3**). The argentophilic Ag···Ag distances shown as thick rods lie in the range 2.70−3.40 Å, and the H and F atoms are omitted for clarity. Silver atoms are drawn as thermal ellipsoids (50% probability level) with atom labeling. (b) Perspective view of the barbell-like $[Ag_5C_6Ag_5]$ aggregate with a pseudo-mirror plane passing through atoms Ag3, Ag4, and Ag5 and their symmetry equivalents. Color scheme: purple, Ag; orange, O; broken lines, Ag−C bonds; the same color scheme for atoms and bonds applies to all other figures.

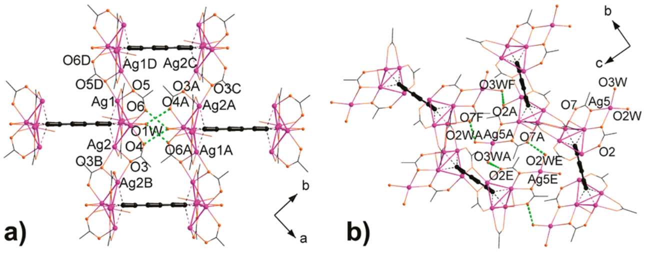


Figure 2. Perspective view of the crystal packing in **3** along (a) the *c*-axis and (b) the *a*-axis, showing notable H-bonds. Green broken lines indicate H-bond interactions; henceforth the same representation will apply to other crystal packing figures.

Further association of neighboring silver−organic layers through additional H-bonding involving the other two aqua ligands and trifluoroacetate groups (O2A···O3WB, 2.743(15) Å; O2WA···O7B, 2.790(14) Å) gives a 3-D supramolecular network (Figure 2b).

Starting material **6** was first added to a concentrated DMSO[17] solution of $AgCF_3CO_2$, quickly yielding an orange Ag_2C_6 precipitate, which gradually dissolved to form a deep red clear solution (Scheme 1). Transparent, orange plates of the double salt $4(Ag_2C_6)\cdot 16AgCF_3CO_2\cdot 14.5DMSO$ (**4**)[8] gradually crystallized through diffusion from atmospheric moisture into this deep red solution. Complex **4** contains five crystallographically independent C_6^{2-} ions, two located at crystallographic inversion centers (Figure 3). Among the five $[Ag_4C_6Ag_3]$ and $[Ag_4C_6Ag_4]$ aggregates, the eight independent terminal ethynide moieties exhibit different coordination modes: μ_4-$\eta^1,\eta^1,\eta^1,\eta^2$ for C1≡C2, C8≡C9, and C10≡C11; μ_3-η^1,η^1,η^1 for C4≡C5 and C20≡C21; μ_4-$\eta^1,\eta^1,\eta^1,\eta^1$ for C14≡C15 and C16≡C17; and μ_4-$\eta^1,\eta^1,\eta^2,\eta^2$ for C22≡C23. Besides this, such supramolecular synthons[18] coalesce with their adjacent units through argentophilic interactions, with Ag···Ag bond distances ranging 2.746(3)−3.573(2) Å, comparable to those observed in a wide variety of silver double and multiple salts,[16] to yield a pair of symmetry-related infinite silver chains (Type I and II), which point in opposite directions (Figure S1). As a result, a 1-D distorted ladder-like silver double-chain structure is generated (Figure S2).

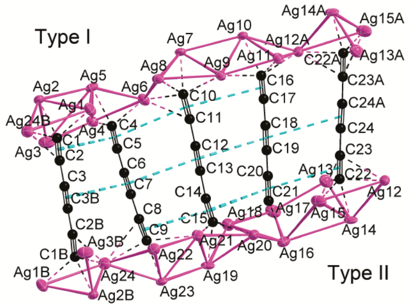


Figure 3. Coordination environment of five independent $[Ag_4C_6Ag_3]$ and $[Ag_4C_6Ag_4]$ aggregates in double salt $4(Ag_2C_6)\cdot 16AgCF_3CO_2\cdot 14.5DMSO$ (**4**), showing notable π−π stacking interactions. The argentophilic Ag···Ag distances shown as thick rods lie in the range 2.70−3.60 Å, and the H and F atoms are omitted for clarity. Silver atoms are drawn as thermal ellipsoids (50% probability level) with atom labeling. Turquoise broken lines indicate π−π stacking interactions; henceforth the same representation will apply to other figures.

