

Pincer and Diamine Ru and Os Diphosphane Complexes as Efficient Catalysts for the Dehydrogenation of Alcohols to Ketones

Walter Baratta,* Gianluca Bossi, Elisabetta Putignano, and Pierluigi Rigo^[a]

Abstract: The ruthenium and osmium complexes $[\text{MCl}_2(\text{diphosphane})(\text{L})]$ ($\text{M} = \text{Ru}, \text{Os}$; $\text{L} = \text{bidentate amino ligand}$) and $[\text{MCl}(\text{CNN})(\text{dppb})]$ ($\text{CNN} = \text{pincer ligand}$; $\text{dppb} = 1,4\text{-bis}(\text{diphenylphosphino})\text{butane}$), containing the N–H moiety, have been found to catalyze the acceptorless dehydrogenation of alcohols in *t*BuOH and in the presence of KO*t*Bu. The compounds *trans*- $[\text{MCl}_2(\text{dppf})(\text{en})]$ ($\text{M} = \text{Ru}$ **7**, Os **13**; $\text{dppf} = 1,1'\text{-bis}(\text{diphenylphosphino})\text{ferrocene}$; $\text{en} = \text{ethylenedia-$

mine) display very high activity and different substrates, including cyclic and linear alcohols, are efficiently oxidized to ketones by using 0.8–0.04 mol% of catalyst. The effect of the base and the comparison of the catalytic activity of the Ru versus Os complexes are reported. The ruthenium

complex **7** generally leads to a faster conversion into ketones with respect to the osmium complex **13**, which displays better activity in the dehydrogenation of 5-en-3 β -hydroxy steroids. The synthesis of new Ru and Os complexes $[\text{MCl}_2(\text{PP})(\text{L})]$ ($\text{PP} = \text{dppb}, \text{dppf}$; $\text{L} = (\pm)\text{-trans-1,2-diaminocyclohexane}$, 2-(aminomethyl)pyridine, and 2-aminoethanol) of *trans* and *cis* configuration is also reported.

Keywords: dehydrogenation • homogeneous catalysis • osmium • phosphane ligands • ruthenium

Introduction

Catalytic alcohol dehydrogenation, through the direct formation of hydrogen and without the need of oxidizing agents, is a straightforward route to achieve carbonyl compounds, such as ketones, aldehydes, and esters.^[1] This process is of great current interest as a potential method for hydrogen production from biomass products.^[1a] A number of transition-metal complexes have been shown to display good to high catalytic activity for both H₂ generation and the preparation of carbonyl compounds from alcohols, ruthenium being the metal of choice. Regarding the hydrogen generation, $[\text{Ru}(\text{OCOCF}_3)_2(\text{CO})(\text{PPh}_3)_2]$, described by Dobson and Robinson, was found to be active for the dehydrogenation of primary and secondary alcohols in the presence of CF₃COOH.^[2] Morton and Cole-Hamilton reported that $[\text{RuH}_2(\text{N}_2)(\text{PPh}_3)_3]$ is active in the dehydrogenation of alcohols in the presence of NaOH.^[3] More recently, Beller and co-workers reported the generation of H₂ from 2-propanol, by use of the systems RuCl₃ hydrate/phosphane and $[\text{RuCl}_2(p\text{-cymene})]_2/\text{nitrogen ligands}$ in strong basic solutions.^[4] For the preparation of carbonyl compounds, Hulshof and co-workers found that the Robinson catalyst^[5] and the related system $[\text{Ru}(\mu\text{-OCOC}_2\text{F}_4\text{OCO})_2(\text{CO})(\text{diphosphane})]_2$ ^[6] can be employed for the acceptorless de-

hydrogenation of secondary alcohols, affording ketones in good yields. Adair and Williams described the dehydrogenation of secondary alcohols using the Grubbs' catalyst $[\text{RuCl}_2(=\text{CHPh})(\text{PCy}_3)_2]$ ($\text{Cy} = \text{cyclohexyl}$) and the $[\text{RuCl}_2(p\text{-cymene})]_2/\text{PPh}_3$ system.^[7] PNP and PNN ruthenium complexes have been reported by Milstein and co-workers as active catalysts for the dehydrogenation of secondary alcohols to ketones^[8] and for the dehydrogenation of primary alcohols to esters and acetals.^[8b,9] Zhao and Hartwig showed that several Ru derivatives, including hydrido-phosphane, diphosphane-diamine, and Shvo complexes are active in the dehydrogenation of 1,4-butanediol to γ -butyrolactone at 205 °C without base.^[10] A few iridium catalysts were also shown to be active in the alcohol dehydrogenation.^[11] It is worth noting that because of the higher redox potentials of aldehydes/primary alcohols relative to those of ketones/secondary alcohols, the dehydrogenation of secondary alcohols is thermodynamically easier.^[12] In addition, the catalytic alcohol dehydrogenation represents a key step for broadening the alcohol reactivity, thus giving access to C–C and C–N bond-forming reactions through a hydrogen borrowing process.^[1e]

Recently, the Ru and Os phosphane complexes *cis*- $[\text{MCl}_2(\text{PP})(\text{ampy})]$ ($\text{M} = \text{Ru},$ ^[13] $\text{Os};$ ^[14] $\text{PP} = \text{diphosphane}$, $\text{ampy} = 2\text{-(aminomethyl)pyridine}$) were found to be highly efficient catalysts for the (asymmetric) transfer hydrogenation and hydrogenation of ketones. Furthermore, the related pincer complexes $[\text{MCl}(\text{CNN})(\text{PP})]$ ($\text{M} = \text{Ru},$ ^[15] Os ^[16]), prepared by using 6-(4'-methylphenyl)-2-pyridylmethylamine (HCNN), catalyze the reduction of carbonyl compounds with high productivity when using 0.05–0.001 mol% of catalyst and a high rate (turnover frequency (TOF) up to

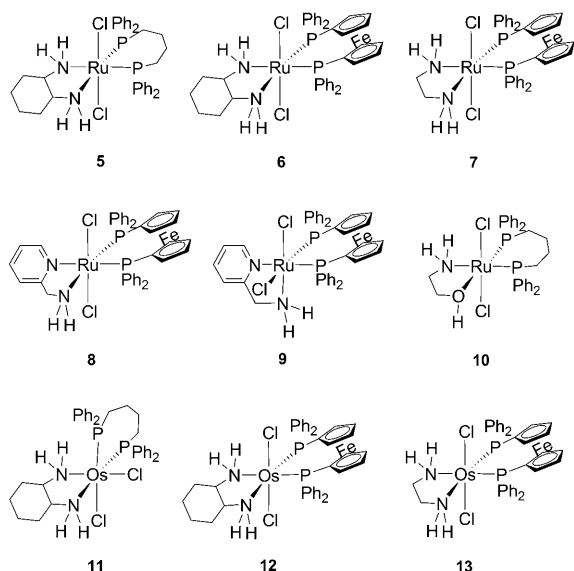
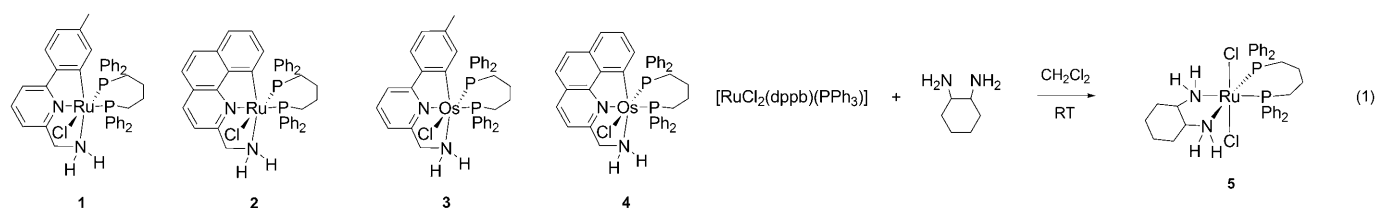
[a] Prof. W. Baratta, Dr. G. Bossi, Dr. E. Putignano, Prof. P. Rigo
Dipartimento di Scienze e Tecnologie Chimiche
Università di Udine
Via Cotonificio 108, 33100 Udine (Italy)
Fax: (+39)0432-558803
E-mail: inorg@uniud.it

10^6 h^{-1}). In addition, *trans*-[OsCl₂(PP)(diamine)]^[17] complexes were found to be extremely active catalysts for the asymmetric hydrogenation of ketones. Based on the microscopic reversibility, it is expected that the hydrogenation catalysts reported above, as well as the classical *trans*-[RuCl₂(PP)(diamine)] described by Noyori et al.,^[18] should also be active in the reverse dehydrogenation process,^[19] even though the concentrations of the reagents are entirely different.

