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Coordination of Tri-Substituted Nona–Germanium Clusters to Cu(I) and Pd(0)

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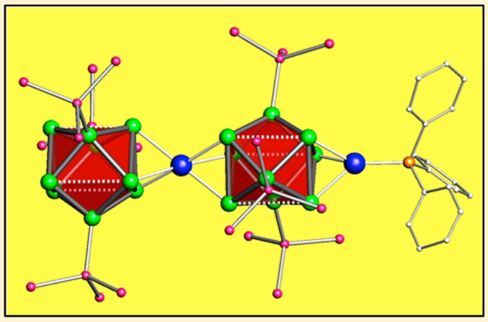
Ⓢ *Supporting Information*

ABSTRACT: The recently developed approach for the rational functionalization of deltahedral nona–germanium clusters Ge_9^{4-} with three substituents to form $Ge_9R_3^-$ (R = $Si(SiMe_3)_3$) in large amounts has made the latter a convenient starting material for further reactivity studies. Reported here are the synthesis, structures, and solution studies of two compounds where $Ge_9R_3^-$ are used as ligands to transition metals, $[(Ge_9R_3)Cu^I(Ge_9R_3)Cu^IPPh_3]$ (**1**) and $[(Ge_9R_3)Pd^0(Ge_9R_3)]^{2-}$ (**2**). The former adds to the families of anionic $[(Ge_9R_3)M^I(Ge_9R_3)]^-$ (M^I = Cu, Ag, and Au) as a neutral member and of the neutral $[(Ge_9R_3)M^{II}(Ge_9R_3)]$ (M^{II} = Zn, Cd, and Hg), while the latter represents the first compound involving a metal from group 10.



INTRODUCTION

The reactivity of group 14 nine-atom deltahedral clusters has been studied quite intensively during the past two decades.[1] Synthesized were many novel clusters centered with transition metals and/or functionalized with transition metal[2−25] and main group[26−33] organometallic fragments as well as with purely organic groups[34−43] with various functionalities. The very first fuctionalization reactions, reported by Eichhorn et al., were those of *nido*-E_9^{4-} (E = Sn, Pb) clusters reacted with $ArM(CO)_3$ (M = Cr, Mo, W; Ar = benzene, mesitylene) to form the 10-atom *closo*-$E_9M(CO)_3^{4-}$.[2,3] In these reactions, the E_9^{4-} cluster, a monocapped square antiprism, plays the role of a six-electron ligand that replaces the labile aryl ligand in the original complex and coordinates by its open square face to the transition metal. Later, it was found that these clusters can "ligate" similarly a number of other transition metal fragments such as −ZnPh, −Ni(CO), $-CuPR_3$, $-PdPPh_3$, etc.[10,20,22,24,25] In addition, in some cases the clusters can be both centered and functionalized at the same time, for example, $[Ni@(Ge_9-NiPPh_3)]^{2-}$,[8] $[Ni@(Sn_9-NiCO)]^{2-}$, and $[Pt@(Sn_9-PtPPh_3)]^{2-}$.[9] It is interesting to note that, unlike the empty clusters, these centered clusters $M@Ge_9$ coordinate to the outside transition metal via one of their triangular faces. The resulting shape of the 10-atom species $(M@Ge_9)M-L$ is that of a tricapped trigonal prism that is additionally capped at one of its trigonal bases resulting in an opening of the latter. Last, treating Ge_9^{4-} with an excess amount of $Ni(cod)_2$ (cod = 1,5-cyclooctadiene) leads to the cluster species $[Ni_3Ge_{18}]^{4-}$ in which two $\{(Ni@Ge_9)Ni\}$ units share the common outside Ni atom, that is, $[(Ni@Ge_9)Ni(Ni@Ge_9)]^{4-}$.[11] The shared Ni atom ends up being octahedrally coordinated by six Ge atoms.

