PREPARATION AND REDUCTIVE ELIMINATION OF DIGERMYPALATINUM COMPLEXES

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Abstract: *cis*- and *trans*-(R₃Ge)₂Pt(PMe₂Ph)₂ complexes as key intermediates of bis-germylation of alkynes have been prepared, and their structures have been established by spectroscopic methods and X-ray crystallography. The *cis* isomers afford digermynes, (R₃Ge)₂ as reductive elimination products in good yields. In contrast, the *trans* isomers lead to monogermynes.

Introduction

A transition metal-catalyzed addition of group 14-element compounds to unsaturated organic substrates is a useful fundamental process in group-14 element chemistry. The addition of Si-Si bonds to C-C triple and double bonds, i.e., bis-silylation, has attracted considerable current interest in the synthesis of fundamental molecules and in application to selective organic synthesis [1-8]. For bis-silylation method and of considerable studies on reaction mechanisms, there have been few reports on bis-germylation reactions [9-11]. We report on the synthesis, characterization, and reactivities of digermypalatinum complexes that assumed as key intermediates in these platinum-catalyzed processes.

Results and Discussion

We set out to prepare model compounds of the intermediate digermypalatinum complexes stabilized by tertiary phosphine ligands. Using dimethylphenylphosphine ligand as supporting ligands, we have been able to prepare digermypalatinum complexes, (Me₂PhGe)₂Pt(PMe₂Ph)₂ (1), (MePh₂Ge)₂Pt(PMe₂Ph)₂ (2), and (Ph₃Ge)₂Pt(PMe₂Ph)₂ (3). The treatment of *cis*-PtCl₂(PMe₂Ph)₂ with two equiv of Me₂PhGeLi, prepared from the corresponding germyl chloride with lithium metal, in THF at room temperature for 12 h afforded yellow crystals with a composition of (Me₂PhGe)₂Pt(PMe₂Ph)₂ (1). NMR examination of a C₆D₆ solution of the yellow crystals showed a single *cis*-isomer: ¹H NMR (C₆D₆) δ 0.73 (d, ²J_{H-P} = 8.1 Hz, ³J_{H-Ge} = 29.9 Hz, PCH₃), 1.05 (s, ³J_{H-Ge} = 17.6 Hz), ³¹P NMR (C₆D₆) δ -10.1 (s, ¹J_{P-P} = 2007 Hz). Complex *cis*-1 in C₆D₆ was stable and did not isomerize to the *trans*-isomer, even at 70 °C. The complex *cis*-PtCl₂(PMe₂Ph)₂ reacted with two equiv of MePh₂GeLi, prepared from the corresponding germyl chloride with lithium metal, in THF at room temperature for 12 h to give yellow crystals with a composition of (MePh₂Ge)₂Pt(PMe₂Ph)₂ (2). A NMR examination of the C₆D₆ solution of the yellow crystals 2 showed the presence of *cis* and *trans* isomers of 2 in an approximately 60:40 ratio. The ¹H NMR of complex *cis*-2 displayed the two methyl signals of the PhMe₂Ph ligands at 0.70 ppm (deformed q, ²J_{H-P} = 8.2 Hz, ³J_{H-P} = 20.8 Hz) and the platinum bound methylphenylgermyl groups at 1.05 ppm (s, ³J_{H-Ge} = 18.6 Hz). The ³¹P NMR showed a singlet signal with satellites at -10.99 ppm (¹J_{P-P} = 2049 Hz). The *trans*-2 isomer exhibited ¹H NMR spectrum of the germanium-bound methyl groups at 1.20 (vt, ²J_{H-P} = 6.0 Hz, ³J_{H-Ge} = 30.8 Hz) and the ³¹P NMR showed a singlet at -10.63 ppm with satellites (¹J_{P-P} = 2731 Hz). The smaller ¹J_{P-P} value in *cis*-2 is consistent with the larger *trans* influence of the germanium ligand situated at the position *trans* to the phosphine ligand. From the *cis* and *trans* mixture, *cis*-2 could be isolated as yellow crystals by recrystallization from a 5:1 mixture of hexane and benzene at room temperature for 3-5 days.

