Dirhodium(II) Tetraacetate Catalysed Hydroboration of Alkenes

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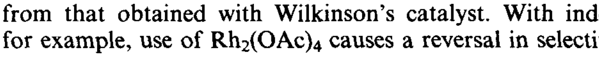
Rhodium(II) compounds are effective catalysts for the hydroboration of alkenes by catecholborane under mild conditions; regioselectivity is dependent on the catalyst, and a facile rhodium hydride catalysed olefin isomerization has been identified.

Transition metal catalysed hydroboration reactions have recently become subjects of considerable synthetic interest[1] and mechanistic controversy.[2] Catecholborane, whose uncatalysed addition to alkenes at room temperature is very slow, reacts virtually quantitatively with alkenes in 2–4 h at 100 °C to afford the corresponding alkaneboronic esters with a regiocontrol that is characteristic of these transformations.[3] With transition metal catalysts, of which those of rhodium(I) are the most active and effective,[4,5] catecholborane hydroboration is rapid at room temperature, and the regioselectivity of its addition is often reversed from that observed in the uncatalysed reaction.[1,4] The potential of dirhodium(II) carboxylates to catalyse hydroboration reactions became evident in investigations that we recently reported for hydrosilylation reactions,[6,7] where association of the hydrosilane at the axial coordination site of the dirhodium(II) compound activated the organosilane for subsequent reactions,[8] and *trans* addition was characteristic.[6] We now provide the first report of the high catalytic activity of dirhodium(II) carboxylates and carboxamides for hydroboration with catecholborane and the facility with which olefin isomerization can occur.

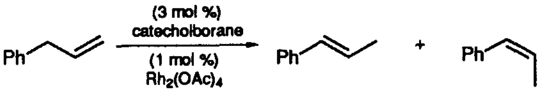
From a refluxing dichloromethane solution of bicyclo[2.2.1]hept-2-ene and 1.1 molar equiv. catecholborane in the presence of only 0.5 mol% dirhodium(II) tetraacetate was obtained, following oxidation with alkaline hydrogen peroxide, bicyclo[2.2.1]heptan-2-ol (*exo*:*endo* = 99.1) in 80% yield without evidence of unreacted alkene, reaction (1). Similarly effective hydroboration–oxidation was performed with a series of representative alkenes (Table 1) under the same reaction conditions. Dichloromethane was the most suitable solvent for reactions performed with $Rh_2(OAc)_4$; THF coordinates with dirhodium(II) compounds to inhibit the catalytic hydroboration reaction. Uncatalysed hydroboration by catecholborane[9] accounted for < 5% product formation.



(1)

As can be seen from Table 1, regioselectivity for hydroboration catalysed by $Rh_2(OAc)_4$ can differ significantly from that obtained with Wilkinson's catalyst. With indene, for example, use of $Rh_2(OAc)_4$ causes a reversal in selectivity from that obtained with $(Ph_3P)_3RhCl$, but with styrene preference for boron attachment at the 1-position was only achieved with rhodium(I).[10] In addition, variation of the dirhodium(II) ligands from perfluorobutyrate to caprolactam, which has been shown to strongly influence regioselection and chemoselection in many, but not all, metal carbene transformations,[11,12] did not cause a significant change in hydroboration regioselectivities with either styrene or indene. The identity of the active catalyst is under investigation.

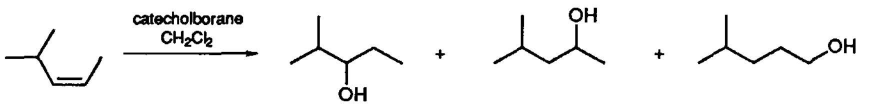
Hydroboration–oxidation of *cis*-4-methylpent-2-ene catalysed by $Rh_2(OAc)_4$ produced 4-methylpentan-2-ol and 2-methylpentan-3-ol but mainly 4-methylpentan-1-ol [reaction (2) > 88% conversion]; with 2-methylpent-2-ene the same product mixture was produced, although with different relative product yields, suggesting the propensity of these alkenes to isomerize under the reaction conditions. A similar complex distribution of products was obtained from allylbenzene. In addition, where *cis*-stilbene was employed, only *trans*-stilbene was isolated, and *trans*-stilbene did not undergo hydroboration. These results, coupled with our earlier discovery of $Rh_2(pfb)_4{\cdot}Et_3SiH$ catalysed olefin isomerization,[7] suggested that a rhodium hydride species might be the cause of olefin isomerization. Accordingly, treatment at 80 °C of neat allylbenzene with catalytic amounts of $Rh_2(OAc)_4$ (1.0 mol %) and catecholborane (3.0 mol %) resulted in its complete isomerization to (*Z*)- and (*E*)-1-phenylprop-1-ene [reaction (3), *Z*:*E* = 19:81 at 22 h]; neither $Rh_2(OAc)_4$ nor catecholborane alone caused this isomerization.



