the ^{31}P NMR spectra of the reaction mixtures at both pH 6 and 7.8. That these new resonances in the 0–2 ppm range are not due to product formation can be shown in Figure 4, as these peaks disappear with time. The intermediate complex **5** possesses five optically active centers—the β-phosphorus atom and the four secondary nitrogens of the macrocyclic ligand—and numerous diastereomers that would be potentially distinguishable by NMR could exist. Thus the interpretations of any new phosphorus resonances in the intermediate (**5**) at 0–2 ppm is greatly complicated by stereochemical considerations and falls outside the scope of this paper.

The exact phosphorus group that is attacked has not yet been determined. Dreiding models of the intermediate (**5**) suggest that the β-phosphate is sterically the most favored, though the work of Lincoln and Stranks[27] suggests that at pH 9 bidentate orthophosphate or a four-membered chelate ring is quite stable, so attack at the α-phosphate is not ruled out. In any case, attack at the γ-phosphate seems unlikely, since as has already been pointed out, orthophosphate from the hydrolysis reaction remains bound to the cyclen species. The stoichiometry experiments show that under the conditions used for these experiments only one molecule of orthophosphate is generated by each molecule of complex 5; thus orthophosphate production is limited by either the β,γ complex concentration or the Co(cyclen) species concentration, whichever is the smaller. Complete hydrolysis of triphosphate to three molecules of orthophosphate can occur if sufficient time is allowed, but over the time scale of the cobalt(III)-assisted reaction these subsequent reactions may be neglected. On basis of the stoichiometry, the pH dependence of the rate, and the NMR species, the following seems a likely reaction scheme:

$$\beta,\gamma\text{ complex } + [\mathrm{Co(cyclen)(OH)_2}]^+ \overset{K_e}{\rightleftharpoons} \text{deprotonated complex } \mathbf{5} \qquad (4)$$

$$\text{deprotonated complex } \mathbf{5} \xrightarrow{k_r} \text{products} \qquad (5)$$

where K_e is an equilibrium constant and k_r is a first-order rate constant for dissociation of the intermediate into products.

Having postulated the existence of a structure of the type suggested in **5**, it becomes apparent from the results of the concentration-dependence experiments that an equilibrium must exist between the catalytic complex **5** (eq 3) and the free β,γ and cyclen complexes, since a 1:1 ratio of these latter two compounds does not give the maximum rate enhancement. An equilibrium of the form in eq 4 could apply.

The following rate law can be derived for the above model:

$$k_{\mathrm{obsd}} = (k_rK_e[\mathrm{C}])/(1 + K_e[\mathrm{C}]) \qquad (6)$$

where [C] is the concentration of cyclen complex and k_{obsd} is the observed rate constant. Equation 5 can be rearrange to give

$$1/k_{\mathrm{obsd}} = 1/(k_rK_e[\mathrm{C}]) + 1/k_r \qquad (7)$$

Thus, by use of the experimentally determined parameters k_{obsd} and [C], values for k_r and K_e can in principle be determined. If the first five linear points in Figure 2 are used in a reciprocal plot as is required by eq 6, a straight line of intercept $1/k_r$ and slope $1/k_rK_e$ is obtained. In practice, large uncertainty in k_r results due to the fact that, as with most reciprocal plots, a small intercept value on a very large ordinate scale is being computed. Even so, an approximate value for K_e was determined to be 3.0 ($\pm$1.5) M^{-1}, and k_r came out to be 0.010 ($\pm$0.006) s^{-1}. Even with the inaccuracies in measuring k_r, the rate enhancement over the rate of hydrolysis of free β,γ complex is very marked at high pH, being of the order of 3×10^4. The enhancement over the rate of hydrolysis of free tripolyphosphate at high pH is of course even more marked and comes out to be about 5×10^5. Although these numbers are subject to uncertainty, the enormous effect of this particular macrocyclic amine complex on the hydrolysis rate of triphosphate in aqueous solution has been effectively demonstrated.

The fact that at high cyclen concentrations the rate of hydrolysis of the β,γ complex appears to slow down (Figure 2) is difficult to rationalize at present. A greater knowledge of the nature of the catalytic intermediate (structure **5**) is required before the mechanism of this apparent inhibition could be postulated. In any event, it seems likely that a tri- or even tetranuclear cobalt(III) species may be involved.

In conclusion the results of this research have shown that cobalt ammines have the ability to greatly enhance the rate of triphosphate hydrolysis, by factors as large as 10^5. Maximum effects appear to be brought about by dinuclear cobalt species that function as templates, positioning the triphosphate ion and incoming nucleophile to facilitate the reaction.

Acknowledgment. We are grateful to Professor Grover Everett of the University of Kansas for provding access to NMR instrumentation. This research was supported by Research Corporation and National Science Foundation Grant No. CHE-8024043.

