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A Heterobimetallic Rhodium(I)−Ruthenium(II) Catalyst for the Oppenauer-Type Oxidation of Primary and Secondary Alcohols under Mild Conditions

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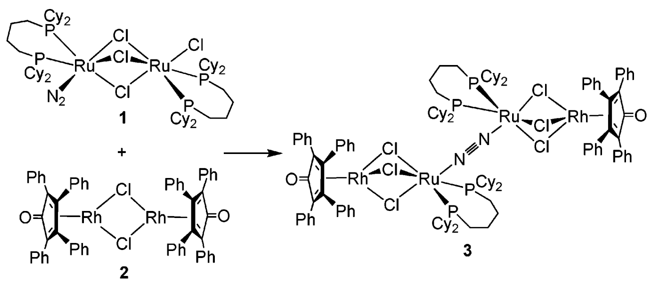
Summary: A heterobimetallic complex, in which a $RuCl_2(acetone)(PPh_3)_2$ fragment is connected via three chloro bridges to a (η^4-C_4Ph_4CO)RhCl fragment, has been identified as a potent catalyst precursor for the Oppenauer-type oxidation of alcohols. With 0.1−0.5 mol % of this complex and K_2CO_3 as the cocatalyst, it is possible to oxidize secondary and primary alcohols at room temperature using acetone as the solvent and oxidation agent.

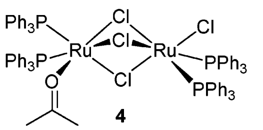
The Oppenauer-type oxidation of alcohols using ketones such as acetone as the solvent *and* oxidation agent is very appealing, from both an environmental and economical point of view. A number of transition metal complexes are known to catalyze this reaction with the interest focused on Ru(II)-phosphine[1,2] and Cp*Ir(III)[3] complexes.[4] With the simple triphenylphosphine complex $[RuCl_2(PPh_3)_3]$, for example, it is possible to oxidize a number of secondary alcohols with turnover numbers exceeding 500 using acetone as the oxidation agent and K_2CO_3 as the cocatalyst.[1] Most of the ruthenium-based catalysts described so far, however, require elevated temperatures[5] and do not work with primary alcohols as substrates.

Scheme 1



Recently, we have shown that the heterometallic Ru(II)−Rh(I) complex **3** can be obtained in a metathesis reaction of the chloro-bridged complexes **1** and **2** (Scheme 1).[6] Complex **3** is a very active and robust catalyst for atom transfer radical additions of CCl_4 to olefins. Under catalytic conditions, the labile dinitrogen ligand is most likely cleaved off to give an electronically unsaturated (dcypb)$RuCl_2$ complex, which is stabilized by a sterically demanding (η^4-C_4Ph_4CO)RhCl fragment. In continuation of these studies, we have investigated whether complex **3** or structurally related complexes can be used as catalyst precursors for Oppenauer-type oxidations.

In chloro bridge metathesis reactions, the ruthenium phosphine complexes **4**[2c] and **5**[7] display a reactivity that is very similar to that of **1**.[8] It thus appeared likely that reactions with the rhodium cyclopentadienone complex **2** would give heterometallic complexes similar to **3**. To increase the structural diversity, we have also included the new rhodium complex **6** in our catalyst screening.[9] Complex **6** has two sterically demanding naphthyl groups attached to the π-ligand.



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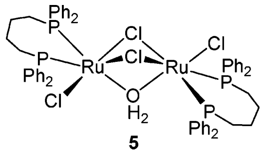

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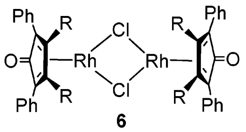

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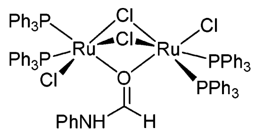
R = naphthyl



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As a benchmark reaction for the catalyst screening, we have employed the oxidation of 1-phenylethanol using acetone as the solvent and K_2CO_3 as the base. Deliberately, the screening was performed at room

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(5) For a Ru-phosphine complex that can be employed at room temperature see ref 2b.

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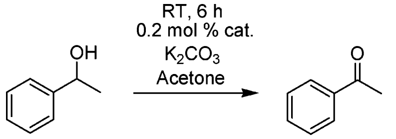
(9) Complex **6** was prepared analogously to the known complex **2** by ligand exchange of $[Rh(C_2H_4)Cl]_2$ with the corresponding cyclopentadienone. See: Bailey, N. A.; Jassal, V. S.; Vefghi, R.; White, C. *J. Chem. Soc., Dalton Trans.* **1987**, 2815−2822.

