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Notes

Ruthenium-Catalyzed Hydroborations of Alkenes

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Summary: The complexes $RuCl_2(PPh_3)_4$ (1), $RuCl_3(PPh_3)_2(MeOH)$ (2), $RuHCl(PPh_3)_3$ (3), $RuH_4(PPh_3)_3$ (4), and $RuHCl(DIOP)_2$ are shown to be catalysts for addition of catecholborane and 3-methyl-1,3,2-oxazaborolane (7) to unhindered alkenes and alkynes. These reactions are slower than the corresponding reactions mediated by rhodium(+1) complexes. Competing hydrogenation reactions occur, just as with hydroborations catalyzed by $RhCl(PPh_3)_3$. Analyses of the hydroboration of cyclohexene mediated by complex 2 reveal that the reaction occurs predominantly via addition of catecholborane, but a small amount of disproportionation of catecholborane to BH_3 and conventional (uncatalyzed) hydroboration also occurs.

Introduction

The evolution of rhodium catalyzed hydroborations of alkenes as a preparative method has increased the potential applications of boron hydrides in synthetic organic chemistry.[1] For instance, highly diastereoselective catalyzed hydroborations have been reported, as have truly *enantioselective* hydroborations of prochiral alkenes (*i.e.* asymmetric transformations wherein all the diastereoselective steps are confined within a catalytic cycle).

Recent mechanistic studies indicate Wilkinson's catalyst combines with catecholborane to give several rhodium complexes, and disproportionation of the boron hydride is also observed (Scheme I).[2] This complication leads to extensive side reactions and can cause diminished stereoselectivities. Competing catalysis by different complexes formed on mixing catalytic precursors with the hydroboration reagent therefore is a major obstacle to the development of more synthetically valuable reactions. Indeed, this complication could account for the almost[3,4] uniformly modest enantioselectivities that have been obtained for catalyzed hydroborations, despite considerable efforts in this area.[3-8] Cleaner catalytic systems must be found if the catalysis is to be harnessed and refined for more advanced applications of catalyzed hydroborations in organic syntheses. Consequently, identification of new catalysts for additions of boron hydrides to alkenes is a priority in this area of research.

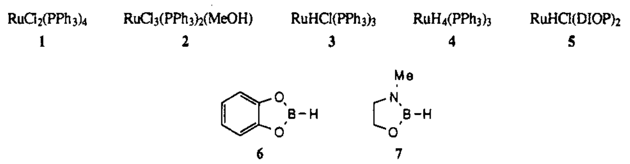
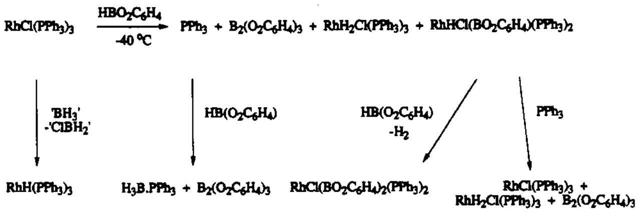


Figure 1. Ruthenium complexes and boron hydrides used in this study.

Scheme I. Reaction of $RhCl(PPh_3)_3$ with Catecholborane



New rhodium-based catalysts for hydroboration reactions are emerging, and the zwitterionic complex $[Rh(\eta^6\text{-}C_6H_4O_2BO_2C_6H_4)\{(^iPr_2PCH_2)_2\}]$ promises to be particularly useful in this regard.[9] Excluding rhodium(+1) complexes, however, only a few transition metals have been reported to accelerate additions of catecholborane to alkenes. Zerovalent palladium- and nickel-based materials mediate hydroborations of conjugated alkenes[10-12] and thioalkynes,[13] but there are no reports concerning additions of catecholborane to alkenes using such systems. Crabtree's catalyst, $[Ir(cod)(PCy_3)(py)]PF_6$,[14] and other iridium complexes have also been used.[15,16] Recently, Marks and Harrison reported the use of $Cp^*{}_2LnR$ {Ln = La or Sm, R = H or $CH(TMS)_2$} as a catalyst for the hydroboration of alkenes.[17] Finally, Männig and Nöth reported low activity for $HRuCl(CO)(PPh_3)_3$, but without providing information concerning the substrate or the experimental conditions.[18]

This manuscript describes a systematic investigation of various ruthenium–phosphine complexes as potential alkene hydroboration catalysts. The goal of this study