The Ag−C bond distances between the Ag caps and C_8^{2-} dianions lie in the ranges 2.12(1)−2.15(2), 2.42(2)−2.45(2), and 2.13(2)−2.86(2) Å for σ, π, and mixed (σ,π) interactions, respectively, according to the classification in our previous studies.[19] The lengths of the C−C triple and single bonds are in the ranges 1.19(3)−1.30(3) and 1.34(3)−1.38(3) Å, respectively, consistent with the corresponding values in our previous observation for those complexes containing C_4^{2-} dianion.[20]

In addition, the ladder-like silver double-chain structures are further consolidated by offset π−π interactions between proximal triple bonds of adjacent C_6^{2-} dianions [bond center−bond center distances (Å) in the range 3.60−4.00 Å: C1≡C2···C4≡C5, 3.683(3); C1B≡C2B···C4B≡C5B, 3.683(3); C3≡C3B···C6≡C7, 3.826(3); C3≡C3B···C7B≡C6B, 3.825(3); C4≡C5···C10≡C11, 3.808(4); C6≡C7···C12≡C13, 3.759(3); C8≡C9···C14≡C15, 3.858(3); C10≡C11···C16≡C17, 3.848(4); C12≡C13···C18≡C19, 3.714(3); C14≡C15···C20≡C21, 3.869(3); C18≡C19···C24A≡C24, 3.650(3); C18A≡C19A···C24≡C24A, 3.825(4); C20≡C21···C23≡C22, 3.823(4); C20A≡C21A···C23A≡C22A, 3.650(3)] (see Figure S4a). These distances are comparable to similar offset face-to-face π−π interactions between phenyl rings.[21]

In complex **4**, the 15 independent co-crystallized DMSO ligand molecules (O33 to O47, the last one exhibiting half site-occupancy) attached to different Ag centers take variable μ_1-η^1, μ_2-η^1,η^1, and μ_3-η^1,η^1,η^1 coordination modes (see Figure S3). Adjacent silver−organic chains are interconnected through additional H-bonding between DMSO molecules and nearby trifluoroacetate groups (C71B−H···F47, 2.875(23) Å) to generate a Ag(I)−organic supramolecular layer (Figure 4a). Cross-linkage of such layers by weak C−H···F bonds between DMSO ligands and trifluoroacetate groups from adjacent layers [C60D−H···F25, 2.781(30) Å; C69−H···F15D, 2.605(21) Å; C68−H···F18D, 2.779(18) Å; C80E−H···F9, 2.672(42) Å] yields a 3-D supramolecular network (Figure 4b).

TMS−C≡C−(C≡C)$_2$−C≡C−TMS (**7**) is synthesized according to a modified literature procedure (Scheme 2).[12] Unfortunately, crude Ag_2C_8 (**2**) cannot be isolated in powder form like **1** due to its high reactivity and explosive properties. Reaction between **7** and $AgCF_3CO_2$ in DMSO produced crude Ag_2C_8 as an orange precipitate, which was later dissolved to give a deep red clear solution. Orange plate-like crystals of double salt $2.5(Ag_2C_8)\cdot 10AgCF_3CO_2\cdot 10DMSO$ (**5**) gradually

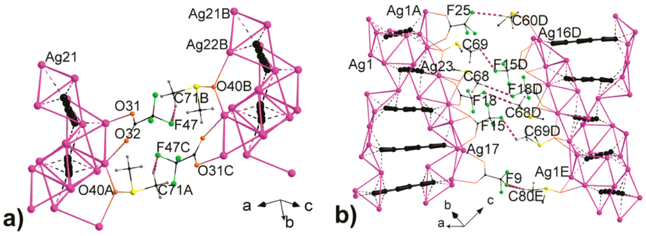
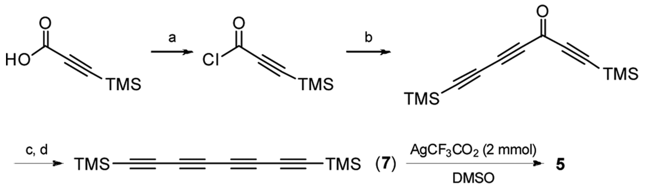


Figure 4. Perspective view of the crystal packing in **4**, along (a) the *c*-axis and (b) the *a*-axis, showing notable H-bonds. Violet broken lines indicate weak C−H···F interactions; henceforth the same representation will apply to other crystal packing figures.