Registry No. $P_3O_{10}^{5-}$, 14127-68-5; $Co(NH_3)_4P_3O_{10}^{2-}$, 63915-32-2; *trans*-$[Co(teta)(H_2O)_2]^{3+}$, 39828-60-9; *trans*-$[Co(Me_6[14]diene)(H_2O)_2]^{3+}$, 17815-30-4; $[Co(NH_3)_5(H_2O)]^{3+}$, 14403-82-8; *cis*-$[Co(cyclen)(H_2O)_2]^{3+}$, 81064-04-2; $[Co(NH_3)_4(H_2O)_2]^{3+}$, 14877-14-6.

Dealkylation of Zirconium(IV) by Borane: The Intimate Mechanism of an Alkyl Transfer Reaction

John A. Marsella and Kenneth G. Caulton*

Contribution from the Department of Chemistry, Indiana University, Bloomington, Indiana 47405. *Received September 21, 1981*

Abstract: The reaction of Cp_2ZrMe_2 with $BH_3 \cdot THF$ ultimately yields $Cp_2Zr(BH_4)_2$. The reaction is sequential in the sense that $Cp_2Zr(BH_4)Me$ has also been detected. By use of ^{11}B NMR spectroscopy, both for resolution of chemically distinct boron-containing species and as an aid to proton counting, it has been possible to show that these reactions proceed through intermediates containing coordinated BH_3Me^- and $BH_2Me_2^-$, and thus the reaction is initially a formal insertion of BH_3 into a $Zr-CH_3$ bond. These intermediates react further with borane to produce a complex equilibrating mixture of alkyldiboranes, $B_2Me_nH_{6-n}$, and $Zr(BH_4)$ groups.

In the course of our investigation of the transfer of hydrogen from transition-metal hydrides to the η^2-acetyl group in $Cp_2Zr[C(O)Me]Me$,[1] it became important to establish the reactivity of a neutral main group hydride toward this same acetyl. Bo-

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rane–tetrahydrofuran, $BH_3 \cdot THF$, was selected for this comparison, since it was known to convert CpFe(CO)(PR$_3$)[C(O)Me] to CpFe(CO)(PR$_3$)Et.[2] It soon became apparent that $BH_3 \cdot THF$ displayed no particular reactivity toward the zirconium η^2-acetyl and that it was instead reactive in an unanticipated manner. We report here the results of this study.

Experimental Section

All operations were performed under N_2 with exclusion of air and moisture. Solvents were dried by conventional methods. Proton NMR spectra were recorded on a Varian T-60 spectrometer. ^{11}B NMR spectra (70.6 MHz) were recorded on a Varian HR-220 spectrometer in the Fourier transform mode. ^{11}B chemical shifts are referenced to $BF_3 \cdot Et_2O$, with shifts downfield of this reference being positive. Boron spectra were variously recorded with digital resolution of 5 and 10 Hz per data point; chemical shifts are therefore accurate to ±5 Hz.

$Cp_2Zr(BH_4)Me$. A solution of 500 mg of $Cp_2ZrMeCl$[3] (1.84 mmol) in ca. 20 mL of toluene was treated with 50 mg of $LiBH_4$ (2.3 mmol). The suspension was stirred for 2 h. At the end of this period, the suspension was filtered and the filtrate was stripped of solvent to yield 440 mg of a white powder. This powder was analyzed by ^1H NMR spectroscopy and was seen to contain ca. 20% starting material. The remainder of the material showed spectroscopic features consistent with $Cp_2Zr(BH_4)CH_3$: ^1H NMR (C_6D_6) δ 5.60 (s, 10 H), 0.24 (q, 4 H, $J_{B-H} = 86$ Hz), 0.17 (s, 3 H) (the methyl resonance at δ 0.17 shows some broadening due to unresolved B···H coupling); ^{11}B NMR (ppm in THF) −3.4 (quintet, $^1J_{BH} = 86$ Hz).

$Cp_2Zr(BH_4)_2$ from Cp_2Zr[C(O)Me]Me. A solution of 50 mg (0.2 mmol) of Cp_2Zr[C(O)Me]Me in 5 mL of THF was stirred at 0 °C with 1 mL of a 1 M $BH_3 \cdot THF$ solution (stabilized with 5% $NaBH_4$) for 1 h. During this time, the very pale yellow color of the acetyl complex disappeared. The solvent was removed, and sublimation (10^{-2} torr, 70 °C) led to the isolation of a white solid, which was shown by ^1H and ^{11}B NMR spectroscopy (−15.8 ppm, quintet, 83 Hz) to be $Cp_2Zr(BH_4)_2$. The same product was obtained in ca. 90% yield when Cp_2ZrMe_2 was treated with excess $BH_3 \cdot THF$.

Standardization of $BH_3 \cdot THF$ Solution. The $BH_3 \cdot THF$ for the following sequential addition experiment was vacuum transferred in order to separate $BH_3 \cdot THF$ from $NaBH_4$ and any nonvolatile impurities (*n*-butyl borate and hydrolysis products).

