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Capping nido-Nonagermanide Clusters with M-PPh₃ and Dynamics in Solution: Synthesis and Structure of closo- $[(Me_3Si)_3Si]_3Et[Ge_9M](PPh_3) (M = Ni, Pt)$

Sabine Frischhut,[†] Felix Kaiser,[‡] Wilhelm Klein,[†][©] Markus Drees,[§] Fritz E. Kühn,[‡][©] and Thomas F. Fässler*,[†]

[†]Lehrstuhl für Anorganische Chemie mit Schwerpunkt Neue Materialien, Fakultät für Chemie, Technische Universität München, Lichtenbergstraße 4, 85747 Garching, Germany

[‡]Professur für Molekulare Katalyse, Fakultät für Chemie, Technische Universität München, Lichtenbergstraße 4, 85747 Garching, Germany

[§]Lehrstuhl für Anorganische und Metallorganische Chemie, Fakultät für Chemie, Technische Universität München, Lichtenbergstraße 4, 85747 Garching, Germany

S Supporting Information

ABSTRACT: In this work, cluster expansion of nine-atomic germanium clusters with nickel and platinum atoms is reported. The compounds $[(Me_3Si)_3Si]_3Et[Ge_9Ni](PPh_3)$ and [(Me₃Si)₃Si]₃Et[Ge₉Pt](PPh₃) are characterized by NMR spectroscopy, elemental analysis, and single crystal Xray structure analysis. The latter represents the first intermetalloid Ge-Pt cluster with a platinum atom as part of a deltahedron. So far, only one compound of this type has been reported for the homologous Pd. Hence, with these new compounds, metal-coordinated deltahedral Geo clusters are



now known for the whole triad of group 10 elements. The cluster compounds are accessible by treating $[(Me_3Si)_3Si]_3EtGe_9$ with η^2 -ethylene-bis-(triphenylphosphine)-nickel(0) and η^2 -ethylene-bis-(triphenylphosphine)-platinum(0), respectively, in toluene. The crystal structure determination reveals ten-vertex-closo- $[Ge_9M]$ -cluster cores (M = Ni, Pt) bearing five exo-bonded ligands. Unlike the nine-vertex-cluster [(Me₃Si)₃Si]₃EtGe₉, the penta-functionalized platinum containing cluster compound $[(Me_3Si)_3Si]_3Et[Ge_9Pt](PPh_3)$ does not show fluctuating behavior in solution over a wide temperature range on the NMR time scale, whereas the $[(Me_3Si)_3Si]_3Et[Ge_9Ni](PPh_3)$ shows highly dynamic processes in solution at ambient temperature.

INTRODUCTION

 $[Ge_{\circ}]^{4-}$ Zintl clusters show multifaceted reactivity toward transition metal compounds. By reacting $[Ge_9]^{4-}$ with diverse transition metal complexes, endohedrally filled cluster species hosting transition metals in the cluster's center, as well as cluster compounds with exohedrally bonded transition metals, are accessible.¹ Therefore, such clusters are candidates to study cluster growth mechanisms for the formation of intermetalloid clusters. The manifold reaction schemes, including stepwise addition and insertion of transition metal atoms to deltahedral cages, flanked by disproportionation reactions allow for the synthesis of a large variety of compounds.²

According to the Wade-Mingos rules, [Ge₉]⁴⁻ represents a nido-cluster containing 22 skeleton-bonding electrons.³ The cluster can be dissolved in highly polar solvents by extraction from the binary Zintl phases A_4 Ge₉ (A = K, Rb), e.g., NH_{3(lia)} or ethylenediamine. The transfer of Ge₉ Zintl cluster compounds into less polar and more convenient solvents was achieved by the silvlation of the $[Ge_9]^{4-}$ Zintl clusters with chloro-silanes. The first representative was reported by Schnepf et al. through metastable Ge(I)Br,⁴ and an even more facile