Herein, we report that the pincer Ru and Os complexes **1–4** and the bidentate amino derivatives **5–13** are highly active in the acceptorless dehydrogenation of alcohols to ke-

Results and Discussion

Preparation of diphosphane Ru and Os complexes with N–H-containing ligands: Preliminary results on Ru and Os complexes [MCl₂(PP)(diamine)] showed that these compounds are catalytically active in the dehydrogenation of alcohols. To extend the number of potential catalysts for this reaction, new derivatives containing the N–H moiety were isolated. The ruthenium compound **5** was promptly prepared in 82% yield by treatment of [RuCl₂(dppb)(PPh₃)] (dppb = Ph₂P(CH₂)₄PPh₂) with one equivalent of (*±*)-*trans*-1,2-diaminocyclohexane (*trans*-dach) in dichloromethane at RT [Eq. (1)].

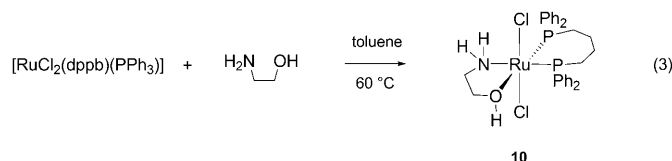
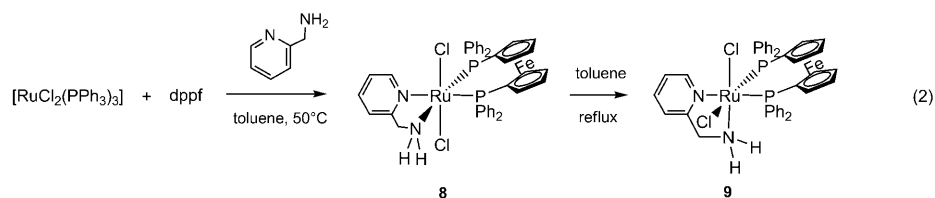


In the ³¹P NMR spectrum, complex **5** shows a singlet at $\delta = 45.1$ ppm, consistent with a *trans* configuration. Treatment of [RuCl₂(PPh₃)₃] with 1,1'-bis(diphenylphosphino)ferrocene (dppf) and ampy in toluene at 50 °C gives the derivative **8** of *trans* configuration, isolated in 92% yield [Eq. (2)].

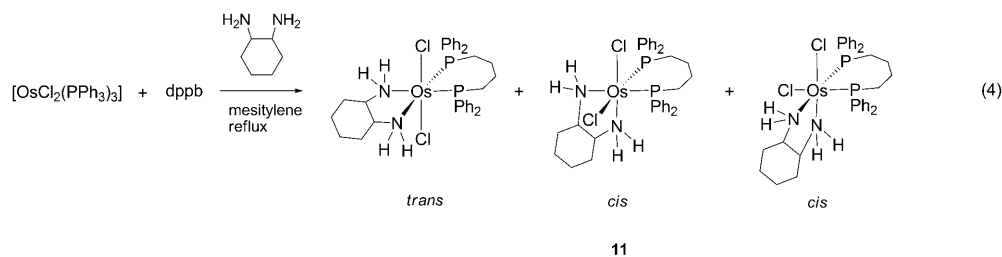
Two doublets at $\delta = 51.6$ and 40.9 ppm with ²J(P,P) = 38.3 Hz were observed in the ³¹P NMR spectrum. Heating of **8** in toluene at reflux temperature for 24 h afforded the thermodynamically more stable *cis* isomer **9**, as inferred from ³¹P NMR spectroscopy ($\delta = 57.8$ and 44.2 ppm, ²J(P,P) = 35.6 Hz), according to previous studies on the Ru/diphosphane/ampy system.^[13a] The Ru derivative **10** containing the NH₂ and OH functions was prepared by reaction of [RuCl₂(dppb)(PPh₃)] with 2-aminoethanol (ae) in toluene at 60 °C and was isolated in 85% yield [Eq. (3)].

The ³¹P NMR spectrum shows two doublets at $\delta = 59.5$ and 44.4 ppm with ²J(P,P) = 42.7 Hz, whereas in the ¹H NMR spectrum the signal at $\delta = 3.53$ ppm is for the OH moiety.

tones. Several alcohols, including 3-hydroxy sterols, have been efficiently oxidized with 0.8–0.04 mol% of catalyst at 130–145 °C. The preparation of some ruthenium and osmium complexes with bidentate nitrogen ligands is also described. This is the first example of the use of Os complexes in the alcohol dehydrogenation reaction.



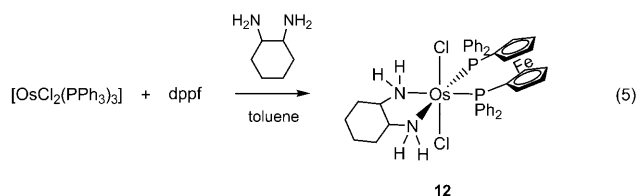
As regards the Os derivatives, reaction of $[\text{OsCl}_2(\text{PPh}_3)_3]$ with dppb and *trans*-dach led to the formation of complex **11** as a mixture of three isomers [Eq. (4)].



The pincer Ru and Os complexes **1–4** catalyze the dehydrogenation of 1,2,3,4-tetrahydro-1-naphthol (α -tetralol), which was taken as model compound for this study, on account of its low redox potential ($E^\circ = 0.080 \text{ V}$).^[12] High conversion of α -tetralol into α -tetralone (93 and 90%) was

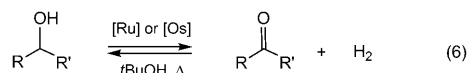
The ^{31}P NMR spectrum obtained at 90°C after 1 h shows one singlet at $\delta = -11.7$ ppm, consistent with a *trans* complex, and four doublets at $\delta = -2.2, -12.8$ ppm ($^2J(\text{P},\text{P}) = 13.4$ Hz) and $\delta = -2.7, -11.7$ ppm ($^2J(\text{P},\text{P}) = 13.3$ Hz) for two *cis* species, on account of the two coordination modes of the *trans*-dach ligand. Upon heating at reflux in mesitylene for 4 h, the *trans* species partially converts to the *cis* isomers, which results in a mixture *trans/cis/cis* = 2:6:1. This result resembles that obtained for the reaction of the Os precursor with dppb and ampy, instead of *trans*-dach, for which a mixture of *cis* and *trans* isomers was observed under similar experimental conditions.^[14] Notably, in the case of ruthenium with *trans*-dach the complex **5** was obtained as a single *trans* isomer.

