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COMMUNICATION

Cationic Dinuclear Platinum and Palladium Complexes with Bridging Hydrogermylene and Hydrido Ligands

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Hydride-abstraction reactions of hydrido(dihydrogermyl) complexes [MH(GeH₂Trip)(dcpe)] [M = Pt, Pd, Trip = 9-triptycyl, dcpe = 1,2-bis(dicyclohexylphosphino)ethane] with B(C₆F₅)₃ led to the unexpected formations of new cationic (μ-germyl)(μ-hydrido) dinuclear platinum and palladium complexes, [{M(dcpe)}₂(μ-GeHTrip)(μ-H)]⁺.

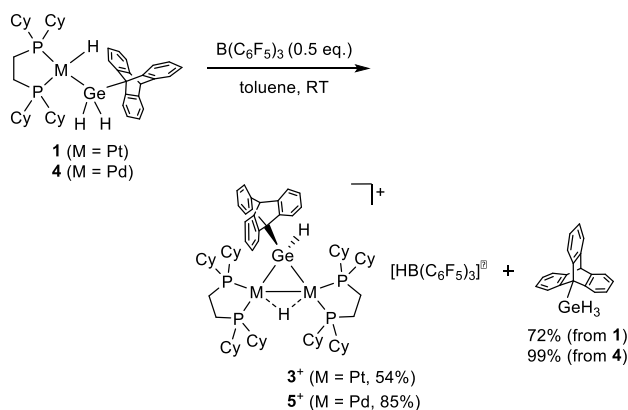
Dinuclear platinum and palladium complexes bearing bridging ligands have attracted attention because of their unusual circumstances arising from the strong electronic effect of two metal centers.¹ In particular, μ-silylene²⁻⁴ and μ-germylene^{5,6} dinuclear Group 10 metal complexes are of considerable interest for their unique structures and reactivity involving various coordination modes. As cationic analogues, although a few number of diplatinum complexes containing μ-alkylidene and μ-hydrido ligands, [{Pt(L-L)}₂(μ-CHR)(μ-H)]⁺ [L-L = chelate phosphine ligand], have been published,⁷ the synthesis and isolation of their μ-silylene or μ-germylene congeners have been scarce until now, probably due to a lack of suitable synthetic methods. Quite recently, Osakada et al. found the formation of cationic (μ₃-hydrido) triplatinum complexes with bridging secondary germylene ligands, [{Pt(PMe₃)}₃(μ-GeR₂)₃(μ₃-H)]⁺, by the protonation of neutral triplatinum complexes [{Pt(PMe₃)}₃(μ-GeR₂)₃] with HBF₄.⁸

Meanwhile, silylene complexes of the type [L_nM=SiR₂] have become of interest as potential intermediates in various transformations of organosilicon compounds.⁹ Among the synthetic strategies for the silylene complexes, 1,2-hydrogen migration from silicon to the metal center has been employed. In 1998, Tilley et al. demonstrated that the methyl-abstraction reaction of the silyl platinum(II) complex, [(dippe)Pt(Me)-(SiHMes₂)] with B(C₆F₅)₃ [dippe = 1,2-bis(diisopropylphosphino)ethane, Mes = 2,4,6-Me₃C₆H₂] to form an observable cationic silylene complex [(dippe)Pt(H)=(SiMes₂)]⁺.¹⁰ Recently, Hillhouse et. al. reported

that the one-electron oxidation of three-coordinated nickel(I) complex [(dtbpe)Ni(SiHMes₂)] [dtbpe = 1,2-bis(di-*tert*-butylphosphino)ethane] with ferrocenium gives a cationic complex [(dtbpe)Ni(μ-H)(SiMes₂)]⁺, which was formed by partial 1,2-hydrogen migration from silicon to nickel.¹¹ Herein, we present hydride-abstraction reactions of platinum(II) and palladium(II) hydrido complexes having a dihydrogermyl ligand, [MH(GeH₂Trip)(dcpe)]^{12,13} [M = Pt, Pd, Trip = 9-triptycyl, dcpe = 1,2-bis(dicyclohexylphosphino)ethane] with B(C₆F₅)₃ to produce the first example of cationic (μ-germyl)(μ-hydrido) dinuclear platinum and palladium complexes, [{M(dcpe)}₂(μ-H)(μ-GeHTrip)]⁺ [M = Pt, Pd]. We also describe substitution reactions of the hydrogen atom on the bridging germylene ligand of the dinuclear complexes by a chlorine atom.

