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Hydrogermylation of alkynes *via* metal–ligand cooperative catalysis†

Marceline Humbert,[a] Arnaud Clerc,[a] Karinne Miqueu, [b] [b] Julien Monot, [b] [a] Blanca Martin-Vaca [b] *[a] and Didier Bourissou [b] *[a]

E–H bond activation (E = B, Ge, Sn) with a (PNS)Pd complex has been investigated theoretically and experimentally. Et₃GeH readily adds across the Pd/S bond. Subsequent transfer to C≡C bonds enables catalytic hydrogermylation. The reaction is most regio and stereoselective with terminal alkynes. Downstream derivatization of silyl-functionalized vinyl germanes is exemplified.

Organo germanium derivatives are much less developed and used than their silicon, boron and tin congeners in organic synthesis. However, they attract growing interest as complementary substrates for coupling reactions and functionalization processes.[1] Most noteworthy is their different and eventually orthogonal reactivity[2] which can enable the rapid construction of complex molecules without the need of protection/deprotection steps.

As a matter of fact, it is needed to develop simple, efficient and selective routes to organo germanium derivatives to further explore and fully exploit their synthetic potential. Significant advances have been reported in the field over the last decades,[3] but hydrogermylation reactions remain sparse and underdeveloped while they certainly represent the most attractive route to vinyl germanes. Transition metal and Lewis acid catalysed, as well as radical approaches have been documented (Chart S1, ESI†),[4] but the transformation is still far from hydrosilylation in terms of scope (with terminal alkynes as substrates essentially) and regio as well as stereo-selectivity (α/β, *syn/anti* additions).[5–8]

Our group has recently reported a PNS pincer Pd complex **I₂** (Scheme 1) that readily activates Si–H bonds thanks to Pd/S

cooperativity and that efficiently catalyzes the hydrosilylation of alkynes.[9] Taking into account that metal–ligand cooperative catalysis has not been applied yet to hydrogermylation, we became interested in testing Pd/S cooperation for the activation of other E–H bonds, in particular Ge–H bonds. As reported hereafter, the (PNS)Pd complex **I₂** was found indeed to activate Et₃Ge–H stoichiometrically and to catalyze alkyne hydrogermylation. Note that the Ru/S cooperative system developed by Ohki, Tatsumi and Oestreich proved to be highly active towards Si, Sn as well as B–H bonds, and compared to our Pd/S system, it tends to favour dehydrogenative coupling over hydroelementation.[10] The activation of Ge–H bonds by this system has only been considered computationally.[11]

The feasibility of E–H bond activation *via* Pd/S cooperation was first probed computationally using Et₃EH (E: Si, Ge, Sn) and HBPin as model substrates (Fig. 1).[4] The first step is the splitting of the Pd/S dimer to form a σ-complex.[12] It is significantly downhill in energy with Ge, about thermoneutral with Sn and endergonic with Si & B (ΔG −6.7, −0.7 and 9.6/17.8 kcal mol⁻¹, respectively). With all the group 14 elements, the σ-complex adopts end-on η¹-type coordination. The shortest E···Pd contact is observed with Ge (2.473 Å), and it is associated with the most elongated E–H bond (2.136 Å). The noticeable degree of Ge–H bond activation is apparent from the Wiberg bond index (0.246) and the significant contribution of Pd → σ*(Ge–H) backdonation (ΔE_{orb} −24.3 *vs.* −59.5 kcal mol⁻¹ for the σ(Ge–H) → Pd donation, according to EDA-NOCV calculations).[4] Comparatively, the HBpin σ-complex tends more to a side-on η²-type structure, with a short B···Pd contact (2.258 Å).

[a] CNRS/Université Paul Sabatier, Laboratoire Hétérochimie Fondamentale et Appliquée (LFA, UMR 5069), 118 Route de Narbonne, 31062 Toulouse Cedex 09, France. E-mail: blanca-maria.martin-vaca@univ-tlse3.fr didier.bourissou@univ-tlse3.fr

