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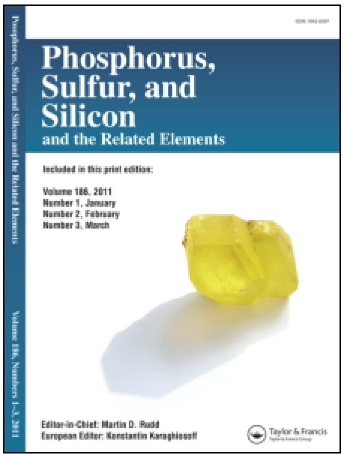

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Organotransition-Metal-Mediated Borane-Cage Expansion

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ORGANOTRANSITION-METAL-MEDIATED BORANE-CAGE EXPANSION

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Attempts were made to synthesize dinuclear Group 6 metal complexes of the arachno-*octahydrotriborate anion. Specifically, the dimer* $[CpW(CO)_3]_2$ *(*$Cp = \eta^5\text{-}C_5H_5$*) was employed as the metal reagent. However, the formation of dinuclear metallaborane complexes did not ensue. Rather, clean, rapid, systematic borane-cage expansion was observed. The* $[B_3H_8]^-$ *cluster was quantitatively converted to* B_5H_9*,* $[B_9H_{14}]^-$*, or* $[B_{11}H_{14}]^-$*, or both, depending on reaction conditions. Refluxing a 1:1 mixture of* $[B_3H_8]^-$ *and* $[CpW(CO)_3]_2$ *in toluene or dioxane lead to the rapid, quantitative conversion of* $[B_3H_8]^-$ *to* B_5H_9*. However, refluxing a 2:1 mixture of* $[B_3H_8]^-$ *and* $[CpW(CO)_3]_2$ *in the same solvents yielded* $[B_9H_{14}]^-$ *and* $[B_{11}H_{14}]^-$ *as the primary products; when glyme was the solvent, only* $[B_9H_{14}]^-$ *was observed, even after prolonged heating.*

Keywords: Borane; clusters; metal dimers; tungsten

INTRODUCTION

Many mononuclear transition-metal complexes of the *arachno*-octahydrotriborate anion, $[B_3H_8]^-$, are known.[1–3] These complexes are synthesized by straightforward, one-step reactions between an organotransition-metal compound and the borane. For example, reacting a Group 6 homoleptic carbonyl with $Cs[B_3H_8]$ in refluxing glyme/diglyme produces the mononuclear complex $[(CO)_4MB_3H_8]^-$ (M = Cr, Mo, W) in high yield.[4] The borane displaces two CO ligands and binds to the metal center in a bidentate fashion via two B—H—M three-center–two-electron bonds.

Attempts were made to synthesize dinuclear Group 6 metal complexes of the *arachno*-octahydrotriborate anion. Specifically, the dimer

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TABLE I Reaction of $[B_3H_8]^-$ with One Equivalent of $[CpW(CO)_3]_2$

$[B_3H_8]^-$	Solvent	Time	Borane(s) Observed by ^{11}B NMR
1 equiv.	Toluene	2 h	B_5H_9 (100%)[a]
1 equiv.	Dioxane	4 h	B_5H_9 (100%)[a]
2 equiv.	Toluene	3 h	$[B_9H_{14}]^-$[b] and $[B_{11}H_{14}]^-$[c]
2 equiv.	Dioxane	12 h	$[B_9H_{14}]^-$ (major), B_5H_9, $[B_{11}H_{14}]^-$
2 equiv.	Glyme	24 h	$[B_9H_{14}]^-$ (>90%), traces of B_5H_9 and $[B_{11}H_{14}]^-$
4 equiv.	Toluene	18 h	$[B_3H_8]^-$ (>50%), B_5H_9, $[B_9H_{14}]^-$, $[B_{11}H_{14}]^-$

[a] −13.4 ppm (d, $J = 163$ Hz); −52.9 ppm (d, $J = 170$ Hz); ^{11}B NMR spectrum of an authentic sample of B_5H_9 (in THF): −11.4 ppm (d, $J = 162$ Hz); −52.9 ppm (d, $J = 175$ Hz).

