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Vinyl C−H Activation Reactions of Vinyl Esters Mediated by $B(C_6F_5)_3$

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Summary: $B(C_6F_5)_3$ *reacts with simple vinyl esters by electrophilic addition to the C*═*C bond and subsequent proton transfer and elimination of* C_6F_5H *to yield the chelated vinylborane products* $(C_6F_5)_2B\{\kappa^2\text{-}CH{=}CHOC({=}O)R\}$ *(R* = *Me, Ph).*

Tris(perfluorophenyl)borane, $B(C_6F_5)_3$,[1] has been used extensively as an activator for metallocene and other single-site olefin polymerization catalysts.[2] In this application, $B(C_6F_5)_3$ abstracts a hydrocarbyl group from an L_nMR_2 precursor to form an active $[L_nMR][RB(C_6F_5)_3]$ ion pair. $B(C_6F_5)_3$ has also been used as a Lewis acid catalyst for the hydrosilation of carbonyl compounds,[3] silation and reduction of alcohols and cleavage of ethers with silanes,[4] addition of silyl enol ethers to carbonyl compounds and other electrophiles,[5] hydrostannation of allenes,[6] and a variety of other reactions.[7] The Lewis acidity of $B(C_6F_5)_3$ is comparable to that of BF_3,[1b] and $XB(C_6F_5)_3^-$ anions are generally more resistant to degradation by X^- transfer than are XBF_3^- anions.[8] Here we describe an unusual reaction in which electrophilic addition of $B(C_6F_5)_3$ to the C═C bond of vinyl esters and subsequent $B-C_6F_5$ bond cleavage results in net vinylic C−H activation and the formation of vinylborane products.

The new chemistry is summarized in Scheme 1.[9] At 23 °C in benzene-d_6, $B(C_6F_5)_3$ reacts immediately with vinyl acetate to form the carbonyl adduct $CH_2{=}CHOC\{{=}OB(C_6F_5)_3\}Me$ (**1a**). Complex **1a** was characterized by multinuclear NMR but was not isolated. Key NMR parameters for **1a** include a low-field ^{13}C carbonyl resonance at δ 179.9 (vs 167.0 for free vinyl acetate), ^{19}F NMR resonances at δ −133.1, −151.6, −161.9, and an ^{11}B NMR resonance at δ 15.6 characteristic of a four-coordinate $B(C_6F_5)_3L$ species.[10] These data are very similar to the data for the ethyl benzoate adduct $EtOC\{{=}OB(C_6F_5)_3\}Ph$ (δ_C, 173.5; δ_B, 19.2) reported by Piers

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[3] Parks, D. J.; Piers, W. E. *J. Am. Chem. Soc.* **1996**, *118*, 9440.

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[5] Ishihara, K.; Hanaki, N.; Funahashi, M.; Miyata, M.; Yamamoto, H. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 1721.

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[7] (a) Ishihara, K.; Hanaki, N.; Yamamoto, H. *Synlett* **1995**, 721. (b) Ishihara, K.; Hanaki, N.; Yamamoto, H. *Synlett* **1993**, 577. (c) Ishihara, K.; Funahashi, M.; Hanaki, N.; Miyata, M.; Yamamoto, H. *Synlett* **1994**, 963.

[8] However, $B(C_6F_5)_3$ and $B(C_6F_5)_3X^-$ anions undergo $B-C_6F_5$ bond cleavage and other reactions under some conditions. For representative examples see: (a) Chernega, A. N.; Graham, A. J.; Green, M. L. H.; Haggit, J.; Lloyd, J.; Mehnert, C. P.; Metzler, N.; Souter, J. *J. Chem. Soc., Dalton Trans.* **1997**, 2293. (b) Pindado, G. N.; Lancaster, S. J.; Thornton-Pett, M.; Bochmann, M. *J. Am. Chem. Soc.* **1998**, *120*, 6816. (c) Barlow, G. K.; Boyle, J. D.; Cooley, N. A.; Ghaffar, T.; Wass, D. F. *Organometallics* **2000**, *19*, 1470. (d) Dagorne, S.; Guzei, I. A.; Coles, M. P.; Jordan, R. F. *J. Am. Chem. Soc.* **2000**, *122*, 274. (e) Vagedes, D.; Fröhlich, R.; Erker, G. *Angew. Chem., Int. Ed.* **1999**, *38*, 3362.

