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Tetrapalladium Complex with Bridging Germylene Ligands. Structural Change of the Planar Pd_4Ge_3 Core

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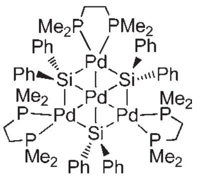
S *Supporting Information*

ABSTRACT: A complex with a planar hexagonal Pd_4Ge_3 core, $[Pd\{Pd(dmpe)\}_3(\mu_3\text{-}GePh_2)_3]$, was synthesized and characterized by X-ray and NMR measurements as well as by DFT calculations. 4-*tert*-Butylbenzenethiol converted the Pd_4 complex into a hexapalladium complex, $[\{Pd_3(\mu\text{-}GePh_2)_2(\mu\text{-}H)(\mu_3\text{-}GePh_2(SC_6H_4{}^tBu\text{-}4))\}_2(\mu\text{-}dmpe)]$, composed of two Pd_3Ge_3 units bridged by a dmpe ligand. The addition of CuI or AgI to the Pd_4 complex yielded $[Pd(\mu\text{-}MI)\{Pd(dmpe)\}_3(\mu_3\text{-}GePh_2)_3]$ (M = Cu, Ag), in which Cu or Ag bridges a Pd−Pd bond of the Pd_4Ge_3 core. The CuI adducts in solution undergo a pivot motion of the CuI on the surface of the Pd_4Ge_3 plane on the NMR time scale.

Multinuclear transition metal complexes containing a planar arrangement of metal centers linked via metal−metal bonds are rare among transition metal clusters.[1] Bridging or semibridging CO or CNR ligands,[2] a pair of planar polyaromatic ligands,[3] and bulky organic ligands were employed as the auxiliary ligands of planar multimetallic complexes.[4] The π-acceptor character of the first two ligands and the steric hindrance of the last one stabilize the respective complexes. Bridging Si ligands[5,6] having electron-releasing character have recently been found to form complexes having a planar multimetallic core.[7−9] We also reported a tetrapalladium complex, $[Pd\{Pd(dmpe)\}_3(\mu_3\text{-}SiPh_2)_3]$ (**1**), which contains a central Pd_4Si_3 unit composed of four Pd centers and three bridging silylene ligands.[10]



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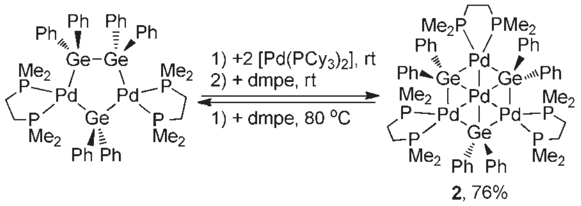
Although these complexes are expected to show unique chemical properties owing to their planar multimetallic core and reactive metal−silicon bonds, there have been few systematic studies of their reactions. In this paper, we present the synthesis and structure of a complex with a similar structure to **1**, but with a heavier group 14 element, Ge, as the coordinating atom.[11] The skeletal change reactions of this complex also form unprecedented multinuclear complexes.

The treatment of a dipalladium complex with bridging digermene and germylene ligands, $[\{Pd(dmpe)\}_2(\mu\text{-}Ge_2Ph_4)(\mu\text{-}GePh_2)]$,[12] with twice the molar amount of $[Pd(PCy_3)_2]$ and then with equimolar dmpe afforded a tetrapalladium complex with bridging germylene ligands, $[Pd\{Pd(dmpe)\}_3(\mu_3\text{-}GePh_2)_3]$ (**2**):



(1)

2, 76%

The reaction product contains only **2**, PCy_3, and $[Pd(dmpe)_2]_n$ ($n = 1, 2$),[13] as revealed by $^{31}P\{^1H\}$ NMR spectroscopy. Heating a mixture of the isolated **2** and dmpe (1:3) at 80 °C regenerates $[\{Pd(dmpe)\}_2(\mu\text{-}Ge_2Ph_4)(\mu\text{-}GePh_2)]$, accompanied by the formation of $[Pd(dmpe)_2]_n$. Although $[Pd(SiHPh_2)_2(dmpe)]$ reacted with $[Pd(PCy_3)_2]$ to produce **1**, the analogous reaction of $[Pd(GeHPh_2)_2(dmpe)]$ with $[Pd(PCy_3)_2]$ yielded a dipalladium complex with bridging germyl ligands $[\{Pd(PCy_3)\}_2(\mu\text{-}GeHPh_2)_2]$[14] rather than **2**. Thus, the use of the dinuclear complex $[\{Pd(dmpe)\}_2(\mu\text{-}Ge_2Ph_4)(\mu\text{-}GePh_2)]$ as one of the starting materials enabled a smooth and selective formation of the Pd_4Ge_3 complex **2**. The reaction in eq 1 is reversible, and proper choice of the reaction conditions resulted in the formation of **2** in high yield.