synthesis of $[{(Me_3Si)_3Si}_3Ge_9]^-$ is carried out by reacting the Zintl phase K₄Ge₉ with chlorotris(trimethylsilyl)silane in a heterogeneous reaction in acetonitrile. This synthesis route provides access to the stable Zintl anion [{Me₃Si}₃Ge₉]⁻, which is highly soluble in acetonitrile, thf, and toluene.⁵ The reactivity of the three-fold silvlated cluster compound $[{(Me_3Si)_3Si}_3Ge_9]^-$ has been studied intensively in recent years, including variation of silvl ligands and the accompanied steric effects. New silvlated cluster compounds emerged, such as $[{(Me_3Si)_2(Ph_3Si)Si}_3Ge_9]^{-,6} [{(Me_3Si)_3Si}_2{(Me_3Si)_2}^{-,6}]$ $(Ph_3Si)Si$ Ge_9 , and $[{HtBu_2Si}_3Ge_9]^{-.8}$ Also, the introduction of specific functionalities to the Ge₉ clusters via the silyl ligand has been shown by the synthesis of $[{(Me_3Si)_3Si}_2 {Ph_2((CH_2)_nCH=CH_2)Si}Ge_9^-$ and $[{Ph_2((CH_2)_nCH=CH_2)Si}Ge_9^-$ CH₂)Si}₃Ge₉]^{-,9} The silyl ligands can also be formally exchanged by other substituents as is shown in [{(Me₃Si)₃-Si}₂PtBu₂Ge₉].¹⁰ Stannyl-decorated Zintl anions were realized in $[(SniPr_3)_3Ge_9]^{-.11}$ More and more attention has been

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Scheme 1. Reaction of $[(Me_3Si)_3Si]_3EtGe_9$ with η^2 -Ethylene-bis-(triphenylphosphine)-platinum(0)/ η^2 -Ethylene-bis-(triphenylphosphine)-nickel(0) in Toluene Yields $[(Me_3Si)_3Si]_3Et[Ge_9Ni](PPh_3)$ (1)/ $[(Me_3Si)_3Si]_3Et[Ge_9Pt](PPh_3)$ (2)



drawn on the three-fold silvlated Ge₉ cluster compounds, as they represent excellent starting materials for follow-up reactions in Zintl cluster chemistry. For example, the threefold silvlated cluster compound $[{(Me_3Si)_3Si}_3Ge_9]^-$ can undergo nucleophilic substitution reactions with XSnPh₃, XSnnBu₃, XR', or Cl(CO)R' (with X = halide and R' = organic substituent) to form neutral cluster compounds, which show dynamic behavior in solution.¹²

Also, $[R_3Ge_9]^-$ (R = silyl ligands) readily reacts with late transition metal halides in metathesis reactions. For example, the linkage of two $[\{(Me_3Si)_3Si\}_3Ge_9]^-$ entities can be realized in $[\{Me_3Si)_3Si\}_3Ge_9MGe_9\{Si(SiMe_3)_3\}_3]^{n-}$ for various metals (M = Cu, Ag, Au, n = 1; M = Zn, Cd, Hg, n = 0), where the cluster cores are coordinated to the metal center in an η^3 -fashion.¹³ With $[\{(Si(SiMe_3)_3)_3Ge_9\}Cu\{Ge_9(Si(SiMe_3)_3)_3\}-CuPPh_3]^{14}$ and $[(CuPiPr_3)_4\{Ge_9(SiPh_3)_2\}_2]_1^{15}$ also larger entities have been reported. Remarkably, the latter contains two CuPiPr_3 entities serving as linker by cluster coordination in both Cu- η^1 and Cu- η^2 fashion. Additionally, each Ge_9 cluster core coordinates to one CuPiPr_3 entity *via* the Cu atom in an η^4 fashion.

Just recently, also the first *N*-heterocyclic carbene (NHC) adducts of Ge₉ Zintl clusters were reported with [NHC^{Dipp}*M*- $(\eta^3$ -Ge₉[{Si(SiMe_3)_3}] (*M* = Cu, Ag, Au) and, thus, for the first time combined NHC and Zintl cluster chemistry, which gave access to several new structures.^{10,16}

Cluster expansions have been realized at bare Ge_9 clusters with Zn, Cu, Sn, Pd and also for the heavier homologues Sn_9 with Zn, Cd, Ir, Cr, Mo, W, Ag, Cu, Au, and for Pb₉ with Cr, Mo, W atoms.^{1b,16d,17}

Similarly, *nido*-cluster core expansion has been achieved for $[{Me_3Si}_3Si]_3Ge_9]^-$, resulting in *closo*- $[[{Me_3Si}_3Si]_3Ge_9M-(CO)_3]^-$ for M = Cr, Mo, W. The transition metal is introduced into the polyhedral arrangement, forming a distorted bicapped square antiprismatic $[MGe_9]$ core.¹⁸

