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Transition Metal-Catalyzed Hydroboration of and CCl$_4$ Addition to Alkenes

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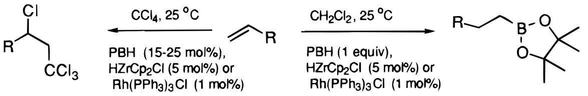
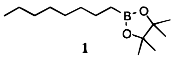
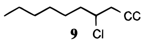
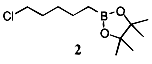
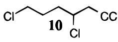
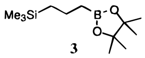
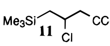
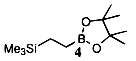
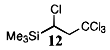
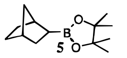
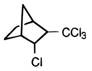
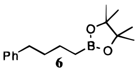
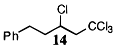
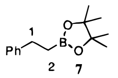
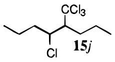
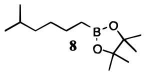
Compounds containing boron and a metal have attracted considerable attention lately as part of the effort directed toward preparing novel compounds for catalysis and organic synthesis.[2] As part of our program involving boron and zirconium, we are always interested in developing or discovering new applications for organometallic reagents in organic synthesis.[3] Recently, we reported that HZrCp$_2$Cl catalyzes the addition of pinacolborane (PBH) to alkynes.[4] As an extension of this work, we now report the HZrCp$_2$Cl-catalyzed addition of PBH to alkenes. A significant solvent effect was observed that changed the course of the reaction. Thus, the fortuitous use of CCl$_4$ as solvent led to a new reaction involving polyhalide addition to alkenes. During the course of this work, we have also cleared some misconceptions surrounding PBH and its hydroborating potential reported in the literature.[5] We also evaluated Wilkinson's catalyst and found it to be superior under the same conditions in both metal-catalyzed hydroboration of and CCl$_4$ addition to alkenes (eq 1).



(1)

Table 1. Products Obtained by Metal-Catalyzed Reactions of Alkenes with Pinacolborane in CH$_2$Cl$_2$ and CCl$_4$

Alkene	Hydroboration Product[a]	Yield, %[b]		CCl$_4$ Addition Product[a]	Yield, %[b]	
		Zr[c]	Rh[d]		Zr[e]	Rh[f]
1-Octene	 **1**	70	99	 **9**	66	95
5-Chloropentene	 **2**	61	99	 **10**	64	96
Allyltrimethylsilane	 **3**	72	99	 **11**	72	95
Vinyltrimethylsilane	 **4**	66	93	 **12**	61	88
Norbornene	 **5**	72	99	 **13**[g]	87	94
4-Phenylbutene	 **6**	39	98	 **14**	41	54
Styrene	 **7**	9	99[h]		21[i]	40[i]
trans-4-Octene	**1**	70	92	 **15**[j]	41	54
cis-2-Methyl-3-hexene	 **8**	69	94			

[a] Assigned structures are consistent with ^{1}H, ^{3}C, ^{13}C APT NMR and MS data. [b] Isolated products. [c] Alkene (1 mmol), PBH (1.1 mmol), and HZrCp$_2$Cl (0.5 mmol) in CH$_2$Cl$_2$, 25 °C, 24 h. [d] Same as in footnote *c*, except that Rh(PPh$_3$)$_3$Cl (0.01 mmol) was used and the reaction worked up after 10 min. [e] Alkene (1 mmol), PBH (0.22 mmol), and HZrCp$_2$Cl (0.05 mmol) in CCl$_4$ (0.5 mL), 25 °C, 24 h. [f] Same as in footnote *e*, except that Rh(PPh$_3$)$_3$Cl (0.01 mmol) and PBH (0.15 mmol) were used. The reaction was stirred for 3 h. [g] Stereochemistry assigned according to: Smart, B. E. *J. Org. Chem.* **1973**, *38*, 2035. [h] In addition to **7** (50%), the α-hydroboration product (35%) and pinacol-*β*-styrenylboronate (15%) were obtained. [i] Inseparable mixture of the addition products was obtained. [j] A 2:1 mixture of *syn:anti* addition products were obtained.

