a change in [Ir] does elicit a change in k_{obs}. However, our present understanding of this effect suffers from poor reproducibility and, thus, provides us with little quantitative insight into the kinetics of oxygen exchange in the less basic regions. Figure 2 shows a plot of k_{obs} vs [OH$^-$], which we describe by the tentative rate law

$$\text{rate}/[\text{Ir(OH)}_6^{3-}] = k_{obs} = k_{OH}[\text{OH}^-]^{-1}$$

Regression analysis of data from runs in which $[\text{OH}^-] \geq 0.5$ M results in $k_{OH} = (1.00 \pm 0.04) \times 10^{-4}$ M s^{-1} at 0 °C and ionic strength near 2 M. A term, independent of [OH$^-$] is statistically insignificant. The temperature dependence of k_{OH} at [OH$^-$] = 3 M indicates that $\Delta H^* = -99 \pm 5$ kJ/mol and $\Delta S^* = 64 \pm 20$ J/(mol K).

The hexaaquairidium(III) ion seems to be one of the, if not the most, inert monomeric 3+ ions in aqueous acidic medium.[13] The hexahydroxoiridate(III) ion is, by comparison, quite labile with $t_{1/2} = 125$ min at 0 °C. Whether this relatively facile exchange is an intrinsic property of Ir(OH)_6^{3-} or a consequence of some catalytic process is not yet known. It is conceivable that this relatively rapid exhange rate is the result of a chemical equilibrium between the monomeric iridium(III) ion and traces of the iridium(IV) ion(s) that are known to form in alkaline solution. Such redox equilibria involving a very exchange-labile impurity of a different oxidation state have been shown to dictate the apparent solvent-exchange rate of the major species in other systems.[14] Though the results of this study do not yet provide sufficient evidence to support mechanistic conclusions, they do establish that the coordination number of iridium(III) in basic solution is 6 and provide the first quantitative rate measurements at the iridium(III) center. We expect that the techniques developed here can be applied to further kinetic studies on the iridium(III) system and to the analogous chromium(III) and rhodium(III) systems.

Acknowledgment. We thank the Austrian Foundation for the Advancement of Scientific Research for financial support (Project No. 4252). Gratitude is also expressed to Heliodor Gschwandle for technical assistance during the course of these investigations.

Registry No. Ir(OH)_6^{3-}, 118111-13-0; H_2O, 7732-18-5.

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Reaction of Intermediate-Sized Boranes with Methylidenetriphenylphosphorane

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Received August 3, 1988

The reactions between alkylidenetriphenylphosphorane ylides and boranes have been the subject of much study.[1-7] The results obtained may be classed into two groups. The lower boranes, including BH_3, B_2H_6, and B_3H_7L (L = Lewis base), form adducts[1-3,5,6] of the type $PR_3CR'_2{\cdot}BH_3$ or $PR_3CR'_2{\cdot}B_3H_7L$, whereas higher boranes such as $B_{10}H_{14}$ and $B_9H_{13}L$ are deprotonated to form the tetraorganylphosphonium salts[1,4] of the borane. The BH_3 adducts undergo interesting thermal rearrangements at higher temperatures.[8,9] There have been no reports of reactions between intermediate-sized boranes and these ylides. This paper describes the reactions of some *nido*-penta- and hexaboranes and the related C_2B_4 *nido*-carboranes with methylidenetriphenylphosphorane. We were particularly interested to see if the products were the borane salts, since the normal method of preparation of these salts involves the use of KH, NaH, or $LiCH_3$ and the products are quite thermally unstable.[10-12] These salts are very useful intermediates, and unless they are prepared in situ for subsequent chemistry, the normal procedure is to convert them to the more stable analogues containing large cations by methathesis.[13,14]

Table I. Triphenylmethylphosphonium Salts of Boranes Prepared in the Reaction between $(C_6H_5)_3PCH_2$ and the Boranes B_5H_9, 1-BrB_5H_8, B_6H_{10}, and $C_2B_4H_8$

species	yield, %	mp,[a] °C	anal.: obsd (calcd) % C	anal.: obsd (calcd) % H
$[(C_6H_5)_3PCH_3][B_5H_8]$	70	187	62.71 (67.20)	7.59 (7.72)
$[(C_6H_5)_3PCH_3][BrB_5H_7]$	40	85	53.55 (54.54)	5.55 (6.04)
$[(C_6H_5)_3PCH_3][B_6H_9]$	20	85–87	65.25 (64.97)	7.59 (7.75)
$[(C_6H_5)_3PCH_3][C_2B_4H_7]$	50	197	68.83 (71.73)	7.12 (7.16)

[a] All species melted with decomposition.

Experimental Section

All manipulations were performed on a high-vacuum line or in a drybox. NMR spectra were run on a Nicolet NT 300 or a Varian XL-300 spectrometer at 300 MHz for ^{1}H, at 96.3 MHz for ^{11}B, and at 121.5 MHz for ^{31}P spectra. Infrared spectra were recorded on a Perkin-Elmer 337 or 783 spectrometer with use of thoroughly dried KBr.

