Stable bis(silyl)nickel complexes with *o*-carboranyl unit: a facile double silylation of alkynes and alkenes

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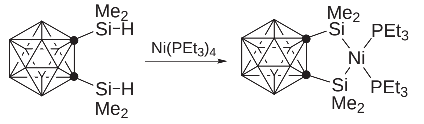
The reaction of *o*-bis(dimethylsilyl)carborane with $Ni(PEt_3)_4$ in pentane affords the reactive intermediate, $[o\text{-}(SiMe_2)_2C_2B_{10}H_{10}]Ni(PEt_3)_2$ 2; the facile double silylation of alkynes catalyzed by 2 is reported.

The double silylation of unsaturated organic substrates catalyzed by group 10 metals has been well documented for two decades.[1] Nickel complexes, in particular, provide excellent catalysts for the transformation of silicon-containing linear compounds. Cyclic bis(silyl)nickel complexes have been implicated as important intermediates in the nickel-catalyzed double silylation of arenes,[3] alkynes,[4] alkenes[5] and aldehydes.[6] However, the intermediates have not been isolated due to their instability. We now describe (i) the isolation of the reactive intermediate cyclic bis(silyl)nickel compound with a bulky *o*-carborane unit; (ii) the facile double silylation of alkynes catalyzed by the intermediate under mild conditions; and (iii) the double silylation of alkenes by the stoichiometric reaction with the intermediate.

Addition of 1.2 equiv. of *o*-bis(dimethylsilyl)carborane, prepared from $1,2\text{-}Li_2C_2B_{10}H_{10}$ and 2 equiv. of $SiMe_2ClH$, to $Ni(PEt_3)_4$ in pentane at 25 °C gave a dark red solution, concomitant with the evolution of gas. Standard workup and crystallization from toluene–pentane gave $[o\text{-}(SiMe_2)_2C_2B_{10}H_{10}]Ni(PEt_3)_2$ **2** as a spectroscopically pure, dark red crystalline solid sensitive to air and stable during brief heating to 100–110 °C in 86% yield [eqn. (1)].† The unusual thermal stability of the nickel bis(silyl) compound is attributed to the advantageous properties of the carboranyl unit, including electronic and steric effect.



(1)

1 **2**

The ^1H, ^{13}C, ^{31}P and ^{29}Si NMR spectra for **2** support the proposed structure. In particular, the ^{29}Si NMR chemical shift of δ 43.19 as a triplet ($J_{\text{Si–P}(cis)}$ 40.11 Hz) resembles the literature value reported for the *cis*-$NiSi_2PC$ complex.[7] 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 P(1)–Ni–P(2) and Si(1)–Ni–Si(2) being 86.03°. Such bis(silyl)nickel complexes are rare as indicated by a search of the Cambridge Data Base which revealed only a few previous examples.[8] As expected, the average Ni–Si bond length [2.2424(9) Å] is slightly longer than that of 2.171(3) Å in $[(\mu\text{-Cl})_2Ni_2(SiCl_3)_4][(CMe_3)_2C_5H_3NH]_2$.[8] The Ni–P bond distance [2.2305(8) Å] is consistent with those observed in other phosphine nickel compounds.[9]

Compound **2** was found to be a good reactive intermediate for the double silylation reaction. The reaction of *o*-bis(dimethylsilyl)carborane **1** with 1-phenylprop-1-yne (1 equiv.) in the presence of a catalytic amount of **2** (0.03 equiv.) for 6 h afforded the double-silylated product **3** in 94% (GC) yield. The reaction was quite sensitive to the reaction conditions. When the same reaction was carried out at higher temperature (70–75 °C), the major component was identified as the acetylene cyclotrimerization product **4** (Scheme 1), which has been characterized by spectroscopic techniques.

When hex-1-yne is employed as a terminal alkyne in the reaction with **1** under the same conditions, the five-membered disilyl ring compound **5** is isolated as a colorless liquid in 71% yield. All the spectral data of **5** was consistent with the proposed formulation.

