

# Tuning the Inorganic Core of a reduced Ni<sub>2</sub>Ge<sub>2</sub> Cluster

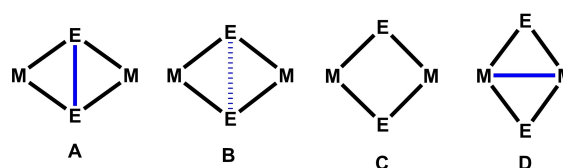
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Tetranuclear cores (M–E)<sub>2</sub> of transition metals (M) and tetrylenes (E<sup>II</sup>=Si, Ge, Sn) are key motifs in homogeneous and heterogeneous catalysis. They exhibit a continuum of M–M and E–E bonding within the inorganic core that leads to a variety of structures for which there are no specific synthetic methods. Herein, we report a series of highly reduced [Ni<sup>0</sup>Ge<sup>II</sup>]<sub>2</sub> squares solely stabilized by bulky terphenyl (C<sub>6</sub>H<sub>3</sub>–2,6–Ar<sub>2</sub>) ligands, for

which we provide complementary and high-yielding syntheses. Reactivity studies with common Lewis bases (carbene and CO) evince that the structure of the (M–E)<sub>2</sub> core can be transformed. We have investigated this core modification by computational means, offering a rationale to better understand the continuum of bonding across these clusters.

The combination of transition metals (M) and heavier tetrylenes, namely divalent heavier group 14 elements (E=Si, Ge, Sn, Pb), has become a frontier research area propelled by the notion of M–E cooperative bond activation and catalysis.<sup>1</sup> Much work has focused on the structure, coordination, bonding and reactivity of monomeric transition metal/tetrylene complexes,<sup>2,3</sup> which in some cases exhibit superior catalytic performance than related tetrylene-free compounds.<sup>4</sup> This boosting effect of the group 14 element is well known in heterogeneous catalysts<sup>5</sup> and has been documented for molecular clusters.<sup>6</sup> In all those, tetrylene-bridged multimetallic moieties ([M(μ-E)<sub>n</sub>M]<sub>m</sub>) are identified as responsible for catalyst efficiency.<sup>7</sup> In fact, isolated molecular fragments of this type are active in, for instance, dehydrogenative coupling of silanes,<sup>8</sup> olefin metathesis<sup>9</sup> or oligomerization of germanes.<sup>10</sup> Interestingly, the simpler dimeric form ([M(μ-E)]<sub>2</sub>) has been mostly investigated for silyl and silylene compounds, but analogous four-membered cores based on germanium and tin are comparatively underdeveloped.<sup>11</sup>

The bonding and structure of [M(μ-E)]<sub>2</sub> four-membered rings can be broadly classified into four groups, represented by structures A–D in Figure 1, each with varying degrees of covalent interactions between the metal atoms. Although not common, structure A is defined by a covalent bond between the tetrylene centers while no interaction is present between the transition metals.<sup>12</sup> More often, a weaker E...E interaction is present in structures of type B,<sup>13</sup> while it is fully absent in compounds of type C,<sup>14</sup> where there is virtually no contact



fsr (E–E)	0.99 - 1.01	1.01 - 1.15	1.15 - 1.45	1.30 - 1.70
fsr (M–M)	1.60 - 1.80	1.50 - 1.80	1.25 - 1.65	0.94 - 1.25

**Figure 1.** Schematic representation of the structures of inorganic four-membered rings comprised of (M–E)<sub>2</sub> dimers (M = transition metal; E = divalent Si, Ge, Sn, Pb). Additional bonding and interactions within the ring are highlighted in blue. fsr = formal shortness ratio = ratio between  $d_{M-M}$  or  $d_{E-E}$  and the sum of the corresponding metallic radii.<sup>[17]</sup>

between atoms on opposite vertices. Nonetheless, structure D is the most common of all,<sup>15</sup> with a covalent bond between transition metals and no contact among the main group atoms. The bonding scheme in these inorganic rings may be associated to their corresponding formal shortness ratio<sup>16</sup> (fsr; Figure 1), defined as the ratio between the M–M or E–E bond distance and the sum of the corresponding metallic radii, though these values must be taken with caution since most reported systems are not accompanied by a computational bonding analysis to corroborate the assignment. Importantly, despite the rich variety of structures, there are no well-defined and selective synthetic approaches, particularly for the heavier congeners (E=Ge and Sn), and their interconversion, highly desirable in the context of catalyst design and understanding, has not yet been realized.

