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COMMUNICATION

A rigid redox-active-ligand-supported bis(germylene) as a two-centre six-electron donor

Jingjing Cui,[a,b,c] Jonas Weiser,[b,c,d] Felipe Fantuzzi,[e] Maximilian Dietz,[b,c] Yelyzaveta Yatsenko,[b,c] Andreas Häfner,[b,c] Samuel Nees,[b,c] Ivo Krummenacher,[b,c] Mingtao Zhang,[f] Kai Hammond,[b,c] Paula Roth,[b,c] Wei Lu,[b,c] Rian D. Dewhurst,[b,c] Bernd Engels,[d] and Holger Braunschweig*[b,c]

A naphthyridine diimine (NDI) supported bis(germylene) NDI-Ge$_2$ containing two dicoordinate, coplanar Ge(II) atoms has been synthesised. Computational investigations on NDI-Ge$_2$ indicated the two Ge(II) atoms are nearly independent. The EDA-NOCV analysis of the [NDI-Ge$_2$][Fe$_2$(CO)$_6$] complex revealed the six-electron donor behavior of NDI-Ge$_2$, the first example for group 14 elements based bidentate ligands.

The potential of bis(tetrylenes), i.e. molecules containing two divalent group 14 atoms, as strong four-electron donors in transition metal catalyst design and low-valent main-group chemistry has been explored extensively.[1] In bis(tetrylenes), the two tetrylene centres, which are separated by a spacer (Fig. 1a), are usually considered independent by default. Little attention has been paid to the possible interaction between the two E(II) (E = group 14 element) centres or between the ligand and the E(II) centres. This is mainly because in bis(tetrylenes): (i) the E(II)…E(II) distance always exceeds the normal single bond range (e.g. 2.358 Å[2] for a Si–Si bond and 2.40 Å[3] for twice the covalent radii of Ge); and/or (ii) the flexible linkages allow sufficient space in between the lone pairs of E(II) (e.g. Fig. 1a, **A** and **B**);[4] or (iii) the lone pairs of the tetrylene centres are oriented away from each other (e.g. Fig. 1a, **C**).[5] To our knowledge, the molecular orbitals (MOs) of neutral, singlet ground state bis(germylene) systems have only been reported for one compound featuring a Ge(II)–O–Ge(II) linkage[6]. The calculations revealed that the highest occupied molecular orbital (HOMO) of this compound is composed of the lone pairs of the Ge(II) atoms, the ligands, and the O linkage, while the

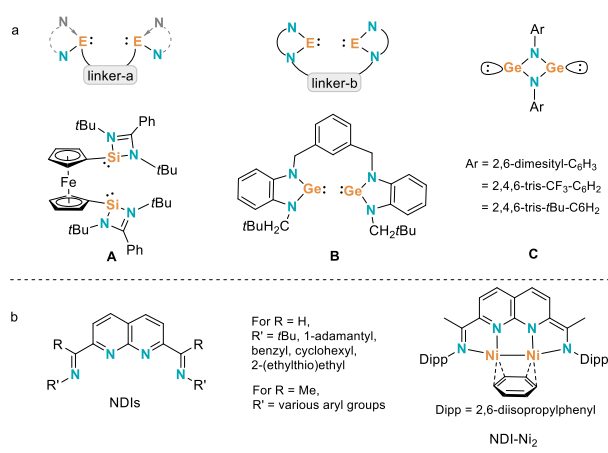HOMO-7 displays the corresponding empty p orbitals overlapping with the filled p orbital of the O linkage.

Fig. 1. (a) Different types of bis(tetrylenes) with one example of each type; (b) Structures of NDIs and NDI-Ni$_2$.

Benefiting from its redox-active and rigid-bidentate nature, naphthyridine diimines (NDIs, Fig. 1b) are well known to facilitate metal-metal cooperative or synergic behavior.[7] Recently, the group of Uyeda reported the nickel NDI complex NDI-Ni$_2$, which is stable in five different oxidation states.[8] The same group also reported the application of NDI-Ni$_2$ in transformations such as alkyne cyclisations,[9] carbene transfer[7c,10] and polymerisation,[11] amongst others.