[9] Characterization data for new compounds are given in the Supporting Information.

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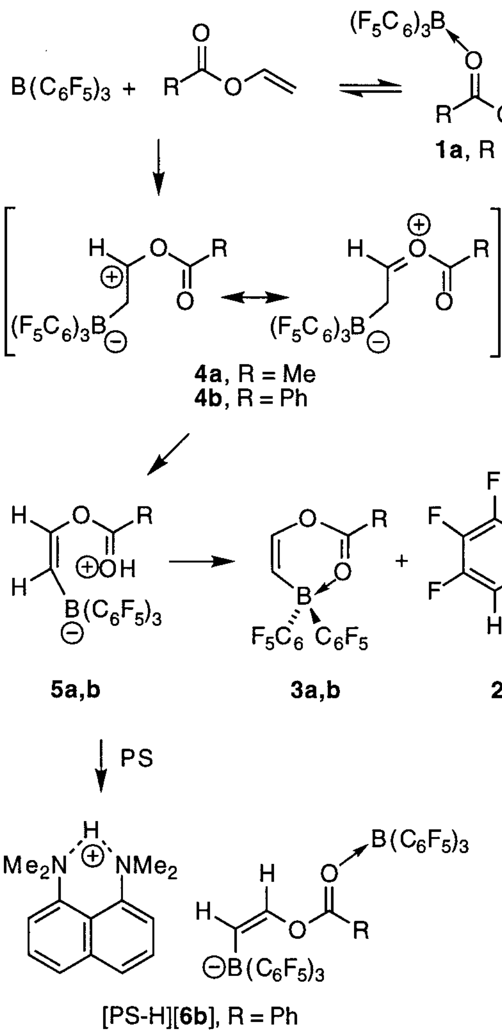
Scheme 1



et al.[10a] Adduct **1a** is stable at room temperature in benzene-d_6 for at least 48 h. However, heating a benzene-d_6 solution of **1a** at 60 °C for 12 h yields a 1/1 mixture of C_6F_5H (**2**) and the chelated vinylborane $(C_6F_5)_2B\{\kappa^2\text{-}CH{=}CHOC({=}O)Me\}$ (**3a**) with a conversion of 93%. Compounds **2** and **3a** were characterized by multinuclear NMR and GC-MS and, for **3a**, elemental analysis. Key NMR parameters for **3a** include (i) a ^{13}C carbonyl resonance at δ 196.0, characteristic of carbonyl oxygen coordination to a Lewis acid, (ii) two doublets for the *cis*-vinyl CH groups (J = 4.0 Hz) in the ^1H spectrum, and (iii) ^{19}F resonances at δ −136.2, −155.5 and −163.4 and a ^{11}B resonance at δ 5.2, consistent with a four-coordinate $RB(C_6F_5)_2L$ species. Very similar NMR data (^{19}F, δ −134.5, −158.1, −163.8; ^{11}B, δ 6.8) were reported for $(C_6F_5)_2B\{\kappa^2\text{-}CH_2(CH_2)_3C({=}O)OEt\}$, in which the ester carbonyl group is coordinated to boron.[11]

A plausible mechanism for this reaction is shown in Scheme 1. The key steps leading to **2** and **3a** are electrophilic attack of $B(C_6F_5)_3$ at the C=C bond to generate the zwitterionic intermediate **4a**, proton transfer to the carbonyl oxygen to generate the carbonyl-protonated species **5a**, and protonolysis of a $B{-}C_6F_5$ bond.

