

Formation and Ring Expansion of Germaplatinacycles via Dehydrogenative Ge-Ge and Ge-Pt Bond-Forming Reactions

Makoto Tanabe, Masaya Hanzawa, Naoko Ishikawa, and Kohtaro Osakada*

Chemical Resources Laboratory, Tokyo Institute of Technology, 4259-R1-3 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

Received June 15, 2009

The bis(germyl)platinum complex [Pt(GeHPh₂)₂(dmpe)] (1) (dmpe = 1,2-bis(dimethylphosphino)ethane) reacts with a small excess of H_2 GePh₂ at 90 °C to produce four-membered germaplatinacycle

[Pt(GePh₂GePh₂GePh₂)(dmpe)] (2). Further reaction of 2 with excess H₂GePh₂ at 90 °C forms

tetragermaplatinacyclopentane [Pt(GePh₂GePh₂GePh₂GePh₂GePh₂)(dmpe)] (3), while 3 is obtained also by the direct reaction of excess H₂GePh₂ with 1 for a prolonged period. Complexes 1-3 were characterized by X-ray crystallography and NMR spectroscopy. Germaplatinacycles 2 and 3 react with H₃GePh to cause cleavage of the Pt–Ge bonds and formation of the oligogermanes H(GePh₂)₃H and H(GePh₂)₄H, respectively.

Introduction

Metallacycles composed of metal-containing four-, five-, and six-membered rings are classified as important organometallic compounds because of their roles as key intermediates in the metal-catalyzed metathesis¹ and oligomerizations² of alkenes. The metallacycloalkanes containing group 10 transition metals have long been investigated for their preparation and chemical properties since the 1970s.^{3–5} In spite of abundant metallacycloalkanes of the late transition metals, there has been a limited number of reports of Si- and Ge-containing metallacycles. Marschner et al. synthesized zirconocena- and hafnocenacyclopentasilanes

 $[M(Si(SiMe_3)_2SiMe_2SiMe_2Si(Me_3)_2)(C_5H_5)_2]$ (M = Zr, Hf) from the metathesis reaction of an oligosilyl dianion with

*To whom correspondence should be addressed. E-mail: kosakada@ res.titech.ac.jp.

(2) (a) Dixon, J. T.; Green, M. J.; Hess, F. M.; Morgan, D. H. J. Organomet. Chem. **2004**, 689, 3641–3668. (b) Wass, D. F. Dalton Trans. **2007**, 816–819.

(3) (a) Grubbs, R. H.; Miyashita, A.; Liu, M.-I. M.; Burk, P. L. J. Am. Chem. Soc. **1977**, 99, 3863–3864. (b) Grubbs, R. H.; Miyashita, A. J. Am. Chem. Soc. **1978**, 100, 1300–1302. (c) Grubbs, R. H.; Miyashita, A.; Liu, M.; Burk, P. J. Am. Chem. Soc. **1978**, 100, 2418–2425.

(4) (a) Diversi, P.; Ingrosso, G.; Lucherini, A. J. Chem. Soc., Chem. Commun. **1978**, 735–736. (b) Diversi, P.; Ingrosso, G.; Lucherini, A.; Murtas, S. J. Chem. Soc., Dalton Trans. **1980**, 1633–1637. (c) Ozawa, F.; Yamamoto, A.; Ikariya, T.; Grubbs, R. H. Organometallics **1982**, *1*, 1481– 1485.

(5) (a) McDermott, J. X.; White, J. F.; Whitesides, G. M. J. Am. Chem. Soc. **1973**, 95, 4451–4452. (b) McDermott, J. X.; White, J. F.; Whitesides, G. M. J. Am. Chem. Soc. **1976**, 98, 6521–6528. (c) Casey, C. P.; Scheck, D. M.; Shusterman, A. J. J. Am. Chem. Soc. **1979**, 101, 4233–4236. (d) Miyashita, A.; Takahashi, M.; Takaya, H. J. Am. Chem. Soc. **1981**, 103, 6257–6259.

Cp₂MCl₂ (Chart 1A).⁶ A similar tetragermacyclopentane invol-

ving a ytterbium center, $[Yb(GePh_2GePh_2GePh_2GePh_2)-(THF)_4]$, was prepared as one of the products from the reaction of metallic Yb with Ph_2GeCl_2 .⁷ Mochida and co-workers synthesized four- and five-membered silagermaplatina-

cycles $[Pt(GePh_2(SiMe_2)_nGePh_2)(PPh_3)_2]$ (n = 1, 2) via the cyclization of the hydrido(germyl)platinum complex

 $[PtH(GePh_2(SiMe_2)_nGeHPh_2)(PPh_3)_2]$.⁸ Recently, Braddock-Wilking reported that the thermal reactions of $[PtMe_2(dppe)]$ (dppe = 1,2-bis(diphenylphosphino)ethane) with sila- and germafluorene H₂ER₂ (ER₂ = SiC₁₂H₈ or GeC₁₂H₈) in 1:4 ratio afforded the two five-membered platinacycles

