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Tetrahedron
Tetrahedron 60 (2004) 1065–1072

Triruthenium dodecacarbonyl/triphenylphosphine catalyzed dehydrogenation of primary and secondary alcohols

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Received 17 July 2003; revised 4 November 2003; accepted 28 November 2003

Abstract—Dehydrogenation of alcohols into aldehydes and ketones by $Ru_3(CO)_{12}/PPh_3$ based homogeneous catalysis has been investigated as an alternative for the classical Oppenauer oxidation. Several catalytic systems have been screened in the Oppenauer-like oxidation of alcohols. A systematic study of various combinations of $Ru_3(CO)_{12}$, mono- and bidentate ligands and hydride acceptors was performed to enable dehydrogenation of primary alcohols to stop at the aldehyde stage. Among many H-acceptors screened, diphenylacetylene (tolane) proved the most suitable judged from its smooth reduction. Electron rich and deficient analogues of tolane have been synthesized and, based on competition experiments between these H-acceptors, a tentative catalytic cycle for the $Ru_3(CO)_{12}/PPh_3$-catalyzed dehydrogenations has been proposed.

1. Introduction

The ever-growing concern to develop more efficient key transformations in organic synthesis has shifted the focus to catalytic processes. Much effort has been expended on the development of novel transition metal complexes to catalyze the oxidation of alcohols to aldehydes and ketones by a variety of inexpensive and environmentally compatible oxidants such as hydrogen peroxide, molecular oxygen and to a lesser extent sodium hypochlorite.[1] Catalytic methods avoiding stoichiometric amounts of inorganic reagents offer environmental benefits. Here, we report a catalytic methodology for dehydrogenation of alcohols using $Ru_3(CO)_{12}/PPh_3$ as catalyst precursor. As H-acceptor tolane was needed resulting in a less than optimal atom economy.

2. Results and discussion

Various commercially available late transition metal complexes were screened in the catalytic dehydrogenation. Although platinum and palladium are well-known dehydrogenation and hydrogenation catalysts, respectively, and platinum has good β-hydrogen elimination properties, they display little or even no activity in the dehydrogenation of 1-octanol or 1-decanol. Catalysts like $Pd(PPh_3)_2(OAc)_2$, $Pd(PPh_3)_4$, $Ir(PPh_3)_3H(CO)$ and $Rh(PPh_3)_3H(CO)$ in combination with tolane gave similar results and also platinum catalysts like $Pt(PPh)_4$ and $PtCl_2(PPh_3)_2$ were completely inactive. The $RuCl_2(PPh_3)_3$ catalyst, which is very active in the hydrogen transfer to acetone as proposed by Bäckvall et al., showed no catalytic activity in the dehydrogenation of primary alcohols.[2,3a] Only one rare example was published by Oshima in the oxidation of dodecanol.[3b] However, when $Ru_3(CO)_{12}$ was employed as catalyst in combination with triphenylphosphine as ligand (Ru/P atomic ratio=1) and tolane as H-acceptor, aldehydes could be obtained in 60–80% yield together with small amounts of ester. $Ru_3(CO)_{12}$ catalyzed dehydrogenations in the absence of additional ligand are known to solely yield esters.[14,22] Initial oxidation experiments with $Ru_3(CO)_{12}/PPh_3$ have been performed in toluene as solvent in an autoclave at 150 °C. Subsequent experiments demonstrated that the same results could be obtained when the reactions were performed in *p*-xylene at 130 °C in standard glassware equipment. The catalytic system can be generalized as depicted in Scheme 1.

The major by-products of the catalytic dehydrogenation of primary alcohols (RCH_2OH) are the corresponding acids

Keywords: Triruthenium dodecacarbonyl catalyst; Catalytic dehydrogenation; Alcohols; Ligands; Hydride acceptors.
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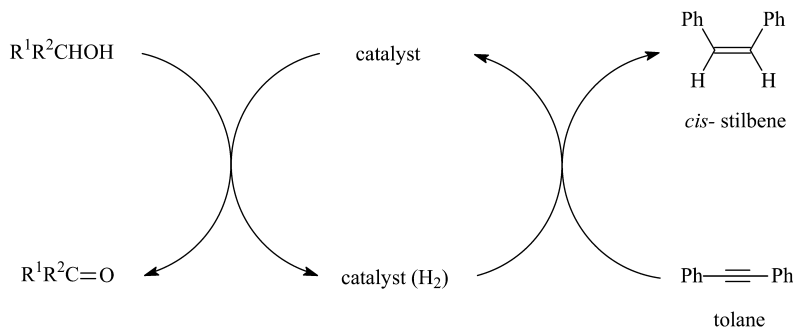
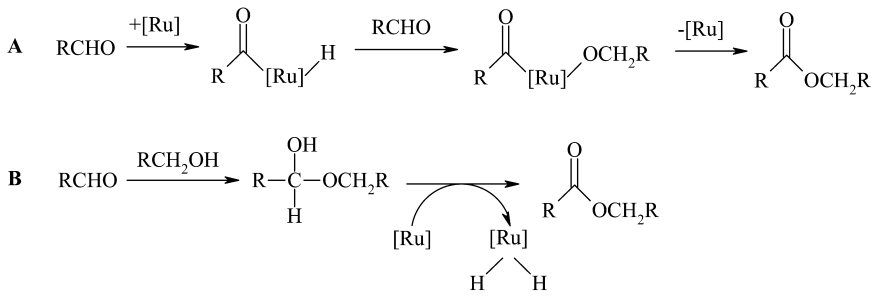
doi:10.1016/j.tet.2003.11.082



Scheme 1. Irreversible hydrogen transfer from alcohols to tolane (diphenylethyne).