The reaction of vinyl acetate with $B(C_6F_5)_3$ to produce **2** and **3a** is much faster in CD_2Cl_2 than in benzene-d_6, and in this case intermediate **5a** can be detected by NMR. Monitoring the reaction in CD_2Cl_2 by NMR at 23 °C revealed the initial formation of carbonyl adduct **1a**, subsequent conversion to **5a**, and ultimate formation of **2** and **3a**. The **1a**/**5a**/**3a** ratio was 1.0/0.72/0.27 after 5 h, and the conversion to **2** and **3a** (1/1 ratio) was complete after 30 h. Key NMR parameters for **5a** include (i) a ^1H resonance at δ 12.87 and a ^{13}C carbonyl resonance at δ 199.1, which are correlated in the 2D-HMBC spectrum and are assigned to the protonated carbonyl group,[12] (ii) two coupled doublets (J = 4.4 Hz) in the ^1H spectrum, which are correlated in the COSY spectrum and are assigned to the *cis*-vinyl CH groups, and (iii) ^{19}F resonances at δ −134.6, −156.7, and −163.8 and a ^{11}B resonance at δ 2.15, for the (vinyl)$B(C_6F_5)_3^-$ unit. The close proximity of the protonated carbonyl group and the methyl group was established by a $^1H{-}^1H$ NOESY spectrum, which exhibited a strong cross-peak between the O−H (δ 12.87) and the Me (δ 2.47) resonances. The acceleration of the reaction in CD_2Cl_2 versus benzene-d_6 is ascribed to stabilization of the zwitterionic intermediates **4a** and **5a** by the more polar solvent.

Similarly, vinyl benzoate reacts with $B(C_6F_5)_3$ in CD_2Cl_2 at room temperature to generate **5b** in 50% yield after 15 min along with 50% of unreacted starting materials (Scheme 1). After 12 h, 93% conversion to a 1/1 mixture of **2** and **3b** was observed.[13] The NMR data for **3b** and **5b** are similar to the data for **3a** and **5a**.[9] To corroborate the structure of intermediates **5a**,**b** and in particular to confirm the presence of a protonated carbonyl group in these species, the 1/1/1 mixture of **5b**, vinyl benzoate, and $B(C_6F_5)_3$ generated at 50% conversion was treated with Proton Sponge (1,8-bis(dimethylamino)naphthalene, PS). An immediate reaction occurred to produce [PS-H][$\{cis\text{-}(C_6F_5)_3BCH{=}CHOC\{{=}OB(C_6F_5)_3\}Ph\}$] ([PS-H][**6b**]) quantitatively (along with unreacted vinyl benzoate). The unreacted $B(C_6F_5)_3$ present in the solution reacts with deprotonated **5b** to form **6b**$^-$. Key NMR parameters for **6b**$^-$ include (i) a low-field ^{13}C carbonyl resonance at δ 196.4, (ii) two sets of ^{19}F signals for the two four-coordinate $-B(C_6F_5)_3$ groups, and (iii) a broad ^{11}B signal centered at δ −1.5 for the two B centers. The ^1H NMR spectrum of [PS-H][**6b**] contains a signal at δ 19.49 for the PS-H$^+$ bridging proton which is correlated with the NMe_2 resonance at δ 3.14 in the COSY spectrum.[14]

Vinyl esters are not generally susceptible to electrophilic attack at the vinyl group, due to the weak ability

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(10) (a) Parks, D. J.; Piers, W. E.; Parvez, M.; Atencio, R.; Zaworotko, M. J. *Organometallics* **1998**, *17*, 1369. (b) Jacobsen, H.; Berke, H.; Döring, S.; Kehr, G.; Erker, G.; Fröhlich, R.; Meyer, O. *Organometallics* **1999**, *18*, 1724. (c) Galsworthy, J. R.; Green, J. C.; Green, M. L. H.; Müller, M. *J. Chem. Soc., Dalton Trans.* **1998**, 15.

(11) Parks, D. J.; Piers, W. E.; Yap, G. P. A. *Organometallics* **1998**, *17*, 5492.

(12) The HMBC (heteronuclear multiple-bond correlation) experiment enables determination of two- and three-bond $^1H{-}^{13}C$ connectivity: Bax, A.; Summers, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 2093.