It was expected that the hydride-abstraction reaction of [PtH(GeH₂Trip)(dcpe)] **1** with B(C₆F₅)₃ would provide a possibility to form the cationic mononuclear hydrogermylene complex, [(Pt=GeHTrip)(μ-H)(dcpe)]⁺ (**2**⁺). When the reaction of **1** was carried out using 0.5 equiv. of B(C₆F₅)₃ in toluene at room temperature, a new cationic (μ-hydrido)(μ-germyl) diplatinum(I) complex, [{Pt(dcpe)}₂(μ-H)(μ-GeHTrip)]⁺ (**3**⁺), which was isolated in the form of a [HB(C₆F₅)₃]⁻ salt as air-stable yellow crystals in 54% yield instead of the expected **2**⁺. In this reaction, trihydrogermane (TripGeH₃) was also produced as a byproduct in 72% yield (Scheme 1).¹⁴ In the ¹H NMR of **3**⁺·[HB(C₆F₅)₃]⁻, the characteristic μ-hydride was observed as a triplet of triplet signal at δ -1.79 (*J*(P(*cis*),H) = 10, *J*(P(*trans*),H) = 67 Hz) accompanying satellites due to ¹⁹⁵Pt-¹H (*J*(Pt,H) = 452 Hz) couplings. This chemical shift is comparable to those of the reported cationic (μ-hydrido)(μ-alkylidene) diplatinum(I) complexes, [{Pt(dppe)}₂(μ-H)(μ-CHCH₂Ph)]⁺ (δ -0.35)^{7a} and [{Pt(dppf)}₂(μ-H)(μ-CHCH₂CH₃OC₆H₄)]⁺ (δ -3.31).^{7c} The germylene proton appeared as a triplet signal at δ 8.00 (*J*(P,H) = 10, *J*(Pt,H) = 135 Hz), which is

significantly shifted to down-field relative to that of the starting complex **1** (δ 5.25)¹². The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $3^+[\text{HB}(\text{C}_6\text{F}_5)_3]^-$ exhibited two nonequivalent singlet signals at δ 61.4 and δ 70.8 corresponding to chemically nonequivalent P atoms in the dcpe ligand. While the singlet at δ 61.4 has broad satellite signals due to the ^{195}Pt isotope ($J(\text{Pt},\text{P}) = 2232$ Hz), the singlet at δ 70.8 accompanies clear satellite signals of an AA'X spin system due to two ^{31}P and one ^{195}Pt nuclei, in which one of the two Pt atoms in 3^+ is NMR active to make two ^{31}P atoms nonequivalent magnetically, to give coupling constants of $^3J(\text{P},\text{P}) = 35$ Hz, $^1J(\text{Pt},\text{P}) = 3848$ Hz, and $^2J(\text{Pt},\text{P}) = 279$ Hz.¹⁵ These ^{195}Pt - ^{31}P coupling constant values are significantly larger than those of the starting complex **1**, indicating that the Pt–P bonds became stronger as a result of weakening of the Pt–H and Pt–Ge bonds due to the bridging coordination of Pt(I) atoms. According to ^{195}Pt - ^{31}P coupling constant values, the lower field resonance (δ 70.8) is assignable to the phosphorus atom lying trans to the bridged hydrido ligand, while the remaining one (δ 61.4) can be attributed to the phosphorus atom lying trans to the germylene ligand. Although the formation mechanism of $3^+[\text{HB}(\text{C}_6\text{F}_5)_3]^-$ is not clear at present, it is possible to speculate that the hydride abstraction from **1** by $\text{B}(\text{C}_6\text{F}_5)_3$ occurs via 1,2-hydrogen migration from germanium to platinum to form the cationic complex, $[(\text{Pt}=\text{GeHTrip})(\mu\text{-H})(\text{dcpe})]^+ \mathbf{2}^+$, as an initial intermediate. Then, the reaction of $\mathbf{2}^+$ with the hydrido complex **1** still remaining in the reaction system took place, followed by the elimination of TripGeH_3 by the resulting Pt–Ge and Pt–Pt bonds to yield the final complex $3^+[\text{HB}(\text{C}_6\text{F}_5)_3]^-$ (see ESI).