Figure 1 shows the molecular structure of **2** with its Pd_4Ge_3 core having one central Pd atom (Pd_{cent}), three edge Pd atoms (Pd_{edge}), and three bridging Ge atoms. These Pd and Ge atoms form a plane, as shown in Figure 1b. The distances between the Pd_{cent} and Ge atoms (2.3207(7)−2.3344(7) Å) are close to the lengths of the Pd=Ge bonds in mononuclear palladium germylene complexes, $[(R_3P)_2Pd{=}Ge\{N(SiMe_3)_2\}_2]$ (R = Et, 2.330(5) Å; R = Ph, 2.3281(4) Å).[15] The Pd and Ge atoms of **2** form a distorted hexagonal core with Pd_{edge}−Ge distances (2.5545(7)−2.6037(7) Å) and Pd−Pd distances (2.7568(6)−2.7904(6) Å) that are longer than the Pd_{cent}−Ge distances. The Pd_4Ge_3 core of **2** is larger than the Pd_4Si_3 core of **1** (Pd_{cent}−Si bond of **1** = 2.2521(8)−2.2674(8) Å). The three Pd_{edge}−Ge−Pd_{edge} bond angles of **2** (136.68(2)−137.78(2)°) are close to the Pd_{edge}−Si−Pd_{edge} angles of **1** (138.00(3)−138.73(3)°), and the hexagonal cores of **1** and **2** have similar shapes.

Density functional theory (DFT) calculations of complex **2** were conducted with the Gaussian 09 quantum chemistry program package (MPWB95/6-31G(d,p)).[16] The geometry of the complex was optimized using the actual atom positions obtained by

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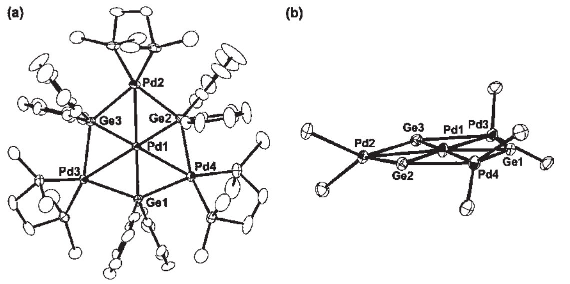
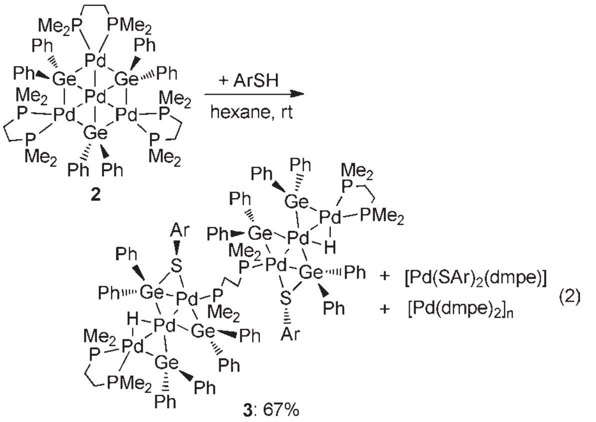


Figure 1. (a) Thermal ellipsoids (50%) of **2** and (b) its Pd_4Ge_3 plane. Two crystallographically independent molecules exist. Selected bond distances (Å) and angles (deg) of one of the molecules: Pd1−Pd2 2.7824(6), Pd1−Pd3 2.7585(6), Pd1−Pd4 2.7836(6), Pd1−Ge1 2.3319(7), Pd1−Ge2 2.3207(7), Pd1−Ge3 2.3338(6), Pd2−Ge2 2.5921(6), Pd2−Ge3 2.5767(7), Pd3−Ge1 2.5637(7), Pd3−Ge3 2.5852(7), Pd4−Ge1 2.5895(7), Pd4−Ge2 2.5788(7), Pd3−Ge1−Pd4 137.05(2), Pd2−Ge2−Pd4 137.67(2), Pd2−Ge3−Pd3 136.71(2).