Inspired by the Ge(0) or Sn(0) species supported by pyridinediimines,[12] we became interested in developing NDI-supported E$_2$ systems (E = group 14 elements) and envisioned that the rigid and aromatic NDI backbone will not only impose a close E(II)…E(II) distance but also hold the two lone pairs of the E(II) centres in a coplanar arrangement. Herein, we report the synthesis of an NDI-supported bis(germylene) NDI-Ge$_2$, in which the Ge centres are held just beyond their covalent bonding limit and thus feature only weak Ge…Ge interactions, resulting in a highly frustrated and electron-rich central binding cavity. As a consequence, NDI-Ge$_2$ acts as a six-electron donor in its diiron complex, making NDI-Ge$_2$ the first known example of such a ligand based on group 14 elements.

a. School of Chemistry and Environmental Engineering, Wuhan Institute of Technology, Wuhan 430205 (P.R. China)

b. Institut für Anorganische Chemie, Julius-Maximilians-Universität Würzburg, Am Hubland, 97074 Würzburg, Germany. E-mail: h.braunschweig@uni-wuerzburg.de

c. Institute for Sustainable Chemistry & Catalysis with Boron, Julius-Maximilians-Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

d. Institute for Physical and Theoretical Chemistry, Julius-Maximilians-Universität Würzburg, Emil-Fischer-Str. 42, 97074 Würzburg (Germany)

e. School of Chemistry and Forensic Science, University of Kent, Park Wood Rd, Canterbury CT2 7NH, UK

f. A201, Centlab, College of Chemistry, Nankai University, Weijin Road, 94, DE 300071 Tianjin (P.R. China)

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We first generated the disodium reagent[13] of **1** in situ and subjected it directly to salt elimination with $GeCl_2$ (Scheme 1). Compound **2** was isolated as a burgundy solid in 40% yield. In the ^{1}H NMR spectrum, the signals corresponding to naphthyridine protons are observed at 6.16 and 5.38 ppm as two doublets ($^3J_{H-H}$ = 8.7 Hz, C_6D_6), which are significantly upfield-shifted from those of ligand **1** (8.62 and 7.47 ppm, $^3J_{H-H}$ = 8.5 Hz, C_6D_6) (Fig. S1-2), indicating a lower degree of aromaticity of the naphthyridine unit in **2**.
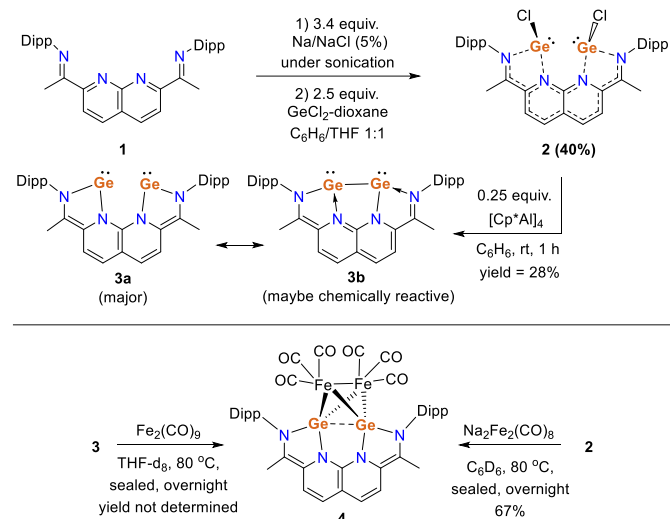
Scheme 1. Synthesis of compounds **2**, **3** and **4**.