Scheme 1 Reactions of $[\text{MH}(\text{GeH}_2\text{Trip})(\text{dcpe})]$ (M = Pt, Pd) with $\text{B}(\text{C}_6\text{F}_5)_3$.

In a similar manner, the palladium congener $[\text{PdH}(\text{GeH}_2\text{Trip})(\text{dcpe})]$ **4** was treated with 0.5 eq. of $\text{B}(\text{C}_6\text{F}_5)_3$ in toluene at room temperature to lead to the formations of the corresponding cationic dinuclear complex $[\{\text{Pd}(\text{dcpe})\}_2(\mu\text{-H})(\mu\text{-GeHTrip})]^+[\text{HB}(\text{C}_6\text{F}_5)_3]^-$ ($5^+[\text{HB}(\text{C}_6\text{F}_5)_3]^-$) and TripGeH_3 in 85% and 99% yields, respectively. Accordingly, a triplet resonance for the bridging μ -hydride was observed in the ^1H NMR spectrum of 5^+ at δ -5.02 with ^{31}P - ^1H ($J(\text{P}(\text{cis}),\text{H}) = 7$, $J(\text{P}(\text{trans}),\text{H}) = 82$ Hz) coupling constants. Compared with the analogous chemical shift of its platinum counterpart 3^+ (δ -1.79), the signal in 5^+ is somewhat high-field shifted because of the smaller electronegativity of palladium (Pd: 2.20

vs. Pt: 2.28).¹⁶ In addition, the corresponding Ge–H resonance also displays a triplet at δ 8.42, which is comparable to that of the platinum analogue 3^+ shown above. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of 5^+ featured two ^{31}P resonances as doublet signals at δ 58.0 and δ 72.9 ($J(\text{P},\text{P}) = 21$ Hz).

The molecular structure of $3^+[\text{HB}(\text{C}_6\text{F}_5)_3]^-$ was supported by a X-ray structure as illustrated in Figure 1. The X-ray diffraction of $3^+[\text{HB}(\text{C}_6\text{F}_5)_3]^-$ revealed that the central Pt_2Ge three-membered ring is an almost isosceles triangle with bond angles of 73.364(19), 53.389(14), and 53.247(15)°, and is orientated perpendicular to the C–Ge–H plane from the germylene moiety. The hydrogen atom bridged between the Pt–Pt bond was located in the Fourier map at ca. 1.85 Å from both platinum atoms and refined isotropically. The Pt1–Pt2 distance of 2.9276(4) Å is substantially elongated compared with that of the neutral (μ -germyl) diplatinum(I) complexes $[\{\text{Pt}(\text{PPh}_3)_2(\mu\text{-HGePh}_2)\}]$ (2.7452(3) Å)^{5a}, and cationic (μ -hydrido)(μ -alkylydenyl) diplatinum(I) complexes, $[\{\text{Pt}(\text{dppe})\}_2(\mu\text{-H})(\mu\text{-CHCH}_2\text{Ph})]^+$ [2.735(1) Å]^{7a} and $[\{\text{Pt}(\text{dppf})\}_2(\mu\text{-H})(\mu\text{-CHCH}_2p\text{-CH}_3\text{OC}_6\text{H}_4)]^+$ [2.7314(4) Å]^{7b}. The μ -bridged Ge–Pt bond lengths (2.4481(6) and 2.4527(6) Å) are slightly longer than those of **1** (2.4162(4) Å) and lie in the range for neutral (μ -germyl) diplatinum(I) complexes (2.3821(4)–2.4785(4) Å).⁵

