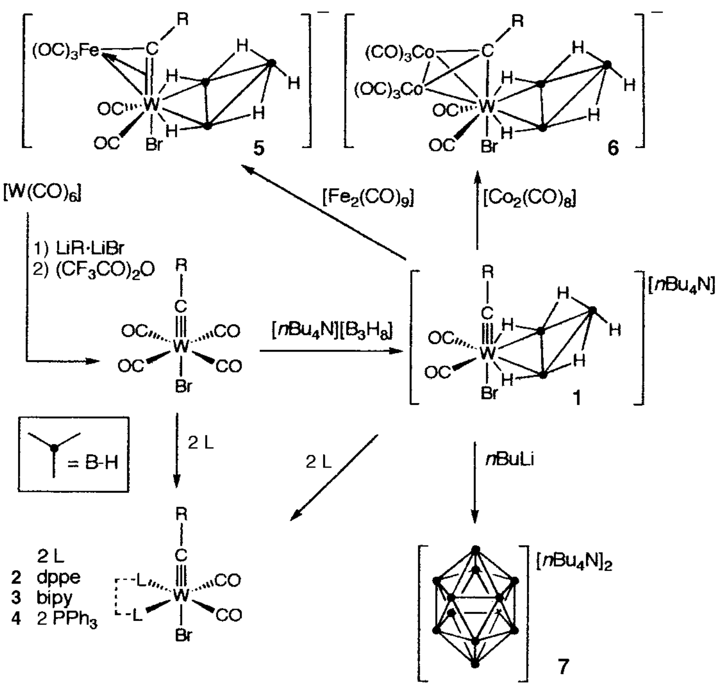
Alkylidyne – Metal Templated Triboronate Condensation[**]

Paul J. Dyson,* Anthony F. Hill,* Alexander G. Hulkes, Andrew J. P. White, and David J. Williams

Dedicated to Professor Warren R. Roper, on the occasion of his 60th birthday

From the earliest reports of high nuclearity boronates,[1] their syntheses have typically involved elevated temperatures, with an attendant loss of selectivity. An attractive alternative would be the condensation of small borohydride-based ligands on a metal template. This has been achieved in a few cases with the preparation of $[L_nMB_2H_5]$[2] and $[L_nMB_3H_8]$[3] ensembles from suitably nucleophilic metal complexes and monoborane precursors. As the oxidation state of boron typically increases with increasing nuclearity, deployment of such a strategy for the preparation of high-nuclearity boranes would require the incorporation of a "hydrogen sink". Stone and co-workers have documented two features of alkylidyne ligands that might predispose them to such a role: Firstly, hydroboration of the metal – carbon multiple bond can be facile, providing access to novel α-boraalkyl and boraalkyne complexes.[4] Secondly, in numerous instances high-nuclearity carbaborane cages couple with alkylidyne coligands, often by complete reduction of the alkylidyne to an alkyl group, which ultimately resides on the carbaborane cage.[5] Furthermore, we have recently shown that dihydrobis(pyrazolyl)borate coligands can also effect such a reduction.[6] We report here the synthesis and structural characterization of the first example of an alkylidyne metallatetraborane and its remarkably facile conversion to $[Bu_4N]_2[B_{12}H_{12}]$ in good yield under exceptionally mild conditions.

Successive treatment of $[W(CO)_6]$ with $Li[2,6\text{-}C_6H_3Me_2]\cdot LiBr$, $(CF_3CO)_2O$ and $[Bu_4N][B_3H_8]$ results in good yields of the somewhat thermolabile salt $[Bu_4N][W(B_3H_8)(\equiv CC_6H_3Me_2)Br(CO)_2]$ (**1**) (Scheme 1). The formulation of the orange, air-sensitive compound follows from spectroscopic data and was confirmed by a crystallographic study.[7] The alkylidyne ligand is manifest in the $^{13}C\{^1H\}$ NMR spectrum as a doublet at $\delta = 252.4$ showing coupling to tungsten [$J(WC) = 193$ Hz], accompanied by a single resonance for the two equivalent carbonyl coligands at $\delta = 217.7$. The molecular symmetry plane results in only two ^{11}B resonances being observed for the triboronate ligand at $\delta = 0.00$ (WB_2) and $\delta = -40.0$ ("wingtip"). The gross composition is reflected in the negative ion FAB-mass spectrum, which includes a molecular ion and fragmentations arising from loss of the carbonyl and triboronate ligands.



