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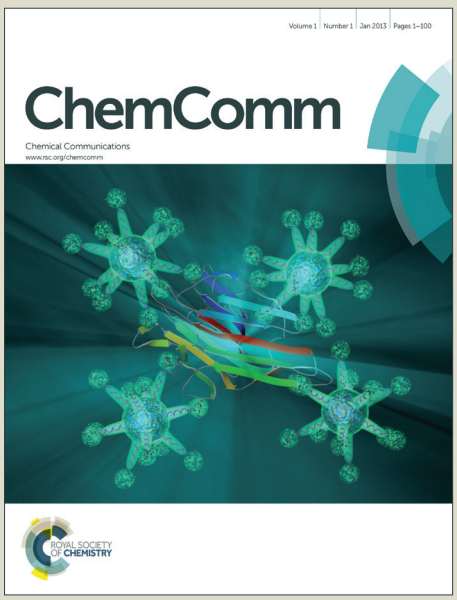

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Triangular Triplatinum(0) Complex with Bridging Germylene Ligands. Insertion of Alkyne into the Pt–Ge Bond Rather Than the Pt–Pt Bond

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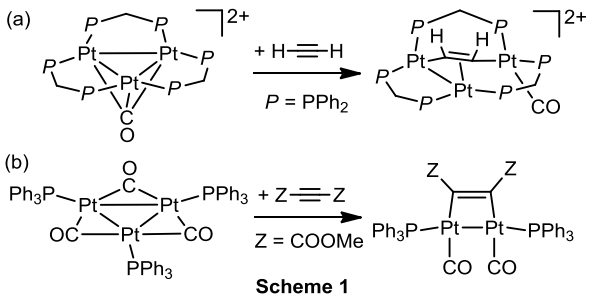
A new triangular triplatinum(0) complex with bridging diphenylgermylene ligands, [{Pt(PMe$_3$)}$_3$(μ-GePh$_2$)$_3$], undergoes insertion of ZC≡CZ (Z = COOMe) into a Pt–Ge bond. The product contains μ_3-η^2(||)-CZ=CZ-GePh$_2$ ligand on the Pt$_3$ plane. Two molecules of HC≡CZ react to afford the Pt$_3$ complex with chelating *C, Ge*- and *Ge, Ge*- ligands.

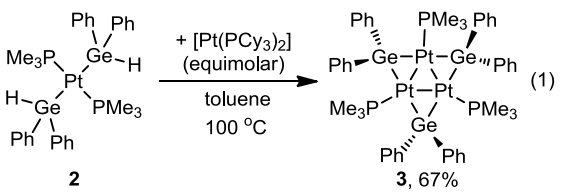
Cyclic triplatinum(0) complexes have long been known[1] and almost all of them contain carbonyl or isonitrile as the bridging ligands. The electron-withdrawing ligands are considered to stabilize the Pt(0)$_3$ core composed of d^{10} metals. The addition of acetylene to cationic triplatinum complexes [Pt$_3$(μ-dppm)$_3$(μ_3-X)]$^{n+}$ (X = CO and n = 2, X = H and n = 1, dppm = Ph$_2$PCH$_2$PPh$_2$), were reported to form their alkyne–coordinated complexes accompanied with cleavage of two Pt–Pt bonds (Scheme 1a).[2] In contrast, the neutral triplatinum carbonyl complex, [{Pt(PPh$_3$)}$_3$(μ-CO)$_3$], reacted with dimethyl acetylenedicarboxylate, ZC≡CZ (Z = COOMe), to afford a 1:1 adduct of the alkyne to the Pt$_3$ core below –50 °C, which was converted to the alkyne-bridged Pt$_2$ complex upon raising the reaction temperature (Scheme 1b).[3]



Scheme 1

Recently, a few number of the complexes were reported by using silylene and germylene ligands instead of the electron-withdrawing bridging ligands. We obtained a triangular triplatinum(0) complex with bridging diphenylsilylene ligands, [{Pt(PMe$_3$)}$_3$(μ-SiPh$_2$)$_3$] (**1**), from the thermal reaction of [Pt(SiHPh$_2$)$_2$(PMe$_3$)$_2$].[4] Braddock-Wilking reported that the reactions of [Pt(CH$_2$=CH$_2$)(PPh$_3$)$_2$] with sila- and germafluorenes yielded [{Pt(PPh$_3$)}$_3${μ-E(C$_{12}$H$_8$)}$_3$] (E = Si, Ge) stabilized by the bridging sila- and germafluorenylidene ligands, although the Ge-containing complex was characterized without X-ray crystallographic results.[5,6] These trinuclear complexes are isoelectronic with those having bridging carbonyl and isonitrile ligands, but may show new chemical properties provided by the less electron-withdrawing silylene and germylene ligands. Herein, we present full characterization of a trinuclear Pt(0) complex with bridging germylene ligands and its reaction with alkynes to afford new triplatinum complexes with germaplatinacyclic structures.

