Synthesis and Kaleidoscopic Reactivities of Bis(tritolylgermyl)bis(dimethylphenylphosphine)platinum(II)

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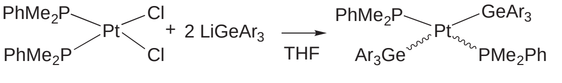
A series of tritolylgermylplatinum complexes $Pt(GeAr_3)_2(PMe_2Ph)_2$ (Ar = *o*-tol, *m*-tol, and *p*-tol) were prepared and kaleidoscopic reactivities were observed by only changing the substituents at the germyl tolyl groups: (1) cis–trans isomerization at platinum, (2) C–H bond activation of ortho methyl group, and (3) reductive elimination at Pt giving Ge–Ge bond.

Group 14 element compounds have attracted growing interest not only as possible synthetic tools in organic chemistry but also for their potential use as new materials. In particular, considerable effort has been devoted to syntheses of group 14 element compounds binding late transition metals, as these complexes are regarded as intermediates in a number of transition-metal-catalyzed transformations of group 14 element compounds. Disilyl– and distannyl–platinum complexes have been intimately studied because it was considered to be an important key intermediate in Pt-catalyzed disilylation or stannylation of unsaturated compounds.[1] Transition-metal-catalyzed germylation in organic synthesis have been also reported.[2] Furthermore, germanium-containing polymers were synthesized by late transition-metal catalysis and their applications for material technology such as conductivity, thermochromism, photoconductivity, and nonlinear optical effect have been investigated.[3] Previously, we have isolated divalent germylplatinum complexes as an intermediate in the digermylation of alkynes catalyzed by zero-valent Pt complexes.[2,4] Herein, we describe the syntheses of a series of tritolylgermylplatinum complexes $Pt(GeAr_3)_2(PMe_2Ph)_2$ (Ar = *o*-tol, *m*-tol, and *p*-tol) and their kaleidoscopic reactivities.

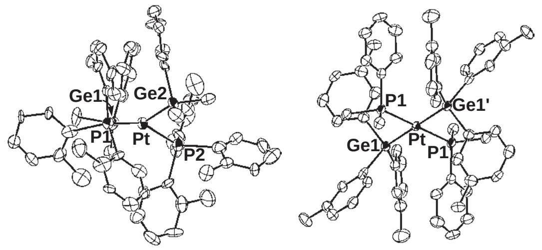
Bis(tritolylgermyl)bis(dimethylphenylphophine)platinum (II), *trans*-$Pt(GeAr_3)_2(PMe_2Ph)_2$ (Ar = *o*-tol (**1**-*trans*), *m*-tol (**2**-*trans*)) were prepared by the treatment of *cis*-$PtCl_2(PMe_2Ph)_2$ with two molar amount of $LiGeAr_3$ in THF at 23 °C for 2 h (eq 1). These complexes were characterized by NMR spectroscopy and elemental analysis.



(1)

Ar = *o*-tol **1**-*trans* (20%)
m-tol **2**-*trans* (87%)
p-tol **3** (*cis*:*trans* = 3:7)

A mixture of *cis*- and *trans*-$Pt[Ge(p\text{-tol})_3]_2(PMe_2Ph)_2$ (**3**) was formed from the reaction of *cis*-$PtCl_2(PMe_2Ph)_2$ with $LiGe(p\text{-tol})_3$ in THF-d_8 at −40 °C in situ. Molecular structures of **1**-*trans* and **2**-*trans* were determined by X-ray structure analysis as shown in Figure 1.[5] **1**-*trans* has a distorted square-planar geometry with a dihedral angle of 34.8° between the plane Ge1–Pt1–P2 and Ge2–Pt–P2, whereas **2**-*trans* has a square-planar structure.



1-*trans* **2**-*trans*

Figure 1. Molecular structures of **1**-*trans* and **2**-*trans*.