Finally, treatment of $[\text{OsCl}_2(\text{PPh}_3)_3]$ with dppf and *trans*-dach affords compound **12** as a single *trans* isomer, as established by ^{31}P NMR spectroscopy ($\delta = -9.9$ ppm), which was isolated in 73% yield [Eq. (5)].



These results agree with the literature data for the compounds $[\text{MCl}_2(\text{PP})(\text{NN})]$ ($\text{M} = \text{Ru}, \text{Os}$). As a matter of fact, although the reaction of Ru phosphane complexes with diamines leads preferentially to the *trans* isomer,^[18] with the ampy ligand the thermodynamically most stable species is the *cis* complex.^[13] With Os and diamines a single *trans* isomer^[17] has been obtained with the ferrocene diphosphane dppf, whereas with dppb a mixture of *trans* and *cis* isomers is formed.

Catalytic results: Ruthenium and osmium/diphosphane/amine complexes, bearing ligands with the N–H functionality, were found to be active in the dehydrogenation of a number of alcohols [Eq. (6)].



observed with the Ru derivatives **1** and **2** (0.4 mol%) and KOtBu (2 mol%) in *t*BuOH at 130°C (bath temperature) within 24 h (Table 1). Under these experimental conditions, the yield of α -tetralone was equal to the conversion of the alcohol, as established by GC and ^1H NMR analyses, thus indicating a high selectivity.

Table 1. Dehydrogenation of α -tetralol with catalysts **1–13** (0.4 mol%) in the presence of KOtBu (2 mol%) in *t*BuOH at 130°C .

Catalyst	Conv. [%] ^[a] after 1 h	Conv. [%] ^[a] after 2 h	Conv. [%] ^[a] (time, h)
1	13	27	93 (24)
2	10	19	90 (24)
3	4	6	44 (24)
4	4	5	36 (24)
5	21	40	97 (22)
6	74	94	97 (3)
7	80	93	98 (3)
8	82	90	97 (4)
9	73	82	90 (4)
10	6	8	86 (45)
11	20	38	93 (22)
12	14	28	96 (24)
13	31	65	98 (6)

[a] The conversion was determined by GC analysis.

To shift the reaction toward the ketone, the reaction was carried out in an open system. Tertiary butanol was chosen as a suitable protic solvent, which by contrast with primary or secondary alcohols is not involved in dehydrogenation reactions. The corresponding pincer osmium complexes **3** and **4** display lower activity, thus leading to incomplete formation of α -tetralone (44 and 36%). The ruthenium derivatives $[\text{RuCl}_2(\text{PP})(\text{diamine})]$ **5–7** show higher activity with respect to the pincer complexes, affording fast and quantitative dehydrogenation of α -tetralol (97–98% conversion) in a shorter time. Interestingly, the diamine derivatives **6** and **7**, which display the dppf diphosphane, exhibit the highest rate, with up to 80% conversion after 1 h. The dppf derivative **8** with the ampy ligand shows activity similar to that of **7**, with 97% conversion after 4 h, thus indicating that both the diamine and the ampy complexes, which are catalysts for hydrogenation and transfer hydrogenation, are highly efficient

catalysts for the dehydrogenation reaction. It is noteworthy that the *cis* isomer **9** shows a slightly lower activity with respect to the *trans* isomer **8** (90% after 4 h), thus differing from the activity of [RuCl₂(dppb)(ampy)] in the transfer hydrogenation of ketones, for which the *cis* isomers gave the highest rate.^[13a] The ruthenium complex **10** containing the 2-aminoethanol ligand is also active, although with lower efficiency (86% conversion in 45 h). As regards osmium, the complexes **11–13** catalyze the dehydrogenation of α -tetralol and their activity was compared with that of the related ruthenium derivatives **5–7**. The osmium complex **11** (*trans* and *cis* isomers), which displays the same set of ligands as **5**, shows much the same activity (93% conversion in 22 h) with respect to **5** (Table 1). Compounds **12** and **13**, which contain the dppf diphosphane, also led to complete conversion (96–98%), even though with a rate lower than that of **6** and **7**. In particular, **13** gave 65% conversion after 2 h and 98% in 6 h, thus indicating that osmium can efficiently be employed in alcohol dehydrogenation. These data show that [RuCl₂(dppf)(ampy)] (**8**, **9**) and *trans*-[MCl₂(dppf)(en)] (M = Ru **7**, Os **13**) are among the most active Ru and Os catalysts. To study the effect of the metal in catalysis, the activity of **7** and **13** was compared.

To investigate the role of the base on the activity of the ruthenium **7** and osmium **13** complexes, the catalytic dehydrogenation was carried out with KO*t*Bu in the range 0 to 40 mol%. Under the same experimental conditions as those previously described, in the absence of base complexes **7** and **13** (0.4 mol%) were found not to be active in the dehydrogenation of α -tetralol ($\leq 1\%$, 2 h; Table 2).

Table 2. Influence of the base (KO*t*Bu) on the dehydrogenation of α -tetralol with catalysts **7** and **13** (0.4 mol%) in *t*BuOH at 130°C.

KO <i>t</i> Bu [mol %]	Complex 7		Complex 13	
	Conv. [%] ^[a] (2 h)	Conv. [%] ^[a] (time, h)	Conv. [%] ^[a] (2 h)	Conv. [%] ^[a] (time, h)
0	0		1	
0.5	1		8	
1	43	91 (21)	45	91 (21)
2	97	98 (3)	65	98 (6)
3	97		60	94 (6)
6	96		58	92 (6)
40	66	96 (24)	47	95 (24)

[a] The conversion was determined by GC analysis.

With 0.5 mol% of base the ruthenium complex is catalytically inactive, whereas osmium led to 8% conversion after 2 h. By use of 1 mol% of KO*t*Bu the two complexes show apparently the same behavior with 43–45% conversion after 2 h and 91% after 21 h. At higher base loading, namely 2–6 mol%, the Ru catalysts afforded almost quantitative conversion after 2 h, whereas the Os complex gave 58–65% of α -tetralone in 2 h and up to 98% in 6 h. It is worth noting that in a closed system (25 mL Schlenk tube) compounds **7** and **13** give incomplete conversion of α -tetralol in 4 h (65 and 56%). At higher loading of KO*t*Bu (40%) the Ru and Os systems are less active and complete conversion is

reached after 24 h. In addition, in the absence of Ru or Os complexes, no dehydrogenation of α -tetralol was observed in basic *t*BuOH at 130°C after 3 h. These data show that the catalysis occurs efficiently when the base/complex ratio is >2 , which suggests that in dehydrogenation, similarly to hydrogenation, the dihydrido system [MH₂(dppf)(en)] (M = Ru, Os), formed by reaction of [MCl₂(dppf)(en)] with potassium α -tetralol alkoxide, is involved in catalysis. To investigate the potential of **7** for synthetic purposes, the dehydrogenation of α -tetralol was carried out at different catalyst loadings, with Ru/KO*t*Bu = 1/5. At 0.4 mol% of Ru quantitative formation of ketone is attained in 3 h, whereas the employment of 0.08 and 0.04 mol% of **7** gives 96 and 93% conversion, respectively, after 21 h (Table 3).

Table 3. Catalytic dehydrogenation of α -tetralol at different loadings of **7** (KO*t*Bu/**7** = 5/1) in *t*BuOH at 130°C.

Complex 7 [mol %]	Conv. [%] ^[a]	Time [h]
0.4	98	3
0.08	96	21
0.04	93	21
0.02	80	46

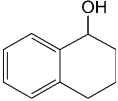
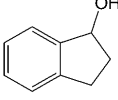
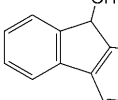
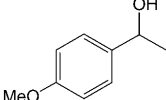
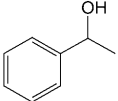
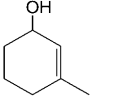
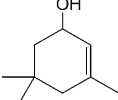
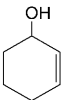
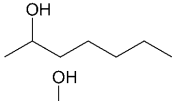
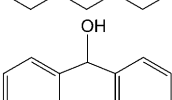
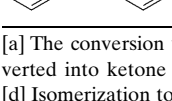
[a] The conversion was determined by GC analysis.