 $[Pt(ER_2ER_2ER_2ER_2)(dppe)]$ (Chart 1B). They proposed $Pt=ER_2$ intermediates formed via 1,2-H migration of silyl or germyl ($Pt-ER_2H$) platinum complexes to account for smooth formation of the metallacycles.⁹ We reported preparation of a five-membered tetragermapalladacycle

[Pd(GePh₂GePh₂GePh₂GePh₂)(dmpe)] (dmpe = 1,2-bis(dimethylphosphino)ethane) (Chart 1C), from the thermal reaction of [Pd(GeHPh₂)₂(dmpe)] in the presence of excess H₂GePh₂.¹⁰ The reaction involves several Ge–Ge bond-forming reactions, but ¹H and ³¹P{¹H} NMR measurements of the reaction mixture did not provide information of the reaction mechanism and their intermediates. In this paper, we present the

 ^{(1) (}a) Chappell, S, D.; Cole-Hamilton, D. J. Polyhedron 1982, 1, 739– 777. (b) Jennings, P. W.; Johnson, L. L. Chem. Rev. 1994, 94, 2241–2290. (c) Eisch, J. J.; Aradi, A. A.; Lucarelli, M. A.; Qian, Y. Tetrahedron 1998, 54, 1169–1184. (d) Cámpora, J.; Palma, P.; Carmona, E. Coord. Chem. Rev. 1999, 193–195, 207–281. (e) Blom, B.; Clayton, H.; Kilkenny, M.; Moss, J. R. Adv. Organomet. Chem. 2006, 54, 149–205.

⁽⁶⁾ Kayser, C.; Kickelbick, G.; Marschner, C. Angew. Chem., Int. Ed. 2002, 41, 989–992.

⁽⁷⁾ Bochkarev, L. N.; Makarov, V. M.; Zakharov, L. N.; Fukin, G. K.;
Yanovsky, A. I.; Struchkov, Y. T. J. Organomet. Chem. 1995, 490, C29–C31.
(8) Usui, Y.; Hosotani, S.; Ogawa, A.; Nanjo, M.; Mochida, K.

⁽⁸⁾ Usui, Y.; Hosotani, S.; Ogawa, A.; Nanjo, M.; Mochida, K. *Organometallics* **2005**, *24*, 4337–4339.

⁽⁹⁾ Braddock-Wilking, J.; Bandrowsky, T.; Praingam, N.; Rath, N. P. Organometallics **2009**, 28, 4098–4105.

⁽¹⁰⁾ Tanabe, M.; Ishikawa, N.; Hanzawa, M.; Osakada, K. Organometallics 2008, 27, 5152–5158.



preparation, structures, and chemical reactions of the four- and five-membered germaplatinacycles.

Results and Discussion

A bis(germyl)platinum complex with diphenylgermyl groups, [Pt(GeHPh₂)₂(dmpe)] (1), was obtained in 86% yield from the reaction of [PtMe2(dmpe)] with H2GePh2 at 60 °C in toluene. Similar reaction of H2SiPh2, giving a bis-(silyl)platinum complex [Pt(SiHPh₂)₂(dmpe)], was reported to proceed at higher reaction temperature (90 °C).¹¹ Treatment of 1 with H₂GePh₂ in 1:1.2 molar ratio at 90 °C produced

trigermaplatinacyclobutane [Pt(GePh₂GePh₂GePh₂)(dmpe)] (2) in 87% yield (Scheme 1). Complexes with monodentate phosphine and triorganogermyl ligands, cis-[Pt(GePh₂R)₂- $(PMe_2Ph)_2$ (R = Ph, Me), undergo thermal isomerization to give an equilibrium mixture of the cis and trans complexes and do not cause any Ge-Ge bond-forming reactions.12 Further reaction of excess H₂GePh₂ with the isolated complex 2 at 90 °C for 48 h afforded the five-membered tetragerma-

platinacycle [Pt(GePh₂GePh₂GePh₂GePh₂)(dmpe)] (3) in 29% yield (Scheme 1). The ¹H NMR spectrum of the reaction mixture in C₆D₆ shows two Ge-H hydrogen signals at δ 5.57 and 5.68, which are assigned to H(GePh₂)₂H¹³ and $H(GePh_2)_3H^{14}$ formed by the reactions. Heating of 1 in the presence of excess H2GePh2 at the same temperature produces 3 directly in 61% yield.

Figure 1 shows the molecular structure of 1 determined by X-ray crystallography. The Pt-Ge bonds of 1 (2.4527(4), 2.4411(6) Å) are within the range of the Pt-Ge bonds of *cis*bis(germyl)platinum complexes with phosphine ligands $(2.4271(15)-2.4985(13) \text{ Å})^{12,15}$ and are longer than the Pd–Ge bonds of the Pd analogue [Pd(GeHPh₂)₂(dmpe)] (2.4259(2), 2.4266(3) Å).¹⁰ The Pt–P bonds of 1 (2.293(1), 2.295(2) Å) are slightly shorter than the Pd-P bonds of the analogous Pd complex (2.3066(6), 2.3147(7) A). Figure 2 shows crystallographic results of square-planar complexes 2 and 3 with fourand five-membered rings composed of Ge and Pt atoms, respectively. The sum of the four bond angles within the PtGe₃

