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Copper(I) β-Boroalkyls from Alkene Insertion: Isolation and Rearrangement

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Summary: The insertion of alkenes into an (NHC)copper(I) boryl affords isolable β-boroalkyl complexes in high yields; competition experiments using substituted styrenes show that electron-donating substituents slow the reaction. Although the insertion products are stable at ambient temperature, a β-hydride elimination/reinsertion sequence affords a rearranged α-boroalkyl complex on heating.

The formation of alkylboron reagents from alkenes has generated notable interest due to the synthetic versatility of the carbon−boron bond.[1] In the catalytic addition of diboron reagents to alkenes, which forms two carbon−boron bonds and permits a wide range of subsequent elaboration, a key step is the insertion of a C═C bond into a metal−boron bond.[2−6] This insertion has been implicated as competitive with metal-hydride insertion in some metal-catalyzed hydroboration reactions.[7] The β-boroalkyl intermediates formed through this insertion are typically prone to β-hydride elimination,[8] and the discrete borometalation of alkenes, in contrast to that of alkynes,[9] has not been reported to date.

We recently reported the first well-characterized copper boryl complex,[10,11] which is highly reactive toward carbon dioxide, and we were interested in examining its reactions with other unsaturated substrates such as alkenes. Although alkyl complexes of d^{10} metal centers undergo β-hydride elimination less readily than those of metals with partially filled d-orbitals, copper(I) alkyls have been shown to decompose by this route as well as by net Cu−C bond homolysis.[12,13] Because N-heterocyclic carbene (NHC) ligands impart considerable stability to σ-organocopper(I) complexes, we hoped that alkene insertion into the (NHC)copper boryl complex would lead to isolable products. Herein we report the regioselective insertion of alkenes into the copper−boron bond, with a Hammett study of substituent electronic effects on the reactivity of vinylarenes. The structurally characterized styrene insertion product does undergo β-hydrogen elimination, resulting in rearrangement to an α-boroalkyl complex, but only at elevated temperatures.

The structurally characterized copper(I) boryl complex (IPr)-CuB(pin)[10] (IPr = 1,3-bis(2′,6′-diisopropylphenyl)imidazol-2-ylidene), pin = pinacolate: 2,3-dimethyl-2,3-butanediolate) reacts rapidly and cleanly with styrene (Scheme 1) to form a single product as judged by ^{1}H NMR spectroscopy. Protonolysis of the styrene insertion product **1** with ethanol produces

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(1) See for example: (a) *Organoboranes for Synthesis*; Ramachandran, P. V., Brown, H. C., Eds.; ACS Symposium Series 783; American Chemical Society: Washington, DC, 2001. (b) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457−2483.

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10.1021/om060131u CCC: $33.50

Scheme 1

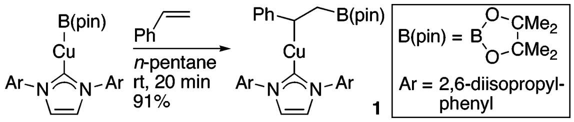
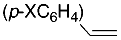
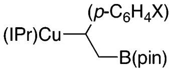
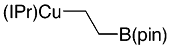
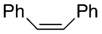
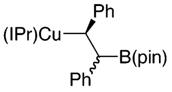
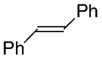
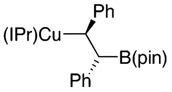


Table 1. Insertion of Alkenes into (IPr)CuB(pin)[a]

Entry	Substrate	Product	Yield (%)
1			
		X = H	91
		F	70
		Me	88
		OMe	92
		NMe$_2$	89
2			86[b]
3		 *syn* : *anti* = 25 :1	76[c,d]
4			81[c,e]

[a] (IPr)CuB(pin) was generated in situ from (IPr)CuO*t*Bu and (pin)BB(pin) (1 equiv). Unless noted otherwise, insertions were carried out in *n*-pentane solvent at room temp for 20 min, using 1.1 equiv of alkene. [b] Carried out under 1 atm of C_2H_4. [c] Reaction time was 15 h. [d] 2 equiv of *cis*-stilbene used; yield refers to both isomers. [e] Indicated stereochemistry is relative.

