Alcohol Synthesis

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High-Yielding Tandem Hydroformylation/Hydrogenation of a Terminal Olefin to Produce a Linear Alcohol Using a Rh/Ru Dual Catalyst System**

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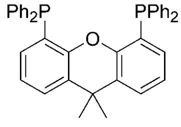
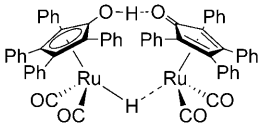
Linear 1-alkanols (*n*-alcohols) are widely used in industry as precursors of detergents and plasticizers.[1] Direct and selective conversion of a terminal olefin into an *n*-alcohol by regioselective hydration is considered an ideal process, and it is referred to as one of the "ten challenges for catalysis".[2] In reality, current industrial production of *n*-alcohols mostly employs a two-step process consisting of hydroformylation of terminal olefins, purification of *n*-aldehydes, and then hydrogenation of *n*-aldehydes to *n*-alcohols. A one-pot tandem hydroformylation/hydrogenation reaction would be an attractive alternative for *n*-alcohol production.[3] A one-pot process would be advantageous over the two-step process in the following way: 1) a one-pot process simplifies the process operation, and 2) syngas (a mixture of H_2 and CO) can be directly used for hydrogenation instead of using hydrogen purified from syngas via membrane separation.[4] Therefore, there have been many reports on the tandem hydroformylation/hydrogenation for direct synthesis of alcohols with alkylphosphine ligands using metal catalysts, such as Co,[5] Rh,[6] Ru,[7] and Pd,[8]. Although these tandem systems gave a mixture of *n*- and *i*-alcohols in good yields (mostly $>90\%$), a significant amount of alkane was often given. The most problematic issue is the low *normal/iso* selectivities ($n/i < 8$) in the hydroformylation step, causing a low *n*-alcohol yield (up to 81%). Recently, a supramolecular catalyst system containing Rh and an acyl guanidine-tethered triphenylphosphine ligand was reported as an effective catalyst for the one-pot conversion of olefins into the corresponding homologated linear alcohols in up to 72% yield.[9] Earlier this year a Cole-Hamilton and co-workers proposed a new strategy wherein two ligands were mixed for Rh-catalyzed hydroformylation/hydrogenation in a one-pot process to provide linear alcohols in up to 87% yield.[6f] While these systems depend on one single metal catalyst to perform the two different reactions, we became interested in the admixture of two catalysts, each of which operates one reaction with high efficiency without disturbing the other reaction.[10] Herein, we report a high-yielding synthesis of *n*-alcohol ($>90\%$) by the reaction of a terminal olefin with syngas using Rh/xantphos[11] and Shvo's catalyst[12] together in one pot.



xantphos



Shvo's catalyst (**1**)

For the linear-selective hydroformylation, we selected an Rh/xantphos catalyst.[11] Xantphos is known to provide the excellent levels of linear selectivity in hydroformylation of terminal olefins and is a triarylphosphine ligand, which is stable in the presence of the generated alcohols. For aldehyde-selective hydrogenation over the coexisting olefins, we selected a ruthenium-based ligand–metal bifunctional catalysts. Such a catalyst converts dihydrogen into two nonequivalent hydrogen atoms; one is protic and the other is hydridic.[13] Both of the hydrogen atoms simultaneously interact with a substrate via a polar transition state in an outer-sphere mechanism. As a result, the hydrogenation of a polar double bond predominates over that of a C=C bond.

Among the Ru catalysts we examined, the use of Shvo's complex **1** gave the best result. Details of the Ru catalysts screening are summarized in Table 1. Under an atmosphere of H_2/CO (1/1, 2.0 MPa), 1-decene was heated at 160°C for 1 hour in the presence of Ru catalysts **1**–**5** and Rh/xantphos. By using Shvo's complex **1**, 1-undecanol (*n*-alcohol) was obtained in 84.9% yield (entry 1). For other Ru catalysts we examined, the use of additional base was required. When Ru complex **2** bearing an amino-Cp ring[14] or a mixture of Cp*Ru complex **3** and $Ph_2PCH_2CH_2NH_2$ (**6**)[15] was used, the formation of byproducts became problematic because of the slow hydrogenation of aldehydes (entries 2 and 3). Significant isomerization of 1-decene into internal olefins were detected with (*p*-cymene)Ru catalyst **4** (entry 4)[16] or with hexacoordinate $RuCl_2$ complex **5**[17] (entry 5).