X-ray crystallography. The average Pd_{cent}−Pd_{edge} and Pd_{cent}−Ge bond distances of 2.796 and 2.363 Å are close to those determined from the X-ray data (2.776 and 2.329 Å, respectively). The Wiberg bond index of **2** (Pd_{cent}−Pd_{edge} = 0.194, Pd_{cent}−Ge = 0.541, and Pd_{edge}−Ge = 0.401−0.442) suggests that the Pd_{cent}−Ge bond is stronger than the Pd_{edge}−Ge bond and is consistent with the X-ray crystallographic results, which also show Pd_{cent}−Ge bonds shorter than the Pd_{edge}−Ge bonds. The charge population analysis of the Pd_4Ge_3 core indicates a higher negative charge of the Pd_{cent} atom (−0.56) than that of the Pd_{edge} atoms (−0.47). The molecular orbitals obtained from the above calculations suggest a large contribution of the Pd_{cent}−Ge and Pd_{edge}−Ge bonds to stabilize the planar Pd_4Ge_3 core (Supporting Information).[17]

The addition of an equimolar amount of $HSC_6H_4{}^tBu$-4 to a hexane solution of **2** caused the separation of $[\{Pd_3(\mu\text{-}GePh_2)_2(\mu\text{-}H)(\mu_3\text{-}GePh_2(SC_6H_4{}^tBu\text{-}4))\}_2(\mu\text{-dmpe})]$ (**3**) as a yellow solid, as shown in eq 2. The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture indicated the accompanying formation of $[Pd(dmpe)_2]_n$ and $[Pd(SC_6H_4{}^tBu\text{-}4)_2(dmpe)]$.[18]



(2)

3: 67%
Ar = $C_6H_4{}^tBu$-4

Complex **3** is composed of two $Pd_3(\mu\text{-}GePh_2)_2(\mu\text{-}H)(\mu_3\text{-}GePh_2(SC_6H_4{}^tBu\text{-}4))$ units and a bridging dmpe ligand, as revealed by X-ray crystallography (Figure 2). Three Pd atoms of each unit are aligned almost linearly (Pd1−Pd2−Pd3 168.54(4)°) and are bridged by two $GePh_2$ ligands and a $GePh_2(SC_6H_4{}^tBu\text{-}4)$ ligand. A hydride ligand derived from the thiol bridges two Pd centers, Pd1 and Pd2. The distance between Pd1 and Pd2 (2.799(2) Å) is longer than that between Pd2 and Pd3 (2.767(2) Å), in spite of the bridging coordination of the hydride to Pd1−Pd2. The thiolato is attached to Ge2 and Pd3, forming the $GePh_2(SC_6H_4{}^tBu\text{-}4)$ ligand. An analogous $\overline{M−Ge−S}$ triangular bonding was reported in the thiolatogermyl iron complex.[19] The dmpe bridges the two Pd_3Ge_3 units to form the hexanuclear molecule, similar to $[\{Ni(\overline{SiH_2C_6H_4SiH_2})(dmpe)\}_2(\mu\text{-dmpe})]$[20] and $[\{Pd\{Pd(dmpe)\}_3(\mu_3\text{-}SiHPh)_3\}_2(\mu\text{-dmpe})]$.[10] The ^1H NMR spectrum of **3** shows the bridging hydrido signal at δ −2.48, with the coupling of two P nuclei of the chelating dmpe ligand (J = 13, 94 Hz). The $^{31}P\{^1H\}$ NMR spectrum of **3** displays three characteristic signals at δ 23.8, 16.3, and −11.9. The first two signals, with a large coupling constant (J_{P-P} = 33 Hz), are assigned to the chelating dmpe ligand, while the last signal is assigned to the bridging dmpe.