(3)

Dirhodium(II) catalysed hydroboration of alkynes is also effective. Treatment of phenylacetylene in dichloromethane with 1.0 equiv. of catecholborane at 25 °C for 2 h in the presence of 2.0 mol % $Rh_2(OAc)_4$ produced, after addition of I_2 (1.2 equiv.) in ether,[13] (*E*)-1-iodo-2-phenylethene in 71% isolated yield. The exclusive formation of the *E*-isomer suggests that rhodium(II)-catalysed hydroboration takes place by *cis*-addition, like its uncatalysed counterpart, but unlike dirhodium(II) catalysed hydrosilylation.[6]

Efforts are being undertaken to expand upon catalytic olefin isomerizations and to determine the applicability of



(2)

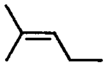
	$Rh_2(OAc)_4$	18%	39%	43%
	$Rh_2(pfb)_4$	11%	40%	49%
	$Rh_2(cap)_4$	9%	38%	53%
	$Rh_2(OAc)_4$	70%	9%	21%

Table 1 Hydroboration–oxidation of representative alkenes with catecholborane catalysed by dirhodium(II) tetraacetate and by $(Ph_3P)_3RhCl$

Alkene	Catalyst[a]	Alcohol	Regioselectivity/ stereoselectivity	Yield (%)[b]
Bicyclo[2.2.1]-hept-2-ene	$Rh_2(OAc)_4$	bicyclo[2.2.1]-heptan-2-ol	*exo*/*endo* = 99	80
Bicyclo[2.2.2]-oct-2-ene	$Rh_2(OAc)_4$	bicyclo[2.2.2]-octan-2-ol		45
Styrene	$Rh_2(OAc)_4$[c]	phenylethanol	2-/1- = 13–19	60
	$(Ph_3P)_3RhCl$[d,e]	phenylethanol	2-/1- = 0.02	80
Indene	$Ph_2(OAc)_4$[f]	indanol	2-/1- = 0.43	45
	$(Ph_3P)_3RhCl$[d]	indanol	2-/1- = 1.7	75
α-Methylstyrene	$Rh_2(OAc)_4$[g]	2-phenylpropan-l-ol		78
	$(Ph_3P)_3RhCl$	2-phenylpropan-l-ol		66
Oct-1-ene	$Rh_2(cap)_4$	octan-1-ol		60

[a] With dirhodium(II) compounds: reactions performed by addition of catecholborane in CH_2Cl_2 to the alkene and catalyst in refluxing CH_2Cl_2; 0.5 mol % catalyst. Neither product yield nor selectivity was dependent on the mode of addition. $(Ph_3P)_3RhCl$: reactions performed at room temperature in THF; 1.0 mol % catalyst. [b] Isolated product yield; less than 10% unreacted alkene. [c] With $Rh_2(pfb)_4$, pfb = perflurobutyrate, 2-/1-phenylethanol = 18; with $Rh_2(cap)_4$, cap = caprolactam, 2-/1-phenylethanol > 20. [d] Freshly prepared, m.p. 157 °C. [e] Reaction performed in CH_2Cl_2. With styrene in THF, 2-/1- = 0.05. [f] With $Rh_2(pfb)_4$, 2-/1-indanol = 0.45; with $Rh_2(cap)_4$, 2-/1-indanol = 0.53. [g] Identical results were obtained with $Rh_2(pfb)_4$ with and $Rh_2(cap)_4$.

chiral dirhodium(II) carboxamides for asymmetric hydroboration reactions. Preliminary results using dirhodium(II) tetrakis(4-*S*-benzyloxazolidinone)[14] for the hydroboration–oxidation of bicyclo[2.2.1]hept-2-ene, which formed the *exo*-alcohol in 56% yield with 28% enantiomeric excess, suggest the potential of these chiral catalysts.

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