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Preliminary communication

Transition metal mediated homologation of $BH_3 \cdot THF$: synthesis and crystal structure of $[WH_3(PMe_3)_3B_3H_8]$

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Abstract

The novel *arachno*-2-tungstametallaborane, $[WH_3(PMe_3)_3B_3H_8]$, has been made in high yield (> 90%) by the reaction of the monoborane $BH_3 \cdot THF$ (THF = tetrahydrofuran) with $[WH_6(PMe_3)_3]$. This represents a controlled transition metal mediated synthesis of a higher borane moiety from a mononuclear precursor. The crystal structure of $[WH_3(PMe_3)_3B_3H_8]$ has been determined.

Oligomerisation and homologation reactions of small hydrocarbon molecules mediated by transition metals are well known, but corresponding reactions are rare in borane(3) and diborane(6) chemistry. We have begun an exploration of transition metal mediated synthesis of higher boranes and metallaboranes from borane(3).

There is one reported example of the reaction of the $BH_3 \cdot THF$ complex with $[Mo_2(CO)_{10}H]^-$ to produce a four vertex metallaborane $[Mo(CO)_4B_3H_8]^-$, which was separated from a tar in undisclosed yield [1].

We report here the high yield synthesis of $[WH_3(PMe_3)_3B_3H_8]$ from the reaction of $[WH_6(PMe_3)_3]$ with $BH_3 \cdot THF$:

$$WH_6(PMe_3)_3 + 3BH_3 \cdot THF = WH_3(PMe_3)_3B_3H_8 + 2H_2 + 3THF$$

Reaction of $[WH_6(PMe_3)_3]$ with $BH_3 \cdot THF$ at room temperature proceeds initially through an uncharacterised deep purple intermediate which in the presence of excess $BH_3 \cdot THF$ reacts rapidly to give a yellow-brown solution, from which $[WH_3(PMe_3)_3B_3H_8]$ can be isolated. Recrystallisation from light petroleum gives an

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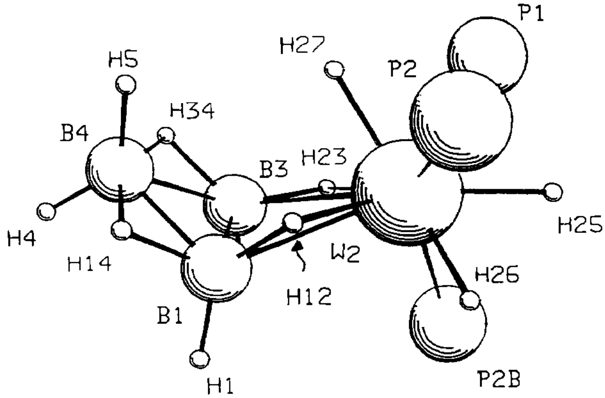

Fig. 1. Crystal structure of $[WH_3(PMe_3)_3B_3H_8]$. For clarity, the carbon atoms bonded to the phosphorus atoms have been omitted. Atom P(2)B is related to atom P(2) by the symmetry operator x, $y-1/2$, z. Selected bond lengths W(2)–P(1) 2.409(1), W(2)–P(2) 2.443(1), W(2)–B(1) 2.520(7), W(2)–B(3) 2.491(8), B(1)–B(3) 1.81(1), B(1)–B(4) 1.76(1), B(3)–B(4) 1.82(2) Å. Selected bond angles B(1)–W(2)–B(3) 42.4(3), P(1)–W(2)–P(2) 98.47(3), P(2)–W(2)–P(2)B 1.38.76(5), B(1)–B(4)–B(3) 60.8(5); dihedral angle between planes B(1), W(2), B(3) and B(1), B(3), B(4) 127.98°.

analytically pure product in $> 90\%$ yield. The structure of the $[WH_3(PMe_3)_3B_3H_8]$ has been determined by single crystal X-ray diffractometry *.

The molecule lies across a crystallographic mirror plane. Atoms W(2), P(1), B(1), H(25) and H(26) lie on the mirror plane. The P(1) methyl groups, H(27), and B_3H_8 ligand (except for B(1)) are disordered with respect to the mirror plane, and Fig. 1 shows only one of the two disordered arrangements. The hydrogen atoms of the B_3H_8 ligand and those attached to W(2) were located in difference Fourier maps, but their positions were poorly determined by the X-ray data.

The compound has been further characterised by multinuclear NMR, F.A.B. mass spectrometry, infrared spectroscopy and chemical analysis. The ^{11}B NMR shows a low field triplet at δ -0.8 (1B) due to the BH_2 group in the 4-position and a highfield doublet at δ -40.5 (2B) due to the two BH groups in the 1- and 3-positions. The ^{1}H and ^{31}P NMR spectra show temperature dependence indicative of a fluxional process involving the terminal hydrogen atoms attached to tungsten. At -40 °C the $^{1}H\{^{11}B\}$ spectrum exhibits six visible resonances in addition to those arising from the PMe_3 methyl protons. Two W–H resonances are observed at δ -0.22 (1H,br.t) and δ -3.33 (2H,m). At room temperature these resonances coalesce to a broad single resonance at δ -2.1 and at higher temperatures