After optimization of the reaction conditions, the yield of *n*-alcohol was elevated up to 90.1%, which is the highest among reported values to date for the one-pot process. A significant solvent effect on the yield was detected. The use of less-polar aprotic solvents such as toluene and THF resulted in the lower yields of *n*-alcohol with an increase of dodecyl formate (compare entry 1 with entries 6 and 7). In contrast, a slight improvement in the yield was achieved in polar aprotic solvents with a suppression of dodecyl formate (entries 8 and

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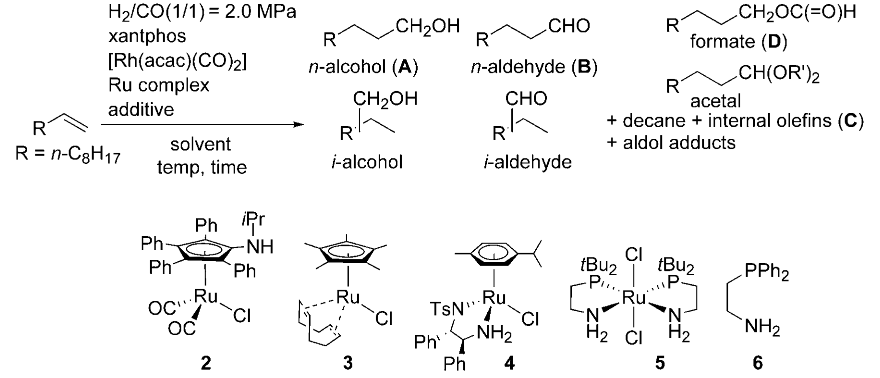
Table 1: Catalyst optimization.[a]



Entry	Ru cat.	Solvent	T [°C]	t [h]	Conv. [%]	Yield [%][b]			
						A (*n*/*i*)	**B** (*n*/*i*)	**C**	**D**
1	**1**	*i*PrOH	160	1	100	84.9 (17)	0.9 (2)	1.7	1.2
2[c]	**2**[d]	*i*PrOH	160	1	100	63.5 (23)	14.0 (9)	2.5	3.3
3[e]	**3** + **6**[d]	*i*PrOH	160	1	100	37.0 (19)	41.0 (0)	2.7	2.0
4[f]	**4**[d]	*i*PrOH	160	1	100	5.4 (–)	64.0 (13)	26.0	0.4
5[g]	**5**[d]	*i*PrOH	160	1	100	59.1 (37)	7.2 (12)	11.0	0.5
6	**1**	toluene	160	1	100	80.1 (20)	2.7 (8)	3.2	9.6
7	**1**	THF	160	1	100	63.5 (14)	4.3 (7)	8.6	11.0
8	**1**	DMF	160	1	100	88.2 (22)	0.6 (1)	3.8	3.5
9	**1**	DMA	160	1	100	89.6 (22)	1.0 (2)	4.9	1.2
10	**1**	DMA	80	1	52.1	24.5 (> 50)	16.7 (> 50)	4.0	0.0
11	**1**	DMA	80	48	100	89.3 (36)	1.5 (4)	2.0	0.3
12	**1**	DMA	120	1	100	49.7 (35)	34.3 (41)	5.4	0.3
13	**1**	DMA	120	12.5	100	90.1 (22)	1.0 (1)	1.9	1.1

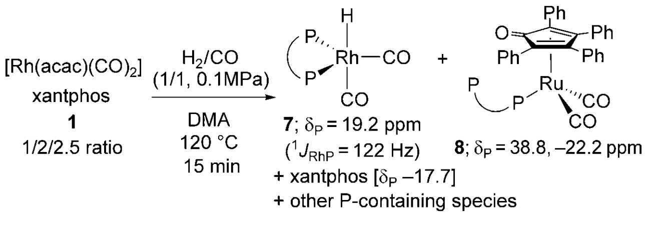
[a] Reaction condition: Ru complex (2.5 mol% of Ru), Rh complex (1 mol%), xantphos (2 mol%), solvent (4 mL). [b] Yields were determined by GC analysis using dodecane as an internal standard after correction for purity of the substrate (96.7% 1-decene + 1.0% decane + 2.3% internal olefins, mainly (*Z*)- and (*E*)-2-decene), [1-decene]/[dodecane] = 2. All values are an average of two independent reactions. Byproducts lower than 4% yield are omitted from this table. Details are reported in the Supporting Information. [c] 4.7% of acetal was detected. [d] *t*BuOK (1 mol%) was added. [e] 4.3% of aldol adduct was detected. [f] The yield of obtained *i*-alcohol was too low to determine the *n*/*i* ratio. [g] 6.4% of acetal was detected. acac = acetylacetonate, DMA = *N*,*N*-dimethylacetamide, DMF = *N*,*N*-dimethylformamide, THF = tetrahydrofuran, Ts = 4-toluenesulfonyl.

