Nuclearity Expansion in Pd Clusters Triggered by the Migration of a Phenyl Group in Cyclooligosilanes

Journal:	*ChemComm*
Manuscript ID	CC-COM-05-2021-002682.R1
Article Type:	Communication

COMMUNICATION

Nuclearity Expansion in Pd Clusters Triggered by the Migration of a Phenyl Group in Cyclooligosilanes

Kento Shimamoto, [b] and Yusuke Sunada*[a,b,c]

Heptanuclear palladium clusters with six palladium atoms in a planar arrangement were obtained from the reaction of [Pd(CN^{t}Bu)$_2$]$_3$ with Ph-substituted cyclotetrasilane or cyclopentasilane via the migration of a phenyl group. The molecular structures of these clusters as well as those of two possible intermediates were determined by single-crystal X-ray diffraction analyses.

Single-atomic-layer nano-materials have attracted substantial attention because they are expected to exhibit unique and remarkable chemical and/or physical properties.[1] In organic chemistry, the synthesis and application of molecular nanocarbon materials with planar or pseudo-planar structures have recently been examined with increasing intensity.[2] In inorganic chemistry, metal nanosheets have been the subject of intensive investigations over the last two decades.[3] Despite this recent progress, only a limited number of well-defined molecular metal nanosheets has been synthesized. One of the recent successes is based on the use of the template synthesis method, where organic molecules act as a template to assemble metal species in a two-dimensional manner.[4] Planar unsaturated hydrocarbons serve as typical examples of template molecules that can assemble metal species to afford metal clusters that exhibit a nanosheet architecture. For instance, Murahashi et al. have described the synthesis of a planar Pd$_5$ cluster supported by naphthacene molecules.[4a] In these reactions, the number of assembled metal atoms generally depends on the number of coordination sites in the template molecule.[‡]

It is known that use of organosilicon ligands can contribute to construct the metal clusters because they can effectively bridge the multiple metal atoms.[5] We have recently demonstrated that planar organosilicon compounds with multiple silicon–silicon bonds are good precursors to afford

metal clusters with two-dimensional architectures.[6] For instance, we successfully synthesized the planar tetranuclear palladium clusters **2** by the reaction of [Pd(CN^{t}Bu)$_2$]$_3$ with the cyclotetrasilanes Si$_4$(^{i}Pr)$_8$ (**1a**) and Si$_4$(cyclopentyl)$_8$ (**1b**) via the insertion of palladium(0) isocyanide species into the four 'Si–Si' bonds (Scheme 1).[6b] This reaction affords exclusively tetranuclear palladium clusters. In contrast, Pd$_{11}$ cluster **3** was obtained from the reaction of [Pd(CN^{t}Bu)$_2$]$_3$ with the bicyclic ladder polysilane decaisopropylbicyclo[2.2.0]hexasilane (Scheme 1).[6a] Moreover, **2** was found to act as an effective catalyst for the hydrogenation of various alkenes.
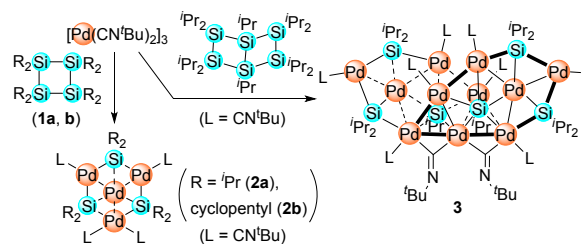
Scheme 1. Construction of Pd$_4$ and Pd$_{11}$ clusters from [Pd(CN^{t}Bu)$_2$]$_3$ and cyclic oligosilanes.