A platinum complex with diphenylgermyl ligands, *trans*-[Pt(GeHPh$_2$)$_2$(PMe$_3$)$_2$] (**2**), was newly obtained and characterized by X-ray crystallography.[7] The heating of an equimolar mixture of **2** and [Pt(PCy$_3$)$_2$] in toluene at 100 °C produced a triplatinum complex with bridging diphenylgermylene ligands, [{Pt(PMe$_3$)}$_3$(μ-GePh$_2$)$_3$] (**3**), in 67% yield (Eqn (1)). Addition of [Pt(PCy$_3$)$_2$] to the solution of **2** increased the yield of **3**.



(1)

The X-ray crystallography of the complex **3** revealed a planar Pt$_3$Ge$_3$ core with a 42-electron cluster incorporating three Pt centers, and the coordination of the bridging GePh$_2$ ligands. The Pt–Pt bonds of **3** (2.7081(6)–2.7194(6) Å) and **1** (2.697(1)–2.716(3) Å) have similar ranges, but are significantly longer than those of the complexes with electron-withdrawing ligands, [{Pt(PCy$_3$)}$_3$(μ-CO)$_3$] (2.653(2)–2.656(2) Å)[8a] and [{Pt(CN^{t}Bu)}$_3$(μ-CN^{t}Bu)$_3$] (2.629(2)–2.637(2) Å).[8b] The Pt–Ge bonds of **3** (2.412(1)–2.423(1) Å) are longer than the Pt–Si bonds of **1** (2.337(5)–2.364(5) Å), which makes the Pt–Ge–Pt angle of **3** (68.10(3)–68.38(3)°) smaller than the Pt–Si–Pt angle of **1** (70.2(1)–70.5(1)°). The Pt–Pt coupling constants of **3** (2633 Hz) and **1** (2950 Hz), estimated from the ^{195}Pt{^{1}H} NMR signals at δ –4195 and –3980, respectively, are larger than those of

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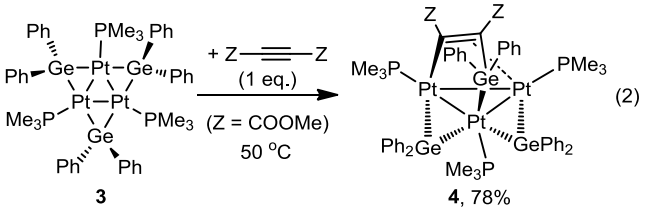
triplatinum complexes with electron-withdrawing CO ligands, [{Pt(PR$_3$)}$_3$(μ-CO)$_3$] (J(Pt,Pt) = 1571–1770 Hz).[8c]

The treatment of **3** with equimolar ZC≡CZ at 50 °C for 1 h yielded a triplatinum complex with the μ_3-germadiplatinacyclopentene structure [{Pt(PMe$_3$)}$_3$(μ_3-η^2(||)-CZ=CZ-GePh$_2$)(μ-GePh$_2$)$_2$] (**4**) in 78% yield, as shown in (Eqn (2)).



The complex **4** maintains a triangular (Pt^I)$_2$(Pt^0)$_1$ core, which is bonded to a μ_3-germavinylene ligand and two bridging germylene ligands at the opposite side of the Pt$_3$ plane (Figure 1). The three Pt–Pt bond distances of **4** (2.700(2)–2.717(2) Å) are similar to those of **3** (2.7081(6)–2.7194(6) Å). The μ_3-germavinylene ligand is σ-bonded to Pt1 and Pt3 and π-bonded to Pt2, with a common μ_3-η^2(||) bonding mode.[9] The bridging GePh$_2$ ligands are unsymmetrically coordinated to two Pt atoms; the Pt1–Ge2 and Pt1–Ge3 bonds (2.799(4) and 2.895(4) Å) are significantly longer than Pt2–Ge2 and Pt3–Ge3 bonds (2.393(4) and 2.419(4) Å).