Scheme 1. Synthesis and reactions of **1**. $R = 2,6\text{-}C_6H_3Me_2$.

Two tungstatetraborane compounds have been previously isolated.[8, 9] One of these, $[WH_3(B_3H_8)(PMe_3)_3]$, has been structurally characterized[9] revealing bond W – B lengths of 2.519 and 2.495 Å within a disordered butterfly unit. The structure of the complex anion of **1** is shown in Figure 1. The "$W(\equiv CC_6H_3Me_2)Br(CO)_2$" component of the anion assumes essentially octahedral geometry with interligand angles in the range 85.5(4) – 90.0(5)°. The W≡C(1) bond at 1.805(13) Å is typical of low-valent tungsten alkylidynes, which are typically in the range 1.76 – 2.02 Å. The angle at C(1) is essentially linear [W-C(1)-C(2) 175(1)°]. The principal structural feature of interest is the tungstatetraborane unit which has W – B separations of 2.53(2) and 2.55(2) Å and a butterfly hinge

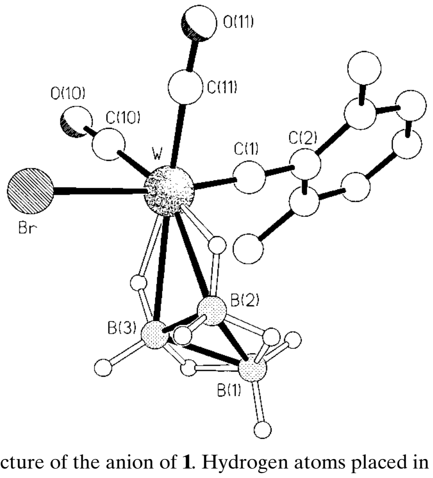


Figure 1. Molecular structure of the anion of **1**. Hydrogen atoms placed in idealized positions.

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angle of 121(1)°. The B(2)–B(3) length of 1.78(3) Å is comparable to the remaining B–B bonds [1.77(3), 1.80(3) Å] in the essentially equilateral triboronate triangle, perhaps reflecting the weak coordination. There are no significant intermolecular interactions between the complex and the $[Bu_4N]$ counterion.