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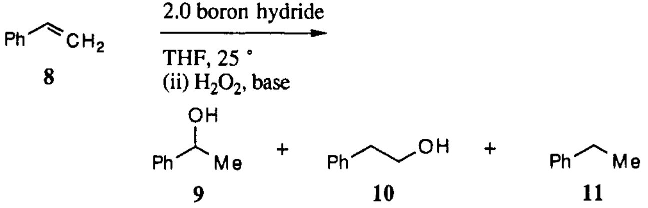
Table I. Catalyzed Hydroborations of Phenylethene



entry	catalyst	boron hydride	time (h)	material balance 8:9:10:11
1	$RuCl_2(PPh_3)_4$	**6**[a]	6	15:0:77:8
2	$RuCl_2(PPh_3)_4$	**7**[a]	6	38:30:11:21
3	$RuCl_3(PPh_3)_2(MeOH)$	**6**	9	0:<1:86:14
4	$RuCl_3(PPh_3)_2(MeOH)$	**7**	9	8:32:19:41
5	$RuHCl(PPh_3)_3$	**6**[a]	6	4:3:84:9
6	$RuHCl(PPh_3)_3$	**7**[a]	6	10:46:13:31
7	$RuH_4(PPh_3)_3$	**6**[b]	3.5	0:0:0:16[c]
8	$RuH_4(PPh_3)_3$	**7**	4	0:71:18:11
9	$RuHCl(DIOP)_2$	**6**[c]	6	36:6:45:13

[a] 1.5 mol % catalyst was used. [b] Polymerization was evident (white solid formed); hence only 16% of product was observed relative to the internal standard. [c] 3.0 mol % catalyst was used.

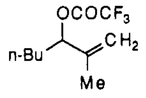
was to compare and contrast any active materials with the established rhodium systems and to highlight characteristics which could be synthetically valuable.

Results

Phenylethene initially was used as a substrate since rhodium catalyzed hydroborations of this alkene have been studied extensively. Five ruthenium complexes (**1**–**5**) were screened as potential catalysts for the addition of catecholborane (**6**) and the 3-methyl-1,3,2-oxazaborolane (**7**); the reaction mixture was then oxidized and the products were monitored by GC (Table I).

Entries 1 and 2 Table I show the ruthenium(+2) dichloride **1** mediates the addition of catecholborane to phenylethene with almost perfect selectivity for the primary alcohol **10** (after oxidation), whereas with the boron hydride **7** the selectivity is reversed and more of the hydrogenation product **11** is formed. Most of these trends were reflected in the experiments using the ruthenium(+3) trichloride catalyst (entries 3 and 4), and the hydridoruthenium(+2) chloride catalyst (entries 5 and 6). Good selectivity for the primary alcohol was observed in the experiments with catecholborane, and more secondary selectivity/hydrogenation resulted when oxazaborolane **7** was used. The tetrahydrido complex **4** gave a mixture of products, and only with boron hydride **7** was evidence for significant hydroboration observed (entries 7 and 8).

Table II summarizes the results obtained for hydroborations of other substrates with catecholborane in the presence of the complexes listed above. Norbornene was mainly converted to *exo*-norborneol (after oxidation), but appreciable hydrogenation product was also observed for complexes **4** and **5** (entries 3 and 4). Use of the enantiopure DIOP complex **5** gave no induction with this substrate (entry 4). A mixture of products resulted from the hydroboration of 1-decyne mediated by complexes **1**–**3**. 1-Decene and decane, the products of addition of 1 and 2 mol of dihydrogen, were detected in all cases, along with both primary and secondary alcohols and decanal (entries 5–7). Three complexes were used to mediate the hydroboration of substrate **12** (entries 8–10); in all cases the reaction was incomplete after 2 days and very low 1,2-induction was observed in favor of the *syn* diastereomer. Complexes **1**–**3** failed to mediate any significant reaction of the more hindered substrate **13** under comparable conditions (48-h reaction time).



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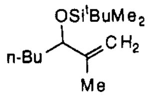

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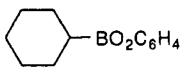
Qualitatively, all the ruthenium mediated processes were observed to be slow relative to be corresponding reactions promoted by rhodium(+1) catalysts, even though up to 5 mol % of the catalysts was often used. An approximate initial turnover number of 780 h^{-1} was determined for the reaction of 1-decene with catecholborane in the presence of $RuCl_3(PPh_3)_2MeOH$ (**2**) whereas for $RhCl(PPh_3)_3$ the turnover number was in the region of 3800 h^{-1}. The rate of decay of substrate in the ruthenium mediated reactions tapers off as the reaction proceeds, indicative of catalyst decomposition. Catalyzed hydroboration of cyclohexene was followed by ^{11}B NMR; the boronate ester product **14** (δ = 35 ppm) formed rapidly in the early stages of the reaction, but after extended periods (*ca.* 10 h) peaks corresponding to BCy_3 (**15**, 81 ppm) and the catecholborane disproportionation product[19] $B_2(O_2C_6H_4)_3$ (**16**) became increasingly prevalent. Consequently, it appears that the reaction proceeds via direct intervention of the metal in the early stages, but hydroboration as a result of catecholborane degradation becomes more important as the catalyst ages. Metal catalyzed degradation reactions of catecholborane have recently been described by others.[20]