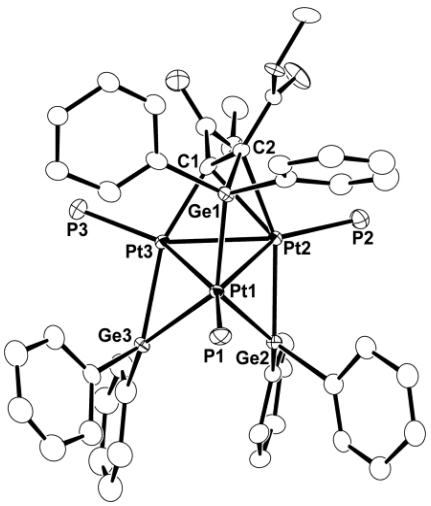
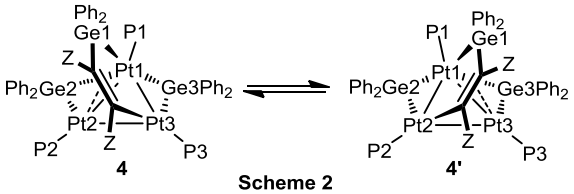


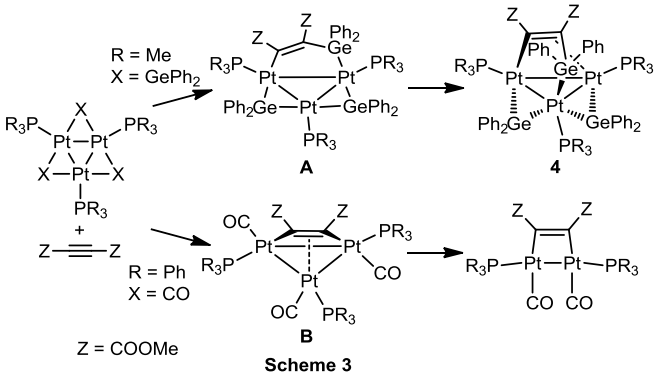
Figure 1. Thermal ellipsoidal plot (50% probability level) of **4**. The PMe$_3$ carbon atoms and all hydrogen atoms are omitted for clarity. Selected bond lengths [Å] for **4**: Pt1–Pt2 2.706(2), Pt1–Pt3 2.717(2), Pt2–Pt3 2.700(2), Pt1–Ge1 2.356(4), Pt1–Ge2 2.799(4), Pt1–Ge3 2.895(4), Pt2–Ge2 2.393(4), Pt3–Ge3 2.419(4), Pt2–C1 2.30(3), Pt2–C2 2.39(3), Pt3–C1 2.06(4), Ge1–C2 2.00(3), C1–C2 1.43(5).

The ^{1}H NMR spectrum of **4** at –50 °C is consistent with the crystal structure. Variable-temperature ^{1}H NMR spectra show fluxional behavior of the molecule, which is interpreted by the interconvertion between the μ_3-germavinylene ligand of **4** and its enantiomer **4'**, as shown in Scheme 2. The dynamic process involves the switching motion of the σ,π-vinyl ligand, which bridges the two Pt centers. Triosmium alkenyl complexes [Os$_3$(CO)$_{10}$(μ-η^2-CR=CHR)(μ-H)] (R = H, Ph) were reported to undergo a similar interconvertion of the σ- and π-bonding alkenyl ligands on the Os$_3$ core.[10] The ^{195}Pt NMR spectrum contains a doublet of triplets assigned as the Pt1 nucleus at δ –4102 (^1J(P,Pt) = 3997 Hz and ^2J(P,Pt) = 307 Hz). Another ^{195}Pt NMR signal of the Pt2 and Pt3 atoms is observed as a severely broadened signal at δ –4466 with J(P,Pt) = ca. 3600 Hz. These nuclei could not be distinguished by NMR spectroscopy in spite of the dynamic motion of the molecule, probably owing to the close signal positions.



