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LETTERS

Rhodium-catalyzed 1,4-addition reactions of diboron reagents to electron deficient olefins

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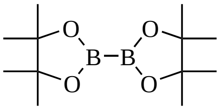
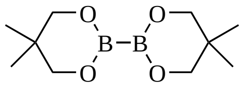
Abstract—The 1,4-addition of bis(pinacolato)diboron and bis(neopentyl glycolato)diboron to α,β-unsaturated ketones, esters, nitriles, and aldehydes was developed using a rhodium catalyst.

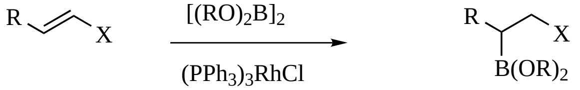
In recent years, the transition metal-catalyzed addition of compounds possessing metal–metal bonds to carbon–carbon multiple bonds has been the subject of intense interest.[1] Examples include metal-catalyzed reactions of diboron reagents such as (pinacolato)diboron.[2] The key step in the reaction of a diboron reagent with an alkene or alkyne is thought to involve oxidative addition of the diboron compound to the transition metal followed by coordination and insertion of the organic precursor and subsequent reductive elimination of the product.[3] The reaction of α,β-unsaturated carbonyl compounds with diboron reagents[4] has not been studied as extensively, but platinum[5] and copper[6] have been used to achieve a 1,4-addition of diboron reagents to α,β-unsaturated carbonyl compounds. Interestingly, no report has appeared concerning the possible use of a rhodium catalyst in the 1,4-addition of diboron agents to α,β-unsaturated carbonyl compounds and related reagents in spite of the fact that rhodium has been used to effectively catalyze the addition of boron hydride derivatives to alkenes and alkynes.[7] We have been investigating the preparation of boronic acids as part of our program focused on boron neutron capture therapy.[8] We now wish to report the use of a rhodium catalyst to achieve the 1,4-diboration of α,β-unsaturated carbonyl compounds and related electron deficient alkenes including esters and nitriles. Both bis(pinacolato)diboron,[9] **1**, and bis(neopentyl glycolato)diboron,[10] **2**, may be utilized in the reaction. Our results are summarized in Table 1.



1



2



Where R = CH_3, Ph, alkyl and X = CHO, CRO, CO_2R, CN

The synthesis of 3-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)cyclohexanone is representative: cyclohexene-2-one (1.9 g, 20 mmol) was added to a nitrogen-flushed, three necked, round-bottomed flask containing toluene (20 ml). Bis(pinacolato)diboron (5.5 g, 22 mmol) and chlorotris(triphenylphosphine)rhodium(I) (10 mol%) were then added and the reaction stirred overnight while maintaining a temperature of 80°C. The reaction mixture was then cooled, water (10 mL) added, and the mixture stirred for 1 h. The organic layer was separated and dried over anhydrous $MgSO_4$. After filtration, the solvent was evaporated and the crude product was purified by column chromatography (silica gel, 5% ethyl acetate in hexane); ^{1}H NMR ($CDCl_3$) δ 2.34–2.26 (m, 4H), 2.04 (m, 1H), 1.64–1.32 (m, 4H), 1.23 (s, 12H); ^{13}C NMR ($CDCl_3$) δ 211.5, 83.1, 42.2, 41.5, 28.1, 26.2, 24.0 (resonance for Cα to B not observed); IR 2978, 2933, 2863, 1711, 1448, 1416, 1325, 1203, 1144, 1058, 978 cm^{-1}; anal. calcd for $C_{12}H_{21}BO_3$; C, 64.31; H, 9.45; found: C, 64.09; H, 9.48.

In conclusion, we have developed a 1,4-addition reaction involving the addition of diboron reagents such as bis(pinacolato)diboron and bis(neopentyl glycolato)diboron to electron deficient alkenes in the presence of rhodium catalyst $(PPh_3)_3RhCl$. This is the first report of the use of a rhodium catalyst for addition of diboron reagents to α,β-unsaturated electron deficient alkenes.

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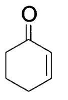
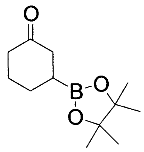
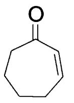
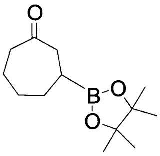
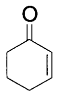
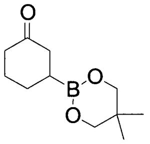
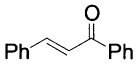
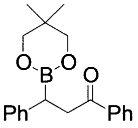
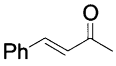
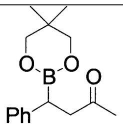
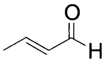
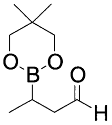
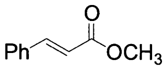
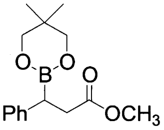
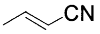
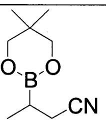
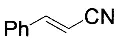
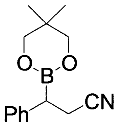
Table 1. 1,4-Addition of diboron reagents to electron deficient olefins catalyzed by rhodium

Acceptor	Diboron Compound	Product	Time in h[a]	Yield (%)[b,c]
	1		13	78
	1		12	75
	2		12	76
	2		13	67
	2		14	64
	2		10	62[d]
	2		14	63
	2		13	72
	2		12	65

[a]Reactions were carried out at 80 °C. [b]Isolated yield. [c]All products were characterized by elemental analysis and/or high resolution mass spectrometry. [d]GC-MS yield.

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