Triphenylphosphine was obtained from Matheson Coleman and Bell. It was converted to the $[(C_6H_5)_3PCH_3]Br$ or I$^-$ salt and treated with n-C_4H_9Li or KH in THF to obtain the ylide. B_5H_9 was obtained from laboratory stock and used without purification. $C_2B_4H_8$,[15] $(CH_3)_2C_2B_4H_6$,[16] B_6H_{10},[17] and 1-BrB_5H_8[18] were prepared by standard methods. KH (Alfa) was washed with C_5H_{12} repeatedly until it was a white, free-flowing powder. All solvents were dried and distilled prior to use.

The preparation of $[(C_6H_5)_3PCH_2][C_2B_4H_7]$ will serve to describe the procedure whereby the salts of B_5H_9, B_6H_{10}, and 1-BrB_5H_8 were prepared. In a typical reaction, in the drybox, a two-neck reaction flask attached to an extractor was charged with KH (0.036 g, 0.792 mmol, 88% active) and sealed with a rotatable solid-addition tube containing $[(C_6H_5)_3PCH_3]^+I^-$ (0.377 g, 0.684 mmol). After evacuation on the vacuum line, 15 mL of THF was condensed into the flask at −196 °C, $(C_6H_5)_3PCH_3]^+I^-$ was added, and the contents were allowed to warm to room temperature. Stirring for 1 h resulted in the formation of a bright yellow solution and the evolution of 0.60 mmol of hydrogen, which was measured by using a Toepler pump. The solution was then filtered to remove KI, unreacted $[(C_6H_5)_3PCH_3]^+I^-$, and KH. $C_2B_4H_8$ (0.32 mmol) was condensed into the mixture at −196 °C, and gradual warming to −35 °C with stirring resulted in rapid decolorization of the bright yellow solution and precipitation of a white solid. The contents of the reaction flask were frozen at −196 °C and transferred under positive flow of nitrogen to a clean extractor. Filtration at −78 °C resulted in the isolation of 0.056 g (50% yield) of the white product, which melted with decomposition at 197 °C. Anal. Calcd for $C_{21}H_{25}B_4P$: C, 71.73; H,

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0020-1669/89/1328-0381$01.50/0

Table II. Spectral Data

species	^{11}B NMR chem shifts,[a] ppm		IR, cm^{-1} (BH region)
	B_{base}	B_{apex}	
$[(C_6H_5)_3PCH_3][B_5H_8]$	−15.2	−51.5	2475 (s, br), 1945 (w), 1845 (w)
$[(C_6H_5)_3PCH_3][BrB_5H_7]$	−13.23	37.30	2497 (s, br), 2238 (w)
$[(C_6H_5)_3PCH_3][B_6H_9]$	10.43	−49.72	not recorded
$[P(C_6H_5)(CH_3)[C_2B_4H_7]$	7.1(1), −5.5(2)	−55.0	2475 (s, br), 1800 (w)

[a] Spectra run in CD_2Cl_2 at −50 °C; numbers in parentheses indicate relative areas.

7.16; B, 12.30. Found: C, 68.83; H, 7.12; B, 12.73. The 96.3-MHz ^{11}B NMR spectrum at −78 °C in CD_2Cl_2 exhibits a doublet at −55.0 ppm (J = 155 Hz) assigned to the apical boron atom and two singlets at 6.7 and −5.9 ppm attributed to B(4,6) and B(5), respectively. The 300-MHz proton NMR spectrum consists of a multiplet at 7.8 ppm and a doublet at 2.74 ppm (J = 13 Hz) assigned to the phenyl and methyl protons, respectively, on $[(C_6H_5)_3PCH_3]^+$, a singlet at −5.0 ppm and a 1:1:1:1 quartet at −1.97 ppm (J = 155 Hz) arising from the bridge hydrogen and the apical terminal hydrogen, respectively, and a singlet at 4.93 ppm attributed to the hydrogens on the carbons of the carborane cage. Two broad overlapping resonances at 3.4 and 2.0 ppm with area ratios of 2:1 are assigned to the hydrogens attached to the basal boron atoms. The 121.5-MHz ^{31}P NMR spectrum exhibits a sharp resonance at 21.8 ppm. The IR spectrum includes a strong band at 2475 cm^{-1} (BH_{term}) and a weak band at 1800 cm^{-1} (BH_{bridge}).

Results and Discussion

The boranes B_5H_9, B_6H_{10}, $C_2B_4H_8$, and 1-BrB_5H_7 were easily deprotonated in the ylide solution, and the results are summarized in Table I. The first three boranes afford white solids that are stable for several hours in the absence of air and moisture. Spectral data for the species are given in Table II.

