

# Dehydrogenative Double C—H Bond Activation in a Germylene-Rhodium Complex

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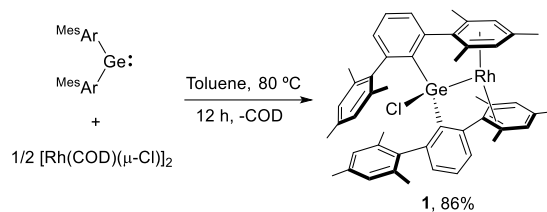
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**Abstract:** Transition metal tetrylene complexes offer great opportunities for molecular cooperation due to the ambiphilic character of the group 14 element. Here we focus on the coordination of germylene  $[(\text{Ar}^{\text{Mes}2})_2\text{Ge}:]$  ( $\text{Ar}^{\text{Mes}} = \text{C}_6\text{H}_3\text{-2,6-(C}_6\text{H}_2\text{-2,4,6-Me}_3)_2$ ) to  $[\text{RhCl}(\text{COD})]_2$  (COD = 1,5-cyclooctadinene), which yields a neutral germyl complex in which the rhodium center exhibits both  $\eta^6$ - and  $\eta^2$ -coordination to two mesityl rings in an unusual pincer-type structure. Chloride abstraction from this species triggers a singular dehydrogenative double C—H bond activation across the Ge/Rh motif. We have isolated and fully characterized three rhodium-germyl species associated to three C—H cleavage events along this process. The reaction mechanism has been further investigated by computational means, supporting the key cooperative action of rhodium and germanium centers.

Transition metal complexes bearing ambiphilic ligands that combine both electron donor and acceptor groups have attracted a great deal of attention in recent times.<sup>1,3</sup> In this regard, heavier tetrylenes ( $\text{:ER}_2$ ; E = Si, Ge, Sn, Pb) offer unique opportunities as single-site ambiphiles ( $\sigma$ -donating lone pair and empty p orbital), revealing unusual coordination modes and reactivity.<sup>4-12</sup> Moreover, they represent the prospects of new avenues for transition metal/P-element cooperation.<sup>13-25</sup> However, the coordination chemistry of tetrylenes remains considerably less explored than their lighter carbene congeners, in no little part due to reduced stability. To overcome this limitation base-stabilized tetrylenes have been explored and their complexes have found relevance in catalysis.<sup>26-29</sup> Nonetheless, quenching their Z-type character by inter- or intramolecular bases hampers their potential to actively cooperate with the transition metal in bond activation processes.

Steric shielding around the tetrel site has also been widely exploited as a strategy to provide kinetic stabilization, being terphenyl ( $\text{C}_6\text{H}_3\text{-2,6-Ar}_2$ ) substituents among the preferred choice.<sup>30</sup> In fact, coordination of terphenyl-stabilized tetrylenes to transition metals has already provided compelling results,<sup>31-37</sup> revealing the tunable donor/acceptor nature of the group 14 element<sup>38,39</sup> and the realization of its highly dynamic binding capacity.<sup>40-45</sup> For instance, the interconversion with tetrylidyne ( $\text{M}\equiv\text{E-R}$ ) and tetryl ( $\text{M-ER}_3$ ) forms drastically modify the bonding with the transition metal and its stereoelectronic properties, producing reactive unsaturated sites amenable for divergent reactivity.<sup>46</sup> In this study, we report the formation of a rhodium germylene/germyl complex based on the bis-terphenyl  $[(\text{Ar}^{\text{Mes}2})_2\text{Ge}:]$  ( $\text{Ar}^{\text{Mes}} = \text{C}_6\text{H}_3\text{-2,6-(C}_6\text{H}_2\text{-2,4,6-Me}_3)_2$ )<sup>47</sup> that promotes a unique intramolecular dehydrogenative double C—H bond activation process in which the germanium center reversibly rearranges from germylene to germyl forming Ge—Cl, Ge—H and Ge—C bonds in concert with the rhodium site.

