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Article

Sila- and Germaplatinacycles Produced from a Stepwise E−E Bond Forming Reaction

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Introduction

The preparation of transition metal complexes containing bonds to the heavier group 14 elements, E = Si, Ge, and Sn, has received considerable attention over the last several decades. Complexes containing transition metal−silicon bonds[1] are by far the most abundant, but many examples are also known for M−Ge and M−Sn containing complexes[2] (M = transition metal). The most versatile method for the preparation of complexes containing a M−E bond involves activation of an E−H bond by the metal center.[3] Metal-promoted activation of the E−H bonds in hydrosilanes, hydrogermanes, and hydrostannanes is also important in dehydrocoupling reactions,[4] as well as addition of E−H bonds to unsaturated organic substrates (e.g., hydrosilylation).[4h,5] The dehydrocoupling of E−H bonds catalyzed by many early transition metal complexes is thought to proceed by a sigma-bond metathesis route,[4b] whereas reactions with late transition metal catalysts have been postulated to involve a cycle of oxidative-addition/reductive-elimination steps[6] but could also involve a sequence of oxidative-addition/reductive-elimination steps, α-hydride abstraction, and migration of ER_3 groups between the metal and the E center in $L_nM{=}ER_2$ intermediates.[4,7] The migration of a group from the metal to the silylene silicon center has been observed with a number of different metal systems.[7b,8] Two alternative pathways for the formation of E−E bonds starting from bis(silyl) or bis(germyl)platinum complexes, either through a platinum−silylene or −germylene intermediate or through a reductive-elimination/oxidative-addition pathway, are shown in Scheme 1. Limited examples of dehydrocoupling of hydrosilanes with late transition metal catalysts such as those containing platinum are known.[9] The formation of Ge−Ge bonds catalyzed by late transition metal complexes is less common compared to silicon due to the decreased reactivity of the M−Ge bond compared to the M−Si bond.[10]

We previously reported the preparation of the digermane complex $(Ph_3P)_2HPt\text{-}GeAr_2GeAr_2\text{-}PtH(PPh_3)_2$ as one of the major products formed from the reaction of germafluorene with $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ through a formal dehydrocoupling reaction (eq 1).[11] A similar diplatinum digermane complex, $[(Et_3P)_2HPtGeAr_2GeAr_2PtH(PEt_3)_2]$, was reported by Banaszak-Holl and co-workers.[12] These reactions likely proceed through pathway a in Scheme 1. Related Ge−Ge bond forming reactions or 1,2-migrations

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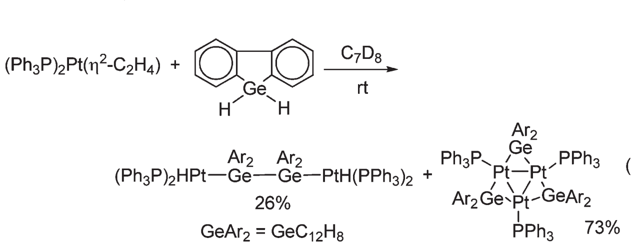
involving Pt=Ge species have been reported by Barrau,[13] Yamashita,[14a] and Mochida.[14b,15–17]

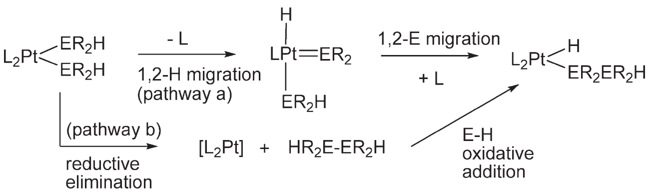


(1)

Mochida and co-workers reported the room-temperature formation of a Ge−Ge bond in *cis*-$(Ph_3P)_2Pt(H)[GeH(Mes)GeH_2Mes]$ from *cis*-$(Ph_3P)_2Pt(GeH_2Mes)_2$ (Mes = 2,4,6-C_6H_2).[16] A related platinum(disilyl) complex, $(Ph_3P)_2Pt(H)(SiPh_2SiPh_2H)$, was found to be stable only at low temperature and underwent a rapid 1,2-migration of a silyl group to give the bis(silyl)complex $(Ph_3P)_2Pt(SiPh_2H)_2$ at −40 °C.[18] In contrast, the related germanium complex $(Ph_3P)_2Pt(H)(GePh_2GePh_2H)$ was found to be stable in toluene or benzene solution.[17] Ishii and co-workers have reported the preparation of stable dihydridogermyl(hydrido)platinum complexes, *cis*-$P_2Pt(H)(GeH_2Trip)$ (Trip=9-triptycyl; P_2= $(Ph_3P)_2$, dppe, dcpe). The dppe complex was found to undergo a thermolysis reaction to produce the digermyl(hydrido)-platinum complex $(dppe)Pt(H)(Ge(HTrip)GeH_2Trip)$.[19] The reaction pathway for the latter complex via reductive elimination of digermane (pathway b, Scheme 1) was preferred since Tilley has reported that 1,2-migrations in four-coordinate Pt−Si complexes without prior ligand dissociation are unfavorable.[20]

Recently, Osakada and co-workers reported the preparation of novel mono- and dinuclear germapalladacycles from a Ge−Ge bond forming reaction that was promoted by palladium (Scheme 2).[21] The dipalladium germacycle was the major product when the starting bis(germyl)palladium complex was heated in toluene. However, upon treatment of the bis(germyl)palladium complex with excess Ph_2GeH_2 and heat, the monopalladium germacycle was the major product. Both reactions were proposed to proceed through the digermyl(hydrido)palladium phosphine complex $(dmpe)Pd(H)(GePh_2GePh_2H)$ via pathway a in Scheme 1. A number of bis(silyl)platinum[1,3] and bis(germyl)platinum[12,13,14a,15–17,22] phosphine complexes have been reported previously.