In the present study, we discovered that a judicious choice of the substituents on the silicon centers in the cyclotetrasilane leads to an expansion of the number of assembled metal atoms. Namely, the reaction of Ph-substituted cyclotetrasilane Si$_4$Ph$_8$ (**1c**) with [Pd(CN^{t}Bu)$_2$]$_3$ led to the formation of a heptanuclear palladium cluster in high yield. During this reaction, the migration of the Ph substituents to afford the silylyne moieties plays a crucial role in inducing the increased metalation. A similar Pd$_7$ cluster was also synthesized using cyclopentasilane Si$_5$Ph$_{10}$ (**4**) instead of **1c**. In this cluster, six of the palladium atoms adopt a planar arrangement, and five of these six palladium atoms are effectively supported by silylyne moieties generated *in situ* by the migration of Ph groups. The generation of the Pd$_5$ and Pd$_6$ clusters **7** and **8**, which could be regarded as possible intermediates to afford the heptanuclear palladium clusters, was observed when the reaction was carried out with a slightly decreased amount of the palladium precursor.

a. Institute of Industrial Science, The University of Tokyo, 4-6-1, Komaba, Meguro-ku, Tokyo 153-8505, Japan.
b. Department of Applied Chemistry, School of Engineering, The University of Tokyo, 4-6-1, Komaba, Meguro-ku, Tokyo 153-8505, Japan.
c. JST PRESTO, 4-1-8 Honcho, Kawaguchi, Saitama, 332-0012, Japan

Treatment of Si_4Ph_8 (**1c**) with 7/3 equiv. of $[Pd(CN^tBu)_2]_3$ in toluene at room temperature led to the formation of heptanuclear palladium cluster **5** in 35% isolated yield as black crystals (Scheme 2). Although the formation of a small amount of an unidentified byproduct was observed, cluster **5** was formed as the major product in this reaction, as confirmed by monitoring the reaction via ^1H NMR spectroscopy. It should be emphasized that the alkyl-substituted cyclotetrasilanes $Si_4(^iPr)_8$ and $Si_4(cyclopentyl)_8$ gave tetranuclear Pd_4 clusters **2** in the reaction with $[Pd(CN^tBu)_2]_3$ as mentioned above, whereas seven palladium atoms were effectively assembled in the reaction with **1c**.
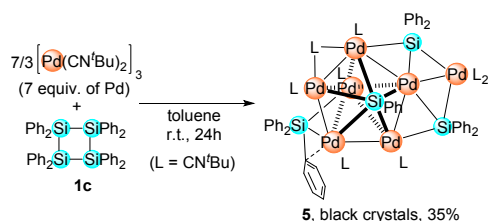
**Scheme 2.** Reaction of $[Pd(CN^tBu)_2]_3$ with **1c** to form Pd_7 cluster **5**.

The molecular structure of **5** was unequivocally determined by a single-crystal X-ray diffraction analysis, and the ORTEP drawing of **5** is shown in Figure 1. Cluster **5** contains seven palladium atoms and four silicon atoms; of these, six palladium and two silicon atoms reside on a plane, with deviations from this Pd_6Si_2 plane in the range of ca. 0.01–0.08 Å. Si(4) apparently acts as a silylyne moiety bearing one Ph substituent, whereas Si(3) bears three Ph groups. In other words, one of the Ph groups that was originally attached to the Si(4) atom migrated to the Si(3) atom to form silylyne (SiPh) and silyl (SiPh$_3$) groups. In the molecular structure of **5**, the Si(4) atom adopts a characteristic heptacoordinated structure consisting of six palladium atoms and a Ph group, and a pentagonal bipyramidal substructure is formed by the overall Pd_6Si unit (cf. Figure S1 in the ESI). Among the six palladium atoms, five are arranged on an equatorial plane, and the Pd(7) and Si(4) atoms are located 1.68 and 0.73 Å out of the plane, respectively. The bond distances of Si(4) and the six palladium atoms (2.3097(14)– 2.563(2) Å) fall within the range of bonding interactions.[7] A similar heptacoordinated silylyne moiety has been observed in the previously reported Pd_{11} cluster **3**.[6a] The Pd(3)–Pd(7) and Pd(6)–Pd(7) bond distances (3.0718(8) and 2.9676(8) Å) are significantly longer than the other Pd–Pd bonds (2.7421(6)– 2.8803(8) Å), suggesting weaker bonding interactions between Pd(3) and Pd(7) as well as Pd(6) and Pd(7) (*vide infra*).[8] An *ipso*-carbon (C(1)) of one of the three Ph rings is coordinated to Pd(5) with a Pd(5)–C(1) bond distance of 2.389(7) Å, which is comparable to previously reported Pd-C(*ipso*) coordination bonds.[9]