A freshly vacuum-transferred solution of $BH_3 \cdot THF$ (Aldrich, 50 mL) in a previously weighed vessel was carefully treated with excess NH_2-*t*-Bu (ca. 2 mL, dried over BaO); adduct formation was evident as a vigorous reaction. The volatiles were then removed (10^{-2} torr), and the weight of the resulting $BH_3 \cdot NH_2$-*t*-Bu adduct was found to be 280 mg (3.2 mmol), indicating the concentration of the original $BH_3 \cdot THF$ solution to be 0.64 M. Because of possible losses of diborane during the vigorous reaction and possible volatilization of $BH_3 \cdot NH$-*t*-Bu (mp 98 °C, with decomposition) during drying, any errors in this method will yield a low assay.

NMR Analysis of the Titration of Cp_2ZrMe with $BH_3 \cdot THF$. To 10 mL of THF was added 0.6 mmol of Cp_2ZrMe_2. To this solution was added (at −78 °C) 0.5-mL or 1.0-mL portions of the 0.64 M $BH_3 \cdot THF$ solution. After each addition, approximately 0.5 mL was transferred to an NMR tube and held at −78 °C until analysis by ^1H and ^{11}B NMR spectroscopy.

Results

Reaction of a THF solution of Cp_2Zr[C(O)Me]Me with excess $BH_3 \cdot THF$ at 0 °C leads to rapid formation of $Cp_2Zr(BH_4)_2$, identified by ^1H and ^{11}B NMR[4] spectroscopy of the isolated solid. Since the acetyl complex is in equilibrium with Cp_2ZrMe_2 (eq 1), and since the zirconium product contained neither ethoxy nor

$$\mathrm{Cp_2Zr[C(O)Me]Me} \rightleftharpoons \mathrm{Cp_2ZrMe_2 + CO} \tag{1}$$

ethyl groups, Cp_2ZrMe_2 itself was treated with $BH_3 \cdot THF$ under the conditions employed above. Since this also resulted in clean formation of $Cp_2Zr(BH_4)_2$, we suggest that the acetyl complex actually reacts with $BH_3 \cdot THF$ via Cp_2ZrMe_2. This reaction is puzzling since it appears to involve interaction of a transition-metal Lewis acid (and one with a d^0 configuration) with a main group acid. The fate of the methyl groups also remained to be established.

Reaction of Cp_2ZrMe_2 with a deficiency of $BH_3 \cdot THF$ produced $Cp_2Zr(BH_4)Me$, identical with a sample synthesized independently from $Cp_2ZrMeCl$ and $LiBH_4$. Since this result did not improve our understanding of the fate of the methyl groups, we next evaluated whether a portion of the methyl groups were lost as methane (or ethane). No gas evolution was observed in the reactions described here. Moreover, production of methane from $BMeH_2$ (or some catalyzed bimolecular methane elimination from its reaction with BH_3) implies production of fragments of average stoichiometry between BH and BH_2. Such fragments would either form the "yellow borane polymer" common to boron chemistry or would condense with BH_n (n = 1–3) fragments to form higher boranes. Boron-11 NMR spectroscopy was employed to search for such products. However, we observe no ^{11}B NMR signal characteristic of B_4H_{10}, B_5H_9, B_6H_{10}, or $B_{10}H_{14}$.[5] Similarly absent are ^{11}B patterns expected for the analogous alkylpolyboranes.[5] These conclusions hold for all B:Zr mole ratios investigated.[6]

Diborane is known to undergo heterolytic base (L) cleavage reactions (eq 2) and in this way serves as a source of BH_4^-.[7]

$$\mathrm{B_2H_6 + 2L \rightarrow L_2BH_2^+ + BH_4^-} \tag{2}$$

Simplified reasoning from this idea led us to consider formal CH_3^- transfer (eq 3), and its replacement by the BH_4^- of eq 2, as a

$$\mathrm{L}_n\mathrm{ZrMe + 2BH_3 \rightarrow L}_n\mathrm{ZrBH_4 + BMeH_2} \tag{3}$$

mchanism for the reaction of borane with Cp_2ZrMe_2. Methylboranes,[8] which are dimeric even in THF,[9,10] were thus sought as the methyl-bearing product of the reaction. Since these are known to be subject to complicated disproportionation[11] (redistribution) reactions[12,13] (eq 4) which are established at varied

$$2\mathrm{B_2H}_n\mathrm{Me}_{6-n} \rightleftharpoons \mathrm{B_2H}_{n+1}\mathrm{Me}_{5-n} + \mathrm{B_2H}_{n-1}\mathrm{Me}_{7-n}\ (n = 3\text{–}5) \tag{4}$$

rates,[14] such a search appeared difficult. Boron-11 NMR spectroscopy was selected as perhaps the most discriminating analytical technique for this purpose.