In the molecular structure of **2** (Fig. 2, top left), the four rings deviate significantly from coplanarity with a dihedral angle of 15.86° between the mean planes of the two C_2N_2Ge five-membered rings. The Ge centres display trigonal pyramidal geometry with a bond angle sum of 273.11(15)°. The distance between the two Ge atoms is 2.8944(9) Å, which is slightly longer than the longest reported Ge−Ge bond in an anionic bis-germylene [2.8774(4) Å],[14] suggesting the absence of a Ge−Ge covalent bond (*vide infra*). The Ge1−N13 bond of 1.9663(15) Å is marginally shorter than the Ge1−N1 bond of 2.0011(16) Å, but both bond lengths are still comparable to the Ge−N bonds in $[LGe(II)Cl]^+[Ge(II)Cl_3]^-$ (L = 2-[C(CH_3)=N(C_6H_3-2,6-iPr_2)]-6-(CH_3O)C_6H_3N) [2.045(4)-2.070(4) Å].[15] Thus, compound **2** is best categorised as a bis(base-stabilised germylene) comprised of two tricoordinate pyramidal Ge(II) centres.

Stirring a benzene solution of **2** and $(Cp^*Al)_4$ (Cp^* = pentamethylcyclopentadienyl) at room temperature generated **3** (Scheme 2). Analytically pure **3** was obtained as black solid by recrystallisation from benzene in 28% yield. The significant difference of the positions of the ^{1}H NMR spectroscopic signals of the naphthyridine backbone protons between **2** (6.16 and 5.38 ppm) and **3** (7.60 and 7.05 ppm) suggests a higher level of aromaticity in the latter.

In the solid-state structure of **3** (Fig. 2, top right), the four annulated rings are approximately coplanar with the largest deviation to the mean plane defined by the four nitrogen atoms (0.146 Å) arising from C3. The distance between the two Ge centres of **3** is 2.9299(4) Å, which is even longer than that of **2**
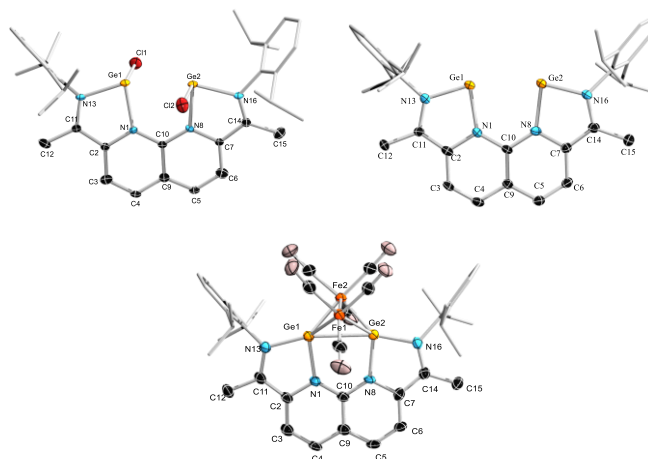
Fig. 2. Solid-state structure of **2** (top left), **3** (top right) and **4** (bottom). Hydrogen atoms and ellipsoids of the Dipp groups are omitted for clarity. Thermal ellipsoids are set at the 50% probability level. Selected bond lengths [Å] and angles [°] of **2**: Ge1…Ge2, 2.8944(9); Ge1−Cl1, 2.2916(7); Ge1−N1, 2.0011(16); N1−C2, 1.414(2); C2−C11, 1.406(2); Ge1−N13, 1.9663(15); C2−C3, 1.389(3); C3−C4, 1.375(3); C4−C9, 1.407(2); C9−C10, 1.434(3); Cl1−Ge1−N13, 99.50(5); Cl1−Ge1−N1, 92.71(4); N1−Ge1−N13, 80.90(6); C10−N1−C2, 120.04(15); N1−C2−C3, 120.18(15). Selected bond lengths [Å] and angles [°] of **3**: Ge1…Ge2, 2.9299(4); Ge1−N1, 1.9455(18); N1−C2, 1.420(3); C2−C11, 1.384(3); Ge1−N13, 1.8911(19); C2−C3, 1.410(3); C3−C4, 1.351(3); C4−C9, 1.427(3); N1−Ge1−N13, 82.76(8); C10−N1−C2, 118.32(18); N1−C2−C3, 120.2(2). Selected bond lengths [Å] and angles [°] of **4**: Ge1−Ge2, 2.7693(7); Fe1−Fe2, 2.7343(10); Ge1−N1, 1.942(3); N1−C2, 1.406(5); C2−C11, 1.407(6); Ge1−N13, 1.922(4); C2−C3, 1.382(6); C3−C4, 1.375(6); C4−C9, 1.416(6); N1−Ge1−N13, 83.02(14); C10−N1−C2, 119.9(3); N1−C2−C3, 120.1(4).