The molecular structure of the previously reported Pd_{11} cluster **3** contains two structurally equivalent Pd_7 subunits connected by a three-palladium axis. It is interesting to note that the structure of cluster **5** can be considered as a substructure that represents half of Pd_{11} cluster **3**. In other words, the use of a bicyclic ladder polysilane in the reaction with $[Pd(CN^tBu)_2]_3$ gave a Pd_{11} cluster consisting of two Pd_7 subunits, whereas the use of cyclotetrasilane **1c**, which can be regarded as a substructure of the ladder polysilane, led to the formation of one Pd_7 subunit with concomitant migration of a Ph group.

One structural characteristic of cluster **3** is that it possesses two $Si(^iPr)$ silylyne moieties with a heptacoordinated structure similar to in **5**. Theoretical calculations of **3** suggested that these silylyne moieties play a crucial role in the assembly of the multiple palladium atoms.[10] Considering these previous results, the generation of the Ph-substituted silylyne (SiPh) moiety on account of the migration of the phenyl group can be regarded as responsible for realizing the nuclearity expansion to afford Pd_7 cluster **5** in the reaction of the **1c** with $[Pd(CN^tBu)_2]_3$.
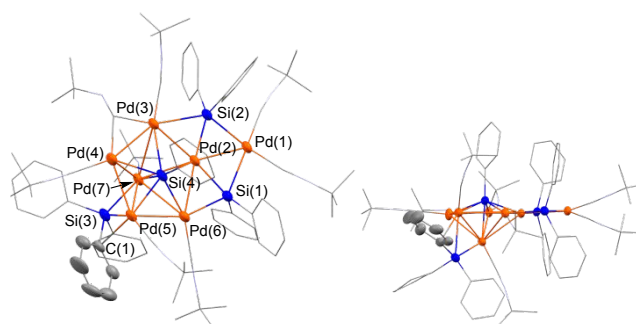
Figure 1. Molecular structure of **5** (left: top view; right: side view) with thermal ellipsoids at 50% probability; all carbon atoms (except for one Ph group) and nitrogen atoms are shown in wireframe style; all hydrogen atoms are omitted for clarity.

The IR spectrum of **5** showed CN absorption bands at 2116 and 2065 cm^{-1}. The ^{29}Si NMR spectrum of cluster **5** showed four sharp signals, one with a significant downfield shift characteristic of silylyne (δ = 332.5 ppm) moieties,[11] as well as a singlet derived from the $SiPh_3$ moiety at -13.7 ppm.
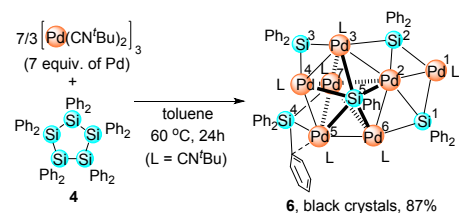
Scheme 3. Reaction of $[Pd(CN^tBu)_2]_3$ with **4** to form Pd_7 cluster **6**.

We then turned our attention to the use of cyclopentasilane Si_5Ph_{10} (**4**) as the oligosilane instead of cyclotetrasilane **1c**. The reaction of 7/3 equiv. of $[Pd(CN^tBu)_2]_3$ with **4** was carried out in toluene at 60 °C. Monitoring the reaction by ^1H NMR spectroscopy confirmed the selective formation of heptanuclear palladium cluster **6** as the sole product, and **6** was isolated in 87% yield as black crystals (Scheme 3). The molecular structure of **6** was determined by single-crystal X-ray diffraction analysis, and its ORTEP drawing is shown in Figure S2.