The thermolability of **1** has been noted above, and the comparatively high values for the $\tilde{\nu}_{(CO)}$ IR absorptions suggest that despite the negative charge on the complex, this is not strongly felt at the metal center but presumably resides substantially on the triboronate ligand. Anionic alkylidyne complexes remain rare, the most celebrated being the carbaborane derivatives $[W(\equiv CR)(CO)_2(Cb)]^-$ (R = alkyl, aryl; Cb = $C_2B_9H_9Me_2$, $C_2B_{10}H_{10}Me_2$), which have been systematically investigated by Stone and co-workers,[5] and it may be argued that for this class of complex, once again much of the negative charge is located within the carbaborane cage. The reactivity of **1** was investigated with respect to both ligand exchange and bridge-assisted metal–metal bond-forming processes. Thus, the reactions of **1** with 2,2′-bipyridyl (bipy) or 1,2-bis(diphenylphosphino)ethane (dppe) lead, unfortunately, to replacement of the triboronate anion and formation of the complexes $[W(\equiv CC_6H_3Me_2\text{-}2,6)Br(CO)_2(bipy)]$ (**2**) and $[W(\equiv CC_6H_3Me_2\text{-}2,6)Br(CO)_2(dppe)]$ (**3**), which are more easily prepared directly from *trans*-$[W(\equiv CC_6H_3Me_2)Br(CO)_4]$.[10] Treating **1** with one equivalent of triphenylphosphane led to a mixture of **1** and *trans,cis,cis*-$[W(\equiv CC_6H_3Me_2)Br(CO)_2(PPh_3)_2]$ (**4**), whilst two equivalents of PPh_3 provided high yields of **4**. The reactions of **1** with $[Co_2(CO)_8]$ and $[Fe_2(CO)_9]$ appeared (color, solution IR) to provide compounds formulated as $[Bu_4N][WFe(\mu\text{-}CC_6H_3Me_2)(B_3H_8)Br(CO)_5]$ (**5**) and $[Bu_4N][WCo_2(\mu_3\text{-}CC_6H_3Me_2)(B_3H_8)Br(CO)_8]$ (**6**). However, these salts were exceedingly air- and temperature-sensitive and decomposed on attempted chromatographic purification, even on silica gel at −40°C. Accordingly, their formulations rest tenuously on limited data and by analogy with related reactions of $[W(\equiv CC_6H_3Me_2)(CO)_2(\eta\text{-}C_5H_5)]$.[10]

The above results taken together would appear to suggest that the coordination of the triboronate ligand in **1** is somewhat fragile. The most intriguing indication of this comes from the reaction of **1** with *n*BuLi and iodomethane. When the reaction is carried out in a dry ice/propanone bath, after 15 minutes a white precipitate forms, which was characterized as $[Bu_4N]_2[B_{12}H_{12}]$ (**7**) and isolated in 70% yield based on incorporated boron. The use of iodomethane in this process is serendipitous, having initially been employed (unsuccessfully) to trap any intermediates. However, whilst not essential to the boronate aggregation, it does serve to solubilize whatever low-valent tungsten side products are formed, thereby expediting work-up. The identity of **7** follows from spectroscopic data and a crystallographic study of the dichloromethane bis(solvate),[7] which shows the $[B_{12}H_{12}]^{2-}$ anion to have crystallographically imposed C_i symmetry and near ideal molecular I_h symmetry. Within the crystal lattice, each dodecaboronate cage is "cupped" between two pairs of cationic "hands" as illustrated in Figure 2.

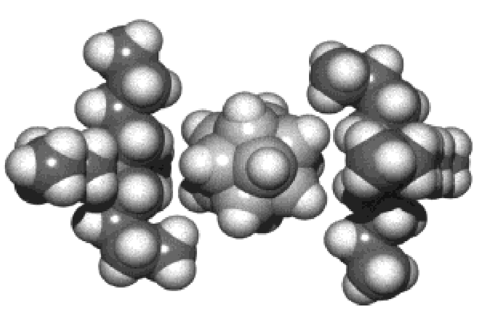

Figure 2. Crystal structure of **7**. Dicholoromethane solvate omitted.

Previously, the extended pyrolysis (200°C, 10 h) of $Na[B_3H_8]$ has been shown to provide (after Na/Cs exchange) $Cs_2[B_{11}H_{14}][BH_4]$.[11] That **7** should form at such a low temperature and in such respectable yields is truly remarkable and clearly implicates the noninnocence of the alkylidyne ligand, presumably as a hydrogen sink by successive hydride transfers, ultimately to afford mesitylene. The closest known relative of **1** is the salt $Cs[W(B_3H_8)(CO)_4]$, which is obtained from the reaction of $[W(CO)_6]$ with $Cs[B_3H_8]$ in 2,2′-dimethoxyethyl ether at reflux;[8] these stringent conditions attest to the stability of the "WB_3H_8" core in the absence of an alkylidyne ligand. The formation of **7** under our exceptionally mild conditions calls to mind the recent discussion by Curl of the assembly of C_{60} from low nuclearity C_x fragments in supersonic jets,[12] although the genesis of the B_{12} skeleton is perhaps more physically tangible than that of the carbon cluster.