2-phenethyl(pinacol)boronate as the only boron-containing product, corroborating its assignment as an α-phenyl-β-boroethyl complex.

The results of insertion reactions using styrenes and other alkene substrates are given in Table 1. A number of *para*-substituted styrenes (entry 1) react efficiently, forming a single regioisomer in each case. Although alkyl-substituted alkenes such as 1-hexene and cyclopentene react very slowly with (IPr)-CuB(pin), ethylene itself undergoes insertion in high yield (entry 2). Both *trans*- and *cis*-stilbene (entries 3, 4) show high selectivity for *syn* addition, although the insertion of *cis*-stilbene leads to a detectable degree of isomerization (~5% as judged by ^{1}H NMR spectroscopy) to form the *anti* product, suggesting that a radical pathway may be involved to some extent. It is worth noting that an internal alkyne, 2-butyne, also inserts readily, affording the corresponding *cis*-2-borovinylcopper complex in an isolated yield of 90%.

Single crystals of **1** were grown by the diffusion of pentane vapor into an ether solution at −40 °C. Analysis by X-ray diffraction revealed a nearly linear two-coordinate structure and confirmed the regiochemistry of the styrene insertion (Figure 1).[14] Although the complex (IPr)CuEt was recently isolated and characterized spectroscopically,[12e] structurally characterized copper alkyl complexes possessing β-hydrogens are rare.[12d,13c,d] The Cu(1)−C$_{\mathrm{alkyl}}$ bond distance in **1** (1.948(3) Å) is similar to that of (IPr)CuCH$_3$ (1.913(6) Å).[15]

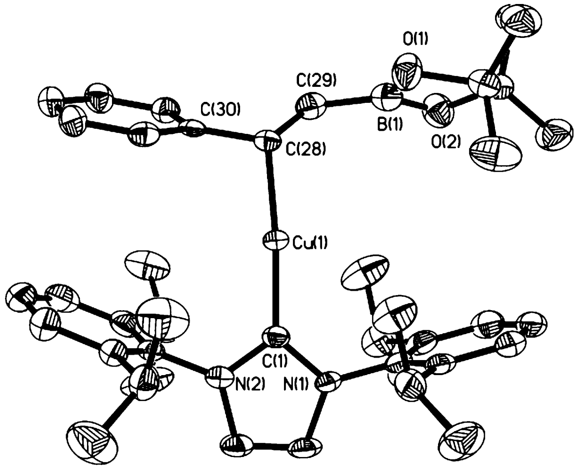


Figure 1. Solid-state structure of $\mathbf{1}\cdot(0.5\ C_5H_{12})$ shown as 50% ellipsoids. For clarity, hydrogen atoms, disorder, and solvent have been omitted. Select bond lengths (Å) and angles (deg): Cu(1)−C(28) 1.948(3), Cu(1)−C(1) 1.898(4), C(28)−C(29) 1.526(5), C(29)−B(1) 1.579(6), B(1)−O(1) 1.353(6), B(1)−O(2) 1.359(5), C(1)−Cu(1)−C(28) 175.07(16), Cu(1)−C(28)−C(29) 114.9(3), Cu-(1)−C(28)−C(30) 104.5(2).

To examine the role of electronic effects, competitive insertion experiments were carried out using *para*-substituted styrenes.[16] A benzene solution containing styrene (2.0 equiv) and 4-XC$_6$H$_4$-CH═CH$_2$ (X = NMe$_2$, OMe, Me, F; 2.0 equiv) was rapidly added to a solution of (IPr)CuB(pin). The relative product ratios, assessed by ^{1}H NMR spectroscopy, indicated that electron-donating substituents slow the reaction: styrene reacts ca. 60 times more rapidly than 4-(dimethylamino)styrene. The reactions were complete within minutes after mixing, and the product ratios did not change over several hours. Competition experiments using more electron-poor styrenes (*p*-Cl, *p*-CF$_3$) gave qualitatively similar results; however, these substrates undergo observable side-reactions[17] and are not included in the study.