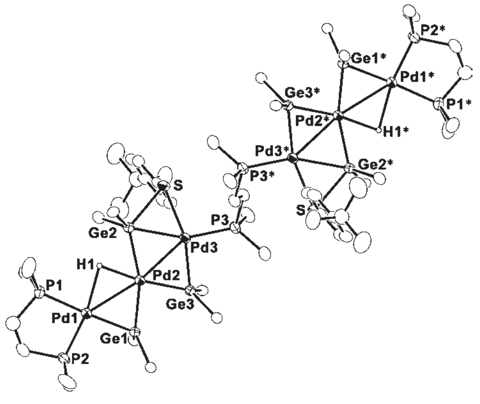
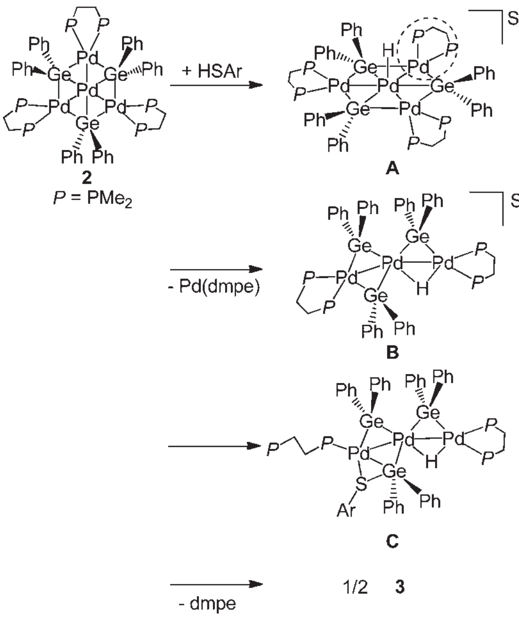


Figure 2. Thermal ellipsoids (30%) of **3**. The molecule has a crystallographic point of symmetry at the midpoint of P3 and P3*. Selected bond distances (Å) and angles (deg): Pd1−Pd2 2.799(2), Pd2−Pd3 2.767(2), Pd3−S 2.501(3), Pd1−Ge1 2.436(2), Pd2−Ge1 2.386(2), Pd2−Ge2 2.411(2), Pd2−Ge3 2.380(2), Pd3−Ge2 2.582(2), Pd3−Ge3 2.407(2), Ge2−S 2.466(3), Pd1−H1 2.2(1), Pd2−H1 2.0(2), Pd1−Pd2−Pd3 168.54(4), Pd2−Pd3−S 110.71(7), Pd1−Ge1−Pd2 70.94(5), Pd2−Ge2−Pd3 67.20(5), Pd2−Ge3−Pd3 70.63(5).

The reaction forming the hexapalladium complex **3** in the presence of the thiol involves the reorganization of the Pd_4Ge_3 core. Scheme 1 summarizes the possible reaction pathway.[21] Protonation of the central Pd atom of **2** by thiol forms the cationic intermediate **A**, which undergoes rearrangement of the Pd_4Ge_3 core and elimination of Pd(dmpe) to produce the tripalladium intermediate **B**. The partial dissociation of a dmpe ligand and coordination of the thiolato forms **C**, which then undergoes dimerization with loss of a dmpe molecule. The formation of $[Pd(dmpe)_2]_n$ and $[Pd(SC_6H_4{}^tBu\text{-}4)_2(dmpe)]$ in the reaction is attributed to further reaction of the Pd(dmpe) intermediate with dmpe and thiol, respectively. The isolated hexanuclear complex **3** is thermally stable and does not change its structure in solution, even at 60 °C. The addition of dmpe to a benzene-d_6 solution of **3** ([dmpe]/[**3**] = 0.5/1), however, formed a mixture of the tetranuclear complex **2** and $[Pd(dmpe)_2]_n$, which were identified from the $^{31}P\{^1H\}$ NMR peaks of the solution.[22] Adams et al. recently reported a reversible structural change of their multinuclear complex. The complex $[Pd\{Re_2(CO)_8(\mu\text{-}SbPh_2)(\mu\text{-}H)\}_2]$ releases its central Pd upon treatment with PCy_3, while the resulting $[\{Re_2(CO)_8(\mu\text{-}SbPh_2)(\mu\text{-}H)\}_2]$ stores the Pd of $Pd(dba)_2$ and regenerates the Re_4Pd complex.[23]

Scheme 1



Equimolar CuI or AgI reacts with complex **2** to cause their addition to a Pd−Pd bond to afford the pentanuclear complexes [Pd(μ-MI){Pd(dmpe)}$_3$(μ_3-GePh$_2$)$_3$] (**4**, M = Cu; **5**, M = Ag):