Experimental Section

1: $[W(CO)_6]$ (1.00 g, 2.84 mmol) in Et_2O (20 cm^3) was treated with a solution of $Li[2,6\text{-}C_6H_3Me_2]\cdot LiBr$ (1.0 mol dm^{-3}, 2.9 cm^3, from Li and $Br[2,6\text{-}C_6H_3Me_2]$). The resulting yellow solution was cooled (dry ice/propanone), and $(CF_3CO)_2O$ (0.40 cm^3) added. The mixture was then allowed to warm to 0°C at which point $[nBu_4N][B_3H_8]$ (0.80 g)[13] was added. The mixture was stirred for 30 min (0°C) to provide a fine yellow precipitate, which was isolated by decantation and dried in vacuo. Yield 0.98 g (49%). IR (Nujol) 2493w, 2437w, 2385w [$\tilde{\nu}$(BH)], 2001vs, 1913vs [$\tilde{\nu}$(CO)] cm^{-1}; ^1H NMR ($CDCl_3$, 25°C, 270 MHz, Bu resonances omitted): −11.0 [s(br), 2H, WHB], 0.85 [m, 2H, BH], 1.23 [m, 2H, BH], 2.44 [m, 2H, BH], 2.51 [s, 6H, $C_6H_3CH_3$], 6.8–7.7 [m, 3H, C_6H_3]. $^{13}C\{^1H\}$ NMR: 252.4 [W≡C, J(WC) = 193.3 Hz], 217.7 [WCO], 140–126 (C_6H_3), 20.8 ($C_6H_3CH_3$); ^{11}B NMR: 0.00 [2 B, WB], −40.0 [1 B, wingtip B]; negative ion FAB-MS m/z = 477 [M^-], 449 [M^--CO], 437 [M^--B_3H_8]. Elemental analysis calcd for $C_{27}H_{53}B_3BrNO_2W$: C 45.1, H 7.4, N 2.0%; found: C 44.4, H 7.4, N 1.9%. The salt was also characterized crystallographically.[7]

7: A suspension of **1** (0.200 g, 0.28 mmol) in THF (10 cm^3) and benzene (5 cm^3) at −78°C was treated with *n*BuLi (0.27 cm^3, 2.0 mol dm^{-3} in cyclohexane), and the mixture stirred for 15 min resulting in the formation of a white precipitate. Iodomethane (0.3 cm^3) was then added, and the mixture allowed to warm to room temperature. The white precipitate was isolated by decantation and recrystallized from a mixture of CH_2Cl_2 and petroleum ether (40/60). Yield 0.031 g (69% based on incorporated boron); IR (Nujol) 2470 vs [$\tilde{\nu}$(BH)] cm^{-1}; negative ion FAB-MS m/z = 141 [M^-]. The salt was also characterized crystallographically.[7]