In a different line of research, Schnepf et al. reported the synthesis of the first tri-functionalized nona–germanium cluster, $[Ge_9(Si(SiMe_3)_3)_3]^-$, by its assembly from small, single Ge atom fragments.[29] Despite the very low yields of these reactions, the same group managed to carry out further studies of the reactivity of the new species toward transitional metal complexes. Thus, fragments such as $M(CO)_3$ and $M(CO)_5$ (M = Cr, Mo, and W) were added to the monoanion to form $[Ge_9R_3M(CO)_x]^-$ where R stands for $Si(SiMe_3)_3$, "hypersilyl".[44,45] Similarly, dimers of tri-substituted clusters linked by a transition metal atom were synthesized as well, $[(Ge_9R_3)M(Ge_9R_3)]^{n-}$, where M = Cu, Ag, and Au for $n = 1$,[46,47] and M = Zn, Cd, and Hg for $n = 0$.[48] The transition metal atom is octahedrally coordinated by six germanium atoms, just like in $[Ni_3Ge_{18}]^{4-}$.

Recently, we reported the rational synthesis of $Ge_9R_3^-$ in nearly quantitative yields starting from preassembled Ge_9 clusters in the intermetallic precursor K_4Ge_9 and reacting its acetonitrile suspension with $(Me_3Si)_3SiCl$.[31] This newly achieved availability of the tri-substituted species in large quantities makes their reactivity studies even more accessible. Herein, we report the results of such studies in which copper and palladium compounds are reacted with $Ge_9R_3^-$ to form $[(Ge_9R_3)Cu^I(Ge_9R_3)Cu^IPPh_3]$ (**1**) and $[(Ge_9R_3)Pd^0(Ge_9R_3)]^{2-}$ (**2**) (R = $Si(SiMe_3)_3$), respectively. The former adds to the families of anionic species $[(Ge_9R_3)M^I(Ge_9R_3)]^-$ (M^I = Cu, Ag, and Au) as a neutral member and of the neutral $[(Ge_9R_3)M^{II}(Ge_9R_3)]$ (M^{II} = Zn, Cd, and Hg), while the latter represents the first compound involving a metal from group 10.

EXPERIMENTAL SECTION

General Methods. All manipulations were carried out under nitrogen atmosphere using a glovebox and standard Schlenk techniques. The Zintl phase K_4Ge_9 was synthesized from a stoichiometric mixture of the elements (K, Strem, 99+%; Ge, Alfa-

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Aesar, 99.999%) heated at 950 °C over 2 days in sealed niobium containers jacketed in evacuated fused silica tubes. Hexanes (Alfa-Aesar, 98.5+%) and toluene (Alfa-Aesar, anhydrous, 99.8+%) were dried by passing over copper-based catalyst and 4 Å molecular sieve, and were then stored in gastight ampules under nitrogen. Acetonitrile (EMD-DriSolv, anhydrous, 99.8+%) was stored over molecular sieves in gastight ampules under nitrogen. The 2,2,2-crypt (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane, Sigma-Aldrich, 98%), "hypersilyl" chloride $(Me_3Si)_3SiCl$ (chlorotris(trimethylsilyl)silane, TCI, 95+%), $(PPh_3)_3CuBr$ (bromotris(triphenylphosphine)copper(I), Sigma-Aldrich, 98%), and $Pd(PPh_3)_4$ (tetrakis(triphenylphosphine)-palladium(0), Acros, 99%) were used as received.

Synthesis of $[\{(Si(SiMe_3)_3)_3Ge_9\}Cu\{Ge_9(Si(SiMe_3)_3)_3\}CuPPh_3]\cdot 2.5hexane$ (1·2.5hex). K_4Ge_9 (92 mg, 0.114 mmol) was weighed out in a test tube in the glovebox, and acetonitrile (3.0 mL) solution of $(Me_3Si)_3SiCl$ (101 mg, 0.356 mmol) was added to the test tube. The reaction mixture was stirred for 4 h at room temperature and was then filtered. $Cu(PPh_3)_3Br$ (85 mg, 0.091 mmol) was added to the clear red filtrate while stirring, and an orange−yellow precipitate formed almost immediately. After 2 h of stirring, the solution became almost colorless, while the color of the precipitate changed somewhat to more brownish. This precipitate was washed with acetonitrile three times and was redissolved in hexanes to give a dark red solution. After any undissolved solid was separated by a centrifuge, the dark red solution was concentrated under vacuum and then stored at −20 °C for crystallization. Large black block-like crystals suitable for single-crystal X-ray crystallography were obtained after 1 week (184 mg, 59.7%). ^1H NMR (d_6-benzene): δ 7.734 (m, phenyl), 7.137 (m, phenyl), 0.433 (s, CH_3). ^{13}C NMR (d_6-benzene): δ 134.48 (phenyl), δ 130.77 (phenyl), δ 129.28 (phenyl), δ 2.769 (CH_3).