Boron−Zirconium. Pinacolborane is a stable, easily stored and prepared hydroborating agent.[4,5] As with other dioxaborolanes and dioxaborinanes,[6] it only sluggishly hydroborates alkenes and alkynes. However, we discovered that HZrCp$_2$Cl is an excellent catalyst for PBH hydroboration of alkynes.[4] At 25 °C and with 1 equiv of PBH, excellent yields of 1-alkenylpinacolboronates were obtained. When PBH was reacted with alkenes under HZrCp$_2$Cl catalysis, moderate to good yields of the hydroborated product were obtained. In an effort to increase the yields, we initiated a solvent study with 1-octene as the substrate. Satisfactory yields of hydroboration products were obtained in CH$_2$Cl$_2$ (Table 1). Low yields were obtained when an aromatic moiety was part of the molecule. Significantly, styrene (although obtained in low yield) gave only the terminally hydroborated product. Vinyltrimethylsilane placed boron exclusively on the terminal carbon. Thus, the present system is equivalent to 9-BBN in its ability.[7] Not unexpectedly, internal alkenes placed boron on the terminal carbon (Table 1). The mechanism of this HZrCp$_2$Cl-catalyzed hydroboration of alkenes with PBH is, therefore, consistent with hydrozirconation as the initial step, isomerization to place zirconium on the least hindered carbon, followed by boron insertion.[4] In our hands, ZrCp$_2$Cl$_2$ did not catalyze hydroboration of alkenes.[8]

However, when the reaction was run in CCl$_4$ (1 equiv of PBH, 0.05 equiv of HZrCp$_2$Cl), the boronate was obtained in only 13.3% relative yield, while the CCl$_4$ addition product was obtained in 86.7% (eq 1). The addition of polyhalogenated alkanes to alkenes is known as the Kharasch reaction.[9] Various metals are known to catalyze this reaction, but acceptable rates are only obtained at relatively high temperatures.[10] After some experimentation, we established a set of conditions for CCl$_4$ addition to alkenes: 0.05 equiv of HZrCp$_2$Cl and 0.22−0.25

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(1) Present address: Fresh Products Inc., 4010 South Ave., Toledo, OH 43615.

(2) Several recent examples: (a) Erker, G.; Noe, R.; Wingbermühle, D.; Petersen, J. L *Angew. Chem., Int. Ed. Engl.* **1993,** *32,* 1213. (b) Erker, G.; Nolte, R.; Aul, R.; Wilker, S.; Krüger, C.; Noe, R. *J. Am. Chem. Soc.* **1991,** *113,* 7594. (c) Iverson, C. N.; Smith, M. R., III. *J. Am. Chem. Soc.* **1995,** *117,* 4403. (d) Fields, L. B.; Jacobsen, E. N. *Tetrahedron: Asymmetry* **1993,** *4,* 2229. (e) Wadepohl, H.; Elliott, G.; Pritzkow, H.; Stone, F. G. A.; Wolf, A. *J. Organomet. Chem.* **1994,** *482,* 243. (f) Spence, R. E. von H.; Parks, D. J.; Piers, W. E.; MacDonald, M.-A.; Zaworotko, M. J.; Rettig, S. J. *Angew. Chem., Int. Ed. Engl.* **1995,** *34,* 1230. (g) Jia, L.; Yang, X.; Ishihara, A.; Marks, T. J. *Organometallics* **1995,** *14,* 3135.

(3) (a) Pereira, S.; Srebnik, M. *J. Org. Chem.* **1995,** *60,* 4316. (b) Zheng, B.; Srebnik, M. *J. Org. Chem.* **1995,** *60,* 1912. (c) Zheng, B.; Srebnik, M. *J. Org. Chem.* **1995,** *60,* 3278. (d) Deloux, L.; Sabat, M.; Srebnik, M. *J. Org. Chem.* **1995,** *60,* 3276. (e) Pereira, S.; Zheng, B.; Srebnik, M. *J. Org. Chem.* **1995,** *60,* 6260.

