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Osmium-catalyzed reduction processes

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Catalytic reduction processes are of vital importance in organic chemistry. Numerous reactions catalyzed by palladium, rhodium, ruthenium, iridium and platinum complexes have been developed. Meanwhile, the use of osmium compounds as catalysts for reduction reactions has received surprisingly little attention, although they can effectively accelerate some processes. In some cases, osmium catalysts are superior to related ruthenium compounds both in activity of the catalytic system and in stability of the catalyst *per se*. This review systematically summarizes reductive transformations catalyzed by organometallic osmium complexes. General trends in this research area followed in the literature are described and prospects in this field of chemistry are discussed. The hydrogen transfer and borrowing hydrogen reactions, hydrogenation, hydroformylation, reductive amination, and water-gas shift reactions are considered.
The bibliography includes 96 references.

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1. Introduction

Osmium and its compounds are extensively used in various fields of chemistry.[1–9] In organic synthesis, these compounds are in demand mainly due to the unique oxidizing properties of OsO_4,[10, 11] in particular, underlying the well-established Sharpless asymmetric dihydroxylation method.

However, in addition to well-known oxidation processes,[12] osmium can also catalyze various reduction reactions. There are a number of reviews [13–19] covering different aspects of the chemistry of osmium derivatives. These reviews either focused on specific types of osmium complexes or covered narrow research on catalytic applications. In this review, we tried to collect as much data as possible

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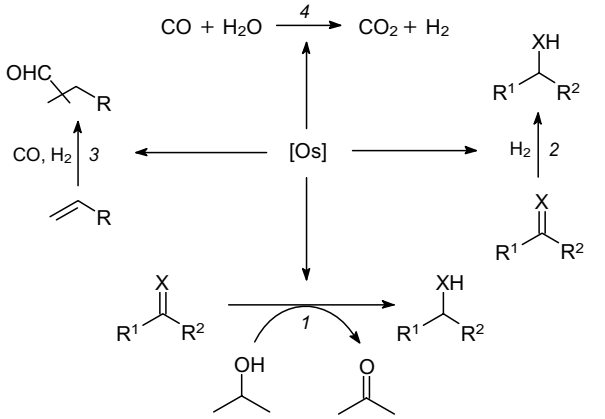
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on the osmium-catalyzed reduction processes without being confined to particular types of complexes or specific transformations. Our purpose was to provide the most comprehensive insight into the current state and development of this little little known but very promising area of chemistry. Examples of reduction reactions, which can be catalyzed by osmium compounds, are presented in Scheme 1.

Scheme 1



X = O, NAlk, NAr, $CAlk_2$; R, R^1 = Alk, Ar; R^2 = Alk

This review addresses the reduction reactions occurring *via* the hydrogen transfer (*1*), hydrogenation (*2*), hydroformylation (*3*) and water-gas shift (*4*) and also some other osmium-catalyzed reductive transformations.

2. Hydrogen transfer reactions using alcohols as reducing agents

Carbonyl compounds are of critical importance in organic synthesis. Therefore, the development of approaches to their modification continues to be a challenge. The reduction of carbonyl compounds, *e.g.*, *via* the hydrogen transfer (see Scheme 1, reaction *1*) hold a special place among such transformations. This reaction is generally carried out in the presence of a catalyst and a base or another additive necessary to activate the catalyst. Isopropyl alcohol is most commonly used as the hydrogen source. An important advantage of this reaction is the possibility of carrying it out in an enantioselective fashion with an optimal catalyst.

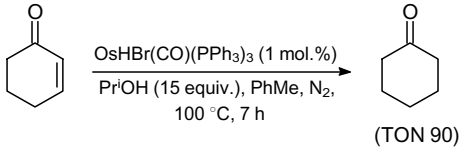
Most of the catalytic systems used for the reduction of carbonyl compounds are based on ruthenium, rhodium or iridium.[20] Meanwhile, osmium systems, despite their great potential, are still neglected.

2.1. Catalysis by osmium complexes with hydrides and molecular hydrogen

In 1985, Sánchez-Delgado *et al.*[21] studied the catalytic activity of the complex $OsHBr(CO)(PPh_3)_3$. It was demonstrated that under hydrogen transfer conditions using isopropyl alcohol as the reducing agent, the reduction of cyclohex-2-en-1-one gives cyclohexanone as the major product (Scheme 2).

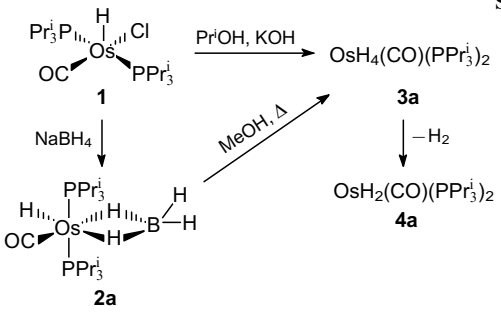
During the long-term study of osmium complexes, Esteruelas *et al.*[22] found that 16-electron compound **1**, being treated with sodium borohydride, first affords complex **2a**, which is transformed into product **3a** in the presence of methanol. A direct reaction between compound **1** and potassium hydroxide in isopropyl alcohol also produces 18-electron hydride complex **3a**, capable of releasing molecular hydrogen to give coordinatively unsaturated complex **4a** (Scheme 3).