Synthesis of $[K(2,2,2\text{-crypt})]_2[\{(Si(SiMe_3)_3)_3Ge_9\}Pd\{Ge_9(Si(SiMe_3)_3)_3\}]\cdot 2CH_3CN$ ($[K(2,2,2\text{-crypt})]_2\cdot 2\cdot 2MeCN$). K_4Ge_9 (92 mg, 0.114 mmol) was weighed out in a test tube in the glovebox, and acetonitrile (3.0 mL) solution of $(Me_3Si)_3SiCl$ (101 mg, 0.356 mmol) was added to the test tube. The reaction mixture was stirred for 4 h at room temperature and was then filtered. $Pd(PPh_3)_4$ (157 mg, 0.136 mmol) suspended in 0.5 mL of acetonitrile was added to the filtrate, and the reaction mixture was allowed to stir for another 6 h at room temperature before filtration. One-half of the filtrate was layered with 5 mL of toluene containing 2,2,2-crypt (72 mg, 0.191 mmol) and stored undisturbed in the drybox. A large amount of dark brown block crystals suitable for single-crystal X-ray crystallography was obtained after 1 week (80 mg, 75.2%). ^1H NMR (d_6-benzene): 0.510 (s, CH_3). ^{13}C NMR (d_6-benzene): δ 3.057 (CH_3). ES−MS: m/z 1397 $[Ge_9R_3]^-$, 1450 $[(Ge_9R_3)Pd^0(Ge_9R_3)]^{2-}$, 1503 $[(Ge_9R_3)Pd^0]^-$, 2939 $\{K-[(Ge_9R_3)Pd^0(Ge_9R_3)]\}^-$.

Structure Determination. X-ray diffraction data sets of single crystals of the compounds **1** and **2** were collected at 120 K on either Bruker D8 APEX-II or Bruker X8 APEX-II diffractometers equipped with CCD area detectors using graphite-monochromated Mo Kα radiation. The single crystals were selected under Paratone-N oil, mounted on Mitegen micromount loops, and positioned in the cold stream of the diffractometer. The structures were solved by direct methods and refined on F^2 using the SHELXTL V6.21 package.[49] Compound **1** exhibited positional disorder of the $-CuPPh_3$ fragment, which was found capping the two available and identical triangular bases of the $[(Ge_9R_3)Cu^I(Ge_9R_3)]^-$ core. It was refined with 50% occupancy of these two positions. The thermal ellipsoids of the corresponding germanium atoms at those capped bases are very slightly elongated toward the capping fragment, suggesting possibly split positions but their refinement as such was not possible. Further details of the data collections and refinements are listed in Table 1.

NMR Spectroscopy. Deuterated benzene (Cambridge Isotope Laboratories, 99.9%) was used as received. ^1H and ^{13}C NMR spectra were recorded on a Varian INOVA 500 MHz spectrometer locked on the signal of deuterium solvent and referenced against Me_4Si (tetramethylsilane, Sigma-Aldrich, 99.9+%).

Mass Spectrometry. Electrospray mass spectra (ES−MS) were recorded in negative-ion mode on a Micromass Quattro-LC triple quadrupole mass spectrometer (typical conditions: 125 °C source temperature, 150 °C desolvation temperature, 2.8 kV capillary voltage, 30−60 V cone voltage). The samples were introduced by direct infusion with a Harvard syringe pump at 10 μL/min. The samples were taken from the corresponding reaction mixtures for the compounds just before setting them aside for crystallization.

Table 1. Selected Data Collection and Refinement Parameters for Compounds 1 and 2

	compound	
	1	2
formula weight	3397.79	3812.67
space group, Z	$C2/c$, 8	$P\bar{1}$, 2
a (Å)	38.399(3)	15.5519(12)
b (Å)	27.380(3)	16.8841(14)
c (Å)	30.128(2)	18.1601(15)
α (deg)	90	64.778(2)
β (deg)	91.359(2)	79.495(3)
γ (deg)	90	89.554(3)
V (Å^3)	31 666(5)	4228.4(6)
radiation, λ (Å)	Mo Kα, 0.71073	
ρ_{calcd} (g cm^{-3})	1.425	1.497
μ (mm^{-1})	3.845	3.551
R1/wR2,[a] $I \geq 2\sigma_I$	0.0440, 0.0937	0.0299, 0.0692
R1/wR2,[a] all data	0.0647, 0.1054	0.0496, 0.0775

[a] $R1 = [\sum||F_0| - |F_0||]/\sum|F_0|$; $wR2 = \{[\sum w[(F_0)^2 - (F_c)^2]^2]/[\sum w(F_0{}^2)^2)]\}^{1/2}$; $w = [\sigma^2(F_0)^2 + (aP)^2 + bP]^{-1}$, where $P = [(F_0)^2 + 2(F_c)^2]/3$.