Cluster **6** exhibits a heptanuclear palladium framework similar to that of **5**, and six palladium atoms and three silicon atoms of the silylene moieties adopt an almost planar arrangement in **6**. The deviation of these atoms from the plane

COMMUNICATION

they define is within 0.265 Å. Similar to in the formation of **5**, the migration of Ph groups occurs during this reaction to afford SiPh and SiPh$_3$ groups. The only difference between **5** and **6** is that three SiPh$_2$ moieties are included in **6**, and one of the three SiPh$_2$ units acts as a ligand that bridges Pd(3) and Pd(4) (Pd(3)–Si(3): 2.3016(10) Å; Pd(4)–Si(3): 2.2400(10) Å). Cluster **6** also possesses a heptacoordinated silicon atom, Si(5), whose bonding parameters are similar to those of that in **5**. The structural parameters, including the bond distances and angles in the Pd$_7$Si$_4$ core, which consists of all the palladium atoms as well as Si(1), Si(2), Si(4) and Si(5), are comparable to those in **5**. Thus, it is feasible to conclude that cluster **6** has a structure analogous to that of **5**, except for the presence of an additional bridging diphenylsilylene moiety (Si(3)).

To elucidate the bonding interactions in **6**, DFT calculations were carried out using the PBE0, B3PW91, M06, and B3LYP functionals. Although some Pd–Pd bond distances were slightly overestimated, the optimized structural parameters obtained using the B3PW91 and PBE0 functionals were in good agreement with the data obtained from the XRD analysis (for details, see the ESI). The calculated Wiberg bond indexes (WBIs) for the Pd–Si(5) bonds in the pentagonal bipyramidal substructure (B3PW91: 0.27-0.49; PBE0: 0.26-0.48) support the presence of bonding interactions between Si(5) and the surrounding six palladium atoms. In addition, the WBIs for the Pd–Pd bonds located at the equatorial plane in this pentagonal bipyramidal substructure (0.12–0.15) indicate the presence of metal–metal bonding interactions. The relatively small WBI values of Pd(7)–Pd(2) and Pd(4)–Pd(5) (0.13–0.19) and those of Pd(7)–Pd(3) and Pd(7)–Pd(6) (< 0.1) in combination with the longer Pd(7)–Pd(3) and Pd(7)–Pd(6) bond distances determined by the XRD analysis suggest that the bonding interactions between Pd(7) and Pd(3)/Pd(6) are relatively weak. The WBIs of the Pd(1)–Si(1) and Pd(1)–Si(2) bonds (ca. 0.42) as well as those of the Pd(2)–Si(1) (0.54) and Pd(2)–Si(2) bonds (0.56) were significantly higher.

The molecular structure of **6** determined by single-crystal X-ray diffraction analysis indicates seven inequivalent CN^{t}Bu ligands. In the ^{1}H NMR spectrum of **6**, six singlets arising from the methyl protons of the ^{t}Bu groups appeared at 0.52, 0.63, 0.77, 0.82, 0.86, and 1.08 ppm, with an integral ratio of 9:9:9:9:18:9. Moreover, five singlets appeared in the ^{29}Si NMR spectrum of **6** (δ = 13.2 for SiPh$_3$, δ = 146.9, 190.7 and 223.5 for SiPh$_2$, δ = 324.0 for SiPh), which is consistent with the solid-state structure.

The cyclooligosilanes with 4- and 5-membered rings both furnished heptanuclear palladium clusters in the reaction with [Pd(CN^{t}Bu)$_2$]$_3$. To gain some insight into the possible intermediates formed in these reactions, we performed the reaction of **1c** or **4** with a decreased amount of [Pd(CN^{t}Bu)$_2$]$_3$. Namely, the reaction of 5/3 equiv. of [Pd(CN^{t}Bu)$_2$]$_3$ (5 equiv. of Pd relative to **4**) with **4** was carried out. Black crystals of **6** were obtained as the major product, albeit that they were accompanied by a small amount of orange crystals. A single-crystal X-ray diffraction analysis of these orange crystals revealed that the pentanuclear palladium cluster **7** was formed as the minor product (Scheme 4). Similarly, when 2 equiv. of