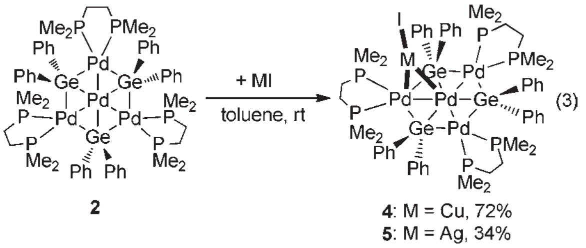


Figure 3 shows the X-ray structure of **4**. Both **4** and **5** retain the bonds between Pd and Ge atoms of the Pd$_4$Ge$_3$ core but lose planarity owing to the bridging of Cu or Ag to a Pd−Pd bond. Two Pd atoms and one Cu or Ag atom form a triangle composed of three d^{10} metals. The Pd1−Pd2 bond (2.7367(8) Å) of **4** is shorter than the Pd1−Pd3 (2.7964(8) Å) and Pd1−Pd4 (2.7738(8) Å) bonds of **4** and the Pd$_{cent}$−Pd$_{edge}$ bonds of **2** (2.7568(6)−2.7904(6) Å). The presence of a Cu−Pd2 bond (2.462(1) Å) shorter than the Cu−Pd1 bond (2.632(1) Å) and of a large I−Cu−Pd2 bond angle (159.15(5)°) suggests a more significant interaction of Pd2 with the Cu atom than that of Pd1. The four Pd atoms of **4** are included in a plane, while one of the Ge atoms (Ge2) deviates from the plane by 0.95 Å because of the elongation of the Pd1−Ge2 bond (2.384(1) Å) compared with the other Pd$_{cent}$−Ge bonds of **4** (Pd1−Ge1 2.358(1), Pd1−Ge3 2.347(1) Å). Trinuclear Pt(0) complexes, [Pt$_3$(μ-CO)$_3$(PR$_3$)$_{3-4}$], were reported to react with Cu(I), Ag(I), and Au(I) to form heterometallic complexes with ML (M = Cu(I), Ag(I); L = phosphine, halides) capping over the Pt$_3$ face. The complexes **4** and **5** show the interaction of Cu and Ag with only the two Pd centers.[24]

The NMR results of **4** below room temperature show the dynamic behavior of the molecule on the NMR time scale. The ^{13}C{^{1}H} NMR spectrum of **4** at room temperature exhibits two *ipso* carbon signals at close positions (δ 156.5 and 155.8) due to the presence of CuI-bonded and CuI-free sides of the Pd$_4$Ge$_3$ core. Although X-ray crystallography showed a clear difference between Pd−Pd bonds with bridging CuI and those without bridging CuI, three phenyl groups on the same face of the Pd$_4$Ge$_3$ core are equivalent in the NMR spectrum. The spectra at low temperature show changes in the aromatic hydrogen peaks of the GePh$_2$ ligands. Two ortho hydrogen signals of the GePh$_2$ ligands are observed at δ 8.31 and 7.74 with equal intensities at 25 °C (Figure 4). Meta hydrogen signals corresponding to three hydrogens are observed at δ 7.33, although the others overlap with the signals of other aromatic hydrogens. On cooling the solution to −90 °C, a set of ortho hydrogen signals (δ 8.31) and the meta hydrogen signal are extremely broadened; these are assigned to the Ph groups on the Cu-coordinated side of the Pd$_4$Ge$_3$ plane. The peak width of the other ortho hydrogen signal at δ 7.74 changes to a much less significant degree.

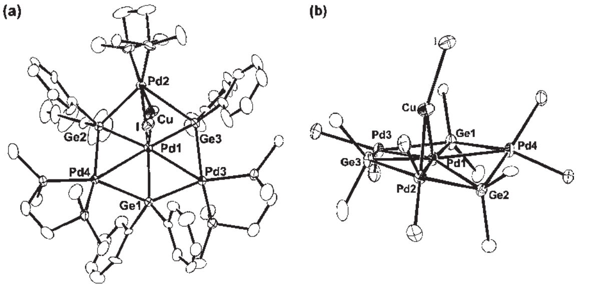


Figure 3. (a) Thermal ellipsoids (50%) of (a) **4** and (b) its Pd$_4$Ge$_3$ plane. Selected bond distances (Å) and angles (deg): Cu−Pd1 2.632(1), Cu−Pd2 2.462(1), Pd1−Pd2 2.7367(8), Pd1−Pd3 2.7964(8), Pd1−Pd4 2.7738(8), Pd1−Ge1 2.358(1), Pd1−Ge2 2.384(1), Pd1−Ge3 2.347(1), Pd2−Ge2 2.597(1), Pd2−Ge3 2.887(1), Pd3−Ge1 2.585(1), Pd3−Ge3 2.532(1), Pd4−Ge1 2.606(1), Pd4−Ge2 2.530(1), I−Cu−Pd2 159.15(5), Pd3−Ge1−Pd4 136.39(4), Pd2−Ge2−Pd4 128.24(3), Pd2−Ge3−Pd3 131.34(3).