Heating an equimolar toluene solution of  $[\text{RhCl}(\text{COD})]_2$  (COD = 1,5-cyclooctadinene) and  $[(\text{Ar}^{\text{Mes}2})_2\text{Ge}:]$  at 80 °C for twelve hours afforded the formation of germyl rhodium complex **1**, which precipitated from the reaction media as a dark orange solid in 86 % yield (Scheme 1). The release of COD, clearly identified by  $^1\text{H}$  NMR, is accompanied by  $\eta^6$ -coordination of the  $\pi$ -system of one of the flanking aryl rings of a terphenyl substituent.<sup>40,43,48-51</sup> This is consistent with a somewhat deshielded  $^1\text{H}$  NMR resonance at 5.16 ppm (2 H) that contrasts with the corresponding resonance in  $[(\text{Ar}^{\text{Mes}2})_2\text{Ge}:]$  found at 6.76 ppm. The associated  $^{13}\text{C}\{^1\text{H}\}$  NMR signal resonates at 119.9 ppm (c.f. 129.0 ppm in  $[(\text{Ar}^{\text{Mes}2})_2\text{Ge}:]$ ) and exhibits scalar coupling to  $^{103}\text{Rh}$  (d,  $J_{\text{CRh}} = 9$  Hz), in line with the proposed coordination. The molecular formulation of **1** was ascertained by X-ray diffraction studies (Figure 1), evidencing insertion of the germylene into the Rh—Cl bond, as previously observed in other rhodium/germylene systems.<sup>52-55</sup> Besides, the rhodium center is  $\eta^2$ -coordinated to a lateral ring of the alternate terphenyl fragment ( $\text{Rh1—C}_{31} = 2.153(2)$  and  $\text{Rh1—C}_{32} = 2.194(2)$  Å), thus resembling an unusual type of pincer-type coordination of the germyl moiety.



Scheme 1. Synthesis of germyl rhodium complex **1**.

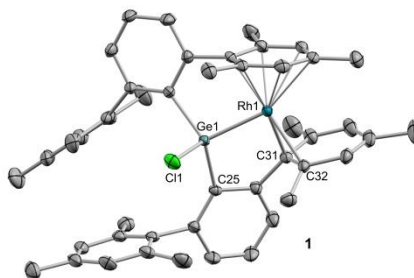
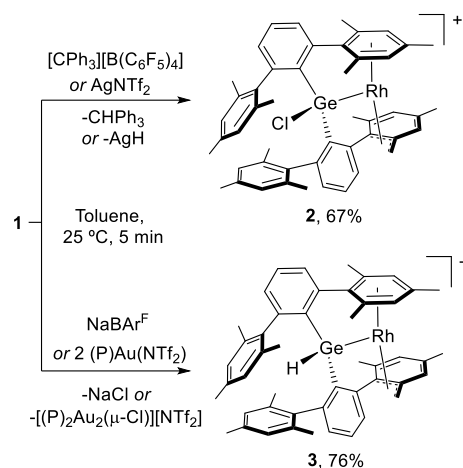


Figure 1. ORTEP diagram of **1**. Hydrogen atoms are excluded for clarity, and thermal ellipsoids are set at 50% probability.

To investigate bond activation processes through Ge/Rh bimetallic cooperation<sup>56</sup> we first targeted chloride abstraction from **1**. Addition of AgNTf<sub>2</sub> (NTf<sub>2</sub> = triflimidate = [N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>]<sup>-</sup>) surprisingly led to the withdrawal of a hydride, inferred by a distinctive <sup>1</sup>H NMR resonance at 0.87 ppm (t, <sup>1</sup>J<sub>HAg</sub> = 7 Hz) attributable to [AgH(NTf<sub>2</sub>)]<sub>n</sub>,<sup>57,58</sup> readily generating germyl-rhodium **2** in good yields (Scheme 2). In fact, an analogous process instantly takes place by treatment of **1** with trityl salt [CPh<sub>3</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>], with concomitant formation of CHPh<sub>3</sub>. The activation of one benzylic C—H bond originates a characteristic AB system in the <sup>1</sup>H NMR spectra due to the diastereotopic Rh—CH<sub>2</sub> protons, with slightly broad signals at 3.93 and 1.36 ppm. Their corresponding <sup>13</sup>C{<sup>1</sup>H} NMR peak resonates at 42.3 ppm (d, <sup>1</sup>J<sub>CRh</sub> = 12 Hz).