Scheme 2



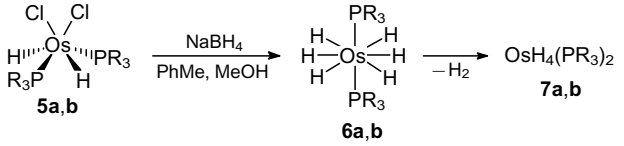
TON is turn-over number

Scheme 3



Similar transformations involving saturated complexes **5a**,**b** produce hydride complexes **6a**,**b**, which can release hydrogen to furnish reactive species **7a**,**b** (Scheme 4).[23]

Scheme 4



R_3 = Pr^i_3 (**a**), $MeBu^t_2$ (**b**)

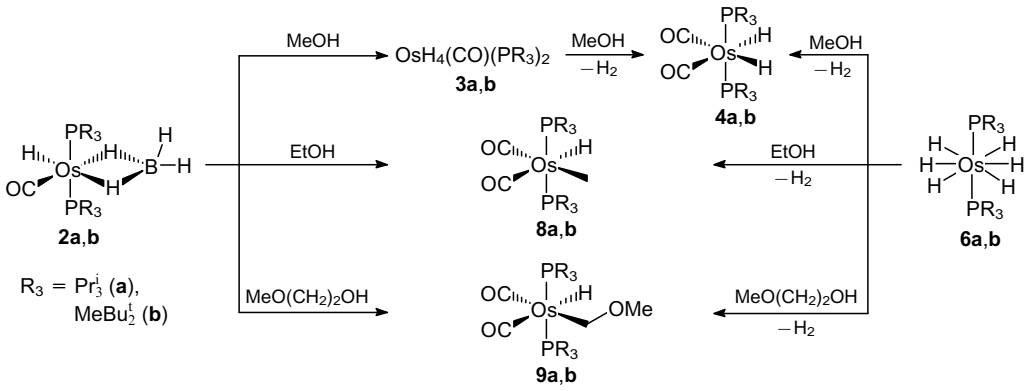
Werner and co-workers[23] also found that the reaction of complexes **2a**,**b** with primary alcohols containing two or more carbon atoms involves the alkylation of the osmium atom. When using methanol, the reacton first affords hydride complexes **3a**,**b** followed by their conversion into compounds **4a**,**b**, in which the second carbonyl ligand is formed as a result of dehydration of the starting alcohol. Complexes **6a**,**b** undergo similar processes to give compounds **8a**,**b** and **9a**,**b** (Scheme 5).[24]

It was shown[22,25] that the use of complex **1** as a pre-catalyst enables the catalytic reduction of double bonds *via* the hydrogen transfer (Schemes 6, 7). It should be noted that in these processes, osmium complexes exhibit a lower activity than their ruthenium counterparts.

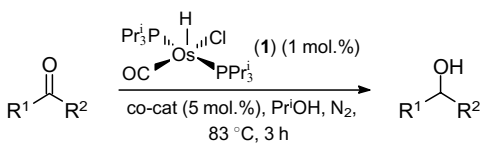
Besides, Werner and co-workers[23,26] showed that osmium complexes **5a**,**b** (Scheme 8) and **10a** (Scheme 9) can also serve as pre-catalysts for the hydrogen transfer reaction, the activity of the catalytic system dramatically increasing upon the addition of $NaBH_4$. For 3-methylcyclohexanone, the process is completed within 15 min. As can be seen from Scheme 9, complexes **10b**,**c** show little catalytic activity, which is attributed to the high acceptor capacity of ester functionalities involved in the ligands.

When attempting to use alcohols other than isopropyl alcohol, the hydrogen transfer reaction hardly ever occurs (Scheme 10).[24] In this case, compounds **1** first generate *in situ* an active species being able to participate in side

Scheme 5

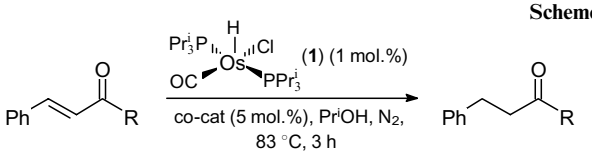


Scheme 6



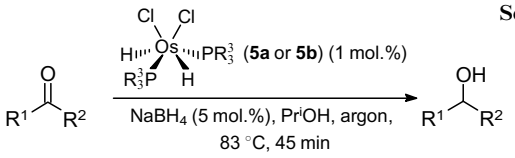
R^1	R^2	Co-catalyst	Yield (in %) or TON
Ph	Me	KOH or $NaBH_4$	37
	$(CH_2)_5$	KOH	67
	$(CH_2)_5$	$NaBH_4$	58

