A Z-type PGeP pincer germylene ligand in a T-shaped palladium(0) complex

Javier A. Cabeza,^{*a} Pablo García-Álvarez,^a Carlos J. Laglera-Gándara^a and Enrique Pérez-Carreño^b

A dipyrromethane-based germylene decorated with two phosphane groups has been used to prepare an unusual T-shaped palladium(0) complex containing a PGeP pincer germylene that acts as a Z-type ligand. This compound is a strong reducing reagent, as it has been easily oxidized to germyl-palladium(II) derivatives with a gold(I) complex, HCl and Ph₂S₂ through processes that involve a formal addition of a bond of the oxidant across the Ge–Pd bond.

Germynes decorated with two phosphane groups having a potential PGeP pincer-type topology¹ are a new class of compounds that are expected to combine the easy tunability of the electronic and steric properties of germynes² and phosphanes³ with the interesting applicability that pincer-type ligands have already demonstrated in organometallic chemistry and catalysis.⁴ Although only a few germynes of this type have been reported to date (compounds **A–F** in Fig. 1),^{5–10} their yet scarce transition metal derivative chemistry^{5–9,11} has already afforded very interesting results, including rare T-shaped PGeP chloridogermyl complexes of gold(I)^{7,8} and silver(I).⁸

However, the transition metal chemistry of PGeP germynes **A–D** is dominated by reactions that, involving the insertion of the germylene Ge atom into M–X bonds (M = metal; X = metal, halogen), lead to complexes comprising PGeP germyl ligands that no longer maintain the original germylene character (Fig. 2).^{5–8,11} In addition, it is also known that the NHC-stabilized (NHC = N-heterocyclic carbene) PGeP germylene **E** has allowed the synthesis of tetrahedral nickel complexes in which a PGeP germylene acts as a tripod (facial) ligand (Fig. 2).⁹ No transition metal derivative of germylene **F** has yet been reported.¹⁰ Therefore, metal complexes containing a genuine PGeP pincer germylene ligand, with coplanar M, Ge and both P atoms, are currently unknown.

Fig. 1 PGeP germynes that are known to be precursors to PGeP pincer-type ligands.

Fig. 2 Known reactivity of germynes **A–D** and **E** with transition metal complexes (X = metal or halogen; M may be attached to additional ligands).

We now report the first metal complex supported by a PGeP pincer germylene. We also describe that this compound presents very unusual and interesting features: (a) it is a rare T-shaped palladium(0) complex, (b) its germylene fragment acts as a Z-type ligand and (c) it behaves as a very strong reducing reagent, as it can be easily oxidized to palladium(II) derivatives with mild oxidants, such as [AuCl(tht)] (tht = tetrahydrothiophene), HCl and Ph₂S₂.

The diposphane-germylene 5,5-dimethyl-1,9-bis(diisopropylphosphanyl)methyl)dipyrromethane-N,N'-diylgermanium(II), Ge(pyrmP'Pr₂)₂CMe₂ (**D** in Fig. 1)⁸ reacted readily at room temperature with [Pd(PPh₃)₄], displacing the four PPh₃ ligands, to give [Pd(κ³-P,Ge,P-Ge(pyrmP'Pr₂)₂CMe₂)] (**1**), which was isolated as a very air- and moisture-sensitive dark green solid in 79 % yield. The structure shown for this complex in Scheme 1 is based on its NMR spectra, DFT calculations and the results of subsequent reactivity studies.

Scheme 1 Synthesis of complex **1**.

The NMR spectra of complex **1** indicated the inequivalence of the CMe₂ methyl groups, the existence of a symmetry plane and the absence of PPh₃ ligands.

