Reaction Mechanisms

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Bond Formation and Coupling between Germyl and Bridging Germylene Ligands in Dinuclear Palladium(I) Complexes**

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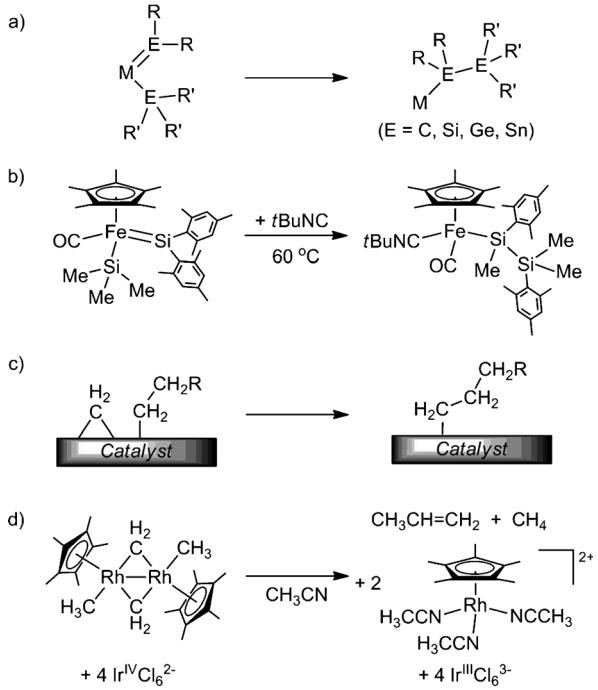
Abstract: *The dinuclear palladium(I) complexes [L-(Ar$_2$HGe)Pd(μ-GeAr$_2$)$_2$Pd(GeHAr$_2$)L] (Ar = Ph, p-Tol; L = PMe$_3$, tBuNC) contain terminal germyl and bridging germylene ligands with the experimentally observed Ge···Ge bond lengths of 2.8263(4) Å (L = PMe$_3$) and 2.928(1) Å (L = tBuNC), which are close to the longest Ge–Ge bond reported to date [2.714(1) Å]. Significant Ge···Ge interactions between the germylene and germyl ligands (PMe$_3$ complexes > tBuNC complexes) are supported by DFT calculations, Wiberg bond indices (WBI), and natural bond orbital (NBO) analyses. Exchanging tBuNC for PMe$_3$ ligands increases the Ge···Ge interaction, and simultaneously activates two Pd–Ge bonds. Adding the chelating diphosphine 1,2-bis(diethylphosphino)-ethane (depe) to the PMe$_3$ complexes results in the intramolecular coupling of germyl and germylene ligands followed by extrusion of a digermane.*

For various transition-metal-catalyzed reactions, such as the polymerization of methylene precursors by palladium catalysts,[1] Fischer–Tropsch reactions on the surface of iron-based catalysts,[2] and the oligomerization of disilanes, trisubstituted germanes, and dialkyl stannanes promoted by platinum, nickel, ruthenium, rhodium, and palladium complexes,[3] bond-formation reactions were proposed between two carbon-, silicon-, germanium-, or tin-containing ligands coordinated to the metal by either a single or double bond (Scheme 1a). Although many research groups have documented and discussed similar reactions for transition-metal complexes with silicon and germanium ligands,[4] only few examples including isolated complexes, for example, a 1,2-silyl migration on an iron complex (Scheme 1b), have been reported.[5] The conversion of in situ prepared mononuclear ruthenium, iridium, and tungsten complexes, containing methylene, methyl, or phenyl ligands, into the corresponding complexes with ethyl or benzyl ligands, was tentatively assigned to C–C bond-formation reactions between methylene and alkyl ligands.[6] The Fischer–Tropsch reaction was proposed to proceed either by an insertion of a methylene, bridging two metal centers, to afford metal–alkyl (M-CH$_2$-R)[7] or metal–alkenyl (M-CH=CHR) bonds[8] (Scheme 1c), or by coupling between the methylene and alkylidene ligands and the alkyl ligand.[9] The former pathway was investigated by Maitlis and co-workers, who used dinuclear rhodium and iridium model complexes containing methyl and bridging methylene ligands.[10] Chemical oxidation of these complexes with [IrCl$_6$]$^{2-}$ resulted in the formation of propylene by insertion of the bridging methylene ligand (Scheme 1d).[11] Bond formation between two different ligands within a bimetallic framework remains a highly important, yet still obscure area in the field of organotransition-metal chemistry. Herein, we report the structure of two bimetallic palladium(I) complexes, each containing a germyl and a bridging germylene ligand, as well as their Ge–Ge bond-forming reactions through an expected reaction mechanism.