The 70.6-MHz Fourier transform ^{11}B NMR spectrum of a solution resulting from the reaction of Cp_2ZrMe_2 with excess $BH_3 \cdot THF$ showed clear evidence for the production of B–Me groups in the 20–36-ppm region.[8] However, it was evident that eq 3 oversimplifies this reaction, since at least four multiplet resonances were present, some of which are indicative of BMe_2 groups. Although such groups might result from secondary (redistribution) reactions, subsequent experiments showed that, in contrast to eq 3, less than 2 mol of $BH_3 \cdot THF$ are required per Zr–Me transformed. This is consistent with *participation* by a reaction of stoichiometry shown in eq 5; direct "dialkylation" of

$$2\mathrm{L}_n\mathrm{ZrMe + 3BH_3 \rightarrow 2L}_n\mathrm{Zr(BH_4) + BMe_2H} \tag{5}$$

$BH_3 \cdot THF$ by zirconium (i.e., transfer to two methyls to a single boron) is suggested as a mechanistic component.

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(6) Similarly absent are resonances that might be attributed to a $B_3H_8^-$ ligand. Finally, we find no evidence that, under our conditions, coordinated BH_4^- is converted by excess borane to $B_2H_7^-$, in spite of the fact that free BH_4^- does bind BH_3.

(7) A small amount (5 mol %) of $NaBH_4$ is added as a stabilizer to commercial (Aldrich) $BH_3 \cdot THF$. It was established, in experiments with only modest excess of $BH_3 \cdot THF$, that $NaBH_4$ was not present in quantities sufficient to be the source of $Cp_2Zr(BH_4)_2$. Moreover, Cp_2ZrMe_2 fails to react with $NaBH_4$ in THF and with $LiBH_4$ in benzene.

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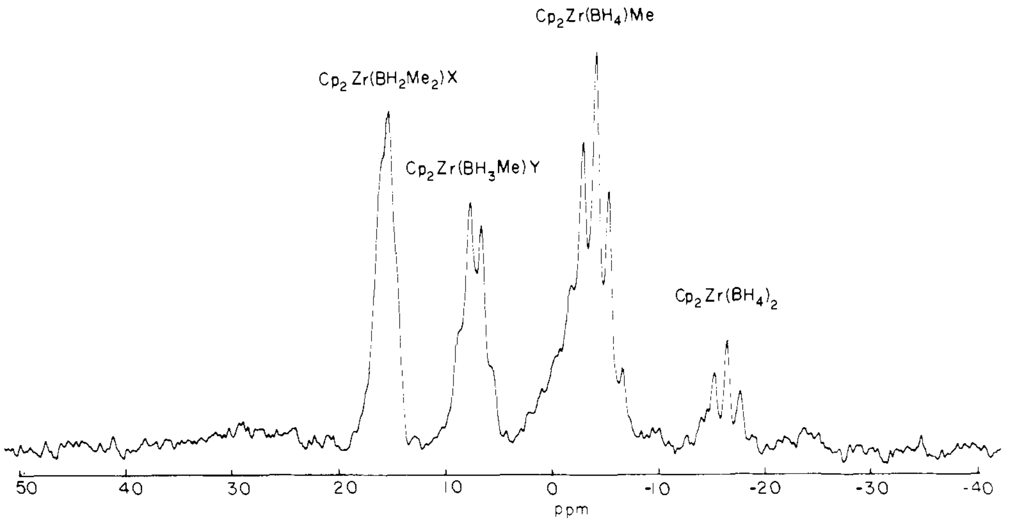


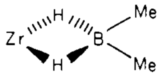
Figure 1. 70.6-MHz ^{11}B NMR spectrum of a THF solution formed from addition of 0.32 mmol of $BH_3\cdot THF$ to 0.64 mmol of Cp_2ZrMe_2. The proton NMR spectrum (not pictured) shows unreacted Cp_2ZrMe_2 to be present.

Direct proof of dialylation of a single boron is available. This experiment is also the first we offer with regard to intimate mechanism (i.e., previously undetected intermediates), as opposed to simply reaction stoichiometry and ultimate products. A THF solution of Cp_2ZrMe_2 was titrated with a standardized $BH_3\cdot THF$ solution. After each incremental addition of borane solution, a sample was taken and frozen for ^{11}B NMR analysis.

A solution in which the overall boron:zirconium ratio is approximately 0.5:1 shows by proton NMR spectroscopy (1) unreacted Cp_2ZrMe_2, (2) the Cp and methyl resonances of $Cp_2Zr(BH_4)Me$, and (3) a trace of the Cp resonance of $Cp_2Zr(BH_4)_2$. The methyl resonance of $Cp_2Zr(BH_4)Me$ is somewhat broad (full width at half-height ~1.5 Hz) as a result of the adjacent quadrupolar boron and possibly unresolved coupling to BH_4 protons. At least one additional Cp resonance is seen very close to those of Cp_2ZrMe_2 and $Cp_2Zr(BH_4)Me$ as well as a number of new peaks (some of which are broad) in the region δ 0–1. The ^{11}B NMR spectrum (Figure 1) of this same solution (which is inherently more sensitive and better resolved than ^1H NMR for a mixture of polyboron compounds) shows (1) a small amount of the quintet due to $Cp_2Zr(BH_4)_2$, (2) a strong quintet due to $Cp_2Zr(BH_4)Me$, (3) a quartet (J = 73 Hz) at +7.7 ppm, and (4) a weakly structured line at +15.8 ppm; $BH_3\cdot THF$ is absent from this solution. Exponential line narrowing of the ^{11}B NMR spectrum clearly reveals triplet structure on the 15.8-ppm resonance, with a line spacing of ca. 40 Hz. The resonances at 7.7 and 15.8 ppm are not caused by any of the alkyldiboranes,[8] which are wholly absent from this solution.