A plot of the relative ratios of the insertion products against σ_p gave a moderate fit ($R^2 = 0.92$) with $\rho = +1.9 \pm 0.4$ (Figure 2).[18] If alkene insertion into the copper−boron bond is rate-determining, the ρ value is consistent with the buildup of negative charge on the incipiently copper-bound carbon. The carbocupration of enones and alkynes by dialkylcuprate(I) reagents has been described in terms of significant electron donation from the electron-rich copper center to the substrate,[19] followed by rate-determining insertion; both substrate binding and insertion are facilitated by the π-acidity of the substrate.[20] Here, the relative rates for the borocupration of styrenes suggest that the substrate likewise behaves essentially as an electrophile.

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(14) Crystal data for $\mathbf{1}\cdot 0.5C_5H_{12}$: $C_{43.50}H_{62}BCuN_2O_2$, monoclinic, space group *P*2(1)/*n*, $a = 20.3264(8)$ Å, $b = 9.6981(4)$ Å, $c = 21.9595(8)$ Å, $\beta = 106.996(2)°$, $V = 4139.8(3)$ Å^3, $Z = 4$, $\rho_{\mathrm{calcd}} = 1.154$ g/cm^3, $\mu = 0.563$ mm^{-1}, λ(Mo Kα) = 0.71073 Å, $T = 100(2)$ K. A total of 46 339 reflections were collected in the θ range 1.94−25.02°, of which 7312 were unique ($R_{\mathrm{int}} = 0.0826$). A semiempirical absorption correction was applied based on equivalent reflections. Least-squares refinement on 544 parameters converged normally with R1($I > 2\sigma(I)$) = 0.0657, wR2(all data) = 0.1449, GOF = 1.133.

(15) Mankad, N. P.; Gray, T. G.; Laitar, D. S.; Sadighi, J. P. *Organometallics* **2004**, *23*, 1191−1193.

(16) For related studies on migratory insertion reactions of *p*-substituted styrenes, see for example: (a) Halpern, J.; Okamoto, T. *Inorg. Chim. Acta* **1984**, *89*, L53−L54. (b) Doherty, N. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1985**, *107*, 2670−2682. (c) Burger, B. J.; Santarsiero, B. D.; Trimmer, M. S.; Bercaw, J. E. *J. Am. Chem.* Soc. **1988**, *110*, 3134−3146. (d) Rix, F. C.; Brookhart, M.; White, P. S. *J. Am. Chem. Soc.* **1996**, *118*, 2436−2448.

(17) The byproducts appear to arise from further reaction between the copper alkyl products and the remaining electron-poor olefins.

(18) σ_p values taken from: Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165−195.

(19) The dominant importance of metal-to-alkene electron donation has been demonstrated both for the binding of substituted styrenes by a d^{10} Pd(0) center and for the associative substitution of Pd(0)-bound styrenes: Popp, B. V.; Thorman, J. L.; Morales, C. M.; Landis, C. R.; Stahl, S. S. *J. Am. Chem. Soc.* **2004**, *126*, 14832−14842.

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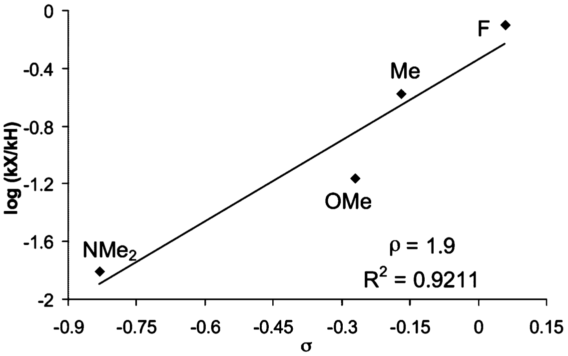
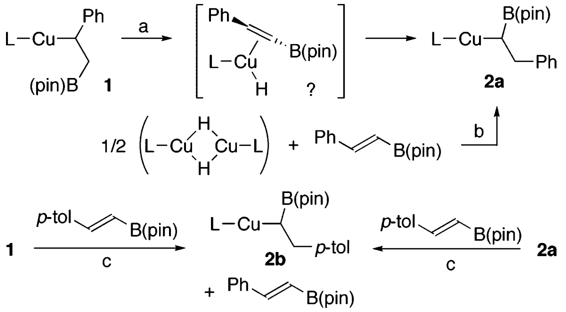


Figure 2. Hammett plot of the relative rates of insertion of 4-substituted styrenes into (IPr)CuB(pin) at room temperature in C_6H_6.