[b] −7.6 ppm (d, $J = 143$ Hz); −20.8 ppm (d, $J = 141$ Hz); −23.5 ppm (d, $J = 132$ Hz); Literature values (from Ref. 5) (in DMSO): −8.3 ppm (d, $J = 140$ Hz); −20.4 ppm (d, $J = 130$ Hz); −23.4 ppm (d, $J = 140$ Hz).

[c] −12.0 ppm (d, $J = 160$ Hz); −14.8 ppm (d, $J = 121$ Hz); −15.8 ppm (d, $J = 132$ Hz); Literature values (from Ref. 6) (in glyme): −12.5 ppm (d, $J = 146$ Hz); −14.1 ppm (d, $J = 156$ Hz); −14.9 ppm (d, $J = 138$ Hz).

$[CpW(CO)_3]_2$ (Cp = η^5-C_5H_5) was employed as the metal reagent. However, the formation of dinuclear metallaborane complexes did not ensue. Rather, clean, rapid, systematic borane-cage expansion was observed. The $[B_3H_8]^-$ cluster was quantitatively converted to B_5H_9, $[B_9H_{14}]^-$, and/or $[B_{11}H_{14}]^-$, depending on reaction conditions.

RESULTS

The conditions and products of our experiments with $[CpW(CO)_3]_2$ are summarized in Table I and detailed below in Parts A—C; other experiments are presented in Parts D—F. The borane products were determined by ^{11}B NMR spectroscopy. (Also, it is noted that in the ^{11}B NMR spectrum of all mixtures with a greater than 1:1 ratio of $[B_3H_8]^-$:$[CpW(CO)_3]_2$ an unidentified singlet ($\delta = 2$ ppm), accounting for about 10% of the total boron content, was present.)

Part A: 1:1 ratio of $[B_3H_8]^-$:$[CpW(CO)_3]_2$

Toluene or Dioxane as Solvent

Refluxing a toluene solution for 2 h resulted in the quantitative conversion of $[B_3H_8]^-$ to B_5H_9. Prolonged reaction times (up to 6 h) did not change the appearance of the ^{11}B NMR spectrum. In the lower-boiling dioxane 4 h of refluxing was required for complete conversion to B_5H_9.

After removal of solvent, NMR spectroscopy of the residue showed the tetracarbonyl dimer* $[CpW(CO)_2]_2$ and some of the starting hexacarbonyl dimer.

Part B: 2:1 Ratio of $[B_3H_8]^-$:$[CpW(CO)_3]_2$

Toluene as Solvent

Refluxing a toluene solution for 3 h yielded $[B_9H_{14}]^-$ and $[B_{11}H_{14}]^-$ as the primary products. Only trace amounts of B_5H_9 were observed.

Dioxane or Glyme as Solvent

Here the difference in rate as a function of solvent boiling point was more pronounced. Dioxane has a boiling point 10 degrees lower than toluene. After a dioxane solution was refluxed for 12 h, the ^{11}B NMR spectrum revealed that B_5H_9 still accounted for about one-fourth of the total boron content; $[B_{11}H_{14}]^-$ is a minor component, with $[B_9H_{14}]^-$ comprising the rest of the mixture. Glyme has a boiling point 26 degrees lower than toluene. At this temperature formation of $[B_{11}H_{14}]^-$ appears to be nearly completely arrested (at least in the time frame of our experiments). Refluxing a glyme solution for 24 h gave $[B_9H_{14}]^-$ as the dominant (>90%) borane cage, with some $[B_3H_8]^-$ and traces of B_5H_9 and $[B_{11}H_{14}]^-$.

Part C: 4:1 Ratio of $[B_3H_8]^-$:$[CpW(CO)_3]_2$

Prolonged reflux times (up to 18 h in toluene) of these solutions facilitated only incomplete conversion (<50%) of the triborane anion to the larger cages; also, the cage expansion proceeds more slowly than for the 2:1 mixtures.

