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Tetrahedron Letters 46 (2005) 1031–1034

Tetrahedron Letters

Ruthenium-catalyzed generation of hydrogen from *iso*-propanol

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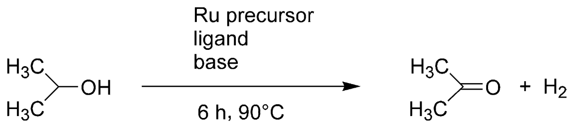
Received 4 November 2004; revised 29 November 2004; accepted 30 November 2004

Abstract—The dehydrogenation reaction of *iso*-propanol has been investigated in the absence of a hydrogen acceptor. Among different transition metals tested various ruthenium precursors in the presence of phosphine ligands proved to be active catalysts. Best results (turnover frequencies up to 155 h^{-1} after 2 h) were achieved with $RuCl_3 \cdot xH_2O$ and 2-di-*tert*-butyl-phosphinyl-1-phenyl-1*H*-pyrrole **4** at low temperature (90 °C).

In recent years hydrogen has become an increasingly attractive feedstock for energy generation.[1] This is in part a consequence of the progressive depletion of fossil fuel reserves and the continuously increasing energy demands. In addition, there exists a strong necessity to reduce the emission of green house gases. Apart from water cleavage,[2] renewable resources such as biomass or its fermentation products, for example, alcohols are promising feedstocks for the generation of hydrogen. However, efficient hydrogen production from renewable resources remains difficult and improved technologies for generating hydrogen at higher reaction rates are required. In this respect the development of new catalysts and their understanding will be a key issue. With regard to catalysts, improvements have been achieved especially in the field of heterogeneous catalysis.[3] For example Davda et al. reported on the generation of hydrogen from sugars and alcohols applying a Pt/Al_2O_3 catalyst at 500 K.[4]

Interestingly, often dehydrogenation reactions in the presence of hydrogen acceptors, for example, transfer-hydrogenations, are performed with homogeneous catalysts due to their higher activity and selectivity compared with heterogeneous catalysts.[5] Nevertheless, the use of soluble transition metal complexes for hydrogen generation has been largely neglected. Hence, in the last three decades only very few molecularly defined catalysts have been reported that allow the production of hydrogen.[6–8] For example Dobson and Robinson and more recently Hulshof and co-workers investigated a catalytic system consisting of $[Ru(O_2CCF_3)_2(CO)(PPh_3)_2]$ and an excess of trifluoroacetic acid.[6] More successfully were the results of Morton and Cole-Hamilton with catalysts of the type $[Ru(H_2)(X_2)(PPh_3)_3]$ ($X_2 = N_2, H_2$).[7] Here turnover frequencies (TOF) of 150 h^{-1} for EtOH, 330 h^{-1} for *iso*-propanol and up to >500 h^{-1} for glycol and *n*-butanol were achieved at 150 °C in the presence of NaOH. In addition, Saito and Shinoda investigated the generation of hydrogen from methanol with several ruthenium precursors and phosphine ligands in the presence of sodium methanolate or acetate. However, the observed TOF was very low (<1.5 h^{-1}).[8]

Based on our experience in the synthesis of new carbene and phosphine ligands and their organometallic complexes for homogeneous catalysis,[9] we became interested in the generation of hydrogen under milder conditions (<100 °C) and the development of more active catalysts for this reaction. To the best of our knowledge there is no catalyst known which is capable to generate hydrogen from renewable feedstocks at sufficient rate (TOF > 100 h^{-1}) at lower temperature (<100 °C). Here, we report for the first time our results towards this goal. As a starting point and model system for renewable alcohols *iso*-propanol was chosen as substrate (Scheme 1) due to easy product analysis and less side-reactions



Scheme 1. Standard reaction conditions: 315 ppm catalyst, 5.0 mL *i*-PrOH, 0.5 mL internal standard (hexadecane), 0.8 M base.

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doi:10.1016/j.tetlet.2004.11.159

compared to other alcohols. In general, the catalytic reactions were performed at 90 °C in the presence of base (NaOH or Na). In all cases reported here only hydrogen and argon (from the inert gas atmosphere) were detected as gaseous products.

In order to identify promising metal precursors a first screening of various metal complexes with different oxidation states has been done. Several ruthenium (oxidation states +2, +3), rhodium (+1, +3), palladium (0, +2) and nickel (+2) complexes were tested. Although almost all of them showed some activity in the model reaction, for more detailed investigations Ru complexes with oxidation states of +2 and +3 have been chosen, since they showed the best activity. In general, besides hydrogen and acetone also minor amounts (1–6%) of aldol condensation products partly followed by hydrogenation (Guerbet reaction[11,12]) could be detected. Thus, a small part of the evolved hydrogen is consumed by this side-reaction.