Scheme 2. Synthesis of Silver(I) Double Salt 5[a]



[a]Reagents: (a) $(COCl)_2$, DMF; (b) $(TMS)_2C_4$, $AlCl_3$, CH_2Cl_2 ;(c) CBr_4, PPh_3, CH_2Cl_2; (d) ^nBuLi, C_6H_{14}.

formed through water diffusion into a concentrated $AgCF_3CO_2/Ag_2C_8$ solution in DMSO. The asymmetric unit of **5** contains three independent $[Ag_4C_8Ag_4]$ aggregates (Figure 5), one occupying a site of symmetry 1, together with 10 independent trifluoroacetate groups and 10 DMSO ligands. The Ag−C bond distances between the Ag caps and C_8^{2-} dianions are in the ranges 2.07(1)−2.11(1), 2.48(1)−2.53(1), and 2.16(1)−2.87(2) Å for σ, π, and mixed (σ,π) interactions, respectively. The lengths of the C−C triple and single bonds lie in the ranges 1.19(1)−1.24(2) and 1.33(2)−1.40(2) Å, respectively.

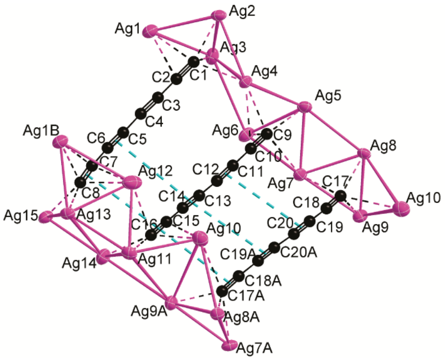


Figure 5. Coordination environment of the Ag(I) atoms in double salt $2.5(Ag_2C_8)\cdot 10AgCF_3CO_2\cdot 10DMSO$ (**5**). The argentophilic Ag···Ag distances shown as thick rods lie in the range 2.70−3.40 Å, and the H and F atoms are omitted for clarity. Silver atoms are drawn as thermal ellipsoids (50% probability level) with atom labeling.

Such Ag_4 caps and their adjacent symmetric-related segments are fused to form a Ag_{15} aggregate through atom sharing, and such Ag_{15} aggregates are further coalesced to generate an infinite Ag chain. The three C_8^{2-} dianions further undergo offset $\pi-\pi$ interactions [$C1\equiv C2\cdots C8B\equiv C7B$, 3.960(3) Å; $C3\equiv C4\cdots C6B\equiv C5B$, 3.891(3) Å; $C5\equiv C6\cdots C4B\equiv C3B$, 3.891(3) Å; $C5\equiv C6\cdots C13\equiv C14$, 4.058(3) Å; $C7\equiv C8\cdots C2B\equiv C1B$, 3.960(3) Å; $C7\equiv C8\cdots C15\equiv C16$, 3.782(3) Å; $C11\equiv C12\cdots C19\equiv C20$, 3.926(3) Å; $C13\equiv C14\cdots C20A\equiv C19A$, 3.825(3) Å; $C15\equiv C16\cdots C18A\equiv C17A$, 3.772(3) Å; $C17\equiv C18\cdots C16A\equiv C15A$, 3.771(3) Å; $C19\equiv C20\cdots C14A\equiv C13A$, 3.825(3) Å; $C20A\equiv C19A\cdots C12A\equiv C11A$, 3.926(3) Å], which provide additional stability to the Ag(I) double-chain structure (Figure S4b).

The 10 independent DMSO ligands chelated on the Ag chain can be classified into three groups according to their corresponding coordination modes: μ_1-η^1, O23; μ_2-η^1,η^1, O21, O22, O24, O26, O27, O29, and O30; and μ_3-η^1,η^1,η^1, O25 and O28 (Figure S5). Adjacent Ag(I)−organic chains are interconnected by additional H-bonds between DMSO ligands and trifluoroacetate groups [C53C−H···F17, 2.666(12) Å; C48−H···F15E, 2.661(13) Å; C59E−H···F24, 2.598(12) Å] to yield a supramolecular layer structure (Figure S6). Further cross-linking of such layer structures by weak C−H···F between DMSO ligands and trifluoroacetate groups [C49A−H···F8B, 2.536(16) Å; C41D−H···F21C, 2.605(12) Å; C42D−H···F27C, 2.619(12) Å] gives a 3-D supramolecular network structure (Figure S7).