[2.8944(9) Å], excluding the possibility of **3** as $NDI^0 \rightarrow Ge^0 = Ge^0 \leftarrow NDI^0$. The $Ge−N_{naphthyridine}$ bonds [Ge1−N1 1.9455(18) Å, Ge2−N8 1.93411(18) Å] and $Ge−N_{imine}$ bonds [Ge1−N13 1.8911(19) Å, Ge2−N16 1.8912(18) Å] of **3** resemble that of α-iminopyridine (IPy) stabilised germylene [IPy-Ge(II)] [$Ge−N_{pyridine}$ 1.907(2) Å and $Ge−N_{imine}$ 1.860(2) Å].[16]

According to our calculations, the computed Ge−Ge Mayer bond order (MBO) of 0.26 for **3** indicates a very weak covalent Ge−Ge interaction. Thus, **3a** (Scheme 2), displaying two nearly independent dicoordinate Ge(II) atoms, represents the major resonance structure. Inspection of the canonical Kohn–Sham MOs indicates that **3** is a highly delocalised system, with the two Ge centres contributing to a large degree to MOs such as HOMO-9, HOMO-2, HOMO-1, and HOMO (Fig. 3). The former two orbitals are associated to the in- and out-of-phase combinations of the Ge lone pairs. In turn, HOMO-1 and HOMO represent the out-of- and in-phase combinations of the p orbitals of the Ge atoms, respectively. These orbitals would likely lead to π and π* interactions if the Ge atoms were closer in space, however, their enforced separation results in only poor orbital overlap. The out-of-phase combination is stabilised due to π delocalisation through the naphthyridine backbone. No clear evidence for a Ge−Ge bond in **2** or **3** was indicated by other theoretical techniques (see ESI). Meanwhile, the lowest unoccupied molecular orbital (LUMO) of **3** is comprised of the in-phase combination of Ge p orbitals, while LUMO+2 is Ge−Ge σ bonding (Fig. 3). The calculated HOMO-LUMO gap of 2.75 eV, although being comparatively small for a germylene (Fig. S14), is in accordance with the closed-shell singlet nature of the system as well as the large computed vertical and adiabatic singlet-triplet gaps (31.8 and 29.0 kcal mol⁻¹, respectively).
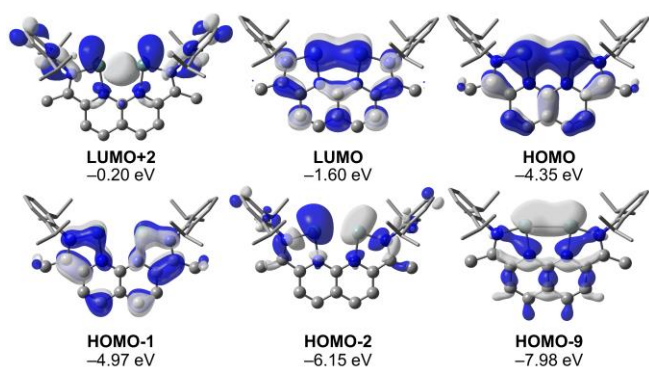
Fig. 3. Selected canonical Kohn–Sham MOs of compound **3** (isovalue: 0.03).