With Pd complexes, introduction of three Pd atoms into the cluster scaffold of $[(SniPr_3)_3Ge_9]^-$, followed by merging with a second $[(SniPr_3)_3Ge_9]^-$ unit, was observed.^{11,19} Just recently, the first example of a cluster expansion of a neutral Ge₉ cluster, which carries five external ligands $[(Me_3Si)_3Si]_3EtGe_9Pd-(PPh_3)$, was reported. The compound with a *closo*-[PdGe₉] core is accessible by the reaction of $[(Me_3Si)_3Si]_3EtGe_9$ with $[Pd(PPh_3)_4]_2^{20}$

In this work, the related *closo*-[*M*Ge₉] cluster derivatives of the lighter homologue M = Ni and the heavier homologue M =Pt are presented. [(Me₃Si)₃Si]₃Et[Ge₉Ni](PPh₃) (1) and [(Me₃Si)₃Si]₃Et[Ge₉Pt](PPh₃) (2) were obtained by reaction of [(Me₃Si)₃Si]₃EtGe₉ with η^2 -ethylene-(bis-triphenylphosphine)-nickel(0) and η^2 -ethylene-(bis-triphenylphosphine)platinum(0), in toluene (Scheme 1), respectively. Both compounds crystallize from *n*-hexane solutions at -32 °C and are investigated by NMR spectroscopy, elemental analysis, and single crystal X-ray diffraction.

RESULTS AND DISCUSSION

Reactions of $[(Me_3Si)_3Si]_3EtGe_9$ with tetrakis(triphenylphosphine)nickel(0) or tetrakis(triphenylphosphine)platinum(0) in analogy to the recently published procedure for the respective palladium species²⁰ leads to the decomposition of $[(Me_3Si)_3-Si]_3EtGe_9$, as monitored in the ¹H NMR spectra of the reaction solutions. Consequently, the reactions were carried out with the more readily reactive η^2 -ethylene-bis-(triphenylphosphine)-nickel(0) and -platinum(0) complexes where the ethylene ligand is easier to replace. The reaction at room temperature in toluene resulted in the formation of the desired products $[(Me_3Si)_3Si]_3Et[Ge_9M](PPh_3)$ with M = Ni (1) and Pt (2). The products were extracted with hexane from the solid after removal of toluene, and recrystallized from the hexane solutions at -32 °C.

Single crystal X-ray diffraction of crystals of 1 and 2 unequivocally revealed the formation of a distorted C_{S^-} symmetric bicapped square-antiprismatic *closo*-[*M*Ge₉] core bearing the *M* atom as a vertex of the square of the antiprism and five ligands that radially point away from the cluster core (Figure 1). The compounds crystallize in the triclinic space group $P\overline{I}$ with one symmetry-independent cluster. The cluster possesses pseudo- C_s symmetry with an approximate mirror plane through the atoms Ni1/Pt1, Ge1, Ge3, Ge6, and Ge8. A triphenylphosphine ligand is coordinated to the Ni/Pt atom which itself coordinates to the five Ge vertices Ge1, Ge2, Ge3, Ge4, and Ge5 of the cluster core. In particular, two hypersilyl groups are bound to the neighboring and opposingly positioned Ge atoms of the square of the antiprism (Ge1 and Ge3).

Both capping atoms bear ligands, namely, the ethyl functionality at the Ge2 atom neighboring the Ni/Pt atom and one of the three hypersilyl groups binds to the Ge6 atom. The Ge–Ge bond lengths within the cluster core in 1 and 2 lie in the range of 2.4682(6)-2.8020(6) Å and 2.4756(8)-2.8885(9) Å, respectively, with Ge1–Ge2 and Ge4–Ge5 being the shortest and longest, respectively. The Ge–Ge bond lengths in 1 appear slightly shorter than the reported ones for the heavier Pd homologue; the Ge–Ge bond lengths in the Pt derivative 2 are similar to those in the lighter Pd homologue.²⁰ The distances Ge4–Ge9 and Ge5–Ge7 appear elongated (1: 3.2429(7) Å and 3.3244(7) Å, 2: 3.2303(9) Å and 3.3053(9)



Figure 1. Molecular structures of 1 (a, b) and 2 (c, d). (a/c) The $[MGe_9]$ -cluster cores are depicted as polyhedrons. All hydrogen atoms as well as CH₃ groups on hypersilyl moieties are omitted for clarity. (b/d) The two squares of the underlying quadratic antiprism of the $[MGe_9]$ -polyhedra are highlighted in red. All ellipsoids are shown at a probability level of 50%. Ge - blue, Si - green, C - gray, P - purple, Ni - turquoise, Pt - brown.