Part D: 1:1 Ratio of $[B_3H_8]^-$:$[CpW(CO)_2]_2$

The tetracarbonyl dimer $[CpW(CO)_2]_2$ was observed at the end of the reflux periods (see Part A). To determine if this were the active species, the tetracarbonyl dimer was allowed to react with the borane. No reaction occurred upon heating a diglyme solution to 110°C for 3 h; only starting material was observed in the ^{11}B NMR spectrum.

Part E: 1:1 Ratio of $[B_3H_8]^-$:$(C_6H_5C(O)\text{-}O\text{-}O\text{-}C(O)C_6H_5)$

To determine if a radical generator could promote cage expansion (see Discussion section), benzoyl peroxide was substituted for the

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*^1H: $\delta = 5.24$ ppm(s); $^{13}C\{^1H\}$: $\delta = 85.3$ ppm(s).

metal dimers. Refluxing a toluene solution overnight resulted in the quantitative conversion (as revealed by ^{11}B NMR spectroscopy) of $[B_3H_8]^-$ to an unknown compound ($\delta = 2$ ppm(s)); this may be the same compound that was observed in the reactions of $[B_3H_8]^-$ with the hexacarbonyl dimers (vide supra). No higher boranes were observed.

Part F: Control Experiments

No reaction occurred upon refluxing solutions of $(Bu_4N)B_3H_8$ in glyme, dioxane, or toluene for 24 h; only starting material was observed in the ^{11}B NMR spectrum.

DISCUSSION

We draw two main, interrelated conclusions from our work. First, the tungsten dimer is directly responsible only for the initial cage expansion of $[B_3H_8]^-$ to B_5H_9. A 1:1 ratio of borane:dimer yields solely B_5H_9. When a 2:1 mixture is allowed to react, half of the $[B_3H_8]^-$ is converted to B_5H_9; the rest is available to react with the newly formed B_5H_9 to generate $[B_9H_{14}]^-$. Then, $[B_9H_{14}]^-$ and $[B_3H_8]^-$ compete for the B_5H_9 to make $[B_{11}H_{14}]^-$ and more $[B_9H_{14}]^-$ respectively. This conclusion is supported by two earlier reports on borane-cage expansion. The conditions were similar to ours, except only the boron-containing reagents were present. Savory and Wallbridge[5] allowed equimolar amounts of B_5H_9 and $[B_3H_8]^-$ in diglyme to stir for 10 days at room temperature; the major product was $[B_9H_{14}]^-$. Later, Shore and coworkers[6] showed that $[B_{11}H_{14}]^-$ is obtained in quantitative yield by refluxing $[B_9H_{14}]^-$ with 0.4 equivalents of B_5H_9 in glyme.

Second, the tungsten dimer appears to be reacting in a 1:1 stoichiometric relationship with the borane anion. As stated above, it appears that one equivalent of $[B_3H_8]^-$ is converted to B_5H_9, and any additional $[B_3H_8]^-$ reacts with the B_5H_9. This is supported by the results when a 4:1 ratio of borane to dimer is employed. Even prolonged reflux times (up to 18 h in toluene) of these higher-ratio solutions facilitated less than 50% conversion of the triborane anion to the larger cages. If indeed a total of two equivalents of $[B_3H_8]^-$ react per mole of tungsten dimer, a theoretical yield of 50% would be predicted for a 4:1 mixture.

We attempted to discern how the tungsten dimer interacted with the $[B_3H_8]^-$. At the reflux temperatures of the solvents employed, the tungsten atoms in the hexacarbonyl starting material ($[CpW(CO)_3]_2$) each lose one CO ligand, leaving the tetracarbonyl complex $[CpW(CO)_2]_2$; indeed, the presence of $[CpW(CO)_2]_2$ in the reaction mixture has been observed by NMR spectroscopy[7] (see Part A, Results section). The possibility of the tetracarbonyl complex being the active form of the dimer was examined by heating solutions of $[CpW(CO)_2]_2$ and $[B_3H_8]^-$. However, only starting material was observed in the ^{11}B NMR spectra.