Scheme 7



R	Co-catalyst	Time, h	Yield (in %) or TON
Me	–	24	28
Me	$NaBH_4$	1	45
Ph	–	24	20
Ph	$NaBH_4$	1	15

Scheme 8

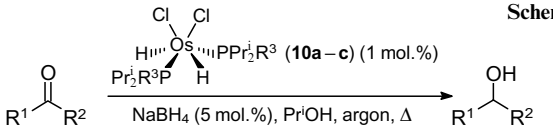


R^3_3 = Pr^i_3 (**a**), $MeBu^t_2$ (**b**)

R^1	R^2	Yield (in %) or TON	
		5a	**5b**
Ph	Me	47	23
	$(CH_2)_5$	93	92
	$CH(Me)(CH_2)_4$	37	22
	$CH_2CH(Me)(CH_2)_3$	82	86
	$(CH_2)_2CH(Me)(CH_2)_2$	90	88

processes to yield complexes of types **3**, **4**, **8** and **9**, which were found to possess low catalytic activity in the said reaction.

Scheme 9

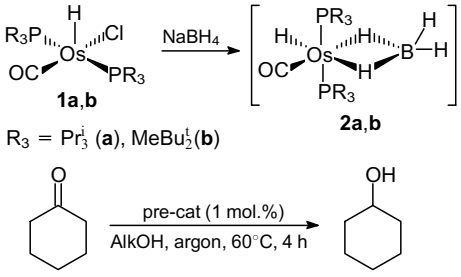


10: R^3 = $(CH_2)_2OMe$ (**a**), CH_2CO_2Me (**b**), CH_2CO_2Et (**c**)

R^1	R^2	Pre-catalyst	Time, h	Yield (in %) or TON
	$(CH_2)_5$	**5a**	15	98
	$(CH_2)_5$	**10a**	5	98
	$(CH_2)_5$	**10b**	360	25
	$(CH_2)_5$	**10c**	360	27
Ph	Me	**5a**	120	60
Ph	Me	**10a**	120	63
Ph	Me	**10b**	120	4 (25) [a]
Ph	Me	**10c**	120	17

[a] The yield is indicated, the TON value is given in parentheses.

Scheme 10



The authors proposed two similar mechanisms for the reduction of carbonyl compounds (Fig. 1 *a*)[27] and C=C bonds in α,β-unsaturated compounds (Fig. 1 *b*).[25] Both routes involve the β-elimination of osmium isoproxides with theregeneration of the Os–H bond necessary for hydrogenation.

Werner's research team[28] reported two approaches to the enantioselective reduction of carbonyl compounds using derivatives of pre-catalyst **2a**. The first approach is based on the addition of optically active acids to the latter species giving complexes **11a**–**d** (Scheme 11). When using these complexes, for the first time for osmium catalytic systems, it has become possible to obtain hydrogen transfer reaction products with a slight enantiomeric excess (*ee*).[28] In this

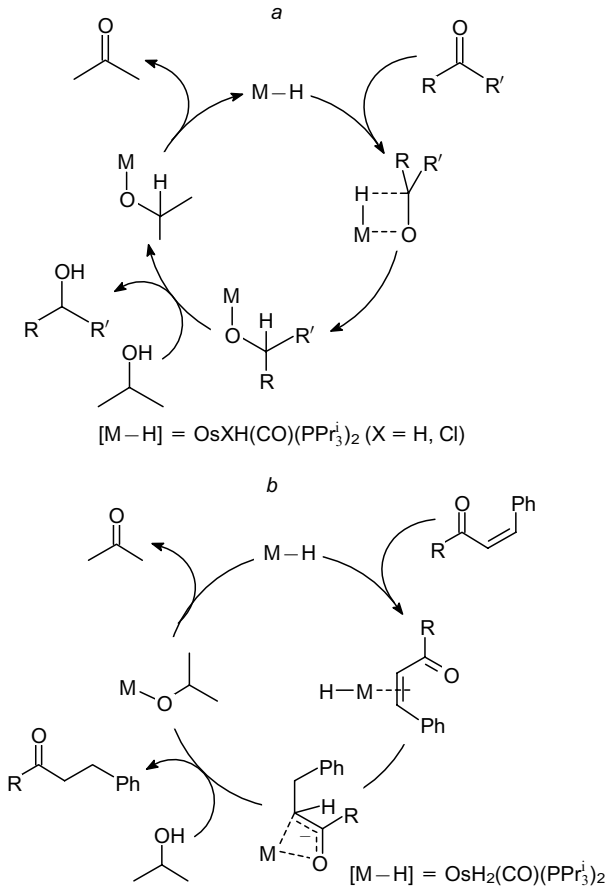
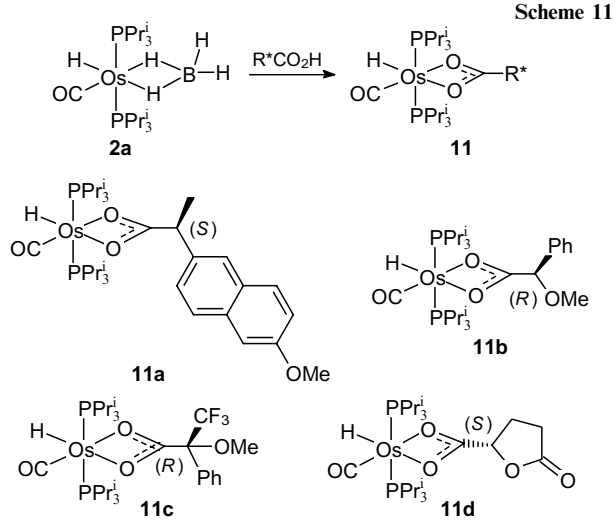


