

The first 1,3-digermyla-2-nickela-carboranylne and the Ni-catalyzed double germylation of unsaturated organic substrates

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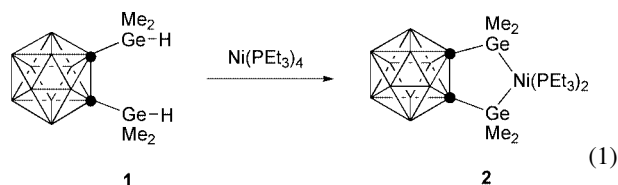
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The reaction of *o*-bis(dimethylgermyl)carborane with Ni(PET₃)₄ in pentane affords the reactive intermediate, [*o*-(GeMe₂)₂C₂B₁₀H₁₀]Ni(PET₃)₂ **2**: the facile double germylation of unsaturated organic substrates catalyzed by **2** is reported.

Although the transition metal-catalyzed double silylation of unsaturated organic substrates has been well documented for three decades,¹ metal-catalyzed double germylation is quite limited.^{2–5} Reactions were carried out mainly in the presence of [Pd(PPh₃)₄] as a catalyst. In the catalytic cycle, bis(germyl)-complexes have been implicated as important intermediates. However, there are only a few precedents for such species⁶ and only bis(chlorogermyl)platinum has been structurally characterized by Tanaka and coworkers.⁷ However, the reactivity towards unsaturated organic substrates was not studied. We found that the bis(germyl)nickel complex is the most efficient and reactive catalyst for the double germylation reaction. We now describe (i) the isolation of the most reactive intermediate cyclic bis(germyl)nickel compound with a bulky *o*-carborane unit; (ii) the facile double germylation of alkyne catalyzed by the intermediate under mild conditions; and (iii) the double germylation of an alkene, aldehyde and nitrile by stoichiometric reaction with the intermediate.

Addition of 1.1 equiv. of *o*-bis(dimethylgermyl)carborane, prepared from 1,2-Li₂C₂B₁₀H₁₀ and 2 equiv. of GeMe₂Cl₂, followed by reduction by NaB(CN)H₃, to Ni(PET₃)₄ in pentane gave a red solution. Standard work-up and crystallization from toluene–pentane gave [*o*-(GeMe₂)₂C₂B₁₀H₁₀]Ni(PET₃)₂ **2** as a spectroscopically pure, red crystalline solid very sensitive to air and water in 60% yield [eqn. (1)].[†]



The ¹H, ¹³C and ³¹P NMR spectra for **2** support the proposed structure. The structure of **2** was unambiguously established by a single-crystal X-ray analysis (Fig. 1).[‡] Complex **2** has a distorted tetrahedral geometry with the dihedral angle between Ge(1)–Ni–Ge(2) and P(1)–Ni–P(2) being 84.60°. This bis(germyl)nickel complex is the first as indicated by a search of the Cambridge Crystallographic Database. As expected, the average Ni–Ge bond length [2.3290(5) Å] is slightly longer than that of 2.248(1) Å in CpNi(PPh₃)GeCl₃.⁸ The Ni–P bond distance [2.2188(10) Å] is consistent with those observed in other phosphine nickel compounds.

Intermediate **2** was found to be an efficient reactant for the double germylation reaction under mild conditions. The reaction of *o*-bis(dimethylgermyl)carborane **1** with hex-1-yne (1 equiv.) in the presence of a catalytic amount of **2** (0.03 equiv.) at room temperature for 14 h afforded the double-germylated

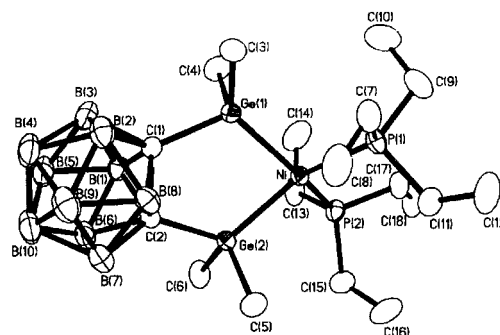
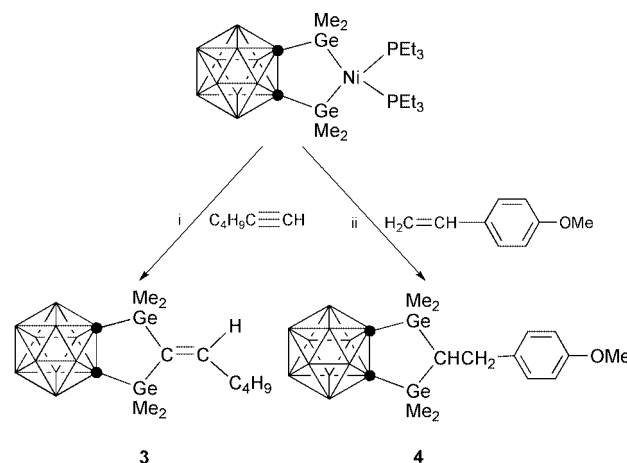