10.1021/om049671m CCC: \$27.50

Table 1. Catalytic Oxidation of 1-Phenylethanol to Acetophenone[a]



entry	Ru complex	Rh complex	conv (%)
1	**1**	**2**	8
2	**1**	**6**	6
3	**4**	**2**	70
4	**4**	**6**	30
5	**5**	**2**	30
6	**5**	**6**	36
7	**4**[b]		<1
8		**2**[b]	1
9	**7**		<1
10	$[RuCl_2(PPh_3)_3]$		2
11	**4**	$[Cp^*RhCl_2]_2$	45

[a] Conditions: a solution of the Ru complex (4.0 μmol) and/or the Rh complex (4.0 μmol) in acetone/CH_2Cl_2 (1.0 mL, 2:8) was added to a mixture of K_2CO_3 (4.0 mmol), 1-phenylethanol (4.0 mmol), and acetone (20 mL). After stirring the mixture for 6 h at RT, the conversion was determined by GC. [b] The complexes were added as a solid directly to the reaction mixture.

temperature to identify catalysts that are effective under mild conditions. The heterometallic catalyst precursors were prepared in situ by mixing equimolar amounts of the ruthenium phosphine complexes **1**, **4**, and **5** with the rhodium complexes **2** and **6**.[10] The conversion after 6 h is listed in Table 1. Catalysts obtained from ruthenium complexes with the ligands PPh_3 (**4**) and diphenylphosphinobutane (**5**) (entries 3–6) displayed higher activities than those obtained from the cyclohexylphosphine complex **1** (entry 1 and 2). The highest conversion was found for the combination of the ruthenium complex **4** with the rhodium complex **2**. Control experiments with the pure homodimeric complexes gave only very low conversions (entries 7 and 8). Complex **4** displays a poor solubility in acetone. To make sure that the low conversion with catalyst **4** was not a result of its limited solubility, we have also employed the formanilide-bridged complex **7**[11] (entry 9). Similar to **4**, complex **7** can be regarded as a solvent-stabilized form of a dimeric "$RuCl_2(PPh_3)_2$". Its reactivity is comparable to that of **4**, but its solubility in organic solvents is much higher.[8] Less than 1% of acetophenone, however, was detected after 6 h with this catalyst precursor, indicating that the "$RuCl_2(PPh_3)_2$" fragment alone is not sufficient for an effective catalytic transformation. A comparison of the results obtained for mixtures of **4** with **2** and **4** with **6** (entries 3 and 4) shows that the introduction of a sterically demanding naphthyl group on the cyclopentadienone ligand is detrimental for catalytic activity.

To put the results into perspective, we have investigated the benchmark reaction with the known catalyst $[RuCl_2(PPh_3)_3]$ (entry 10). Although this complex is a good catalyst at elevated temperatures, it gives a very poor conversion at room temperature. For comparison, we have also investigated the reactivity of the Rh(III)–Ru(II) complex $[Cp^*Rh(\mu\text{-}Cl)_3RuCl(PPh_3)_2]$ (entry 11). This heterobimetallic complex can be obtained from **4** and $[Cp^*RhCl_2]_2$ and has previously been used by our group for Oppenauer-type oxidations (2-butanone, 80 °C).[2c] Its activity is clearly higher than that of $[RuCl_2(PPh_3)_3]$ but still inferior to what is found for the combination of complexes **4** and **2**.