(4) Pereira, S.; Srebnik, M. *Organometallics* **1995,** *14,* 3127.

(5) Tucker, C. E.; Davidson, J.; Knochel, P. *J. Org. Chem.* **1992,** *57,* 3482.

(6) (a) Woods, W. G.; Strong, P. L. *J. Am. Chem. Soc.* **1966,** *88,* 4667. (b) Fish, R. H. *J. Am. Chem. Soc.* **1968,** *90,* 4435.

(7) (a) Brown, H. C.; Liotta, R.; Scouten, C. G. *J. Am. Chem. Soc.* **1976,** *98,* 5297. (b) Brown, H. C.; Chen, J. C. *J. Org. Chem.* **1981,** *46,* 3978. (c) Soderquist, J. A.; Hassner, A. *J. Organomet. Chem.* **1978,** *156,* C12.

(8) Evans, D. A.; Muci, A. R.; Stürmer, R. *J. Org. Chem.* **1993,** *58,* 5307.

(9) Kharasch, M. S.; Reinmuth, O.; Urry, W. H. *J. Am. Chem. Soc.* **1947,** *69,* 1105.

(10) (a) Asscher, M.; Vofsi, D. *J. Chem. Soc.* **1963,** 1887. (b) Martin, P.; Steiner, E.; Winkler, T.; Bellus, D. *Tetrahedron* **1985,** *41,* 4057. (c) Davis, R.; Khazaal, N. M. S.; Maistry, V. *J. Chem. Soc., Chem. Commun.* **1986,** 1387. (d) Davis, R.; Durrant, J. L. A.; Khazal, M. S. *J. Organomet. Chem.* **1990,** *386,* 229. (e) Davis, R.; Khazal, N. M. S.; Bitterwolf, T. E. *J. Organomet. Chem.* **1990,** *397,* 51. (f) Ma, S.; Lu, X. *J. Chem. Soc., Perkin Trans. 1* **1990,** 2031.

0002-7863/96/1518-0909$12.00/0

equiv of PBH at 25 °C. This is a significant advance in polyhalogenated methane addition to alkenes, as this reaction can be effected at 25 °C. The products obtained from this reaction are useful synthetic intermediates that can be converted to α,β-unsaturated acids.[10b] Yields of CCl_4 addition to a series of alkenes are summarized in Table 1. The yields are good to excellent. In all cases (where applicable), the CCl_3 moiety attaches itself to the terminal carbon of the alkene. The reaction of *trans*-4-octene is especially interesting. Unlike the hydroboration of *trans*-4-octene, the internal chloro trichlormethylated compound was obtained as a 2:1 mixture of diastereomers (eq 2).

(2)

Thus, hydrozirconation is apparently not the initial step in CCl_4 addition.[11] Both galvinoxyl free radical and butylated hydroxytoluene did not inhibit the reaction.[12] In addition, zirconium hydride and boron hydride are required.[13] Cp_2ZrCl_2/PBH, $HZrCp_2Cl/R_3B$, $HZrCp_2Cl/(RO)_3B$, PBH, and R_3B or $(RO)_3B$ were ineffective in catalyzing the CCl_4 addition to alkenes. The boron-containing species identified at the end of the CCl_4 reaction is *B*-chloropinacolboronate.[14] The final zirconium product is $ZrCp_2Cl_2$. However, use of $HZrCp_2Cl$ or $ZrCp_2Cl_2$ and *B*-chloropinacolboronate in the CCl_4 addition to 1-octene did not result in any product. The mechanism, therefore, is complex and may involve a non free radical pathway; if a free radical mechanism does occur, it is a step in the catalytic process that does not involve the alkene.[9,10,12,13]