Scheme 1



Five-membered metallacycles containing a transition metal or main group metal and two or more group 14 elements (Si or Ge) have been prepared by a variety of synthetic pathways. For example, reactions involving oxidative addition of E−H bonds at a transition metal center have produced ME_4 complexes as reported by Osakada,[21] Mochida,[17] Schram,[23] and Barrau.[13a,13c] Barrau and co-workers have also synthesized a number of cyclic complexes, $L_2Pt[GeMe_2XGeMe_2]$ (L = PPh_3, diphos; X=$(CH_2)_n$, S, O, NPh, $(\eta^5\text{-}C_5H_4)_2Fe$) by reaction of bis(chlorogermyl)platinum complexes with alkali-metal reagents.[13a,13b] Marschner and co-workers have prepared $Cp_2M[Si(SiMe_3)_2(SiMe)_2Si(SiMe_3)_2]$ complexes (M = Zr, Hf) and related Mg metallacycles from a salt-elimination reaction.[24,25] Mochida and co-workers have suggested the formation of $PdGe_4$ metallacycles from the palladium-catalyzed ring-opening reactions of tetragermetanes and the subsequent addition reactions with alkynes.[26] Bochkarev et al. reported the preparation of a$YbGe_4$ metallacycle from the reaction of elemental Yb and Ph_2GeCl_2 in THF.[27] Herein, we report the preparation of two platinacycles containing five-membered PtE_4 rings, $(dppe)Pt(ER_2)_4$ (ER_2 = $SiC_{12}H_8$ or $GeC_{12}H_8$), from the stepwise thermal reaction of H_2ER_2 with $(dppe)PtMe_2$.

Results and Discussion

Reaction of 9,9-dihydridosilafluorene ($H_2SiC_{12}H_8$, **1**) with the chelating phosphine complex $(dppe)PtMe_2$[28] (**2**) in ca. 4:1 ratio in toluene-d_8 at 70 °C resulted in the formation of the bis(silyl)platinum complex $(dppe)Pt(SiHC_{12}H_8)_2$ as an orange solid in 56% yield (eq 2). However, when the reaction was carried out at 75 °C for a period of 19 h, the

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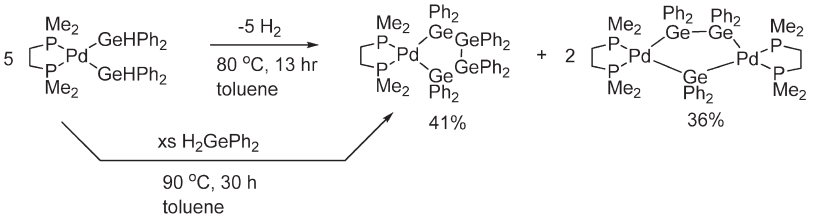
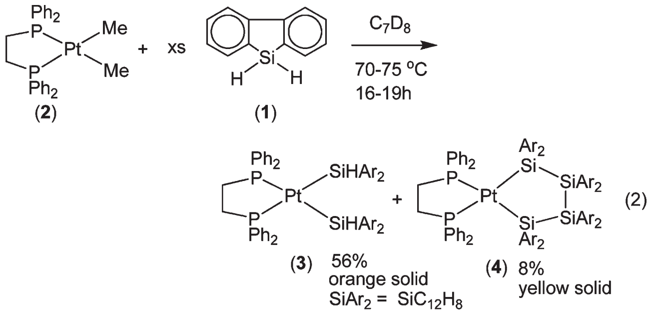
Scheme 2

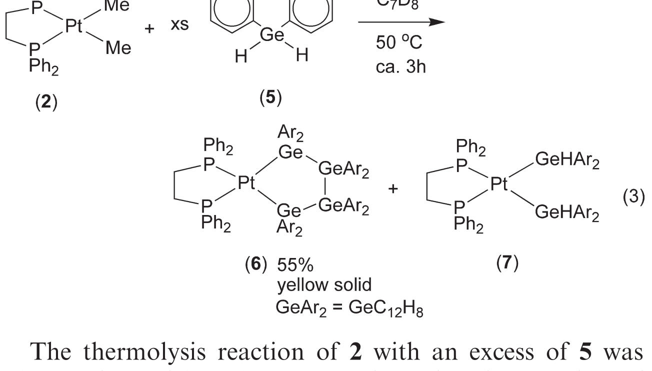


novel platinatetrasilacycle **4** was obtained as a minor product in 8% yield as a yellow solid (eq 2).



The ^1H NMR spectrum of **3** in CD_2Cl_2 exhibited a Si−H resonance at 5.23 ppm ($^2J_{PtH}$ = 83 Hz) in addition to the aryl and methylene proton signals of the complex. The $^{31}P\{^1H\}$ NMR spectrum of **3** shows a singlet with platinum satellites at 59.3 ppm ($^1J_{PtP}$ = 1704 Hz) and a similar shift for **4** at 57.6 ppm ($^1J_{PtP}$ = 1683 Hz). The molecular structure of **4** was confirmed by X-ray crystallography (vide infra).

The corresponding reaction between 9,9-dihydridogermafluorene **5** and the platinum complex **2** in toluene-d_8 at lower temperature (50 °C) produced the platinatetragermacycle **6** as the major product in 55% yield (eq 3). The molecular structure of **6** was confirmed by X-ray crystallography (vide infra). The ^1H and $^{31}P\{^1H\}$ NMR spectra of **6** were similar to those of **4**, but the phosphorus resonance of **6** appeared at 55.9 ppm and exhibited a significantly larger Pt−P coupling of $^1J_{PtP}$ = 2177 Hz compared to **4**. The bis(germyl)platinum complex **7** was observed at the early stages of the reaction, as determined by NMR spectroscopy (vide infra). Complex **7** was isolated as the major product in 67% yield in a separate experiment involving the reaction of **2** with **5** in toluene-d_8 at 27 °C in the presence of 2 equiv of CD_3CN (vide infra).



