

Two birds with one stone: anion templated ball-shaped Ag₅₆ and disc-like Ag₂₀ clusters†Cite this: *Dalton Trans.*, 2013, **42**, 6281

Received 3rd February 2013,

Accepted 6th March 2013

DOI: 10.1039/c3dt50342a

www.rsc.org/dalton

Di Sun,^{*a} Hua Wang,^a Hai-Feng Lu,^a Sheng-Yu Feng,^a Zhen-Wei Zhang,^b
Guo-Xin Sun^b and Dao-Feng Sun^a

One-pot reaction of AgSBU^t and AgOAc in the methanol–ethanol–DMF solvent system under room temperature gave a ball-shaped Ag₅₆ cluster and a disc-like Ag₂₀ cluster. The formations of clusters 1 and 2 are templated by an *in situ* generated S²⁻ ion from the cleavage of the S–C bond of SBU^t and CO₃²⁻ ion from the fixation of atmospheric carbon dioxide, respectively. Interestingly, cluster 1 only emits bright-red light in the solid state at 77 K and is not emissive at room temperature.

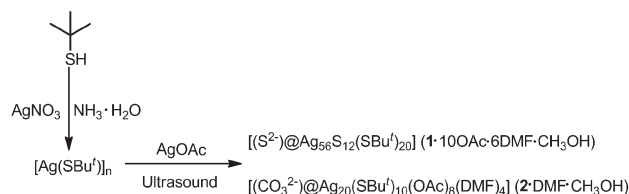
In recent years, increased attention has been focused on the high-nuclearity metal clusters due to not only their fascinating structures,¹ but also their various potential applications.² Among them, giant silver chalcogenide clusters are important members and have been studied extensively due to their rich photophysical properties and their role as intermediates between mononuclear complexes and binary bulk phases.³ Employing the reaction of various silver salts with high-reactive S(SiMe₃)₂ and analogues in the presence of phosphane reagents, the Fenske group has made great advances in the synthesis of a series of giant silver clusters, for example, [Ag₁₂₃S₃₅(SBU^t)₅₀], [Ag₂₆₂S₁₀₀(SBU^t)₆₂(dppp)₆], [Ag₃₂₀S₁₃₀(SBU^t)₆₀(dppp)₁₂], [Ag₃₄₄S₁₂₄(SBU^t)₉₆], [Ag₃₅₂S₁₂₈(S^tC₅H₁₁)₉₆] and [Ag₄₉₀S₁₈₈(S^tC₅H₁₁)₁₁₄].⁴ However, the difficulties in both synthesis and structural determination of these huge clusters still prevent researchers from deeply understanding them.^{4c} Thus, much effort should be continuously devoted to the construction of the silver chalcogenide clusters. Thanks to their good affinity for silver atoms and the ability to stabilize silver clusters, thiolates including *t*-butylmercaptan (HSBU^t), 4-*t*-butylthiophenol (HSC₆H₄BU^t) and 3,4-difluoro-benzenethiol have been widely

used to cap the exterior silver shell to form truly monodispersed clusters in size and shape, which enable one to determine the precise molecular structure of the clusters.⁵

As we know, only a few Ag–S clusters based on the small HSBu^t ligand have been found in the literature.⁶ Moreover, luminescent Ag–S nanoclusters are still sparse. Wang *et al.* unmasked the first luminescent molecular Ag–S nanocluster, [Ag₆₂S₁₃(SBU^t)₃₂](BF₄)₄, which could be defined as a core–shell cluster with an interior μ₆-S²⁻ centered eight-capped octahedral silver core and a [Ag₄₈(SBU^t)₃₂] shell.⁷ They and the Mak group also pioneered the anion-templated silver clusters, proving the powerful template approach for the synthesis of high-nuclearity silver(I) clusters.⁸

As an ongoing investigation on structurally charming silver clusters and their luminescent properties,⁹ we have now succeeded in preparing two novel clusters, ball-shaped [(S²⁻)@Ag₅₆S₁₂(SBU^t)₂₀] (1·10OAc·6DMF·CH₃OH; main product) and disc-like [(CO₃²⁻)@Ag₂₀(SBU^t)₁₀(OAc)₈(DMF)₄] (2·DMF·CH₃OH; by-product) clusters. The formations of them are templated by an *in situ* generated S²⁻ ion from the cleavage of the S–C bond of SBU^t and a CO₃²⁻ ion from the fixation of atmospheric carbon dioxide, respectively. Interestingly, cluster 1 only emits bright-red light in the solid state at 77 K and is not emissive at room temperature. In this communication, we report the synthesis, crystal structure, and luminescent properties of 1 as well as the crystal structure of the by-product 2.