The ^1H NMR of a solution in which the B:Zr ratio is 1:1 shows that Cp_2ZrMe_2 is now completely consumed. Both ^1H and ^{11}B NMR spectra reveal that the amount of $Cp_2Zr(BH_4)Me$ has increased, as has $Cp_2Zr(BH_4)_2$. In the ^{11}B NMR spectrum, the 7.7 ppm quartet has now declined in relative intensity, while the 15.8 ppm triplet has grown. Coincident with the growth of the 15.8 ppm triplet, the previously unidentified Cp proton resonance is now resolved from the very similar resonance of $Cp_2Zr(BH_4)Me$. The δ 0–1 region of the ^1H NMR spectrum (Me and B–H) remains complex. By ^{11}B NMR, the $BH_3\cdot THF$ quartet is now weakly in evidence.

At this point, it is useful to discuss a working hypothesis for the identity of the unidentified boron resonances at 7.7 and 15.8 ppm. Note first that these chemical shifts and J values are inconsistent with all $B_2H_nMe_{6-n}$ species. The quartet structure of the 7.7 ppm resonance indicates boron with three attached hydrogens. It is downfield of $BH_3\cdot THF$, a direction consistent with that resulting from alkylation.[5] It is also downfield from the −25.7 ppm shift of $KBH_3(thexyl)$,[15] downfield shifts being the normal consequence of coordination to Zr(IV). We assign this to a BH_3Me^- species coordinated to zirconium. The triplet structure of the 15.8 ppm resonance requires a BH_2 group. The chemical shift is downfield of the −13 to −18 ppm range found for $BR_2H_2^-$ salts;[15,16] we assign this to a coordinated $BH_2Me_2^-$ unit. This single proposal rather naturally accounts not only for boron NMR chemical shifts and coupling constants (see below) but also for the fate of the methyl groups and the deviations from the stoichiometry shown in eq 3; BMe_2 groups lower the required B:Zr stoichiometry below 2:1. The coupling constants of the BH_3Me^- and $BH_2Me_2^-$ resonances are inconsistent with these being isolated anions with terminal hydrogens. That of $BH_2Me_2^-$ (40 Hz) is consistent with both hydrogens playing a bridging role as in I (cf. 40–50 Hz in $B_2H_nMe_{6-n}$[8] as well as in higher boranes[5]).



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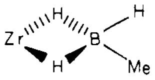

II

This is in accord with the fact that $(C_5H_4Me)_2Hf(BH_4)_2$ is known[17] to have only bidentate (i.e., doubly hydride bridged) BH_4 ligands. The coupling constant measured here in the BH_3Me^- resonance, 73 Hz, is consistent with a fluxional unit of structure II. Bridge/terminal B–H exchange is a characteristic[17,18] fluxional process of both $Cp_2Zr(BH_4)_2$ and $Cp_2Zr(BH_4)Me$, as shown by the quintet pattern. The increased J_{B-H} value (compared to coordinated $BH_2Me_2^-$) results from averaging one (larger) terminal B–H J value with two bridging B–H coupling constants. The observed value is inconsistent with (i.e., too large for) a tridentate BH_3Me^- ligand.

What remains is to establish the partner ligands X and Y in the complexes $Cp_2Zr[(\mu-H)_2BMe_2]X$ and $Cp_2Zr[(\mu-H)_2BHMe]Y$ proposed above. We immediately rule out any boron ligand as the partner, since the appropriate boron resonance is not observed; all observed resonances have been accounted for. It is not possible to claim that a single compound, $Cp_2Zr[(\mu-H)_2BMe_2][(\mu-H)_2BHMe]$, is present, since the 7.7 and 15.8 ppm boron resonances do not always exhibit equal intensities. The partner ligands which remain as viable candidates are H and Me. These will be discussed in more detail below, after we return to a description of the results of further incremental addition of $BH_3\cdot THF$ of Cp_2ZrMe_2.

Further sequential additions of $BH_3\cdot THF$ to the reaction mixture now containing only the four complexes of $BH_nMe_{4-n}^-$ ligands show the first evidence of B–Me groups being released