The T-shaped coordination environment of the palladium atom of complex **1** was indicated by a DFT study at the wB97XD/SDD/cc-pVDZ theory level (Fig. 3), which showed and almost lineal P–Pd–P arrangement (175.35°) and that the Pd–Ge distance (2.507 Å) is longer than the Pd–P distances (2.347 Å) and also significantly longer than the Pd–Ge distances found in non-pincer three-coordinate germylene-palladium(0) complexes, for example [Pd(PET₃)₂{Ge(HMDS)₂}] (HMDS = N(SiMe₃)₂; Pd–Ge 2.333 Å).¹² T-shaped palladium(0) complexes are very rare; in fact, we have found only three examples in the

CSD,¹³ and they all involve a [Pd(phosphane)₂] fragment attached to a very strong Lewis acid: [Pd(PBz₃)₂(SO₂)] (Bz = benzyl),¹⁴ [Pd(PCy₃)(^tBu)(AlCl₃)] (Cy = cyclohexyl; ^tBu = 1,3-bis(*tert*butyl)imidazol-2-ylidene)¹⁵ and [Pd{κ³P,*B*,*P*-BPh(C₆H₄PCy₂)₂}]¹⁶ the latter being a PBP pincer complex.

Fig. 3 DFT-optimized molecular structure (left; H atoms omitted for clarity) and NBO images of the HOMO (center) and HOMO-12 (right) orbitals of complex **1**.

The unusual T-shaped coordination of the palladium atom and the fact that disubstituted (not donor-stabilized) germynes present an ambiphilic character (they can behave as both Lewis acids and bases),¹⁷ led us to investigate the electronic structure of complex **1**. A Natural Bond Orbital (NBO) analysis indicated that the HOMO of **1** (Fig. 3) is the molecular orbital responsible for the Pd–Ge interaction, as it consists of a bonding interaction between a filled *ds* hybrid orbital of the palladium and an empty *p* orbital of the germanium (the latter is almost perpendicular to the GeN₂ plane). The orbital holding the germylene lone pair, HOMO-12 (Fig. 3), is mostly constituted by a Ge *s* orbital and does not participate in any bonding. Therefore, the germylene scaffold of complex **1** behaves as an uncommon σ-acceptor ligand (*Z*-ligand¹⁸). This situation contrasts with that observed for the related nickel complex shown in Fig. 2 (derived from germylene **E**), which has been reported to present a Ge=Ni double bond with a σ-donor π-acceptor behavior of the germylene fragment (bond length 2.2876(3) Å).⁹ As far as we are aware, a *Z*-ligand behavior of a germylene has been previously claimed only once, for a diamidinogermylene nickel(0) complex that serendipitously resulted in low yield from the reduction of a bis(chloro(amidinato)germylene-phosphane)nickel(0) complex with potassium metal,¹⁹ but the Ni–Ge bond length of this complex, 2.2559(4) Å, is unexpectedly much shorter than the Pd–Ge bond length of complex **1**.

Complex **1** did not react with the strong σ-donor 4-dimethylaminopyridine (dmap), confirming the unavailability of an accessible empty orbital on the Ge atom of **1**. Consequently, the reaction of [Pd(PPh₃)₄] with the donor-stabilized germylene **D**-dmap, which was prepared on purpose (ESI), afforded a mixture of complex **1**, dmap and PPh₃. This reactivity contrasts with the Lewis acid behavior observed for the nickel complex shown in Fig. 2 (derived from germylene **E**), which is prone to add an NHC to its Ge atom.⁹

Attempting the displacement of tht from [AuCl(tht)] by the Ge lone pair of complex **1**, these reagents were mixed in 1:2 mol ratio in THF. This reaction led to the precipitation of gold metal (violet solid) and to a solution that contained the new complex [PdCl{κ³P,*Ge*,*P*-GeCl(pyrmP'Pr₂)₂CMe₂}] (**2**; Scheme 2). The use of a 1:1 **1** to [AuCl(tht)] mole ratio led to the incomplete

consumption of **1**. Therefore, the reaction is a redox process in which the Pd⁰ atom of **1** is oxidized to Pd^{II} by the Au^I atom of [AuCl(tht)]. Alternatively, complex **2** was also prepared from germylene **D** and [PdCl₂(MeCN)₂] via an insertion of the Ge atom of **D** into a Pd–Cl bond. An X-ray diffraction (XRD) structure (Scheme 2) confirmed that **2** is a square planar palladium(II) complex containing a PGeP pincer chloridogermyl ligand.^{7,11c}