Syntheses and structures of *cis*- and *trans*-digermylplatinum complexes have been reported.[2,6] Preferential cis geometry of $Pt(SiR_3)_2(PR'_3)_2$ was attributed to a large trans influence of organosilyl ligand,[7] while Kim et al. reported the isolation of *trans*-$Pt(SiHPh_3)_2(PMe_3)_2$.[8] In addition, bulky germyl groups, in comparison with the corresponding silyl groups, presumably disfavor the sterically congested cis form. Three different types of selective reactions were observed by only changing the substituents at the germyl tolyl groups: (1) cis–trans isomerization at platinum, (2) C–H bond activation of ortho methyl group, and (3) reductive elimination at Pt giving Ge–Ge bond.

Firstly, photoinduced and thermal isomerization of digermylplatinum complexes were observed. Irradiation of **2**-*trans* ($\lambda_{max} = 310$ nm in CH_2Cl_2) with a Xenon lamp ($h\nu > 450$ nm) in 1,2-dichloroethane-d_4, $(CD_2Cl)_2$, at room temperature for 30 min induced the smooth isomerization to give the corresponding cis isomer, *cis*-$Pt[Ge(m\text{-tol}_3)]_2(PMe_2Ph)_2$ (**2**-*cis*) (**2**-*cis*/**2**-*trans* = 98/2).

In order to investigate the mechanism for the photoisomerization of **2**-*trans* without dissociation or association of PMe_2Ph, ab initio molecular orbital calculations at the CASSCF level were performed for the model complex, $Pt(GeH_3)_2(PH_3)_2$. The results suggest that the photoisomerizaion is possible to proceed via a conical intersection (the crossing point of the ground and excited potential energy surfaces) with the tetrahedral structure.[9]

2-*cis* was thermally converted to the trans isomer in $(CD_2Cl)_2$ at 50 °C for 5 h (**2**-*trans*/**2**-*cis* = 80/20) (eq 2). The thermal isomerization of **2**-*cis* to **2**-*trans* at various temperature (40–60 °C) was followed by observing the change in the two methyl signals of the PMe_2Ph ligands by means of ^1H NMR spectroscopy. The isomerization of **2**-*cis* showed the first-order kinetics. Rate constant in $(CD_2Cl)_2$ at 50 °C was $1.32 \times 10^{-4}\,s^{-1}$ with apparent activation energy of 99.0 kJ mol^{-1} from Arrhenius plot. Activation enthalpy and entropy from Eyring

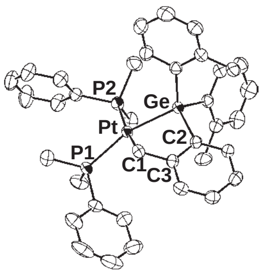
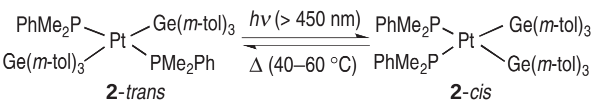


Figure 2. Molecular structure of **4**.

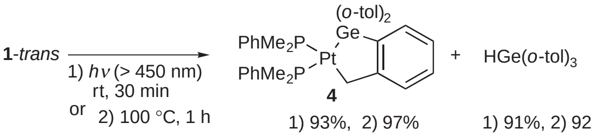
plot were 96.3 kJ mol^{-1} and -20.7 J mol^{-1} K^{-1}, respectively. Addition of PMe_2Ph caused acceleration of the isomerization of **2**-*cis*. This result suggests that the isomerization of **2**-*cis* proceeds through an associative pathway involving a five coordinate intermediate formed upon association of PMe_2Ph to **2**-*cis*.



(2)

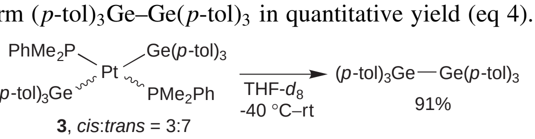
We have also carried out ab initio molecular orbital calculations to confirm such an associative five-coordinated mechanism with a Berry pseudorotation and located the transition state for the model complex $Pt(GeH_3)_2(PH_3)_2$.[10] There has been little study about precise determination of relative thermodynamic stability between cis and trans isomers for $Pt(ER_3)_2L_2$ ($E =$ Si, Ge, and Sn; $L = PR'_3$), except for ref 8, while the intramolecular twist-rotational motion between two ER_3 group was observed with *cis*-$Pt(ER_3)_2L_2$ ($E =$ Si and Sn; $L = PR'_3$).[1]

