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Hydroboration Reactions Mediated by Bis(mesityl)niobium: Beware of the Trojan Horse

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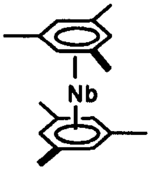
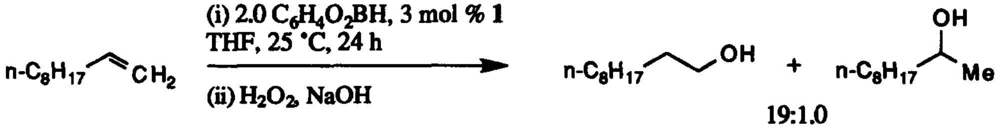
Abstract: Bis(mesityl)niobium (**1**) promotes hydroborations of alkenes by catecholborane but via an indirect mechanism.

Transition-metal catalysis of hydroboration reactions opens new avenues for chemo-, regio-, and stereoselective reactions in organic syntheses.[1] Most work in this area has focused on the use of rhodium(+1) catalysts, but the performance of these is far from ideal. For instance, hydroboration of allylic silyl ethers mediated by $RhCl(PPh_3)_3$ can give substantial amounts of alkane (via hydrogenation) and aldehyde (after oxidation of the dehydrogenative borylation products, *ie* vinylboronate esters) besides the desired material.[2] Such side reactions reflect the fact that reactions of $RhCl(PPh_3)_3$ with catecholborane are exceedingly complex.[2] It is evident that new catalysts for hydroboration reactions would be highly desirable, particularly if they follow mechanistic pathways which differ significantly from the rhodium promoted processes.

In the present study, bis(mesityl)niobium (**1**)[3] was tested as a potential catalyst for the following reaction.



1



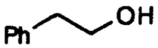
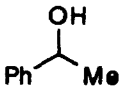
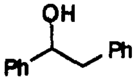
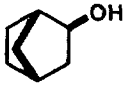
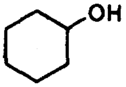
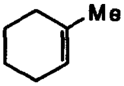
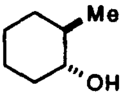
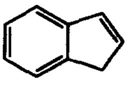
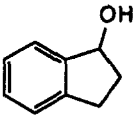
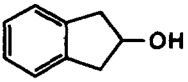
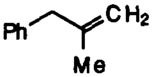
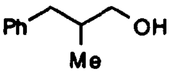
eq. 1

Hydroboration did indeed occur, giving 76 % isolated yield of the corresponding primary alcohol. Monitoring the reaction via GC indicated that the alkene was consumed without generation of hydrogenation product, and predominantly one silyl ether was formed after oxidation and silylation.

Several other substrates were subjected to niobium-mediated hydroborations, and the results are shown in the Table. In each case, GC analyses indicated the reactions were exceptionally clean.

Table. Hydroboration Reactions Promoted by Niobium Complex **1**.

$$\text{alkene} \xrightarrow[\text{(ii) } H_2O_2\text{, NaOH}]{\text{(i) 2.0 } C_6H_4O_2BH\text{, 3 mol \% } \mathbf{1} \text{; THF, 25 °C, 24 h}} \text{alcohol(s)}$$

entry	starting alkene	product(s)	yield (%)
1		 5.4:1.0 	77
2[b]			61
3			69
4			74
5			71
6[c]		 1.0:3.2 	78
7[c]			84

[a] Product ratios indicated were accessed by GC after silylation and calibration, but the yields quoted are for isolated materials. [b] 10 mol % catalyst used. [c] 6 mol % catalyst.

At face value, these results seem particularly encouraging. Bis(mesityl)niobium was easily prepared from niobium pentachloride in one step,[3] and at a cost which is considerably less than for $RhCl(PPh_3)_3$. Only small quantities of the complex were required, although the reaction was slower than with rhodium(+1) catalysis.

Most importantly, bis(mesityl)niobium is unlikely to catalyze hydroborations via oxidative addition of catecholborane, addition of alkene, migratory insertion, and reductive elimination {*ie* via a mechanism which parallels that of the rhodium(1+) catalysis}; consequently, it would appear that the reaction should give chemo-, regio-, and stereo-selectivities characteristic of its unique mechanism.