The reaction of **2** with 1 equiv. of styrene takes place at a higher temperature (80 °C) and affords a moderate yield of the five-membered disilyl ring compound **6** (Scheme 2). A key feature in the ^1H NMR spectrum of **6** includes a singlet at δ 7.71 assigned to the vinyl proton. A characteristic low frequency ^{13}C NMR resonance at δ 139.75 provides evidence for a tethered carbon atom of the two silicon moieties. The structure of **6** has been determined by X-ray crystallography.‡ Such formation of the disilyl ring compound has been observed during the nickel-catalyzed reaction of benzo-disilacyclobutene with styrene.[5] Treatment of **2** with 1 equiv. of 1,1-diphenyl-ethylene in toluene at 80 °C resulted in a brown solution from which the five-membered disilyl ring compound **7** was isolated in a yield of

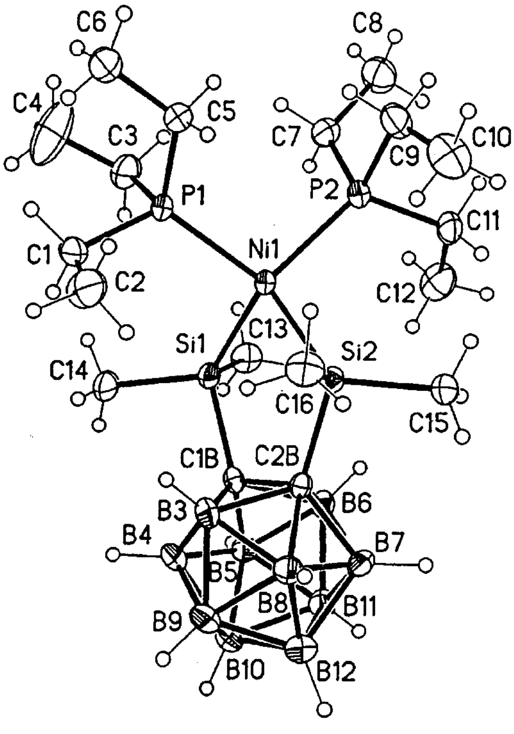
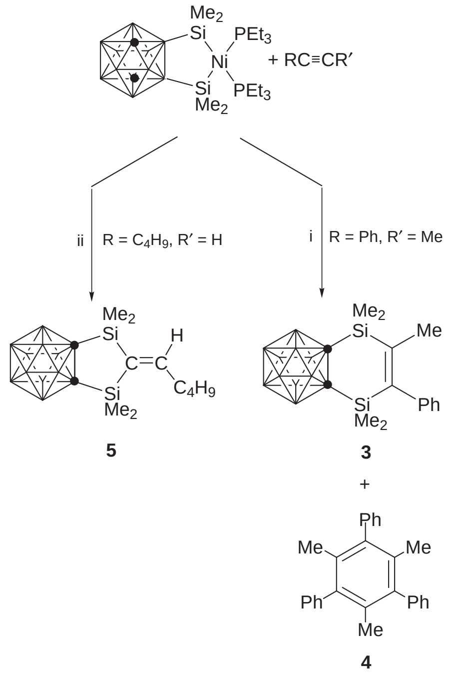
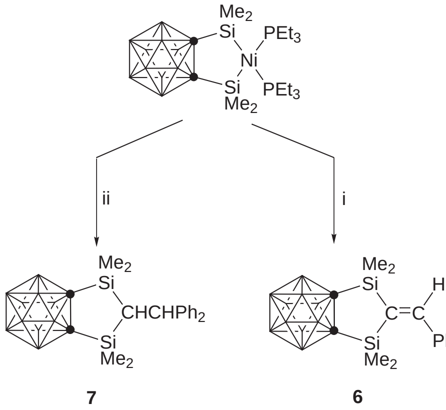


Fig. 1 Molecular structure of **2** showing the atom numbering scheme. Selected distances (Å) and angles (°): Ni(1)–P(1) 2.2265(8), Ni(1)–P(2) 2.2346(8), Ni(1)–Si(1) 2.2371(9), Ni(1)–Si(2) 2.2477(9), Si(1)–C(1B) 1.941(3), Si(2)–C(2B) 1.940(3), C(1B)–C(2B) 1.669(4); P(1)–Ni(1)–P(2) 101.95(3), Si(1)–Ni(1)–Si(2) 83.69(3), P(1)–Ni(1)–Si(1) 96.06(3), P(2)–Ni(1)–Si(1) 140.35(4).



