

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

Received 00th Month 20xx,
Accepted 00th Month 20xx

DOI: 10.1039/x0xx00000x

A dipyrromethane-based germylene decorated with two phosphane groups has been used to prepare an unusual T-shaped palladium(0) 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.

Germylenes 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 germylenes² and phosphanes³ with the interesting applicability that pincer-type ligands have already demonstrated in organometallic chemistry and catalysis.⁴ Although only a few germylenes 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 germylenes **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.

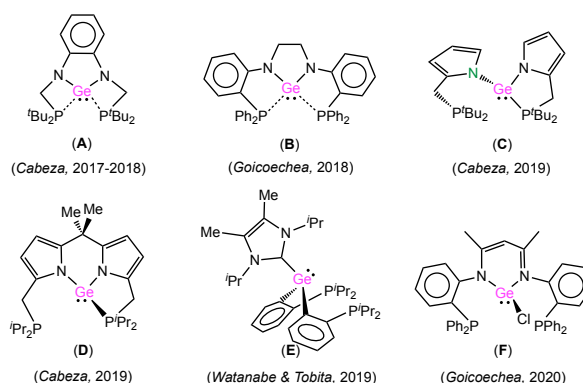


Fig. 1 PGeP germylenes that are known to be precursors to PGeP pincer-type ligands.

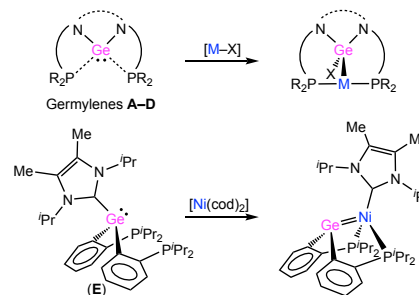


Fig. 2 Known reactivity of germylenes **A–D** and **E** with transition metal complexes (X = metal or halogen; M may be attached to additional ligands).

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.

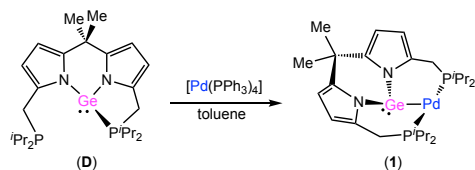
The diposphane-germylene 5,5-dimethyl-1,9-bis(diisopropylphosphanyl)methyl)dipyrromethane-N,N'-diylgermanium(II), Ge(pyrmPⁱPr₂)₂CMe₂ (**D** in Fig. 1)⁸ reacted readily at room temperature with [Pd(PPh₃)₄], displacing the four PPh₃ ligands, to give [Pd{κ³P,Ge,P-Ge(pyrmPⁱPr₂)₂CMe₂}] (**1**), which was isolated as a very air- and moisture-sensitive dark

^aCentro de Innovación en Química Avanzada (ORFEO-CINQA) and Departamento de Química Orgánica e Inorgánica, Universidad de Oviedo, 33071 Oviedo, Spain. E-mail: jac@uniovi.es.

^bDepartamento de Química Física y Analítica, Universidad de Oviedo, 33071 Oviedo, Spain.

[†]Electronic supplementary information (ESI) available: CCDC 2035174-2035175, experimental, analytical and complementary NMR, XRD and DFT data. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x

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 CMe_2 methyl groups, the existence of a symmetry plane and the absence of PPh_3 ligands.