For comparison we also tested Cole-Hamilton's catalyst $[Ru(H_4)(PPh_3)_3]$[7] (Table 1, entries 1 and 2), which belongs to the most active catalysts published for the dehydrogenation of alcohols in the absence of a hydrogen acceptor. However, the activity of this catalyst diminishes to approximately 15% by decreasing the temperature from 150 °C to 90 °C. Hence, a turnover frequency of about 50 h^{-1} was obtained after 2 h. Applying $RuCl_3 \cdot xH_2O$ without a ligand or $RuBr_3 \cdot xH_2O$, $Ru(acac)_3 \cdot xH_2O$ and $[RuCl_2(COD)]$ with two equivalents of PCy_3 even lower activity is observed (Table 1, entries 3, 4, 6, 7). However, using $RuCl_3 \cdot xH_2O$ or $[RuCl_2(p\text{-cymene})]_2$ in the presence of two equivalents of PCy_3 an increase in the activity (TOF after 2 h: 78 and 94 h^{-1}, respectively) is seen (Table 1, entries 5 and 8).

On the basis of these promising results, the influence of several reaction parameters was investigated in more detail (Table 2). Due to the availability and easy handling $RuCl_3 \cdot xH_2O$ has been selected as the metal precursor for the following studies. Changing the ligand:ruthenium ratio from 2 to 4 and 8 causes a decrease of the catalytic activity (Table 2, entries 1 and 2). Further attempts were made concerning the base concentration. Without base hydrogen generation is slow (Table 2, entry 3). In between 0.1 and 0.8 mol L^{-1} NaOH (Table 2, entries 4–6) there is basically no change of reactivity, however at an NaOH concentration of 1.5 M a significantly lower TOF is obtained due to precipitation of ruthenium species (dark brown solid).

Table 2. Influence of reaction conditions with the catalyst system $RuCl_3 \cdot xH_2O/PCy_3$

Entry	P:Ru ratio	Base	Reaction time h	Hydrogen volume[a] mL	TOF[b] h^{-1}
1	4	0.8 M NaOH	2	26	28
			6	43	16
2	8	0.8 M NaOH	2	37	40
			6	67	24
3	2	—	2	10	11
4	2	0.1 M NaOH	2	79	86
			6	124	45
5	2	0.2 M NaOH	2	78	85
			6	130	47
6	2	0.5 M NaOH	2	70	76
			6	119	43
7	2	1.5 M NaOH[c]	2	31	34
			6	54	20

Standard reaction conditions: 315 ppm catalyst precursor $RuCl_3 \cdot xH_2O$, ligand PCy_3, 5.0 mL *i*-PrOH, 0.5 mL internal standard (hexadecane); 6 h 90 °C.[10]

[a] Measured by gas burette.

[b] Calculated concerning to values measured by gas burette.

[c] Brown precipitate is formed.

Next, the influence of different phosphine ligands was investigated (Table 3). While PPh_3, P^tBu_3 and 1,1′-bis(diphenylphosphino)-ferrocene (dppf) were less active (TOF approximately 53–66 h^{-1} after 2 h and 32–42 h^{-1}

Table 1. Performance of different catalysts for the dehydrogenation of *iso*-propanol

Entry	Ru-precursor	P:Ru ratio	Ligand	Base	Reaction time h	Hydrogen volume[a] mL	TOF[b] h^{-1}
1	$[Ru(H_4)(PPh_3)_3]$	—	—	NaOH	2	45	49
					6	74	27
2	$[Ru(H_4)(PPh_3)_3]$	—	—	Na	2	50	54
					6	89	32
3	$[RuCl_2(COD)]$	2	PCy_3	NaOH	2	33	36
					6	54	20
4	$RuCl_3 \cdot xH_2O$	—	—	NaOH	2	22	24
					6	54	20
5	$\mathbf{RuCl_3 \cdot xH_2O}$	**2**	$\mathbf{PCy_3}$	**NaOH**	**2**	**72**	**78**
					6	**148**	**54**
6	$RuBr_3 \cdot xH_2O$	2	PCy_3	NaOH	2	20	22
					6	39	14
7	$Ru(acac)_3 \cdot xH_2O$	2	PCy_3	NaOH	2	15	16
					6	30	11
8	$\mathbf{[RuCl_2(p\text{-cymene})]_2}$	**2**	$\mathbf{PCy_3}$	**NaOH**	**2**	**86**	**94**
					6	**120**	**43**

Standard reaction conditions: 315 ppm catalyst, 5.0 mL *i*-PrOH, 0.5 mL internal standard (hexadecane), 0.8 M base, 6 h 90 °C.[10]

[a] Measured by gas burette.

[b] Calculated concerning to values measured by gas burette.