Figure 1. Mechanisms for the multiple bond reduction *via* the hydrogen transfer for carbonyl (*a*) and α,β-unsaturated compounds (*b*).[25, 27]

Scheme 11



case, acetophenone was reduced without adding KOH or $NaBH_4$ as the co-catalyst (Scheme 12, Table 1). Moreover, it is important to note that related ruthenium complexes provided even lower enantioselectivity in this reaction. The authors only determined the conversion of the substrate, while the enantiomeric excess of the product was calculated from the optical rotation of its mixture with the starting compound, which complicated the interpretation of the results and even casts doubt on the reliability of the obtained data to some extent.

Scheme 12

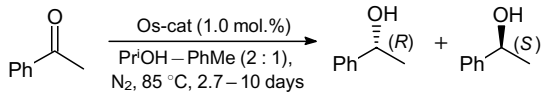


Table 1. Catalytic activity of Os compexes **11** in the reduction of acetophenone (see Scheme 12).[28]

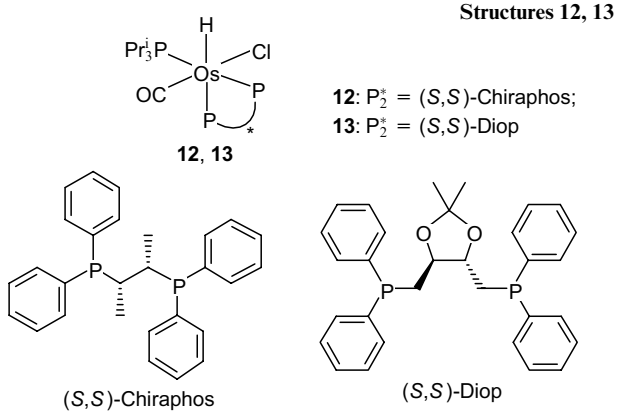
Catalyst	Time, days	Conversion (%)	TON	*ee* (%)	Configuration of the major product
11a	8.7	41	< 41	7	*R*
11b	5.7	60	< 60	13	*S*
11c	2.7	82	< 82	12	*R*
11d	9.9	22	< 22	1	*S*

The second approach is based on the synthesis of precatalysts, which are similar to osmium complexes **1** and contain bidentate optically active phosphines.[29]

The highest catalytic activity and high selectivity were observed for osmium complexes **12** and **13**. For example, the use of catalyst **12** enabled the preparation of (*S*)-1-phenylethanol with a 20% enantiomeric excess, while in the presence of KOH, a 17% enantiomeric excess of the (*R*)-isomer was observed (Scheme 13, Table 2). As in the previous example, it is difficult to estimate the yield of the product and the process selectivity in the cited publication.

In 1993, Bianchini's team [30] carried out a comparative study of the catalytic activity of a family of the Group VIII

Structures 12, 13



Scheme 13

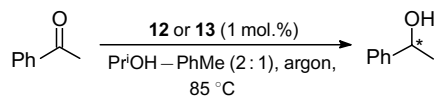
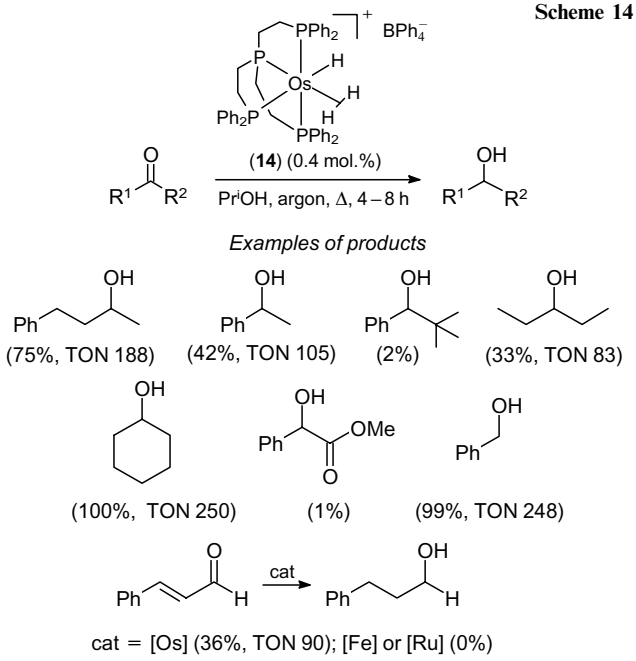