The Ag−C≡C (σ-type interaction) and C≡C−C angles in **3**−**5** lie in the ranges 160.3(2)−171.4(2)° and 173.6(2)−179.4(2)°, respectively, which show larger deviation from linearity (<10° in general) than those reported in other C_6/C_8-bridged transition metal (Re,[1a] Au,[1b] Fe,[1c] Ru,[2] Os,[3] Pt[4]) complexes that are mostly dinuclear, indicating the effect of multinuclear Ag−ethynide interactions on the $AgC_{2n}Ag$ ($n = 3, 4$) segments.

Among complexes **3**−**5**, the coordination mode of either C_6^{2-} or C_8^{2-} retains the highest ligation number[20] of 8, consistent with those established for C_2^{2-} and C_4^{2-}, featuring the co-existence of Ag(I)−C σ- and π-type bonding. Such high-nuclearity coordination mode is further stabilized by ionic as well as argentophilic interactions. The internal ethynyl groups in both C_6^{2-} and C_8^{2-} are found to have no interaction with the Ag(I) ions. Notably, they gain stabilization via offset $\pi-\pi$ stacking between adjacent ethynyl groups, which is seldom observed in polymeric coordination networks. The coordination modes of the trifluoroacetate groups vary from the common μ_2-η^2 kind to the μ_2-η^1,η^1, μ_3-η^1,η^2, and μ_4-η^2,η^2 varieties. The trifluoroacetate ligand generally plays two important roles: either spanning an edge of the Ag_n basket to consolidate the $[Ag_nC\equiv C]^{(n-1)+}$ cationic moiety, or bridging adjacent Ag_n baskets to generate an infinite chain or layer structure. Complexes **3**−**5** all contain solvated water or DMSO molecules in their crystalline lattices. In these complexes, regular or weak C−H···F hydrogen bonds confer enhanced stability to a coordination chain/layer or connect the chains into a higher-dimensional supramolecular structure.

In summary, the present study provides the first examples of polymeric organosilver(I) frameworks assembled with the linear multinuclear Ag(I)−polyynediide supramolecular synthons $Ag_n\subset C\equiv C-(C\equiv C)_m-C\equiv C\supset Ag_n$ ($m = 1, 2$; $n = 3, 4$). Seen in a different light, the new Ag(I) carbides Ag_2C_6 and Ag_2C_8, despite their inherent instability, are potentially useful as structure building units for the construction of new coordination networks in combination with coinage-metal ions, inorganic/organic anionic bridging anions, and ancillary ligands.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, additional figures, ^{1}H NMR spectra, and X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

tcwmak@cuhk.edu.hk

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work is dedicated to the memory of Dr. Hson-Mou Chang (1923−2000). We gratefully acknowledge financial support by the Hong Kong Research Grants Council (GRF CUHK 402710) and the Wei Lun Foundation, and the award of a Postdoctoral Research Fellowship to S.C.K.H. by The Chinese University of Hong Kong.

■ REFERENCES

(1) (a) M = Re: Yam, V. W.-Y.; Chong, S. H.-F.; Ko, C.-C.; Cheung, K.-K. *Organometallics* **2000**, *19*, 5092. (b) M = Au: Lu, W.; Xiang, H.-F.; Zhu, N.; Che, C.-M. *Organometallics* **2002**, *21*, 2343. (c) M = Fe: Akita, M.; Sakurai, A.; Moro-oka, Y. *Chem. Commun.* **1999**, 101.

(2) M = Ru: (a) Qi, H.; Gupta, A.; Noll, B. C.; Snider, G. L.; Lu, Y.; Lent, C.; Fehlner, T. P. *J. Am. Chem. Soc.* **2005**, *127*, 15218. (b) Gao, L.-B.; Kan, J.; Fan, Y.; Zhang, L.-Y.; Liu, S.-H.; Chen, Z.-N. *Inorg. Chem.* **2007**, *46*, 5651. (c) Xu, G.-L.; Zou, G.; Ni, Y.-H.; DeRosa, M. C.; Crutchley, R. J.; Ren, T. *J. Am. Chem. Soc.* **2003**, *125*, 10057. (d) Xu, G.-L.; Wang, C.-Y.; Ni, Y.-H.; Goodson, T. G., III; Ren, T. *Organometallics* **2005**, *24*, 3247. (e) Xi, B.; Xu, G.-L.; Fanwick, P. E.; Ren, T. *Organometallics* **2009**, *28*, 2338. (f) Xi, B.; Liu, I. P.-C.; Xu, G.-L.; Choudhuri, M. M. R.; DeRosa, M. C.; Crutchley, R. J.; Ren, T. *J. Am. Chem. Soc.* **2011**, *133*, 15094.