The T-shaped coordination environment of the palladium atom of complex **1** was indicated by a DFT study at the $\text{wb97XD/SDD/cc-pVDZ}$ theory level (Fig. 3), which showed and almost lineal P-Pd-P arrangement (175.35°) and that the Pd-Ge distance (2.507 \AA) is longer than the Pd-P distances (2.347 \AA) and also significantly longer than the Pd-Ge distances found in non-pincer three-coordinate germylene-palladium(0) complexes, for example $[\text{Pd}(\text{PET}_3)_2\{\text{Ge}(\text{HMDS})_2\}]$ ($\text{HMDS} = \text{N}(\text{SiMe}_3)_2$; Pd-Ge 2.333 \AA).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 $[\text{PdL}_2]$ ($\text{L} = \text{phosphane}$ or NHC) fragment attached to a very strong Lewis acid: $[\text{Pd}(\text{PBz}_3)_2(\text{SO}_2)]$ ($\text{Bz} = \text{benzyl}$),¹⁴ $[\text{Pd}(\text{PCy}_3)(\text{t}^i\text{Bu})(\text{AlCl}_3)]$ ($\text{Cy} = \text{cyclohexyl}$; $\text{t}^i\text{Bu} = 1,3\text{-bis}(\text{tertbutyl})\text{imidazol-2-ylidene}$)¹⁵ and $[\text{Pd}\{\kappa^3\text{P},\text{B},\text{P-BPh}(\text{C}_6\text{H}_4\text{PCy}_2)_2\}]$,¹⁶ the latter being a PBP pincer complex.

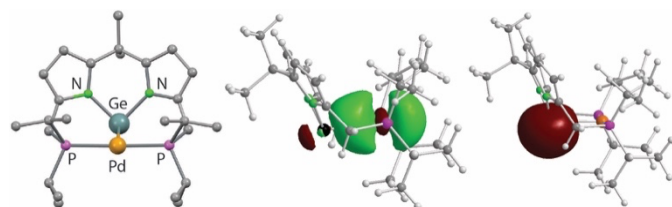


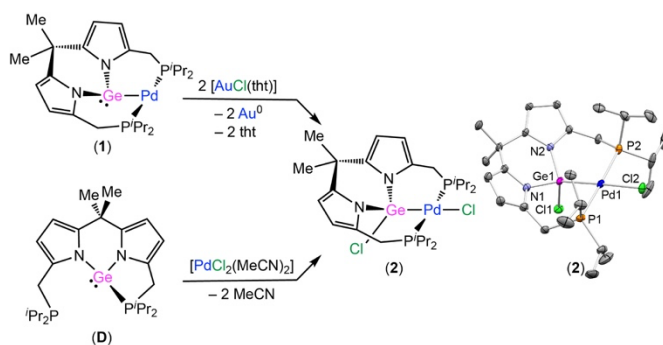
Fig. 3 DFT-optimized molecular structure (left; H atoms omitted for clarity) and NBO images of the HOMO (center) and HOMO-12 (right) orbitals of complex 1.

The unusual T-shaped coordination of the palladium atom and the fact that disubstituted (not donor-stabilized) germylenes 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 GeN_2 plane). The orbital holding the germylene lone pair, HOMO-12 (Fig. 3), is mostly constituted by a $\text{Ge } s$ 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 $2.2876(3) \text{ \AA}$).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, $2.2559(4) \text{ \AA}$, 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 $[\text{Pd}(\text{PPh}_3)_4]$ with the donor-stabilized germylene **D-dmap**, which was prepared on purpose (ESI), afforded a mixture of complex **1**, dmap and PPh_3 . 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