Table 2. Catalytic activity of Os compexes **12** and **13** in the enantioselective reduction of acetophenone (see Scheme 13).[29]

Catalyst	Co-catalyst	Time, h	Conversion (%)	TON	*ee* (%)	Configuration of the product
12	–	168	85	< 85	20	*S*
12	KOH	22	62	< 62	17	*R*
13	–	18	94	< 94	4	*R*
13	KOH	40	35	< 35	1	*S*

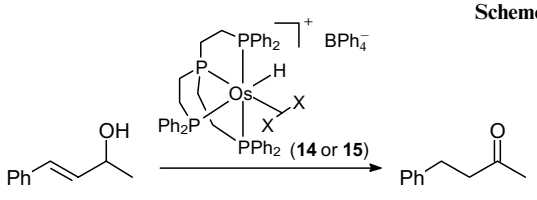
transition metal complexes in the reduction of multiple bonds. Among the catalysts being investigated, osmium complex **14** is of special note. The authors showed that in contrast to the iron and ruthenium complexes, complex **14** remained active in the presence of aldehyde moieties in the substrate, for example, in the reduction of benzaldehyde and cinnamaldehyde (Scheme 14).

Scheme 14



Moreover, when studying the reduction of multiple bonds in other α,β-unsaturated compounds, it was found that, unlike its ruthenium and iron counterparts, complex **14** can catalyze isomerization of allylic alcohols into saturated ketones (Scheme 15). The replacement of the H_2 ligand with more labile N_2 (complex **15**) leads to an increase in the catalytic activity.

Scheme 15



The possibility of such isomerization suggests that the reduction of α,β-unsaturated carbonyl compounds occurs through the initial reduction of the carbonyl group followed by the isomerization of the newly formed allylic alcohol into a saturated ketone. It is essential to point out that in this case, H_2 and N_2 molecules are not directly involved in the hydrogenation but serve as leaving ligands, thus setting free the coordination site at the osmium atom for its interaction with the substrate.

Bianchini *et al.*[30] studied the reduction of a series of α,β-unsaturated ketones in the presence of complex **14** and isopropyl alcohol, which can provide an access to saturated ketones (**A**) and alcohols (**B**), as well as to unsaturated (allylic) alcohols **C** (Scheme 16, Table 3).

Scheme 16

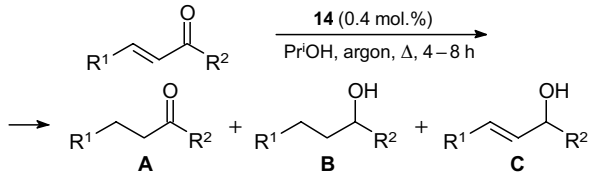
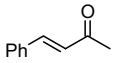
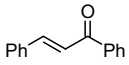
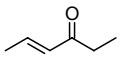
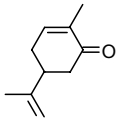
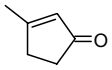
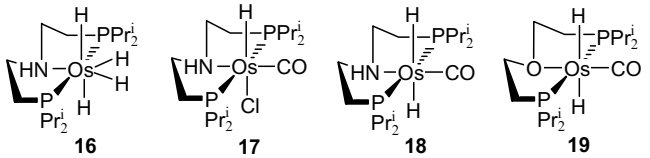


Table 3. Catalytic activity of Os compex **14** in the reduction of α,β-unsaturated ketones (see Scheme 16).[30]

No.	Substrate	Total yield (%)	Time, h	Yield of **A** (%) (TON)	Yield of **B** (%) (TON)	Yield of **C** (%) (TON)
1		91	3	72 (180)	10 (25)	9 (23)
2		93	7	64 (160)	29 (73)	0 (0)
3		11	7	11 (28)	0 (0)	0 (0)
4		100	8	95 (238)	5 (13)	0 (0)
5		91	3	9 (23)	77 (193)	5 (13)
6		43	7	0 (0)	6 (15)	37 (93)
7		2	7	0 (0)	0 (0)	2 (5)
8		98	1	84 (210)	14 (28)	0 (0)
9		2	7	2 (5)	0 (0)	0 (0)

The results of studying the catalytic activity of complex **14** in the reduction reactions of other unsaturated bonds are presented in Table 4. Complex **14** was found to be highly active in the reduction of the carbon—carbon triple bonds as compared to the double ones (see line No. 7), which can possibly be attributed to the higher energy of the triple bond. This helps to avoid the exhaustive hydrogenation of triple bonds.