To our delight, treatment of **1** with NaBAr<sup>F</sup> immediately effects the initially targeted chloride abstraction. The resulting compound **3** is spectroscopically similar to chloride-containing **2**. Thus, an analogous AB pattern is present, but accompanied by an additional resonance at 6.02 due to a Ge—H terminus. Interestingly, addition of two equivalents of (PMe<sub>2</sub>Ar<sup>Dipp2</sup>)Au(NTf<sub>2</sub>)<sup>59,60</sup> (Ar<sup>Dipp2</sup> = C<sub>6</sub>H<sub>3</sub>-2,6-(C<sub>6</sub>H<sub>3</sub>-2,6-<sup>i</sup>Pr<sub>2</sub>)<sub>2</sub>) to precursor **1** generates as well compound **3** along with the chloride-bridged digold species [(PMe<sub>2</sub>Ar<sup>Dipp2</sup>)<sub>2</sub>Au<sub>2</sub>(μ-Cl)]. This contrasts with the aforementioned inability of silver salts to abstract the chloride substituent. Besides, we found slight NMR spectroscopic differences for the products derived from reactions of **1** with AgNTf<sub>2</sub> vs [CPh<sub>3</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] and those with NaBAr<sup>F</sup> vs (PMe<sub>2</sub>Ar<sup>Dipp2</sup>)Au(NTf<sub>2</sub>) that we attribute to counteranion effects (see Figure S1).

It is clear from these latter experiments that yield compound **3** that the formation of a transient cationic germanium site is central for the facile activation of a benzylic C—H bond, which does not take place from **1** even under harsh conditions (100 °C, 48 h). In fact, germynes are highly reluctant to insertion into C—H bonds<sup>61</sup> and the only other example of terphenyl benzylic C—H bond activation in a tetraylene relied on the use of an extremely σ-donating boryl ligand,<sup>62</sup> while herein the cooperative participation of both Ge and Rh sites is crucial. The mechanism by which compound **3** is formed has been investigated and shall be discussed along these lines.



Scheme 2. Synthesis of compounds **2** and **3** from germyl-rhodium **1** by hydride and chloride abstraction, respectively.

Compounds **2** and **3** were unequivocally characterized by X-ray diffraction as pseudoallylic species (Figure 2 and S2), with  $\eta^6$ -coordination to the alternate terphenyl substituent being retained. Pseudoallylic coordination is defined by average  $\text{Rh}-\text{C}$  bond distances of 2.28 ( $\text{CH}_2$ ), 2.13 ( $\text{C}_{\text{orto}}$ ) and 2.18 Å ( $\text{C}_{\text{ipso}}$ ), while other geometric parameters are comparable to those of **1**.