(13) Compounds **2** and **3b** (1/1 ratio) are generated quantitatively by heating a CD_2Cl_2 solution of $B(C_6F_5)_3$ and vinyl benzoate to 80 °C for 3 h (sealed tube). In benzene-d_6 solution, 86% conversion to **2** and **3b** is observed after 5 days at 80 °C.

(14) This assignment is consistent with literature data: (a) Pietrzak, M.; Wehling, J.; Limbach, H.-H.; Golubev, N. S.; López, C.; Claramunt, R.; Elguero, J. *J. Am. Chem. Soc.* **2001**, *123*, 4338. (b) Grech, E.; Stefaniak, L.; Ando, I.; Yoshimizu, H.; Webb, G. H.; Sobczyk, L. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 2716. (c) Brzezinski, B.; Schroeder, G.; Jarczewski, A.; Grech, E.; Nowicka-Scheibe, J.; Stefaniak, L.; Klimkiewicz, J. *J. Mol. Struct.* **1996**, *377*, 149.

of the −OC(═O)R group to stabilize the carbocation intermediate. Thus, while vinyl ethers undergo facile cationic polymerization, vinyl esters do not.[15] Nevertheless, electrophilic attack at the C═C bond of vinyl esters has been established in several cases. For example, Noyce and Pollack showed by kinetic, substituent effect, and solvent isotope effect studies that acid hydrolysis of vinyl esters proceeds by two competing mechanisms: (i) initial protonation at the carbonyl oxygen followed by H_2O attack and collapse to products ($A_{AC}2$ mechanism), analogous to the mechanism for saturated esters, or (ii) initial protonation at the C═C bond followed by H_2O attack and collapse to products ($A_{SE}2$ mechanism), analogous to the normal mechanism for vinyl ethers.[16] The latter process is important under highly acidic conditions and when the carbocation resulting from protonation at carbon is strongly stabilized by substituents (e.g. α-acetoxy styrenes). Landgrebe showed by NMR H/D exchange studies that isopropenyl acetate undergoes fast reversible protonation at the C═C bond in concentrated H_2SO_4/D_2SO_4 solution.[17−19] In the present case, the kinetic product of the reaction of $B(C_6F_5)_3$ with vinyl acetate is the carbonyl adduct, but formation of the vinylborane product derived from C═C attack is driven by the irreversible protonolysis of the $B-C_6F_5$ bond.

The formation of **5a**,**b** from $B(C_6F_5)_3$ and the appropriate vinyl ester is a net electrophilic substitution of a vinyl hydrogen by a $B(C_6F_5)_3$ group. This reaction bears some similarity to the reaction of metal cyclopentadienyl complexes with electrophilic boranes to yield $M\{C_5H_4B^-X_3\}$ products.[20] For example, the reaction of the zirconacyclopentadiene complex $Cp_2Zr(C_4Me_4)$ with $B(C_6F_5)_3$ yields $Cp\{\eta^5\text{-}C_5H_4B^-(C_6F_5)_3\}Zr^+(\sigma\text{-CMe=CMe-CMe=CHMe})$, presumably via electrophilic attack of $B(C_6F_5)_3$ at a Cp ligand to generate $Cp\{(1\text{-}exo\text{-}B^-(C_6F_5)_3\text{-cyclopentadiene})Zr^+(C_4Me_4)$ followed by protonolysis of a Zr−C σ bond by the endo C−H group.[20b]

Supporting Information Available: Text giving synthetic procedures and characterization data for new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) (a) Noyce, D. S.; Pollack, R. M. *J. Am. Chem. Soc.* **1969**, *91*, 7158. (b) Noyce, D. S.; Pollack, R. M. *J. Am. Chem. Soc.* **1969**, *91*, 119. (c) Euranto, E. *Pure Appl. Chem.* **1977**, *49*, 1009 and references therein.

(17) Landgrebe, J. A. *J. Org. Chem.* **1965**, *30*, 2105.

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(19) The −OC(═O)R group is a mildly activating ortho, para director in electrophilic aromatic substitution: Smith, M. B.; March, J. *Advanced Organic Chemistry*, 5th ed.; Wiley: New York, 2001; p 684.

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