Formation of the Novel Neopentylidenoborane $Me_3Si(Bu^t)N{=}B{=}CHBu^t$ from the Tantalum Neopentylidene Complex $[(\eta\text{-}C_5H_5)Cl_2Ta{=}CHBu^t]$ by Metathesis

Ian Manners and Peter Paetzold*

Institut für Anorganische Chemie der Technischen Hochschule Aachen, Templergraben 55, D-5100 Aachen, West Germany

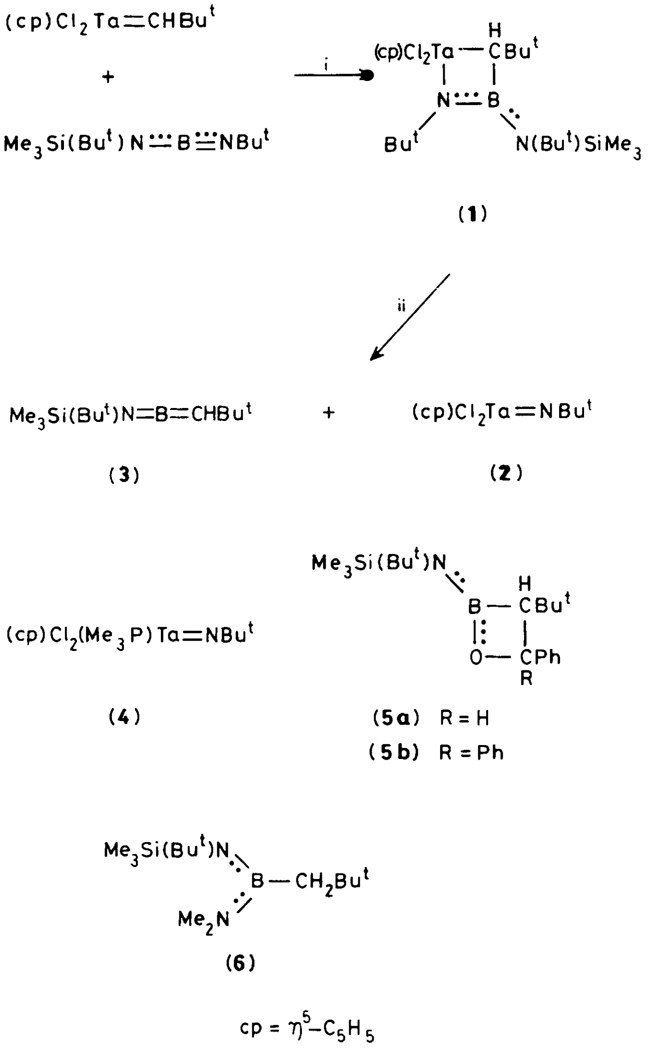
The aminoiminoborane $Me_3Si(Bu^t)N\overset{..}{-}B\overset{..}{\equiv}NBu^t$ reacts with the alkylidene complex $[(\eta\text{-}C_5H_5)Cl_2Ta{=}CHBu^t]$ at −50 °C to give a (2 + 2) cycloadduct containing a $\overline{\text{TaCBN}}$ ring; on warming to 0 °C cleavage occurs, affording the metathesis products $Me_3Si(Bu^t)N{=}B{=}CHBu^t$ and $[(\eta\text{-}C_5H_5)Cl_2Ta{=}NBu^t]$.

Iminoboranes $RB{\equiv}NR$ are isoelectronic with alkynes $RC{\equiv}CR$, to which they often show a close chemical similarity.[1] In the process of developing their co-ordination chemistry[1,2] we have carried out metathesis type reactions with transition metal alkylidene complexes[3] which provide a new synthetic route to compounds containing boron–carbon double bonds $RB{=}CR_2$ (alkylideneboranes), of which only a few examples are known.[4] In this paper we report our initial observations.

On warming a mixture of the aminoiminoborane $Me_3Si(Bu^t)N\overset{..}{-}B\overset{..}{\equiv}NBu^t$[5] and the 14-electron neopentylidene complex $[(\eta\text{-}C_5H_5)Cl_2Ta{=}CHBu^t]$[6] (1 : 1, in toluene) from −78 to −50 °C the solution rapidly darkened in colour. Addition of hexane and cooling to −80 °C gave a green crystalline precipitate, identified as the compound (**1**) (Scheme 1), containing a TaCBN four-membered ring, by low temperature n.m.r. spectroscopy (yield, 80%). In particular, a low field ^{13}C signal typical for a Ta=C bond was absent; instead, a resonance at δ 90.4 [d, *J*(CH) 107 Hz], assignable to an sp^3 hybridised carbon atom bonded to one hydrogen, was observed.