Scheme 1



tetragon of 2 is equal to 359.49(4)°, indicating high planarity of the four-membered ring. This contrasts with most metallacyclobutanes, which contain a puckered four-membered ring. Molecule 3 contains a five-membered PtGe₄ ring with an envelope conformation. Chart 2 summarizes bond parameters

of complexes 1-3, [Pt(GeR₂GeR₂GeR₂GeR₂)(dppe)] (GeR₂=

GeC₁₂H₈),⁹ and [Pd(GePh₂GePh₂GePh₂GePh₂)(dmpe)].¹⁰

The two Pt-Ge bonds of **3** (2.4643(4), 2.4769(4) A) are slightly longer than those of bis(germyl)platinum complex 1 (2.4411(6), 2.4527(4) Å), trigermaplatinacycle 2 (2.451(1),

2.4542(9) Å), and [Pt(GeR₂GeR₂GeR₂GeR₂)(dppe)] (GeR₂ = GeC₁₂H₈) (2.4426(7), 2.4384(7) Å).⁹ The Ge–Ge distances of 2 (2.456(1), 2.578(1) Å) and **3** (2.4174(5)-2.4646(5) Å) are similar to cyclic Ge compounds such as cyclopentagermane $(2.438(3)-2.473(2) \text{ Å})^{16}$ and cyclohexagermane (2.456(2)-2.466(2) Å).¹⁷ Although the Ge-Pt-Ge and Ge-Ge-Ge bond angles of 2 (83.14(3)°, 80.53(3)°) are significantly smaller than the two Pt-Ge-Ge bond angles $(96.32(3)^\circ, 99.50(3)^\circ)$, two coordinating Ge atoms are at too remote positions to have a Ge···Ge interaction (3.255(1) Å). The four-membered Pt

complex with a disiloxy ligand, [Pt(SiMe₂-O-SiMe₂)(dppe)],¹⁸ was reported to exhibit a Si · · · Si contact with a shorter distance $(2.549(2) \text{ \AA})$ than the Si–Si bond of Bu^t₃Si–SiBu^t₃ (2.697 Å).¹⁹

The ¹H NMR spectrum of **1** shows a Ge-H hydrogen signal at δ 5.82 with reasonable coupling constants (${}^{3}J_{P-H} =$ 14.4 Hz, ${}^{2}J_{Pt-H} = 101$ Hz). The ${}^{31}P{}^{1}H{}$ NMR spectra of 1–3 contain a single signal flanked with ${}^{195}Pt$ satellites (1: $J_{\text{Pt-P}} = 1895 \text{ Hz}, 2: J_{\text{Pt-P}} = 1819 \text{ Hz}, 3: J_{\text{Pt-P}} = 1851 \text{ Hz}).$ $[Pt(SiHPh_2)_2(dmpe)]$ exhibits a small coupling constant (δ 37.0, $J_{Pt-P} = 1456 \text{ Hz})^{11}$ due to the larger *trans* influence of the Si than the Ge ligands. Integration of the ¹H NMR peaks gives a ratio of the ortho hydrogens of the µ-GePh2 ligands of 2 and 3 that is consistent with the respective four- and fivemembered metallacyclic structures. The ${}^{13}C{}^{1}H$ NMR spectrum of 2 exhibits two signals assigned to the ipso carbon of the GePh₂ groups. The signal at δ 147.2 with a large coupling constant (63 Hz) is attributed to the GePh₂ groups

^{(11) (}a) Tanabe, M.; Osakada, K. J. Am. Chem. Soc. 2002, 124, 4550-4551. (b) Tanabe, M.; Osakada, K. Chem.-Eur. J. 2004, 10, 416-424.

^{(12) (}a) Mochida, K.; Wada, T.; Suzuki, K.; Hatanaka, W.; Nishiyama, Y.; Nanjo, M.; Sekine, A.; Ohashi, Y.; Sakamoto, M.; Yamamoto, A. Bull. Chem. Soc. Jpn. 2001, 74, 123-137. (b) Mochida, K.; Fukushima, T.; Suzuki, M.; Hatanaka, W.; Takayama, M.; Usui, Y.; Nanjo, M.; Akasaka, K.; Kudo, T.; Komiya, S. J. Organomet. Chem. 2007, 692, 395-401.

⁽¹³⁾ Fehér, F.; Plichta, P. Inorg. Chem. 1971, 10, 609–610.
(14) (a) Castel, A.; Riviére, P.; Satgé, J.; Ko, Y. H. J. Organomet. *Chem.* **1988**, *342*, C1–C4. (b) Castel, A.; Riviére, P.; Satgé, J.; Ko, H. Y. Organometallics 1990, 9, 205-210.

^{(15) (}a) Yamashita, H.; Kobayashi, T.; Tanaka, M.; Samuels, J. A.; Streib, W. E. Organometallics **1992**, *11*, 2330–2333. (b) Mochida, K.; Karube, H.; Nanjo, M.; Nakadaira, Y. Organometallics **2005**, *24*, 4734– 4741. (c) Usui, Y.; Hosotani, S.; Ogawa, A.; Nanjo, M.; Mochida, K. Organometallics 2005, 24, 4337-4339.