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* Crystal data: $C_9H_{38}WP_3B_3$, M = 455.6, monoclinic, space group $P2_1/m$, a 9.247(3), b 15.546(6), c 7.221(2) Å, β 101.61(2)°, U 1016.82 Å^3, $Z = 2$, $D_c = 1.488$ g cm^{-3}, $F(000) = 452$, μ(Mo-K_α) 60.2 cm^{-1}, crystal size ca. 0.7×0.2×0.2 mm. Data were collected (2θ max 56°) on an Enraf–Nonius CAD4 diffractometer, using monochromated Mo-K_α radiation. An empirical absorption correction was applied and structure solution and refinement were carried out using 2220 observed reflections ($I > 3\sigma(I)$) from the 2537 independent reflections measured. The structure was solved by Patterson and Fourier methods. Full matrix least squares refinement has led to final agreement factors of $R = 0.024$ and $R_w = 0.026$.

The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

decomposition rapidly ensues. Resonances at δ 3.3 and δ 4.8 are assigned to the *exo*-H4 and *endo*-H5 terminal protons; complete assignment of these is not possible *. The W–H–B and B–H–B bridges resonate at δ −7.9 and δ 0.28 respectively, the latter being at unusually low field. The terminal B(1)–H(1) and B(3)–H(3) proton resonances are obscured by the PMe_3 resonances. However, careful spectral subtraction of $^1H\{^{11}B\}$ on- and off-resonance decoupled spectra [2] allowed their position to be established at δ 1.3 (2H). This was confirmed by $^{11}B\{^1H\}$ experiments. The $^{31}P\{^1H\}$ NMR at −40 °C shows two environments for the phosphine ligands; δ −19.4 (2P,d) and δ −31.0 (1P,t).

The butterfly geometry is well known for four vertex *arachno*-2-metallaborane analogues of tetraborane(10), and has been reviewed along with structures of other metallaboranes [3]. Generally these species are prepared by displacement reactions involving the *arachno*-$B_3H_8^-$ anion. Reported examples of such tungsten subrogated ** tetraborane(10) analogues are rare, but include $[NMe_4][W(CO)_4B_3H_8]$ [4] and the partially characterised $[W(\eta\text{-}C_5H_5)(CO)_2B_3H_8]$ [5].

The structure of $[WH_3(PMe_3)_3B_3H_8]$ is consistent with cluster electron counting procedures [6] which predict an *arachno*-four vertex cluster, the $\{W(PMe_3)_3H_3\}$ fragment subrogating for a $\{BH_2\}$ unit in the 2-position of the parent tetraborane(10). Alternatively the compound may be considered as an eighteen electron d^2 tungsten (IV) complex with a $[B_3H_8]^-$ moiety acting as a bidentate ligand via bridging hydrogen atoms.

Only one previous example of the use of $[WH_6(PR_3)_3]$ as a synthon for metallaboranes has been reported namely that in the synthesis of the decaborane(14) analogue $[W(PMe_2Ph)_3H_2B_9H_{13}]$ [7]. However, this work and related studies suggest that a variety of transition metal hydride complexes can act as synthons for metallaboranes [8].

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References

1 S.W. Kirtley, M.A. Andrews, R. Bau, G.W. Grynkewich, T.J. Marks, D.L. Tipton and B.R. Whittlesey, J. Am. Chem. Soc., 99 (1977) 7154.
2 J.D. Kennedy and J. Staves, Z. Naturforsch, B, 34 (1979) 808.
3 J.D. Kennedy, Prog. Inorg. Chem., 32 (1984) 519; Ibid., 34 (1986) 211.
4 F. Klanberg, E.L. Muetterties and L.H. Guggenberger, Inorg. Chem., 7 (1968) 2272.
5 D.F. Gaines and S.J. Hildebrandt, Inorg. Chem., 17 (1978) 794.
6 K. Wade, Adv. Inorg. Chem. Radiochem., 18 (1976) 1 and D.M.P. Mingos, Acc. Chem. Res., 17 (1984) 311.

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* For tetraborane(10) the chemical shift difference between these *exo*- and *endo*-protons is very small [9]. The chemical shift difference of δ 1.5 between H(4) and H(5) is unusually large. For the analogous $(\eta\text{-}C_5H_5)Fe(PMe_3)B_3H_8$ there is also a very large chemical shift difference between these *exo*- and *endo*-hydrogens [8].

** Subrogation is used as a term to indicate the replacement of a vertex and its attached groups in a polyhedral cluster by a moiety which maintains the same cluster electron count.

7 M.A. Beckett, N.N. Greenwood, J.D. Kennedy and M. Thornton-Pett, J. Chem. Soc., Dalton Trans., (1986) 801.

8 M.L.H. Green, M.A. Kelland, L.L. Wong, P.D. Grebenik and J.B. Leach, Abstract CA13, VI. International Meeting on Boron Chemistry, Bechyne, Czechoslovakia, June 1987, and unpublished results.

9 J.B. Leach, T. Onak, J. Spielman, R.R. Rietz, R. Schaeffer and L.G. Sneddon, Inorg. Chem., 9 (1970) 2170.