Clusters 1 and 2 were synthesized by a one-pot reaction of equimolar amounts of the AgSBU^t precursor¹⁰ and AgOAc in methanol–ethanol–DMF (v : v : v = 2 : 4 : 3) under the ultrasonic condition (160 W, 40 kHz, 40 min, room temperature, Scheme 1).



Scheme 1 Schematic presentation of stepwise synthesis of 1 and 2.

^aKey Laboratory of Special Functional Aggregated Materials, Ministry of Education, School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100, People's Republic of China. E-mail: dsun@sdu.edu.cn; Fax: +86-531-88364218

^bSchool of Chemistry and Chemical Engineering, University of Jinan, 106 Jiwei Road, 250022 Jinan, PR China

†Electronic supplementary information (ESI) available: Synthetic and crystallographic details, additional measurements, figures and tables. CCDC 884502 (1) and 913216 (2). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt50342a

The red **1** and colourless **2** suitable for X-ray crystallography were obtained by slow evaporation at room temperature (see ESI†). The crystals of **1** are stable in the mother liquor and become brittle once exposed to air. The composition of **1** was further deduced from X-ray single crystal diffraction, elemental analysis, and IR spectra. The phase purity of **1** is sustained by its powder X-ray diffraction pattern, which is consistent with that simulated on the basis of the single-crystal X-ray diffraction data. These results are well in agreement with the crystal structure of **1** (Fig. S1, ESI†). Colorless crystals of **2** were picked up from a large quantity of **1** with a very low yield (below 5%). Due to extremely low yield, only structure determination was carried out for this cluster.

X-ray single-crystal diffraction analysis† reveals that **1** is a ball-shaped cluster. It crystallizes in the cubic crystal system with a space group of $Pa\bar{3}$. As depicted in Fig. 1a, the C_{3i} -symmetric cluster is comprised of 56 Ag(I) ions, 20 SBU^f ligands, and 13 S²⁻ ions *in situ* generated from the cleavage of the S–C bond of SBU^f. There is a 3-fold axis through the atoms S1–Ag10–S5 and S5 also sits on the inversion center. Owing to the size of the cluster, there is a significant interstitial space of 37.0% (calculated using the PLATON/VOID routine¹¹) accommodating the counteranion OAc⁻ and solvents in a severely disordered fashion.

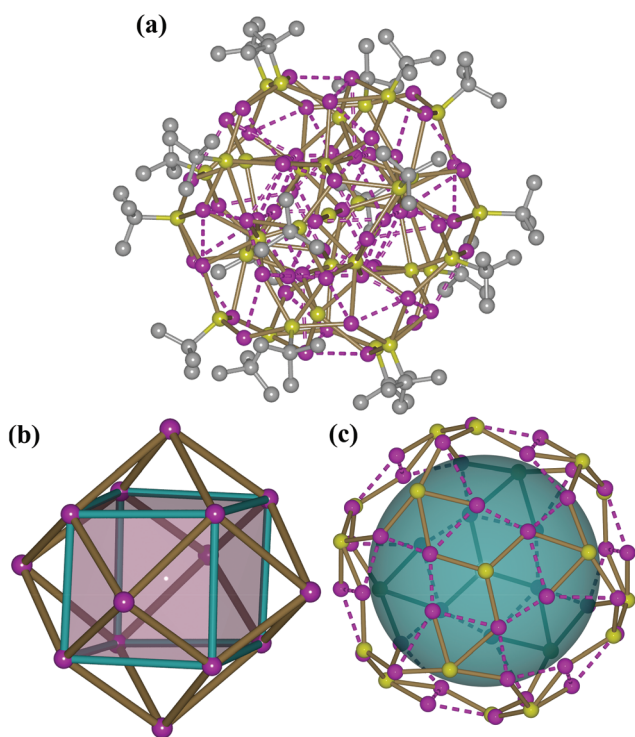


Fig. 1 (a) Crystal structure of cluster **1**, the Ag(I)...Ag(I) interactions are highlighted with the purple dashed lines. (b) The hexacapped cube Ag₁₄ core (the μ_2 -S²⁻ ion in its center is omitted). (c) The [Ag₄₂(SBU^f)₂₀] shell structure and the Bu^f groups are omitted for clarity, and the artificial large yellow sphere shows the inner space occupied by the Ag₁₄ core. Color legend: Ag, purple; S, yellow; C, gray.