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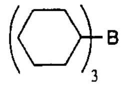

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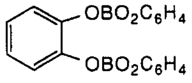

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Discussion

Addition of catecholborane to phenylethene mediated by Wilkinson's catalyst gives predominantly 1-phenylethanol (**9**).[2] Hayashi and co-workers have suggested formation of this product occurs via a η^3-benzylic ligand.[3] Apparently, such intermediates are unimportant in the ruthenium mediated hydroborations of the same substrate wherein the secondary alcohol was a minor product (Table I). Good selectivity was observed for 2-phenylethanol in hydroborations with catecholborane mediated by complexes **1**–**3** (entries 1, 3, and 5). All of the ruthenium-mediated processes gave some hydrogenation product, more so when 3-methyl-1,3,2-oxazaborolane was used in place of catecholborane.

Norbornene reacts relatively quickly with catecholborane in the presence of Wilkinson's catalyst. The incomplete reactions of this substrate in the presence of complexes **1**–**3** and **5** is further evidence that the ruthenium complexes give less rate acceleration (Table II, entries 1–4). Formation of reduction products in the hydroboration of 1-decyne is analogous to the corresponding rhodium mediated reactions, and the 1- and 2-decanol formed (after oxidation) probably result from hydroboration of 1-decene generated by reduction of the parent alkyne *in situ* (entries 5–7).[2] The ratio of alcohols to

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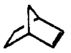
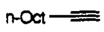
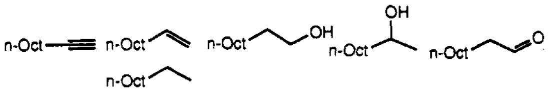
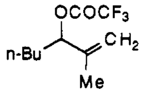
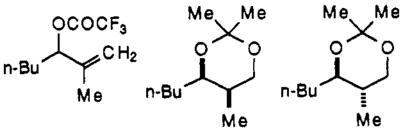
Table II. Catalyzed Hydroborations of Other Substrates

$$\text{substrate} \xrightarrow[\text{(ii) } H_2O_2\text{, base}]{\text{(i) 0.05 M catalyst, 2.0 equiv catecholborane, THF, 25 °C}} \text{products}$$

entry	substrate	catalyst	time (h)	products (ratios)
				
1		$RuCl_2(PPh_3)_4$	5	10:*c*:87
2		$RuCl_3(PPh_3)_2(MeOH)$	6	15:*c*:77
3		$RuHCl(PPh_3)_3$	5	6:12:82
4		$RuHCl(DIOP)_2$	6	20:11:54[a]
				 (inseparable)
5		$RuCl_2(PPh_3)_4$	5	0:4:25:5:13[b]
6		$RuCl_3(PPh_3)_2(MeOH)$	5	0:4:24:3:20[b]
7		$RuHCl(PPh_3)_3$	5	0:3:40:10:14[b]
	 **12**			
8		$RuCl_2(PPh_3)_4$	48	32:41:28 (*i.e.* 19% de)
9		$RuCl_3(PPh_3)_2(MeOH)$	48	41:33:24 (*i.e.* 16% de)
10		$RuHCl(PPh_3)_3$	48	27:40:32 (*i.e.* 11% de)

[a] ee = 0% determined by $Eu(hfc)_3$ NMR shift experiment. [b] Decane and 1-decene were inseparable by GC; ratios quoted are relative to internal standard and do not add to 100, apparently some polymerization products were formed. [c] Trace hydrogenated product inseparable from the solvent peak in the GC.

decanal indicates reduction is relatively facile in comparison with the hydroboration process. Finally, the incomplete reaction of the 1,1-disubstituted alkene **12** and lack of reaction of alkene **13** underline the observation that the ruthenium promoted processes are relatively slow in relation to the rhodium promoted ones and are less diastereoselective for this particular substrate.