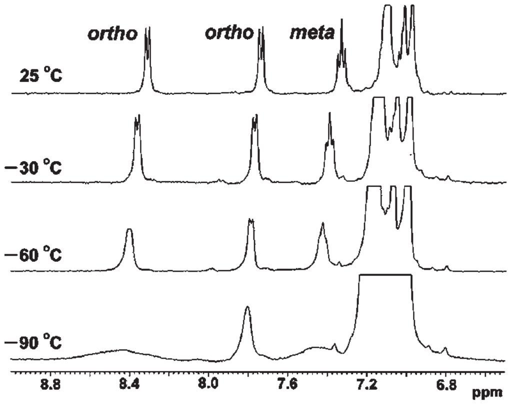
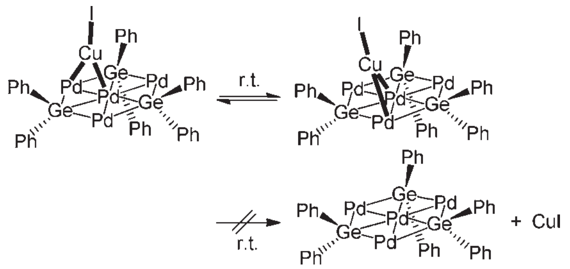


Figure 4. ^{1}H NMR spectra of **4** at −90, −60, −30, and 25 °C in toluene-d_8.

Scheme 2 shows a plausible mechanism to account for the results: the cleavage and formation of a Cu−Pd$_{edge}$ bond occur rapidly and reversibly to cause the apparent pivot motion of CuI on the surface of the Pd$_4$Ge$_3$ plane. The dissociation of CuI from **4** can be excluded on the basis of the two ^{1}H and ^{13}C{^{1}H} NMR signals of the phenyl groups. The ^{1}H NMR spectrum of **5** at −90 °C shows the broadening of the two ortho hydrogen peaks to a similar extent. Thus, CuI and AgI produce the complexes **4** and **5**, respectively, with similar structures in the solid state, but the behaviors of the two adducts are different in solution.[25]

Scheme 2



In summary, we succeeded in isolating **2**, characterizing its structure, and carrying out its DFT analysis. The striking findings in this study are the formation of the tetrapalladium complex **2** from the mono- and dinuclear Pd complexes and the skeletal change of the planar Pd_4Ge_3 core caused by thiol and CuI, which have the character of Brønsted and Lewis acids, respectively. The combination of low-valent Pd and the Ge ligand enabled the formation of the multinuclear complexes with various structures and their smooth conversion involving the skeletal change.

■ ASSOCIATED CONTENT

S Supporting Information. Experimental details and characterization data; MO interaction diagram for **2**; and complete ref 16. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) Theoretical calculation of planar $[Ni(SiH_2)_6]$ was reported to form the planar $NiSi_6$ core stabilized by the Ni—Si and Si—Si bonds. See: Tang, H.; Hoffman, D. M.; Albright, T. A.; Deng, H.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1616–1618.

(18) We characterized $[Pd(SC_6H_4{}^tBu\text{-}4)_2(dmpe)]$ by comparison of its NMR data with those of the complex which was isolated from the reaction of $[Pd(SiHPh_2)_2(dmpe)]$ with excess $HSC_6H_4{}^tBu\text{-}4$. See Supporting Information.

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(21) Several other pathways also lead to the formation of **3**. For example, the oxidative addition of thiol to a Pd—Pd bond of **2** and the subsequent rearrangement of the complex would result in formation of **3** via the neutral intermediates corresponding to **A**—**C**.

(22) The reaction in eq 2 is formally reversible, but its detailed processes are different between the forward and the backward reactions. The reaction of dmpe with **3** forming tetranuclear **2** should involve a Pd(0)-dmpe species that reacts with the hexanuclear or trinuclear Pd complexes. Direct elimination of the thiol from **3** upon coordination of the added dmpe may be responsible.

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(25) There are several possible details of the dynamic behavior of **5** in solution because no coalescence signals were observed above −90 °C. The dynamic motion of the AgI fragment in solution was suggested involving a rapid pivot motion over the NMR time scale, monodentate coordination of AgI to the Pd center, or the smooth dissociation/recoordination of AgI to the Pd_4Ge_3 core.