9). Reaction temperature was also essential for the product distribution. At 80°C, both hydroformylation and hydrogenation steps were very slow (entries 10 and 11).[11] At 120°C in 1 hour, 1-decene was completely consumed but the main product was the aldehyde with a high *n*/*i* ratio (entry 12). Finally, prolonged reaction time at 120°C gave *n*-alcohol in 90.1% yield (entry 13).

Although the active species for catalysis is not yet fully characterized, the following studies suggest that the hydroformylation is catalyzed by Rh/xantphos and the hydrogenation is operated by Ru catalyst **1** with/without xantphos. When an admixture of [Rh(acac)(CO)$_2$], xantphos, and complex **1** in a ratio of 1:2:2.5 was heated at 120°C for 15 minutes under a syngas atmosphere, several phosphorus-containing species were detected including [(xantphos)Rh(H)(CO)$_2$] (**7**), [(κ^1-xantphos)Ru(Cp′)(CO)$_2$] (**8**) (Cp′ = tetraphenylcyclopentadienone), free xantphos, and other minor species (Scheme 1).[18] Considering that all examples offered high *n*/*i* ratios (> 15) of the resulting alcohols, the step responsible for the high linear selectivity is hydroformylation catalyzed by **7**.[11] Notably, all catalysts **1**–**5** showed catalytic activity in the coexistence of CO, although the catalytic activity was lower than the originally reported values under pure H$_2$. The deceleration of hydrogenation may be attributed to the reversible ligation of either CO or xantphos to the Ru catalyst, which lowers the concentration of the active Ru species available for hydrogenation.

The following features were further elucidated by control experiments described in the Supporting Information. Formation of decane could be attributed to the direct hydrogenation of 1-decene by both Rh and Ru hydride species.[19] The Ru catalyst is responsible for the olefin isomerization because the isomerization product increased at a higher Ru/Rh ratio. Undecyl formate formed by insertion of CO into RuOC$_{11}$H$_{23}$ bond of the alkoxide intermediate during the hydrogenation of the aldehyde by **1**.

In conclusion, a new dual catalyst system—a combination of xantphos/[Rh(acac)(CO)$_2$] and Shvo's catalyst—has accomplished a highly efficient production of *n*-alcohol by a simple one-pot process utilizing syngas for hydrogenation. Under the best conditions, 1-undecanol was produced from 1-decene in 90.1% yield, which is the highest yield to date. The best yield achieved with **1** is a result of the following factors: 1) the highest hydrogenation activity of **1** under CO, 2) well-suited Rh/L/Ru ratio, 3) the absence of any additional base, and 4) the best solvent (DMA).



Scheme 1. Expected species in the present tandem catalyst system.

Experimental Section

Standard procedure of tandem hydroformylation/hydrogenation. [Rh(acac)(CO)$_2$] (5.2 mg, 20 μmol), xantphos (23.1 mg, 40.0 μmol), and DMA (1.0 mL) were added to a 50 mL stainless autoclave under an argon atmosphere. The autoclave was flushed with H_2/CO (1/1) gas, and the mixture was stirred at RT for a few minutes. A solution of **1** in DMA (25 µmol, 50 µmol of Ru, 3.0 mL) was added to the reaction mixture followed by a mixture of substrate 1-decene and dodecane ([1-decene]/[dodecane] = 2.00; 550 µL, ca. 450 mg, ca. 2 mmol). Before and after the addition of substrate 1-decene and dodecane, the weight of the syringe was recorded for the yield calculation. The autoclave was pressurized by H_2/CO (1/1, 2.0 MPa), and stirred at the required temperature for the desired time. After the autoclave was cooled to RT and depressurized, the crude product was diluted with toluene and was analyzed by GC analysis. All yields were calculated from the area ratio of each product vs. the internal standard (dodecane). Yields were also compensated for with respect to the purity of starting 1-decene (96.7% 1-decene, 1.0% decane, 2.3% internal olefins) as judged by GC analysis. All the results are summarized in Table S1 in the Supporting Information, where more information about byproducts can be found.

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