Scheme 2 Syntheses and XRD molecular structure of complex **2** (H atoms have been omitted for clarity; 20% displacement ellipsoids). Selected bond lengths (Å) and angles (°) in **2**: Pd1–Ge1 2.3001(4), Pd1–Cl2 2.3707(7), Pd1–P1 2.3138(9), Pd1–P2 2.3197(9), Ge1–Cl1 2.2070(8); Ge1–Pd1–Cl2 178.00(3), Pd1–Ge1–Cl1 113.07(3).

As the formation of compound **2** from **1** and [AuCl(tht)] suggested a very strong reducing character for complex **1**, we decided to investigate its use as a source of palladium(II) complexes by treating it with reagents that could oxidatively add to either the palladium atom (to end in germylene-palladium(II) complexes) or across the Ge–Pd bond (to end in germyl-palladium(II) derivatives). As a proof of concept, we report herein the reactions of complex **1** with hydrogen chloride and with diphenyl disulfide (Scheme 3). While the use of one equivalent of HCl (solution in diethyl ether) immediately led to the hydrido complex [PdH{κ³P,*Ge*,*P*-Ge(OH)(pyrmP'Pr₂)₂CMe₂}] (**3**; Scheme 3), an excess of HCl led, as expected,²⁰ to the chloride complex **2**. The PdH signal of **3** was observed in its ¹H NMR spectrum as a triplet at –5.09 ppm. The bis(phenylsulfide) complex [Pd(SPh){κ³P,*Ge*,*P*-Ge(SPh)(pyrmP'Pr₂)₂CMe₂}] (**4**; Scheme 3), whose molecular structure was determined by XRD, was the only product of the reaction of **1** with Ph₂S₂. These reactions confirm not only the strong reducing character of complex **1** but also that the oxidative addition of the appropriate oxidizing reagent bond does not occur to the Pd atom (normal oxidative addition that would lead to germylene-palladium(II) products) but across the Ge–Pd bond, leading to germyl-palladium(II) derivatives.

Scheme 3 Reactions of complex **1** with hydrogen chloride and diphenyl disulfide and XRD molecular structure of complex **4** (H atoms have been omitted for clarity; 50% displacement ellipsoids). Selected bond lengths (Å) and angles (°) in **4**: Pd1–Ge1 Pd1–Ge1 2.3680(2), Pd1–S2 2.4003(4), Pd1–P1 2.3488(4), Pd1–P2 2.3343(4), Ge1–S1 2.2673(4); Ge1–Pd1–S2 175.35(1), Pd1–Ge–S1 121.94(1).

In conclusion, we have herein reported the synthesis of a palladium(0) compound (**1**) that is the first transition metal complex containing a genuine PGeP pincer germylene ligand, with coplanar Pd, Ge and both P atoms. Interestingly, this complex (a) features an unusual T-shaped coordination geometry of its Pd atom, (b) contains a germylene moiety that behaves as a σ -acceptor Z-ligand, and (c) its reactivity is dominated by a very strong reducing character of its Ge–Pd scaffold, as **1** easily leads to germyl-palladium(II) complexes, upon reacting with [AuCl(tht)], HCl and Ph₂S₂, through processes that involve an uncommon addition of an oxidant bond across the Ge–Pd bond.

Conflicts of interest

There are no conflicts to declare.

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An unusual T-shaped palladium(0) complex having a σ -acceptor (Z-type) germylene scaffold has been prepared from a dipyrromethane-based PGeP germylene