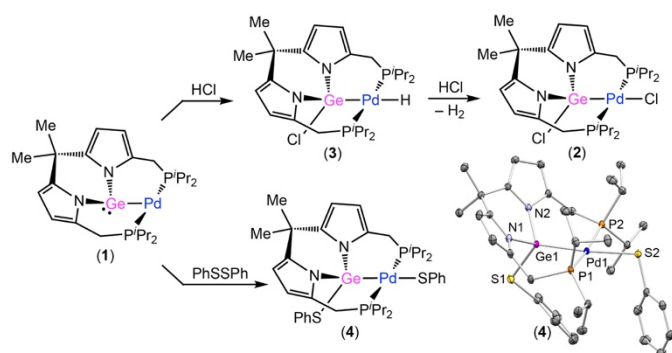
Attempting the displacement of tht from $[\text{AuCl}(\text{tht})]$ by the Ge lone pair of complex **1**, these reagents were mixed in 1:2 mol ratio in THF. This reaction led to the precipitation of gold metal (violet solid) and to a solution that contained the new complex $[\text{PdCl}\{\kappa^3\text{P},\text{Ge},\text{P-GeCl}(\text{pyrmP}^i\text{Pr}_2)_2\text{CMe}_2\}]$ (**2**; Scheme 2). The use of a 1:1 **1** to $[\text{AuCl}(\text{tht})]$ mole ratio led to the incomplete consumption of **1**. Therefore, the reaction is a redox process in which the Pd^0 atom of **1** is oxidized to Pd^{II} by the Au^{I} atom of $[\text{AuCl}(\text{tht})]$. Alternatively, complex **2** was also prepared from germylene **D** and $[\text{PdCl}_2(\text{MeCN})_2]$ 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 (\AA) and angles ($^\circ$) 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-Ge-Cl1 $113.07(3)$.

As the formation of compound **2** from **1** and $[\text{AuCl}(\text{tht})]$ 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 $[\text{PdH}\{\kappa^3\text{P,Ge,P-Ge}(\text{OH})(\text{pyrmP}^i\text{Pr}_2)_2\text{CMe}_2\}]$ (**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 $[\text{Pd}(\text{SPh})\{\kappa^3\text{P,Ge,P-Ge}(\text{SPh})(\text{pyrmP}^i\text{Pr}_2)_2\text{CMe}_2\}]$ (**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 $[\text{AuCl}(\text{tht})]$, 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.

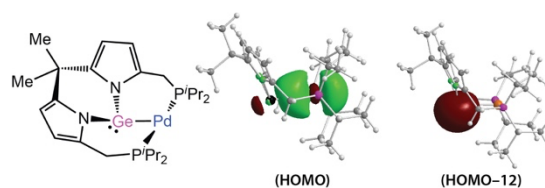
Acknowledgements

This work was supported by MINECO (CTQ2016-75218-P, MAT2016-78155-C2-1-R and RED2018-102387-T) and AEI (PID2019-104652GB-I00) projects.