Stoichiometric reactions of catecholborane with bis(mesityl)niobium are not easily followed by NMR because the complex is paramagnetic (17*e*). The catalytic reaction is more easily studied, since this can be done by following the substrates and products via ^{11}B NMR. For a THF solution of catecholborane and 6 mol % bis(mesityl)niobium, ^{11}B NMR[4,5] showed around 90 % of the catecholborane (26 ppm, relative to $BF_3.OEt_2$ external reference throughout) remained after 24 h at 25 °C. However, two other products formed: a trace of BH_3 (*ca* 5 %, 0.4 ppm) and a material giving a peak at 19 ppm which we assign to $B_2(O_2C_6H_4)_3$ [6] (2, *ca* 5 %). The ^{11}B NMR spectrum of this material is shown in the Figure.

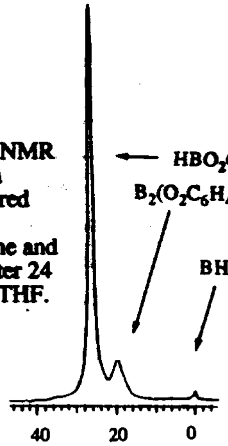
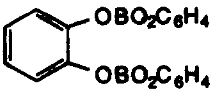
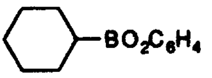


Figure. ^{11}B NMR spectrum of a sample prepared from catecholborane and 6 mol % 1 after 24 h at 25 °C in THF.

A THF solution of cyclohexene, catecholborane, and bis(mesityl)niobium (20:15:1.0) after 6 h at 25 °C gave several ^{11}B NMR peaks. *The expected boronate ester 3 was not the major product* (for an authentic sample of this material: ^{11}B, δ = 36 ppm). An intense resonance was observed for $B_2(O_2C_6H_4)_3$, and three other peaks were seen corresponding to $CyBO_2C_6H_4$ (3, 36 ppm), Cy_2BH (5, 51 ppm), and Cy_3B (6, 81 ppm).



2



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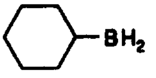

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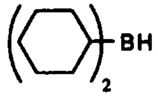

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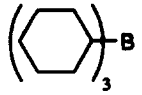

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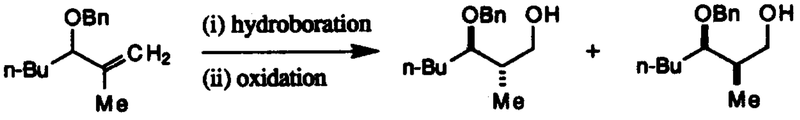
The possibility that bis(mesityl)niobium causes extensive disproportionation between catecholborane and the boronate ester 3 to give 4 - 6 was ruled out on the basis of other ^{11}B NMR experiments. Consequently, we conclude bis(mesityl)niobium facilitates the disproportionation of catecholborane[6] into an equilibrium concentration of BH_3 and $B_2(O_2C_6H_4)_3$; *BH_3 is the major active hydroborating agent and its concentration is rejuvenated as reactions proceed, via an equilibrium established in the presence of complex 1.* This assertion is supported by equation 1 and entry 1 in the Table wherein the observed ratio of regioisomers formed in the hydroboration process is very similar for the ratios reported for hydroboration of the same substrates with BH_3.[7,8] Moreover, diastereoselectivities for the hydroboration of the allylic ether 6 with BH_3, and with catecholborane/catalytic bis(mesityl)niobium, were very similar.



6

BH_3 56:44
$C_6H_4O_2BH$/cat. 1 53:47

It appears that the formation of BH_3 is the rate limiting step in these niobium promoted hydroborations because all the substrates are consumed at approximately the same rate (turnover ~2 h^{-1}); by contrast, rhodium(+1) catalyzed hydroboration of phenylethene, for instance, is much faster than the corresponding Rh-catalyzed reaction of 1,2-diphenylethene.

Besides rhodium(+1), $Rh_2(OAc)_4$,[9] complexes of iridium,[10,11] palladium,[12,13] nickel,[14] samarium,[15] lanthanum,[15] and titanium[16-18] (see following paper) have been reported to catalyze addition of boron-hydrides to alkenes and/or alkynes. Other new catalysts for hydroborations will undoubtedly be reported in the near future. However, the boron hydride must be delivered to the substrate via a mechanism that intimately involves the metal if the reaction is to be useful in organic chemistry; generation of BH_3 in a Trojan horse-like manner will not provide useful alternative chemo-, regio-, and stereo-selectivities. Formation of BH_3 in these niobium mediated reactions reaction might easily have been missed because such small amounts are formed (see Figure). Characterization of the boron-containing products in catalyzed hydroborations therefore is a prerequisite for progress in this area. We feel that this has not been adequately emphasized in the literature to date, although Baker, Marder, and co-workers have stressed the importance of monitoring reaction products by multinuclear NMR with respect to rhodium catalyzed hydroborations.[19,20]

Acknowledgments

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