On allowing a toluene solution of (**1**) to warm to 0 °C a bright orange solution containing the metathesis products [(η-C_5H_5)Cl_2Ta=NBu^t] (**2**) and Me_3Si(Bu^t)N=B=CHBu^t (**3**) formed. The imido complex (**2**)† was isolated as orange-red crystals (80% yield) by removal of the solvent and recrystallisation from pentane at −80 °C. Pure (**3**) (a colourless liquid at −30 °C) was isolated in *ca.* 70% yield by the flash vacuum pyrolysis of (**1**) (65 °C, 10^{-3} Torr) using a short path length apparatus and a trap at −196 °C. The structure of (**3**) was established by its low temperature ^{1}H, ^{11}B, and ^{13}C n.m.r. spectra† and i.r. spectroscopy. Thus, for example, the ^{1}H n.m.r. spectrum of (**3**) shows a relatively low field resonance at δ 2.92 due to the hydrogen bonded to the sp^2 hybridised carbon atom, and the i.r. spectrum (hexane) two bands at 1705 cm^{-1}, and 1758 cm^{-1} (intensity ratio 4 : 1), characteristic[4] of N^{11}BC and N^{10}BC asymmetric stretching modes, respectively. The known compounds possessing a two co-ordinate boron atom doubly bonded to carbon all contain sterically demanding groups.[4] Thus (**3**) is the first example of such a compound with a hydrogen substituent at the multiply bonded carbon atom. In view of this, it is not surprising that (**3**) is unstable at room temperature, decomposing to as yet unidentified products ($t_{\frac{1}{2}}$ = *ca.* 12 h for a 5 × 10^{-4} M solution in hexane).‡

We have begun to investigate the chemistry of (**3**). For such studies, toluene solutions of (**3**) free of (**2**) were most conveniently generated by the addition of PMe_3, which led to the precipitation of the sparingly soluble white adduct (**4**).



Scheme 1. *Reaction conditions:* i, toluene, −78 to −50 °C, 1 h, then hexane, −78 °C; ii, 0 °C.

Benzaldehyde (PhCHO)§ and benzophenone (Ph_2CO) undergo [2 + 2] cycloaddition to the unsaturated B=C bond of (**3**) to give the oxaboretanes† (**5a**) [stereoselectively *anti*, *J*(HH) 3.5 Hz] and (**5b**), respectively (both compounds were isolated as colourless crystals in *ca.* 60% yield from pentane at −80 °C). The N–H bond of dimethylamine (Me_2NH) also adds across the B=C bond, affording the bis(amino)borane (**6**)† (colourless crystals from diethyl ether at −80 °C, 55% yield).

The remarkable formation of (**3**) may be attributed to the relative strength of the tantalum–nitrogen multiple bond, and