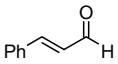
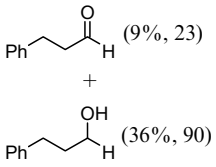
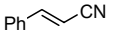
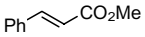
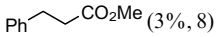
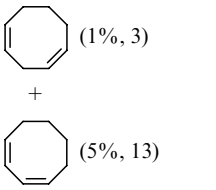
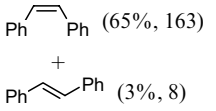
Structures 16 – 19



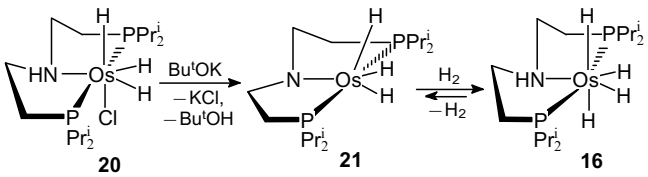
Gusev and co-workers[31,32] synthesized four osmium pincer complexes **16** – **19**.

Complex **16** is formed through dehydrohalogenation of compound **20** followed by hydrogenation of the initially formed amide complex **21** (Scheme 17).[31]

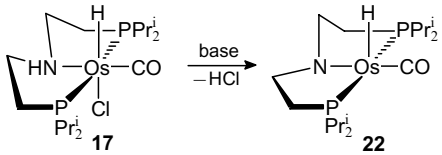
Table 4. Catalytic activity of Os compex **14** in the reduction of unsaturated bonds in different classes of compounds.[30]

No.	Substrate	Total yield (%)	Time, h	Products (yield, TON)
1		45	3	 (9%, 23) + (36%, 90)
2		0	7	–
3		3	7	 (3%, 8)
4		0	7	–
5		6	7	 (1%, 3) + (5%, 13)
6		0	7	–
7		68	6	 (65%, 163) + (3%, 8)

Scheme 17



Scheme 18



Being treated with a base, *e.g.*, $NaN(SiMe_3)_2$, compound **17** produces an extremely air-sensitive amide complex **22** (Scheme 18),[32] which is apparently a key intermediate in catalytic hydrogen transfer reactions.

Studies on the catalytic properties of such complexes showed that compounds **16**–**18** are highly active in the reduction of ketones *via* the hydrogen transfer (Scheme 19).[31, 32]

Moreover, osmium complex **16** is superior in activity to its iridium analogue,[31] while complex **18** surpasses its ruthenium analogue.[32] For some reason, the activity of

Scheme 19

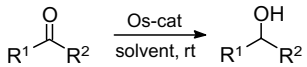


Table 5. Catalytic activity of Os compexes **16**–**18** in the reduction of carbonyl compounds (see Scheme 19).

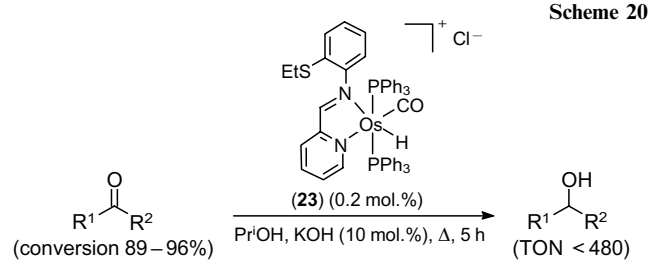
Catalyst	Loading of [Os] (mol.%)	Alcohol	Base (mol.%)	TOF,[a] h^{-1}	Ref.
		Product — 1-phenylethanol (R^1 = Ph, R^2 = Me)			
16	0.016	Pr^iOH	–	1900	31
16	0.01	Pr^iOH	Bu^tOK (0.05)	5700	31
16	0.16	EtOH	–	420	31
16	0.04	Pr^iOH	Bu^tOK (0.4)	1800	31
17		Pr^iOH	Bu^tOK (1.0)	14 000	32
17		EtOH	Bu^tOK (1.0)	100	32
18		Pr^iOH	Bu^tOK (1.0)	16 000	32
18		Pr^iOH	–	13 000	32
18		EtOH	–	300	32
		Product — cyclohexanol ($R^1 - R^2 = (CH_2)_5$)			
16	0.13	Pr^iOH	–	4600	31
16	0.0016	Pr^iOH	Bu^tOK (0.5)	32 700	31
16	0.07	EtOH	–	430	31
18		Pr^iOH	Bu^tOK (1.0)	63 000	32
18		Pr^iOH	–	19 000	32
18		EtOH	–	550	32

[a] TOF is the turnover frequency for the 50% conversion of the substrate, the time is 1–2 h.

hydride complexes **16** and **18** is raised in the presence of potassium *tert*-butoxide. Although it was shown[33] that the base can independently catalyze the reduction of acetophenone upon heating in isopropyl alcohol *via* the hydrogen transfer, Gusev and co-workers[31, 32] tend to believe that in the system they used, the addition of Bu^tOK promotes the process due to a synergistic effect, since the reactions occur without heating in the presence of a low concentration of the said base. It is also important to note that Gusev and co-workers[31, 32] succeeded in developing one of the few catalytic systems for the hydrogen transfer, making it possible to use ethanol as a hydrogen source (Table 5).