The thermolysis reaction of **2** with an excess of **5** was also performed in toluene-d_8 and produced a number of complexes during the course of the reaction as determined by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy (Figure 1). The reaction proceeded to a small extent at room temperature but was accelerated by heating at 323 K. The initial products observed at room temperature in the $^{31}P\{^1H\}$ NMR spectrum were assigned to the bis(germyl) platinum complex (dppe)Pt($GeAr_2H)_2$ (**7**) at δ 56.9 ($^1J_{PtP}$ = 2139 Hz) and three products that were assigned to six-coordinate complexes based on the chemical shift to higher field and significantly reduced $^1J_{PtP}$ coupling values (< 1350 Hz).[29] These high-field resonances were assigned to six-coordinate complexes that would arise from the oxidative-addition of H_2GeAr_2 (**5**) to (dppe)$PtMe_2$ (**2**) and the subsequent six-coordinate complexes that would result after reductive elimination of CH_4 or $MeGeAr_2H$ followed by oxidative addition of a second molecule of **5**. The ^{31}P NMR chemical shifts and tentative assignments for the six-coordinate complexes are 30.6 and 24.9 ppm (**C**, (dppe)Pt(CH_3)(H)$_2$($GeAr_2H$); 26.1 and 25.8 ppm (**D**, (dppe)Pt(CH_3)(H)($GeAr_2H)_2$); and 16.1 ppm (**E**, (dppe)Pt($CH_3)_2$(H)($GeAr_2H$)). The unreacted platinum complex **2** (δ 46.8, $^1J_{PtP}$ = 1779 Hz) was also present in a significant amount in the reaction solution.

As the reaction mixture was heated gradually to 323 K, a number of new resonances emerged while some of the original resonances slowly disappeared in both the ^1H and $^{31}P\{^1H\}$ NMR spectra, and no new resonances assignable to six-coordinate intermediates were observed. The sequential appearance of five new sets of doublet resonances in the $^{31}P\{^1H\}$ NMR spectra in the region of 50−60 ppm during the course of the reaction indicated the formation of unsymmetrical complexes (labeled as products **A**, **B**, **F**, **H**, and **I** in Figure 1 and Supporting Information). This supports a stepwise process in the formation of the metallacycle **6**.

A reaction pathway similar to the one proposed by Osakada and co-workers for the formation of the related palladacycle, (dmpe)Pd($GePh_2)_4$, starting from the bis(germyl)palladium complex (dmpe)Pd($GePh_2H)_2$[21] may be occurring in the formation of the platinum metallacycle **6** through a stepwise sequence beginning with the bis(germyl)platinum complex **7** as shown in Scheme 1. Dissociation of a phosphine group from **7**, followed by a 1,2-hydride migration from Ge to Pt, would produce the germyleneplatinum intermediate as shown in Scheme 3. A subsequent 1,2-migration of a ($GeAr_2H$) group from Pt to the germylene followed by recoordination of the phosphine to platinum would generate the complex (dppe)Pt(H)($GeAr_2$-$GeAr_2H$). However, dissociation of a phosphine unit in a chelating phosphine would be less favorable than a complex containing a monodentate phosphine. Another possible

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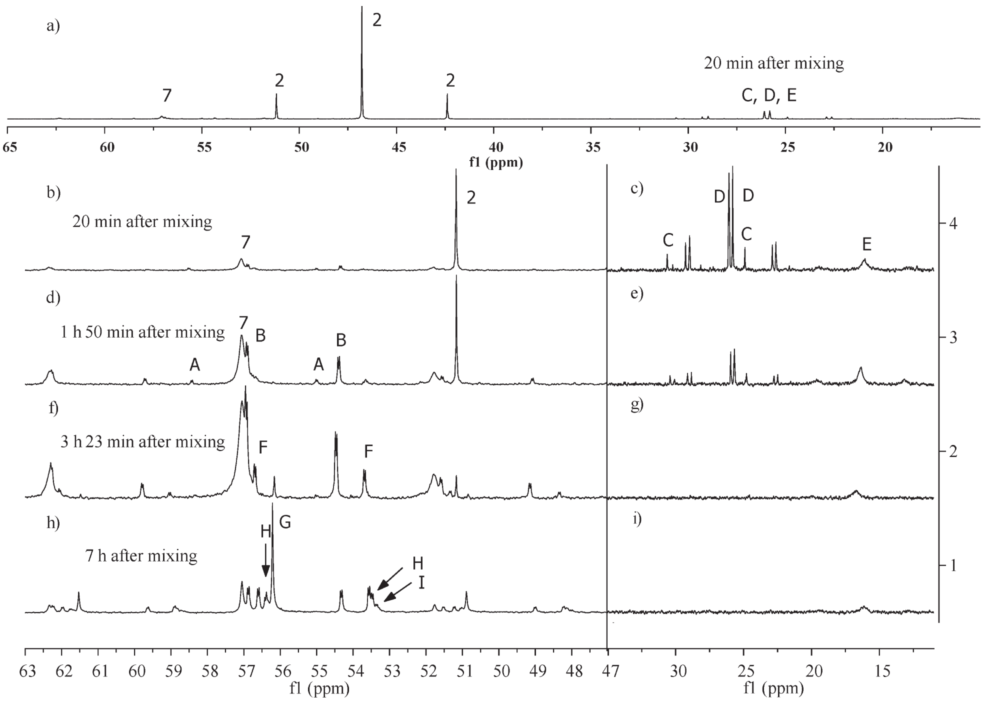
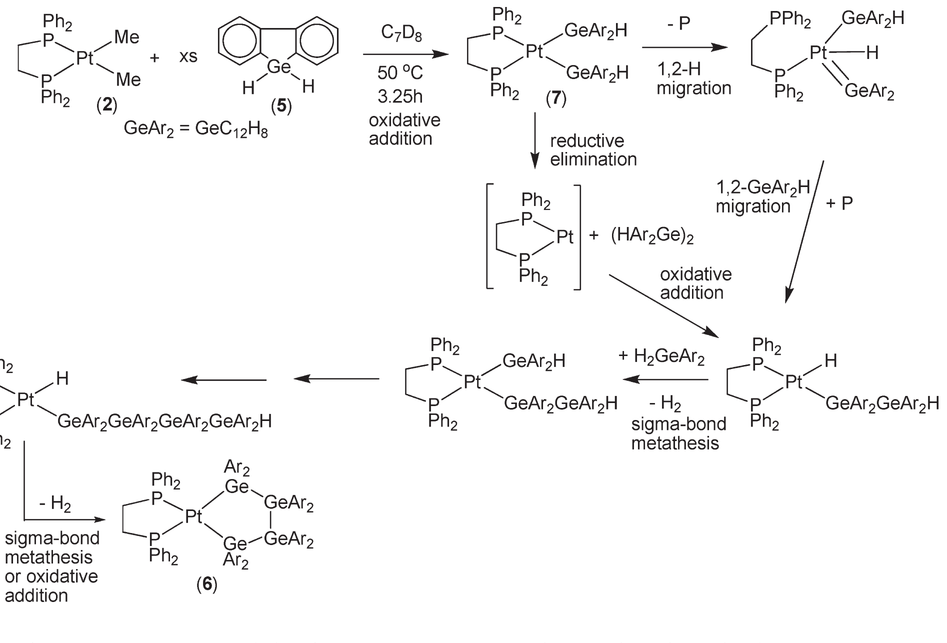