^{(16) (}a) Ross, L.; Dräger, M. Z. Naturforsch. 1983, 38b, 665-673. (b) Ross, L.; Dräger, M. Z. Anorg. Allg. Chem. 1984, 519, 225-232.

^{(17) (}a) Dräger, M.; Ross, L.; Simon, D. Z. Anorg. Allg. Chem. 1980, 466, 145-156. (b) Dräger, M.; Ross, L. Z. Anorg. Allg. Chem. 1981, 476, 95 - 104

⁽¹⁸⁾ Pham, E. K.; West, R. Organometallics 1990, 9, 1517-1523.

⁽¹⁹⁾ Wiberg, N.; Schuster, H.; Simon, A.; Peters, K. Angew. Chem., Int. Ed. Engl. 1986, 25, 79-80.



Figure 1. ORTEP drawing of 1 with thermal ellipsoids shown at the 50% probability level. Selected bond distances (Å) and angles (deg): Pt-Ge1 2.4527(4), Pt-Ge2 2.4411(6), Pt-P1 2.293(1), Pt-P2 2.295(2), Ge1-H1 1.57(4), Ge2-H2 1.87(3), Ge1-Pt-Ge2 90.63(2), Ge1-Pt-P2 93.40(3), Ge2-Pt-P1 90.97(4), P1-Pt-P2 85.06(4).



Figure 2. ORTEP drawings of (a) 2 and (b) 3 with thermal ellipsoids shown at the 50% probability level. Selected bond distances (Å) and angles (deg) for 2: Pt–Gel 2.451(1), Pt–Ge3 2.4542(9), Pt–P1 2.282(2), Pt–P2 2.278(3), Ge1–Ge2 2.578(1), Ge2–Ge3 2.456(1), Ge1–Pt–Ge3 83.14(3), Pt–Ge1–Ge2 96.32(3), Ge1–Ge2–Ge3 80.53(3), Pt–Ge3–Ge2 99.50(4). Selected bond distances (Å) and angles (deg) for 3: Pt–Ge1 2.4643(4), Pt–Ge4 2.4769(4), Pt–P1 2.285(1), Pt–P2 2.285(1), Ge1–Ge2 2.4251(5), Ge2–Ge3 2.4174(5), Ge3–Ge4 2.4646(5), Ge1–Pt–Ge4 89.76(1), Pt–Ge1–Ge2 108.91(2), Ge1–Ge2–Ge3 101.25(2), Ge2–Ge3–Ge4 99.79(2), Pt1–Ge4–Ge3 116.34(2).

bonded with the Pt atom, while the signal at δ 147.5 with a small ${}^{2}J_{\text{Pt-C}}$ value (40 Hz) is due to the central GePh₂ group. Two *ipso* carbon signals of **3** at δ 148.4 (${}^{2}J_{\text{Pt-C}} = 39$ Hz) and 141.9 (${}^{2}J_{\text{Pt-C}} = 14$ Hz) are assigned on the basis of comparison of the peak positions to those of **2**.



Figure 3 shows the ³¹P{¹H} NMR spectrum during the ring expansion reaction from **2** to **3** in the presence of H₂GePh₂ in C₆D₆ at 100 °C. The signal of **2** (δ 36.2) is decreased upon heating the reaction mixture, and a new signal due to complex **3** is observed at δ 33.6. After 11 days, the signal of **2** becomes negligible, while complex **3** was formed as the major product of the reaction (Figure 3c). Small signals with an AB pattern ($J_{P-P} = 8.9$ Hz) at δ 34.5 ($J_{Pt-P} = 1946$ Hz) and δ 35.8 ($J_{Pt-P} = 1815$ Hz) may be assigned to unsymmetrical Pt intermediates having different Ge ligands, although ¹H and ¹³C NMR data for the species were not obtained due to small intensity and/ or overlapping of the peaks. We reported the conversion of a dinuclear Pd complex with bridging germylene and digermene ligands, [{Pd(dmpe)}₂(μ -Ge₂Ph₄)(μ -GePh₂)], into palladager-

macycle [Pd(GePh₂GePh₂GePh₂GePh₂)(dmpe)], in which the ³¹P{¹H} NMR spectrum of the mixture shows analogous minor signals due to an intermediate with two different Ge ligands.¹⁰