Scheme 2

Scheme 3 shows a comparison of the reactions of ZC≡CZ with **3** and [{Pt(PPh$_3$)}$_3$(μ-CO)$_3$].[3] The complex with bridging GePh$_2$ ligands undergoes insertion of ZC≡CZ into a Pt–Ge bond to yield a germadiplatinacyclopentene (**A**, upper route). The migration of the germyl group of the GePh$_2$-CZ=CZ ligand to the other Pt affords more stable **4** as the isolable product. An alternative pathway exists involving the shift of the bridging GePh$_2$ ligand of **A** to the Pt bonded with the vinyl group.[11] The Pt–Pt bonds are kept during the reaction. In contrast, the carbonyl-bridged Pt$_3$ complex forms adducts of the alkyne on the Pt$_3$ plane with the μ_3-η^2(||) bonding mode and terminal carbonyl ligands (**B**, lower route), and undergoes the fragmentation of the trinuclear complex to the dinuclear complex. The two distinct reactions are initiated by insertion of the alkyne and addition of the alkyl to a Pt–Pt bond, respectively. The interaction of π-orbitals of the alkynes with LUMO of the complexes should be important in determining the reaction pathway. In order to elucidate the details, we compared molecular orbitals of **3** and [{Pt(PMe$_3$)}$_3$(μ-CO)$_3$].[12]



Scheme 3

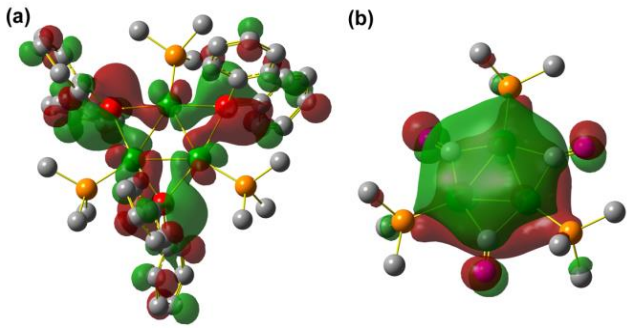


Figure 2. LUMO of (a) **3** and (b) [{Pt(PMe$_3$)}$_3$(μ-CO)$_3$], optimized by DFT calculations.

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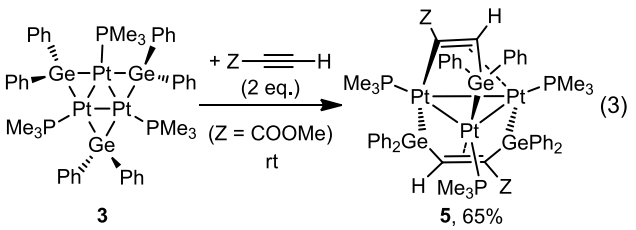
The HOMOs of these complexes are similar, and exist along the Pt–EPh_2 and Pt–CO bonds. As shown in Figure 2, the LUMO of **3** is located along the Pt–Ge bonds, and may take on the character of the *anti*-bonding orbital of the Pt-germylene bonds, whereas the LUMO of $[\{Pt(PMe_3)\}_3(\mu\text{-}CO)_3]$ spreads over the $Pt_3(CO)_3$ plane, which includes the Pt(0)–Pt(0) bonds. Thus, complex **3** undergoes facile insertion of the alkyne into the Pt–Ge bond, whereas $[\{Pt(PMe_3)\}_3(\mu\text{-}CO)_3]$ prefers addition of the alkyne to a Pt–Pt bond.

The reaction of **3** with methyl propiolate (ZC≡CH) in 1:2 ratio at room temperature afforded a triplatinum complex with a digermadiplatinacyclohexene moiety through the Ge–C bond-forming reactions, $[\{Pt(PMe_3)\}_3(\mu_3\text{-}\eta^2(\|)\text{-}CZ{=}CH\text{-}GePh_2)(\mu_3\text{-}\eta^2(\|)\text{-}GePh_2\text{-}CZ{=}CH\text{-}GePh_2)]$ (**5**, 65%) (Eqn (3)). An equimolar reaction of ZC≡CH with **3** forms a mixture of **5** and unreacted **3** instead of intermediates corresponding to **4**. It suggests that the reaction of the second alkyne molecule occurs rapidly than the first. Alkynes without strongly electron-withdrawing groups, such as PhC≡CPh and PhC≡CH, did not react with **3** even with heating at 70 °C.