Figure 1. $^{31}P\{^1H\}$ NMR data collected during the reaction of **2** + **5** showing (a) the full spectrum at 300 K, 20 min after mixing. Expanded regions between 47 and 63 ppm and 11−35 ppm collected at (b, c) 300 K, 20 min; (d, e) 310 K, 1 h 50 min; (f, g) 323 K, 3 h 23 min; (h, i) 300 K after heating, 7 h. The expanded spectra are scaled to the largest peak.

Scheme 3



route would involve reductive elimination of the digermane HAr_2Ge-$GeAr_2H$ from **7** followed by subsequent oxidative-addition of the Ge−H bond by (dppe)Pt. Reaction between H_2GeAr_2 (**5**) and (dppe)Pt(H)($GeAr_2GeAr_2H$) either by an oxidative-addition reaction involving a Ge−H bond of **5** or more likely through a pathway involving a sigma-bond metathesis reaction followed by elimination of H_2 would produce (dppe)Pt($GeAr_2H$)($GeAr_2GeAr_2H$). A similar sequence of steps would then ultimately generate the complex (dppe)Pt(H)[$(GeAr_2)_3GeAr_2H$]. The latter complex could then undergo a final step involving intramolecular oxidative-addition of the terminal Ge−H bond at the Pt atom or react by a σ-bond methathesis step to give product **6** along with elimination of H_2. The $^{31}P\{^1H\}$ NMR spectra collected during the course of the reaction of **2** + **5** showed several sets of doublet resonances (Figure 1) that may be due to Pt (germyl)(di- or trigermyl) or Pt(hydridro)(germyl) complexes as shown in Scheme 3. However, no NMR evidence was observed for the presence of either platinum-germylene or four-coordinate or six-coordinate (hydrido)platinum(germyl) species, but this may be due to high instability or reactivity of these complexes. Deuterium labeling studies for the reaction of **5-d_2** with **2** did not provide any new NMR signals in the ^2H spectrum that were not observed in the reaction of **5** with **2** as determined by ^{1}H NMR spectroscopy. A singlet was observed in the ^{1}H NMR spectrum from the beginning of the reaction that may be due to the digermane $HAr_2Ge\text{-}GeAr_2H$,[30] but signals due to other possible reductive-elimination products, $H(GeAr_2)_xH$ ($x = 3-4$), were not assigned. Complexes containing smaller [$Pt(GeAr_2)_3$] or larger [$Pt(GeAr_2)_5$] metallacycles were not observed in the reaction, and this is probably due to the formation of the thermodynamically favorable five-membered metallacycle in **6**. The formation of the metallacycles **4** and **6** and (dmpe)Pd$(GePh_2)_4$[21] appear to be influenced by the use of chelating phosphine groups at the metal center and not the substituents at the group 14 center. Attempts to trap any platinum-germylene intermediates with 1,3-dimethyl-2-imidazolidinone (DMI) or CD_3CN were unsuccessful.[31] In the reaction with added DMI, complex **6** was isolated in 30% yield, and an unidentified product was observed in solution after heating at 323 K that exhibited a singlet resonance with Pt satellites at δ 57.3 in the $^{31}P\{^{1}H\}$ NMR spectrum ($^{1}J_{PtP}$ = 2013 Hz). In the reaction with 1 equiv of CD_3CN, the formation of the major product **7** suggests that the CD_3CN may interfere with the reaction pathway by reversible coordination to the germylene center in the intermediate species $(Ph_2PCH_2CH_2PPh_2)(H)Pt({=}GeAr_2)(GeAr_2H)$. This would make the subsequent germyl migration to the germylene center unfavorable, thus inhibiting the reaction from proceeding further. In fact, only a minor amount of **6** (< 10%) was produced from this reaction.

X-ray Crystallography. The molecular structures of **4**, **6**, and **7** were determined by X-ray crystallography and are shown in Figures 2−4, respectively. Both structures **4** and **6** contain two five-membered rings in puckered envelope conformations. The two five-membered rings in **4** and **6** are twisted relative to each other by 9.6° and 1.6°, respectively. The platinum centers in **4**, **6**, and **7** exhibit a distorted square-planar environment.