Scheme 2. Proposed pathways towards ester formation.

(RCO_2H) and esters (RCO_2CH_2R). When the reactions are performed under oxygen-free conditions, over-oxidation into the acid is prevented. However, ester formation still occurs. For the ester formation two pathways have been proposed, both starting from the aldehyde (Scheme 2).[4,5]

Product formation might be significantly influenced by variation of the ligands and also the cone or bite angles of the ligands in the catalytically active complex as it has long been recognized that changing the ligands may cause marked changes in the behavior of the free ligands and of their transition metal complexes.[6–10] To our knowledge the exact nature of the coordination of diphosphines at $Ru_3(CO)_{12}$ was not yet studied. Thus, $Ru_3(CO)_{12}$ was tested in combination with several ligands having different cone angles and electronic properties in order to favor aldehyde formation and to suppress the ester formation, the results of which are collected in Table 1.

Table 1. Conversion and yield for monodentate ligands differing in cone angle and electronic properties in the dehydrogenation of 1-octanol[a]

Entry	Ligand	Cone angle	Conv. (%)	$Y_{aldehyde}$[b] (%)	Y_{ester} (%)
1	$P(OEt)_3$	109	73	0	31
2	$P(OPh)_3$	130	68	0	22
3	PPh_3	145	100	80	0
4	$(p\text{-}CH_3C_6H_4)_3P$	145	100	64	8
5	$(p\text{-}CH_3OC_6H_4)_3P$	145	100	60	9
6	$(p\text{-}CF_3C_6H_4)_3P$	145	82	60	3
7	$(o\text{-}CH_3C_6H_4)_3P$	194	93	46	0
8	$(n\text{-}Bu)_3P$	132	42	12	0
9	$(C_6H_{11})_3P$	170	100	11	0
10	tri-(2-Furyl)phosphine	—	75	9	21

[a] All experiments were performed at 100 °C with 1-octanol as substrate in the presence of 5 mol% catalyst, 17 mol% of ligand (Ru/P atomic ratio=0.88) and with 200 mol% of tolane. *p*-Xylene was used as solvent and the reactions were stopped after 4 h.

[b] $Y_{aldehyde}$=yield$_{ald}$=conversion×selectivity$_{aldehyde}$.

With PPh_3, $(p\text{-}CH_3OC_6H_4)_3P$ or $(o\text{-}CH_3C_6H_4)_3P$ as ligand a fair amount of desired aldehyde and only a very small amount of ester were formed. The other ligands tested gave lower conversions or more ester.

Ligands with different bite angles were also tested in combination with $Ru_3(CO)_{12}$. The results of these experiments are collected in Table 2.

The bidentate ligands tested did not suppress the ester formation and did not yield aldehyde. The yield of ester formation depends on the bite angle as demonstrated by the results in Figure 1. Increasing flexibility of a ligand backbone raises the chance of an arm-off η^1 coordination (entries 4, 5 and 6 compared to 1, 2, and 3). Ligands with good chelating properties display high and very similar catalytic activities within a range of bite angles from 72 to 92°. Lower activity is afforded by potentially non-chelating

Table 2. Conversion and yield for bidentate ligands differing in bite angles in the dehydrogenation of 1-octanol[a]

Entry	Ligand	Bite angle	Conv. (%)	Y_{ester}[b]	$Y_{aldehyde}$
1	$Ph_2PCH_2PPh_2$	72	100	50	0
2	$Ph_2P(CH_2)_2PPh_2$	83	100	47	0
3	$Ph_2P(CH_2)_3PPh_2$	92	100	47	0
4	$Ph_2P(CH_2)_4PPh_2$	97	72	12	0
5	$Ph_2P(CH_2)_5PPh_2$	—	85	22	0
6	$Ph_2P(CH_2)_6PPh_2$	—	88	26	0
7	Diphenyl-2-pyridylphosphine	—	80	0	30
8	2,2′-Dipyridyl	—	100	0	50

[a] All experiments were performed in *p*-xylene at 130 °C with 1-octanol as substrate in the presence of 5 mol% catalyst, 5 mol% of bidentate ligand (Ru/P atom ratio=1.5) and 200 mol% of tolane. Furthermore, all experiments were performed in *p*-xylene and were stopped after 5 h.

[b] Fifty percent yield corresponds to 100% conversion of 1-octanol (RCH_2OH) into ester (RCO_2CH_2R).

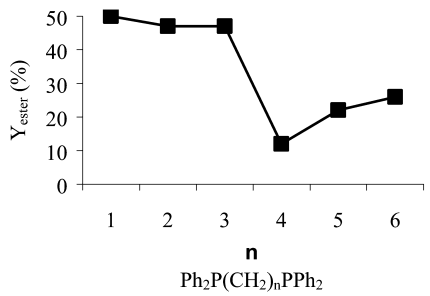


Figure 1. Effect of bite angle on ester formation in the ligand series $Ph_2P(CH_2)_nPPh_2$. For reaction conditions see Table 2.