In this work, we focus on the synthesis of unreported [Ni<sup>0</sup>Ge<sup>II</sup>]<sub>2</sub> squares, inspired by precedents on its lighter Si analogues,<sup>18</sup> and encouraged by the outstanding reactivity revealed by the handful of highly reduced nickel(0)-germylene complexes reported.<sup>19</sup> We provide complementary and high-yielding syntheses that are effective for the sterically congested [Ni<sup>0</sup>Ge<sup>II</sup>]<sub>2</sub> explored herein and demonstrate that their structures can be readily converted, offering a convenient approach for the synthesis of inorganic square-type complexes.

Synthetically, we decided to exploit the capacity of Power's terphenyl germylene dimers ([Ar\*GeCl]<sub>2</sub>; Ar\* = C<sub>6</sub>H<sub>3</sub>–2,6–Ar<sub>2</sub>) to coordinate transition metals.<sup>20</sup> The terphenyl flanking aryl rings

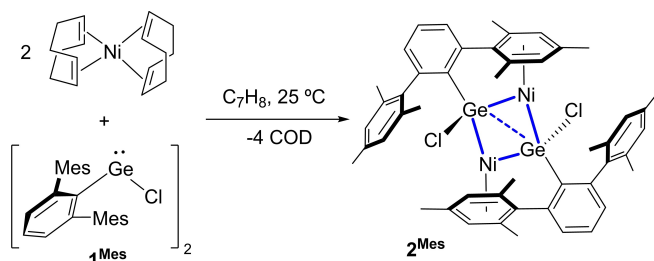
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enable stabilizing metals with low-coordination numbers through reversible  $\pi$ -arene binding,<sup>21</sup> a key aspect to modulate the targeted four-membered rings. Besides, [Ar\*Sn]-based species have already shown success in stabilizing related structures,<sup>13,22</sup> though no nickel examples are known.

We first investigated the equimolar reactions of Ni(COD)<sub>2</sub> (COD = 1,5-cyclooctadiene) with dimers [Ar<sup>Mes</sup>GeCl]<sub>2</sub> (**1**<sup>Mes</sup>) and [Ar<sup>Dipp</sup>GeCl]<sub>2</sub> (**1**<sup>Dipp</sup>) (Scheme 1) (Ar<sup>Mes</sup> = C<sub>6</sub>H<sub>3</sub>-2,6-(C<sub>6</sub>H<sub>2</sub>-2,4,6-Me<sub>3</sub>)<sub>2</sub>; Ar<sup>Dipp</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>). The corresponding toluene solutions turned dark brown after two hours and the formation of free COD was discernible in both cases. The reaction with **1**<sup>Mes</sup> cleanly produced the aimed dimeric compound **2**<sup>Mes</sup> after ca. 15 hours at 25 °C, isolated in pure form in 67% yield (Scheme 1). Spectroscopic analysis concurs with a symmetric but rigid structure with two inequivalent mesityl groups.  $\pi$ -arene bonding with the Ni centers is evidenced by <sup>1</sup>H NMR, as the resonances due to the *meta*-protons of the mesityl rings are shifted to lower frequencies (6.13 and 5.75 ppm) compared to the non-coordinating mesityl rings (6.96 and



Scheme 1. Synthesis of compound **2**<sup>Mes</sup> from Ni(COD)<sub>2</sub> and **1**<sup>Mes</sup>.