■ RESULTS AND DISCUSSION

Structure. The neutral molecule **1**, $[(Ge_9R_3)Cu^I(Ge_9R_3)-Cu^IPPh_3]$ ($R = Si(SiMe_3)_3$), is a dimer of two tri-silylated clusters (Ge_9R_3), each with the shape of a tricapped trigonal prism where the three capping Ge atoms are *exo*-bonded to the three "hypersilyl" R groups (Figure 1). The two clusters are linked by a copper atom, which is coordinated to one trigonal prismatic base from each cluster. The two triangular faces are staggered with respect to each other resulting in *pseudo* octahedral geometry around that copper atom. In addition, the second trigonal prismatic base of one of the clusters is capped by the $CuPPh_3$ fragment. The $[(Ge_9R_3)Cu^I(Ge_9R_3)]^-$ core is the same as in the previously reported anionic $[(Ge_9R_3)-Cu^I(Ge_9R_3)]^-$ (**3**).[47] The anion is obviously "neutralized" by the additional $CuPPh_3{}^+$ fragment in **1**. The distances at the central Cu atom are also very similar in **1** and **3** with averages of 2.571 and 2.622 Å, respectively. On the other hand, the three Ge−$CuPPh_3$ distances in **1**, an average of 2.399 Å, are understandably shorter due to the lower coordination number of that Cu atom, that is, three Ge atoms and the PPh_3 group. These distances are also shorter than those to Cu atoms capping an open square face of nine−atom germanium clusters where they are five-coordinate, for example, $[(\eta^4\text{-}Ge_9)\text{-}CuPCy_3]^{3-}$, $[(\eta^4\text{-}Ge_9)\text{-}CuP^iPr_3]^{3-}$, and $[(\eta^4\text{-}Ge_9)\text{-}Cu\text{-}(\eta^1\text{-}Ge_9)]^{7-}$ with average Ge−Cu distances of 2.488, 2.499, and 2.501 Å, respectively.[22]

The linking and capping Cu atoms also affect the Ge−Ge distances within the capped faces by significantly elongating them. Thus, these distances of the Cu-linked triangular faces in **1** and **3** are noticeably long at 2.816 and 2.847 Å, respectively. Also, the average distance within the triangular base capped by $CuPPh_3$ in **1**, 2.755 Å, is substantially longer than the corresponding noncapped base in **3**, 2.640 Å.

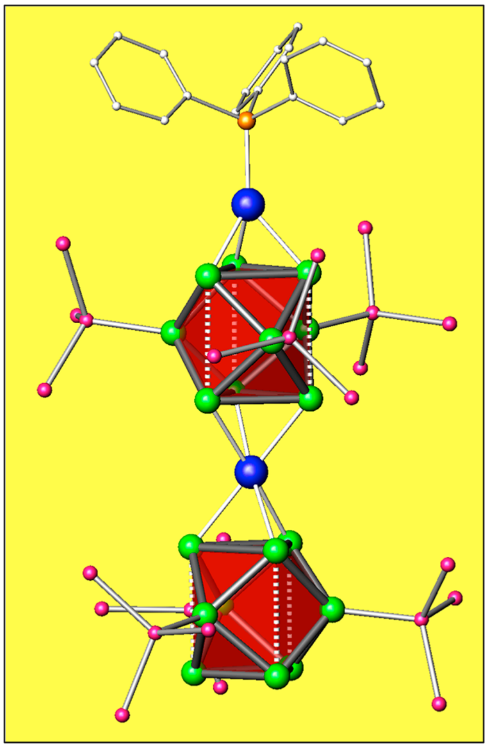

Figure 1. Structure of the neutral $[(Ge_9R_3)Cu^I(Ge_9R_3)Cu^IPPh_3]$ (**1**) where R = $Si(SiMe_3)_3$. The methyl groups on the "hypersilyl" groups are omitted for clarity. Ge, green; Si, purple; Cu, blue; P, orange; C, white.