Finally, at 0.02 mol% of **7** α -tetralone (80%) is formed after 46 h, affording a turnover number (TON) of 4000 and suggesting that **7** can be used for the preparation of ketones. It is worth noting that complete dehydrogenation of α -tetralol (95% conversion in 2 h) was also achieved by using **7** (0.4 mol%), obtained in situ by treatment of [RuCl₂(PPh₃)₃] with dppf (1 h at 110°C) and ethylenediamine (1 h at 110°C) in *t*BuOH. By contrast, no conversion ($<1\%$) was observed under the same experimental conditions when using Me₂NCH₂CH₂NMe₂ instead of H₂NCH₂CH₂NH₂, which indicates that the N–H functionality is crucial for the fast catalytic dehydrogenation. These results differs from those obtained for the [RuCl₂(*p*-cymene)]/amine system, for which tertiary amines display higher activity than primary ones.^[4b]

Ruthenium and osmium complexes **7** and **13** (0.4 mol%) were efficient catalysts for the dehydrogenation of a number of alcohol substrates to the corresponding ketones at 130°C, achieving TOF values up to 300 h⁻¹. As a matter of fact, quantitative conversion of α -tetralol into α -tetralone is achieved with **7** and **13** in 3 and 6 h with TOF = 200 and 80 h⁻¹, respectively (Table 4).

The cyclic 1-indanol and fluorenol were also dehydrogenated with 88–99% conversion, ruthenium being faster than osmium. The ketone 4-methoxyacetophenone was formed quantitatively (up to 97%) with **7** in 4 h and with **13** in 20 h, starting from the corresponding alcohol. Notably, 1-phenylethanol, which exhibits a higher redox potential than 4-methoxy-1-phenylethanol, led to 58 and 68% of ketone with **7** and **13** after 20 h, respectively. Also the cyclic 3-methyl-2-cyclohexenol was rapidly converted to ketone (92% in 2 h) with TOF = 300 h⁻¹ by using **7**, whereas with **13** the reaction was considerably slower. Complete dehydrogenation was

Table 4. Dehydrogenation of alcohols with catalysts **7** and **13** (0.4 mol %) in the presence of KO*t*Bu (2 mol %) in *t*BuOH at 130 °C.

Alcohol	Complex 7			Complex 13		
	conv. [%] ^[a]	time [h]	TOF [h ⁻¹] ^[b]	conv. [%] ^[a]	time [h]	TOF [h ⁻¹] ^[b]
	98	3	200	98	6	80
	95	7	100	98	6	50
	99 ^[c]	5	95	88 ^[c]	20	20
	97	4	130	96	20	40
	58	20	–	68	20	–
	92	2	300	82	20	30
	95	2	120	97	20	70
	86 ^[d]	5	100	91 ^[d]	2	220
	72 ^[e]	45	–	91 ^[e]	20	15
	73	20	–	40	30	–
	5	20	–	41	30	–

[a] The conversion was determined by GC and NMR analyses. [b] Turnover frequency (moles of alcohol converted into ketone per mole of catalyst per hour) at 50% conversion. [c] Substrate/catalyst/KO*t*Bu = 125:1:5. [d] Isomerization to cyclohexanone. [e] Substrate/catalyst/KO*t*Bu = 50:1:5.

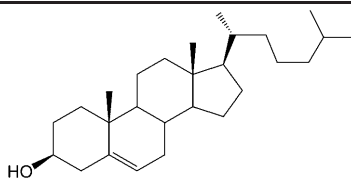
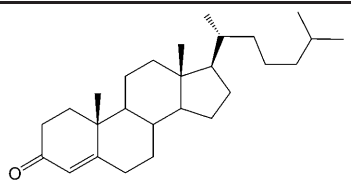
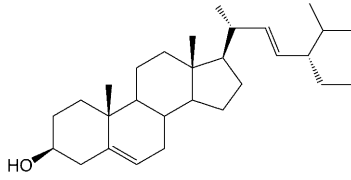
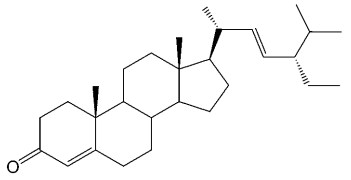
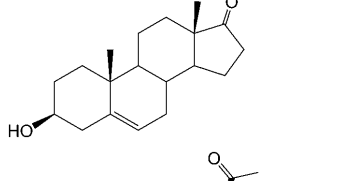
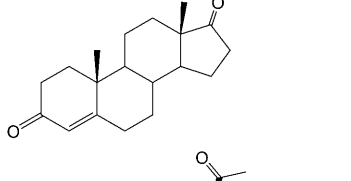
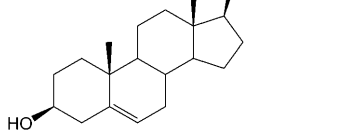
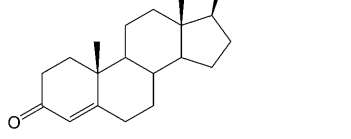
also observed with 3,5,5-trimethyl-2-cyclohexenol, achieving 95 and 97% conversion with **7** and **13** in 2 and 20 h, respectively. It should be pointed out that the unfunctionalized alcohol 2-cyclohexenol isomerizes to cyclohexanone (86%) in 5 h with **7**, whereas the osmium complex **13** gave 91% conversion in 2 h. In addition, the substrate 2-heptanol was converted (72%) into 2-heptanone with **7** in 45 h, whereas **13** led to 91% conversion in 20 h. On the other hand, 3-heptanone was obtained from 3-heptanol (73% conversion in 20 h) with **7**, whereas with **13** poor conversion was observed (40% in 30 h). Finally, **7** was found to be almost inactive in

the dehydrogenation of benzhydrol, whereas **13** led to poor conversion (41% in 30 h). The comparison of the GC and NMR data for these reactions showed that the yield is much the same as the conversion and that the reactions occur with high selectivity.

Steroidal compounds containing the 4-en-3-one functionality, such as progesterone, have been prepared by oxidation of 5-en-3 β -hydroxy steroids with concomitant C=C double-bond isomerization. Different routes, including the use of Cr^{VI},^[20a,b] MnO₂,^[20c] and the Oppenauer oxidation with ketones mediated by [Al(O*i*Pr)₃], have been described.^[21] In the middle of the 1990s Bäckvall et al. reported the oxidation of sterols by using acetone as oxidant through a hydrogen-transfer reaction, catalyzed by [RuCl₂(PPh₃)₃] and [Ru₂(CO)₄(μ -H)][(η^5 -C₄Ph₄CO)₂H] complexes.^[22] Interestingly, the ruthenium and osmium derivatives **7** and **13** in the presence of KO*t*Bu have proven to efficiently catalyze the dehydrogenation of sterols in *t*BuOH/toluene mixture at 145 °C (bath temperature; Table 5).