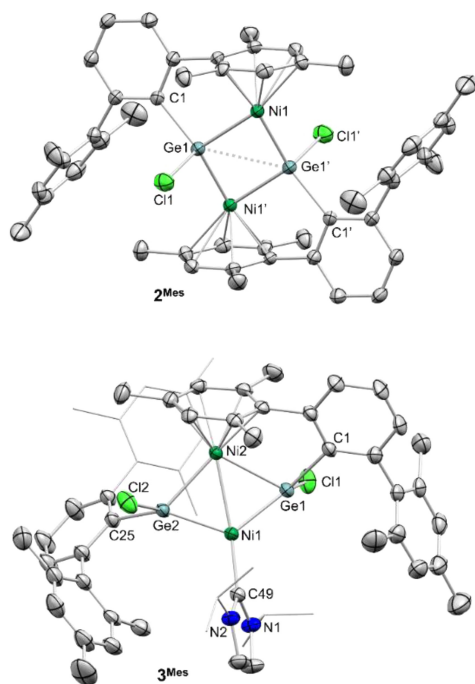


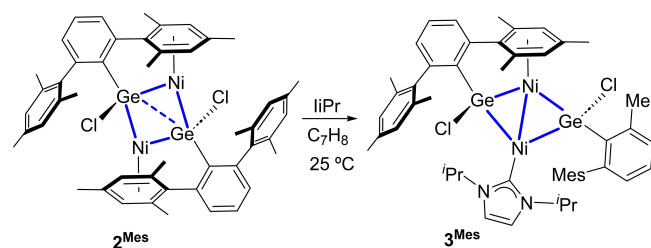
Figure 2. ORTEP diagram of compounds **2**<sup>Mes</sup> and **3**<sup>Mes</sup>. Hydrogen atoms are excluded, and some fragments are represented in wireframe format for clarity. Thermal ellipsoids are set at 50% probability.

6.88 ppm). In contrast, reaction with **1**<sup>Dipp</sup> led to a complex <sup>1</sup>H NMR spectra due to the asymmetric nature of the resulting product, where two different types of contacts between lateral aryl rings and nickel atoms led to particularly high shielded <sup>1</sup>H NMR resonances (see SI for details). Nevertheless, this species readily decomposes in solution and attempts to isolate dimer **2**<sup>Dipp</sup> from the reaction media just led to black precipitates.

The structure of **2**<sup>Mes</sup> was authenticated by X-ray diffraction studies<sup>23</sup> after growing crystals from toluene/pentane solutions at -30 °C (Figure 2). Interestingly, a tiny crop of crystals grew during our attempts to isolate the thermally unstable compound resulting from **1**<sup>Dipp</sup> and Ni(COD)<sub>2</sub>, allowing us to characterize **2**<sup>Dipp</sup> by X-ray diffraction, though the method could not be scaled-up. Nonetheless, redissolution of these crystals allowed us to confirm its dissimilar structure in solution (asymmetric) and solid-state (symmetric), since it led to the same complex <sup>1</sup>H NMR pattern discussed above, which readily evolved into intractable mixtures.

The structures of both compounds **2** are characterized by a planar Ni<sub>2</sub>Ge<sub>2</sub> core (Figure 2) defined by two sets of Ni–Ge bond distances (Ni1–Ge1: **2**<sup>Mes</sup>, 2.3797(6), **2**<sup>Dipp</sup>, 2.3552(8); Ni1–Ge1': **2**<sup>Mes</sup>, 2.2697(6); **2**<sup>Dipp</sup>, 2.2678(9) Å). While one of them is slightly shorter than the sum of the corresponding covalent radii (2.44 Å)<sup>24</sup>, the latter is closer to the calculated double bond distance (2.12 Å).<sup>25</sup> The Ge–Ge bond lengths account for 2.869(1) Å and 2.757(1) in **2**<sup>Mes</sup> and **2**<sup>Dipp</sup>, respectively, notably elongated compared to precursors [Ar\*GeCl]<sub>2</sub> (ca. 2.45 Å)<sup>26</sup> and singly bonded terphenyl germylene dimers (*d*<sub>GeGe</sub> ≈ 2.3–2.6 Å).<sup>27</sup> Nonetheless, the distance is short enough to anticipate a direct Ge...Ge interaction,<sup>12a,28</sup> though there is no contact between the nickel atoms (*d*<sub>NiNi</sub> 3.66 (**2**<sup>Mes</sup>) and 3.71 (**2**<sup>Dipp</sup>) Å), in agreement with structures of type B in Figure 1. These structures clearly differ from the single reported example of a [Ni–Ge]<sub>2</sub> dimer, [(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>Ge<sup>II</sup>Ni<sup>I</sup>(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>], which presents a butterfly structure with a strong Ni<sup>I</sup>–Ni<sup>I</sup> bond (2.49 Å).<sup>29</sup>