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[7] Crystal data for **1**: $[(C_4H_9)_4N][C_{11}H_{17}O_2B_3BrW]$, $M = 719.9$, monoclinic, space group $P2_1/c$ (no. 14), $a = 12.958(2)$, $b = 16.665(2)$, $c = 15.924(2)$ Å, $\beta = 101.07(1)^\circ$, $V = 3375.0(7)$ Å^3, $Z = 4$, $\rho_c = 1.42$ g cm^{-3}, $\mu(\mathrm{Mo_{K\alpha}}) = 46.3$ cm^{-1}, $F(000) = 1448$. An orange prism of dimensions $0.77 \times 0.70 \times 0.70$ mm was used. For **7**: $[(C_4H_9)_4N]_2[B_{12}H_{12}] \cdot 2\,CH_2Cl_2$, $M = 796.6$, monoclinic, space group $P2_1/c$ (no. 14), $a = 9.504(1)$, $b = 16.262(1)$, $c = 16.581(2)$ Å, $\beta = 99.67(1)^\circ$, $V = 2526.1(4)$ Å^3, $Z = 2$, $\rho_c = 1.05$ g cm^{-3}, $\mu(\mathrm{Cu_{K\alpha}}) = 22.9$ cm^{-1}, $F(000) = 868$. A clear rhomb of dimensions $0.43 \times 0.33 \times 0.20$ mm was used. Independent reflections: 5887 (3749); Siemens P4 diffractometers; graphite-monochromated $\mathrm{Mo_{K\alpha}}$ (**1**) and $\mathrm{Cu_{K\alpha}}$ radiation (**7**); ω scans. The structures were solved by the heavy atom and direct methods for **1** and **7**, respectively, and all the major occupancy non-hydrogen atoms were refined anisotropically (there being slight disorder in one of the butyl chains of the cation in **1**) with absorption corrected data using full-matrix least-squares based on F^2 to give $R_1 = 0.059$ (0.069), $wR_2 = 0.133$ (0.178) for 3734 (2555) independent observed reflections $[|F_o| > 4\sigma(|F_o|), 2\theta \leq 50^\circ\ (120^\circ)]$ and 325 (236) parameters for **1** and **7**, respectively. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101158. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Synthesis and Structure of $(CH_3Si)_6(NH)_9$: A Si–N Cage Made from Methyltrichlorosilane and Ammonia

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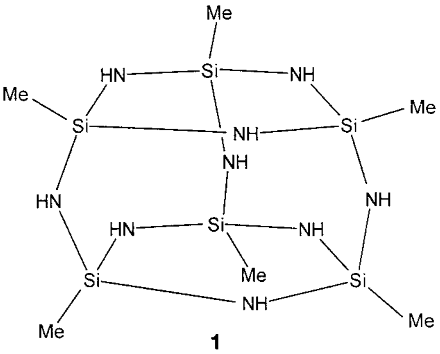
Dedicated to Professor Hans Bock on the occasion of his 70th birthday

Silicon–nitrogen compounds are being increasingly used for industrial purposes. Silicon nitride, for example, forms an integral part of many materials due to its high mechanical stability.[1] In recent years there has been an increasing effort to study nitridosilicates. These compounds consist of a highly polymeric three-dimensional silicon–nitrogen framework with incorporated cations.[2] We recently reported on cagelike silicon–nitrogen compounds with covalently bonded heteroatoms.[3, 4] Cyclopolyalkylsilazanes and alkylsilsesquiazanes have been known for a long time,[5] however these compounds have not been structurally characterized. Single crystals of $(MeSi)_6(NH)_9$ (**1**)[6] have now been investigated by X-ray structure analysis for the first time. They were obtained by developing a synthetic route in which no ammonium chloride is formed; our experience has shown that NH_4Cl hinders the growth of single crystals and is difficult to remove.



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Ammonia was condensed onto elemental sodium at −78 °C, and methyltrichlorosilane was added. This led to NaCl (which can be easily removed) and **1,** which was characterized by NMR and IR spectroscopy, mass spectrometry, and elemental analysis [Eq. (a)]. We assume that in the course of the reaction sodium amide is initially formed, which then reacts with methyltrichlorosilane under formation of sodium chloride. According to the single-crystal X-ray structure analysis, **1** consists of two six-membered Si_3N_3 rings in the chair conformation with alternating silicon and nitrogen atoms. The rings are linked to one another by bridging NH groups connected to the Si centers, resulting in a prismatic

$$6\,\mathrm{MeSiCl_3} + 18\,\mathrm{Na} \xrightarrow[-\,18\,\mathrm{NaCl}]{\mathrm{NH_3\ liq.}} (\mathrm{MeSi})_6(\mathrm{NH})_9\ \mathbf{1} \qquad \text{(a)}$$

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