(3) M = Os: Bruce, M. I.; Kramarczuk, K. A.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **2010**, *695*, 469.

(4) M = Pt: (a) Stahl, J.; Bohling, J. C.; Bauer, E. B.; Peters, T. B.; Mohr, W.; Martín-Alvarez, J. M.; Hampel, T.; Gladysz, J. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1871. (b) Zheng, Q.; Gladysz, J. A. *J. Am. Chem. Soc.* **2005**, *127*, 10508. (c) Stahl, J.; Mohr, W.; de Quadras, L.; Peters, T. B.; Bohling, J. C.; Martín-Alvarez, J. M.; Owen, G. R.; Hampel, F.; Gladysz, J. A. *J. Am. Chem. Soc.* **2007**, *129*, 8282. (d) de Quadras, L.; Bauer, E. B.; Mohr, W.; Bohling, J. C.; Peters, T. B.; Martín-Alvarez, J. M.; Hampel, F.; Gladysz, J. A. *J. Am. Chem. Soc.* **2007**, *129*, 8296. (e) Owen, G. R.; Stahl, J.; Hampel, F.; Gladysz, J. A. *Chem.—Eur. J.* **2008**, *14*, 73. (f) Owen, G. R.; Gauthier, S.; Weibach, N.; Hampel, F.; Bhuvanesh, N.; Gladysz, J. A. *Dalton Trans.* **2010**, *39*, 5260. (g) Yam, V. W.-Y.; Wong, K. M.-C.; Zhu, N. *Angew. Chem., Int. Ed.* **2003**, *42*, 1400. (h) Lu, W.; Mi, B.-X.; Chan, M. C. W.; Hui, Z.; Che, C.-M.; Zhu, N.; Lee, S.-T. *J. Am. Chem. Soc.* **2004**, *126*, 4958.

(5) For reviews, see: (a) Mak, T. C. W.; Zhao, X.-L.; Wang, Q.-M.; Guo, G.-C. *Coord. Chem. Rev.* **2007**, *251*, 2311. (b) Mak, T. C. W.; Zhao, L. *Chem. Asian J.* **2007**, *2*, 456. (c) Mak, T. C. W.; Zhao, L.; Zhao, X.-L. Supramolecular Assembly of Silver(I) Complexes with Argentophilic and Silver···Carbon Interactions. In *The Importance of Pi-Interactions in Crystal Engineering—Frontiers in Crystal Engineering III*; Tiekink, E. R. T., Zukerman-Schpector, J., Eds.; Wiley: Chichester, 2012; Chap. 13, pp 323−366.

(6) (a) Zhao, X.-L.; Mak, T. C. W. *Inorg. Chem.* **2010**, *49*, 3676. (b) Hu, T.; Zhao, L.; Mak, T. C. W. *Organometallics* **2012**, *31*, 7539. (c) Hu, T.; Mak, T. C. W. *Inorg. Chem.* **2013**, *52*, 9066. (d) Hu, T.; Mak, T. C. W. *Cryst. Growth Des.* **2013**, *13*, 4957.

(7) Crystal data for **3**: $C_{22}H_{12}Ag_{10}F_{24}O_{22}$, $M = 2163.02$, monoclinic, space group $P2_1/c$ (No. 14), $a = 10.871(7)$ Å, $b = 10.844(7)$ Å, $c = 20.337(20)$ Å, $\beta = 97.983(10)°$, $V = 2374.3(3)$ Å^3, $Z = 2$, $T = 173$ K, $R_1 = 0.0761$, $wR_2 = 0.2052$ for 4290 reflections $[I > 2\sigma(I)]$. IR (KBr): 1928, 2047, 2129 cm^{-1} ($\nu_{C\equiv C}$, w).