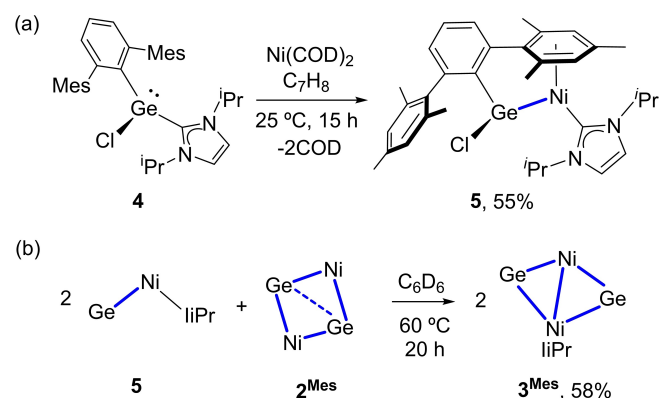
We next aimed at tuning the geometry and bonding of the metallic Ni<sub>2</sub>Ge<sub>2</sub> core, a long-sought goal in the chemistry of planar multimetallic species.<sup>30</sup> First, we treated **2**<sup>Mes</sup> with carbene 1,3-diisopropylimidazol-2-ylidene (IiPr), as a 2-electron strong  $\sigma$ -donor. Only one equivalent of IiPr per dimer reacts, leading to compound **3**<sup>Mes</sup> (Scheme 2), isolated in ca. 62% yield and whose lower symmetry is evinced by <sup>1</sup>H NMR (see SI) and from a high-frequency <sup>13</sup>C{<sup>1</sup>H} NMR resonance at 187.9 ppm due to the Ni-carbene. The structure of **3**<sup>Mes</sup> was authenticated by X-ray diffraction studies (Figure 2), demonstrating that the



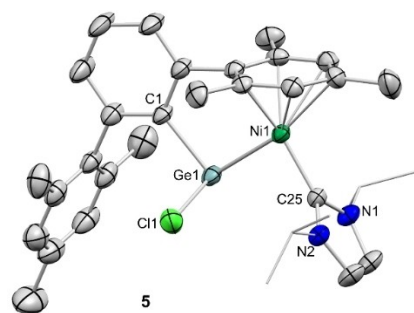
Scheme 2. Tuning the structure and bonding of the four-membered Ni<sub>2</sub>Ge<sub>2</sub> core in compound **2**<sup>Mes</sup> by addition of IiPr to form species **3**<sup>Mes</sup>.

tetrametallic core can indeed be modified, in particular from **B** to **D** in Figure 1. Structurally, the Ni<sub>2</sub>Ge<sub>2</sub> planar square in **2**<sup>Mes</sup> is transformed into a butterfly-type Ni<sub>2</sub>Ge<sub>2</sub> core in which the weak Ge...Ge contact has disappeared ( $d_{\text{GeGe}} = 3.855(1) \text{ \AA}$ ) and a short Ni–Ni distance (2.5190(6) Å) emerges, likely to compensate the loss of  $\pi$ -arene bonding (i.e., formally moving from a 16-electron Ni fragment in **2**<sup>Mes</sup> to a 12-electron one in **3**<sup>Mes</sup>).

Attempts to introduce a second liPr ligand were unsuccessful and only led to decomposition under more forcing conditions (80 °C). Therefore, we wondered whether a potential and highly unusual (liPr)Ni–Ge monomer would be synthetically attainable and if so, whether its dimerization could generate the intended bis-NHC dimeric structure. We synthesized the envisaged monomer by preparing adduct (Ar<sup>Mes</sup>)ClGe(liPr) (**4**; see SI for details; XRD structure in Figure SX2) and subsequent treatment with one equivalent of Ni(COD)<sub>2</sub>. <sup>1</sup>H NMR monitoring revealed the formation of the new compound **5** accompanied by liberation of COD (Scheme 3a). As foreseen, a high-frequency shift of the distinct <sup>13</sup>C{<sup>1</sup>H} NMR resonance of the carbenic carbon from 172.4 ppm in **4** to 183.8 ppm in **5** was diagnostic of transmetalation of the NHC ligand to nickel, a transformation already described.<sup>31</sup> Overall, this reaction can be understood as the formal insertion of Ni<sup>0</sup> across the NHC–Ge bond. However, this insertion seems to be favored by stabilization of the Ni center through  $\pi$ -arene bonding (NMR pattern comparable to



**Scheme 3.** (a) Synthesis of monomeric Ni–Ge compound **5**; (b) Schematic representation of the reaction between monomer **5** and dimer **2**<sup>Mes</sup> leading to Ni<sub>2</sub>Ge<sub>2</sub> core rearrangement in dimer **3**<sup>Mes</sup>.