The compound cholest-4-en-3-one is formed quantitatively in 20 h by heating cholest-5-en-3 β -ol (Table 5, entry 1) with **7** (0.8 mol %) and KO*t*Bu (4 mol %), as inferred from ¹H and ¹³C NMR analyses, thus showing that this reaction occurs with excellent selectivity without formation of side products. Complete conversion of this 3-hydroxy sterol, which displays a very low redox potential (0.063 V),^[12] is also obtained with the osmium derivative **13**. In addition, cholest-4-en-3-one is also formed (90% conversion in 20 h) by using complex **7** in polyethylene glycol (PEG, 3400 MW) as reaction medium. Stigmasterol is dehydrogenated with **7** in *t*BuOH/toluene, affording 80% conversion after 36 h, whereas with **13** quantitative conversion is achieved after 20 h (Table 5, entry 2). With **7**, androstenedone is formed from *trans*-dehydroandrosterone in low amount (45% conversion in 46 h), whereas **13** afforded a higher conversion

Table 5. Catalytic dehydrogenation of sterols with complexes **7** and **13** (0.8 mol %) in the presence of KO^tBu (4 mol %) in *t*BuOH/toluene (2:1, v/v) at 145 °C.

Entry	Substrate	Product	Complex 7			Complex 13		
			conv. [%] ^[a]	time [h]	TOF [h ⁻¹] ^[b]	conv. [%] ^[a]	time [h]	TOF [h ⁻¹] ^[b]
1			> 98 ^[c]	20	15	> 98 ^[c]	20	15
2			80	36	5	> 98 ^[c]	20	8
3			45	46	–	86	20	6
4			87	20	11	95	20	25

[a] The conversion was determined by ¹H and ¹³C NMR analysis. [b] Turnover frequency (moles of alcohol converted into ketone per mole of catalyst per hour) at 50% conversion. [c] No signal of the starting material was observed.

(86% in 20 h; Table 5, entry 3). Interestingly, pregnenolone was also efficiently oxidized to progesterone after 20 h with 87 and 95% conversion when using **7** and **13**, respectively (Table 5, entry 4). These results indicate that osmium led to a better conversion with respect to the analogous ruthenium complex, which may be ascribed to the stronger thermal stability of the Os species relative to Ru, the deactivation being retarded. Apparently, this is the first report on the catalytic dehydrogenation of sterols promoted by a transition-metal complex, without using an oxidizing agent.

To show the potential of these dehydrogenation catalysts for synthetic applications, a few ketones were prepared. Thus, 1-indanone, α -tetralone, and 4-methoxyacetophenone were isolated in 80, 83, and 77% yield by using **7** (0.4 mol %) at 130 °C, starting from the corresponding alcohols. In addition, cholest-4-en-3-one was obtained from cholest-5-en-3 β -ol by using **7** (0.8 mol %) at 145 °C and isolated in 90% yield, in agreement with the high selectivity of this process.

As regards the catalytic cycle, it is likely that the mechanism may resemble that proposed for the reverse hydrogenation reaction with ruthenium, which entails the dihydride species [MH₂(PP)(diamine)] (M = Ru, Os) and the N–H functionality.^[23]

These results indicate that the ruthenium and osmium complexes [RuCl₂(PP)(ampy)] and [MCl₂(PP)(diamine)]

(M = Ru, Os), which are among the most active catalysts for transfer hydrogenation and hydrogenation of ketones, also display high activity in the reverse reaction of dehydrogenation of alcohols. Because complexes **7–9** and **13** can be easily obtained from commercially available ligands through a straightforward synthesis, these systems may find applications in the synthesis of ketones by dehydrogenation.

Conclusion

In summary, we have found that the pincer [MCl(dpp)(CNN)(diphosphane)] and [MCl₂(diphosphane)(L)] (M = Ru, Os; L = bidentate nitrogen ligand) complexes, which contain the N–H functionality, are catalysts for the oxidation of alcohols through acceptorless dehydrogenation. Particularly active are the compounds [MCl₂(dppf)(en)] (M = Ru **7**, Os **13**), which efficiently dehydrogenate several substrates, including cyclic and linear alcohols, by using 0.8–0.04 mol % of Ru or Os catalyst at 130–145 °C. The comparison of the reactivity of the Ru and Os systems shows that although **7** gives generally faster reduction than **13**, the latter derivative displays higher activity in the oxidation of 5-en-3 β -hydroxy steroids. These investigations indicate that Os can be efficiently employed in the alcohol dehydrogenation reaction and is a valid complement to Ru. Studies are under way to

broaden the scope of these complexes for other catalytic transformations, including hydrogen-borrowing reactions, through alcohol activation.

Experimental Section

General: All reactions were carried out under an argon atmosphere by using standard Schlenk techniques. The solvents were carefully dried by standard methods and distilled under argon before use. The diphosphanes, the nitrogen ligands, and all other chemicals were purchased from Aldrich and Strem and used without further purification. The compounds $[\text{MCl}_2(\text{PPh}_3)_3]$ ($\text{M} = \text{Ru}$,^[24] Os ^[25]), $[\text{RuCl}_2(\text{dppb})(\text{PPh}_3)_2]$,^[26] and **1**,^[15a] **2**,^[16b] **3**,^[16a] **4**,^[16b] **6**,^[27] **7**,^[10] and **13**^[17] were prepared according to the literature procedure. NMR measurements were recorded on a Bruker AC 200 spectrometer and the chemical shifts, in ppm, are relative to TMS for ^1H and $^{13}\text{C}\{^1\text{H}\}$, and 85% H_3PO_4 for $^{31}\text{P}\{^1\text{H}\}$. Elemental analyses (C, H, N) were carried out with a Carlo Erba 1106 elemental analyzer, whereas the GC analyses were performed with a Varian GP-3380 gas chromatograph.

Synthesis of *trans*-[RuCl₂(dppb)(*trans*-dach)] (5): $[\text{RuCl}_2(\text{dppb})(\text{PPh}_3)]$ (100 mg, 0.116 mmol) and (\pm)-*trans*-diaminocyclohexane (*trans*-dach; 13.9 μL , 0.116 mmol) were dissolved in dichloromethane (2.0 mL) and the solution was stirred for 24 h at room temperature. The resulting solution was concentrated (0.5 mL) and addition of heptane (2 mL) afforded a yellow precipitate, which was washed with 1-propanol (3×1 mL) and dried under reduced pressure. Yield: 68 mg (82%); ^1H NMR (200.1 MHz, CDCl_3 , 20°C): $\delta = 7.71\text{--}7.26$ (m, 20H; aromatic protons), 2.89 (m, 4H; CH_2P), 2.49 (m, 6H; CHN , NH_2), 1.67–1.49 (m, 8H; $\text{CH}_2\text{CH}_2\text{P}$, CH_2CH), 0.99 ppm (m, 4H; CH_2); $^{13}\text{C}\{^1\text{H}\}$ NMR (50.3 MHz, CDCl_3 , 20°C): $\delta = 133.1\text{--}127.5$ (m; aromatic carbons), 57.1 (s; CHNH_2), 35.7 (s; CH_2CH), 24.4 (s; CH_2), 24.3 (d, $J(\text{C,P}) = 29.0$ Hz; PCH_2), 22.0 ppm (s; CH_2); $^{31}\text{P}\{^1\text{H}\}$ NMR (81.0 MHz, CDCl_3 , 20°C): $\delta = 45.1$ ppm (s); elemental analysis calcd (%) for $\text{C}_{34}\text{H}_{42}\text{Cl}_2\text{N}_2\text{P}_2\text{Ru}$: C 57.30, H 5.94, N 3.93; found: C 57.15, H 5.73, N 3.60.