Å), compared to the shorter distances Ge4–Ge5 and Ge7–Ge9 (1: 2.7638(6) Å and 2.7785(6) Å, 2: 2.8885(9) Å and 2.7497(9) Å), resulting in a considerably distorted "square", formed by the Ge4-Ge5-Ge7-Ge9 atoms. This has already been observed for neutral, functionalized Ge₉ Zintl clusters.^{12a,20} As expected, the average Ni–Ge distance of

2.476 Å in 1 is smaller compared to the average Pd–Ge distance of 2.577 Å and the average Pt–Ge distance of 2.592 Å in 2. The latter two are rather similar due to similar atom radii of Pd and Pt.²¹ The shorter Ni–Ge distances lead to a stronger distortion of the *closo*-cluster core accompanied by a compression of the Ge–Ge distances.

The ¹H NMR spectrum of the platinum cluster **2** shows all expected signals at r.t. including the phenyl groups of the phosphine ligands in the range of 7.90–6.99 ppm, the ethyl group, which shows the two expected signals at 2.66 and 2.36 ppm with an integral ratio of 2:3, and two sharp signals at 0.65 and 0.26 ppm in a 1:2 integrals ratio for the three hypersilyl groups. According to the approximate C_S symmetry of the polyhedron, two hypersilyl groups are chemically equivalent (Figure 2).

Even at elevated temperatures up to 90 $^{\circ}$ C, 2 does not show a change in its nondynamic behavior, as is revealed by temperature-resolved NMR studies (Figure S15, Supporting Information). Thus, the two signals for the hypersilyl groups remain virtually unchanged throughout a wide temperature range.

The ¹H NMR spectrum of 1 at r.t. shows broad signals in the region of the H atoms of the hypersilyl ligands at 0.61 and 0.27 ppm, and the ethyl group at 2.86 and 2.25 ppm. The large line widths hint for a dynamic process in solution (Figure S5). Temperature-dependent NMR spectra of 1 show sharp signals at lower temperature up to 0 °C (Figures 2 and 3). The hypersilyl ligands appear as two signals in a 1:2 ratio as expected for a $C_{\rm s}$ -symmetric cluster. Upon warming to 25 °C, the signals for the hypersilyl and the ethyl ligand progressively broaden and are visually shifted at 25 °C. When further heated up to 80 °C, sharp signals for the hypersilyl ligands at 0.52 and 0.29 ppm in a 1:2 ratio appear in the ¹H NMR spectrum (Figure 3a). Also, a new signal set for the ethyl ligand at 2.60 and 1.90 ppm appears with an integrals ratio of 2:3 which still does not show the expected multiplicity at 80 °C (Figure 3b). The signal set of the bound triphenylphosphine ligand does not significantly change in the described temperature range;



Figure 2. ¹H NMR spectrum of dissolved crystals of compound 2, recorded in $[D_6]$ benzene at r.t. The regions of the phenyl and ethyl groups are shown enlarged. The signals of the hypersilyl groups are marked with "hyp"; the signals of hexane are marked with "hex".

Organometallics

Article



Figure 3. Variable temperature ¹H NMR study of crystals of 1 in $[D_8]$ toluene in the range from -40 to 80 °C and subsequent cooling to -40 °C. (a) The signals of the hypersilyl ligands ("hyp") are shown. (b) The signals of the ethyl ligand ("Et") are shown.

however, after increasing time of heating, a signal of low intensity corresponding to free PPh₃ appears (Figure S7). Subsequent cooling to -40 °C leads to the same sharp signal sets as before warming (Figure 2 and Figure S6). Yet, the very weak signal of free PPh₃ remains visible in the ¹H NMR spectrum, which hints at slow and irreversible PPh₃ abstraction of **1**. Remarkably, compound **1** is the major component again after heating to 80 °C and subsequent cooling. Variable temperature ³¹P NMR studies also reveal dynamic temperature-dependent processes in solution (Figure S8, Supporting Information).

Hence, the clusters 1 and 2 do not show the fluctuating behavior as is observed for $[(Me_3Si)_3Si]_3EtGe_9$ in solution at r.t., since the silyl ligands are not all identical. Nevertheless, 1 shows a different dynamic process in solution at r.t., whereby the C_S -symmetry of 1 remains unchanged. This can be concluded from the signal set of two signals for the hypersilyl ligands as well as the corresponding integrals ratio of 1:2 at temperatures above 60 °C in the temperature-dependent ¹H NMR spectrum.