Scheme 1. Representative examples for 1,1-insertion of carbene analogues into M–E (E = C, Si, Ge, Sn) bonds.

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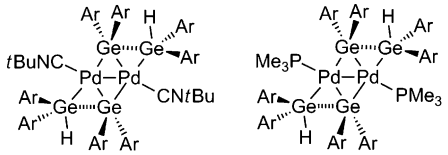
Dipalladium complexes [(*t*BuNC)(Ar_2HGe)Pd(μ-$GeAr_2$)$_2$Pd($GeHAr_2$)(CN*t*Bu)] (**1a**: Ar = Ph; **1b**: Ar = *p*-Tol) and [(Me_3P)(Ar_2HGe)Pd(μ-$GeAr_2$)$_2$Pd($GeHAr_2$)(PMe_3)] (**2a**: Ar = Ph; **2b**: Ar = *p*-Tol) were prepared from *cis*-[$PdMe_2(PMe_3)_2$], H_2GeAr_2, and *t*BuNC. Single crystals, suitable for X-ray diffraction analysis,[12] were obtained from



1a: Ar = Ph
1b: Ar = *p*-Tol

2a: Ar = Ph
2b: Ar = *p*-Tol

the diffusion of *n*-hexane into toluene (**1a**, **1b**) or THF (**2a**) solutions containing the respective target compound.

The complexes **1a** and **2a** adopt similar structures with a planar [Pd_2Ge_4] core exhibiting a close contact between the Ge atoms of the germyl and germylene ligands (Figure 1a). The observed Ge···Ge bond lengths [**1a**: 2.928(1) Å; **2a**: 2.8263(4) Å] are close to the longest Ge–Ge σ bond reported

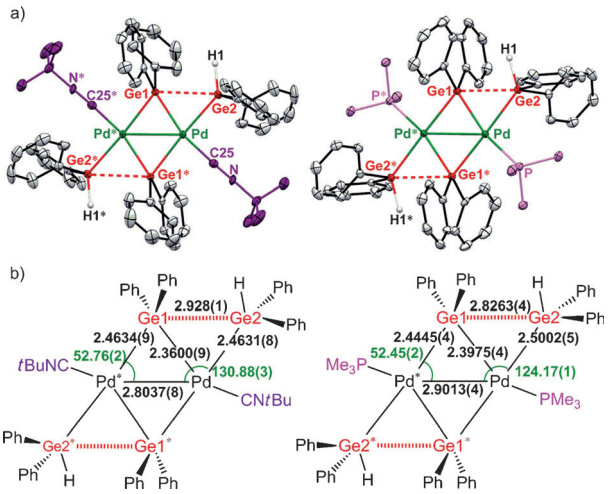


Figure 1. a) ORTEP representation of **1a** and **2a** with thermal ellipsoids set at 50% probability. Carbon-bound hydrogen atoms are omitted for clarity. **1a** and **2a** contain a crystallographic center of symmetry in the middle of the Pd–Pd* bond. Atoms with asterisks are crystallographically equivalent to those having the same number without asterisks. b) Selected bond lengths [Å] and angles [°] for **1a** and **2a**.

so far [2.714(1) Å],[13,14] and much shorter than the corresponding bond lengths in other dinuclear transition-metal complexes, such as [{(OC)(Ph_3Ge)Pt}(μ-$GePh_2$)$_2${Pt($GePh_3$)(CO)}] [3.1803(5) Å][15] or [{(OC)$_2$(Ph_2HGe)HIr}(μ-$GePh_2$)$_2$[IrH($GeHPh_2$)(CO)$_2$}] [3.179(1) Å].[16] For the complex **2a**, containing PMe_3 ligands, a shorter Ge···Ge distance and a smaller Pd*-Pd-Ge2 angle [124.17(1)°] were observed relative to those in **1a** which has *t*BuNC ligands [130.88(3)°], thus suggesting significantly higher levels of interaction between the Ge atoms of the former complex relative to the latter. Important metric parameters of the [Pd_2Ge_4] moiety in **1a** and **2a** are summarized in Figure 1b. The Pd–Ge1 bond lengths in **1a** [2.3600(9) Å] and **2a** [2.3975(4) Å] are comparable to the Pd=Ge bond lengths in mononuclear palladium complexes with germylene ligands, such as [(R_3P)$_2$Pd=Ge{N($SiMe_3$)$_2$}$_2$] [R = Et: 2.330(5) Å; R = Ph: 2.3281(4) Å],[17] and shorter than in other complexes with Pd–Ge bonds [2.4259(2)–2.5024(4) Å].[4c] The complex **2a** contains a shorter Pd*–Ge1 bond [2.4445(4) Å], and longer Pd–Ge1 [2.3975(4) Å] and Pd–Ge2 [2.5002(5) Å] bonds compared to those of **1a** [2.4634(9) Å, 2.3600(9) Å, and 2.4631(8) Å, respectively].