2,3-Dimethyldicarbahexaborane(8) did not react with the ylide, and we presume that the inductive effect of the methyl groups reduces the acidity of the carborane such that deprotonation does not occur. $(CH_3)_2C_2B_4H_6$ is easily deprotonated with NaH, as others have noted.[19,20] The reaction between 1-BrB_5H_8 and $(C_6H_5)_3PCH_2$ is much more complicated than those of the other species. If the reaction is carried out exactly as it was for $C_2B_4H_8$, two products appear to be formed, one a white powder and the other a yellow oil. We were not able to separate and identify these species satisfactorily, and the eventual elemental analysis of the two species gave inconclusive results. The relative quantities of the two species appeared to be temperature dependent, suggesting that perhaps some thermal reaction or arrangement occurs. A possibility is that there are two simultaneous reactions occurring: deprotonation and adduct formation. A third possibility is that these two products may interconvert according to

$$[(C_6H_5)_3PCH_3][B_5H_7Br] \rightarrow [(C_6H_5P)_3PCH_3\cdots B_5H_8Br]$$

Another possible side reaction, which has precedent in the chemistry of bromoboranes,[17] is the elimination of $[(C_6H_5)_3PCH_3]Br$ from either the adduct or the salt to form higher boranes according to

$$[(C_6H_5)_3PCH_3]B_5H_7Br \rightarrow [(C_6H_5)_3PCH_3]Br + \text{“}B_5H_7\text{”}$$

$$\text{“}B_5H_7\text{”} \rightarrow \text{higher boranes} + H_2$$

"B_5H_7" could form $B_{10}H_{14}$ or any of a series of higher boranes. The final product mixture always contained materials that we presumed to be higher boranes. Their ^{11}B NMR spectra were complex but resembled spectra of mixtures of higher boranes. Allowing the reaction to proceed in an NMR tube and monitoring it by NMR were not easy, since 1-BrB_5H_8 rearranges to the 2-isomer in ethers, as noted previously.[21] Because the ylide is not soluble in other solvents such as C_5H_{12} or CH_2Cl_2, the reaction could not be followed in these. The $[1\text{-}BrB_5H_7]^-$ salt was prepared by carrying out the reaction with the ylide at −78 °C and isolating the product without warming the reaction mixture above −78 °C until the solvent-free solid was isolated. This substance was a yellowish solid, and its spectral and other data are given in Tables I and II. In order to demonstrate that deprotonation took place at −78 °C, the reaction between 1-BrB_5H_8 and $(C_6H_5)_3PCH_2$ was allowed to proceed at that temperature and then to warm slowly to room temperature while the spectrum was monitored. In the range −80 to −20 °C, the separation between the two ^{11}B resonances did not change although there was a small (0.46 ppm) shift upfield. The spectrum of the parent 1-BrB_5H_8 under the same conditions has different peak separations and chemical shifts. At −20 °C, significant decomposition had taken place; however, the spectrum still resembled that of the anion. The resultant salt is much less stable than the other $[(C_6H_5)_3PCH_2]^+$ salts reported herein.

In summary, intermediate boranes react with methylidenetriphenylphosphorane to give products resulting from deprotonation of the borane. The yields are quite low, and thus, the reaction is not a useful method for directly preparing the stable borane salts and will not serve as an alternative to methods using alkali-metal hydrides.

Acknowledgment. We acknowledge support from the Grant Incentive and Weldon Spring Funds of the University of Missouri—St. Louis and the National Science Foundation for an instrumentation grant (Grant No. CHE-8506671), and P.N. acknowledges support from NSF-REU Grant CHE-8712558.

Registry No. $[(C_6H_5)_3PCH_3]Br$, 1779-49-3; $[(C_6H_5)_3PCH_3]I$, 2065-66-9; B_5H_9, 19624-22-7; $C_2B_4H_8$, 18972-20-8; $(CH_3)_2C_2B_4H_6$, 20741-68-8; B_6H_{10}, 23777-80-2; 1-BrB_5H_8, 23753-67-5; $[(C_6H_5)_3PCH_3][C_2B_4H_7]$, 118043-04-2; $(C_6H_5)_3PCH_2$, 3487-44-3; $[(C_6H_5)_3PCH_3][B_5H_8]$, 67495-88-9; $[(C_6H_5)_3PCH_3][BrB_5H_7]$, 118043-02-0; $[(C_6H_5)_3PCH_3][B_6H_9]$, 57298-52-9.

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Synthesis of $Cp_2Ti[C\equiv CSi(CH_3)_3]_2$ and Synthesis and Molecular Structure of $[Cp_2TiC\equiv CSi(CH_3)_3]_2$

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Received August 17, 1988

Titanium compounds of the general type $Cp_2Ti[C\equiv CR]_2$, where R = alkyl or aryl substituents, have been synthesized and shown to exhibit limited stability.[1-4] These alkynyltitanium complexes have been characterized by various methods, including IR spectroscopy (which revealed a $\nu_{C\equiv C}$ absorption in the range 2040–2000 cm^{-1}), elemental analyses, and NMR spectroscopy.

The reaction of titanium(III) complexes with acetylides has proven more interesting. Teuben found that the reaction of $[Cp_2TiCl]_2$ with $Na[C\equiv C(Ph)]$ resulted in the formation of a green material that no longer exhibited a $\nu_{C\equiv C}$ stretch.[2] A dimeric species was proposed as the structure in which the acetylene group acted as a σ donor to one metal center and a bridging group with the adjacent titanium atom.[2] It was later determined by Stucky that the complex had actually undergone an oxidative coupling reaction to form μ-(1-3η:2-4η-*trans*,*trans*-1,4-diphenyl-

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