Isomerization resulting from rotation of the ethyl group in **1** is feasible, but the reason for the lack of rotational isomerism in **2** in the analogous Pt complex remains unclear. Therefore, we also take constitutional isomerism into account. Scheme **2** shows the two at elevated temperatures possibly formed isomers **1**' and **1**'', which fulfill the C_{s} -symmetry.

On the basis of quantum chemical DFT calculations, the energy difference between the two isomers 1 and 1', where the position of the Ge2-ethyl fragment is changed with the only ligand-free adjacent Ge8-vertex, is only as high as +7.6 kcal/mol (energy difference between the Pt-analogous isomers 2 and 2': +8.1 kcal/mol). Retention of the C_s -symmetry in 1 would also be given when the fragments Ni-PPh₃ and Ge2-ethyl undergo a formal positional change to form the isomer 1''. Here, the energy difference of the isomers 1 and 1'' is +7.2 kcal/mol (energy difference between the Pt-analogous isomers 2 and 2'': +9.2 kcal/mol). The energy differences for the isomerization of 1 and 2 are in the same range; however, we do not have any information about transition states. The

Scheme 2. Two Feasible C_S -Symmetric Isomers of 1' and 1'' Which Can Be Achieved Based on 1 by the Formal Exchange of Vertices



isomerization of **1** most likely proceeds according to a diamond-square-diamond (DSD) rearrangement mechanism. Such cluster rearrangement processes have been described for boranes and carboranes,²² which are structurally and electronically related to the Ge₉ clusters. Isomerizations analogous to the formation of **1**^{''} out of **1** are already reported in the literature for *closo*-[Sn₉Mo(CO)₃]⁴⁻, where the corresponding η^4 - and η^5 -structures show a dynamic equilibrium.^{17g}

The formation of the *closo*- $[MGe_9]$ cluster core (M = Ni, Pt) of 1 and 2 is, similarly to $[(Me_3Si)_3Si]_3Et[Ge_9Pd](PPh_3)$, believed to be initiated by an $M(PPh_3)$ entity capping the triangular face Ge2-Ge4-Ge5 of the *nido*-Ge₉ cluster core, followed by a cluster-opening displacement of the ethyl-functionalized Ge2 vertex.²⁰

Currently, investigations on follow-up reactions are ongoing in our laboratories. Among others, the behavior of the PPh_3 ligand and its exchangeability for other ligands is of particular interest to us.

CONCLUSION

In this work, we were able to complete the triad of the compounds $[(Me_3Si)_3Si]_3Et[Ge_9M](PPh_3)$ with M = Ni-Pt. The deltahedral Ge₉ Zintl cluster compounds $[(Me_3Si)_3Si]_3-Et[Ge_9M](PPh_3)$ [M = Ni (1), M = Pt (2)] are synthesized by reaction of $[(Me_3Si)Si]_3EtGe_9$ with η^2 -ethylene-bis-(triphenyl-phosphine)-nickel(0) or η^2 -ethylene-bis-(triphenylphosphine)-platinum(0). Both compounds 1 and 2 are characterized in solution by NMR spectroscopy as well as in the solid state by elemental analysis and single crystal X-ray diffraction. The nickel derivative 1 shows a strongly distorted *closo*-[NiGe_9] cluster core and most likely undergoes a framework rearrangement in solution at r.t., if compared to the *closo*-[MGe_9] cluster cores of the heavier homologues.

Further investigating the neutral deltahedral Ge₉ Zintl cluster compounds in follow-up reactions is of special interest as neutral, functionalized cluster compounds can be used to build up higher cluster aggregates. After saturating the whole coordination sphere of the neutral Zintl cluster compound $[(Me_3Si)Si]_3EtGe_9$, new interesting structures might be available.

EXPERIMENTAL SECTION

General. All manipulations were carried out under a purified argon atmosphere using standard Schlenk techniques. The Zintl phase with the nominal composition K₄Ge₉ was synthesized heating a stoichiometric mixture of the elements K and Ge (99.999%, Chempur) at 650 °C for 46 h in a stainless steel autoclave.²³ The solvents acetonitrile, toluene, and hexane were dried over molecular sieve in a solvent purification system MB-SPS. cis-Dichloro-bis-(triphenylphosphine)-platinum(II) (Sigma-Aldrich), ethylene (\geq 99.5%, Sigma-Aldrich), chlorotris(trimethylsilyl)silane (\geq 95.0%, TCI Chemicals), and bromoethane (98%, Sigma-Aldrich) were used as received. Ni(acac)₂ was sublimed in vacuo $(10^{-3} \text{ mbar}, 160 \degree \text{C})$, PPh₃ was recrystallized twice from hot ethanol, and diethyl ether was saturated with ethylene by vigorously passing a stream of ethylene gas through the liquid over a period of 10 min. The deuterated solvents [D₆]benzene and [D₈]toluene were purchased from Deutero GmbH and stored over molecular sieves (3 Å) for at least 1 day.