[Pd(CN^{t}Bu)$_2$]$_3$ (6 equiv. of Pd relative to **1c**) was treated with **1c**, subsequent recrystallization furnished black crystals of **5** containing a small amount of red crystals. A X-ray diffraction analysis of these crystals revealed that they consist of hexanuclear palladium cluster **8** (Scheme 4). The OTREP drawings of **7** and **8** are shown in the ESI. Strikingly, as in **5** and **6**, the migration of a Ph group to form SiPh and SiPh$_3$ groups also took place in **7** and **8**. In the molecular structure of **7**, all the palladium atoms are positioned on the same plane, and the deviation of all the atoms from the plane is less than 0.18 Å. It should be emphasized here that there is a Si–Si bond between the Si(4) and Si(5) atoms in **7** with a bond distance of 2.4514(10) Å. DFT calculations revealed that the estimated WBI of the Si(4)–Si(5) bond was ca. 0.7, which indicates single-bond character. The Si(5) atom adopts a hexacoordinated structure, and Si(5) forms a unique distorted pentagonal monopyramidal substructure with four surrounding palladium atoms and a silicon atom (Si(4)) (Figure S3). A similar distorted pentagonal monopyramidal substructure was confirmed in the molecular structure of **8** with five equatorially arranged palladium atoms (Figure S4). Previously reported theoretical calculations of the Pd$_{11}$ cluster **3** suggested that such a pentagonal monopyramidal substructure would be unstable, and geometry optimization calculations indicated it to be converted into an octahedral substructure.[10] This instability would explain why clusters **7** and **8** are observed only as minor products.
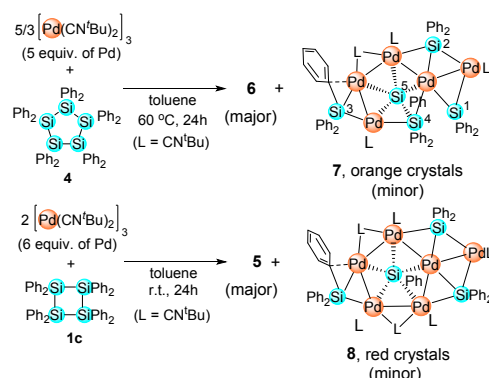
Scheme 4. Formation of Pd$_5$ cluster **7** and Pd$_6$ cluster **8** as the minor products in the reaction of [Pd(CN^{t}Bu)$_2$]$_3$ with **1c** or **4**.

Based on the structural features of **5-8**, a plausible reaction mechanism for the production of heptanuclear palladium clusters could be proposed: First, five palladium atoms are arranged to form cluster **7** via the insertion of palladium species into four of the five Si–Si bonds of **4**. The sixth palladium atom could then be incorporated to form the hexanuclear framework shown in **8** by assuming that the remaining Si–Si bond in **7** undergoes the insertion of an additional palladium species. Subsequently, metalation could occur to form heptanuclear palladium cluster **6**. In other words, the insertion of palladium species into the Si–Si bonds of **4** and Ph group migration take place concomitantly to afford a pentanuclear palladium cluster as the primary product. Then, sequential metalation could form heptanuclear cluster **6** via the formation of a hexanuclear cluster.

We have previously reported that the planar tetranuclear palladium clusters such as **2** act as effective homogenous catalysts for the hydrogenation of alkenes.[6b] Because the development of molecular palladium compounds that can catalyze the hydrogenation of alkenes is surprisingly underexplored,[12] we applied cluster **6** the catalytic hydrogenation of alkenes (cf. Table S1). These hydrogenations were effectively realized in cyclopentylmethylether (CPME) in the presence of a catalytic amount of **6** (2 mol% for Pd). For example, the hydrogenation of 1-octene, styrene, cyclohexene, and *trans*-stilbene were performed in CPME for 6 h at room temperature under 1 atm of H_2 with a catalytic amount of **6**, and the corresponding alkanes were formed in high to quantitative yield. Although the conversion of methylcyclohexene was relatively low (34%), the hydrogenation of sterically hindered ethyl-3,3-dimethylacrylate proceeded smoothly in CPME even at room temperature. Notably, cluster **6** showed higher catalytic performance than the conventional Pd/C catalyst in the hydrogenation of ethyl-3,3-dimethylacrylate.