Fig. 1 Molecular structure of **2**. Selected bond lengths (Å) and angles (°): Ge(1)–C(1) 2.028(3), Ge(2)–C(2) 2.035(3), Ge(1)–Ni 2.3316(5), Ge(2)–Ni 2.3264(5), Ni–P(1) 2.2146(10), Ni–P(2) 2.2230(10); C(1)–Ge(1)–Ni 116.01(10), C(2)–Ge(2)–Ni 116.52(9), P(1)–Ni–P(2) 103.10(4), P(1)–Ni–Ge(2) 146.73(3), P(2)–Ni–Ge(2) 92.08(3), Ge(2)–Ni–Ge(1) 84.231(8).

product **3** in 62% yield. All the spectral data of **3** were consistent with the proposed formulation.[§] A key feature in the ¹H NMR spectrum includes a singlet at δ 6.24 assigned to the vinyl proton. A characteristic high-field ¹³C NMR signal at δ 142.82 provides evidence for a tethered carbon atom of the two germanium moieties. Formation of the digermyl ring compound **3** can be related to nickel-catalyzed double silylation.⁹

The reaction of **2** with 1 equiv. of 4-vinylanisole takes place at room temperature and affords a moderate yield of the five-membered digermyl ring compound **4** (Scheme 1). One doublet (δ 2.80) in the ¹H NMR spectrum of **4** is assigned to the methine proton. A low-frequency ¹³C NMR resonance at δ 55.41 provides evidence for the tethered carbon atom of the two germanium moieties. The structure of **4** has been determined by X-ray crystallography (Fig. 2).[‡] The formation of **4** may



Scheme 1 Reagents and conditions: i, HCCCH₂C₄H₉ (1 equiv.), **1** (0.5 equiv.), **2** (0.03 equiv.), toluene, 25 °C; ii, H₂C=CH–C₆H₄–OMe (1 equiv.), **2** (1 equiv.), toluene, 80 °C.

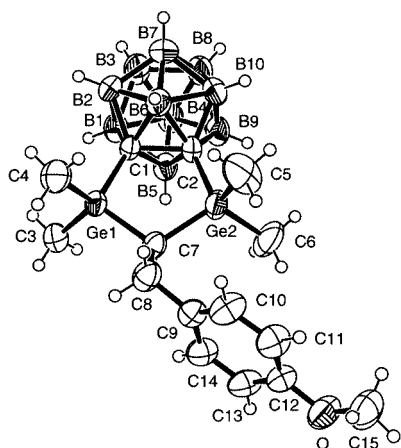
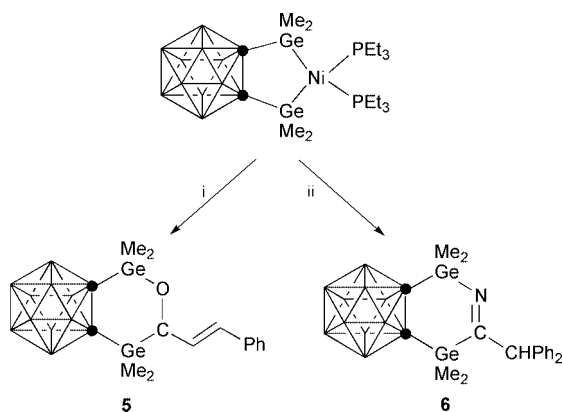


Fig. 2 Molecular structure of **4**. Selected bond lengths (Å) and angles (°): Ge(1)–C(1) 1.990(3), Ge(2)–C(2) 1.997(3), Ge(1)–C(7) 1.967(3), Ge(2)–C(7) 1.954(3), C(1)–C(2) 1.679(3); Ge(1)–C(7)–Ge(2) 110.04(14), Ge(1)–C(1)–C(2) 112.30(16).

involve an initial oxidative addition reaction of an olefinic C–H bond to the nickel center, followed by the shift of a phenyl group from the nickel atom to one of two germanium atoms. Such a C–H activation has been observed in Ni-catalyzed double silylation.¹⁰ Treatment of **2** with 1 equiv. of *trans*-cinnamaldehyde at room temperature gave the 1,2-double germylation product **5** (Scheme 2). The ¹H NMR spectrum of **5** contained a distinguishing low-field methine resonance (δ 4.61) as a doublet of doublets which was used to monitor its formation. This result is in contrast with that of double silylation which gave the insertion product of two carbonyl ligands into the C–Si bond.¹¹



Scheme 2 Reagents and conditions: i, PhCH=CHCHO (1 equiv.), **2** (1 equiv.), toluene, 25 °C, 70%; ii, Ph₂CHCN (1.3 equiv.), **2** (1 equiv.), toluene, 25 °C, 66%.