The conversion and selectivity to the aldehyde were nearly the same when a Ru/P atomic ratio of 0.5 or 0.88 was chosen. Lower Ru/P atomic ratios rendered the reaction slower and the selectivity lower. Presumably, excess of ligand is blocking free coordination sites on the catalyst and consequently retards the reaction. The optimal amount of PPh_3 would be in between a Ru/P atomic ratio of 0.5 and 0.88. Due to the small difference in selectivity between the two ratios, all other experiments where performed with a Ru/P ratio of 0.88. Furthermore, the optimum amount of tolane was found to be 200 mol%. Less tolane led to lower reaction rates and more ester formation. Larger amounts

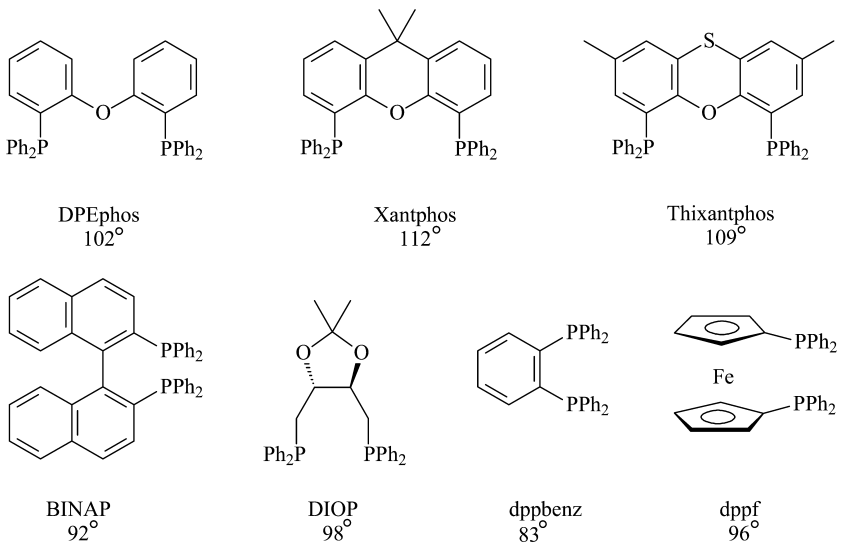


Figure 2. Additional bidentate ligands screened for $Ru_3(CO)_{12}$-catalyzed dehydrogenation of 1-octanol including their bite angles.

ligands. Less ester formation seems to go hand in hand with a slower reaction.

Several other bidentate ligands screened like DPEphos, xantphos, thixantphos, BINAP, DIOP, dppbenz and dppf (see Figure 2 for structures and bite angles) in equimolar amounts with respect to the Ru-catalyst did not give satisfactory results and no clear trends in the conversion rate or yield of the aldehyde could be observed.

From the results collected in Tables 1 and 2, it can be concluded that ester formation is almost completely suppressed when $Ru_3(CO)_{12}$ is used as catalyst in combination with PPh_3 as ligand (cone angle 145°). The effect of the amount of PPh_3 on the ester formation was also investigated (Table 3) in the aforementioned conditions. The Ru/P atomic ratio was changed in every experiment. Furthermore, all experiments were performed in *p*-xylene and were stopped after 5 h.

Table 3. Conversion and yields in the dehydrogenation of 1-octanol searching for the optimal amount of PPh_3[a]

Ru/P ratio	Conv. (%)	Y_{ald} (%)	Y_{ester} (%)	S_{ald} (%)
0.88	100	59	0	59
0.5	100	62	0	62
0.25	88	41	0	47

[a] Reaction conditions as in Table 1.

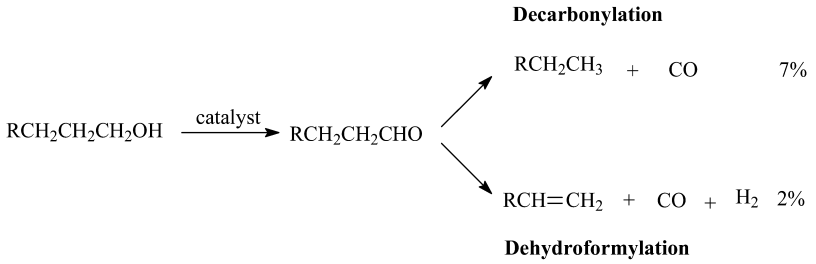
(400 mol%) diminished reaction rates but did not affect the selectivity. The observation that lower concentrations of the H-acceptor led to more ester formation indicates that tolane is not only acting as a H-acceptor but is also playing the role of ligand. Ester formation could also be suppressed by keeping the alcohol concentration as low as possible, that is, working under substrate starving conditions. This was accomplished by adding the alcohol over a period of 1 h to a mixture of 5 mol% $Ru_3(CO)_{12}$, 17 mol% PPh_3 (Ru/P atomic ratio of 0.88) and 200 mol% of tolane.

To widen the scope of the $Ru_3(CO)_{12}/PPh_3$ catalyzed dehydrogenations, several primary and secondary alcohols

Table 4. Oxidation of primary and secondary alcohols with $Ru_3(CO)_{12}$[a]

Entry	Substrate	Catalyst (mol%)	Temp. (°C)	Time (h)	Conv. (%)	*Y* (%)
1[b]	1-Octanol	5	130	5	100	80
2	1-Octanol	5	130	5	100	59
3	1-Decanol	5	130	5	100	54
4	Geraniol	5	100	4	100	82
5	(*S*)-Citronellol	5	130	5	100	77
6	Benzyl alcohol	5	100	4	100	71
7	*p*-Methoxy-benzyl alcohol	5	100	4	100	99
8	Cinnamyl alcohol	5	100	2	100	90
9	2-Decanol	0.5	100	4	94	92
10	Cholesterol	5	150	12	100	94
11	4-*t*-Butyl-cyclohexanol	0.5	130	12	100	88

[a] See Section 4 for the reaction conditions.
[b] Slow addition experiment.