To examine the stability of these bonds and the interaction in the complexes, density functional theory (DFT) calculations were carried out for **1a** and **2a** at the ωB97X-D/6-31G(d) and SDD (for Pd) level of theory using Gaussian 09. The Ge···Ge bond lengths in **1a** (2.931 Å) and **2a** (2.811 Å) obtained from DFT calculations are in good agreement with the metric parameters obtained from the X-ray diffraction experiments [2.928(1) Å and 2.8263(4) Å, respectively]. The HOMO of both complexes was found to be localized on the Ge···Ge moieties and the Pd*–Ge1 bonds, thus corroborating the presence of bonding interactions between the Ge atoms. The Wiberg bond indices (WBI) of **1a** (0.397) and **2a** (0.487) suggest Ge···Ge interactions in both complexes, whereby the interaction in **2a** is significantly more pronounced than that in **1a**.

Natural bond orbital (NBO) second-order perturbation energy analysis of **1a** and **2a** revealed that the dominant interaction corresponds to a donation of electron density from the Ge···Ge σ orbital to an empty 5s orbital of the Pd center (Figure 2a).[18] The calculated NBO interaction energies (193.6 kcal mol^{-1}) and the back-donation from the occupied $d_{x^2-y^2}$ orbital of the Pd center to the Ge···Ge σ* orbital of **2a** (22.8 kcal mol^{-1}; Figure 2b) are significantly smaller than those of **1a** (315.1 and 35.9 kcal mol^{-1}, respectively), while the

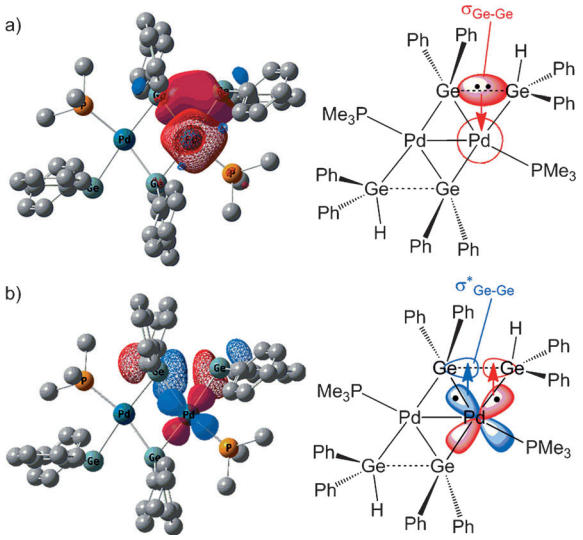
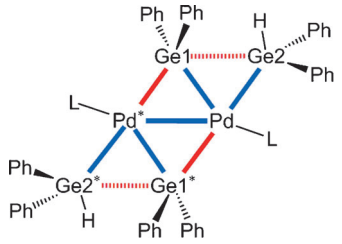


Figure 2. Results of the NBO analysis for **2a**. a) Electron donation from the filled Ge···Ge σ orbital into the empty 5s orbital on palladium. b) Electron back-donation from a filled $d_{x^2-y^2}$ orbital on palladium into the empty σ* orbital of the Ge···Ge bond.

electron occupancy for the Ge···Ge σ orbital of **1a** (1.552) is smaller than that of **2a** (1.621). Thus, electron localization in the Ge···Ge σ orbital is significantly higher for **2a** relative to **1a**. All these results suggest that the increase of Ge···Ge interaction is directly correlated to the activation of both the Pd–Ge1 and Pd–Ge2 bonds. They also suggest that these changes are closely associated to their bond lengths and strengths, and that the interaction occurs in a concerted manner. The formation of a three-center-two-electron Ge–H···Ge bond as an explanation for the observed close contact of the Ge atoms can be excluded based on the analysis of the X-ray diffraction experiments [Pd-Ge2-C angles for **1a**: 106.1(2)°/104.8(2)°; **2a**: 111.56(7)°/108.95(8)°], the chemical shift of the Ge–H hydrogen atoms ($\delta_H = 5.28$–5.37 ppm) in the ^{1}H NMR spectra, and the results of the NBO analysis between the Ge–H bonding orbital and the orbitals of the bridging germylene ligands.