[b] CNRS/Université de Pau et des Pays de l'Adour, Institut des Sciences Analytiques et Physico-Chimie pour l'Environnement et les Matériaux (IPREM, UMR 5254) Hélioparc, 2 Avenue du Président Angot, 64053 Pau Cedex 09, France
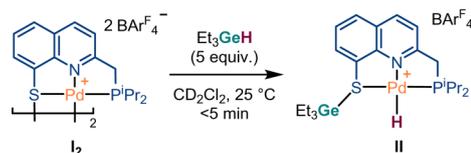
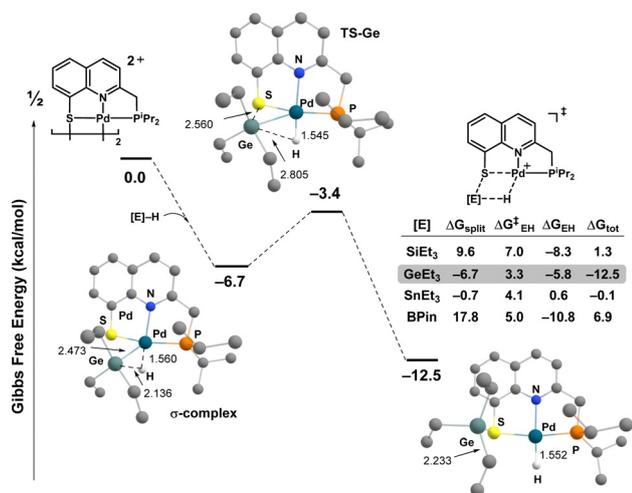Scheme 1 Stoichiometric reaction of triethylgermane with complex **I₂**.

Fig. 1 Reaction profiles (ΔG in kcal mol^{-1}) computed for the Pd/S cooperative activation of E−H bond (E: Si, Ge, Sn, B). Only the structures associated with the activation of Et$_3$GeH are shown. For clarity, the hydrogen atoms are omitted, except that at Ge/Pd. Optimizations performed at the SMD(DCM)-B3PW91-D3(BJ)/SDD+f(Pd), SDD+d(Sn), 6-31G** (other atoms) level of theory. Main distances in Å.

[E]	ΔG_{split}	$\Delta G^{\ddagger}_{EH}$	ΔG_{EH}	ΔG_{tot}
SiEt$_3$	9.6	7.0	−8.3	1.3
GeEt$_3$	−6.7	3.3	−5.8	−12.5
SnEt$_3$	−0.7	4.1	0.6	−0.1
BPin	17.8	5.0	−10.8	6.9

Heterolytic cleavage of the E−H bond then proceeds in a concerted manner thanks to Pd/S cooperativity.[4] The activation barriers are low and follow the same trend as the Ru/S system:[11] Ge < Sn < B < Si ($\Delta G^{\neq}$ 3.3, 4.1, 5.0 and 7.0 kcal mol^{-1}, respectively). With the group 14 elements, the cleavage of the E−H bond is asynchronous. At the transition state, the H atom is nearly transferred to Pd (Pd···H ∼ 1.55 Å) whereas the EEt$_3$ group is on the way to S with E − S distances of 2.6 to 2.9 Å. IBO analyses confirm this picture, showing a covalent Pd−H bond and a S lone pair starting to mix with E. The H−Bpin activation

process is more synchronous. The formation of the Pd−H and S−B bonds are both highly advanced at the TS (Pd···H 1.57 Å, B···S 2.19 Å). From the σ-complex, the E−H activation step is exergonic for all computed [E]−H bonds except Et$_3$Sn−H. Taking into account the splitting of the Pd/S dimer, the process is thermodynamically favored for Ge, about thermoneutral for Sn & Si, and uphill in energy for B (ΔG −12.5, −0.1/1.3 and 6.9, respectively).

The activation of pinacolborane, tributyltin hydride and triethylgermane by the [(PNS)Pd]$_2$ complex I$_2$ was then investigated experimentally under the same conditions as for hydrosilanes.[9] No reaction was observed with HBpin after 48 h at 25 °C, even with 5 equiv.[4] In marked contrast, nBu$_3$SnH led to an instantaneous gas evolution (H$_2$), even at low temperature (−78 °C), with concomitant appearance of a ^{119}Sn NMR signal at δ −83 ppm diagnostic of the dehydrogenative coupling product Bu$_3$SnSnBu$_3$.[4,13] The best result was actually obtained with Et$_3$GeH (Scheme 1). Here, NMR monitoring revealed rapid and quantitative reaction, with a marginal shift of the ^{31}P{^{1}H} signal (from δ 75.8 to 74.8 ppm), as previously observed upon hydrosilane activation.[9] The structure of the obtained complex II was unambiguously established by multi-nuclear NMR spectroscopy. The hydride at Pd resonates as a doublet at δ −12.6 ppm (J_{PH} 4.9 Hz) in the ^{1}H NMR spectrum and germylation of the thiolate moiety is apparent from a ^{1}H–^{1}H NOESY experiment.[4]