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from the metal. Doubling the total amount of BH_3·THF previously added changes the mole ratio of $Cp_2Zr(BH_4)_2$ to $Cp_2Zr(BH_4)Me$ to nearly 1.4:1. $Cp_2Zr(BH_3Me)Y$ is gone completely and $Cp_2Zr(BH_2Me_2)X$ is now a minor component. Free BH_3·THF is evident, as are multiplets at 39, 33, 25, 7, 15, and 8 ppm, all being consistent with alkyldiboranes.[8] No BMe_3 is seen (+84 ppm[12]). Most readily identified are the narrow multiplets (coupling to μ-H only) of the Me_2B ends of 1,1-dimethyldiborane, trimethyldiborane, and tetramethyldiborane. Significantly absent are the two compounds with only one methyl per boron: B_2MeH_5 and 1,2-dimethyldiborane. A final addition of further BH_3·THF merely accomplishes alkyl redistribution chemistry that is predictable from mass-action principles: $B_2Me_4H_2$ is consumed and 1,2- and 1,1-dimethyldiborane grow in relative abundance. $Cp_2Zr(BH_4)Me$ is essentially gone, leaving $Cp_2Zr(BH_4)_2$ as the only metal complex. The separation of alkylhydridoborates from zirconium is thus accomplished as a secondary reaction by abstraction of BR_nH_{3-n} from zirconium with BH_3·THF.

Discussion

BH_3·THF reacts with Cp_2ZrMe_2 not by a single pathway but rather by a complex series of competitive Lewis acid-base reactions that share the feature of alkyl transfer (also called transmetalation).[11] There is no evidence that the production of a BH_4^- complex proceeds by a zirconium-independent preequilibrium heterolytic formation of BH_4^- (eq 2). Similarly, there is no evidence that the reaction is as simple as the two steps of eq 6[19] and 7. The crucial mechanistic information follows from the

$$L_nZrMe + BH_3 \rightarrow L_nZrH + BMeH_2 \tag{6}$$

$$L_nZrH + BH_3 \rightarrow L_nZrBH_4 \tag{7}$$

observation of coordinated alkylborohydride anions at low B:Zr ratios. The intermediacy of these is proven by their observed consumption by additional BH_3·THF.

Consider now the fragment $Cp_2Zr[(\mu\text{-}H)_2BHMe]Y$, where Y does not contain boron. We propose that Y = CH_3, mainly on the basis that the simple "Cp_2ZrMe_2·BH_3" stoichiometry that this formula implies. If we assume, for simplicity, that alkyl transfer between two zirconium centers is not operative, then a reasonable identification of X in the $Cp_2Zr[(\mu\text{-}H)_2BMe_2]X$ is X = H. That is, this is a structural isomer of $Cp_2Zr[(\mu\text{-}H)_2BHMe]Me$ in which transposition of Zr-Me and B-H has taken place. The formation of a Zr-H unit (and not Zr-BH_4) is consistent with the low B:Zr ratio in such solutions. Moreover, the dimethyldihydridoborate-ligated complex is a likely precursor to $Cp_2Zr(BH_4)_2$ at low B:Zr ratios and with net consumption of less than 2 BH_3 per methyl transferred (eq 5 or 8). This proposal also explains the

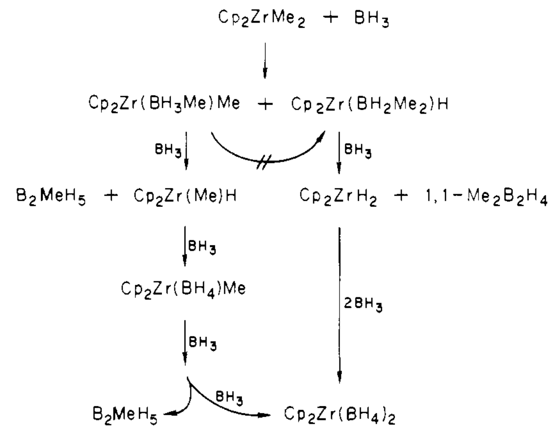
$$Cp_2ZrMe_2 + BH_3 \rightarrow Cp_2Zr(H_2BMe_2)H \xrightarrow{+2BH_3} Cp_2Zr(BH_4)_2 + BMe_2H \tag{8}$$

significant production of alkylboranes containing BMe_2 (as opposed to BMeH) groups. In a like manner, $Cp_2Zr(BH_3Me)Me$ is the obvious precursor to $Cp_2Zr(BH_4)Me$ after reaction with an additional molecule of BH_3 (eq 9). The ^{11}B NMR spectra

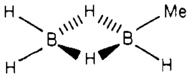
$$Cp_2Zr(BH_3Me)Me + BH_3 \rightarrow Cp_2Zr(BH_4)Me + BMeH_2 \tag{9}$$

observed over the course of sequential BH_3·THF addition support this scheme of reactions. Addition of increasing amounts of borane to a solution with an initial B:Zr ratio of 0.5:1 consumes $Cp_2Zr(BH_3Me)Me$ in preference to $Cp_2Zr(BH_2Me_2)H$. Note also that it is possible to produce solutions with greatly varying porportions of the structurally isomeric species $Cp_2Zr(BH_3Me)Me$ and $Cp_2Zr(BH_2Me_2)H$. This indicates that these compounds do not readily interconvert (equilibrate) at ≤25 °C and thus suggests that they are not sequential intermediates on the route to BH_4^- complexes but are instead formed from Cp_2ZrMe_2 by distinct paths.[20] It is for this reason that we do not propose either spontaneous or borane-induced conversion of $Cp_2Zr(BH_3Me)Me$ into $Cp_2Zr(BH_2Me_2)H$. The complete sequence of reactions observed is displayed in Scheme I.