**Figure 3.** ORTEP diagram of compound **5**. Hydrogen atoms are excluded, and some fragments are represented in wireframe format for clarity. Thermal ellipsoids are set at 50% probability.

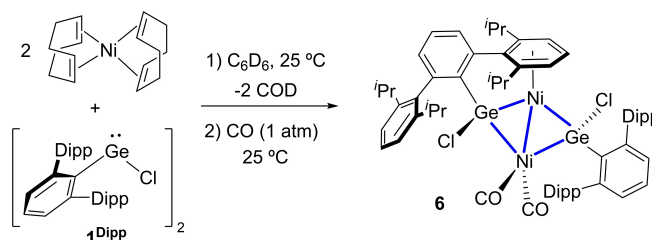
that described above for **2**, see SI for details), which indicates that the structure does not spontaneously dimerize.

The monomeric nature of **5** was corroborated by X-ray diffraction studies (Figure 3). It is characterized by coordination of liPr onto Ni ( $d_{\text{NiC}} = 1.896(2) \text{ \AA}$ ) and  $\eta^6$ -mesityl bonding defined by a short Ni–centroid distance of 1.683 Å. The Ni–Ge distance (2.4252(4) Å) is indicative of a bonding interaction. The sum of the angles around Ni accounts for an ideal 359.99(5)°, in perfect agreement with a trigonal planar geometry at Ni. Besides, angles at Ge are between 90° and 109.5° suggesting a trigonal pyramidal geometry. This last observation suggests a strong Ni→Ge interaction with minimal Ge→Ni back-donation, in accordance with our computational studies (see SI, Figures SC4). The dimeric and monomeric nature of compounds **2**<sup>Mes</sup>, **3**<sup>Mes</sup> and **5** was maintained in solution, as we could verify by diffusion-ordered NMR spectroscopy (DOSY; see SI for details).

A rapid inspection of intermetallic bonding distances in compounds **2**<sup>Mes</sup>, **3**<sup>Mes</sup> and **5**, along with the impossibility of accessing monomer **5** from Ni<sub>2</sub>Ge<sub>2</sub> structures, suggest compound **3**<sup>Mes</sup> as the thermodynamic product of the series. In accordance, the reaction of **2**<sup>Mes</sup> and **5** in benzene-*d*<sub>6</sub> in a 1:2 ratio worked successfully to produce **3**<sup>Mes</sup> in 58% spectroscopic yield upon heating at 60 °C for 20 h (Scheme 3b), demonstrating that tuning the geometry and bonding in metallic square-type structures is accessible through complementary routes.

Although the Ar<sup>Dipp</sup>-system exhibits a considerably decreased stability, we wondered whether it would still lead to isolable products by ligand coordination, once again looking to modulate the electronic structure of the Ni<sub>2</sub>Ge<sub>2</sub> core. Naturally, limited stability led to less tractable reactions than for the Ar<sup>Mes</sup>-system. The *in situ* generated product from **1**<sup>Dipp</sup> and Ni(COD)<sub>2</sub> readily reacts with liPr and carbon monoxide. In the former case it seems that the analogue **3**<sup>Dipp</sup> is the major product, though it could not be isolated in pure form. At variance, addition of CO (1 atm) results in cleaner formation of the bis-carbonyl structure **6** (Scheme 4), as corroborated by X-ray diffraction studies (Figure SX3), highlighting the versatility of the method to modulate the tetrametallic core.