Cluster **1** could be defined as a core–shell structure containing a hexacapped cube Ag₁₄ (Fig. 1b) in the interior and a [Ag₄₂(SBU^f)₂₀] shell in the exterior (Fig. 1c). Eight Ag(I) ions congregate to a cube, and six additional Ag(I) ions further cap its six rectangular faces to give a fascinating polyhedron with a hexacapped cube configuration through Ag(I)...Ag(I) contacts of 2.978(3), 3.0044(12), 3.181(3), and 3.188(3) Å. These distances are shorter than the sum of Ag(I) van der Waals radii (3.44 Å), indicating unambiguously the presence of metal...metal contacts.¹² The central S²⁻ ion is in a perfectly linear binding mode, with a long Ag–S bond length of 2.9476(17) Å. An alternative description for the hexacapped cube is that 14 Ag₄ quadrangles built up a rhombic dodecahedron. This interior polyhedron geometrically resembles a previously reported Ni-centered Ni₈(μ_4 -Ge)₆ cage in Ni₉(μ_4 -GeEt)₆(CO)₈,^{13a} a heterometallic Cl-centered Ag₈Cu₄ cage covered by an FcC≡C ligand,^{13b} and an X-centered (X = Cl and Br) Ag₁₄ cage covered by a C≡CBu^f ligand,^{13c} but obviously different from the eight-capped octahedral Ag₁₄ core in [Ag₆₂S₁₃(SBU^f)₃₂](BF₄)₄.⁷ Twelve *in situ* generated S²⁻ ions are embedded in the lacuna between the interior hexacapped cube and the exterior [Ag₄₂(SBU^f)₂₀] silver shell. The whole cluster is completed by the linkage of S²⁻ ions (including μ_4 -, μ_5 - and μ_6 -modes) as well as the Ag(I)...Ag(I) interactions between the core and the shell. This ball-shaped cluster has a diameter of *ca.* 1.7 nm. Disorder of the Ag(I) ions on the outermost shell made accurate discussions about the Ag...Ag separations and Ag–S bond lengths distributed on the shell meaningless, although the data were collected at 100 K. It is of note, however, that the outermost shell of 20 SBU^f groups is ordered. The disordered distributions of Ag(I) ions within the core or shell of the high-nuclear cluster have usually occurred with the structural determination of many other silver-rich clusters.⁴

It is noteworthy that the core structures in **1** and [Ag₆₂S₁₃(SBU^f)₃₂](BF₄)₄⁷ are completely different (Fig. S2†), despite both of them having fourteen Ag(I) ions and one central S²⁻. During the self-assembly process, the Ag(I) ions may firstly enclose the highly polarizable S²⁻ ions to aggregate into the low-nuclear silver cluster, which is highly reactive and quickly grows with the organic ligand covered on the outermost shell. As described above, syntheses of **1** and [Ag₆₂S₁₃(SBU^f)₃₂](BF₄)₄ are performed in different solvents, reaction conditions, and additives, which is responsible for the formation of the different core structures, as a consequence, the different clusters are obtained. These comparison results give us a preliminary insight into the growth mechanism of core–shell Ag–S clusters.