The Pt−Si bond distances of **4** (2.34−2.37 Å) fall in the range of known Pt−Si single bonds[3] and are similar to those observed in (dppe)Pt$(SiH^{i}Pr_2)_2$,[32] [(dppe)Pt(μ-$SiPh_2$)]$_2$,[33] and {(dppe)Pt[μ-SiH(IMP)]}$_2$.[34] As expected, the Pt−Ge distances for **6** and **7** (2.43−2.44 Å) are similar to those reported for (dppe)Pt$(GeMePh_2)_2$,[15c] *cis*-$(PhMe_2P)_2Pt(GeR_3)_2$ (GeR_3 = $GeMePh_2$, $GeMe_2Ph$),[15c] and (dmpe)Pt$(GeMePh_2)_2$[15c] but are slightly longer than the Pt−Si distances in **4** due to the larger size of Ge compared to Si. The digermaplatinacycle complex $(Ph_3P)_2Pt[GePh_2(SiMe_3)_2GePh_2]$ showed significantly longer Pt−Ge distances (2.49 Å) compared to **6**.[17]

The Pt−P distances in **4** and **7** (2.28−2.30 Å) are similar to those observed for (dppe)Pt$(GeMePh_2)_2$[15c] and are only marginally longer than those in complex **6** (2.27 Å), resulting from the smaller *trans* influence of Ge compared to Si; likewise, larger Pt−P coupling values were observed for **6** and **7** ($^{1}J_{PtP}$ = 2177, and 2131 Hz, respectively) compared to **4** ($^{1}J_{PtP}$ = 1683 Hz) and are consistent with the stronger *trans* influence of silicon. The dihedral angle for the

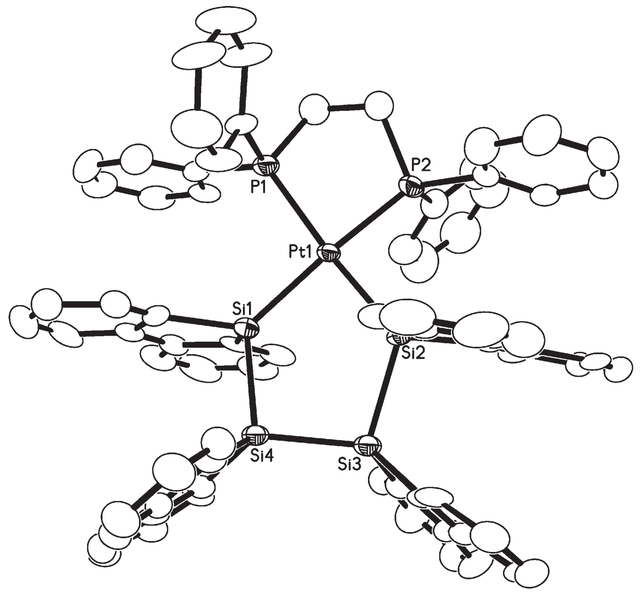


Figure 2. Molecular structure of **4** (with thermal ellipsoids shown at the 50% probability level). Selected bond distances (Å) and angles (deg): Pt(1)−P(1) = 2.294(2), Pt(1)−P(2) = 2.3042(19), Pt(1)−Si(1) = 2.346(3), Pt(1)−Si(2) = 2.375(3), Si(1)−Si(4) = 2.365(3), Si(3)−Si(4) = 2.327(3), Si(2)−Si(3) = 2.357(4); P(1)−Pt(1)−P(2) = 85.32(8), Si(1)−Pt(1)−Si(2) = 88.85(7), P(1)−Pt(1)−Si(2) = 169.46(8), P(2)−Pt(1)−Si(1) = 164.23(9), Pt(1)−Si(1)−Si(4) = 122.23(13), Pt(1)−Si(2)−Si(3) = 121.04(13), P(1)−Pt(1)−Si(1) = 96.17(9), P(2)−Pt(1)−Si(2)=92.37(9), Si(2)−Si(3)−Si(4)=100.57(13), Si(1)−Si(4)−Si(3) = 99.40(13).

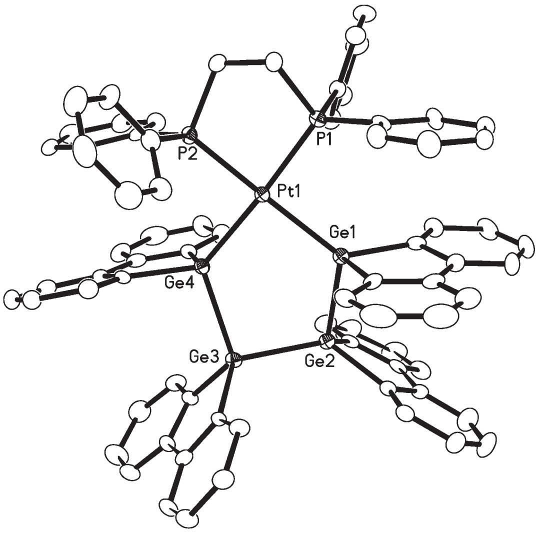


Figure 3. Molecular structure of **6** (with thermal ellipsoids shown at the 50% probability level). Selected bond distances (Å) and angles (deg): Pt(1)−P(1) = 2.2711(15), Pt(1)−P(2) = 2.2768(15), Pt(1)−Ge(1) = 2.4426(7), Pt(1)−Ge(4) = 2.4384(7), Ge(1)−Ge(2) = 2.4383(9), Ge(2)−Ge(3) = 2.3964(9), Ge(3)−Ge(4) = 2.4434(9); P(1)−Pt(1)−P(2) = 86.05(5), Ge(1)−Pt(1)−Ge(4) = 90.61(2), P(1)−Pt(1)−Ge(4) = 170.36(4), P(2)−Pt(1)−Ge(1) = 174.51(4), P(1)−Pt(1)−Ge(1) = 92.10(4), P(2)−Pt(1)−Ge(4) = 92.09(4), Pt(1)−Ge(1)−Ge(2) = 118.72(3), Pt(1)−Ge(4)−Ge(3) = 120.43(3), Ge(1)−Ge(2)−Ge(3) = 101.79(3), Ge(2)−Ge(3)−Ge(4) = 98.67(3).