Experimental Section

High field NMR spectra were recorded on a Bruker AF300 spectrometer (^1H at 300 MHz, ^{13}C at 75.4 MHz) using $CHCl_3$ as internal reference (δ 7.25 ppm and δ 77.0 ppm, respectively). Low resolution mass spectra (EI) were obtained on a Finnigan 3300 mass spectrometer. Gas chromatography was performed on a Shimadzu GC-9A with a flame ionization detector using a 50-m Quadrex fused silica capillary column (0.25-mm internal diameter, 0.25-μm film of methyl phenyl (5%) silicone, Catalog No. 007-2-50-0.25F) at a flow rate of 1.5 atm of He. Reaction mixtures contained 10 mol % of naphthalene as an internal standard. Starting alkenes, hydrogenation products (where possible), trimethylsilylated product alcohols, and the diol acetonides were calibrated independently against naphthalene. Tetrahydrofuran was distilled under N_2 from sodiobenzophenone ketyl immediately before use. Catecholborane, purchased from Aldrich, was distilled at reduced pressure before use. The ruthenium complexes $RuCl_2(PPh_3)_4$,[21] $RuCl_3(PPh_3)_2(MeOH)$,[22] $RuHCl(PPh_3)_3$,[23] $RuH_4(PPh_3)_3$,[24] and $RuHCl(DIOP)_2$[25] were synthesized by procedures reported in the literature. ^{11}B NMR spectra were recorded on a Varian XL 200 BB at 64.17 MHz using $BF_3 \cdot OEt_2$ as an external reference.

Screening Procedure. A Schlenk tube charged with the ruthenium complex (0.05 mmol) was evacuated/filled with Ar 3×, after which a solution of the alkene (1 mmol) and naphthalene (12.8 mg, 0.1 mmol) in THF (3 mL) was added followed by the addition of 3-methyl-1,3,2-oxazaborolane (1.5 M in THF, 1.5 mL, 2.3 mmol) or catecholborane (240 mg, 2 mmol). The progress of the reaction was monitored by GC and the decrease of alkene noted with respect to the naphthalene standard {in a separate GC experiment with decane as the internal standard, naphthalene was shown not to react with catecholborane in the presence of complex **2**}. The reaction mixture was subjected to a basic oxidative workup of EtOH (1 mL), NaOH (3 M, 1 mL), and H_2O_2 (30%, 1 mL) for 2-12 h, followed by extraction (Et_2O), washing (1 M NaOH, 3× and saturated aqueous NaCl, 1×), and drying ($MgSO_4$) of the extract followed by removal of the solvent. A small quantity of the crude mixture was derivatized as the trimethylsilyl alcohol using pyridine/1,1,1,3,3,3-hexamethyldisilazane/chlorotrimethylsilane and subjected to analysis by GC. In the case where the expected product was a 1,3-diol the mixture was turned into the acetonide by reacting a small amount of the mixture in Et_2O with 2,2-dimethoxypropane (~5 equiv) and toluenesulfonic acid (~0.1 equiv) for 24 h, after which it was subjected to analysis by GC.

3-Methyl-1,3,2-oxazaborolane. To borane–dimethyl sulfide (0.24 mol, 24.0 mL) at 0 °C under Ar was added *N*-methylethanolamine (16.7 g, 0.23 mol, 18 mL) at a rate of 0.44 mL min^{-1}. The mixture was left to stir until evolution of H_2 had ceased (~1 h). The dimethyl sulfide was removed at high vacuum over a period of about 1 h, giving a very viscous liquid. The mixture was heated to 120 °C over a period of 90 min and left at this temperature for 1.5 h. (*Caution: check the pressure bleed regularly for blockages to avoid an explosive buildup of pressure.*) After cooling, the resulting white solid was distilled under Ar, bp 107–109 °C (lit.[26] bp 82–84 °C at 155 torr). ^{13}C NMR (75.4 MHz,

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$CDCl_3$): δ 61.9 (CH_2), 57.9 (CH_2), 42.1 (CH_3/CH). MS (EI, 70 eV): *m*/*e* (%) 169 (100, dimer-1), 141 (60), 84 (monomer-1,30).

Determination of Turnover Numbers. A Schlenk tube charged with $RuCl_3(PPh_3)_2MeOH$ (22.8 mg, 0.03 mmol) was evacuated and filled with Ar three times, after which a solution of decene (420 mg, 3 mmol) and naphthalene (38.4 mg, 0.3 mmol) in THF (9 mL) was added followed by the addition of catecholborane (720 mg, 6 mmol). Samples were withdrawn at known periods of time, and these were analyzed by GC. A graph of decene concentration versus time gave an exponential decay curve fit with a correlation coefficient of 0.953. Differentiating the equation of the curve for *t* = 0 gave a turnover number of 780 h^{-1}. After 120 min the mixture was subjected to the usual oxidative workup. The final mixture contained decane (13%), decene (6%), 1-decanol (77%), and no 2-decanol.

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