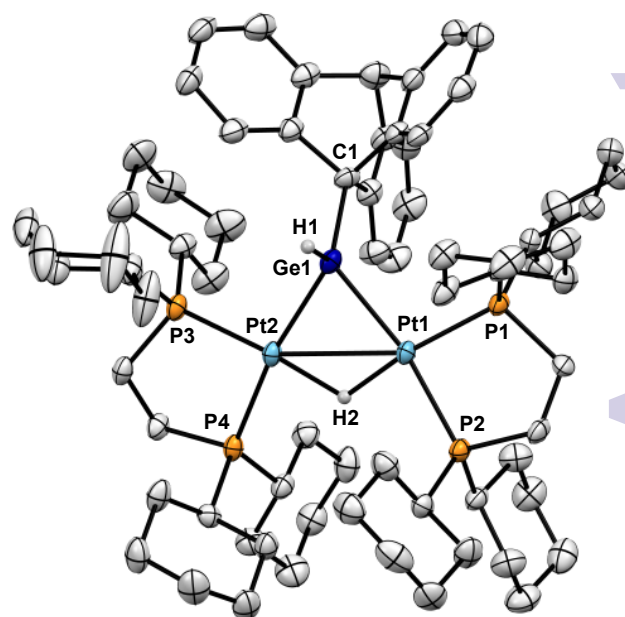


Fig. 1 ORTEP diagram of 3^+ (50% thermal ellipsoid, counter anion $[\text{HB}(\text{C}_6\text{F}_5)_3]^-$ and hydrogen atoms except H1 and H2 were omitted for clarity). Selected bond lengths [Å] and angles [°]: Pt1–Pt2 2.9321(3), Pt1–Ge1 2.4534(5), Pt2–Ge1 2.4492(5), Pt1–P1 2.2547(12), Pt1–P2 2.3296(12), Pt2–P3 2.3135(13), Pt2–P4 2.2610(12), Pt1–H2 1.853(10), Pt2–H2 1.846(10), Pt1–Ge1–Pt2 73.464(16), Ge1–Pt1–Pt2 53.203(13), Ge1–Pt2–Pt1 53.333(12).

To understand the nature of bonding in 3^+ , a DFT calculation was carried out using $[\{\text{Pt}(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)\}_2(\mu\text{-H})(\mu\text{-GeH}^t\text{Bu})]^+$ (6^+) as a model complex (Figure 2).¹⁷ The optimized structural parameters for 6^+ are in fairly good agreement with the experimentally observed values of 3^+ (e.g., Ge–Pt = 2.464 and 2.471 Å, Pt–Pt = 2.920 Å, Pt–H = 1.783 and 1.846 Å).

1.785 Å). Both HOMO and LUMO+1 of 6^+ are exclusively assigned to the bonding and antibonding interactions, respectively, between the d_{xy} -orbitals on the platinum atoms and the 4p-orbital on the germanium atom. In sharp contrast, LUMO of 6^+ is represented by the delocalized vacant d-orbital on the Pt–Pt bond. Additionally, both HOMO-7 and LUMO+3 of 6^+ participate in a three-center two-electron bond using the 1s-orbital of the hydrogen atom and the 6d-orbitals on each platinum atom.