Next, catalytic hydroelementation tests were carried out with diphenylacetylene as benchmark substrate (using 2.5 mol% of I$_2$). No reaction occurred with HBpin at 25 °C, but rising the temperature to 70 °C resulted in 82% alkyne conversion after 4 h and 78% isolated yield of the expected addition products with a *syn*/*anti* addition ratio of 28/72.[4,14] With nBu$_3$SnH, dehydrogenative Sn−Sn coupling prevailed even
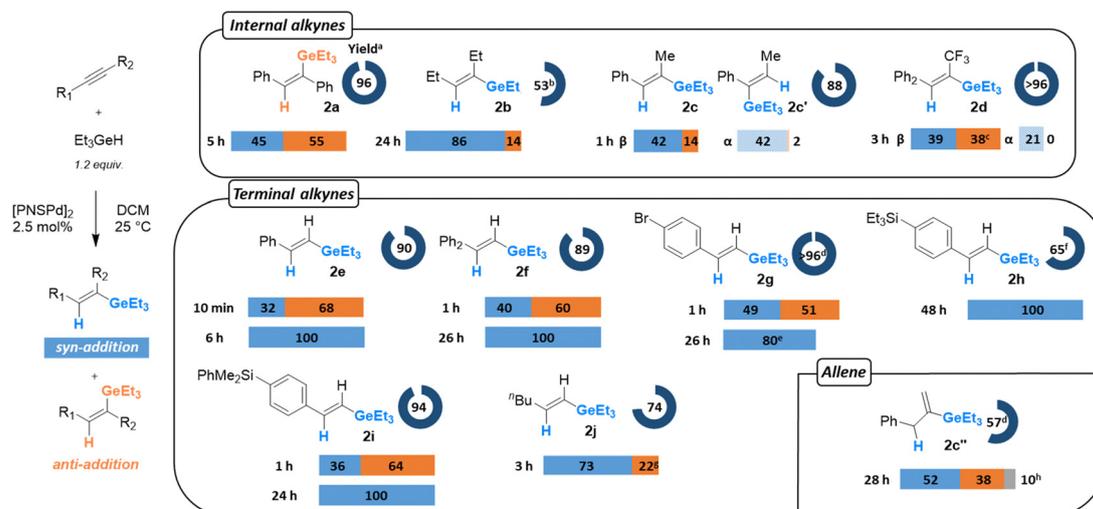

Chart 1 Hydrogermylation of alkynes catalyzed by the Pd complex I$_2$ at 25 °C. The major vinyl germane product obtained is shown. ^{a} Isolated as mixture of isomers. ^{b} With 3 equiv. of Et$_3$GeH. ^{c} 2% of not identified secondary product. ^{d} Determined by ^{1}H NMR spectroscopy with 1,2,4,5-tetramethylbenzene as internal standard or GS/MS. ^{e} 20% of secondary product from dehalogenation reaction. ^{f} Reaction performed at 1.8 mmol scale (400 mg of alkyne). ^{g} 5% of secondary product from chain-walking. ^{h} Ratio **2c''**/**2c**/Z-PhCH=CH(CH$_3$)GeEt$_3$.

under catalytic conditions and in the presence of the alkyne. Only traces of hydrostannylation product were detected in the ^{119}Sn NMR spectrum.[4] Once again, the best result was obtained with Et_3GeH, for which near full alkyne conversion was achieved in 5 h at 25 °C to yield a 45/55 mixture of the *syn*/*anti* addition products (96% isolated yield) (Chart 1).[4,15] A good conversion (82%) and similar *syn*/*anti* selectivity (40:60) was obtained by decreasing the catalyst loading to 0.5 mol% and extending the reaction time (24 h).[16] These first catalytic tests suggest that catalytic hydrogermylation *via* Pd/S cooperativity is indeed feasible. Complex I_2 seems to be slightly less reactive in hydrogermylation than hydrosilylation, but substantially more than in hydroboration. We thus focused on hydrogermylation for the catalytic study to assess the synthetic potential of this system to access vinyl germanes.