X-ray single-crystal diffraction analysis† reveals that **2** is a disc-like structure with the outer diameter and the thickness of *ca.* 10 and 4 Å, respectively. As depicted in Fig. 2a, the centrosymmetric cluster is comprised of 20 Ag(I) ions, 10 SBU^f ligands, 8 OAc⁻, 4 DMF and one CO₃²⁻ ion from the atmosphere lying on the inversion center. The ten SBU^f ligands adopt μ_4 - η^1 , η^1 , η^1 , η^1 binding mode and link four silver(I) ions to form ten Ag₄S square pyramids, each of which consists of a silver rectangle base and four Ag₂S triangle faces. The ten Ag₄S

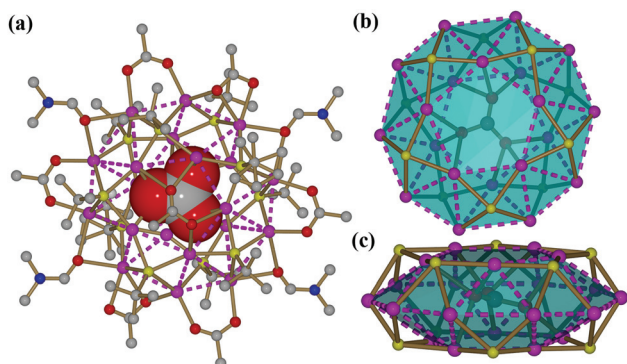


Fig. 2 (a) Crystal structure of cluster **2**. (b) and (c) The disc-like Ag_{20} cluster viewed along the different directions. Color legend: Ag, purple; S, yellow; C, gray; N, blue; O, red.

square pyramids share their corners to form the Ag_{20} cluster. Furthermore, ten silver triangles are alternately inserted into the interspace among every three Ag_4S square pyramids. The eight OAc^- ions show three kinds of coordination modes, four are $(\kappa^1)-(\kappa^1)-\mu_2$, two are $(\kappa^2)-(\kappa^1)-\mu_2$ and two are $(\kappa^2)-(\kappa^1)-\mu_3$, which combine with μ_2 -DMF to seam the $\text{Ag}_{20}\text{S}_{10}$ cluster in the periphery. The overall geometry of the $\text{Ag}_{20}\text{S}_{10}$ cluster can be described as a disc (Fig. 2b and 2c). In addition, the $\text{Ag}\cdots\text{Ag}$ distances in **2** fall in the range of 2.9053(9) to 3.375(3) Å, indicating the important argentophilicity $\text{Ag}\cdots\text{Ag}$ interactions. The CO_3^{2-} ion was encapsulated as a template in the center of **2** and ligated with the exterior Ag shell through the $(\kappa^3)-(\kappa^3)-(\kappa^3)-\mu_6$ mode. The origination of enthetic CO_3^{2-} is unambiguously proved by the contrast experiments. The crystal of **2** is exclusively formed in the atmosphere and only **1** could be obtained when evaporating in an inert N_2 atmosphere without CO_2 under darkness in the desiccator.

It is noteworthy that both **1** and **2** are formed by the directions of S^{2-} and CO_3^{2-} templates, respectively, which are not added into the reaction but originate from *in situ* C–S single bond cleavage of SBU^f and the fixation of atmospheric carbon dioxide,^{8c,9a} respectively. In this one-pot reaction, two different anion templates are generated from two different routes, which has been rarely observed in the self-assembly process previously. The present work opens up a new chapter for the assembly of multiple anion-templated high-nuclearity silver thiolate clusters in complicated reaction systems.

The electronic absorption spectrum of **1** exhibits one broad peak covering the visible region from 400 to 800 nm (Fig. S3†), which contains a maximum absorption peak centered at 413 nm and two shoulders at *ca.* 481 and 626 nm, respectively. The wide absorption in the visible region is consistent with the dark-red color of its crystals. The low-energy band in the visible region is assigned to the charge transfer from the S 3p to Ag 5s orbitals, as a similar assignment was made in $[\text{Ag}_{62}\text{S}_{13}(\text{SBU}^f)_{32}](\text{BF}_4)_4$.⁷

The luminescent properties of **1** were investigated in the solid state at room temperature and 77 K, respectively. There is no detectable luminescence at room temperature for **1**.