3 **5**, 65%

The molecule of **5** also contains a triplatinum core with a μ_3-germavinylene ligand, and a digermadiplatinacyclohexene ligand is bonded at the opposite side of the Pt_3 plane (Figure 3). Two of the Pt–Pt bonds of **5** (2.749(1), 2.816(1) Å) are longer than those of the complexes **3** and **4**.[13] The six-membered digermadiplatinacycle is stabilized by two Ge–Pt σ-bonds and π-coordination of the vinylene group. A bis(silylene)-bridged diruthenium complex $[\{(C_5Me_5)Ru\}_2(\mu\text{-}H)_2(\mu\text{-}SiPh_2)_2]$ reacted with acetylene to give a dinuclear complex with a disilaruthenacyclopentene structure $[\{(C_5Me_5)Ru\}_2(\mu\text{-}H)_2(\mu\text{-}\eta^2\text{-}SiPh_2\text{-}CH{=}CH\text{-}SiPh_2)]$, which involved two Ru–Si σ-bonds and the C=C π-bond interaction with the Ru_2 centers.[14] The ^{1}H NMR spectrum of **5** at room temperature shows three inequivalent PMe_3 hydrogen signals (δ 1.24, 1.01, and 0.84) and six C_6H_5 *ortho* signals of each Ph group in the range of δ 8.42–7.96. In the $^{13}C\{^1H\}$ NMR spectra of **5**, six independent signals assignable to the C_6H_5 *ipso* carbon are observed at δ 150.5–142.3. These NMR spectroscopic data of **5** prove that there is no dynamic behavior below 80 °C. The vinylene carbon signal bonded to Pt of **5** at δ 185.8 involves a large ^{195}Pt satellite signal of 658 Hz, compared with the J(Pt,C) value of the Pt–C bond of **4** (δ 193.3, 394 Hz).

In summary, we prepared and completely characterized triplatinum complexes with bridging germylene ligands. The coordination of the electron-releasing germylene ligands with the Pt(0)-phosphine units composed of the d^{10} configuration may enhance reactivity for the alkyne insertion into the Pt–Ge bond. Several research groups have employed silylene and germylene ligands in the synthesis of multinuclear complexes of Fe,[15] Ru,[16] Os,[17] Rh,[18] Ir,[19] Ni,[20] Pd,[21] Pt,[22] and Au.[23] The reactivities of these complexes, however, were reported in only a part of them.[21] Further studies of this area will provide new chemistry of the cluster compounds.

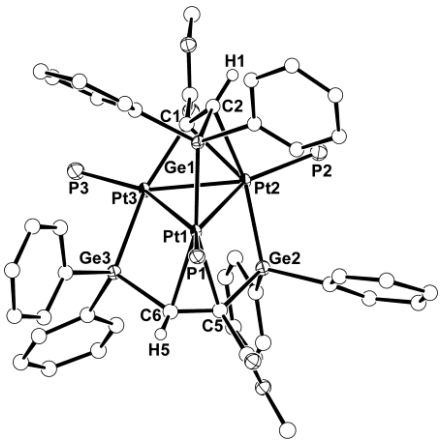


Figure 3. Thermal ellipsoidal plot (50% probability level) of **5**. The PMe_3 carbon atoms and all hydrogen atoms, except =CH hydrogen, are omitted for clarity. Selected bond lengths [Å] for **5**: Pt1–Pt2 2.749(1), Pt1–Pt3 2.816(1), Pt2–Pt3 2.695(1), Pt1–Ge1 2.418(2), Pt2–Ge2 2.370(2), Pt3–Ge3 2.389(2), Pt1–C5 2.44(2), Pt1–C6 2.381(2), Pt2–C1 2.20(2), Pt2–C2 2.31(2), Pt3–C1 2.08(2), Ge1–C2 1.95(2), Ge2–C5 1.98(2), Ge3–C6 2.01(2), C1–C2 1.45(2), C5–C6 1.34(2).

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Notes and references

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† Electronic Supplementary Information (ESI) available: Detailed experimental procedures, crystal structures, NMR spectra and DFT data for complexes. CCDC 979331 (**2**), 979332 (**3**), 979333 (**4**) and 979334 (**5**). See DOI: 10.1039/c000000x/

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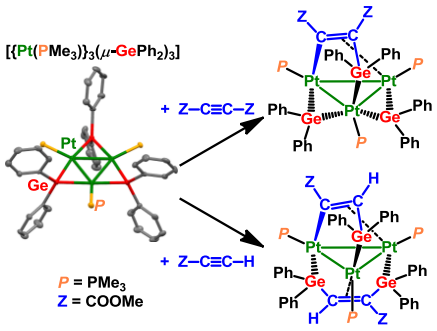
Summary "for table of contents for summary"

A triangular triplatinum(0) complex with bridging germylene ligands was prepared and fully characterized. The Pt_3Ge_3 core is bonded with electron-releasing $GePh_2$ and PMe_3 ligands. Insertion of electron-deficient alkyne molecules into the Pt–Ge bonds forms the germaplatinacyclic compounds, which was suppoted by DFT calculation.

Graphical abstract



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