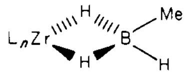
Scheme I



Although monoalkylboranes with larger alkyl groups are partially monomeric in THF,[12,13] this is not true of methyl- and ethylboranes (even in THF).[9,10] It was therefore overly simplistic to write a reaction such as eq 3 in that the production of monomeric $BMeH_2$ (even if THF solvated) is energetically expensive. In fact, since the products described here as zirconium alkylhydridoborate *complexes* are formal transition-metal analogues of alkyldiboranes (III and IV), the need to stabilize a $BMeH_2$ monomer is satisfied in the immediate product of a bimolecular contact between Cp_2ZrMe_2 and BH_3. Our data suggest that this is a stable entity in the absence of an abundance of the competitive Lewis acid BH_3 and that additional borane is required to *complete* the separation of the methyl group from zirconium. Thus, transfer of the methyl group from the transition-metal center occurs not to a translationally independent main group center, but rather to a main group center which is simultaneously evolving into a ligand. In this sense, our results are consistent with observations on the reaction of $Cp_2Zr(X)R$ with diisobutylaluminum hydride.[21]

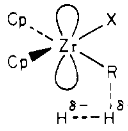


III

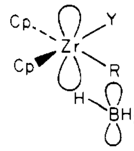


IV

The nature of this initial alkyl transfer therefore deserves comment, since it returns us to the anomalous point that the two reagents Cp_2ZrMe_2 and BH_3 are both Lewis acids. We see some similarity to the equally problematic reaction of H_2 with the d^0 (i.e., oxidation resistant) complexes Cp_2ZrRH and Cp_2ZrH_2.[22] The mechanism proposed for hydrogenolysis involves donation from only one atom of dihydrogen into the empty metal orbital, thereby polarizing H_2 in a manner which initiates bonding between the second hydrogen (now δ+) and the alkyl group (V). Borane is ideally constituted to react in this manner since the external atom *enters* the bimolecular contact with an empty orbital; $H^{\delta-}$-$B^{\delta+}H_2$ polarization by zirconium will assist the reaction, but



V



VI

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(19) In every case where a methylborane monomer is written, it will receive temporary stabilization by THF prior to dimerization.

(20) A possible difference might be approach of BH_3 between the two methyl groups and also from the outside of the $ZrMe_2$ angle. Alternatively, one could form under conditions where local heating on borane addition does allow some isomerization.

(21) Shoer, L. I.; Gell, K. I.; Schwartz, J. *J. Organomet. Chem.* **1977**, *136*, C19.

(22) Gell, K. I.; Posin. B.; Schwartz, J. *J. Am. Chem. Soc.* **1982**, in press.

J. Am. Chem. Soc. 1982, 104, 2365-2372

there should be less of an activation barrier to the approach of these two Lewis acids precisely because of all of those factors which make borane a dimer instead of a monomer (VI). The two mechanisms (hydrogenolysis vs. the BH_3 reaction) diverge subsequent to achieving transition states V and VI, again due to the higher valence of the BH_2 fragment than the H. Thus, while the emerging RH in hydrogenolysis has no unsatisfied valence orbitals (and is therefore a superb leaving group), the emerging BRH_2 has obvious reasons to remain. In the latter case, the inferiority of akyl relative to hydrogen as a bridging group necessitates only an intramolecular rearrangment of VI to form the product $Cp_2Zr[(\mu\text{-}H)_2BHR]Y$. The BH_3 reaction observed here gives a primary product which evokes the label "insertion reaction".[23] While such a generic name has limitations, it does point out the unimolecular nature of the product, a feature lacking in the labels "alkyl transfer" and "transmetalation".

Conclusion

The idea that the empty d orbital of unsaturated Cp_2ZrMe_2 is the initial site of attack by $BH_3{\cdot}THF$[24] may also explain the initially anomalous observation that $Cp_2Zr[C(O)Me]Me$, which lacks this empty orbital, is unreactive toward borane. Because of the operation of equilibrium 1, borane is rapidly consumed by Cp_2ZrMe_2 and any reactivity of $Cp_2Zr[C(O)Me]Me$ is so slow as to be kinetically imperceptible. The absence of such an empty metal orbital in $CpFeCO(PR_3)[C(O)Me]$ does not diminish its reactivity toward $BH_3{\cdot}THF$, a result which speaks for a mechanism involving initial coordination of the "acidic hydride" borane to the η^1-C(O)Me oxygen lone pair.[2] On the other hand, $CpFeCO(PR_3)Et$, once formed, is observed to be stable to ethyl transfer to BH_3; this follows from our mechanistic proposal since BH_3 finds no empty iron orbital to initiate ethyl transfer (i.e., BH_3 insertion).[25]

We have argued that π donation by chlorine in Cp_2ZrCl_2 diminishes the Lewis acidity of this complex relative to Cp_2ZrMe_2.[26] It is therefore significant that we find $BH_3{\cdot}THF$ to leave Cp_2ZrCl_2 unchanged under our reaction conditions. It has also been noted[27] that transmetalation from Cp_2ZrClR to stoichiometric (1:1) $AlCl_3$ yields *free* $(RAlCl_2)_n$ and Cp_2ZrCl_2 and that the latter compound is only weakly coordinated to added $AlCl_3$. π-donor ligands can thus effectively diminish the unsaturation of Zr(IV).