Electron-Dispersive X-ray (EDX) Analysis. The elemental composition in the single crystals of 1 and 2 which were used to determine the crystal structure was analyzed with a Hitachi TM-1000 tabletop microscope.

Elemental Analysis. Elemental analysis was performed by the microanalytical laboratory at the Department of Chemistry of the Technische Universität München. The elements C and H were determined with a combustion analyzer (elementar vario EL, Bruker Corp.). Platinum was determined photometrically with tin(II) chloride at 404 nm. Nickel was determined by atomic absorption spectroscopy.

NMR Spectroscopy. All NMR spectra were recorded on a BRUKER Avance Ultrashield AV400 spectrometer. The signals were referenced to the residual proton signal of the deuterated solvents [D₆]benzene ($\delta = 7.16$ ppm) and [D₈]toluene ($\delta_{CH3} = 2.09$ ppm). The chemical shifts are given in δ values in parts per million (ppm). Variable temperature ³¹P NMR studies were performed on a BRUKER AV500 cryo spetrometer. Crystals of 1 were dissolved in the deuterated solvent at -78 °C.

DFT Calculations. All calculations have been carried out with the software package Gaussian 09.²⁴ The level of theory contains the gradient approximated functional PBE²⁵ and the def2-SV(P)²⁶ basis set for all elements except Pt. For the latter element, the Dresden-Stuttgart ECP²⁷ has been used. All optimized structures have been proved by frequency analysis, if we have a ground state (NImag = 0) or a transition state (NImag = 1). All energy values are unscaled ΔG values. Detailed information about the calculated structures

(geometry, absolute energy) can be found in the Supporting Information.

Synthesis of η^2 -Ethylene-bis-(triphenylphosphine)-nickel-(0). The product was synthesized according to a literature procedure.²⁸ Ni(acac)₂ (1.00 g, 3.89 mmol) and PPh₃ (2.04 g, 7.78 mmol) are dissolved in diethyl ether, and a stream of ethylene gas is passed through the suspension at 0 °C. AlEt₃ (469 mg, 4.11 mmol) dissolved in 6.5 mL of hexanes is added over a period of 30 min and stirred for 5 h. The canary yellow precipitate is filtered off with a Schlenk frit, washed three times with diethyl ether, and dried in a vigorous stream of ethylene. The product is isolated as a canary yellow solid. The analytical data match those reported in the literature.

Synthesis of [(SiMe₃)Si]₃Ge₉Et. The compound [(SiMe₃)₃Si]₃-Ge₉Et was synthesized according to a modified literature procedure.^{12a} A solution of chlorotris(trimethylsilyl)silane (357 mg, 1.26 mmol) in 12 mL of acetonitrile is added to K₄Ge₉ (341 mg, 0.42 mmol). The reaction solution is stirred for 21 h at r.t. and filtered over a glass fiber filter. Bromoethane (156 μ L, 2.10 mmol) dissolved in 2 mL acetonitrile is added dropwise under vigorous stirring. A brown precipitate is formed; the suspension is stirred for 5 h and then set aside to allow the precipitate to settle down. The supernatant is decanted, and the precipitate is washed three times with a total amount of 24 mL of acetonitrile. The residue is dried *in vacuo* and characterized by NMR spectroscopy (see the Supporting Information).

Synthesis of $[(SiMe_3)Si]_3Et[Ge_9Ni](PPh_3)$ (1). The obtained brown solid of $[(SiMe_3)_3Si]_3Ge_9Et$ (150 mg, 0.11 mmol) and η^2 ethylene-bis-(triphenylphosphine)-nickel(0) (65 mg, 0.11 mmol) are dissolved in 3.2 mL of toluene and stirred for 2 h at r.t. After filtration over a glass fiber filter, the solvent is removed. The residue was extracted with hexane to give a dark-brown solution which was filtered again. After concentration, the solution is stored at -32 °C for crystallization. After 5 days, brown block-shaped crystals of 1 (yield: 27%) suitable for X-ray structure analysis formed. For NMR spectroscopic investigations, crystals of 1 were separated from the mother liquor, washed with acetonitrile, dried *in vacuo*, and dissolved in a deuterated solvent.