Scheme 3. Consecutive reactions observed during the dehydrogenation of primary alcohols.[11,12]

have been subjected to oxidation, see Table 4. For the dehydrogenation of primary alcohols, 17 mol% PPh_3 was always used to suppress ester formation. In contrast, from secondary alcohols ketones can be produced with relatively high rates and selectivities. In these oxidations, no ligand is needed to suppress side reactions and lower concentrations of the catalyst can be used.

The yield of 1-octanal could be enhanced from 59 to 80% when the alcohol was slowly added to the catalyst (entries 1 and 2). Alcohols containing functional groups like double bonds could be oxidized, leaving the double bond intact (entries 4, 5, 8 and 10). When primary alcohols are oxidized, a considerable loss of material takes place except in the case of *p*-methoxybenzyl or cinnamyl alcohol. Part of the product loss may result from dehydroformylation and decarbonylation of the aldehyde as a consequence of the high temperature (see Scheme 3). When 1-dodecanol was oxidized, these consecutive reactions accounted for ~10% loss. When lower boiling alcohols depicted in Table 4 were oxidized, the decarbonylated and dehydroformylated products evaporated from the reaction mixture before analysis. Also high boiling aldol condensation products might have been formed although no experimental evidence was found. However, the undesired decarbonylation and dehydroformylation as well as aldol condensation reactions can only occur when the primary alcohols are first oxidized into the aldehydes. In the case of entries 7 and 8, decarbonylation and dehydroformylation are prevented due to conjugation between carbonyl and the carbon–carbon double bond or aromatic ring.

There is also some evidence for coordination of the formed ester molecules to the metal center of the catalyst. When half the amount of catalyst was used less material was missing than with double the amount of catalyst. However, attempts to release material from the catalyst by adding strongly coordinating ligands, like cyanide or by phosphine ligands failed. So it remains unclear what the fate of the missing material is.

All alcohols containing unsubstituted ethylene or acetylene groups, yielded a substantial number of by-products and were not further investigated. Even alcohols with substituted acetylenes like 6-phenyl-5-hexyn-3-ol yielded mixtures of products. The hydride has the option to transfer intra- or intermolecularly either to the triple bond of 6-phenyl-5-hexyn-3-ol or to that of the actual H-acceptor tolane.

Another aspect investigated is the performance of alternatives to tolane as H-acceptor. Tolane is initially transformed into *cis*-stilbene that slowly isomerizes to *trans*-stilbene at elevated temperatures. Both isomers are difficult to separate from the product. For this reason other cheap H-acceptors like nitrobenzene, *m*-dinitrobenzene, azobenzene, phenazine, diisopropyl azodicarboxylate, *tert*-butylperoxide, dehydrolinalol, nicotinamide and analogues were screened. The results with these alternative H-acceptors are, however, disappointing. Surprisingly, when tolane was replaced by 1-phenylpropyne, high yields of ester and only small amounts of the aldehyde were obtained, indicating that small changes in H-acceptor may have a dramatic effect on the selectivity. Furthermore, it also suggests that tolane is not only acting as H-acceptor but is also suppressing ester formation efficiently. Subsequently, other substituted analogues of tolane with electron withdrawing or electron releasing substituents have been synthesized. These analogues might provide information about the catalytic cycle. In this cycle, the H-acceptor has to coordinate to the metal center first. After coordination, a hydride is transferred from the metal center to the H-acceptor. Electron rich H-acceptors coordinate well to the metal center but are poor hydride acceptors. The opposite is true for electron deficient H-acceptors. Electron deficient compounds would take up the hydride easily but do not coordinate very well.

For this reason, the MeO (electron rich) and CF_3 (electron deficient) substituted analogues of tolane have been synthesized.[13] Both substituted tolane analogues could be isolated in 80% yield and were studied in the dehydrogenation of 1-octanol.

The reactions performed at 130 °C in *p*-xylene as solvent in the presence of the catalytic system $Ru_3(CO)_{12}/PPh_3$ (Ru/P atomic ratio of 0.88) were stopped after 5 h. The results of the experiments with different H-acceptors are collected in Table 5.

In the catalytic systems, tolane is the best H-acceptor followed by the electron rich 4-MeO-tolane. Both tolane and 4-MeO-tolane coordinate better to the metal center than 4-CF_3-tolane does. Due to the considerably lower fraction of complexed 4-CF_3-tolane, the overall rate of hydride insertion is lower compared to that of the other two

Table 5. $Ru_3(CO)_{12}/PPh_3$ catalyzed dehydrogenation of 1-octanol with tolane and substituted analogues

H-acceptor	Conv. alcohol (%)	Yield aldehyde (%)
Tolane	100	72
4-MeO-tolane	93	61
4-CF_3-tolane	50	22

H-acceptors. The difference between tolane and the electron rich 4-MeO-tolane may originate from the more difficult H-uptake by the latter, despite its easier complexation. In addition, experiments with equimolar mixtures of two H-acceptors were conducted and the catalyst performance after 5 h reaction time is collected in Table 6.