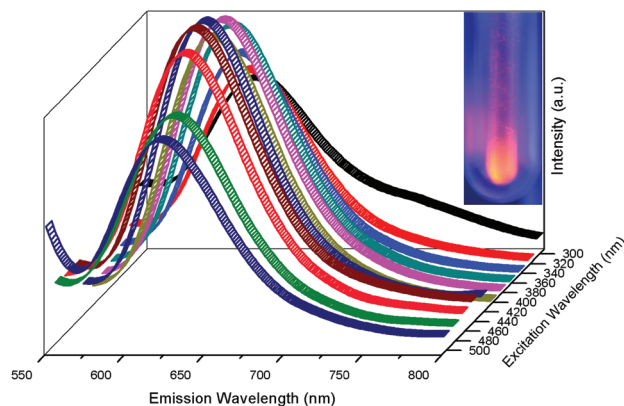


Fig. 3 Emission spectra of **1** at 77 K under different excitation wavelengths. Insert: Photograph of the luminescence taken at 77 K excited with a hand-held UV lamp (365 nm).

However, the brilliant red luminescence was observed at 77 K when **1** was illuminated with a hand-held UV lamp ($\lambda_{\text{ex}} = 365$ nm). As shown in Fig. 3, complex **1** exhibits a low energy emission band with λ_{max} at 623 nm at 77 K. Although when the excitation wavelengths vary from 300 to 500 nm, the maximum emission position is still kept. The red emission from **1** is very probably associated with the ligand-to-metal charge transfer (LMCT) excited state, that is charge transfer from the S 3p to Ag 5s orbitals, perturbed by $\text{Ag}\cdots\text{Ag}$ interactions,¹⁴ which is characteristic of the polynuclear d^{10} complexes with metallophilic interactions.¹⁵ Notably, disordered silver atoms may provide channels for nonemissive vibrational relaxation of the emissive excited state, which are attributed to the nonemissive behavior of **1** at room temperature. At 77 K, the degree of disorder of silver atoms was, to some extent, inhibited, which reduced the nonradiative decay of the emitting excited state, giving **1** the bright red emission.

In summary, two novel high-nuclear silver clusters have been synthesized using a facile one-pot approach at room temperature. The formations of clusters **1** and **2** are templated by an *in situ* generated S^{2-} ion from the cleavage of the S–C bond of SBU^f and a CO_3^{2-} ion from the fixation of atmospheric carbon dioxide, respectively. Interestingly, cluster **1** only emits bright-red light in the solid state at 77 K and is not emissive at room temperature.

This work was supported by the NSFC (Grant No. 21201110), the Independent Innovation Foundation of Shandong University (2011GN030), the Special Fund for Postdoctoral Innovation Program of Shandong Province (201101007) and the China Postdoctoral Science Foundation (2012M511492).

Notes and references

†Crystal data for **1**: $\text{C}_{80}\text{H}_{180}\text{Ag}_{56}\text{S}_{33}$, cubic, space group $P\bar{a}3$ (no. 205), $M = 8240.94$, $a = 29.022(6)$ Å, $V = 24\,444(8)$ Å³, $T = 100(2)$, $Z = 4$, $\mu(\text{Mo K}\alpha) = 4.666$, 26 664 reflections measured, 7126 unique ($R_{\text{int}} = 0.0489$) which were used in all calculations. The final R_1 was 0.0829 ($>2\sigma(I)$) and wR_2 was 0.2648 (all data).

Crystal data for 2: $C_{69}H_{142}Ag_{20}N_4O_{23}S_{10}$, monoclinic, space group $P2_1/n$ (no. 14), $M = 3873.97$, $a = 11.887(2)$ Å, $b = 19.864(4)$ Å, $c = 25.881(5)$ Å, $\beta = 91.49(3)^\circ$, $V = 6109(2)$ Å³, $T = 173(2)$ K, $Z = 2$, $\mu(\text{Mo K}\alpha) = 3.347$ mm⁻¹, 38 879 reflections measured, 10 716 unique ($R_{\text{int}} = 0.0577$) which were used in all calculations. The final R_1 was 0.0485 ($>2\sigma(I)$) and wR_2 was 0.1223 (all data).