The bonds between the Pd^I centers in these complexes exhibit smaller WBI indices (**1a**: 0.174, **2a**: 0.149) and are longer [**1a**: 2.8037(8) Å, **2a**: 2.9013(4) Å] compared to other dinuclear palladium(I) complexes such as [(PCy$_3$)Pd(μ-GeHPh$_2$)$_2$Pd(PCy$_3$)] [2.752(1) Å][19] or [(Me$_3$P)Pd(μ-SiHPh$_2$)$_2$Pd(PMe$_3$)$_n$] [$n = 1$, 2.691(1) Å; $n = 2$, 2.740(1) Å].[20] Based on X-ray and DFT results, the metal–metal bonds in the PMe$_3$-containing complexes (**2a**, **b**) are significantly more destabilized compared to those in **1a**, **b**. Thus, it can be concluded that all the bond distances between the Pd and Pd(Ge) atoms are influenced by the auxiliary ligands. A color-coded scheme based on the X-ray crystallography and DFT analyses (Scheme 2) shows which bonds are elongated and shortened as a result of exchanging *t*BuNC for PMe$_3$ ligands. In comparison with the electron-accepting *t*BuNC ligand, the electron-donating PMe$_3$ ligand activates the Pd–Ge1, Pd–Ge2, and Pd–Pd* bonds, whereas it stabilizes the Pd*–Ge1 bond and the Ge1···Ge2 interaction.

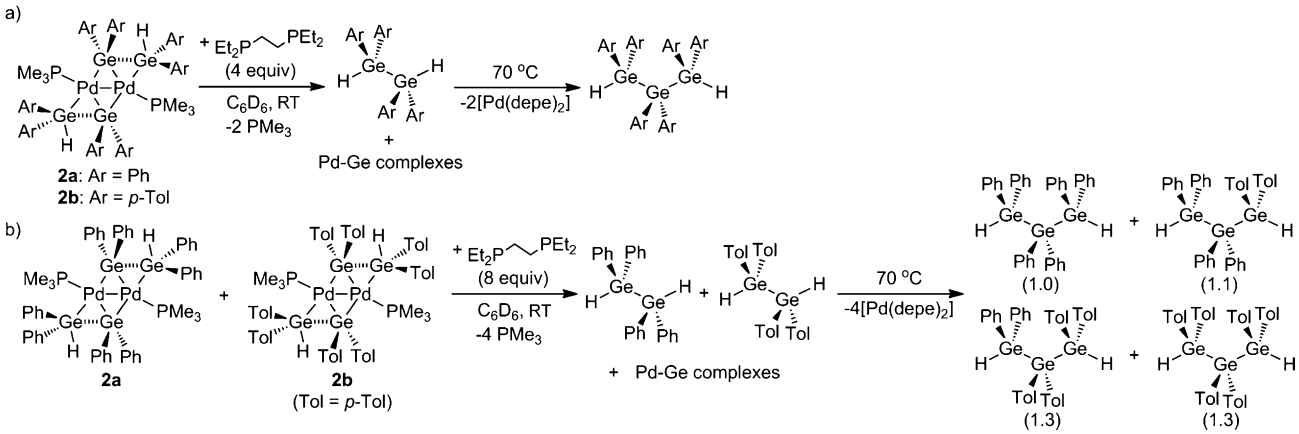
Upon addition of the bidentate diphosphine 1,2-bis(diethylphosphino)ethane (depe), **2a** released 1,1,2,2-tetraphenyldigermane H(GePh$_2$)$_2$H, which was observed in the ^{1}H NMR spectrum of the reaction mixture after 30 minutes. Further reaction slowly converted a proportion of this



Scheme 2. The effect of the auxiliary ligand L (PMe$_3$ or *t*BuNC) on the bond lengths in **1a** and **2a**. Exchanging *t*BuNC with PMe$_3$ results in a contraction of the red bonds and an elongation of the blue bonds.

digermane into 1,1,2,2,3,3-hexaphenyltrigermane H(GePh$_2$)$_3$H, and heating the reaction mixture to 70 °C completed the reaction, thus affording H(GePh$_2$)$_3$H and [Pd(depe)$_2$] as the final products (Scheme 3a). A crossover experiment using a mixture of **2a** and **2b** revealed that the formation of the digermane involved an intramolecular Ge–Ge bond-forming process as outlined below (Scheme 3b; Tol = *p*-Tol). The addition of an excess of depe (8 equiv) to an equimolar mixture of **2a** and **2b** produced homodigermanes H(GePh$_2$)$_2$H and H(GeTol$_2$)$_2$H as the major products of the initial period ($t < 30$ min), and two additional minor ^{1}H NMR signals ($\delta_H = 5.617$ and 5.622 ppm) were assigned to the Ge–H hydrogen atoms of the heterodigermane 1,1-diphenyl-2,2-ditolyldigermane H(GePh$_2$GeTol$_2$)H (Figure 3).