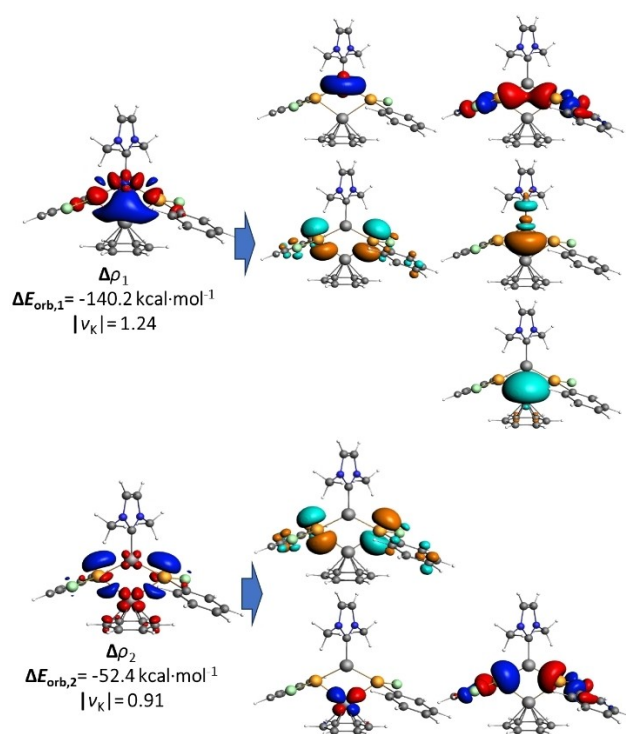
We then carried out computational studies to ascertain the nature of the bonding regarding modifications of the Ni<sub>2</sub>Ge<sub>2</sub> core. We considered singlet electronic ground states of the dimeric species described above, obtaining optimized molecular geometries in good agreement with the XRD data.<sup>32</sup> In addition, we included in the study model systems as shown in



**Scheme 4.** Synthesis of compound **6** by exposing a solution of **1**<sup>Dipp</sup> and Ni(COD)<sub>2</sub> to carbon monoxide.







**Figure 6.** EDA-NOCV analysis of the bonding in  $3_M$ . Figures on the left represent the major deformation channels, in which regions in red and blue are being depleted of, and accumulating electron density, respectively, upon formation of the dimers. To their right blue arrows point to representations of fragment orbitals contributing to each deformation channel (red and blue lobes are for donor orbitals and light blue and orange lobes are for acceptor orbitals).

polarization (electron density transfer between orbitals of the same fragment) within the Ni–NHC moiety. These are orbital contributions are now shown to the right of the deformation channels. The second orbital interaction ( $\Delta\rho_2$ ) has a comparatively minor contribution to  $\Delta E_{\text{orb}}$  and involves back donation from the Ni( $C_6H_6$ ) to an antisymmetric combination of p orbitals on the germanium atoms, and polarization within the  $[\text{PhGeCl}]_2$  fragment. This contribution suggests that  $3_M$  might be described as well as a Ni( $C_6H_6$ ) adduct of NHC–Ni( $\text{PhGeCl}$ ) $_2$ .

Overall, the bonding situations in  $2_M$  and  $3_M$  are clearly different. In the former it is related to the Dewar-Chatt-Duncanson model for transition metal-olefin complexes, which has been applied to related systems.<sup>36</sup> The weakened Ge...Ge bond and the absence of significant Ni...Ni interaction is consistent with the type-B structure of Figure 1. On the contrary, the bonding in  $3_M$  can be likened to two non-interacting, ambiphilic  $\mu$ -germylene moieties bonding to both Ni fragments, (with stronger donation to Ni–NHC) which, in addition to the non-negligible degree of Ni–Ni bond formation, as indicated by the blue region between both Ni atoms showing in  $\Delta\rho_1$ , permits classifying the structure as type\_D. The latter bonding model also applies to species  $6_M$  and details are given in the SI.

In summary, this work offers a family of unprecedented and highly reduced  $[\text{Ni}^0\text{Ge}^{\text{II}}]_2$  squares. This type of metallic core has been highlighted as key motif in homogeneous and heteroge-

neous catalysts and in the chemistry of larger inorganic clusters, but their study has been limited in large part by the absence of efficient synthetic methods, particularly for heavier Ge and Sn analogues. Our work provides several downstream benefits for further investigations. First, we describe two complementary and convenient synthetic approaches, including a more exotic one that highlights the potential of reactions between monomeric and dimeric precursors, which works well for the congested  $[\text{Ni}^0\text{Ge}^{\text{II}}]_2$  systems reported herein. Besides, the addition of exogeneous bases as a *liPr* and CO allows to transform the inorganic Ni $_2$ Ge $_2$  core among two different structures defined by a Ni–Ni bond (and no Ge...Ge interaction) vs a Ge...Ge interaction (and no Ni–Ni bond). This offers a straightforward approach for structural tuning in small inorganic clusters and to explore their particular effects in catalysis, an avenue that we are now pursuing in our laboratories.

## Supporting Information

The authors have cited additional references within the Supporting Information.<sup>[37–49]</sup>

## Acknowledgements

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## Conflict of Interests

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

**Keywords:** Cluster · Square · Tetrametallic · Germylene · Nickel

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