- 1 (a) G. E. Kostakis and A. K. Powell, *Coord. Chem. Rev.*, 2009, **253**, 2686; (b) X. J. Kong, L. S. Long, Z. P. Zheng, R. B. Huang and L. S. Zheng, *Acc. Chem. Res.*, 2010, **43**, 201; (c) D. L. Long, R. Tsunashima and L. Cronin, *Angew. Chem., Int. Ed.*, 2010, **49**, 1736; (d) C. Schäffer, A. M. Todea, H. Bögge, E. Cadot, P. Gouzerh, S. Kopilevich, I. A. Weinstock and A. Müller, *Angew. Chem., Int. Ed.*, 2011, **50**, 12326; (e) H.-W. Lerner, G. Margraf, J. W. Bats and M. Wagner, *Chem. Commun.*, 2005, 4545; (f) H. B. Wu, Z. J. Huang and Q. M. Wang, *Chem.-Eur. J.*, 2010, **16**, 12321; (g) X.-J. Kong, Y. Wu, L.-S. Long, L.-S. Zheng and Z. Zheng, *J. Am. Chem. Soc.*, 2009, **131**, 6918; (h) X.-J. Kong, Y.-P. Ren, L.-S. Long, Z. Zheng, R.-B. Huang and L.-S. Zheng, *J. Am. Chem. Soc.*, 2007, **129**, 7016; (i) X.-J. Kong, Y.-P. Ren, W.-X. Chen, L.-S. Long, Z. Zheng, R.-B. Huang and L.-S. Zheng, *Angew. Chem., Int. Ed.*, 2008, **47**, 2398; (j) X.-J. Kong, L.-S. Long, R.-B. Huang, L.-S. Zheng, T. D. Harris and Z. Zheng, *Chem. Commun.*, 2009, 4354; (k) M.-H. Zeng, M.-X. Yao, H. Liang, W.-X. Zhang and X.-M. Chen, *Angew. Chem., Int. Ed.*, 2007, **46**, 1832; (l) Y. Xiao and Q. M. Wang, *Chem.-Eur. J.*, 2012, **18**, 11184; (m) L. Q. Mo, J. H. Jia, L. J. Sun and Q. M. Wang, *Chem. Commun.*, 2012, **48**, 8691; (n) T. U. Connell, S. Sandanayake, G. N. Khairallah, J. M. White, R. A. J. O'Hair, P. S. Donnelly and S. J. Williams, *Dalton Trans.*, 2013, **42**, 4903; (o) H. Yang, J. Lei, B. Wu, Y. Wang, M. Zhou, A. Xia, L. Zheng and N. Zheng, *Chem. Commun.*, 2013, **49**, 300.
- 2 (a) B. S. Bassil, M. H. Dickman, I. Römer, B. von der Kammer and U. Kortz, *Angew. Chem., Int. Ed.*, 2007, **46**, 6192; (b) F. Xu, R. A. Scullion, J. Yan, H. N. Miras, C. Busche, A. Scandurra, B. Pignataro, D. L. Long and L. Cronin, *J. Am. Chem. Soc.*, 2011, **133**, 4684; (c) D. Mansfeld, L. Miersch, T. Ruffer, D. Schaarschmidt, H. Lang, T. Böhle, R. W. Troff, C. A. Schalley, J. Müller and M. Mehring, *Chem.-Eur. J.*, 2011, **17**, 14805; (d) T. Wu, F. Zuo, L. Wang, X. H. Bu, S. T. Zheng, R. Ma and P. Y. Feng, *J. Am. Chem. Soc.*, 2011, **133**, 15886; (e) Y. Shichibu, Y. Kamei and K. Konishi, *Chem. Commun.*, 2012, **48**, 7559; (f) X. K. Wan, Z. W. Lin and Q. M. Wang, *J. Am. Chem. Soc.*, 2012, **134**, 14750.
- 3 J. F. Corrigan, O. Fuhr and D. Fenske, *Adv. Mater.*, 2009, **21**, 1867.
- 4 (a) D. Fenske, C. Persau, S. Dehnen and C. E. Anson, *Angew. Chem., Int. Ed.*, 2004, **43**, 305; (b) D. Fenske, C. E. Anson, A. Eichhöfer, O. Fuhr, A. Ingendoh, C. Persau and C. Richert, *Angew. Chem., Int. Ed.*, 2005, **44**, 5242; (c) C. E. Anson, A. Eichhöfer, I. Issac, D. Fenske, O. Fuhr, P. Sevillano, C. Persau, D. Stalke and J. T. Zhang, *Angew. Chem., Int. Ed.*, 2008, **47**, 1326.