Next, we studied the coordination chemistry of **3**. The ^{1}H NMR spectrum of the reaction between [Fe$_2$(CO)$_9$] and **3** showed the disappearance of **3** concomitant with the generation of a new peak at 6.40 ppm in THF-d$_8$, corresponding to the naphthyridine backbone protons (the other one overlaps with signals of the Dipp group). We subsequently found that the same product could be achieved by the salt elimination between **2** and Na$_2$[Fe$_2$(CO)$_8$] with a higher yield (Scheme 2). In the ^{13}C NMR spectrum, a single carbonyl group resonance appears at 217.9 ppm, which is comparable to those of the reported Fe$_2$(CO)$_6$ complexes of cumulenes.[17]

The molecular structure of compound **4** (Fig. 2, bottom) shows that ligand **3** coordinates to the two Fe centres via two Ge centres in a bridging fashion, forming a tetrahedron geometry. This arrangement fits the prediction of a *nido*-4-vertex cluster by applying the Wade-Mingos rules with **3** functioning as a six-electron donor. This suggests that **3** can react following resonance structure **3b**, which might be chemically active due to the redox-active nature of the NDI ligand and the enforced proximity of the hypovalent Ge centres. It is impossible to compare the coordination chemistry of **3** and IPy-Ge(II) due to the limited reactivity study of the latter species.[16, 18] It is worth mentioning that although the heavy group 14 element alkyne analogues (RE≡ER, E = Ge or Sn) can also donate six electrons to group 6 carbonyls, all these six electrons are from the total cleavage of the E≡E triple bond.[19]

In compound **4**, each Fe centre displays a distorted octahedral geometry, and the Fe–Fe bond of 2.7343(10) Å is slightly shorter than those of other reported six-electron-ligand-(e.g. diphosphene, trienes[20]) stabilised Fe$_2$(CO)$_6$ complexes (2.740–2.872 Å). After coordination, the Ge…Ge distance shrinks significantly from 2.9299(4) Å in **3** to 2.7693(7) Å in **4**. The Ge–Fe bonds of **4**, ranging from 2.3187(9) Å to 2.3324(9) Å, are comparable to previously reported examples (2.34–2.43 Å).[18, 21] The CO stretching bands of **4** in the IR spectrum (2037, 2004, 1956, 1938, and 1911 cm^{-1}) is comparable to those of [Fe$_2$(CO)$_6$(P$_2$tBu$_2$)][22] (2053, 2015, 1988, 1968, and 1958 cm^{-1}) which features a six-electron-donating diphosphene ligand, implying a similar electron-donating ability of **3** with diphosphene.

For **4**, we carried out computations based on the energy decomposition analysis with natural orbitals for chemical valence (EDA-NOCV) approach (see ESI for details). All energy

values associated with the EDA-NOCV decomposition scheme are shown in Table S3, while Fig. 4 shows the deformation densities of the four most important NOCV pairs.

At the BP86-D3(BJ)/TZ2P level of theory, an interaction energy (ΔE_{int}) value of −160.8 kcal mol^{-1} is found between the [NDI-Ge$_2$] and [Fe$_2$(CO)$_6$] fragments. The decomposition of ΔE_{int} reveals that the electrostatic term (ΔE_{elstat}) contributes to 50.1% of the Ge–Fe stabilising contributions, while the corresponding orbital interaction (ΔE_{orb}) term corresponds to 44.6%. Inspection of the NOCV pairs indicates that four of those contribute to roughly 84% of ΔE_{orb}, the three largest of which comprise Ge$_2$→Fe$_2$ donation interactions. The first and largest term is related to Ge→Fe σ donation due to the interaction between the HOMO-2 of **3** (see Fig. 3) with the LUMO+2 of Fe$_2$(CO)$_6$ (see Fig. S22 in the ESI for the MOs of Fe$_2$(CO)$_6$). This