Boron−Rhodium. Metal-catalyzed hydroboration is generally done with catecholborane (CBH).[15] However, 1.5 equiv of CBH is required due to degradation during the course of the reaction.[15e] It has been reported that hydroboration with PBH is not catalyzed by rhodium.[5] Having successfully used PBH in conjunction with zirconium, it appeared to us that PBH should serve as a suitable substrate in rhodium-catalyzed hydroboration of alkenes.[15] Indeed, this has now proven to be the case. As little as 0.2 mol % $Rh(PPh_3)_3Cl$ is effective. The reaction is very fast (10 min at 25 °C) and essentially quantitative in methylene chloride. Aqueous workup of the water- and chromatography-stable pinacolboronates gave almost pure product (Table 1). As is the case with CBH, metal-catalyzed hydroboration of styrene with PBH gave a mixture of boronates (C1, 35%; C2, 50%; and a β-vinyl boronate, 15%).[16] Two internal alkenes were investigated. Surprisingly, **1** was also obtained when rhodium was used as the catalyst in the hydroboration of *trans*-4-octene (Table 1) in CH_2Cl_2. We prepared genuine pinacol-4-octylboronate (**16**) by hydroboration of *trans*-4-octene with $HBBr_2{\cdot}SMe_2$, followed by treatment with pinacol. Reaction of **16** with $Rh(PPh_3)_3Cl$ or $Rh(PPh_3)_3Cl$/PBH did not provide **1.** Furthermore, rhodium-catalyzed hydroboration of *cis*-2-methyl-3-hexene furnished **8.** It seems, therefore, that with internal alkenes, rhodium-catalyzed hydroboration with PBH behaves similarly to hydrozirconation of internal alkenes.[17] In the case of *cis*-2-methyl-3-hexene, isomerization had occurred at the nonbranched carbon of the chain. This contrasts with the report in the literature for the enantioselective hydroboration of *cis*-3-hexene with catecholborane, which gave the expected internal boronate.[18] We attribute the difference between PBH and CBH in the hydroboration of internal alkenes to the much larger steric requirements of pinacolborane, apparently resulting in a fast β-hydride elimination/recomplexation sequence that places rhodium on the least hindered carbon of the chain, followed by a relatively slow boron insertion. Careful examination of the reaction mixture failed to reveal any PBH degradation products, indicating that it is much more stable than CBH in metal-catalyzed hydroborations. Degradation of catecholborane is a major problem.[15e] Metal-catalyzed hydroboration of alkenes with PBH requires 1.05 equiv of borane versus 1.5 equiv with catecholborane to produce the same yield over an identical period of time. The products of PBH hydroboration are air-, moisture-, and chromatography-stable boronates, facilitating the separation of isomers. It is well known that catecholboronates are notoriously sensitive to moisture and cannot be chromatographed. For these reasons, PBH is superior to CBH.

We next turned our attention to CCl_4 addition to alkenes in the presence of rhodium.[19] As was the case in the zirconium−boron system, $Rh(PPh_3)_3Cl$ by itself was ineffective, and a complex reaction mixture was obtained, dominated by oligomers. However, $Rh(PPh_3)_3Cl$ (1 mol %) in the presence of catalytic amounts of PBH (10−15 mol %) gave an almost quantitative yield of CCl_4 addition product at 25 °C. Only trace amounts of hydroborated products were observed. Results are summarized in Table 1. Again, the final boron-containing compound was *B*-chloropinacolboronate, which was completely ineffective in catalyzing CCl_4 addition to alkenes in the presence of $Rh(PPh_3)_3Cl$. As was the case with the zirconium system, various free radical inhibitors did not inhibit or slow the rate of the reaction. It is premature to speculate on a mechanism, especially regarding the role of PBH in the course of the reaction.

In summary, we have developed two systems consisting of metal/PBH. In hydroboration, PBH is used stoichiometrically. In CCl_4 addition, PBH is used catalytically, and the reaction occurs at ambient temperature. Hydroboration of alkenes furnishes terminal boronates. Chloro trichloromethylation, on the other hand, provides the internal addition products. We have also clarified the literature surrounding PBH and predict that PBH will enter organic synthesis alongside such venerable hydroborating reagents as CBH and 9-BBN.