In conclusion, we have synthesized two Pd_7 clusters, **5** and **6**, in which six palladium atoms are arranged in a planar fashion. Although alkyl-substituted cyclotetrasilanes are known to afford planar tetranuclear Pd clusters in the reaction with [Pd(CN^{t}Bu)$_2$]$_3$, the use of Ph-substituted cyclooligosilanes opens the way to expand the nuclearity to afford heptanuclear clusters. During this cluster-formation reaction, the generation of a silylyne (SiPh) group via the migration of a Ph group induced the expansion of the nuclearity to form **5** and **6**. In addition, the generation of the pentanuclear and hexanuclear clusters **7** and **8** was observed when the reaction was performed in the presence of a decreased amount of the Pd source. Although clusters **7** and **8** are the minor products in these reactions, the observation of these clusters might be regarded as a snapshot of the intermediates formed during the palladium-assembly reactions. These results suggest that the use of appropriate template molecules may open the way to construct a series of transition-metal clusters with higher nuclearity and unique architectures, as well as assist in obtaining detailed insight into the sequential metalation steps during the formation of the clusters. Research in this direction is currently in progress in our laboratories.

Conflicts of interest

There are no conflicts to declare.

Notes and references

‡ Murahashi et al. have recently reported the ligand-free accommodation of extra metal moieties in a planar tetranuclear palladium cluster; for details, see ref. 4b.

1   (a) C. Tan, X. Cao, X. -J. Wu, Q. He, J. Yang, X. Zhang, J. Chen, W. Zhao, S. Han, G. -H. Nam, M. Sindoro and H. Zhang, *Chem. Rev.* 2017, **117**, 6225-6331; (b) R. Dong, T. Zhang and X. Feng, *Chem. Rev.* 2018, **118**, 6189-6235; (c) A. H. Khan, S. Ghosh, B. Pradhan, A. Dalui, L. K. Shrestha. S. Acharya and K. Ariga, *Bull. Chem. Soc. Jpn.* 2017, **90**, 627-648; (d) E. P. Nguyen, C. de C. C. e. Silva and A. Merkoçi, *Nanoscale* 2020, **12**, 19043-19067; (e) L. Fu, Z. Yan, Q. Zhao and H. Yang, *Adv. Mater. Interfaces.* 2018, **5**, 1/1801094-21/1801094.

2   (a) M. Stępień, E. Gońka, M. Żyła and N. Sprutta, *Chem. Rev.* 2017, **117**, 3479-3716; (b) K. Sato, Y. Segawa and K. Itami, *Synlett* 2019, **30**, 370-377; (c) J. Wu, W. Pisula and K. Müllen, *Chem. Rev.* 2007, **107**, 718-747.

3   (a) R. Kempt, A. Kuc and T. Heine, *Angew. Chem. Int. Ed.* 2020, **59**, 9242-9254; (b) S. Bertolazzi, M. Gobbi, Y. Zhao, C. Backes and P. Samori, *Chem. Soc. Rev.* 2018, **47**, 6845-6888; (c) G. H. Han, D. L. Duong, D. H. Keum, S. J. Yun and Y. H. Lee, *Chem. Rev.* 2018, **118**, 6297-6336.