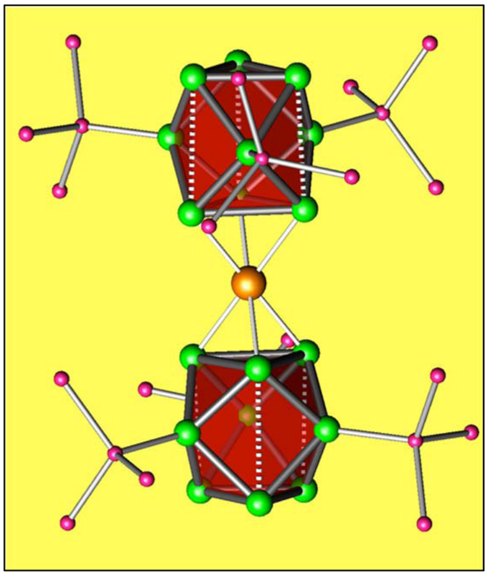

Figure 2. Structure of $[(R_3Ge_9)Pd(Ge_9R_3)]^{2-}$ (**2**) where R = $Si(SiMe_3)_3$. The methyl groups on the "hypersilyl" groups are omitted for clarity. Ge, green; Si, purple; Pd, orange.

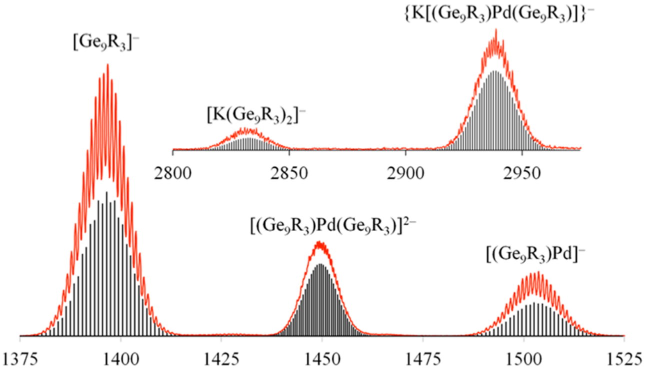

Figure 3. Electrospray mass spectrum (negative-ion mode) of acetonitrile solution of the potassium salt of **2**, that is, $K_2[(Ge_9R_3)Pd^0(Ge_9R_3)]$ (R = $Si(SiMe_3)_3$). The experimental and calculated spectra are shown in red and black, respectively.

The second molecule, the anionic $[(Ge_9R_3)Pd^0(Ge_9R_3)]^{2-}$ (**2**) (R = $Si(SiMe_3)_3$), can be viewed as a part of the series $[(Ge_9R_3)M(Ge_9R_3)]^{n-}$ where the charge n depends on the oxidation state of M. Thus, $n = 0$ for the dications of group 12, that is, Zn^{2+}, Cd^{2+}, and Hg^{2+}, and $n = 1$ for the monocations of group 11, that is, Cu^+, Ag^+, and Au^+. In our case, we have a metal of group 10 with a closed d-shell zero oxidation state Pd^0, which results in a charge of $n = 2$. The new dianion is a dimer of two tri-silylated clusters linked by the metal atom, just like the other reported species as well as in **1** (Figure 2). The central Pd atom is octahedrally coordinated by the trigonal prismatic bases of the two clusters with an average Ge−Pd distance of 2.568 Å. Again, due to the interaction with the Pd atom, the triangular bases are significantly expanded with an average Ge−Ge distance of 2.870 Å. In contrast, the average at the noncapped triangular bases is 2.631 Å.