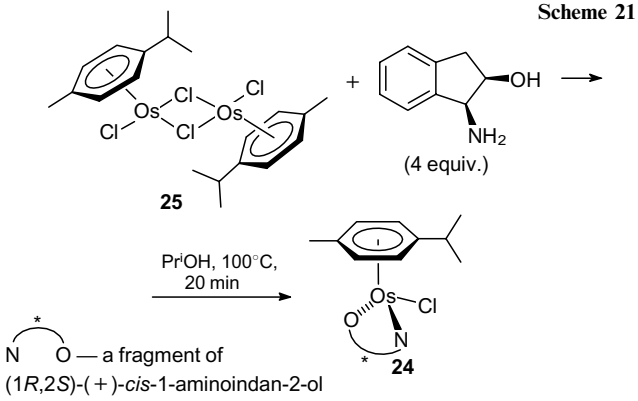
In 2017, Mondal and co-workers[34] prepared osmium complex **23** bearing a Schiff base as a ligand (Scheme 20) and demonstrated its high catalytic activity in hydrogen transfer reactions.

Scheme 20



This complex provided the reduction of a number of *para*-substituted acetophenones and other aromatic and cyclic aliphatic ketones with a high conversion.

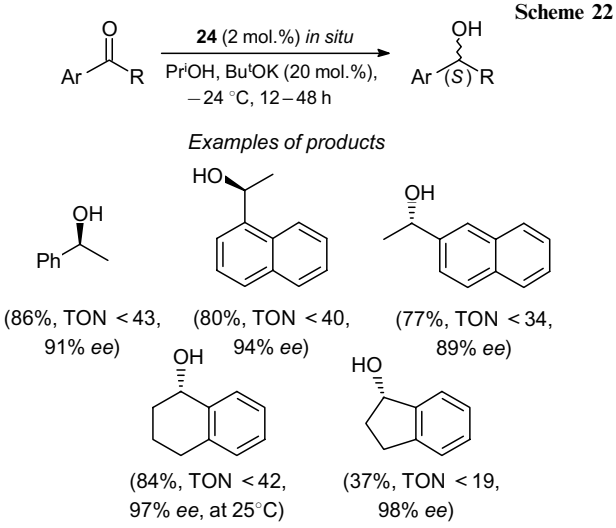
Scheme 21



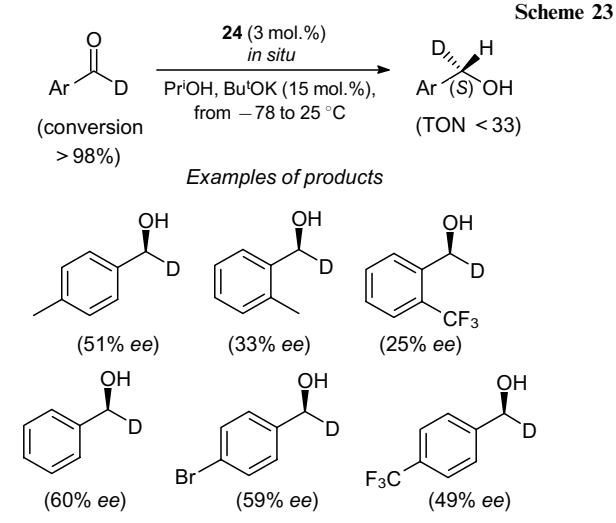
2.2. Catalysis by osmium arene complexes

Faller and Lavoie [35, 36] proposed a catalytic system for the enantioselective reduction of aromatic ketones and α-deuteriobenzaldehydes through a hydrogen transfer mechanism based on active species **24** generated *in situ* from $[(\eta^6\text{-cymene})OsCl_2]_2$ (**25**) and (1*R*,2*S*)-(+)-*cis*-1-aminoindan-2-ol (Scheme 21).

Scheme 22



Scheme 23



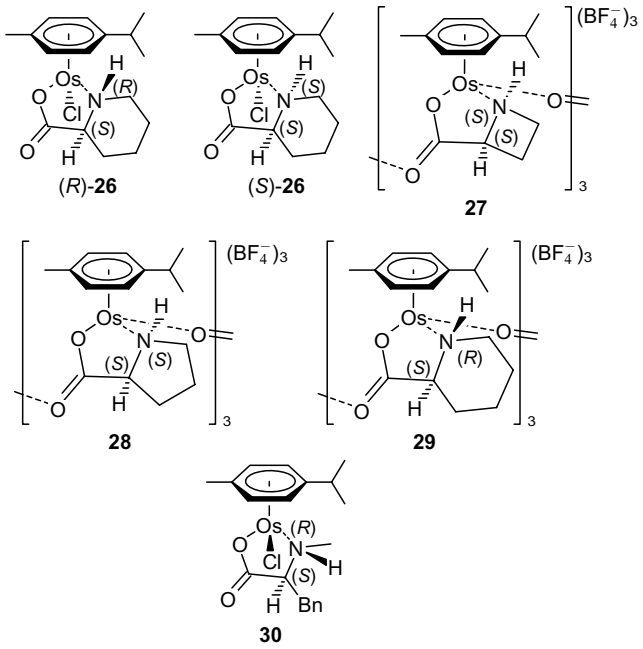
Using this catalyst, the authors prepared a series of optically active alcohols with a high enantiomeric excess (Scheme 22).