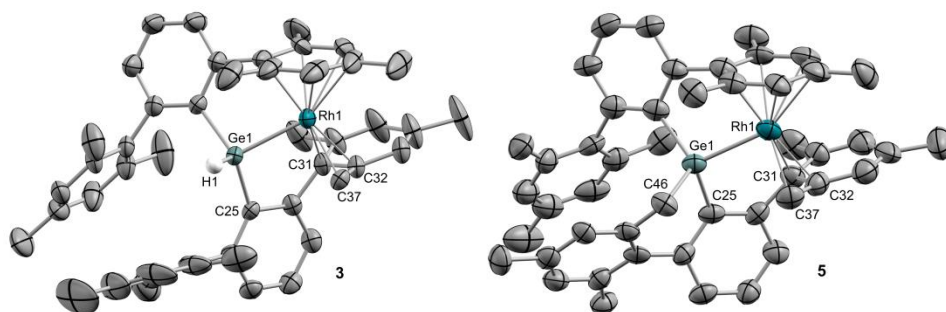
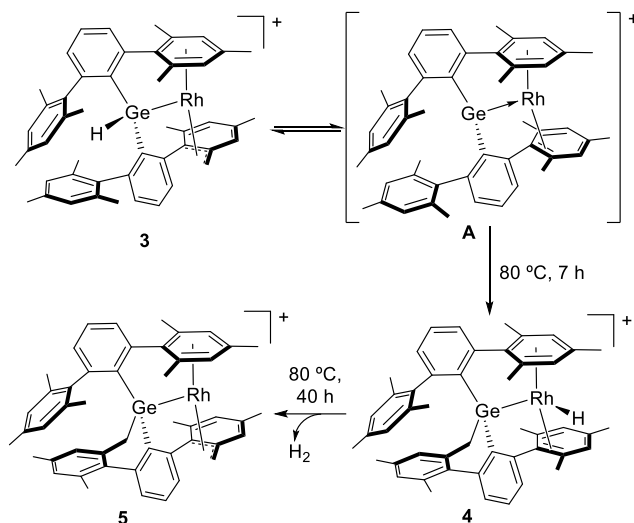


Figure 2. ORTEP diagrams of **3** and **5**. Counteranions, solvent molecules and most hydrogen atoms are excluded for clarity, and thermal ellipsoids are set at 50% probability.

Heating compound **3** in benzene or toluene solution for seven hours results in its quantitative conversion into **4**, characterized by a distinctive low-frequency  $^1\text{H}$  NMR signal at  $-18.12$  ppm ( $^1J_{\text{HRh}} = 21.6$  Hz) due to a hydride ligand bound to rhodium (Scheme 3). A thorough analysis of multinuclear mono and bidimensional NMR spectra reveals that only one of the benzylic positions of the mesityl rings is activated, although it has migrated to the germanium center. This double hydride/methylene migration between germanium and rhodium represents a rare example of the potential for cooperation in this type of hybrid main group/transition metal complexes. The formation of **4** most likely implies accessing a reactive germylene intermediate as **A** in Scheme 3, in turn the parent species from which the initial  $\text{C}-\text{H}$  activation to yield **3** after chloride abstraction would take place.



Scheme 3. Formation of compounds **4** and **5** by stepwise double hydride/methylene migration followed by dehydrogenative C—H bond activation.

The appearance of **4** was accompanied by minute amounts (<5%) of another species (**5**) for which the hydride ligand vanishes from the <sup>1</sup>H NMR spectrum. Further heating for 40 hours results in clean and complete conversion into **5**. This compound conserves the AB system observed by <sup>1</sup>H NMR in complex **4**, with two signals at 2.50 (d, <sup>3</sup>J<sub>HRh</sub> = 14.4 Hz) and 2.06 ppm, while also incorporates a related AB pattern (broad signals at 3.37 and 0.54 ppm) analogous to that found in compounds **2** and **3**. This suggests that two benzylic positions have now been activated with concomitant release of dihydrogen. This is in accordance with a total number of ten resonances accounting for three protons each between 1.24 and 2.21 ppm due to the methyl groups. This assumption was corroborated by X-ray diffraction studies (Figure 2), where one of the terphenyl substituents is doubly cyclometalated to both germanium and rhodium in  $\eta^1$  and  $\eta^3$ -fashion, respectively, a transformation that finds no precedent in the chemistry of tetrylenes.

Mechanistic understanding on this dehydrogenative double C—H bond activation is central to further explore the cooperative potential of this kind of tetraphenyl-transition metal systems. Investigation of the formation of species **3**–**5** by DFT methods (SMD- $\omega$ B97XD/6-31g(d,p)/SDD level; see the Supporting Information for details) were carried out starting from the cationic germylene-rhodium **A** that results from elimination of the chloride atom in **1** (Figure 3). The species retains the coordination environment around rhodium in **1**, whereas the expected trigonal planar geometry is found around the germanium, and the Ge—Rh distance is 2.25 Å. The calculations favor initial C—H activation at rhodium, which occurs through a low energy barrier ( $\Delta G$  from **A**) of ca. 10 kcal·mol<sup>-1</sup> to afford a new germyl intermediate, **B**, featuring a formally Rh(III) hydride moiety. Species **3** would in turn result from hydride migration from Rh to Ge, having the transformation an overall barrier of ca 16 kcal·mol<sup>-1</sup> from **A**. AIM and NBO analyses (SMD- $\omega$ B97XD/Def2TZVP level) were used to probe the germanium-rhodium interaction throughout the reaction pathway, showing an increase in the double bond character of the Ge—Rh bond in **A**, as a result of Rh to Ge back donation, which decreases in **B** as expected (see the SI for details).