The proposed mechanism for the formation of the tetracarbonyl dimer from the hexacarbonyl dimer involves homolytic fission of the W—W bond, and the production of monomeric radicals.[8,9] However, the apparent inability of benzoyl peroxide to foster formation of the larger boranes would indicate that radicals ipso facto do not promote the cage expansion of $[B_3H_8]^-$. The mechanism remains obscured.

The solvent does not appear to play a direct role in the cage expansion. A hydrocarbon (toluene), a nonpolar cyclic ether (dioxane), and a polar straight-chain ether (glyme) gave similar results. The solvents did seem to have an effect on the kinetics of the cage expansion. However, the rates are proportional to the boiling point of each solvent, and any kinetic effect can be attributed readily to that physical property.

Finally, a comment on our control experiments. Only starting material was observed in the ^{11}B NMR spectrum after refluxing solutions of $(Bu_4N)B_3H_8$ in glyme, dioxane, or toluene for up to 24 h. However, when a solution of $(Bu_4N)B_3H_8$ in diglyme was refluxed for 15 h, $[B_3H_8]^-$ was quantitatively converted to $(CH_3BO)_3$, $B(OCH_3)_3$, and $CH_3OB(CH_3)_2$ in an approximately 2:2:1 ratio, as revealed by ^{11}B NMR spectroscopy.[10,*] In an earlier study, Schaeffer and coworkers[11] reported that refluxing NaB_3H_8 in diglyme produced the icosohedral dianion $B_{12}H_{12}^{2-}$. The one obvious difference between the two experiments is the cation; otherwise, we cannot explain this discrepancy.

EXPERIMENTAL

All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques. Solvents were distilled from sodium benzophenone ketal. $[CpW(CO)_3]_2$ (Strem) and benzoyl peroxide (Aldrich) were used as received. $(Bu_4N)B_3H_8$ was prepared by the method described by Ryschkewitsch and Nainan.[12] $[CpW(CO)_2]_2$ was synthesized in diglyme as proscribed by Curtis et al.[7]; these solutions were used in subsequent reactions without further purification.

NMR spectra were measured at room temperature on a Varian-300 FT-NMR spectrometer operating at 96.3 MHz for ^{11}B spectra,

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[*] ^{11}B NMR resonances: $(CH_3BO)_3$ (obs. +32.0(s); lit. +33), $B(OCH_3)_3$(obs. +18.7(s); lit. +18), and $CH_3OB(CH_3)_2$ (obs. +54.3(s); lit. +54).

300 MHz for ^{1}H spectra, and 75.5 MHz for ^{13}C spectra. Boron trifluoride etherate ($\delta = 0$ ppm) was used as an external reference for ^{11}B spectra; tetramethylsilane ($\delta = 0$ ppm) was used as an internal reference for ^{1}H NMR spectra; and the solvent peak ($\delta = 77.0$ ppm) was used as an internal reference for ^{13}C NMR spectra.

The following describes a typical experiment: A 100-mL two-necked flask equipped with a reflux condenser was charged with $[CpW(CO)_3]_2$ (0.333 g, 0.500 mmol), $(Bu_4N)B_3H_8$ (0.283 g, 1.00 mmol), and a stir bar. A stopcock-adapter was attached to the condenser, and the second neck was plugged with a septum. The system was evacuated on a Schlenk line, then filled with nitrogen; a nitrogen atmosphere was maintained throughout the experiment. Toluene (30 mL) was added via syringe. The stirred mixture was brought to reflux. Samples were removed periodically for ^{11}B NMR measurements. Next, the solvent was removed in vacuo, and the residue was dissolved in $CDCl_3$ for the ^{1}H and ^{13}C spectra.

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