Synthesis of *trans*-[RuCl₂(dppf)(ampy)] (8): $[\text{RuCl}_2(\text{PPh}_3)_3]$ (200 mg, 0.209 mmol) and dppf (127 mg, 0.229 mmol) were treated with toluene (2.0 mL) and the suspension was stirred for 1 h at 50°C. After addition of ampy (23 μL , 0.223 mmol) the suspension was stirred for 2 h at 50°C and then concentrated to about 0.5 mL. Addition of heptane (2 mL) afforded a yellow precipitate, which was washed with heptane (3×1 mL) and diethyl ether (3×1 mL) and dried under reduced pressure. Yield: 160 mg (92%); ^1H NMR (200.1 MHz, CD_2Cl_2 , 20°C): $\delta = 8.51$ (m, 1H; *o*- $\text{C}_5\text{H}_4\text{N}$), 8.10 (pseudo t, $J(\text{H,H}) = 7.9$ Hz, 4H; aromatic protons), 7.60–7.03 (m, 18H; aromatic protons), 6.58 (t, $J(\text{H,H}) = 6.6$ Hz, 1H; aromatic proton), 4.73 (m, 2H; C_5H_4), 4.31 (m, 2H; CH_2NH_2), 4.22 (m, 2H; C_5H_4), 4.14 (m, 2H; C_5H_4), 4.03 (m, 2H; C_5H_4), 3.05 ppm (m, 2H; NH_2); $^{13}\text{C}\{^1\text{H}\}$ NMR (50.3 MHz, CD_2Cl_2 , 20°C): $\delta = 163.8$ (m, NCCH_2), 156.3 (d, $J(\text{C,P}) = 3.7$ Hz; NCH), 139.2–120.1 (m, aromatic carbons), 89.9 (dd, $J(\text{C,P}) = 46.0$ and 4.9 Hz; *ipso*- C_5H_4), 82.4 (dd, $J(\text{C,P}) = 46.8$ and 0.8 Hz; *ipso*- C_5H_4), 77.9 (d, $J(\text{C,P}) = 7.7$ Hz; C_5H_4), 75.7 (d, $J(\text{C,P}) = 7.1$ Hz; C_5H_4), 71.5 (d, $J(\text{C,P}) = 5.8$ Hz; C_5H_4), 69.1 (d, $J(\text{C,P}) = 5.0$ Hz; C_5H_4), 50.4 ppm (t, $J(\text{C,P}) = 2.3$ Hz; CH_2); $^{31}\text{P}\{^1\text{H}\}$ NMR (81.0 MHz, CD_2Cl_2 , 20°C): $\delta = 51.6$ (d, $J(\text{P,P}) = 38.3$ Hz), 40.9 ppm (d, $J(\text{P,P}) = 38.3$ Hz); elemental analysis calcd (%) for $\text{C}_{40}\text{H}_{36}\text{Cl}_2\text{FeN}_2\text{P}_2\text{Ru}$: C 57.57, H 4.35, N 3.36; found: C 58.32, H 4.43, N 3.16.

Synthesis of *cis*-[RuCl₂(dppf)(ampy)] (9): Compound **8** (120 mg, 0.144 mmol) was treated with toluene (2.0 mL), stirred for 24 h at 120°C, and then the suspension was dried under reduced pressure. Yield: 110 mg (92%); ^1H NMR (200.1 MHz, CD_2Cl_2 , 20°C): $\delta = 8.91$ (m, 1H; *o*- $\text{C}_5\text{H}_4\text{N}$), 8.49 (pseudo t, $J(\text{H,H}) = 7.8$ Hz, 2H; aromatic protons), 8.16 (pseudo t, $J(\text{H,H}) = 8.1$ Hz, 2H; aromatic protons), 7.64–6.70 (m, 18H; aromatic protons), 6.56 (s, 1H; aromatic proton), 4.95 (m, 1H; C_5H_4), 4.45 (m, 1H; C_5H_4), 4.22 (m, 1H; C_5H_4), 4.08 (m, 1H; C_5H_4), 3.96 (m, 1H; C_5H_4), 3.77–3.58 (m, 3H; CH_2N , C_5H_4), 3.32 (m, 1H; C_5H_4), 3.09 (m, 1H; CH_2N), 1.70 (m, 1H; NH_2), 1.57 ppm (m, 1H; NH_2); $^{13}\text{C}\{^1\text{H}\}$ NMR (50.3 MHz, CD_2Cl_2 , 20°C): $\delta = 158.6$ (m, NCCH_2), 151.0 (s, NCH), 137.7–

120.0 (m, aromatic carbons), 78.3 (d, $J(\text{C,P}) = 12.8$ Hz; C_5H_4), 77.6 (d, $J(\text{C,P}) = 8.4$ Hz; C_5H_4), 76.1 (d, $J(\text{C,P}) = 2.9$ Hz; C_5H_4), 74.9 (d, $J(\text{C,P}) = 6.9$ Hz; C_5H_4), 73.2 (d, $J(\text{C,P}) = 5.8$ Hz; C_5H_4), 70.6 (d, $J(\text{C,P}) = 3.9$ Hz; C_5H_4), 70.1 (d, $J(\text{C,P}) = 5.5$ Hz; C_5H_4), 69.9 (d, $J(\text{C,P}) = 5.6$ Hz; C_5H_4), 52.2 ppm (d, $J(\text{C,P}) = 2.6$ Hz; CH_2); $^{31}\text{P}\{^1\text{H}\}$ NMR (81.0 MHz, CD_2Cl_2 , 20°C): $\delta = 57.8$ (d, $J(\text{P,P}) = 35.6$ Hz), 44.2 ppm (d, $J(\text{P,P}) = 35.6$ Hz); elemental analysis calcd (%) for $\text{C}_{40}\text{H}_{36}\text{Cl}_2\text{FeN}_2\text{P}_2\text{Ru}$: C 57.57, H 4.35, N 3.36; found: C 57.14, H 4.25, N 3.17.

Synthesis of *trans*-[RuCl₂(dppb)(ae)] (10): $[\text{RuCl}_2(\text{dppb})(\text{PPh}_3)]$ (150 mg, 0.174 mmol) and 2-aminoethanol (12 μL , 0.200 mmol) were treated with toluene (2.0 mL). The suspension was stirred for 2 h at 60°C and concentrated to 0.5 mL. Addition of heptane (2 mL) afforded a yellow precipitate, which was washed with heptane (3×1 mL) and diethyl ether (3×1 mL) and dried under reduced pressure. Yield: 98 mg (85%); ^1H NMR (200.1 MHz, CD_2Cl_2 , 20°C): $\delta = 7.69\text{--}7.18$ (m, 20H; aromatic protons), 3.86 (br s, 2H; CH_2OH), 3.53 (br s, 1H; OH), 2.93 (br s, 2H; CH_2N), 2.69 (br s, 6H; CH_2P , NH_2), 1.65 (br s, 2H; $\text{CH}_2\text{CH}_2\text{P}$), 1.56 ppm (br s, 2H; $\text{CH}_2\text{CH}_2\text{P}$); $^{31}\text{P}\{^1\text{H}\}$ NMR (81.0 MHz, CD_2Cl_2 , 20°C): $\delta = 59.5$ (d, $J(\text{P,P}) = 42.7$ Hz), 44.4 ppm (d, $J(\text{P,P}) = 42.7$ Hz); elemental analysis calcd (%) for $\text{C}_{30}\text{H}_{35}\text{Cl}_2\text{NOP}_2\text{Ru}$: C 54.63, H 5.35, N 2.12; found: C 54.38, H 5.61, N 2.15.