The product mixture obtained after heating to 70 °C contained the four trigermanes [H(GePh$_2$)$_3$H], [H(GePh$_2$)$_2$(GeTol$_2$)H] ($\delta_H = 5.719$ and 5.727 ppm), [H(GePh$_2$)(GeTol$_2$)$_2$H] ($\delta_H = 5.744$ and 5.750 ppm), and [H(GeTol$_2$)$_3$H] in a 1.0:1.1:1.3:1.3 ratio. Symmetrically mixed trigermanes [H(GePh$_2$)(GeTol$_2$)(GePh$_2$)H] and [H(GeTol$_2$)(GePh$_2$)(GeTol$_2$)H], which could be formed from [H(GePh$_2$GeTol$_2$)H], were obtained in much smaller amounts. Scheme 4 shows a possible pathway for the formation of the digermanes. Initial coordination of the chelating diphosphine to a palladium center enhances the bond formation between the germyl and germylene ligands (**A**). The resulting digermyl ligand and a hydride, formed by α-



Scheme 3. Ge–Ge bond-formation reactions in dipalladium complexes with terminal germyl and bridging germylene ligands. a) Reaction of **2a** and **2b** with depe at room temperature. b) Crossover experiment between **2a** and **2b** and depe.

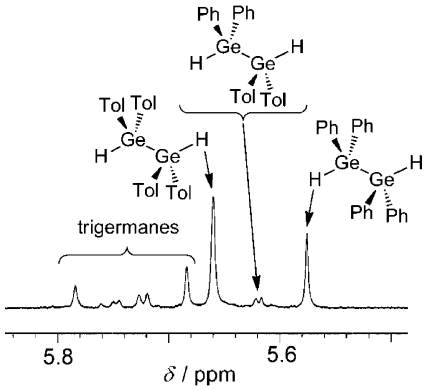
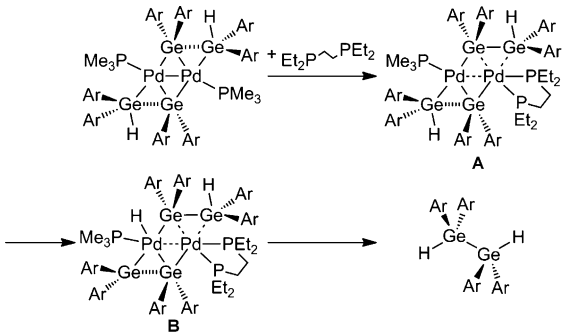


Figure 3. ^{1}H NMR spectrum of the crossover reaction (reaction mixture) in C_6D_6 after 1 hour at room temperature.



Scheme 4. A possible pathway for the Ge–Ge bond formation in dipalladium(I) complexes.

hydrogen elimination from the other germyl ligand (**B**), undergo coupling to form the digermane. Thus, the intramolecular coupling of the terminal germyl and bridging germylene ligands to form a digermyl ligand occurs initially, and is followed by intra- or intermolecular hydrogen abstraction to produce the extruded digermanes.

In summary, the structures of dipalladium(I) complexes with bridging germylene and terminal germyl ligands and auxiliary *t*BuNC or PMe_3 ligands, revealed that the electron-donating PMe_3 ligands increase Ge···Ge interactions under concomitant activation of two Pd–Ge bonds. Rather than considering this reactivity as an insertion of a reactive germylene ligand into a metal–germyl bond, the synchronized activation and bond-formation reactions should be classified similar to the reductive elimination of a molecule from the corresponding diorgano transition-metal complexes under formation of a new C–C bond. It is well known, that the stability and reactivity of a metal–carbon bond in mononuclear transition-metal complexes varies significantly depending on the auxiliary ligand.[21] In the dinuclear complexes of this study, the two metal centers change their respective coordination bonds in a different but cooperative way, and thus achieve bond formation and activation. Shimada, Tanaka, and co-workers reported nickel(0)-promoted cyclodimerization of 1,2-disilabenzene, which may also involve formation of Si–Si bonds from the terminal silyl and bridging silylene ligands of a dinickel intermediate.[4a,22] Because of the cooperative interaction of the metal centers in di- or multinuclear transition-metal complexes, new reactions and reaction pathways should be possible and expected for these complexes.

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