Scheme 2 shows the plausible pathway for ring expansion from four- to five-membered germaplatinacycles. Addition of H₂GePh₂ to the solution leads to cleavage of a Pt-Ge bond of 2 to form a trigermyl(germyl)platinum intermediate A. This intermediate may correspond to the minor ³¹P NMR signals at δ 34.5 and 35.8 in Figures 3b and c. α -Hydrogen migration of GePh₂H groups accompanied with partial dissociation of dmpe ligands forms a platinum-germylene structure **B**. Subsequent migration of the trigermyl unit to the Ge center in the Pt=Ge bond affords a tetragermyl-(hydrido)platinum intermediate C. Tetragermaplatinacyclopentane 3 is obtained by the intramolecular cyclization of C, together with elimination of H₂. A similar pathway was proposed to account for formation of analogous Pt⁹ and Pd¹⁰ complexes. Braddock-Wilking et al. reported that Pt(0) complex $[Pt(\eta^2-C_2H_4)(PPh_3)_2]$ caused dehydrogenative Ge-Ge bond formation of $H_2GeC_{12}H_8$ to give a diplatinum complex with bridging digermene ligands, $[{PtH(PPh_3)_2}_2 - (\mu-GeC_{12}H_8GeC_{12}H_8)]^{20}$ Banaszak Holl,²¹ Mochida,²² and Ishii²³ reported conversion of the bis(germyl)platinum to (digermyl)platinum complexes via facile rearrangement of

^{(20) (}a) Braddock-Wilking, J.; Corey, J. Y.; White, C.; Xu, H.; Rath, N. P. *Organometallics* **2005**, *24*, 4113–4115. (b) White, C. P.; Braddock-Wilking, J.; Corey, J. Y.; Xu, H.; Redekop, E.; Sedinkin, S.; Rath, N. P. *Organometallics* **2007**, *26*, 1996–2004.

 ⁽²¹⁾ Bender, J. E.IV; Litz, K. E.; Giarikos, D.; Wells, N. J.;
 Banaszak Holl, M. M.; Kampf, J. W. Chem.—Eur. J. 1997, 3, 1793–1796.
 (22) Arii, H.; Nanjo, M.; Mochida, K. Organometallics 2008, 27, 4147–

^{4151.} (23) Nakata, N.; Fukazawa, S.; Ishii, A. Organometallics 2009, 28,

⁽²³⁾ Nakata, N.; Fukazawa, S.; Ishii, A. Organometallics 2009, 28, 534–538.



Figure 3. ³¹P{¹H} NMR spectra during the conversion of 2 into 3 in the presence of H₂GePh₂ (a) at 0 h, (b) after 4 days at 100 °C, and (c) after 11 days at 100 °C. The two doublets (δ 34.5 and 35.8) labeled with an asterisk may be assigned as an intermediate complex with two different Ge ligands.



the primary or secondary germyl ligands, as shown in Scheme 3. The Ge–Ge bond formation promoted at the Pt center was considered to proceed through Pt=Ge intermediates, which underwent insertion of $GeAr_2$ units into the Pt-Ge bond, or to undergo reductive elimination of digermane and subsequent reoxidative addition of the Ge–H bonds.

The Pt-Ge bond cleavage of the four- and five-membered

digermaplatinum complexes [Pt(GeMe₂(CH₂)₂GeMe₂)L₂]

Scheme 3



(L = (PPh₃)₂, PPh₂(CH₂)₂PPh₂) was promoted by various nucleophilic or electrophilic reagents, and the complexes released organogermyl compounds upon the reactions.²⁴ Addition of excess H₃GePh to the solution of **2** or **3** produces tri- and tetragermanes H(GePh₂)₃H and H(GePh₂)₄H in 76% and 66% yields, respectively (eq 1). Elimination of trigermane from the ring-strained complex **2** easily occurs at room temperature, while the Pt–Ge bond cleavage of the five-membered complex **3** requires heating for 36 h at 90 °C and affords the tetragermane. The isolated oligogermanes were characterized on the basis of the ¹H and ¹³C{¹H} NMR spectroscopic data and their comparison with authentic data.¹⁴ The Pt-containing product was not isolated nor characterized due to facile conversion into mixtures of the insoluble di- or multinuclear complexes with bridging Ge ligands.



The above reaction suggests exchange of the chelating Ge ligands with primary germyl groups derived from PhGeH₃. Scheme 4 shows the plausible pathway for preparation of

^{(24) (}a) Barrau, J.; Rima, G.; Cassano, V.; Satgé, J. *Inorg. Chim. Acta* **1992**, *198–200*, 461–467. (b) Barrau, J.; Rima, G.; Cassano, V.; Satgé, J. *Organometallics* **1995**, *14*, 5700–5703. (c) Barrau, J.; Rima, G.; Cassano, V. *Main Group Met. Chem.* **1996**, *19*, 283–299.