Scheme 2[a]



[a] (a) C_6H_6, 70 °C, 24 h; 54%. (b) $[(IPr)CuH]_2$ generated in situ from (IPr)CuO*t*Bu and $(EtO)_3SiH$; *n*-pentane, room temp, 1 h; 91%. (c) C_6D_6, 70 °C, 24 h; mixture of **2b** and **2a** observed.

In contrast, the small and negative ρ values determined for hydroboration reactions suggest the buildup of some positive charge in the substrate during insertion.[21,22] A more detailed mechanistic discussion must await further investigation.

Although **1** is stable for prolonged periods at ambient temperature, heating in benzene solution at 70 °C for 20 h resulted in the formation of a new complex, along with some deposition of elemental copper (Scheme 2). Analysis by ^1H NMR spectroscopy indicated the formation of the rearranged alkyl complex (IPr)CuCH[B(pin)]CH_2Ph (**2a**). This rearrangement presumably occurs via β-hydride elimination followed by reinsertion of the resulting olefin into a Cu–H bond. In a separate experiment, *trans*-2-phenylvinyl(pinacol)boronate, which should be formed by β-hydride elimination from **1**, reacted cleanly and rapidly with the previously characterized[23] copper hydride $[(IPr)CuH]_2$ to form **2a**. The rapidity of this hydrometalation suggests that β-hydride elimination is the slow step in the rearrangement of **1** to **2a**. The thermal rearrangement of **1** was also conducted in the presence of *trans*-2-(*p*-tolyl)vinyl(pinacol)boronate (1.5 equiv). The resulting ^1H NMR spectrum indicated the formation of both **2a** and (IPr)CuCH[B(pin)]CH_2(*p*-tolyl) (**2b**) and the presence of free *trans*-2-phenylvinyl(pinacol)boronate. This observation is consistent with the generation of a copper-alkene complex, in which the alkene is substitutionally labile, as an intermediate in the rearrangement. Heating a benzene solution of **2a** in the presence of 2-(*p*-tolyl)vinyl(pinacol)boronate (1.5 equiv) for 20 h likewise leads to a mixture of **2a** and **2b**,[24] indicating that the α-boroalkyl complexes can also undergo β-hydride elimination and hinting at the participation of a similar intermediate.

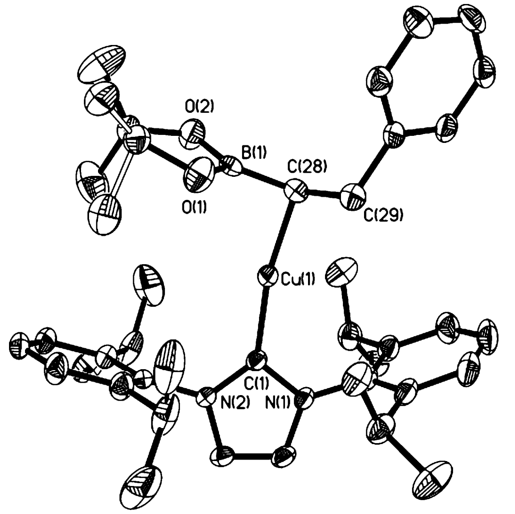


Figure 3. Solid-state structure of **2a**·$(0.5C_7H_8)$ shown as 50% ellipsoids. For clarity, hydrogen atoms, disorder, and solvent have been omitted. Select bond lengths (Å) and angles (deg): Cu(1)–C(28) 1.959(3), Cu(1)–C(1) 1.895(3), Cu(1)–B(1) 2.608(3), C(28)–C(29) 1.536(5), C(28)–B(1) 1.520(5), B(1)–O(1) 1.393(5), B(1)–O(2) 1.371(4), C(1)–Cu(1)–C(28) 169.51(13), Cu(1)–C(28)–C(29) 106.9(2), Cu(1)–C(28)–B(1) 96.3(2).