4   (a) T. Murahashi, M. Fujimoto, M. Oka, Y. Hashimoto, T. Uemura, Y. Tatsumi, Y. Nakao, A. Ikeda, S. Sakaki and H. Kurosawa, *Science* 2006, **313**, 1104-1107; (b) T. Ishikawa, A. Kawamura, T. Sugawa, R. Moridaira, K. Yamamoto and T. Murahashi, *Angew. Chem. Int. Ed.* 2019, **58**, 15318-15323; c() T. Murahashi, R. Inoue, K. Usui and S. Ogoshi, *J. Am. Chem. Soc.* 2009, **131**, 9888-9889; (d) T. Murahashi, R. Inoue, K. Usui and S. Ogoshi, *J. Am. Chem. Soc.* 2009, **131**, 9888-9889; (e) T. Murahashi, N. Kato, T. Uemura and H. Kurosawa, *Angew. Chem. Int. Ed.* 2007, **46**, 3509-3512; (f) T. Sugawa, K. Yamamoto and T. Murahashi, *Chem. Commun.* 2018, **54**, 5875-5878; g) K. Yamamoto, J. Sawada, T. Murahashi, T. *Chem. Eur. J.* 2020, **26**, 8388-8392.

5   (a) J. Y. Corey, *Chem. Rev.* 2016, **116**, 11291-11435; (b) J. Y. Corey, *Chem. Rev.* 2011, **111**, 863-1071; (c) J. Y. Corey and J. Braddock-Wilking, *Chem. Rev.* 1999, **99**, 175-292; (d) K. Osakada, Y. Tsuchido, and M. Tanabe. *Coord. Chem. Rev.* 2020, **412**, 213195.

6   (a) Y. Sunada, R. Haige, K. Otsuka, S. Kyushin and H. Nagashima, *Nat. Commun.* 2013, **4**, 3014/1-3014/7; (b) C. Yanagisawa, S. Yamazoe and Y. Sunada, *ChemCatChem* 2021, **13**, 169-173; (c) Y. Sunada, N. Taniyama, K. Shimamoto, S. Kyushin and H. Nagashima, *Inorganics* 2017, **5**, 84/1-84/12; (d) K. Shimamoto and Y. Sunada, *Chem. Eur. J.* 2019, **25**, 3761-3765; (e) R. Usui and Y. Sunada, *Chem. Commun.* 2020, **56**, 8464-8467.

7   (a) T. Yamada, A. Mawatari, M. Tanabe, K. Osakada and Tanase, *Angew. Chem. Int. Ed.* 2009, **48**, 568-571; (b) M. Tanabe, R. Yumoto, T. Yamada, T. Fukuta, T. Hoshino, K. Osakada and T. Tanase, *Chem. Eur. J.* 2017, **23**, 1386-1392; (c) M. Tanabe, J. Jiang, H. Yamazawa, K. Osakada, T. Ohmura and M. Suginome, *Organometallics* 2011, **30**, 3981-3991.

8   T. Murahashi and H. Kurosawa, *Coord. Chem. Rev.* 2002, **231**, 207-228.

9   T. Schindler, M. Lux, M. Peters, L. T. Scharf, H. Osseili, L. Maron and M. E. Tauchert, *Organometallics* 2015, **34**, 1978-1984.

10 Y. Chen, Y. Sunada, H. Nagashima and S. Sakaki, *Chem. Eur. J.* 2016, **22**, 1076-1087.

11 H. Ogino and H. Tobita, *Adv. Organomet. Chem.*, 1998, **42**, 223-290.

12 (a) Q. -A. Chen, Z. -S. Ye, Y. Duan and Y. -G. Zhou, *Chem. Soc. Rev.* 2013, **42**, 497-511; (b) V. Jurčík, S. P. Nolan and C. S. J. Cazin, *Chem. Eur. J.* 2009, **15**, 2509-2511; (c) O. Songis and C. S. J. Cazin, *Synlett* 2013, **24**, 1877-1881; (d) J. W. Sprengers, J. Wassenaar, N. D. Clement, K. J. Cavell and C. J. Elsevier, *Angew. Chem. Int. Ed.* 2005, **44**, 2026-2029; (e) M. W. van Laren and C. J. Elsevier, *Angew. Chem. Int. Ed.*, 1999, **38**, 3715-3717; (f) J. Yu and J. B. Spencer, *J. Am. Chem. Soc.* 1997, **119**, 5257-5258.