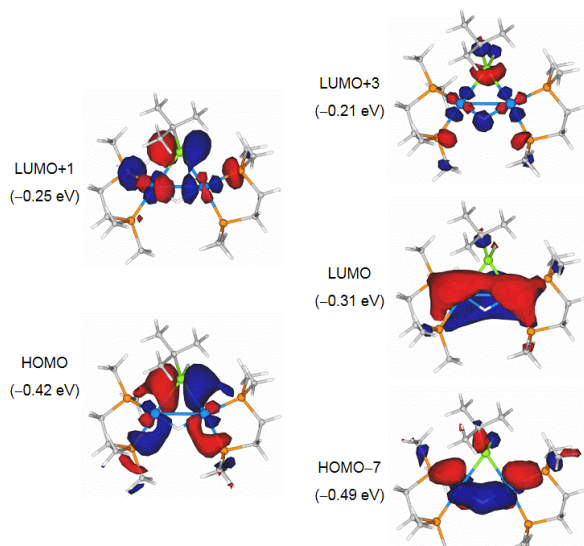
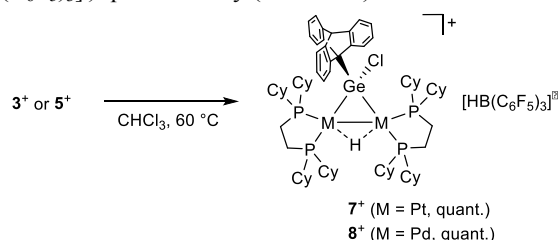


Fig. 2 Molecular orbital diagrams of $[\{Pt(Me_2PCH_2CH_2PMe_2)\}_2(\mu-H)(\mu-GeH^tBu)]^+ 6^+$.

It was reported that cationic or neutral hydrogermylene complexes undergo hydrogermylation reactions with alkenes, alkynes, carbonyl compounds, and nitriles.¹⁸ Moreover, neutral hydrogermylene species incorporated in bulky β -diketimido ligands have exhibited small-molecule activations toward the Ge–H bond.¹⁹ Thus, since it is of interest to explore the potential for the reactivity of hydrogermylene compounds, we next examined the reactivity of cationic dinuclear complexes 3^+ ·[HB(C₆F₅)₃] and 5^+ ·[HB(C₆F₅)₃]. Chlorination reactions of the bridging hydrogermylene moiety of 3^+ and 5^+ proceeded gradually in CHCl₃ at 60 °C to afford the corresponding chlorogermylene complexes, $[\{M(dcpe)\}_2(\mu-H)(\mu-GeClTrip)]^+ \cdot [HB(C_6F_5)_3]^-$ (M = Pt, 7^+ ·[HB(C₆F₅)₃], M = Pd, 8^+ ·[HB(C₆F₅)₃]) quantitatively (Scheme 2).²⁰



Scheme 2 Chlorination of 3^+ or 5^+ in CHCl₃.

In the ¹H NMR spectra of 7^+ and 8^+ , indeed, the low-field shifted germylene protons disappeared completely and the bridging μ -hydrides give rise to a triplet of triplet signal at δ –2.34 ($J(P(cis),H) = 10$, $J(P(trans),H) = 66$ Hz) with ¹⁹⁵Pt