References

- For a recent review on PGeP pincer complexes, see: J. A. Cabeza, P. García-Álvarez and C. J. Laglera-Gándara, *Eur. J. Inorg. Chem.*, 2020, 784.
- M. Asay, C. Jones and M. Driess, *Chem. Rev.*, 2011, **111**, 354.
- (a) J. F. Hartwig, *Organotransition Metal Chemistry: from Bonding to Catalysis*, University Science Books, New York, 2010; (b) C. A. Tolman, *Chem. Rev.*, 1977, **77**, 313; (c) *Transition Metal Complexes of Phosphorus, Arsenic, and Antimony Ligands*, ed. C. A. McAuliffe, J. Wiley, New York, 1973.
- Selected recent reviews on pincer complexes and their applications: (a) *Pincer Compounds: Chemistry and Applications*, ed. D. Morales-Morales, Elsevier, Amsterdam, 2018. (b) E. Peris and R. H. Crabtree, *Chem. Soc. Rev.*, 2018, **47**, 1959; (c) *The Privileged Pincer–Metal Platform: Coordination Chemistry & Applications*, ed. G. van Koten and R. A. Gossage, Springer, Cham, 2016; (d) M. Asay and D. Morales-Morales, *Dalton Trans.*, 2015, **44**, 17432; (e) C. Gunanathan and D. Milstein, *Chem. Rev.*, 2014, **114**, 12024; (f) *The Chemistry of Pincer Compounds*, ed. K. J. Szabó and O. F. Wendt, Wiley-VCH, Weinheim, 2014; (g) *Organometallic Pincer Chemistry*, ed. G. van Koten and D. Milstein, Springer, Heidelberg, 2013; (h) G. Bauer and X. Hu, *Inorg. Chem. Front.*, 2016, **3**, 741; (i) H. A. Yonus, W. Su, N. Ahmad, S. Chen and F. Verpoort, *Adv. Synth. Catal.*, 2015, **357**, 283; (j) *Catalysis by Pincer Complexes: Applications in Organic Synthesis and Catalysis*, ed. K. J. Szabó and O. F. Wendt, Wiley-VCH, Weinheim, 2014; (k) Q.-H. Dend, R. L. Melen and L. H. Gade, *Acc. Chem. Res.*, 2014, **47**, 3162; (l) *The Chemistry of Pincer Compounds*, ed. D. Morales-Morales and C. Jensen, Elsevier Science, Amsterdam, 2007.
- L. Álvarez-Rodríguez, J. Brugos, J. A. Cabeza, P. García-Álvarez, E. Pérez-Carreño and D. Polo, *Chem. Commun.*, 2017, **53**, 893.
- S. Bestgen, N. H. Rees and J. M. Goicoechea, *Organometallics*, 2018, **37**, 4147.
- J. A. Cabeza, I. Fernández, J. M. Fernández-Colinas, P. García-Álvarez and C. J. Laglera-Gándara, *Chem. Eur. J.*, 2019, **25**, 12423.
- J. A. Cabeza, P. García-Álvarez, C. J. Laglera-Gándara and E. Pérez-Carreño, *Dalton Trans.*, 2019, **48**, 13273.
- T. Watanabe, Y. Kasai and H. Tobita, *Chem. Eur. J.*, 2019, **25**, 13491.
- S. Bestgen, M. Mehta, T. C. Johnstone, P. W. Roesky and J. M. Goicoechea, *Chem. Eur. J.*, 2020, **26**, 9024.
- (a) J. Brugos, J. A. Cabeza, P. García-Álvarez, E. Pérez-Carreño and D. Polo, *Dalton Trans.*, 2018, **47**, 4534; (b) J. Brugos, J. A. Cabeza, P. García-Álvarez and E. Pérez-Carreño, *Organometallics*, 2018, **37**, 1507; (c) L. Álvarez-Rodríguez, J. Brugos, J. A. Cabeza, P. García-Álvarez and E. Pérez-Carreño, *Chem. Eur. J.*, 2017, **23**, 15107.
- Z. T. Cygan, J. E. Bender IV, K. E. Litz, J. W. Kampf and M. M. B. Holl, *Organometallics*, 2002, **21**, 5373.
- CSD version 5.41, updated August 2020.
- S. Arifhodzic-Radojevic, A. D. Burrows, N. Choi, M. McPartlin, D. M. P. Mingos, S. V. Tarlton and R. Vilar, *J. Chem. Soc., Dalton Trans.*, 1999, 3981.
- J. Bauer, H. Braunschweig, A. Damme, K. Gruss and K. Radacki, *Chem. Commun.*, 2011, **47**, 12783.
- P. Steinhoff and M. E. Tauchert, *Beilstein J. Org. Chem.*, 2016, **12**, 1573.
- (a) E. Rivard, *Dalton Trans.*, 2014, **43**, 8577; (b) L. Álvarez-Rodríguez, J. A. Cabeza, P. García-Álvarez and D. Polo, *Coord. Chem. Rev.*, 2015, **300**, 1.
- A. Amgoune and D. Bourissou, *Chem. Commun.*, 2011, **47**, 859.
- Z. Feng, Y. Jiang, H. Ruan, Y. Zhao, G. Tan, L. Zhang and X. Wang, *Dalton Trans.*, 2019, **48**, 14975.
- The elimination of H₂ has been observed upon protonation of a PCP pincer Pd^{II}–H complex: R. Gerber, T. Fox and C. M. Frech, *Chem. Eur. J.*, 2010, **16**, 6771.

Figure and Text for the Table of Contents



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