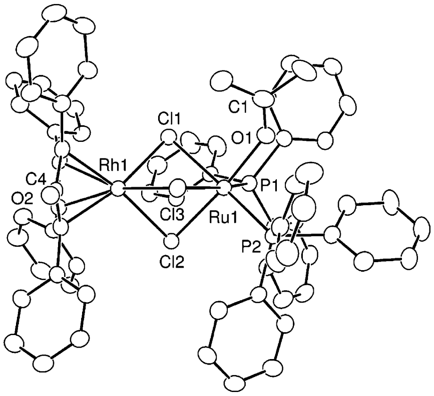


Figure 1. Graphic representation of the molecular structure of **8** in the crystal. The solvent molecules and the hydrogen atoms are not shown for clarity. Selected bond length (Å) and angles (deg): Rh1–Cl1 = 2.4700(14), Rh1–Cl2 = 2.4698(14), Rh1–Cl3 = 2.5275(14), Ru1–Cl1 = 2.4588(12), Ru1–Cl2 = 2.4013(16), Ru1–Cl3 = 2.4994(15), Ru1–P1 = 2.3314(15), Ru1–P2 = 2.3303(13), Ru1–O1 = 2.114(4); P1–Ru1–P2 = 104.15(5), P1–Ru1–O1 = 88.88(11), P1–Ru1–Cl1 = 85.93(5).

To identify the catalyst precursor that is formed after mixing complexes **4** and **2**, we have carried out this reaction on a larger scale.[12] In situ ^{31}P NMR spectroscopic investigations indicated that a single complex, **8**, was obtained in >95% yield. After isolation, this complex was crystallized from CH_2Cl_2/acetone/pentane and analyzed by single-crystal X-ray analysis.[13]

The overall structure of **8** is similar to what was found for **3**: a $RuCl_2L_2$ fragment is connected via three chloro bridges to a (η^4-C_4Ph_4CO)RhCl fragment (Figure 1). The remaining coordination site at the ruthenium complex, however, is not occupied by a bridging dinitrogen ligand but by an acetone ligand. The resulting octahedral Ru center is slightly distorted as a result of the two sterically demanding phosphine ligands. The rhodium exhibits a five-coordinated, electronically saturated configuration. This is in agreement with the known tendency of cyclopentadienone rhodium complexes to form piano-stool type complexes.[14]

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[10] Chloro bridge metathesis reactions are generally very fast. See: Severin, K. *Chem. Eur. J.* **2002**, *8*, 1514–1518, and references therein.

[11] Kondo, T.; Kotachi, S.; Tsuji, Y.; Qatanabe, Y.; Misudo. *Organometallics* **1997**, *16*, 2562–2570.

[12] A solution of complex **4** (148 mg, 98 μmol) and complex **2** (102 mg, 98 μmol) in CH_2Cl_2 (8 mL) was stirred for 30 min. After evaporation of the solvent under reduced pressure, the product was washed with pentane and dried under vacuum (isolated yield: 92%). Orange crystals were obtained by slow diffusion of pentane into a solution of **8** in dichloromethane and acetone. IR: ν (cm^{-1}) 1643 (CO). ^1H NMR (400 MHz, acetone-d_6): δ (ppm) 7.1–7.9 (m, 50 H, phenyl). ^{13}C NMR (101 MHz, acetone-d_6): δ (ppm) 67.37 [d, $^1J_{RhC}$ = 12 Hz, *C*-Ph], 93.97 [d, $^1J_{RhC}$ = 12 Hz, *C*-Ph], 127.29–136.24 (m, Ph), 166.72 (CO). ^{31}P NMR (162 MHz, acetone-d_6): δ (ppm) 46.84 (s). Anal. calcd for $C_{68}H_{56}Cl_3O_2P_2RhRu$: C 63.93, H 4.42. Found: C 63.66, H 4.32.

[13] Crystal data for complex **7**: $C_{68}H_{56}Cl_3O_2P_2RhRu\cdot C_3H_6O\cdot 0.5CH_2Cl_2$, M = 1377.94, monoclinic, a = 13.620(4) Å, b = 21.2001(15) Å, c = 22.096(6) Å, β = 101.74(2)°, V = 6246(3) Å^3, T = 140(2) K, space group $P2_1/n$ (no. 14), Z = 4, μ(Mo Kα) = 0.776 mm^{-1}, 38 599 reflections collected, 10 901 independent reflections, R_{int} = 0.0536, R_1 [$I > 2\sigma(I)$] = 0.0477, wR_2 (all data) = 0.1389.