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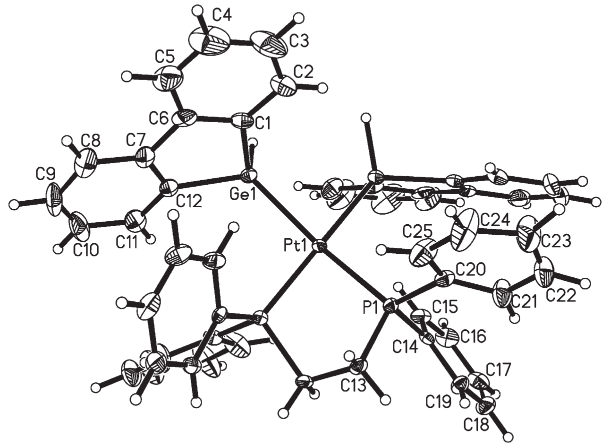

Figure 4. Molecular structure of **7** (thermal ellipsoids shown at the 50% probability level). Selected bond distances (Å) and angles (deg): Pt(1)−P(1) = 2.2893(8), Pt(1)−P(1)#1 = 2.2893(8), Pt(1)−Ge(1) = 2.4346(4), Pt(1)−Ge(1)#1 = 2.4347(4), Ge(1)−H(1) = 1.49(3); P(1)−Pt(1)−P(1)#1 = 85.58(4), Ge(1)−Pt(1)−Ge(1)#1 = 82.347(17), P(1)−Pt(1)−Ge(1)#1 = 96.91(2), P(1)#1−Pt(1)−Ge(1) = 96.91(2), P(1)−Pt(1)−Ge(1) = 169.90(2), P(1)#1−Pt(1)−Ge(1)#1 = 169.90(1).

planes composed of P1−Pt−P1′ and Ge1−Pt−Ge1′ for **7** is 14.9°. The Si−Si[35] and Ge−Ge[36] distances in the ring in complexes **4** and **6**, respectively, are within the expected range.

There are a few examples of structurally characterized complexes containing a five-membered MSi_4 or MGe_4 ring including $Cp_2M(SiMe_2)_4$ (M = Zr and Hf),[24] $(THF)_2Mg(SiMe_3)_4$,[25] $(dmpe)Pd(GePh_2)_4$,[21] and $(THF)_4Yb(GePh_2)_4$.[27]

Conclusion

The thermolysis of sila- and germafluorene (**1** and **5**, respectively) with $(dppe)PtMe_2$ (**2**) produced new five-membered metallacycles $(dppe)Pt(ER_2)_4$ (E = Si (**4**), Ge (**6**); R = $C_{12}H_8$). The use of the chelating dppe ligand at Pt facilitates the E−E bond forming reaction starting from $(dppe)Pt(ER_2H)_2$ (**3** and **7**, respectively). The reaction pathway of **4** and **6** likely involves Pt=E intermediates formed from silyl or germyl group migrations and a series of oxidative-addition or sigma-bond metathesis steps, as suggested by multinuclear NMR spectroscopy.

Experimental Section

General Procedures. All reactions were carried out under an argon atmosphere using standard Schlenk techniques or a drybox. The solvents THF, diethyl ether, and methylene chloride were distilled according to standard procedures. The NMR solvents, toluene-d_8, benzene-d_6, and methylene-d_2, were purchased from Cambridge Isotopes, Inc., and degassed by freeze/thaw pump cycles and dried over activated molecular sieves. Acetonitrile-d_3 was obtained as 1 g vials from Cambridge Isotopes Inc. and used as received. 1,3-Dimethyl-2-imidazolidinone (DMI) was purchased from Aldrich Chemical Co. and degassed before use. 9,9-Dihydridogermafluorene[11] was prepared by the lithium aluminum hydride reduction of dichlorogermafluorene,[30] and 9,9-dideuterogermafluorene was prepared from an analogous reaction by reduction of $Cl_2GeC_{12}H_8$ with $LiAlD_4$. 9,9-Dihydridosilafluorene was prepared by a literature method.[37] The platinum complex $(dppe)PtMe_2$[28] was prepared by a modified literature procedure using $(cod)PtMe_2$ and dppe in toluene.[38] The ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker ARX-300 MHz and Bruker ARX-500 MHz at room temperature unless otherwise specified. Proton chemical shifts (δ) were referenced to the residual peaks of the solvents used. Phosphorus chemical shifts are referenced relative to external H_3PO_4. Infrared spectra were recorded on a Thermo-Nicolet Avatar 360 ESP FT-IR spectrometer. Elemental analysis determinations were obtained from Atlantic Microlabs, Inc., Norcross, GA. X-ray crystallographic determinations were performed on a Bruker Apex II diffractometer equipped with a CCD area detector.

General Procedure for the Addition Reactions. In a drybox, a solution of the platinum precursor $(dppe)PtMe_2$ was prepared in C_7D_8 in a vial. In a separate vial, $H_2SiC_{12}H_8$ or $H_2GeC_{12}H_8$ was dissolved in C_7D_8 and then added dropwise to the $(dppe)PtMe_2$ solution. The reaction mixture was transferred to a NMR tube and heated in the NMR probe or in an oil bath. NMR data were collected at various reaction times after addition.

Preparation of $(dppe)Pt(SiHC_{12}H_8)_2$ (3). To a solution of $(dppe)PtMe_2$ (0.064 g, 0.10 mmol, **2**) in 0.5 mL of C_7D_8 was added a solution of $H_2SiC_{12}H_8$ (0.080 g, 0.44 mmol, **1**) in 1 mL of C_7D_8. The sample was heated at 70 °C in an oil bath for 16 h. An orange solid (**3**, 55 mg, 56% yield) precipitated and was washed with pentane and then dried. ^1H NMR data (300 MHz, CD_2Cl_2): δ 7.50−6.80 (br, overlapping resonances, aromatic H), 5.23 (s, $^2J_{PtH}$ = 83 Hz, SiH), 1.88 (br, m, CH_2). $^{31}P\{^1H\}$ NMR data (121 MHz, CD_2Cl_2): δ 59.3 (s, $^1J_{PtP}$ = 1704 Hz). Selected IR data (solid, cm^{-1}): ν 2044 (Si−H). Anal. Calcd for $C_{50}H_{42}P_2PtSi_2$: C, 62.81; H, 4.43. Found: C, 62.24; H, 4.46.