Scheme 1 *Reagents and conditions*: i, PhCCMe (1 equiv.), **1** (1 equiv.), **2** (0.03 equiv.), toluene, 25 °C, 94%; ii, $HCCC_4H_9$ (1 equiv.), **1** (1 equiv.), **2** (0.03 equiv.), toluene, 25 °C, 71%.



Scheme 2 *Reagents and conditions*: i, $PhCHCH_2$ (1 equiv.), **2** (1 equiv.), toluene, 80 °C, 84%; ii, Ph_2CCH_2 (1 equiv.), **2** (1 equiv.), toluene, 80 °C, 74%.

74%. The formulation of **7** was confirmed by a spectrometric analysis. The mass spectrum of the product showed a molecular ion at *m/z* 440.

Two doublets (δ 3.93, 1.81) in the ^1H NMR spectrum of **7** are assigned to the methine protons. A low-frequency ^{13}C NMR resonance at δ 49.87 provides evidence for the tethered carbon atom of the two silicon moieties.

In summary, we have isolated the reactive intermediate, the cyclic bis(silyl) nickel complex, which reacts with unsaturated organic substrates such as an alkyne and alkene, generating a new class of heterocyclic compounds. The intermediate **2** is quite reactive and readily attacked by a variety of organic substrates. 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** (0.48 g, 1.85 mmol) in 20 ml of pentane was added to a stirred solution of $Ni(PEt_3)_4$ (0.98 g, 1.85 mmol) in 20 ml of pentane pentane at −20 °C. The solution was warmed to room temperature for 2 h. The solution was filtered. The residue was dissolved in toluene (20 ml) and this solution was covered with a layer of a pentane (20 ml) at −15 °C. Dark red crystals of **2** formed over a period of several days (0.88 g, 86% yield). ^1H NMR (C_6D_6): δ 1.13 (dq, J_{HH} 5.6, J_{HP} 6.4 Hz, CH_2), 0.63 (dt, J_{HH} 5.6 Hz, J_{HP} 14.2 Hz, CH_3), 0.42(s, $SiCH_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 71.08, 17.05 (d, J_{CP} 16.64 Hz, CH_2), 6.737 (s, CH_3), 4.105 (s, $SiCH_3$). $^{31}P\{^1H\}$ NMR (C_6D_6) : δ 5.58. ^{29}Si NMR(C_6D_6) : δ 43.19 (t, J_{SiP} 40.11 Hz).

‡ *Crystal data*: **2**: $C_{18}H_{52}B_{10}NiP_2Si_2$, M = 553.53, monoclinic, space group $P2_1/n$, a = 9.4833(6), b = 19.2061(13), c = 16.8724(10) Å, β = 93.029(2), V = 3068.8(3) Å^3, Z = 4, D_c = 1.198 g cm^{-3}, μ(Mo-Kα) = 0.823 mm^{-1}, 6498 reflections observed [$I > 2\sigma(I)$], 298 parameters, largest difference peak 0.401 e Å^{-3}. final R, R_w on [$I > 2\sigma(I)$] data were 0.0545, 0.1072, goodness of fit on F^2 = 1.083.

7: $C_{14}H_{28}B_{10}Si_2$, M = 360.64, monoclinic, space group $P2_1/n$, a = 9.6874(4), b = 18.2763(15), c = 12.7310(7) Å, β = 106.587(4)°, V = 2160.2(2) Å^3, Z = 4, D_c = 1.109 g cm^{-3}, μ(Mo-Kα) = 0.160 mm^{-1}, 4239 reflections observed [$I > 2\sigma(I)$], 255 parameters, largest difference peak 0.243 e Å^3, final R, R_w on [$I > 2\sigma(I)$] data were 0.0506, 0.1316, goodness of fit on F^2 = 0.967. CCDC 182/1017.

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