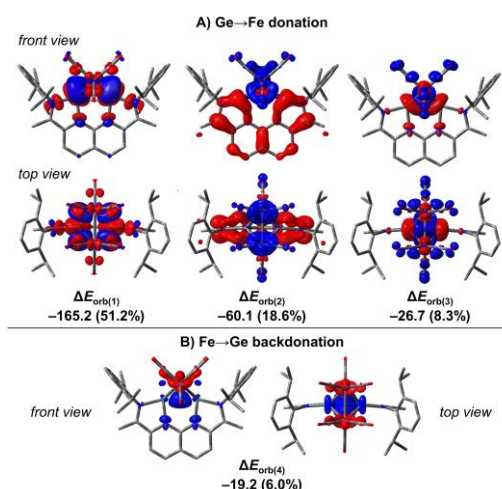**Fig. 4.** NOCV deformation densities and the corresponding individual orbital interaction energies ($\Delta E_{orb(i)}$, kcal mol^{-1}) related to Ge→Fe donation (top panel) and Fe→Ge backdonation (bottom panel) at the BP86-D3/TZ2P level of theory. Values in parentheses indicate the $\Delta E_{orb(i)}$ percentage with respect to ΔE_{orb}. Charge flows from red to blue. Isovalues: 0.003.

represents more than half (51.2%) of ΔE_{orb}. Furthermore, electron depletion from the HOMO-2 of **3**, which is antibonding with respect to the Ge–Ge axis, would formally lead to an increase of the Ge–Ge bonding character and nicely correlates with the Ge–Ge bond length decrease observed in **4**.

The second most important NOCV pair is related to donation of π symmetry from the HOMO of **3** to the LUMO+1 of Fe$_2$(CO)$_6$. This interaction contributes to −60.1 kcal mol^{-1} (18.6% of ΔE_{orb}). The third most important contribution, which is also of the Ge→Fe type, is related to donation of the HOMO-9 of **3** to the LUMO of the Fe$_2$(CO)$_6$ motif, which includes an Fe–Fe σ bonding contribution due to mixing of the Fe $3p$ orbitals. This NOCV pair stabilises **4** by −26.7 kcal mol^{-1} (8.3% of ΔE_{orb}). Finally, the fourth NOCV term is related to backdonation from the Fe$_2$(CO)$_6$ fragment to the LUMO+2 of **3**, which comprises Ge–Ge σ bonding character. This contribution stabilises **4** by −19.2 kcal mol^{-1} (6.0% of ΔE_{orb}). Thus, the three main NOCV contributions to ΔE_{orb} are in line with a quantitative description of the bis(germylene) as a six-electron donor ligand, while the fourth interaction accounts for the bond-strengthening Fe$_2$→Ge$_2$

backdonation that ultimately contributes to decreasing the Ge–Ge distance in **4**. Similar bonding effects have been observed in other systems, including transition metal complexes of diborenes[23] and aminoborylene-stabilised aminoborylenes.[24]

In summary, starting from a reported naphthyridine diamine, we prepared bis-germylenes NDI-Ge$_2$ featuring planar dicoordinated Ge(II) atoms. Both X-ray diffraction and theoretical studies suggest weak interaction between Ge atoms with no appreciable covalent bond. According to our EDA-NOCV results, NDI-Ge$_2$ donates six electrons to the diiron fragment in its complex with Fe$_2$(CO)$_6$, making it the first example of a six-electron-donating bidentate ligand based on group 14 elements. At the same time, NDI-Ge$_2$ accepts electron density from the iron centres by backdonation. The results showcase the benefits of the rigid NDI backbone, which is able to adapt to a range of electronic situations.[25]

Conflicts of interest

There are no conflicts to declare.

Author Contributions

J.C. designed the project and performed experiments with Y.Y. A.H. and S.N. improved the synthetic route to **3**. I.K. did the electrochemical measurements. M.D. and W.L. performed the X-ray diffraction experiments. K.H. and P.R. prepared the starting material for NDI. F.F. and B.E. supervised the theoretical calculations, which were performed by J.W., F.F. and M.Z. J.C., R.D. and F.F. wrote the manuscript. H.B. supervised the project. All authors read and commented on the manuscript.

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