Secondly, irradiation ($h\nu > 450$ nm, room temperature) or heating (100 °C) of **1**-*trans* caused C–H bond activation of *o*-tolyl group to give a germaplatinacycle complex $Pt[Ge(o\text{-tol})_2(o\text{-}C_6H_4CH_2)](PMe_2Ph)_2$ (**4**) and hydrogermane $HGe(o\text{-tol})_3$ quantitatively (eq 3). Molecular structure of **4** was determined by X-ray structure analysis as depicted in Figure 2.[11] An ORTEP drawing of **4** clearly shows formation of the new Pt–CH_2 bond by C–H activation of the methyl group at *o*-tolyl moiety. This is probably enhanced by close proximity of the Me group to Pt or another germyl group leading to C–H bond cleavage.



(3)

Lastly, clean Ge–Ge bond formation at Pt was observed for tris(*p*-tol)germylplatinum derivative **3**. A mixture of cis and trans isomers **3** was immediately generated from the reaction of *cis*-$PtCl_2(PMe_2Ph)_2$ with $LiGe(p\text{-tol})_3$ at -40 °C in situ and characterized by multinuclear NMR spectra. Interestingly, on warming to room temperature, reductive elimination proceeded to form $(p\text{-tol})_3Ge\text{–}Ge(p\text{-tol})_3$ in quantitative yield (eq 4).



(4)

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5 Preliminary crystallographic data for **1**-*trans*: $C_{74}H_{96}O_4Ge_2P_2Pt$, $M_r = 1451.72$, triclinic, $P1$, $a = 13.2860(15)$, $b = 14.1620(14)$, $c = 17.7320(14)$ Å, $\alpha = 96.177(5)$, $\beta = 103.711(6)$, $\gamma = 111.638(5)°$, $V = 2941.8(5)$ Å^3, $Z = 2$, $D_{calcd} = 1.639$ g cm^{-3}, $F(000) = 1488$, $\mu = 3.496$ mm^{-1}, $R = 0.0584$ ($I > 2\sigma(I)$), $wR2 = 0.1634$ (all data), GOF = 1.206. Crystallographic data for **2**-*trans*: $C_{58}H_{64}Ge_2P_2Pt$, $M_r = 1163.30$, triclinic, $P\bar{1}$, $a = 12.5600(8)$, $b = 13.8290(10)$, $c = 17.4500(17)$ Å, $\alpha = 104.025(5)$, $\beta = 102.670(5)$, $\gamma = 112.854(4)°$, $V = 2537.7(3)$ Å^3, $Z = 2$, $D_{calcd} = 1.522$ g cm^{-3}, $F(000) = 1168$, $\mu = 4.026$ mm^{-1}, $R = 0.0545$ ($I > 2\sigma(I)$), $wR2 = 0.1526$ (all data), GOF = 0.990.

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9 The conical intersection is found to be 218 kJ mol^{-1} less stable than the trans isomer in the ground state at the CASSCF(6,6)/LANL2DZ level.

10 The energy barrier from the trans isomer is estimated to be 120 kJ mol^{-1} at the HF/LANL2DZ+6-31G(d) level.

11 Crystallographic data for **4**: $C_{49}H_{54}GeP_2Pt$, $M_r = 972.54$, triclinic, $P1$, $a = 10.4030(2)$, $b = 12.7170(4)$, $c = 16.8210(6)$ Å, $\alpha = 80.411(2)$, $\beta = 79.010(2)$, $\gamma = 87.075(2)°$, $V = 2153.57(11)$ Å^3, $Z = 2$, $D_{calcd} = 1.500$ g cm^{-3}, $F(000) = 976$, $\mu = 4.049$ mm^{-1}, $R = 0.0481$ ($I > 2\sigma(I)$), $wR2 = 0.1531$ (all data), GOF = 1.369.

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