Table 1. Crystallographic Data and Details of Refinement of 1, 2, and 3

	1	2	3
formula	$C_{30}H_{38}Ge_2P_2Pt \cdot 1/2$ toluene	C ₄₂ H ₄₆ Ge ₃ P ₂ Pt	C ₆₁ H ₆₄ Ge ₄ P ₂ Pt
fw	846.99	1025.63	1344.57
cryst size/mm	0.08 imes 0.15 imes 0.17	0.35 imes 0.36 imes 0.53	$0.25 \times 0.41 \times 0.52$
cryst syst	monoclinic	monoclinic	orthorhombic
cryst color	colorless	yellow	colorless
space group	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)	<i>P</i> 2 ₁ 2 ₁ 2 ₁ (No. 19)
a/Å	17.672(4)	17.783(7)	11.927(2)
$b/\text{\AA}$	11.870(2)	15.928(8)	20.208(4)
$c/\text{\AA}$	17.501(3)	15.164(5)	23.619(4)
β/deg	118.373(3)	102.04(3)	
$V/Å^3$	3230(1)	4201(3)	5693(2)
Z	4	4	4
$D_{\rm calcd}/{\rm g}~{\rm cm}^{-3}$	1.740	1.622	1.569
F(000)	1676	2008	2664
μ/mm^{-1}	6.2724	5.344	4.6184
no. of reflns measd	22 578	11456	47 180
no. of unique reflns	7072	9618	12 988
R _{int}	0.032	0.051	0.034
no. of obsd reflns $(I \ge 2.00\sigma(I))$	6404	5059	12248
no of variables	361	434	614
$R_1, R_{\rm m} (I \ge 2\sigma(I))$	0.0351, 0.0938	0.0443. 0.1097	0.0273, 0.0479
R_1, wR_2 (all data)	0.0386, 0.0963	0.1378. 0.1416	0.0293, 0.0487
GOF on F^2	1.044	1.009	1.001
Scheme 4		Experimental Section	



oligogermanes from germaplatinacycles. Addition of PhGe- H_3 causes metathesis reaction between the Pt–Ge bonds of the Pt complexes and H–Ge bonds of the additive to form a trigermyl(germyl)platinum complex (A'), similar to structure A in Scheme 2. Primary organogermanes show high reactivity toward exchange reaction of the germyl ligands to release oligogermanes.

Conclusion

We presented the preparation and structure of four- or five-membered germaplatinacycles from a bis(germyl)platinum complex depending on the amount of added H₂GePh₂. Compared to analogous reactions of related Pt⁹ and Pd¹⁰ complexes, the four-membered Pt complex 2 was newly isolated and formed the five-membered complex 3 upon reaction with H2GePh2. The results established the route involving ring-expansion of the four-membered Ge-containing metallacycle to the five-membered one, although it is not clear whether the reaction route is dominant in the direct reaction of 1 with H_2GePh_2 , yielding 3 or not. These isolated germacycles also react with excess PhGeH₃ to lead to the Pt-Ge bond cleavage of the cyclic oligogermyl ligands rather than the rearrangement for Ge-Ge bond formation. All these results demonstrate a new route to prepare linear oligogermane dihydrides directly from diarylgermanes.

General Procedures. All manipulations of the complexes were carried out using standard Schlenk techniques under an argon or nitrogen atmosphere. Hexane and toluene were purified by using a solvent purification system (Glass Contour). The ¹H, ¹³C{¹H}, and ³¹P{¹H} NMR spectra were recorded on Varian Mercury 300 and JEOL EX-400 spectrometers. Chemical shifts in ¹H and ¹³C{¹H} NMR spectra were referenced to the residual peaks of the solvents used. The peak positions of the ³¹P{¹H} NMR spectra were referenced to external 85% H₃PO₄ (δ 0) in C₆D₆. IR absorption spectra were recorded on a Shimadzu FT/IR-8100 spectrometer. Elemental analysis was carried out using a LECO CHNS-932 or Yanaco MT-5 CHN autorecorder. H₂GePh₂ was obtained from reduction of Cl₂GePh₂ (Sigma-Aldrich) by LiAlH₄. [PtMe₂(dmpe)]²⁵ was prepared according to the reported pro-

cedure. **Preparation of** [**Pt(GeHPh₂)₂(dmpe**)] (1). To a toluene solution (6 mL) of [**PtMe**₂(dmpe)] (296 mg, 0.79 mmol) was added excess H₂GePh₂ (542 mg, 2.37 mmol) in one portion. The solution was stirred for 6 h at 60 °C. Removal of the solvent under reduced pressure gave a solid, which was washed three times with hexane/toluene (3:1) and dried *in vacuo* to give **1** as a white solid (545 mg, 86%). Recrystallization of **1** from hexane/toluene (3:1) at room temperature (rt) gave colorless crystals suitable for X-ray crystallography. Anal. Calcd for $C_{33}H_{45}Ge_2P_2Pt \cdot (1/2C_6H_{14})$: C, 46.96; H, 5.37. Found: C, 46.96; H, 4.97. ¹H NMR (300 MHz, C₆D₆, rt): δ 7.82 (dd, 8H, C₆H₅ ortho, J_{H-H}= 7.5, 1.8 Hz), 7.23–7.16 (m, 12H, C₆H₅ meta and para, J_{H-H}= 6.9 Hz), 5.82 (m, 2H, GeH, ³J_{P-H} = 14.4 Hz, ²J_{Pt-H}= 101 Hz), 0.85 (d, 12H, PCH₃, ²J_{P-H}= 9.3 Hz, J_{Pt-H}= 24.6 Hz), 0.63 (m, 4H, CH₂, J_{P-H} = 17.1 Hz). ¹³C{¹H} NMR (75 MHz, C₆D₆, rt): δ 146.6 (t, C₆H₅ *ipso*, ³J_{P-C} = 5.5 Hz, ²J_{Pt-C} = 44 Hz), 137.0 (t, C₆H₅ ortho, ³J_{Pt-C} = 16 Hz), 127.6 (C₆H₅ para), 127.0 (C₆H₅ meta), 29.9 (m, PCH₂), 13.0 (m, PCH₃, ²J_{Pt-C} = 29 Hz). ³¹P{¹H} NMR (121 MHz, C₆D₆, rt): δ 35.6 (J_{Pt-P} = 1895 Hz). IR (KBr): 1869, 1935 (v_{Ge-H}) cm⁻¹.