We find that $Cp_2Zr(C_6H_5)_2$ does not react with $BH_3{\cdot}THF$ under the reaction conditions employed here. This is consistent with a mechanism passing from Zr–R through the intermediate $Zr(\mu\text{-}H)(\mu\text{-}R)BH_2$, *if* we postulate that phenyl is inferior to methyl in bridging to zirconium. This suggests that selective conversion of $Cp_2Zr(Me)Ph$ to $Cp_2Zr(BH_4)Ph$ might be achieved.

Finally, we suggest that insertion of Lewis acidic main group hydrides into M–X bonds (M = an unsaturated transition metal) may be a generally mechanistic feature of alkyl transfer (transmetalation). The Schwartz group has established this point for several reactions of diisobutylaluminum hydride.[21] Nöth and co-workers have reported several preparations of BH_4^- complexes that also fit this pattern (eq 10[28] and 11[29]), with the added feature

$$Cr(O\text{-}t\text{-}Bu)_4 + BH_3{\cdot}THF \rightarrow Cr(BH_4)_2{\cdot}2THF + \ldots \quad (10)$$

$$Ti(OR)_4 + 5BH_3(THF) \rightarrow Ti(BH_4)_3 + 2HB(OR)_2 + 0.5H_2 \quad (11)$$

of reduction of the metal.

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Registry No. Cp_2ZrMe_2, 12636-72-5; $BH_3{\cdot}THF$, 14044-65-6; $Cp_2Zr(BH_4)Me$, 81064-02-0; $Cp_2Zr(BH_4)_2$, 12083-77-1; $Cp_2Zr[C(O)Me]Me$, 60970-97-0; $Cp_2ZrMeCl$, 1291-45-8.

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(23) Calderazzo, F. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 299.

(24) A referee suggests that this reaction might instead be viewed as a "simple nucleophilic attack on a relatively positive boron center" by (anionic) methyl carbon. We are reluctant to ignore the potential of the empty zirconium orbital for stabilizing the transition state.

(25) For examples of alkyl group exchange between free BR_3 and metal-bound borohydride ligands, see: Schlesinger, H. I.; Brown, H. C.; Horvitz, L.; Bond, A. C.; Tuck, L. D.; Walker, A. O. *J. Am. Chem. Soc.* **1953**, *75*, 222. Marks, T. J.; Kolb, J. R. *Ibid.* **1975**, *97*, 27.

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Structure of Oxonium Ions: An X-ray Crystallographic Study of Triethyloxonium Hexafluorophosphate and Triphenyloxonium Tetraphenylborate[1]

Michael I. Watkins, Wai Man Ip, George A. Olah,* and Robert Bau*

Contribution from the Department of Chemistry and the Hydrocarbon Research Institute, University of Southern California, Los Angeles, California 90007. *Received July 15, 1981*

Abstract: Single-crystal X-ray diffraction data were collected on two tricoordinate oxonium salts, triethyloxonium hexafluorophosphate and triphenyloxonium tetraphenylborate. While the triethyloxonium ion is established as being pyramidal, the triphenyloxonium ion is nearly flat but deviates significantly from planarity. The average O–C distances are 1.499 (10) Å for Et_3O^+ and 1.472 (9) Å for Ph_3O^+. For the triphenyloxonium ion, the phenyl rings are tilted by an average of 59.7° from the equatorial plane. This value indicates nearly no p–π interaction between oxygen and its aromatic ligands. The unusually large ipso angle, 125.8°, of the triphenyloxonium ion suggests that the oxonium substituent (i.e., $^+OPh_2$) on the aromatic ring is a powerful σ-electron-withdrawing group. $Ph_3O^+BPh_4^-$ crystallizes in the monoclinic space group $P2_1/n$, with $a = 21.101$ (5) Å, $b = 11.107$ (3) Å, $c = 13.603$ (7) Å, $\beta = 90.75$ (3)°, $V = 3188$ (4) Å^3, and $Z = 4$. The final R factor is 0.048 for 1379 reflections with $I > 3\sigma(I)$. $Et_3O^+PF_6^-$ crystallizes in the orthorhombic space group $Pnma$, with $a = 16.475$ (3) Å, $b = 9.965$ (2) Å, $c = 6.557$ (1) Å, $V = 1076.5$ (3) Å^3, and $Z = 4$. The final R factor is 0.058 for 618 reflections with $I > 3\sigma(I)$.

The synthesis and structural characterization of compounds containing a tricoordinate, positively charged oxygen (R_3O^+, oxonium ions) has remained a long-term challenge for chemists ever since Meerwin's pioneering work in 1937.[2a] The only

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