Complex *cis*-PtCl₂(PMe₂Ph)₂ reacted with two equiv of Ph₃GeLi, prepared from Ph₃GeCl and lithium metal, in THF under similar conditions to give yellow crystals of only one species (Ph₃Ge)₂Pt(PMe₂Ph)₂ (3) having a *trans* geometry: ¹H NMR (C₆D₆) δ 1.24 (vt, ²J_{H-P} = 29.3 Hz, ³J_{H-P} = 6.6 Hz, PCH₃), ³¹P NMR (C₆D₆) δ -11.0 (s, ¹J_{P-P} = 2616 Hz). The complex *trans*-3 in C₆D₆ was stable and did not isomerize to the *cis* isomer, even at 70 °C. Thus, the stable geometry for (R₃Ge)₂Pt(PMe₂Ph)₂ complexes varies dependent on the number of phenyl groups on the germanium atom. The structure of *cis*-1, *cis*-2, and *trans*-3 were established by NMR, IR, and X-ray analysis. Although crystallized 2 has a *cis* geometry, the dissolution of *cis*-2 in benzene caused a gradual isomerization to give a *cis-trans* equilibrium mixture.

The isomerization of *cis*-2 to *trans*-2 in C₆D₆ at various temperatures was followed by observing the change in the two methyl signals of the PMe₂Ph ligands by means of ¹H NMR spectroscopy. From the concentrations of the *cis* and *trans* isomers after equilibria were reached, the following thermodynamic parameters were obtained: ΔH°, 6.0 kJ mol⁻¹ and ΔS°, 13.0 J mol⁻¹ K⁻¹.

As a representative example, Fig. 1 shows the molecular structure of *cis*-1, confirmed by X-ray diffraction analysis.

Fig. 1. Molecular structure of the *cis*-bis(dimethylphenylgermyl)bis(dimethylphenylphosphine)platinum (1). (30% probability thermal ellipsoids). Hydrogen atoms are omitted for clarity.

Fig. 2 shows the summary of selected bond lengths, bond angles, and dihedral angles in *cis*-1, *cis*-2, and *trans*-3 complexes.

Fig. 2. A summary of selected bond lengths, bond angles, and dihedral angles of *cis*-1, *cis*-2, and *trans*-3.

Both *cis*-1 and *cis*-2 have distorted square-planar *cis* geometries, with the dihedral angles between the planes composed of P(1)-Pt(1)-P(2) and Ge(1)-Pt(2)-Ge(2) being 21.6 and 37.8°, respectively. The deformation from planarity is considered to be caused by a steric repulsion between the bulky ligands. The two germyl groups are bound to the platinum center in position *cis* to each other, with the bite angle, Ge(1)-Pt(1)-Ge(2), being 88.6° for *cis*-1 and 85.2° for *cis*-2. On the other hand, the complex *trans*-3 has a somewhat distorted square-planar geometry with a dihedral angles of 8.1° between the plane composed of P(1)-Pt-Ge(1) and P(2)-Pt-Ge(2). The four bond angles of Ge-Pt-P are close to 90°. The bond lengths of Pt-Ge (2.5207(3) and 2.5239(4) Å of *trans*-3 are longer than those of *cis*-1 and *cis*-2 (2.4455(9) and 2.4410(7) Å, respectively). On the contrary, the Pt-P lengths of *trans*-3 (2.3011(9) and 2.3120(9) Å are shorter than those of *cis*-1 and *cis*-2 (2.334(2) and 2.324(1) Å, respectively). These results indicate the greater *trans* influence of the germyl ligand than the phosphine ligand.

The thermolysis behavior of these digermylplatinum complexes, 1-3, was examined in sealed NMR tubes. Thermolysis of *cis*-1 at 80 °C for 12 h and *cis*-2 at 120 °C for 5 h led to the formation of digermanes (65 and 60%, respectively) as the major coupling products of the two germyl ligands. Two monogermenes and other unidentified germanium-containing oligomers were produced as by-products.

On the other hand, heating of *trans*-3 at 70 °C for 24 h gave tetraphenylgermane (60%) as main products. Other unidentified products were also detected.

For examining the reactivity of the digermylplatinum complexes that are assumed to be involved in the platinum-catalyzed bis-germylation of alkynes, we treated *cis*-2 with 5.0 equiv. of phenylacetylene at 65 °C for 24 h. The reaction gave *Z*-1-phenyl-1,2-bis(diphenylmethylgermyl)ethene in 31% yields.