Preparation of $(dppe)Pt(SiC_{12}H_8)_4$ (4). To a solution of $(dppe)PtMe_2$ (0.028 g, 0.045 mmol, **2**) in 0.5 mL of C_7D_8 was added a solution of $H_2SiC_{12}H_8$ (0.030 g, 0.16 mmol, **1**) in 0.75 mL of C_7D_8. The sample was heated at 75 °C for 19 h in an oil bath. A yellow crystalline solid (**4**, 5 mg, 8% yield) formed and was washed with benzene and then dried. ^1H NMR data (500 MHz, CD_2Cl_2): δ 7.80−6.90 (br, overlapping resonances, aromatic H), 1.89 (br, m, CH_2). $^{31}P\{^1H\}$ NMR data (202 MHz, CD_2Cl_2): δ 57.6 (s, $^1J_{PtP}$ = 1683 Hz). Attempts to obtain a significant quantity of analytically pure **4** were unsuccessful.

Reaction of $H_2GeC_{12}H_8$ (5) with $(dppe)PtMe_2$ (2). Formation of $(dppe)Pt(GeC_{12}H_8)_4$ (6). To a solution of $(dppe)PtMe_2$ (0.046 g, 0.074 mmol, **2**) in 0.4 mL of C_7D_8 was added $H_2GeC_{12}H_8$ (0.045 g, 0.22 mmol, **5**) in 0.4 mL of C_7D_8 at room temperature. Then the temperature was raised to 50 °C and maintained for 3.25 h. After heating, the sample tube contained a yellow solution and a light yellow crystalline solid. The solid was dissolved in CD_2Cl_2 and analyzed by NMR spectroscopy. Pale yellow crystals of **6** containing one molecule of CD_2Cl_2 solvate were isolated from the NMR sample and were suitable for X-ray crystallographic analysis. Anal. Calcd for $C_{74}H_{56}P_2PtGe_4\cdot CD_2Cl_2$: C, 57.02; H, 3.83. Found: C, 57.82; H, 3.93. In a separate reaction, $(dppe)PtMe_2$ (0.048 g, 0.077 mmol, **2**) and $H_2GeC_{12}H_8$ (0.052 g, 0.23 mmol, **5**) in ca. 1.0 mL of C_7D_8 were heated for approximately 3 h at 50 °C. Complex **6** was isolated as a light yellow solid in 55% yield (63 mg). Anal. Calcd for $C_{74}H_{56}P_2PtGe_4$: C, 59.04; H, 3.78. Found: C, 59.01; H, 3.97.

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(38) Clark, H. C.; Manzer, L. E. *J. Organomet. Chem.* **1973**, *59*, 411–428.

Table 1. Crystallographic Data and Structure Refinement for 4, 6, and 7

	4	**6**	**7**
formula	$C_{74}H_{56}P_2PtSi_4$	$C_{74}H_{56}Ge_4P_2Pt \cdot CD_2Cl_2$	$C_{50}H_{42}Ge_2P_2Pt$
fw	1314.58	1577.50	1045.05
cryst size/mm	0.19 × 0.14 × 0.11	0.35 × 0.09 × 0.05	0.17 × 0.13 × 0.08
cryst syst	orthorhombic	monoclinic	tetragonal
space group	$Pna2_1$	$P2_1/n$	$I4_1/acd$
a/Å	23.4146(13)	16.714(3)	17.9479(3)
b/Å	10.3148(6)	19.448(3)	17.9479(3)
c/Å	24.4550(12)	20.010(3)	52.441(3)
β/deg	90	102.905(7)	90
V/Å^3	5906.3(6)	6340.2(17)	16892.6(9)
D_{calcd}/g cm^{-3}	1.478	1.653	1.644
Z	4	4	16
abs coeff/mm^{-1}	2.556	4.252	4.829
θ range/deg	1.93 to 26.47	2.71 to 26.02	2.83 to 25.07
reflns collected/indep reflns	173 667/12 023 [R(int) = 0.108]	115 163/12 479 [R(int) = 0.11]	134 807/3745 [R(int) = 0.109]
abs correct	semiempirical from equivalents	numerical	numerical
max. and min. transmn	0.7663 and 0.6423	0.8155 and 0.3176	0.7777 and 0.6096
final R indices [$I > 2\sigma(I)$]	0.0442	0.0434	0.0234
R indices (all data)	0.0971	0.1052	0.0402
largest diff peak and hole/e Å^{-3}	2.905 and −1.655	2.238 and −2.312	0.469 and −0.519

(dppe)Pt($GeC_{12}H_8$)$_4$ (6). ^{1}H NMR (500 MHz, CD_2Cl_2, 27 °C): δ 7.60−7.03 (overlapping resonances, ArH), 1.91 (m, CH_2). $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2, 27 °C): δ 55.9 (s, $^1J_{PtP}$ = 2177 Hz).

Reaction of $D_2GeC_{12}H_8$ (5-*d*$_2$) with (dppe)PtMe$_2$ (2). A solution of **5-*d*$_2$** (0.050 g, 0.22 mmol) in 0.4 mL of C_7H_8 was added to a solution of **2** (0.046 g, 0.73 mmol) in 0.4 mL of C_7H_8. A small drop of C_6D_6 was added to the solution as a reference. The reaction was monitored by ^{2}H NMR. The NMR spectra were recorded approximately 40 min after addition at 27 °C. Then the solution was heated in 5 °C increments every 10 min to 52 °C and held at that temperature for 1 h.

^{2}H NMR (76 MHz, C_7H_8 + C_6D_6, 37 °C, 1 h after addition): δ 6.3 (br), 6.1 (br), 5.4 (s), 5.3 (s), 5.2 (s), 4.9 (s, **5-*d*$_2$**, major component), 4.5 (s, D_2), 4.3 (s), 4.16 (s), 2.1 (t, $C_7(H/D)_8$, 1.75 (br), 1.6 (br), 1.4 (br), 0.1 (q, CH_3D), −9.1 (br). As the sample was heated, the signals at δ 6.3 and −9.1 disappeared and most of **5-*d*$_2$** had been consumed. The other resonances listed above were still present in the solution. After heating, complex **6** precipitated in the NMR tube and was isolated in a 41% yield.