Table 3. Screening of ligands for the dehydrogenation of *iso*-propanol with $RuCl_3{\cdot}xH_2O$ as precursor

Entry	Ligand	Base	Reaction time h	Hydrogen volume[a] mL	TOF[b] h^{-1}
1	PPh_3	NaOH	2	56	61
			6	106	38
2	PPh_3	Na	2	61	66
			6	117	42
3	PCy_3	Na	2	93	101
			6	157	57
4	PCy_2Ph	NaOH	2	69	75
			6	128	46
5	P^tBu_3	NaOH	2	49	53
			6	88	32
6	dppf	NaOH	2	51	55
			6	103	37
7	**BuPAd$_2$**	**NaOH**	**2**	**96**	**104**
	1		**6**	**152**	**55**
8	**2**	NaOH	2	6	7
9	**2**	Na	2	105	114
			6	169	61
10	**3**	NaOH	2	28	30
11	**3**	Na	2	110	120
			6	176	64
12	**4**	**Na**	**2**	**143**	**155**
			6	**216**	**78**

Standard reaction conditions: 315 ppm catalyst precursor $RuCl_3{\cdot}xH_2O$, ratio P:Ru = 2:1 (except for entry 6; P:Ru = 1:1), 5.0 mL *i*-PrOH, 0.5 mL internal standard (hexadecane), 0.8 M base; 6 h 90 °C.[10]

[a] Measured by gas burette.

[b] Calculated concerning to values measured by gas burette.

after 6 h) (Table 3, entries 1, 2, 5, 6), dicyclohexylphenylphosphine is as effective as tricyclohexylphosphine.

Best results with NaOH as the base were obtained with the recently at our institute developed BuPAd$_2$ **1**[13] and $RuCl_3{\cdot}xH_2O$ (TOF after 2 h: 104 h^{-1}; Table 3, entry 7). By application of sodium instead of NaOH as base a slight increase in activity of the system $RuCl_3{\cdot}xH_2O$/2 equiv PCy_3 is obtained (Table 3, entry 3). More significant effects were observed in case of the ligands **2** and **3** (Fig. 1; Table 3, entries 8–11).

Noteworthy, the Buchwald ligand **2**[14] as well as 2-dicyclohexylphosphinyl-1-phenyl-1*H*-pyrrole **3** and 2-di-*tert*-butylphosphinyl-1-phenyl-1*H*-pyrrole **4**[15] are not effective in the NaOH containing reactions, however they form active catalyst systems with $RuCl_3{\cdot}xH_2O$ if sodium is used as the base. These results seem to be mainly due to the different sensitivity of the ligands against water. While with NaOH as base water is generated by the reaction of NaOH and *iso*-propanol, applying sodium the generation of water is avoided. In addition, an increased concentration of NaO^iPr exhibits a stronger positive influence on the reactivity of catalysts containing **4** compared to PCy_3.

The highest turnover frequency after 2 h (TOF = 155 h^{-1}) is obtained in the presence of **4**. In general, the TOF values decrease for all catalytic systems after 6 h. This deactivation seems to correlate with the formation of aldol by-products. These are generated by the self-condensation of acetone. In agreement with this finding, addition of mesityloxide decreases the rate of hydrogen formation.

In conclusion, we have shown for the first time, that it is possible to generate hydrogen from *iso*-propanol below 100 °C with turnover frequencies >150 h^{-1}. Interestingly, adamantylphosphines and biarylphosphines, which have so far never applied for such reactions, give best results. Hence, these ligands might be also of interest for transfer hydrogenation reactions or dynamic kinetic resolution processes of chiral alcohols.[16]

Acknowledgements

This work has been supported by the State of Mecklenburg-Western Pommerania, the Arbeitsgemein schaft industrieller Forschungsvereinigungen 'Otto von Guericke' e. V. (AIF) and the Fonds der Chemischen Industrie (FCI). We thank Mrs. H. Baudisch, Mrs. A. Lehmann and Mrs. S. Buchholz (all IfOK) for their excellent analytical support.

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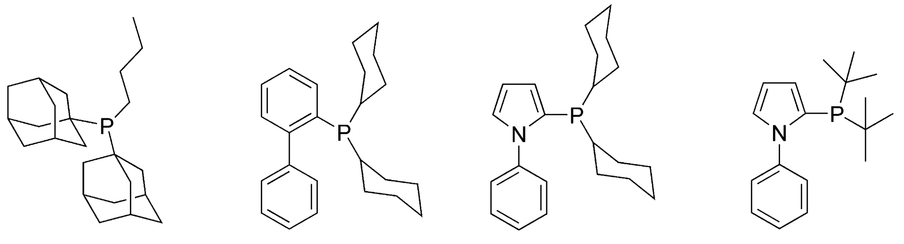

Di-adamantan-1-yl -butyl-phosphine BuPAd$_2$ **1**

Biphenyl-2-yl -dicyclohexyl -phosphine *Buchwald ligand* **2**

2-Dicyclohexyl-phosphinyl-1 -phenyl-1*H*-pyrrole **3**

2-Di-*tert*-butyl-phosphinyl-1-phenyl-1*H*-pyrrole **4**

Figure 1. Monodentate phosphine ligands applied in the dehydrogenation of *iso*-propanol.

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