- 5 (a) H. Yang, J. Lei, B. Wu, Y. Wang, M. Zhou, A. Xia, L. Zheng and N. Zheng, *Chem. Commun.*, 2013, **49**, 300; (b) X. Liu, H. Yang, N. Zheng and L. Zheng, *Eur. J. Inorg. Chem.*, 2010, 2084.
- 6 (a) J. Arnold, *Prog. Inorg. Chem.*, 1995, **43**, 353; (b) K. Tang, X. Xie, Y. Zhang, X. Zhao and X. Jin, *Chem. Commun.*, 2002, 1024; (c) K. Zhou, C. Qin, H.-B. Li, L.-K. Yan, X.-L. Wang, G.-G. Shan, Z.-M. Su, C. Xu and X.-L. Wang, *Chem. Commun.*, 2012, **48**, 5844; (d) K. Zhou, X.-L. Wang, C. Qin, H.-N. Wang, G.-S. Yang, Y.-Q. Jiao, P. Huang, K.-Z. Shao and Z.-M. Su, *Dalton Trans.*, 2013, **42**, 1352.
- 7 G. Li, Z. Lei and Q.-M. Wang, *J. Am. Chem. Soc.*, 2010, **132**, 17678.
- 8 (a) G. G. Gao, P. S. Cheng and T. C. W. Mak, *J. Am. Chem. Soc.*, 2009, **131**, 18257; (b) S.-D. Bian, H.-B. Wu and Q.-M. Wang, *Angew. Chem., Int. Ed.*, 2009, **48**, 5363; (c) S.-D. Bian, J.-H. Jia and Q.-M. Wang, *J. Am. Chem. Soc.*, 2009, **131**, 3422; (d) S.-D. Bian and Q.-M. Wang, *Chem. Commun.*, 2008, 5586; (e) J. Qiao, K. Shi and Q. M. Wang, *Angew. Chem., Int. Ed.*, 2010, **49**, 1765; (f) Y. P. Xie and T. C. W. Mak, *J. Am. Chem. Soc.*, 2011, **133**, 3760; (g) Y. P. Xie and T. C. W. Mak, *Chem. Commun.*, 2012, **48**, 1123; (h) Y. P. Xie and T. C. W. Mak, *Inorg. Chem.*, 2012, **51**, 8640.
- 9 (a) D. Sun, G.-G. Luo, N. Zhang, R.-B. Huang and L.-S. Zheng, *Chem. Commun.*, 2011, **47**, 1461; (b) D. Sun, D.-F. Wang, X.-G. Han, N. Zhang, R.-B. Huang and L.-S. Zheng, *Chem. Commun.*, 2011, **47**, 746; (c) D. Sun, F.-J. Liu, R.-B. Huang and L.-S. Zheng, *Inorg. Chem.*, 2011, **50**, 12393; (d) D. Sun, L. Zhang, Z. Yan and D. Sun, *Chem.-Asian J.*, 2012, **7**, 1558; (e) D. Sun, Z.-H. Wei, C.-F. Yang, N. Zhang, R.-B. Huang and L.-S. Zheng, *Inorg. Chem. Commun.*, 2010, **13**, 1191.
- 10 AgSBU^t was prepared by reacting equivalent amounts of AgNO₃ and HSBu^t in the presence of 25% ammonia.
- 11 A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7.
- 12 (a) A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441; (b) M. Jansen, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 1098; (c) P. Pykkö, *Chem. Rev.*, 1997, **97**, 597.
- 13 (a) J. P. Zebrowski, R. K. Hayashi, A. Bjarnason and L. F. Dahl, *J. Am. Chem. Soc.*, 1992, **114**, 3121; (b) Q.-H. Wei, G.-Q. Yin, L.-Y. Zhang and Z.-N. Chen, *Organometallics*, 2006, **25**, 4941; (c) D. Rais, J. Yau, D. M. P. Mingos, R. Vilar, A. J. P. White and D. J. Williams, *Angew. Chem., Int. Ed.*, 2001, **40**, 3464.
- 14 A. Barbieri, G. Accorsi and N. Armaroli, *Chem. Commun.*, 2008, 2185.
- 15 V. W.-W. Yam, *Acc. Chem. Res.*, 2002, **35**, 555.