Vinyl-germyl type platinum complex is a possible intermediate species in the reactions of digermylplatinum complexes 1-3 with phenylacetylene in the process to liberate a bis-germylation product of the alkyne. Complex 2 reacted with phenylacetylene (2 equiv) at 65 °C for 1.5 h in C₆D₆ to give regioselectively the corresponding insertion complex 4 in quantitatively yields, as confirmed by NMR spectroscopy.

Fig. 3. Molecular structure of the methyldiphenylgermyl(1-phenyl-2-methyldiphenylgermyl-ethylenyl)bis(dimethylphenylphosphine)platinum (4). (30% probability thermal ellipsoids). Hydrogen atoms are omitted for clarity.

Complex **4** was isolated as a yellow solid in 88% yield and characterized by NMR spectroscopy and X-ray diffraction analysis. The ^{31}P NMR of complex **4** exhibited two sets of doublets ($^2J_{\text{P-P}} = 18 \text{ Hz}$) at δ -15.0 and -18.7 with $^1J_{\text{P-P}}$ values of 1811 and 1819 Hz, respectively.

Figure 3 shows the molecular structure of **4**. The platinum atom in **4** has a square-planar geometry, the sum of the four angles about platinum being 360.2° . The C(1)-C(2) distance (1.351(13) Å) is in the typical range of a carbon-carbon double bond. The Z arrangement of the platinum and germanium atoms bound to the C=C double bond clearly shows the occurrence of the *cis* insertion of phenylacetylene into one of the two Pt-Ge bonds.

Heating of *cis*-**4** in C_6D_6 at 80°C for 8 h led to the decomposition of *cis*-**4** (45%) with the formation of Z-1-phenyl-1,2-bis(diphenylmethylgermyl)ethene in 40% yield.

As a mechanism for the bis-germylation of alkynes with a digermene, we propose a catalytic cycle (Scheme 1) driven by a Pt(0) species generated from a catalyst precursor. The catalytic cycle is composed of (a) the oxidative addition of digermene to the platinum species to form a digermylplatinum intermediate (**A**), (b) the coordination of an alkyne to **A** to form an alkyne-coordinated bis-germylation complex (**B**), (c) the insertion of the coordinated alkyne into one of the Pt-Ge bonds to form the insertion product (**C**) having the germly and vinyl ligands, (d) the reductive elimination of the bis-germylation product of alkyne with the regeneration of the active platinum species that further carries the catalytic cycle.

Scheme 1.

For obtaining further information we attempted the detection of an intermediate species involved in the process by a NMR examination of the reaction system.

The formation of the bis-germylation product of phenylacetylene upon a treatment of *cis*-**2** with phenylacetylene at 65°C lends support to the involvement of the digermylplatinum complex in the catalytic bis-germylation of alkynes, as proposed in Scheme 1. For examining whether the isolated digermylplatinum complex **2** in fact acts as a catalyst for the bis-germylation of phenylacetylene, hexamethyldigermene $\text{Me}_3\text{GeGeMe}_3$ was treated with phenylacetylene in the presence of **2** at 65°C for 24 h. The bis-germylation product of phenylacetylene was obtained in 2% yield. The low yield may be partly due to an interference

effect of the phosphine ligand, which was used to stabilize the digermylplatinum complex in the oxidative addition of the digermene to a Pt(0) species.

The regioselective formation of the germyl(germylvinyl)platinum complex **4** upon the treatment of *cis*-**2** with phenylacetylene supports on the involvement of possible intermediates corresponding **B** and **C** in Scheme 1.

As an alternative route to give **C**, a process involving a prior coordination of the alkyne to a Pt(0) species followed by the oxidative addition of a digermene is conceivable. However, a phenylacetylene-coordinated triphenylphosphine complex did not react with MePh₂GePh₂Me or Me₃GeGeMe₃ upon heating at 60–120 °C for 16 h, and no bis-germylation product of phenylacetylene was produced.

Presumably, the coordination of phenylacetylene to the Pt(0) complex through a π bond makes the platinum complex less electron-rich by back-donation, and renders it less susceptible to an oxidative addition reaction with the digermene.

References and Notes

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