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† *Selected spectroscopic data* (in $CDCl_3$ at 25 °C unless otherwise stated, ^{11}B n.m.r. reference $Et_2O{\cdot}BF_3$): (**1**) (All data in [$^2H_8$]toluene at −50 °C) ^{1}H, δ 0.15 (s, 9H, SiMe$_3$), 0.62 (s, 9H, CCMe$_3$), 1.16 (s, 9H, NCMe$_3$), 1.42 (s, 9H, NCMe$_3$), 1.84 (s, 1H, CH), 5.80 (s, 5H, C_5H_5); ^{11}B, δ 25; ^{13}C, δ 7.6 (q, SiMe$_3$), 32.3 (q, 2NC*Me*$_3$), 33.2 (q, CC*Me*$_3$), 36.7 (s, C*C*Me$_3$), 54.7 (s, SiN*C*Me$_3$), 62.5 (s, TaN*C*Me$_3$), 90.4 (d, J_{CH} 107 Hz, CH), 116.2 (d, C_5H_5). (**2**) (All data in C_6D_6) ^{1}H, δ 1.11 (s, 9H, NCMe$_3$), 5.83 (s, 5H, C_5H_5); ^{13}C, δ 32.2 (q, NC*Me*$_3$), 66.3 (s, N*C*Me$_3$), 111.1 (d, C_5H_5). (**3**) (All data at −50 °C) ^{1}H, δ 0.26 (s, 9H, SiMe$_3$), 1.01 (s, 9H, CCMe$_3$), 1.19 (s, 9H, NCMe$_3$), 2.92 (s, 1H, CH); ^{11}B, δ 60 ; ^{13}C, δ 3.7 (q, SiMe$_3$), 30.6 (s, C*C*Me$_3$), 32.7 (q, CC*Me*$_3$), 34.4 (q, NC*Me*$_3$), 55.2 (s, N*C*Me$_3$), 69.1 (br. s, B=C). (**4**) ^{1}H (CD_2Cl_2), δ 1.44 (s, 9H, NCMe$_3$), 2.03 (d, J_{HP} 15 Hz, 9H, PMe$_3$), 5.33 (s, 5H, C_5H_5); ^{13}C, δ 15.8 (dq, J_{CP} 28 Hz, PMe$_3$), 32.1 (q, NC*Me*$_3$), 68.3 (s, N*C*Me$_3$), 108.6 (d, C_5H_5). (**5a**) ^{1}H (CD_2Cl_2), δ 0.32 (s, 9H, SiMe$_3$), 1.12 (s, 9H, CCMe$_3$), 1.48 (s, 9H, NCMe$_3$), 1.68 (d, J_{HH} 3.5 Hz, 1H, BCH), 5.26 (d, J_{HH} 3.5 Hz, 1H, OCH), 7.30—7.38 (m, 5H, Ph); ^{11}B, δ 40.4; ^{13}C, δ 5.4 (q, SiMe$_3$), 30.2 (q, CC*Me*$_3$), 33.0 (q, NC*Me*$_3$), 33.9 (s, C*C*Me$_3$), 54.7 (s, N*C*Me$_3$), 55.1 (d, BCH), 79.3 (d, OCH), 124.9, 126.8, 128.3 (3d, Ph), 145.2 (s, Ph). (**5b**) ^{1}H, δ 0.09 (s, 9H, SiMe$_3$), 0.85 (s, 9H, CCMe$_3$), 1.46 (s, 9H, NCMe$_3$), 2.50 (s, 1H, BCH), 7.03—7.76 (m, 10H, Ph); ^{11}B, δ 43.1; ^{13}C, δ 5.5 (q, SiMe$_3$), 31.2 (q, CC*Me*$_3$), 33.2 (q, NC*Me*$_3$), 33.8 (s, C*C*Me$_3$), 55.1 (s, N*C*Me$_3$), 57.5 (d, CH), 88.5 (s, *C*Ph$_2$), 126.1, 126.2, 126.2, 127.1, 127.7, 130.0 (6d, 2Ph), 144.1, 150.1 (2s, 2Ph). (**6**) ^{1}H, δ 0.16 (s, 9H, SiMe$_3$), 1.04 (s, 9H, CC*Me*$_3$), 1.27 (s, 9H, NC*Me*$_3$), 1.45 (s, 2H, CH$_2$), 2.76, 2.79 (2s, 6H, NMe$_2$); ^{11}B, δ 38.7; ^{13}C 4.9 (q, SiMe$_3$), 33.3 (q, CC*Me*$_3$), 33.8 (q, NC*Me*$_3$), 39.7, 40.5 (2q, NMe$_2$), 52.6 (s, N*C*Me$_3$).

‡ A white solid product has been isolated with a broad ^{11}B signal (in $CDCl_3$) at 46 p.p.m. [suggestive[7] of a cyclodimer of (**3**)]. However, the ^{1}H and ^{13}C n.m.r. spectra are too complex to interpret.

§ Experimental conditions; under N_2 using rigorously dry solvents. To [(η-C_5H_5)Cl_2Ta=CHBu^t] (2.74 mmol) in toluene (20 ml) at −78 °C was added dropwise a solution of Me_3Si(Bu^t)N=B=NBu^t (2.74 mmol) in the same solvent (5 ml). The solution was warmed to −50 °C, stirred for 1 h, and PMe_3 (2.76 mmol) added. After slow warming to 0 °C the reaction mixture was stirred for 5 min, cooled to −78 °C, and (**4**) filtered. To the filtrate was added excess PhCHO (5.46 mmol) and the reaction mixture allowed to warm to room temperature and stirred overnight. Solvent removal followed by multiple recrystallisation from minimal pentane at −80 °C gave colourless crystalline (**5a**) (0.56 g, 62%).

is, to the best of our knowledge, the first example of the synthesis of a novel multiply bonded main group element compound *via* a transition metal mediated metathesis reaction. Known routes to neutral species containing B=C double bonds typically involve the induced elimination of small molecules such as HCl or $SiMe_3F$ from suitable precursors and appear, at present, to be of somewhat limited scope. However, the metathesis route exemplified by the synthesis of (**3**) *via* (**1**) has considerable potential versatility, which is being investigated; substituent control is possible, in principle, by variation of both the alkylidene ligand and the iminoborane.

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