Solution Studies. Both compounds are soluble in fairly nonpolar solvents such as benzene and toluene. However, while the neutral **1** is also soluble in the very nonpolar hexane and is insoluble in polar solvents such as acetonitrile, the anionic species **2** is exactly the opposite, that is, soluble in acetonitrile and insoluble in hexane. Both compounds were characterized by ^1H and ^{13}C NMR spectroscopy of their deuterated benzene solutions, and both showed single signals for the "hypersilyl" hydrogens and carbons. The phenyl groups of **1** were also clearly visible in the ^1H NMR. In addition, **2** was characterized by electrospray mass spectrometry in negative ion mode of its acetonitrile solution (Figure 3). The spectra exhibited the dianions both alone, that is, $[(Ge_9R_3)Pd(Ge_9R_3)]^{2-}$, and ion-paired with potassium cations, that is, $\{K[(Ge_9R_3)Pd(Ge_9R_3)]\}^-$, as well as their fragments, for example, $[Ge_9R_3]^-$ and $[(Ge_9R_3)Pd]^-$ (the analogous $[(Ge_9R_3)Pt]^-$ has already been identified by ES−MS[50]). It should be pointed out that polyanionic Zintl ions appear in electrospray mass spectra almost exclusively as monoanions, apparently due to their partial oxidation by the attracting positive electrode in the mass spectrometer. It is very rare to observe species with higher charges, which most likely attest to the stability of the ion with that particular charge. This is the case for **2** as it appeared in the spectrum with its real charge of 2− at $m/z = 1450$ where $z = 2$, and the isotope lines are separated by a one-half of a unit. The only other time we have observed a similar situation was with a solution of $[(K(2,2,2\text{-crypt})]_4[Ni_3@(Ge_9)_2]\cdot 2tol$, which showed the dianion $[Ni_3@(Ge_9)_2]^{2-}$.[11] Thus, the NMR of both **1** and **2** and the ES−MS of the latter suggest strongly that the species are intact in solutions and are not formed simply upon crystallization.

Synthesis. The formation of **1** can be viewed in light of the previously suggested formation of the gold analogue of **3**, that is, $[(Ge_9R_3)Au^I(Ge_9R_3)]^-$ (**4**).[46] While **3** is made by reacting $Ge_9R_3^-$ with the salt-like Cu(I) compound with weakly coordinating anions, $Cu(Al(OR)_4)$,[47] **4** is made by a reaction with a salt with ligated Au(I), $(PPh_3)AuCl$, just like the reaction with $(PPh_3)_3CuBr$ for the formation of **1**. It has been speculated that the formation of **4** begins with a salt-metathesis reaction to form the neutral $[(Ge_9R_3)Au{-}PPh_3]$, which then exchanges the neutral PPh_3 ligand with another anionic $Ge_9R_3^-$ to form $[(Ge_9R_3)Au^I(Ge_9R_3)]^-$, that is:[46]

$$[(Ge_9R_3)Au{-}PPh_3] + Ge_9R_3^- \rightarrow [(Ge_9R_3)Au^I(Ge_9R_3)]^- + PPh_3$$

Following this analogy, we suggest that the formation of **1** begins with the formation of $[(Ge_9R_3)Cu{-}PPh_3]$, which then replaces the PPh_3 ligand with exactly the same species of $[(Ge_9R_3)Cu{-}PPh_3]$, that is:

$$[(Ge_9R_3)Cu{-}PPh_3] + [(Ge_9R_3)Cu{-}PPh_3] \rightarrow [(Ge_9R_3)Cu(Ge_9R_3)Cu{-}PPh_3] + PPh_3$$

Notice that the latter reaction will be possible only in the absence of free $Ge_9R_3^-$ anions, which, in turn, is possible if the amount of transition metal reagent is enough to coordinate to all cluster anions. In the gold reaction, this is not the case as the ratio of $Ge_9R_3^-$:$(PPh_3)AuCl$ is 2:1, while in the copper reaction the two species are approximately equimolar.[46]

It is instructive to compare the synthesis of **2** with that of the endohedral $[Pd_2@Ge_{18}]^{4-}$ as they are both synthesized by a reaction with $Pd(PPh_3)_4$.[12] The difference, of course, is that reacted in the latter are naked Ge_9^{4-} clusters while the former uses the tri-substituted $Ge_9R_3^-$. Clearly, the results show that palladium atoms can be inserted into the naked clusters but not into the substituted species. It should be pointed out that this is also the case for all known mono- and di-substituted species; that is, metal atoms have not yet been inserted into already substituted clusters independent of how many substituents they have. It is likely that once substituted, the cluster loses the flexibility that might be needed for the insertion.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b01371.

X-ray data for compound **1**·2.5hex (CIF)
X-ray data for compound $[K(2,2,2\text{-crypt})]_2\cdot\mathbf{2}\cdot 2MeCN$ (CIF)

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Notes

The authors declare no competing financial interest.

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