Acknowledgment. We thank the University of Toledo for support of this work. Special thanks to Dr. Craig Blankenship of Boulder Scientific for providing generous quantities of Cp_2ZrCl_2.

Supporting Information Available: General experimental procedures and representative spectra for compounds in Table 1 (39 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(11) Addition of 5 mol % $HZrCp_2Cl$ to the alkene, followed by the addition of PBH *after* 2 h, leads to results identical to those obtained under the conditions in Table 1. Other transition metal catalysts that we tried in the hydroboration of 1-octene are $Rh(CO)(PPh_3)_2Cl$ (80% **1**) and $Ru(PPh_3)_3Cl$ (0% **1**).

(12) Hydroquinone was shown not to inhibit the rate of addition of CX_4 to alkenes: Suzuki, T.; Tsuji, J. *J. Org. Chem.* **1970,** *35,* 2982.

(13) However, in a study using $RuH_3(SiMe_2Ph)(PPh_3)_3$ and $RuH_2(PPh_3)_4$, no enhanced catalytic activity for haloalkene addition to alkenes was observed: Davis, R.; Furze, J. D.; Cole-Hamilton, D. J.; Pogorzelec, P. *J. Organomet. Chem.* **1992,** *440,* 191.

(14) We prepared *B*-chloropinacolboronate from pinacol and BCl_3 according to the procedure of: Gennari, C.; Colombo, L.; Poli, G. *Tetrahedron Lett.* **1984,** *25,* 2279. ^{11}B NMR ($CDCl_3$): δ +28.2.

(15) (a) Männig, D.; Nöth, H. *Angew. Chem., Int. Ed. Engl.* **1985,** *25,* 878. (b) For a review, see: Burgess, K.; Ohlmeyer, M. J. *Chem. Rev.* **1991,** *91,* 1179. (c) Bijpost, E. R.; Duchateau, R.; Teuben, J. H. *J. Mol. Catal. A: Chem.* **1995,** 121. (d) With lanthanides, see: Harrison, K. N.; Marks, T. J. *J. Am. Chem. Soc.* **1992,** *114,* 9220. (e) For mechanistic studies and degradation of catecholborane, see: Wescott, S. A.; Blom, H. P.; Marder, T. B.; Baker, R. T.; Calabrese, J. C. *Inorg. Chem.* **1993,** *32,* 2175. (f) New rhodium catalysts for hydroboration: Westcott, S. A.; Blom, H. P.; Marder, T. B.; Baker, R. T. *J. Am. Chem. Soc.* **1992,** *114,* 8863.

(16) (a) For a study of selectivity of hydroboration of vinylarenes with rhodium catalysts, see: Burgess, K.; Donk, van der, W.; Westcott, S. A.; Marder, T. B.; Baker, R. T.; Calabrese, J. C. *J. Am. Chem. Soc.* **1992,** *114,* 9350. (b) Westcott, S. A.; Marder, T. B.; Baker, R. T. *Organometallics* **1993,** *12,* 975.

(17) Hart, D. W.; Schwartz, J. *J. Am. Chem. Soc.* **1974,** *96,* 8115.

(18) Sato, M.; Miyaura, N.; Suzuki, A. *Tetrahedron Lett.* **1990,** *31,* 231.

(19) $RhBr(CO)(PMe_3)_2$ was reported to catalyze $CBrCl_3$ addition to 1-octene: Cable, C. J.; Adama, H.; Bailey, N. A.; Crosby, J.; White, C. *J. Chem. Soc., Chem. Commun.* **1991,** 165. In our hands, $RhCl(CO)(PMe_3)_2$/PBH gave <10% addition product with CCl_4 and 1-octene, while $Ru(PPh_3)_3Cl$ was completely ineffective.