satellites ($J(Pt,H) = 449$ Hz) for 7^+ and at δ –5.57 ($J(P(cis),H) = 5$, $J(P(trans),H) = 81$ Hz) for 8^+ , respectively, which are high-field shifted in comparison with those of 3^+ and 5^+ . Crystals of 7^+ ·[HB(C₆F₅)₃] and 8^+ ·[HB(C₆F₅)₃] were grown from a saturated toluene or fluorobenzene solution at room temperature and the crystal structures of 7^+ ·[HB(C₆F₅)₃] and 8^+ ·[HB(C₆F₅)₃] were confirmed by X-ray analysis to show that they were almost isomorphous (see ESI). As depicted in Figure 3, the Pd1–Pd2 distance [2.9075 (6) Å] of 8^+ was significantly longer than those in the related 9-triptyceneselenolato-bridged dinuclear palladium(I) complex, $[\{Pd(PPh_3)\}_2(\mu-SeTrip)]^+$ [2.5821(6) Å],²¹ and the cationic (μ -carbonyl)(μ -hydrido) dipalladium(I) complexes, $[\{Pd(dipp)\}_2(\mu-H)(\mu-CO)]^+$ [2.767(4) Å]²² and $[\{Pd(bipy)\}_2(\mu-H)(\mu-CO)]^+$ [2.691(3) Å].²³ Both of the Pd1–Ge1 and Pd2–Ge1 distances [2.4166(7) and 2.4314(7) Å] were close to those observed in neutral (μ -germyl)(μ -hydrido) di- and tetrapalladium(I) complexes $[\{Pd(PCy_3)\}_2(\mu-HGePh_2)_2]$ [2.440(1) and 2.415(1) Å]^{6a} and $[\{Pd_3(\mu-GePh_2)_2(\mu-H)(\mu_3-GePh_2(SC_6H_4^tBu-4))\}_2(\mu-dmpe)]$ [2.386(2) and 2.436(2) Å].²⁴ The bridging hydrogen atom was located in the electron density map and has Pd–H distance of 1.89(5) and 1.67(5) Å. Of interest is the fact that there exist intramolecular interactions between the chlorine atom and the aromatic hydrogen atoms on the 9-triptycyl group [2.758 and 2.814 Å]. In fact, in the ¹H NMR for 7^+ and 8^+ , three phenyl groups in the 9-triptycyl group appeared as non-equivalent signals in the ratio of 2 : 1 due to the observed interactions. Thus, this non-equivalence would be due to slow rotation by the steric effect on the NMR time scale.

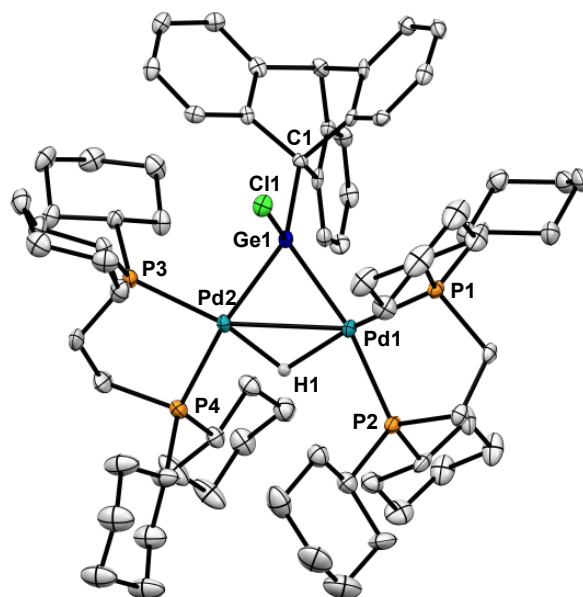


Fig. 3 ORTEP diagrams of 8^+ (50% thermal ellipsoid, counter anion [HB(C₆F₅)₃], a solvated C₆H₅F molecule, and hydrogen atoms except H1 were omitted for clarity). Selected bond lengths [Å] and angles [°]: Pd1–Pd2 2.9075(6), Pd1–Ge1 2.4166(7), Pd2–Ge1 2.4314(7), Pd1–P1 2.3014(14), Pd1–P2 2.3336(13), Pd2–P3 2.2936(14), Pd2–P4 2.3700(15), Pd1–H1 1.89(5), Pd2–H1 1.67(5), Pd1–Ge1–Pd2 73.70(2), Ge1–Pd1–Pd2 53.383(16), Ge1–Pd2–Pd1 52.918(16).

In summary we demonstrated that the cationic (μ -germyl)(μ -hydrido) dinuclear complexes, $[\{M(dcpe)\}_2(\mu-GeHTrip)(\mu-H)]^+$ [M = Pt, Pd] were obtained unexpectedly by the hydride-abstraction reactions of $[MH(GeH_2Trip)(dcpe)]^+$ with B(C₆F₅)₃. These complexes are of particular interest as

they represent the first cationic diplatinum and dipalladium complexes bridging both the germyl and hydrido ligands. Further investigations on these complexes are currently underway.

Electronic supplementary information (ESI) available: Experimental section, spectral data, crystallographic data, plausible formation mechanism, and computational details. CCDC 1055408–1055410. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c000000x/

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