(8) Crystal data for **4**: $C_{170}H_{150}Ag_{48}F_{96}O_{93}S_{29}$, $M = 11612.40$, triclinic, space group $P\bar{1}$ (No. 2), $a = 15.124(18)$ Å, $b = 22.255(3)$ Å, $c = 26.642(3)$ Å, $\alpha = 102.224(2)°$, $\beta = 97.582(2)°$, $\gamma = 108.848(2)°$, $V = 8097.3(16)$ Å^3, $Z = 1$, $T = 173$ K, $R_1 = 0.1072$, $wR_2 = 0.3001$ for 29 018 reflections $[I > 2\sigma(I)]$.

(9) Crystal data for **5**: $C_{60}H_{60}Ag_{15}F_{30}O_{30}S_{10}$, $M = 3769.73$, monoclinic, space group $C2/c$ (No. 15), $a = 58.133(4)$ Å, $b = 11.814(9)$ Å, $c = 39.378(3)$ Å, $\beta = 129.787(10)°$, $V = 20782(3)$ Å^3, $Z = 8$, $T = 173$ K, $R_1 = 0.0803$, $wR_2 = 0.2266$ for 18 835 reflections $[I > 2\sigma(I)]$.

(10) Anthony, J.; Boldi, A. M.; Rubin, Y.; Hobi, M.; Gramlich, V.; Knobler, C. B.; Seiler, P.; Diederich, F. *Helv. Chim. Acta* **1995**, *78*, 13.

(11) We are indebted to a reviewer for drawing our attention to an alternative route that gives **6** in gram scale. See: Rubin, Y.; Lin, S. S.; Knobler, C. B.; Anthony, J.; Boldi, A. M.; Diederich, F. *J. Am. Chem. Soc.* **1991**, *113*, 6943.

(12) Eisler, S.; Slepkov, A. D.; Elliott, E.; Luu, T.; McDonald, R.; Hegmann, F. A.; Tykwinski, R. R. *J. Am. Chem. Soc.* **2005**, *127*, 2666.

(13) Corey, E. J.; Fuchs, P. L. *Tetrahedron Lett.* **1972**, *13*, 3769.

(14) Xu, G.-L.; Xi, B.; Updegraff, J. B.; Protasiewicz, J. D.; Ren, T. *Organometallics* **2006**, *25*, 5213.

(15) (a) Pyykkö, P. *Chem. Rev.* **1988**, *88*, 563. (b) Pyykkö, P. *Chem. Rev.* **1997**, *97*, 597. (c) Pyykkö, P. *Chem. Soc. Rev.* **2008**, *37*, 1967. (d) Grimme, S.; Djukic, J.-P. *Inorg. Chem.* **2010**, *49*, 2911. (e) Muñiz, J.; Wang, C.; Pyykkö, P. *Chem.—Eur. J.* **2011**, *17*, 368.

(16) (a) Guo, G.-C.; Zhou, G.-D.; Mak, T. C. W. *J. Am. Chem. Soc.* **1999**, *121*, 3136. (b) Guo, G.-C.; Zhou, G.-D.; Wang, Q.-G.; Mak, T. C. W. *Angew. Chem., Int. Ed.* **1998**, *37*, 630. (c) Wang, Q.-G.; Mak, T. C. W. *J. Am. Chem. Soc.* **2001**, *123*, 1501. (d) Wang, Q.-M.; Mak, T. C. W. *Angew. Chem., Int. Ed.* **2001**, *40*, 1130. (e) Wang, Q.-M.; Mak, T. C. W. *Chem. Commun.* **2001**, *37*, 807.

(17) DMSO was employed as it has been proven to be a good solvent by functioning as a co-ligand in our previous studies. See: Cheng, P.-S.; Marivel, S.; Zang, S.-Q.; Gao, G.-G.; Mak, T. C. W. *Cryst. Growth Des.* **2012**, *12*, 4519.

(18) (a) Desiraju, G. R. *Angew. Chem., Int. Ed.* **1995**, *34*, 2311. (b) Desiraju, G. R. *Angew. Chem., Int. Ed.* **2007**, *46*, 8342.

(19) Hau, S. C. K.; Mak, T. C. W. *Chem.—Eur. J.* **2013**, *19*, 5387.

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

(21) Janiak, C. *J. Chem. Soc., Dalton Trans.* **2000**, 3885.

(22) Guo, G.-C.; Mak, T. C. W. *Chem. Commun.* **1999**, 813.