Preparation of $[Pt(GePh_2GePh_2GePh_2)(dmpe)]$ (2). To a toluene solution (3 mL) of 1 (330 mg, 0.41 mmol) was added H_2GePh_2 (113 mg, 0.49 mmol). The reaction mixture was stirred

⁽²⁵⁾ Smith, D. C. Jr.; Haar, C. M.; Stevens, E. D.; Nolan, S. P.; Marshall, W. J.; Moloy, K. G. Organometallics **2000**, *19*, 1427–1433.

for 1.5 h at 90 °C. Removal of the solvent under reduced pressure and washing the resulting pale yellow solid with hexane (3 × 3 mL) yielded **2** (366 mg, 87%). Recrystallization from hexane/toluene (3:1) at rt gave yellow crystals of **2** suitable for X-ray crystallography. Anal. Calcd for $C_{42}H_{46}Ge_3P_2Pt$: C, 49.18; H, 4.52. Found: C, 48.39; H, 4.31. ¹H NMR (300 MHz, C₆D₆, rt): δ 7.79 (dd, 8H, C₆H₅ *ortho*, J_{H-H} = 7.4, 1.6 Hz), 7.70 (m, 4H, C₆H₅ *ortho*), 7.13–7.04 (m, 18H, C₆H₅ *meta* and *para*), 0.85 (d, 12H, PCH₃, ²J_{P-H} = 9.3 Hz, J_{Pt-H} = 25.5 Hz), 0.62 (m, 4H, PCH₂, ²J_{P-H} = 16.7 Hz). ¹³C{¹H} NMR (75 MHz, THF-d₈, rt): δ 147.5 (t, C₆H₅ *ipso*, ³J_{P-C} = 5.2 Hz, ²J_{Pt-C} = 40 Hz), 147.2 (t, C₆H₅ *ipso*, ³J_{P-C} = 5 Hz, ²J_{Pt-C} = 63 Hz), 137.8 (C₆H₅ *ortho*, ²J_{Pt-C} = 18 Hz), 136.5 (C₆H₅ *ortho*), 127.9, 127.6, 127.3, 127.1 (C₆H₅ *meta* and/or *para*), 30.6 (m, PCH₂), 14.7 (m, PCH₃, ³J_{P-C} = 28 Hz, ²J_{Pt-C} = 44 Hz). ³¹P{¹H} NMR (121 MHz, C₆D₆, rt): δ 36.2 (J_{Pt-P} = 1819 Hz).

Preparation of [Pt(GePh₂GePh₂GePh₂GePh₂)(dmpe)] (3). A mixture of **2** (101 mg, 0.098 mmol) and excess H₂GePh₂ (112 mg, 0.49 mmol) in toluene solution (3 mL) was heated for 48 h at 90 °C. The solvent was evaporated to dryness, and the resulting white solid was recrystallized from toluene/hexane (1:4) to yield **3** as colorless crystals (35 mg, 29%). The ¹H NMR spectrum of the reaction mixture in C₆D₆ before purification showed two Ge–H hydrogen signals at δ 5.57 and 5.68, which were assigned to H(GePh₂)₂H¹³ and H(GePh₂)₃H¹⁴ (literature: δ 5.58 and 5.65). Anal. Calcd for C₅₄H₅₆Ge₄P₂Pt: C, 51.78; H, 4.51. Found: C, 50.96; H, 4.57. ¹H NMR (300 MHz, C₆D₆, rt): δ 7.72 (dd, 8H, C₆H₅ ortho, J_{H–H} = 6.6, 2.7 Hz), 7.50 (dd, 8H, C₆H₅ ortho, J_{H–H} = 7.7, 1.7 Hz), 7.07–6.92 (m, 24H, C₆H₅ meta and para), 0.79 (m, 12H, PCH₃, ²J_{P–H} = 9.6 Hz, J_{Pt–H} = 21.7 Hz), 0.61 (m, 4H, CH₂, ²J_{P–H} = 17 Hz). ¹³C{¹H} NMR (75 MHz, THF-d₈, rt): δ 148.4 (t, C₆H₅ ipso, ³J_{P–C} = 5.5 Hz, ²J_{Pt–C} = 39 Hz), 141.9 (t, C₆H₅ ipso, ³J_{Pt–C} = 14.4 Hz), 138.5 (C₆H₅ ortho, ²J_{Pt–C} = 17.3 Hz), 137.6 (C₆H₅ ortho), 127.7 (C₆H₅ meta), 127.5 (C₆H₅ meta), 127.2 (C₆H₅ para), 127.1 (C₆H₅ para), 30.8 (m, PCH₂), 13.9 (d, PCH₃, ²J_{P-C} = 29 Hz, ²J_{Pt–C} = 39 Hz). ³¹P{¹H} NMR (121 MHz, C₆D₆, rt): δ 33.6 (J_{Pt–P} = 1851 Hz).