An X-ray diffraction study was performed on single crystals grown by vapor diffusion of pentane into a toluene solution of **2a** (Figure 3).[25] Other metal α-boroalkyls show varying degrees of metal–boron orbital interaction.[26] The somewhat acute Cu(1)–C(28)–B(1) angle of 96.3(2)° might indicate an attractive copper–boron interaction; however, the long Cu(1)–B(1) bond distance of 2.608(3) Å (the only measured Cu–B σ-bond is 2.002(3) Å) and the trigonal planar geometry about boron imply that any such interaction is weak in this case. In solution, no boron–copper interaction is observed for **2a** on the basis of its ^{11}B NMR spectrum: The chemical shift observed for **2a** (33.4 ppm) is typical of neutral, three-coordinate boron[27] and differs only slightly from that of **1** (34.7 ppm).

In conclusion, alkenes insert cleanly and regioselectively into (IPr)CuB(pin) to give isolable β-boroalkyl complexes. A Hammett study using 4-substituted styrenes showed that electron-releasing substituents slow the reaction markedly. At elevated

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(21) Vishwakarma, L. C.; Fry, A. *J. Org. Chem.* **1980**, *45*, 5306–5308. (b) Garner, C. M.; Chiang, S.; Nething, M.; Monestel, R. *Tetrahedron Lett.* **2002**, *43*, 8339–8342.

(22) We thank a reviewer for calling our attention to ref 21a, which plots relative rates against σ^+. This reviewer astutely points out the somewhat better correlation ($R^2 = 0.95$) obtained when our data are plotted against σ^+, which would give $\rho = +1.0 \pm 0.2$. The use of σ^+ in our study, however, would imply direct resonance between the aryl group and a significant positive charge on the carbon forming a bond to boron. While we cannot rule out such a contribution, we find it difficult to reconcile with the overall trend in rates, in which electron-rich styrenes react more slowly.

(23) Mankad, N. P.; Laitar, D. S.; Sadighi, J. P. *Organometallics* **2004**, *23*, 3369–3371.

(24) Under the reaction conditions, some decomposition occurs with deposition of metallic copper and formation of uncharacterized byproducts.

(25) Crystal data for **2a**·$0.5C_7H_8$: $C_{44.50}H_{60}BCuN_2O_2$, monoclinic, space group $P2(1)/n$, $a = 12.5994(8)$ Å, $b = 19.7548(15)$ Å, $c = 17.9349(14)$ Å, $\beta = 110.025(2)°$, $V = 4194.1(5)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.155$ g/cm^3, $\mu = 0.557$ mm^{-1}, λ(Mo Kα) = 0.71073 Å, $T = 100(2)$ K. A total of 75 308 reflections were collected in the θ range 1.59–26.37°, of which 8592 were unique ($R_{int} = 0.0409$). A semiempirical absorption correction was applied based on equivalent reflections. Least-squares refinement on 586 parameters converged normally with $R1(I > 2\sigma(I)) = 0.0671$, wR2(all data) = 0.1672, GOF = 1.029.

(26) Scollard, J. D.; McConville, D. H.; Rettig, S. J. *Organometallics* **1997**, *16*, 1810–1812. (b) Zhang, S.; Piers, W. E.; Gao, X.; Parvez, M. *J. Am. Chem. Soc.* **2000**, *122*, 5499–5509. (c) Cook, K. S.; Piers, W. E.; Woo, T. K.; McDonald, R. *Organometallics* **2001**, *20*, 3927–3937.

(27) Kennedy, J. D. In *Multinuclear NMR*; Mason, J., Ed.; Plenum Press: New York, 1987; pp 221–258.

temperatures, the styrene insertion product rearranges via β-hydrogen elimination and reinsertion to give an (α-boroalkyl)-copper(I) complex.

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Supporting Information Available: Text and figures giving experimental procedures, spectroscopic data, and structure refinement details; tables giving crystal structure data, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters for **1** and **2a**. Data for the structures are also available as a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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