Reaction of $H_2GeC_{12}H_8$ (5) with (dppe)PtMe$_2$ (2) in the Presence of DMI. A solution of **5** (0.042g, 0.18 mmol) and DMI (0.007 g, 0.06 mmol) in 0.4 mL of C_7D_8 was added to a solution of **2** (0.038 g, 0.061 mmol) in 0.4 mL of C_7D_8. After 50 min at room temperature, the solution was then heated to 50 °C for approximately 3 h in the NMR probe. Complex **6** precipitated in the NMR tube after heating and was isolated in 30% yield (27 mg). Analysis of the reaction mixture during the heating period by ^{1}H and $^{31}P\{^1H\}$ NMR spectroscopy showed essentially all of the same resonances observed in the 6:1 germafluorene/(dppe)PtMe$_2$ reaction described above, but the $^{31}P\{^1H\}$ NMR spectrum for the reaction solution after heating for 3 h showed that the major component was complex **2** along with one new signal at 57.3 (s, $^1J_{PtP}$ = 2012 Hz, unassigned). No Ge−H or Pt−H signals and only signals for uncoordinated DMI were observed in the ^{1}H spectrum after heating for 3 h.

Reaction of $H_2GeC_{12}H_8$ (5) with (dppe)PtMe$_2$ (2) in the presence of CD_3CN. Formation of (dppe)Pt($GeHC_{12}H_8$)$_2$ (7). A solution of **5** (0.043 g, 0.19 mmol) and CD_3CN (0.005 g, 0.12 mmol) in 0.4 mL of C_7D_8 was added to a solution of **2** (0.038 g, 0.061 mmol) in 0.4 mL of C_7D_8 in an NMR tube. The solution was heated in the NMR probe starting at 27 °C, and ^{1}H and $^{31}P\{^1H\}$ NMR spectra were collected beginning 15 min after addition. Fifty minutes after addition the solution was heated to 50 °C for 6.5 h. The NMR spectra were recorded every 15 min after heating was initiated. Analysis of the reaction mixture during the initial heating period by $^{31}P\{^1H\}$ NMR spectroscopy showed signals for **2**, **7**, **D**, and **E**. As the reaction progressed, some of the other resonances observed in the 6:1 germafluorene/(dppe)PtMe$_2$ reaction were observed but in a much smaller amount. After heating, the NMR tube contained a clear yellow solution, a colorless solid, and a fine yellow solid. The solution was decanted, and the solid mixture was washed with a small amount of CD_2Cl_2 to give a clear crystalline solid (**7**, 43 mg, 67% yield) that was suitable for X-ray crystallography. A minor amount of **6** (< 10%) was produced from the reaction as an impure solid. Anal. Calcd for $C_{50}H_{42}P_2PtGe_2$: C, 57.46; H, 4.05. Found: C, 57.53; H, 4.05.

(dppe)Pt($GeHC_{12}H_8$)$_2$ (7). ^{1}H NMR (500 MHz, CD_2Cl_2, 27 °C): δ 7.8−6.8 (overlapping resonances, ArH), 6.52 (m, GeH), 1.55 (m, CH_2). $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2, 27 °C): δ 56.9 (s, $^1J_{PtP}$=2139 Hz). Selected IR data (solid, cm^{-1}): ν 1945 (Ge−H).

X-ray Structure Determination of 4, 6, and 7. Crystals of appropriate dimension were obtained by room-temperature crystallization in toluene-*d*$_8$ (**4** and **7**) or methylene chloride-*d*$_2$ (**6**). Crystals of appropriate dimensions were mounted on a Mitgen loop in random orientations. Preliminary examination and data collection were performed using a Bruker Kappa Apex II charge coupled device (CCD) detector system single-crystal X-ray diffractometer equipped with an Oxford Cryostream LT device at 100(2) K. All data were collected using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) from a fine-focus sealed tube X-ray source. Preliminary unit cell constants were determined with a set of 36 narrow frame scans. Typical data sets consist of combinations of ϖ and ϕ scan frames with typical scan widths of 0.5° and counting times of 15−30 s/frame at a crystal to detector distance of 4.0 cm. The collected frames were integrated using an orientation matrix determined from the narrow frame scans. Apex II and SAINT software packages[39] were used for data collection and data integration. Analysis of the integrated data did not show any decay. Final cell constants were determined by global refinement of reflections from the complete data set. Collected data were corrected for systematic errors using SADABS[40] based on the Laue symmetry using equivalent reflections.

Crystal data and intensity data collection parameters are listed in Table 1.

Structure solution and refinement were carried out using the SHELXTL- PLUS software package.[41] The structures

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(39) *Apex II* and *SAINT*; Bruker Analytical X-Ray: Madison, WI, 2008.

(40) Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33–38.

(41) Sheldrick, G. M. (Bruker-SHELXTL) *Acta Crystallogr.* **2008**, *A64*, 112−122.

were solved by direct methods and refined successfully in the space groups $Pna2_1$, $P2_1/n$, and $I4_1/acd$, respectively. Full matrix least-squares refinement was carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$. All non-hydrogen atoms were refined anisotropically to convergence except C1 and C2 in the case of **4**. Some twinning was observed in the case of **4**. Twin refinement was carried out with the use of BASF/TWIN (SHELXTL). All hydrogen atoms were treated using an appropriate riding model (AFIX m3). Disorder in a phenyl ring in the structure of **7** was resolved with 50% occupancy atoms. The crystal data and structure refinement parameters for **4**, **6**, and **7** are listed in Table 1.

Complete listings of geometrical parameters, positional and isotropic displacement coefficients, and anisotropic displacement coefficients for the non-hydrogen atoms are in the Supporting Information. A table of the calculated and observed structure factors is available in electronic format.

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Supporting Information Available: Crystallographic data for complexes **4**, **6**, and **7** as a CIF file and VT NMR data for the reaction of (dppe)PtMe$_2$ (**2**) with H$_2$GeAr$_2$ (**5**). This material is available free of charge via the Internet at http://pubs.acs.org.