Direct Preparation of 3 from 1. Direct preparation of **3** from complex **1** is as follows: Complex **1** (88 mg, 0.11 mmol), H_2GePh_2 (251 mg, 1.10 mmol), and toluene (3 mL) were added to a 25 mL Schlenk and stirred for 28 h at 90 °C. The solvent was removed under reduced pressure to produce the residual solid, which was recrystallized from toluene/hexane (1:4) to remove oligogermanes as byproduct. The product **3** was obtained as colorless crystals (84 mg, 61%).

Reaction of 2 with PhGeH₃. When a 4-fold amount of PhGeH₃ (108 mg, 0.71 mmol) was added to a 5 mL toluene solution of **2** (182 mg, 0.18 mmol), the reaction mixture turned from yellow to colorless and was stirred for 2 h at rt. The reaction mixture was filtered, and the solvent removed under reduced pressure. The resulting solid material was reprecipitated with hexane repeatedly to give H(GePh₂)₃H¹⁴ as a white solid (92.4 mg, 76%). ¹H NMR (300 MHz, C₆D₆, rt): δ 7.60 (m, 4H, C₆H₅

ortho), 7.44 (m, 8H, C_6H_5 ortho), 7.03 (m, 18H, C_6H_5 meta and para), 5.68 (s, 2H, GeH). ¹³C{¹H} NMR (75 MHz, THF- d_8 , rt): δ 137.9 (C_6H_5 ipso), 136.6 (C_6H_5 ipso), 136.6 (C_6H_5 ortho), 136.3 (C_6H_5 ortho), 129.5 (C_6H_5 meta or para), 129.4 (C_6H_5 para), 129.1 (C_6H_5 meta or para), 129.0 (C_6H_5 meta). IR (KBr): 2012 (ν_{Ge-H}) cm⁻¹.

Reaction of 3 with PhGeH₃. To a stirred suspension of complex **3** (81.4 mg, 0.065 mmol) in 3 mL of toluene was added a 6-fold amount of PhGeH₃ (59.6 mg, 0.39 mmol). The reaction mixture was allowed to stir for 36 h at 60 °C, then filtered to remove unreacted compounds and evaporated to give a pale yellow solid. The resulting material was washed twice with 20 mL of hexane, dissolved in 5 mL of ether, then passed through a Florisil column. The solvent was removed from the eluted solutions *in vacuo* to give the tetragermane H(GePh₂)₄H¹⁴ as a white solid (39 mg, 66%). ¹H NMR (300 MHz, C₆D₆, rt): δ 7.50 (d, 8H, C₆H₅ *ortho*, J_{H-H} = 6.3 Hz), 7.38 (d, 8H, C₆H₅ *ortho*, J_{H-H} = 6.0 Hz), 6.99 (m, 24H, C₆H₅ *meta* and *para*), 5.62 (s, 2H, GeH). ¹³C{¹H} NMR (75 MHz, THF-*d*₈, rt): δ 138.1 (C₆H₅ *ipso*), 137.0 (C₆H₅ *ipso*), 136.9 (C₆H₅ *ortho*), 129.3 (C₆H₅ *para*), 129.2 (C₆H₅ *para*), 128.9 (C₆H₅ *meta*). IR (KBr): 1998 (v_{Ge-H}) cm⁻¹.

X-ray Crystallography. Crystals of 1, 2, and 3 suitable for an X-ray diffraction study were mounted on Micro-Mounts (MiTeGen). The crystallographic data of 1 and 3 were collected on a Rigaku Saturn CCD area detector equipped with monochromated Mo K α radiation ($\lambda = 0.71073$ Å) at 150 K. The data of 2 were collected on a Rigaku AFC-7R automated four-cycle diffractometer at rt. Calculations were carried out using the program package Crystal Structure, version 3.8, for Windows. The positional and thermal parameters of nonhydrogen atoms were refined anisotropically on F^2 by the fullmatrix least-squares method using SHELXL-97.²⁶ Hydrogen atoms, except for the GeH hydrogens of 1, were placed at calculated positions and refined with a riding mode on their corresponding carbon atoms. Crystallographic data and details of refinement of 1, 2, and 3 are summarized in Table 1.

Acknowledgment. This work was financially supported by Grants-in-Aid for Scientific Research for Young Chemists (No. 21750057), for Scientific Research (No. 1925008), and for Scientific Research on Priority Areas (No. 19027018), from the Ministry of Education, Culture, Sport, Science, and Technology, Japan. We are grateful to Dr. Norio Nakata (Saitama University) for helpful discussions.

Supporting Information Available: Crystallographic data for **1**, **2**, and **3** as a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

(26) Sheldrick, G. M. SHELXL-97: Program for Crystal Structure Refinement; University of Gottingen: Germany, 1997.