Synthesis of [OsCl₂(dppb)(*trans*-dach)] (11): $[\text{OsCl}_2(\text{PPh}_3)_3]$ (150 mg, 0.143 mmol) and dppb (70 mg, 0.164 mmol) were treated with mesitylene (2.0 mL) and the suspension was stirred for 2 h at room temperature. *Trans*-dach (18 μL , 0.150 mmol) was added and the resulting suspension was stirred at 135°C for 4 h and concentrated to 0.5 mL. Addition of heptane (2 mL) afforded a dark-green precipitate, which was washed with heptane (3×1 mL) and diethyl ether (3×1 mL) and dried under reduced pressure. Yield: 72 mg (63%); ^1H NMR (200.1 MHz, CD_2Cl_2 , 20°C): $\delta = 8.00\text{--}6.90$ (m; aromatic protons), 3.98–0.90 (m; CH, CH_2 , NH_2); $^{31}\text{P}\{^1\text{H}\}$ NMR (81.0 MHz, CD_2Cl_2 , 20°C): $\delta = -2.7$ (d, $J(\text{P,P}) = 13.4$ Hz, major *cis* complex), -11.7 (d, $J(\text{P,P}) = 13.4$ Hz), -2.2 (d, $J(\text{P,P}) = 13.3$ Hz, minor *cis* complex), -12.8 (d, $J(\text{P,P}) = 13.3$ Hz), -11.7 ppm (s; *trans* complex); elemental analysis calcd (%) for $\text{C}_{34}\text{H}_{42}\text{Cl}_2\text{N}_2\text{OsP}_2$: C 50.93, H 5.28, N 3.49; found: C 49.96, H 5.44, N 3.48.

Synthesis of *trans*-[OsCl₂(dppf)(*trans*-dach)] (12): $[\text{OsCl}_2(\text{PPh}_3)_3]$ (200 mg, 0.191 mmol) and dppf (117 mg, 0.211 mmol) were treated with toluene (3.0 mL) and the suspension was heated at reflux for 4 h. After addition of *trans*-dach (23.0 μL , 0.191 mmol) the yellow suspension was stirred for 24 h at RT and then concentrated to 0.5 mL. Addition of heptane (2 mL) afforded a yellow precipitate, which was washed with heptane (3×1 mL) and diethyl ether (3×1 mL) and dried under reduced pressure. Yield: 130 mg (73%); ^1H NMR (200.1 MHz, CD_2Cl_2 , 20°C): $\delta = 7.79\text{--}7.10$ (m, 20H; aromatic protons), 4.60 (s, 2H; C_5H_4), 4.55 (s, 2H; C_5H_4), 4.16 (s, 4H; C_5H_4), 3.10 (d, $J(\text{H,H}) = 8.9$ Hz, 2H; NH_2), 2.86 (t, $J(\text{H,H}) = 9.0$ Hz, 2H; NH_2), 2.61 (m, 2H; CH), 1.71 (m, 2H; CH_2), 1.47 (m, 2H; CH_2), 1.05 ppm (m, 4H; CH_2); $^{13}\text{C}\{^1\text{H}\}$ NMR (50.3 MHz, CD_2Cl_2 , 20°C): $\delta = 140.9$ (m; *ipso* aromatic carbons), 140.1 (m; *ipso* aromatic carbons), 134.7 (t, $J(\text{C,P}) = 4.8$ Hz; aromatic carbons), 134.3 (t, $J(\text{C,P}) = 4.9$ Hz; aromatic carbons), 129.1–127.2 (m; aromatic carbons), 90.2 (dd, $J(\text{C,P}) = 60.9$ and 5.6 Hz; *ipso*- C_5H_4), 76.5 (t, $J(\text{C,P}) = 3.9$ Hz; C_5H_4), 76.3 (t, $J(\text{C,P}) = 3.8$ Hz; C_5H_4), 74.1 (br s; C_5H_4), 70.1 (s; C_5H_4), 57.9 (s; CHNH_2), 35.6 (s; CH_2), 25.0 ppm (s; CH_2); $^{31}\text{P}\{^1\text{H}\}$ NMR (81.0 MHz, CD_2Cl_2 , 20°C): $\delta = -9.9$ ppm (s); elemental analysis calcd (%) for $\text{C}_{40}\text{H}_{42}\text{Cl}_2\text{FeN}_2\text{OsP}_2$: C 51.68, H 4.55, N 3.01; found: C 50.96, H 4.63, N 2.87.

Procedure for the catalytic dehydrogenation of alcohols: The Ru or Os complex (0.01 mmol) was dissolved in *t*BuOH (2 mL). After addition of the alcohol substrate (2.5 mmol) and $\text{KO}t\text{Bu}$ (0.05 mmol) the solution was heated at 130°C (bath temperature) under argon in an open system and the conversion was determined by GC and NMR analyses, which revealed the absence of side products (Ru or Os 0.4 mol%, $\text{KO}t\text{Bu}$ 2 mol%).

Procedure for the catalytic dehydrogenation of 3 β -hydroxy steroids: The ruthenium **7** or osmium **13** complex (0.01 mmol), the sterol substrate (1.25 mmol), and $\text{KO}t\text{Bu}$ (0.05 mmol) were dissolved in *t*BuOH (2 mL) and toluene (1 mL). The solution was heated at 145°C (bath temperature) under argon in an open system and the conversion into the 4-en-3-

one derivative was determined by ^1H and ^{13}C NMR analysis (Ru or Os 0.8 mol %, KOtBu 4 mol %).

Preparation of 1-indanone: Complex **7** (7.9 mg, 0.01 mmol) was dissolved in *t*BuOH (2 mL). After addition of 1-indanol (335 mg, 2.5 mmol) and KOtBu (5.6 mg, 0.05 mmol) the solution was heated at 130 °C (bath temperature) under argon in an open system for 7 h. Diethyl ether was added to the solution (1:1, v/v), the mixture was filtered through a short celite pad, and the solvent was evaporated. The product was purified by flash chromatography ($\text{CH}_2\text{Cl}_2/\text{ether}=30:1$) to give the ketone (265 mg, 80% yield).

Preparation of α -tetralone: The ketone α -tetralone was obtained by following the procedure used for 1-indanone but using α -tetralol and heating the solution for 4 h to afford the product (302 mg, 83% yield).

Preparation of 4-methoxyacetophenone: The ketone 4-methoxyacetophenone was obtained by following the procedure used for 1-indanone but using 4-methoxy-1-phenylethanol and heating the solution for 5 h to afford the product (290 mg, 77% yield).

Preparation of cholest-4-en-3-one: Complex **7** (7.9 mg, 0.01 mmol) was dissolved in *t*BuOH (2 mL) and toluene (1 mL). After addition of cholest-5-en-3 β -ol (483 mg, 1.25 mmol) and KOtBu (0.05 mmol) the solution was heated at 145 °C (bath temperature) under argon in an open system for 20 h. Diethyl ether was added to the solution (1:1, v/v), the mixture was filtered through a short celite pad, and the solvent was evaporated to give the ketone (435 mg, 90% yield).

Acknowledgements

This work was supported by the Ministero dell'Università e della Ricerca (MIUR) and the Regione Friuli Venezia Giulia. We thank Johnson–Matthey/Alfa Aesar for a generous loan of ruthenium, and Mr. P. Polese for carrying out the elemental analyses.