First, we confirmed the relevance of the Ge–H activation product to the catalytic transformation. Following the formation of complex **II** by reaction of I_2 with 5 equiv. of Et_3GeH, the addition of 5 equiv. of diphenylacetylene led to rapid and quantitative consumption of the substrates and formation of **2a** with again 45/55 *syn*/*anti* selectivity. A blank reaction performed with diphenylacetylene in the absence of the (PNS)Pd complex showed no reaction, even after 24 h or heating at 70 °C for 6 h. Hydrogermylation of hex-3-yne **1b**, a more challenging substrate, was then surveyed (Chart 1). Here, the use of 3 equiv. of Et_3GeH was beneficial to maintain a reasonable reaction time (24 h) and an acceptable isolated yield (53%) with 85/15 selectivity in favour of the *syn* addition product.[17] Then, the internal dissymmetric alkynes $PhC≡CMe$ **1c** and $Ph–PhC≡CCF_3$ **1d** were tested. In both cases, only 1.2 equiv. of Et_3GeH was sufficient to achieve good yields (>88%) in maximum 3 h. While β addition (the germyl group being introduced in the β position to the aromatic substituent) was largely favoured for **1d** (>75/25 *vs.* 56/44 for **1c**), higher *syn*/*anti* selectivity was observed for **1c** than for **1d** (84/16 and 60/40, respectively). The (PNS)Pd complex I_2 also proved efficient in promoting the hydrogermylation of terminal alkynes at room temperature, here with complete regioselectivity for β addition (Chart 1). Of note, no C–Ge dehydrogenative coupling was detected. Typically, full conversion of phenylacetylene **1e** was achieved within only 10 min. The ensuing vinyl germane **2e** then slowly isomerizes so that *syn* selectivity increases from 40/60 to 100/0 after 6 h at 25 °C. Attempts to selectively obtain the *anti* addition product by decreasing the catalyst loading to 0.5 mol% or lowering the temperature to −78 °C were unsuccessful. The biphenylene substituted alkyne **1f** behaves similarly, except a longer isomerization time (26 h). With 4-bromophenylacetylene **1g**, full conversion was reached in 10 min at 25 °C with a high selectivity for β addition. However, a dehalogenation side-product was detected (*ca.* 20%). Of particular interest is the ability of I_2 to catalyze the hydrogermylation of aryl-silylated substrates such as **1h** and **1i** without any trace of desilylation. Again, a mixture of β-*syn*/β-*anti* addition products is initially formed but prolonged reaction times resulted in complete isomerization into the β-*syn* addition product. Good to excellent yields (65–94%) were obtained for these functionalized vinyl compounds **2h** and **2i**. Selective β-addition was also achieved with hex-1-yne **1j** (73/22 *syn*/*anti* addition ratio),
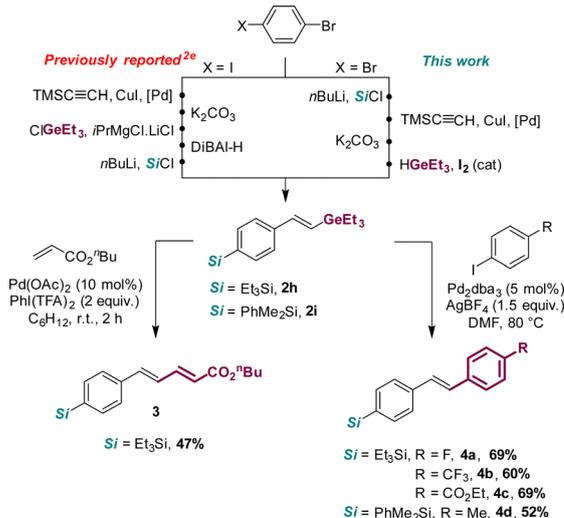
Scheme 2 Preparation of Si-functionalized vinylgermanes (comparison of the hydrogermylation route with the known method) and subsequent derivatization of their carbon–germane bond.

although full conversion required longer time (3 h *vs.* 10 min for **1e**). Note that isomerization into the β-*syn* isomer does not proceed so cleanly in this case, a secondary product resulting from chain-walking of the C=C bond forms concomitantly.[18] Finally, an allene, $PhC≡C≡CH_2$, was also tested. It could be hydrogermylated at 25 °C with good conversion (80% in 28 h), yielding the terminal vinyl germane **2c″** (resulting from β-addition) as major product.[19]

Although the hydrogermylation of internal alkynes lacks stereoselectivity, the total β-regioselectivity observed with terminal alkynes and the *syn* to *anti* isomerization occurring from aryl alkynes make the transformation synthetically valuable. The hydrogermylation route is particularly attractive and efficient to access silylated products such as **2h** and **2i**. It nicely complements the known synthetic route involving DiBAl-H reduction of alkynyl germanes (see Scheme 2).[2e] This prompted us to investigate further skeleton diversification of **2h** and **2i**.[2a,2d] Based on a recent report of Schoenebeck *et al.*,[2e] the olefination of vinyl germane **2h** with *n*-butyl acrylate was successfully carried out under oxidative Pd-catalyzed conditions, giving the desired product **3** with exclusive E-selectivity. Furthermore, using *in situ* generated Pd nanoparticles,[2d] **2h** and **2i** could be efficiently converted to the functionalized stilbenes **4a–d** using aryl iodides. The cross-coupling reaction works with electron-enriched and deprived substrates,[2e] it is fully E-selective and occurs only at the Ge site, leaving the silyl moiety intact for downstream derivatization.

In conclusion, complex I_2 was found to readily activate $Et_3Ge–H$ thanks to Pd/S cooperativity. The synthetic demand for vinyl germane derivatives has driven our investigations towards the catalytic hydrogermylation of alkynes. The PNS pincer Pd complex turned active towards internal and terminal alkynes, as well as allenes under mild conditions (25 °C). Most synthetically useful is the hydrogermylation of aryl alkynes which affords the corresponding vinyl germanes with exquisite

regio and stereoselectivity (β *syn* addition). The compatibility with silyl moieties and selective derivatization of the vinyl germane functionality are also noteworthy.

Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

There are no conflicts to declare.

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