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Table 2. Oxidation of Secondary Alcohols to Ketones Catalyzed by 8[a]

entry	substrate	substrate/catalyst	time (h)	conv (%)
1	1-phenylethanol	200:1	6	94
		1000:1	24	78
		1000:1	24	55[b]
2	1-indanol	200:1	6	>99
		1000:1	24	96
3	cylopentanol	200:1	6	67
		1000:1	1	64
4	cyclohexanol	200:1	24	77
		1000:1	24	50
5	benzhydrol	200:1	24	97
		1000:1	24	47
6	cycloheptanol	200:1	24	>99
		1000:1	24	51
7	2-octanol	200:1	24	77
		1000:1	24	77

[a] Conditions: a solution of complex **8** (2.0 μmol or 0.4 μmol) in acetone/benzene (0.2 mL, 1:1) was added to a mixture of K_2CO_3 (0.4 mmol), the secondary alcohol (0.4 mmol), and acetone (2 mL). After stirring the mixture for the given time at RT, the conversion was determined by GC. [b] 0.4 mmol K_2CO_3 was employed.

Table 3. Oxidation of Primary Alcohols to Aldehydes Catalyzed by 8[a]

entry	substrate	conv (%)
1	benzyl alcohol	54
2	4-methylbenzyl alcohol	74
3	4-methoxybenzyl alcohol	90
4	3,5-methoxybenzyl alcohol	60
5	3,4,5-methoxybenzyl alcohol	80
6	4-chlorobenzyl alcohol	20
7	1-octanol	10

[a] Conditions: a solution of complex **8** (2.0 μmol) in acetone/benzene (0.2 mL, 1:1) was added to a mixture of K_2CO_3 (0.4 mmol), the primary alcohol (0.4 mmol), and acetone (10 mL). After stirring the mixture for 24 h at RT, the conversion was determined by GC.

The scope of the new heterobimetallic Rh(I)−Ru(II) catalyst precursor **7** was investigated in reactions with a number of secondary (Table 2) and primary alcohols (Table 3). Using a substrate:catalyst ratio of 200:1, aromatic and aliphatic secondary alcohols were oxidized at room temperature to the corresponding ketones with good to excellent conversions. Stoichiometric amounts of K_2CO_3 were employed since reactions with catalytic amounts of K_2CO_3 (10 mol %) gave slightly lower conversions (entry 1c). NEt_3 was found unsuited for catalytic oxidations with complex **8**. Experiments with only 0.1 mol % catalyst demonstrate that turnover numbers of more than 500 can be achieved for several substrates (Table 2).

Primary alcohols can likewise be oxidized to the corresponding aldehydes (Table 3). Using 0.5 mol % of complex **8**, 54% of benzaldehyde was obtained from benzyl alcohol after 24 h. Typical side products such as the aldol condensation product $PhCH{=}CHCOCH_3$ or the Tishchenko reaction product $PhCO_2CH_2Ph$ could not be observed by gas chromatography. In agreement with previous reports,[3] electron-donating groups on the aromatic ring increased the conversion (entries 2−5), whereas electron-withdrawing groups reduced the conversion (entry 6). As expected, aliphatic primary alcohols such as 1-octanol (entry 7) gave only low conversions as a results of their unfavorable redox potential with respect to the acetone/2-propanol pair.[15]

A plausible coordination site for the substrate is the electronically unsaturated ruthenium center, which is generated after liberation of the labile acetone ligand. The base K_2CO_3 is expected to facilitate the formation of a metal-alkoxide complex,[16] which could then undergo β-hydride elimination to give a hydride complex. It is also conceivable that the (η^4-C_4Ph_4CO)Rh fragment participates actively in catalysis since it has been described for (η^4-C_4Ph_4CO)Ru complexes that the carbonyl group of the π-ligand is able to accept hydrogen.[17] Attempts to identify intermediates of the catalytic cycle by NMR spectroscopy were so far not successful. It is important to point out, however, that both the rhodium as well as the ruthenium fragment are essential constituents of the new catalyst. This is evidenced by the fact that (a) the homobimetallic complexes **2**, **4**, and **7** are not active at all and (b) the activity of the heterobimetallic catalyst precursors is modulated by variations of the co-ligands on ruthenium *and* on rhodium (Table 1). Our system thus represents one of the still rare examples of a successful application of a heterobimetallic complex in homogeneous catalysis.[18]

Supporting Information Available: Crystallographic data in CIF format of complex **7**. This material is available free of charge on the Internet at http://pubs.acs.org.

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(16) For our experiments, stoichiometric amounts of K_2CO_3 were employed. Reactions with catalytic amounts of K_2CO_3 (10 mol %) gave nearly identical conversions. NEt_3 was found unsuited for catalytic oxidations with complex **7**.

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