¹H NMR (400 MHz, [D₈]toluene, 233 K): δ (ppm) 7.76 (m, 6H, phenyl), 7.03 (m, superimposed with signal of toluene, phenyl), 7.951 (m, superimposed with signal of toluene, phenyl), 2.86 (q, 2H, ${}^{3}J$ = 7.6 Hz, CH₂), 2.36 (t, 3H, ${}^{3}J$ = 7.6 Hz, CH₃), 0.65 (s, 27H, SiCH₃), 0.28 (s, 54H, SiCH₃); ${}^{31}P{}^{1}H$ NMR (162 MHz, [D₈]toluene, 233 K): δ (ppm) 50.99; elemental analysis calcd for 1.0.5 hex (%): C 33.55, H 6.08, Ni 3.28; found: C 33.23, H 6.08, Ni 3.7.

Synthesis of η^2 -Ethylene-bis-(triphenylphosphine)platinum(0). The compound was synthesized according to a modified literature procedure.²⁹*cis*-Dichloro-bis-(triphenylphosphine)-platinum(II) (2.03 g, 2.57 mmol) is suspended in a mixture of 25 mL of dichloromethane and 25 mL of ethanol, cooled to 5 °C, and ethylene is vigorously passed through the stirred suspension *via* cannula. NaBH₄ (0.48 g, 12.6 mmol) is added in portions within a period of 10 min, and the solution is stirred at 5 °C for 30 min. 85 mL of ethanol is added, the suspension is stirred for 5 min, and the ethylene stream is turned off. The white precipitate is filtered off, washed with water, ethanol, and pentanes, and slowly dried on air. 1.82 g (2.43 mmol, 95%) of η^2 -ethylene-bis-(triphenylphosphine)platinum(0) is isolated as a white solid. The analytical data match those reported in the literature.^{29,30}

Synthesis of [(SiMe₃)Si]₃Et[Ge₉Pt](PPh₃) (2). [(SiMe₃)₃Si]₃-Ge₉Et (150 mg, 0.11 mmol) and η^2 -ethylene-bis-(triphenylphosphine)-platinum(0) (79 mg, 0.11 mmol) are dissolved in 3.2 mL of toluene and stirred for 3.5 h at r.t. The reaction solution is filtered over a glass fiber filter. After solvent-removal from the red-brown filtrate *in vacuo*, the product is extracted with 2 mL of hexane. After filtration, the solution is concentrated *in vacuo* and stored at -32 °C for crystallization. Red-brown plates of 2 (yield: 32%) suitable for X-ray structure analysis formed within 4 weeks. For NMR spectroscopic investigations, crystals of 2 were separated from the mother liquor, washed with acetonitrile, dried *in vacuo*, and dissolved in a deuterated solvent.

¹H NMR (400 MHz, $[D_6]$ benzene, 298 K): δ (ppm) 7.88 (m, 6H, phenyl), 7.09 (m, 6H, phenyl), 7.01 (m, 3H, phenyl), 2.66 (q, 2H, ³J = 7.6 Hz, CH_2), 2.36 (t, 3H, ³J = 7.6 Hz, CH_3), 0.65 (s, 27H, SiCH₃), 0.26 (s, 54H, SiCH₃); ¹H ¹H COSY (400 MHz, [D₆]benzene, 298 K): δ (ppm)/ δ (ppm) 7.88/7.09 (phenyl), 2.65/2.37 (³J, CH₂/CH₃); ¹³C{¹H} NMR (101 MHz, $[D_6]$ benzene, 298 K): δ (ppm) 140.8 (s, phenyl), 140.4 (s, phenyl), 134.8 (s, phenyl), 134.7 (s, phenyl), 129.9 (s, phenyl), 129.8 (s, phenyl), 128.3 (superimposed with signal of C₆D₆, revealed by HMBC and HSQC, phenyl), 47.7 (t, CH₂), 16.1 (q, CH₃), 3.1 (q, SiCH₃); ¹H ¹³C HSQC (400 MHz, 101 MHz, $[D_6]$ benzene, 298 K): δ (ppm)/ δ (ppm) 7.88/134.4, 7.89/128.0, 7.09/134.4, 7.09/129.6, 7.09/128.0, 7.01/129.6, 2.66/47.3 (¹J, CH₂/ CH₂), 2.66/15.70 (²J, CH₂/CH₃), 2.36/47.35 (²J, CH₃/CH₂), 2.36/ 15.70 (¹J, CH₃/CH₃), 0.65/2.72 (¹J, SiCH₃/SiCH₃), 0.26/2.74 (¹J, SiCH₃/SiCH₃); ¹H ¹³C HMBC (400 MHz, 101 MHz, [D₆]benzene, 298 K): δ (ppm)/δ (ppm) 7.88/134.6, 7.88/129.9, 7.11/140.7, 7.10/ 134.7, 7.09/128.4, 7.00/134.8, 2.65/16.5, 2.36/47.7, 0.65/3.2, 0.26/ 3.3; ${}^{31}P{}^{1}H$ NMR (162 MHz, [D₆]benzene, 298 K): δ (ppm) 37.79 (s, PtPPh₃); ²⁹Si NMR (79 MHz, 298 K): -9.08 (s, Si[$Si(CH_3)_3$]₃), -9.83 (s, Si[Si(CH₃)₃]₃), -87.04 (s, Si[Si(CH₃)₃]₃), -94.66 (s, $Si[Si(CH_3)_3]_3)$; elemental analysis calcd for 2.1.5 hex (%): C 33.42, H 6.11, Pt 9.69; found: C 32.84, H 5.80, Pt 9.6.