Table 6. $Ru_3(CO)_{12}/PPh_3$ catalyzed dehydrogenation of 1-octanol with equimolar mixtures of H-acceptors

H-acceptor	Conv. alcohol (%)	Yield aldehyde (%)
Tolane/4-MeO-tolane	93	58
Tolane/4-CF_3-tolane	56	22
4-MeO-tolane/4-CF_3-tolane	100	70

Compared to the oxidations with tolane, 4-MeO-tolane or the mixture of tolane and 4-MeO-tolane, the reaction with a mixture of 4-MeO-tolane and 4-CF_3-tolane is surprisingly fast. The conversion of 4-CF_3-tolane into 4-CF_3-stilbene is even faster than those of tolane or 4-MeO-tolane into the corresponding stilbene compounds, see Table 7.

Table 7. Conversion of mixtures of H-acceptor in the $Ru_3(CO)_{12}/PPh_3$ catalyzed dehydrogenation

H-acceptor mixture[a]	Conv. (%)
Tolane/4-MeO-tolane	46/51
4-MeO-tolane/4-CF_3-tolane	35/64

[a] Molar ratio is 1, but total ratio tolane/substrate is 2.

The conversions of tolane and 4-MeO-tolane are comparable indicating that both compounds are comparable in coordinating and accepting the hydride. The higher conversion of 4-CF_3-tolane with respect to 4-MeO-tolane indicates that both H-acceptors play an important but different role in the dehydrogenation of the alcohols. First, the electron rich 4-MeO-tolane will coordinate to the metal center and this increases the electron density on the metal center. As a result the electron deficient 4-CF_3-tolane can coordinate and will then be reduced very fast. The asymmetry introduced by the substituents on the hydride acceptor may also play an important role in the coordinating and hydride accepting properties of the H-acceptor. Unfortunately, the effect of a symmetrically disubstituted tolane was not studied and this leaves room for speculation.

Furthermore, experiments were performed with a radical scavenger to determine whether the oxidation of alcohols is a one or a two-electron process. Standard reaction conditions were used with the exception that in these experiments 2,6-di-*tert*-butyl-4-methylphenol (BHT) was added as a radical scavenger. The results are comparable to the experiments, which were performed under standard reaction conditions without radical scavenger. Hence, it can be concluded that the oxidation is not of a radical nature.

Attempts to unravel the mechanistic pathway of the catalytic reaction were also initiated. Ruthenium complexes formed during the $Ru_3(CO)_{12}/PPh_3$ catalyzed dehydrogenation of 1-octanol in combination with tolane as H-acceptor precipitated from the reaction mixture. The MALDI-TOF MS spectrum of the solid showed 4 different molar masses, see Figure 3.

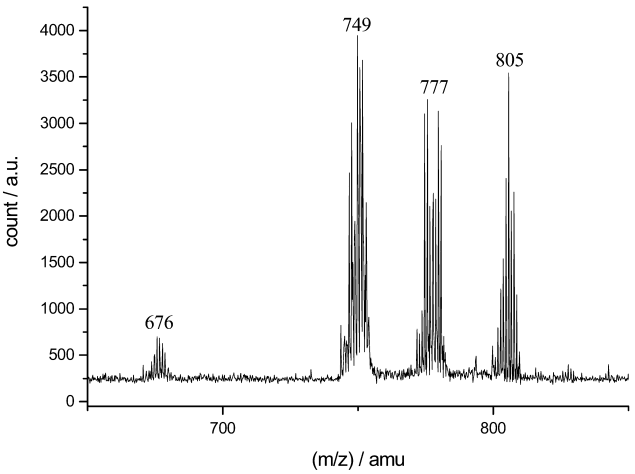


Figure 3. MALDI-TOF MS spectrum obtained from a ruthenium complex isolated during $Ru_3(CO)_{12}/PPh_3$ catalyzed dehydrogenation of 1-octanol.

In this particular case, crystals were grown from one isolated Ru-complex. The X-ray structure of these crystals revealed a mass of 804 corresponding to the structure depicted in Figure 4. The analyzed crystals turned out to be a dichloromethane solvate of the Ru-complex. The molecular structure of the Ru-complex is very similar to that observed in the benzene solvate reported earlier by Yamazaki and Taira.[22]