- [1] a) T. C. Johnson, D. J. Morris, M. Wills, *Chem. Soc. Rev.* **2010**, 39, 81; b) G. E. Dobreiner, R. H. Crabtree, *Chem. Rev.* **2010**, 110, 681; c) A. Friedrich, S. Schneider, *ChemCatChem* **2009**, 1, 72; d) B. Loges, H. Junge, B. Spilker, C. Fischer, M. Beller, *Chem. Ing. Tech.* **2007**, 79, 741; e) M. H. S. A. Hamid, P. A. Slatford, J. M. J. Williams, *Adv. Synth. Catal.* **2007**, 349, 1555; f) A. J. Esswein, D. G. Nocera, *Chem. Rev.* **2007**, 107, 4022; g) J. H. Choi, N. Kim, Y. J. Shin, J. H. Park, J. Park, *Tetrahedron Lett.* **2004**, 45, 4607; h) C. P. Casey, J. B. Johnson, S. W. Singer, Q. Cui, *J. Am. Chem. Soc.* **2005**, 127, 3100.
- [2] A. Dobson, S. D. Robinson, *Inorg. Chem.* **1977**, 16, 137.
- [3] a) D. Morton, D. J. Cole-Hamilton, *J. Chem. Soc. Chem. Commun.* **1988**, 1154; b) D. Morton, D. J. Cole-Hamilton, I. D. Utuk, M. Panque-Sosa, M. Lopez-Poveda, *J. Chem. Soc. Dalton Trans.* **1989**, 489.
- [4] a) H. Junge, M. Beller, *Tetrahedron Lett.* **2005**, 46, 1031; b) H. Junge, B. Loges, M. Beller, *Chem. Commun.* **2007**, 522.
- [5] G. B. W. L. Lighthart, R. H. Meijer, M. P. J. Donners, J. Meuldijk, J. A. J. M. Vekemans, L. A. Hulshof, *Tetrahedron Lett.* **2003**, 44, 1507.
- [6] J. van Buijtenen, J. Meuldijk, J. A. J. M. Vekemans, L. A. Hulshof, H. Koojiman, A. L. Spek, *Organometallics* **2006**, 25, 873.
- [7] G. R. A. Adair, J. M. J. Williams, *Tetrahedron Lett.* **2005**, 46, 8233.
- [8] a) J. Zhang, M. Gandelman, L. J. W. Shimon, H. Rozenberg, D. Milstein, *Organometallics* **2004**, 23, 4026; b) J. Zhang, M. Gandelman, L. J. W. Shimon, D. Milstein, *Dalton Trans.* **2007**, 107.
- [9] a) J. Zhang, G. Leitus, Y. Ben-David, D. Milstein, *J. Am. Chem. Soc.* **2005**, 127, 10840; b) C. Gunanathan, L. J. W. Shimon, D. Milstein, *J. Am. Chem. Soc.* **2009**, 131, 3146.
- [10] J. Zhao, J. F. Hartwig, *Organometallics* **2005**, 24, 2441.
- [11] a) K.-I. Fujita, N. Tanino, R. Yamaguchi, *Org. Lett.* **2007**, 9, 109; b) C. Crotti, J. Kaspar, E. Farnetti, *Green Chem.* **2010**, 12, 1295.
- [12] H. Adkins, R. M. Eloffson, A. G. Rossow, C. C. Robinson, *J. Am. Chem. Soc.* **1949**, 71, 3622.
- [13] a) W. Baratta, E. Herdtweck, K. Siega, M. Toniutti, P. Rigo, *Organometallics* **2005**, 24, 1660; b) W. Baratta, G. Chelucci, E. Herdtweck, S. Magnolia, K. Siega, P. Rigo, *Angew. Chem.* **2007**, 119, 7795; *Angew. Chem. Int. Ed.* **2007**, 46, 7651; c) T. Ohkuma, C. A. Sandoval, R. Srinivasan, Q. Lin, Y. Wei, K. Muñiz, R. Noyori, *J. Am. Chem. Soc.* **2005**, 127, 8288.
- [14] W. Baratta, M. Ballico, A. Del Zotto, K. Siega, S. Magnolia, P. Rigo, *Chem. Eur. J.* **2008**, 14, 2557.
- [15] a) W. Baratta, G. Chelucci, S. Gladiali, K. Siega, M. Toniutti, M. Zannette, E. Zangrando, P. Rigo, *Angew. Chem.* **2005**, 117, 6370; *Angew. Chem. Int. Ed.* **2005**, 44, 6214; b) W. Baratta, K. Siega, P. Rigo, *Adv. Synth. Catal.* **2007**, 349, 1633; c) W. Baratta, G. Chelucci, S. Magnolia, K. Siega, P. Rigo, *Chem. Eur. J.* **2009**, 15, 726; d) W. Baratta, M. Ballico, A. Del Zotto, E. Herdtweck, S. Magnolia, R. Peloso, K. Siega, M. Toniutti, E. Zangrando, P. Rigo, *Organometallics* **2009**, 28, 4421; e) W. Baratta, L. Fanfoni, S. Magnolia, K. Siega, P. Rigo, *Eur. J. Inorg. Chem.* **2010**, 1419; f) W. Baratta, F. Benedetti, A. Del Zotto, L. Fanfoni, F. Felluga, S. Magnolia, E. Putignano, P. Rigo, *Organometallics* **2010**, 29, 3563.
- [16] a) W. Baratta, M. Ballico, G. Chelucci, K. Siega, P. Rigo, *Angew. Chem.* **2008**, 120, 4434; *Angew. Chem. Int. Ed.* **2008**, 47, 4362; b) W. Baratta, M. Ballico, S. Baldino, G. Chelucci, E. Herdtweck, K. Siega, S. Magnolia, P. Rigo, *Chem. Eur. J.* **2008**, 14, 9148.
- [17] W. Baratta, C. Barbato, S. Magnolia, K. Siega, P. Rigo, *Chem. Eur. J.* **2010**, 16, 3201.
- [18] a) R. Noyori, T. Ohkuma, *Angew. Chem.* **2001**, 113, 40; *Angew. Chem. Int. Ed.* **2001**, 40, 40; b) H. Doucet, T. Ohkuma, K. Murata, T. Yokozawa, M. Kozawa, E. Katayama, A. F. England, T. Ikariya, R. Noyori, *Angew. Chem.* **1998**, 110, 1792; *Angew. Chem. Int. Ed.* **1998**, 37, 1703.
- [19] M. L. S. Almeida, M. Beller, G. Z. Wang, J. E. Bäckvall, *Chem. Eur. J.* **1996**, 2, 1533.
- [20] a) L. F. Fieser, M. Fieser, *Steroids*, Reinhold, New York, **1959**; b) G. H. Rasmusson, G. E. Arth in *Organic Reactions in Steroid Chemistry, Vol 1* (Eds.: J. Fried, J. A. Edwards), Van Nostrand, New York, **1972**, p. 222; c) U. Karlsson, G. Z. Wang, J. E. Bäckvall, *J. Org. Chem.* **1994**, 59, 1196.
- [21] a) C. Djerassi, *Org. React.* **1951**, 6, 207; b) R. Skoda-Földes, L. Kollár, *Chem. Rev.* **2003**, 103, 4095.
- [22] M. L. S. Almeida, P. Kočovský, J. E. Bäckvall, *J. Org. Chem.* **1996**, 61, 6587.
- [23] a) K. Abdur-Rashid, S. E. Clapham, A. Hadzovic, J. N. Harvey, A. J. Lough, R. H. Morris, *J. Am. Chem. Soc.* **2002**, 124, 15104; b) C. A. Sandoval, T. Ohkuma, K. Muñiz, R. Noyori, *J. Am. Chem. Soc.* **2003**, 125, 13490; c) R. J. Hamilton, S. H. Bergens, *J. Am. Chem. Soc.* **2006**, 128, 13700.
- [24] T. A. Stephenson, G. Wilkinson, *J. Inorg. Nucl. Chem.* **1966**, 28, 945.
- [25] G. P. Elliott, N. M. McAuley, W. R. Roper, *Inorg. Synth.* **1989**, 26, 184.
- [26] C. W. Jung, P. E. Garrou, P. R. Hoffman, K. G. Caulton, *Inorg. Chem.* **1984**, 23, 726.
- [27] G. Ma, R. McDonald, M. Ferguson, R. G. Cavell, B. O. Patrick, B. R. James, T. Q. Hu, *Organometallics* **2007**, 26, 846.

Received: October 19, 2010
Published online: February 21, 2011