X-ray Data Collection and Structure Determination. A few crystals were transferred from the mother liquor into perfluoropolyalkylether under a cold N₂ stream. A single crystal was fixed on a glass fiber and positioned in a 150 K (compound 1) or 100 K (compound 2) cold N₂ stream. The single crystal intensity data were recorded on a Stoe StadiVari diffractometer (Mo K α radiation ($\lambda = 0.71073$), Pilatus 300 K detector), by using the X-Area software package.³¹ The crystal structure was solved by Direct Methods using the SHELX software.³² The positions of the hydrogen atoms were calculated and refined using a riding model. All non-hydrogen atoms were treated with anisotropic displacement parameters. Solvent molecules appear partially disordered in the crystal structure of 2. Crystallographic details of compounds 1 and 2 are listed in Table 1. CCDC 1812801 (1) and CCDC 1812802 (2) contain the supplementary crystallographic data.

Table 1. Crystallographic Details of Compounds 1.1.5 hex and 2.1.5 hex

	1.1.5 hex	2 ·1.5 hex
formula	C56H122Ge9NiPSi12	C56H122Ge9PtPSi12
fw (g⋅mol ⁻¹)	1875.60	2011.98
space group (no.)	$P\overline{1}(2)$	$P\overline{1}(2)$
a (Å)	15.167(1)	15.191(1)
b (Å)	15.847(1)	15.708(1)
c (Å)	19.892(2)	19.723(2)
α (deg)	99.133(6)	98.925(7)
β (deg)	106.666(6)	106.532(6)
γ (deg)	99.076(6)	99.084(6)
$V(Å^3)$	4416.3(6)	4354.5(6)
Z	2	2
T (K)	150(2)	100(2)
λ (Å)	0.71073	0.71073
$\rho_{\rm calcd}~({\rm g}{\cdot}{\rm cm}^{-3})$	1.410	1.535
$\mu (\text{mm}^{-1})$	3.435	4.872
collected reflns	119203	77381
independent reflns	20306	17104
R _{int}	0.066	0.093
parameters/restraints	698/0	752/49
R_1 [all data/ $I > 2\sigma(I)$]	0.067/0.040	0.065/0.041
wR ₂ [all data/ $I > 2\sigma(I)$]	0.099/0.083	0.097/0.089
goodness of fit	1.072	0.96
max./min diff. el. density	0.96/-0.78	2.75/-0.85

The presence of the elements Si, Ge, P, and Pt or Ni in the measured single crystal was confirmed by EDX.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.8b00459.

Further details on the crystal structures of **1** and **2**, as well as NMR spectra are provided (PDF) Cartesian coordinates (XYZ)

Accession Codes

CCDC 1812801 and 1812802 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Author

*Fax: +49-89-289-13186. E-mail: Thomas.Faessler@lrz.tumuenchen.de.

ORCID 💿

Wilhelm Klein: 0000-0002-6351-9921

Fritz E. Kühn: 0000-0002-4156-780X

Thomas F. Fässler: 0000-0001-9460-8882

Notes

The authors declare no competing financial interest.

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