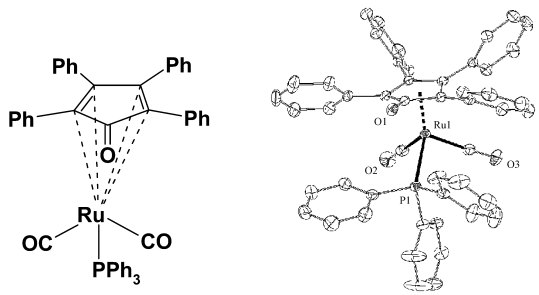
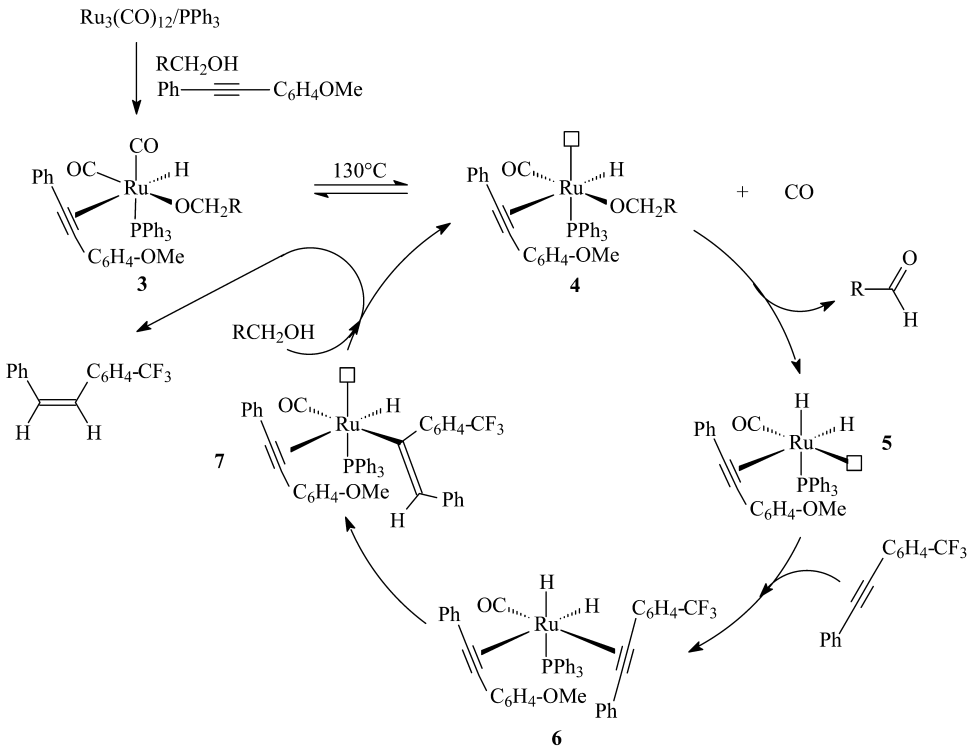


Figure 4. X-ray structure of the isolated ruthenium complex from $Ru_3(CO)_{12}/PPh_3$ catalyzed dehydrogenation of 1-octanol. H atoms and solvent molecule are omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.

In this complex tetracyclone, formally composed of two tolane molecules and one carbon monoxide molecule as depicted in Figure 4, acts as a ligand. An envelope structure is adopted by the tetracyclone ring. The carbonyl carbon atom is located 0.236(2) Å from the least-squares plane through the atoms of the diene system, who all lie within 0.03(2) Å of this plane. The distances between the diene carbons are similar in length (C–C 1.44–1.45 Å, observed range: 1.438(3)–1.453(3) Å; the C–C (carbonyl) bonds are significantly longer: 1.480(3) and 1.482(3) Å), indicating delocalization of the double bonds over the four atoms. The isolated ruthenium complex has been investigated for its catalytic activity. Unfortunately, it turned out that this complex is not the active species in the catalytic cycle and hence, its formation is expected to reduce the activity of the catalytic system.

Since little mechanistic information about the $Ru_3(CO)_{12}$ catalyzed reactions is available, it was difficult to obtain information about the catalytic cycle. Nevertheless, based



Scheme 4. Proposed catalytic cycle for the $Ru_3(CO)_{12}$ catalyzed dehydrogenations.

on the results obtained so far, particularly those from the competition experiments with the electron rich and electron deficient tolane analogues, a tentative catalytic cycle can be proposed, see Scheme 4.

Before entering the catalytic cycle, the $Ru_3(CO)_{12}$ metal cluster is proposed to be defragmented into the mono-metallic complex **3** by PPh_3, the electron rich 4-MeO-tolane and the alcohol. Due to high temperature, a CO molecule is released generating a free coordination site in **4**. β-Hydride elimination from the alkoxide gives rise to a ruthenium hydride species **5** and one aldehyde or ketone molecule is released. Subsequently, the electron deficient 4-CF_3-tolane can coordinate to the metal center **6** due to the higher electron density on the metal induced by the electron rich 4-MeO-tolane. One hydride is inserted in the 4-CF_3-tolane ligand and a free coordination site is generated in **7**. Concomitant reductive elimination from the 4-CF_3-tolane followed by oxidative addition of an alcohol molecule restores ruthenium complex **4** and in this way the catalytic cycle is closed.

3. Conclusions

In contrast to the classical Oppenauer and the Oppenauer-like oxidation presented by Bäckvall,[2,3] it was found that the dehydrogenations of primary and secondary alcohols are catalyzed by $Ru_3(CO)_{12}$ in the presence of tolane as H-acceptor.[23] Screening experiments with several ligands demonstrated that ester formation is almost completely suppressed with triphenylphosphine as ligand and the selectivity towards the aldehyde never exceeded 80%. For the dehydrogenation of primary alcohols, additional ligand (PPh_3) is needed to suppress ester formation. Non-conjugated aldehydes often give decarbonylation and dehydroformylation as consecutive reaction.

No PPh_3 and less $Ru_3(CO)_{12}$ are needed for the oxidation of secondary alcohols and still high conversions and selectivities for ketones are obtained.

Taking into account all the experimental results a catalytic cycle has been proposed.