When diphenylacetonitrile is employed in the reaction with **1**, the six-membered digermyl ring compound **6** is isolated as colorless crystals in 74% yield. All the spectral data of **6** were consistent with the proposed formulation.^{||}

In summary, we have isolated a reactive intermediate, a cyclic bis(germyl)nickel complex, which readily reacts with unsaturated organic substrates such as alkynes, alkenes, alde-

hydes and nitriles, generating a new class of heterocyclic compounds. This potential has been further exploited in a series of novel chemical transformations with this system.

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Notes and references

† *Experimental procedure*: for **2**: compound **1** (0.14 g, 0.38 mmol) in 5 ml of pentane was added to a stirred solution of Ni(PEt₃)₄ (0.1 g, 0.37 mmol) in 10 ml of pentane at –15 °C. The solution was warmed to room temperature and stirred for 2 h. The solution was then evaporated *in vacuo* and the residue extracted with toluene (8 ml) and then the solution was covered with a layer of pentane (10 ml) at –5 °C. Red crystals of **2** were formed over a period of several days (0.14 g, 60% yield). ¹H NMR (C₆D₆): δ 1.14 (dq, *J*_{HP} 7.42, *J*_{HH} 5.48 Hz, CH₂), 0.86 (dt, *J*_{HP} 7.04, *J*_{HH} 5.48 Hz, CH₃) and 0.21 (s, GeCH₃). ³¹P{¹H} NMR (C₆D₆): δ 6.18.

‡ *Crystal data*: for **2**: C₁₈H₅₂B₁₀P₂Ge₂Ni, *M* = 641.52, monoclinic, space group P2₁/*n*, *a* = 11.28880(10), *b* = 14.2049(3), *c* = 20.6930(4) Å, β = 104.7760(10)°, *V* = 3208.52(10) Å³, *Z* = 4, *D*_c = 1.328 g cm^{–3}, μ (Mo–K α) = 2.550 mm^{–1}, 5038 reflections observed [*I* > 2 σ (*I*)], 338 parameters, final *R*, *R*_w on [*I* > 2 σ (*I*)] data were 0.0339, 0.0809, goodness of fit on *F*² = 1.059.

For **4**: C₁₅H₃₂B₁₀Ge₂O, *M* = 481.69, orthorhombic, space group *Pbca*, *a* = 16.6363(9), *b* = 15.3576(8), *c* = 18.9404(10) Å, *V* = 4839.2(4) Å³, *Z* = 8, *D*_c = 1.322 g cm^{–3}, μ (Mo–K α) = 2.488 mm^{–1}, 5992 reflections observed [*I* > 2 σ (*I*)], 253 parameters, final *R*, *R*_w on [*I* > 2 σ (*I*)] data were 0.0378, 0.0781, goodness of fit on *F*² = 0.951. CCDC reference numbers 166073 and 168186. See <http://www.rsc.org/suppdata/cc/b1/b105026p/> for crystallographic data in CIF or other electronic format.

§ **3**: ¹H NMR (CDCl₃): δ 6.24 (s, C=CH), 2.13 (t, *J*_{HH} 9.40 Hz, CH₂), 1.59–1.27 (m, CH₂CH₂), 0.92 (t, *J*_{HH} 4.46 Hz, CH₃), 0.48 (s, GeCH₃) and 0.45 (s, GeCH₃). ¹³C{¹H} NMR (CDCl₃): δ 159.20 (C=CH), 142.82 (Si–C=CH), 41.00, 31.49, 22.69, 14.22, –0.68 and –0.84.

¶ **5**: ¹H NMR (CDCl₃): δ 7.34–7.25 (m, Ph), 6.52 (dd, *J*_{HH} 15.88, *J*_{HH} 1.82 Hz, C=CHPh), 6.22 (dd, *J*_{HH} 15.88, *J*_{HH} 5.44 Hz, CH=C), 4.61 (dd, *J*_{HH} 5.44 Hz, *J*_{HH} 1.82 Hz, OCH), 0.75 (s, GeCH₃), 0.73 (s, GeCH₃), 0.44 (s, GeCH₃) and 0.42 (s, GeCH₃). ¹³C{¹H} NMR (CDCl₃): δ 137.04, 131.64, 128.74, 128.43, 127.44, 127.21, 126.26, 70.01, –0.07, –1.85, –3.63 and –6.91.

|| **6**: ¹H NMR (CDCl₃): δ 7.35–7.06 (m, Ph), 4.75 (s, CH), 0.64 (s, GeCH₃) and 0.61 (s, GeCH₃). ¹³C{¹H} NMR (CDCl₃): δ 143.54, 132.86, 130.22, 128.58, 128.34, 128.22, 125.92, 54.59, 5.85 and 1.29.

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