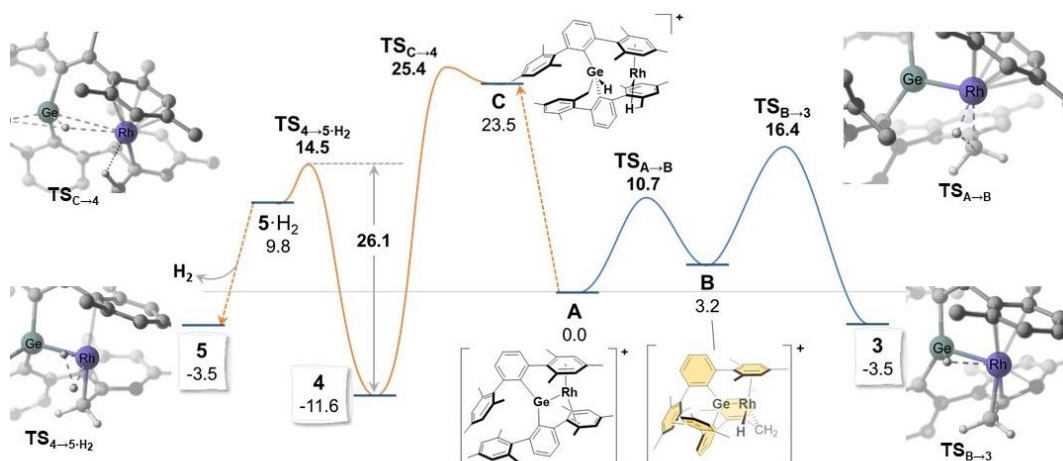


FIGURE 3.  $\Delta G^{\text{sol}}$  profile ( $\text{kcal}\cdot\text{mol}^{-1}$ ; benzene) for the formation of **3** and **4** from intermediate **A**, as well C—H dehydrogenative activation towards **5** and calculated geometries of transition states.

Formation of **4** and **5** from **3** under forcing conditions implies accessing the reacting germylene intermediate **A**, from which the addition product, the germyl **C**, may be accessible, located  $23.5 \text{ kcal}\cdot\text{mol}^{-1}$  above **A**. Then **4** would result from H migration from Ge to Rh, which is predicted to be almost barrierless. This species is located  $-11.6 \text{ kcal}\cdot\text{mol}^{-1}$  below **A** in agreement with experiments. Finally,  $\text{H}_2$  release implies a third C—H activation event, this time again at the rhodium center, which has a barrier of ca  $26 \text{ kcal}\cdot\text{mol}^{-1}$  from **4**.

In summary, the reactivity studies described in the foregoing sections constitute a remarkable illustration of the cooperative potential of transition metal tetrylenes. Chloride abstraction from a rhodium-embraced germyl compound initiates a highly unusual series of bond breaking events that result in the double C—H bond activation of two benzylic positions with concomitant release of dihydrogen. Computational studies provide a mechanistic picture for the above transformation, emphasizing the key cooperative action between rhodium and germanium. The process involves up to three C—H bond cleavage steps, as well as reversible hydride migration and formal hydrocarbyl migration between germanium and rhodium. These observations highlight the prospects for cooperative bond activation and catalysis of transition metal tetrylenes, which may surpass the more widely explored base-stabilized tetrylenes as ligands for transition metals.

**Supporting Information.** Synthesis and characterization of new compounds, X-ray diffraction information, computational details and NMR spectra.

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