4. Experimental

4.1. General

All starting materials were obtained from commercial suppliers and used as received. All reactions were performed under an atmosphere of dry argon. Analytical thin layer chromatography was performed on Kieselgel 60 F-254 precoated silica gel plates. Visualization was accomplished with UV light or iodine vapour. Column chromatography was performed on Merck silica gel 60 or on Merck aluminum oxide 90. ^1H, ^{13}C and ^{31}P NMR spectra were recorded on a 400 MHz NMR (Varian Mercury, 400 MHz for ^1H NMR and 100 MHz for ^{13}C NMR), or on a 300 MHz NMR (Varian Gemini, 300 MHz for ^1H NMR and 75 MHz for ^{13}C NMR). Proton chemical shifts (δ) are reported in ppm downfield from tetramethylsilane (TMS), whereas the carbon chemical shifts are reported in ppm downfield of TMS using the resonance of the deuterated solvent as internal standard. The phosphorus shifts were referenced to 85% H_3PO_4. IR-spectra were recorded on a Perkin Elmer ATR-IR Spectrum One. MALDI-TOF-spectra were obtained on a PerSeptive Biosystems Voyager DE PRO spectrometer using α-cyano-4-hydroxycinnamic acid

as a matrix. GC analyses were performed using a Zebron ZB-35 or a Chirasil-Dex-CB column on a Perkin Elmer Autosystem in combination with a flame ionization detector. Conversion and yields were determined by using 1,3,5-tri-*tert*-butylbenzene as internal standard. GC/MS measurements were obtained with a Shimadzu GC/MS-QP5000 using a Zebron ZB-35 column.

4.1.1. $Ru_3(CO)_{12}$ catalyzed dehydrogenations of primary alcohols with monodentate ligands, general procedure. All monodentate ligands were obtained from Aldrich, Acros or Strem. All catalytic oxidation experiments were performed in a dry, oxygen-free argon atmosphere. A typical experiment was performed as follows. An oven-dry 40 mL Radley carousel reaction tube was flushed with argon before it was charged with $Ru_3(CO)_{12}$ (61.2 mg, 0.096 mmol), tolane (684 mg, 3.84 mmol) as H-acceptor and triphenylphosphine (85.6 mg, 0.326 mmol) as metal ligand. Alcohol (1.92 mmol) and internal standard (1,3,5-tri-*tert*-butylbenzene, 81 mg, 0.33 mmol) dissolved in *p*-xylene (2.50 mL) were added to the mixture. A small aliquot was taken from the alcohol/internal standard solution for GC analysis. The reaction tube was placed in a 12 tube Radley reaction carousel and the mixture was heated and stirred with a magnetic stirrer for several hours. Small aliquots of reaction mixture were taken for GC analysis. The products were characterized by GLC and GC/MS by comparison with authentic samples. The conversions and yields were determined with GLC (Tables 1, 2 and 4).

4.1.2. $Ru_3(CO)_{12}$ catalyzed dehydrogenations of primary alcohols with bidentate ligands, general procedure. All bidentate ligands were obtained from Aldrich, Acros or Strem. In a typical experiment, the oven-dry 40 mL Radley carousel reaction tube was charged with $Ru_3(CO)_{12}$ (61.2 mg, 0.096 mmol), tolane (684 mg, 3.84 mmol) and 0.096 mmol bidentate ligand. 1-Octanol (250 mg, 1.92 mmol) and internal standard (1,3,5-tri-*tert*-butylbenzene, 81 mg, 0.33 mmol) dissolved in *p*-xylene (2.50 mL) were added to the mixture. GC analysis was performed after 5 h as described above.

4.1.3. $Ru_3(CO)_{12}$ catalyzed dehydrogenations of secondary alcohols, general procedure. The procedure was analogous to that of the primary alcohols with monodentate ligands (see Section 4.1.1). In all of the examples, no ligand was added.

4.1.4. Octanal. 1-Octanol was dehydrogenated according to the procedure described above. The product was characterized (GC) by comparison with an authentic sample. After 5 h, octanal was obtained in 80% yield after bulb-to-bulb distillation. Spectral data were in accordance with the literature.

4.1.5. Benzaldehyde. Benzyl alcohol was dehydrogenated according to the procedure described above. The product was characterized (GC) by comparison with an authentic sample. After 5 h, benzaldehyde was obtained in 71% yield after bulb-to-bulb distillation. Spectral data were in accordance with the literature data.

4.1.6. 2-Decanone. 2-Decanol was dehydrogenated according to the procedure described above. The product was characterized (GC) by comparison with an authentic sample. After 5 h, 2-decanone was obtained in 92% yield after bulb-to-bulb distillation. Spectral data were in accordance with the literature data.

4.1.7. 4-Cholestene-3-one. Cholesterol was dehydrogenated according to the procedure described above. The product was characterized (GC) by comparison with an authentic sample. The yield was determined with GLC. Purification of the reaction mixture by flash column chromatography (silica gel, with dichloromethane/diethyl ether (20:1)) yielded 4-cholestene-3-one as a light brown/white powder (94%). The spectral data was in accordance with literature data.[15]

4.1.8. Screening of H-acceptors. Analogous to the general procedure, the dehydrogenation of 1-octanol was performed with 2 equiv. of the alternative H-acceptors. All reactions were stopped after 5 h. The conversion was monitered by GC analysis.

4.1.9. 4-Methoxy-diphenylethyne. A mixture of phenylacetylene (6.0 g, 58.74 mmol), 4-iodoanisole (11.7 g, 53.42 mmol), CuI (1.0 g, 5.25 mmol), dichlorobis(triphenylphosphine)palladium (II) (1.5 g, 2.14 mmol) and triethylamine (65 mL, 466 mmol) was stirred at RT. After stirring overnight, the mixture was poured into H_2O (200 mL) and extracted with diethyl ether (200 mL). The organic layer was washed successively with H_2O (100 mL) and brine (100 mL) before drying ($MgSO_4$). Evaporation of the solvent followed by bulb-to-bulb distillation under reduced pressure (150 °C/0.03 Torr), gave 4-methoxy-diphenylethyne (8.4 g, 81%) as a light yellow solid. The spectral data was in accordance with literature data.[17] Mp 58 °C (lit.[17] 52–54 °C).

4.1.10. 4-Trifluoromethyl-diphenylethyne. A mixture of phenylacetylene (2.50 g, 24.48 mmol), 4-iodobenzotrifluoride (5.50 g, 20.22 mmol), CuI (0.5 g, 2.63 mmol), dichlorobis(triphenylphosphine)palladium (II) (0.70 g, 0.10 mmol) and triethylamine (30 mL, 220 mmol) was stirred at RT. After stirring overnight, the mixture was poured into H_2O (100 mL) and extracted with diethyl ether (100 mL). The organic layer was washed successively with H_2O (50 mL) and brine (50 mL) before drying ($MgSO_4$). Evaporation of the solvent followed by bulb-to-bulb distillation under reduced pressure (150 °C/0.03 Torr), gave 4-trifluoromethyl-diphenylethyne (3.9 g, 78%) as an off-white solid. Mp 97 °C (lit.[24] 104–106 °C, dec.). The spectral data was in accordance with literature data.[16]

4.1.11. Dehydrogenation in the presence of equimolar mixtures of H-acceptor. Analogous to the general procedure, the dehydrogenation of 1-octanol was performed with a 1 to 1 mixture of H-acceptor (total 2 equiv. of H-acceptor). All reactions were stopped after 5 h. The conversion was monitored by GC analysis (Tables 5–7).

4.1.12. Dehydrogenation in the presence of radical scavenger. The dehydrogenation of 1-octanol was performed according to the general procedure including 2,6-di-*tert*-butyl-4-methylphenol (427 mg, 1.94 mmol). The conversion was monitored by GC analysis.

4.1.13. Isolation of $(Ph_4C_5O)Ru(CO)_2PPh_3$ formed during the dehydrogenation of 1-octanol. After the dehydrogenation of 1-octanol according to the standard procedure, the reaction mixture was allowed to cool to room temperature overnight. A yellow solid had precipitated. Removal of the mother liquor by filtration yielded a yellow solid that was purified by column chromatography (silica gel, CH_2Cl_2) and crystallized from CH_2Cl_2:hexane, the product was obtained as a few yellow crystals. ^{1}H NMR ($CDCl_3$): δ=7.44–6.94 (m, 35H); ^{13}C NMR ($CDCl_3$): δ=202.2, 202.1, 133.5, 133.1, 133.0, 132.6, 132.6, 132.1, 131.2, 130.3, 130.1, 130.0, 128.2, 128.1, 127.6, 126.7, 125.9, 105.6, 105.5, 81.8; ^{31}P NMR ($CDCl_3$): δ=39.0; IR (ATR): ν=3051, 2006, 1951, 1605, 1575, 1498, 1486, 1445, 1435, 1401, 1312, 1091, 1072, 1029, 1001, 838, 805, 757, 740, 727, 708, 690 cm^{-1}. MALDI-TOF *m/z* 777, 749, 805. R_f=0.22 (CH_2Cl_2). Mp 205 °C (dec.).

4.2. Crystals structure determination of $(Ph_4C_5O)Ru(CO)_2PPh_3$

A yellow crystal having approximate dimensions of 0.27×0.42×0.54 mm^3 mounted on top of a glass capillary was used for X-ray study. The data were collected on a Nonius KappaCCD diffractometer. A correction for absorption was considered unnecessary. Reduced-cell calculations did not indicate higher lattice symmetry. All data were collected at 150 K using graphite-monochromated Mo Kα radiation (λ=0.71073 Å). The structure was solved by automatic Patterson methods (DIRDIF99).[18] The structure was refined on F^2, using full-matrix least squares techniques (SHELXL97).[19] Neutral atom scattering factors and anomalous dispersion corrections were taken from the International Tables for Crystallography.[20] Validation, geometrical calculations and illustrations were performed with PLATON.[21]

The crystal structure has been deposited at the Cambridge Crystallographic Data Center as (η4-2,3,4,5-tetraphenyl-2,4-cyclopentadien-1-one)-dicarbonyl-triphenylphosphine-ruthenium(0) dichloromethane solvate and allocated the deposition number CCDC 223319.

Crystal data: $C_{49}H_{35}O_3PRu{\cdot}CH_2Cl_2$, M=888.74, tetragonal, space group $I4_1/a$ (No. 88), a=22.1040(1), c=33.2826(2) Å, V=16261.44(14) Å^3, Z=16, D_{calc}=1.452 g cm^{-3}, μ(Mo Kα)=0.600 mm^{-1}, F(000)=7264, T=150 K.

Data collection and refinement: θ_{min}, θ_{max}=1.8, 27.5°, data set (*hkl*-range)=−28:28, −28:28, −43:42, total data=123,055, total unique data=9325 (R_{int}=0.050), number of refined parameters=514, final R=0.0312 [for 8043 $I > 2\sigma(I)$], final $wR2$=0.0803, goodness of fit=1.03, min. and max. residual density=−0.86, 0.68e Å^{-3}.

Acknowledgements

The authors gratefully acknowledge the support by the Ministry of Economic Affairs as part of the Innovation Oriented Research Program on Catalysis (IOP Catalysis). The crystal structure work was supported by the Council for the Chemical Sciences of the Netherlands Organization for Scientific Research (CW-NWO).

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