Also, the authors carried out the reduction of α-deuteriobenzaldehydes bearing electron-donating or -withdrawing substituents in the *ortho* and *para* positions (Scheme 23). In this case, the enantiomeric excess of the resulting products the enantiomeric excess did not exceed 60%. For the systems based on the osmium catalyst, *para*-substituents in α-deuteriobenzaldehydes led to a decrease in enantioselectivity regardless of their electronic factors, whereas for the systems based on ruthenium, rhodium and iridium catalysts, the introduction of electron-withdrawing substituents at the *para* position of α-deuteriobenzaldehyde improved the enantiomeric excess of the product.

The presence of substituents in the *ortho* position of α-deuteriobenzaldehyde induces a significant decrease in enantioselectivity of the process for the osmium system regardless of the electronic effects of these substituents, whereas for the catalysts based on other metals, the trend is reversed.

In 2002, Carmona *et al.*[37] synthesized optically activeosmium complexes **26**–**30** starting from $[(\eta^6\text{-cymene})OsCl_2]_2$ (**25**) and the appropriate amino acids. An important feature of complexes (*R*)-**26**, **29** and **30** is that both the original optical centre at the carbon atom and the newly formed optical centre at the carbon atom adopt an S_CR_N configuration, whereas other complexes have the S_CS_N configuration.

Structures 26–30



The authors investigated the activity of these complexes in the enantioselective reduction of ketones *via* a hydrogen transfer mechanism (Table 6). The use of complexes **29** and **30** having S_CR_N configurations of the optical centres in the reduction of acetophenone led to the formation of an *S* enantiomer, while the S_CS_N-complexes produced an *R* enantiomer. However, when 4-phenylbutan-2-one (benzylacetone) was reduced, the situation was reversed. In the case of S_CR_N-complex **30**, an *R* enantiomer was obtained,

Scheme 24

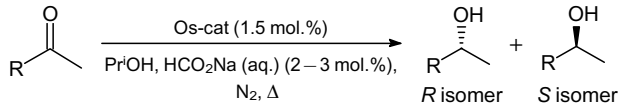


Table 6. Catalytic activity of Os compexes **26**–**30** in the reduction of acetophenone and benzylacetone (see Scheme 24).[37]

R	Catalyst	Time, h	Configuration of the major product	*ee* (%)	TOF, h^{-1}
Ph	(*S*)-**26**	1.0	*R*	66	57
Ph	**27**	1.25	*R*	50	24
Ph	**28**	1.25	*R*	72	47
Ph	**29**	1.0	*S*	52	47
Ph	**30**	2.0	*S*	37	60
$Ph(CH_2)_2$	(*S*)-**26**	3.0	*S*	30	45
$Ph(CH_2)_2$	**30**	6.0	*R*	5	36

whereas S_CS_N-complex (*S*)-**26** gave an *S* enantiomer. It is noteworthy that ruthenium analogues of such complexes showed higher activity and enantioselectivity in the reduction of ketones.

Based on these findings, transition states were proposed for hydrogen transfer reactions, which account for the observed stereoselectivity (Fig. 2).[37] The authors hypothesized that one reason for this arrangement of acetophenone in the transition states is the favourable CH – π-interaction of cymene with the benzene ring of acetophenone. This fact confirms the stereospecificity of the reaction with 4-phenylbutan-2-one, for which such an interaction is impossible for steric reasons.

Thus, Carmona *et al.*[37] developed a new enantioselective approach to the reduction of ketones amd demonstrated that it is possible to generate an optical centre at the nitrogen atom with a configuration other than that of the nearby optical center at the carbon atom. However, the major drawback limiting the application of this approach is a low enantiomeric excess in the reactions involving aliphatic ketones.

In 2012, in the follow-up investigation of osmium complexes with amino acids, the scope of reduction catalysts was significantly expanded. Carmona *et al.*[20] gave a detailed proof of their mechanistic suggestions put forward as early as 2002[37] but they failed to surpass the activity of complexes (*S*)-**26** and **28**.

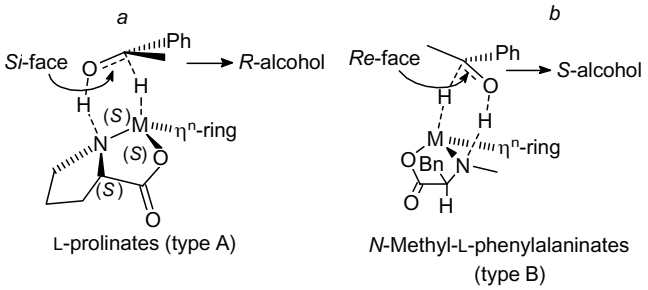
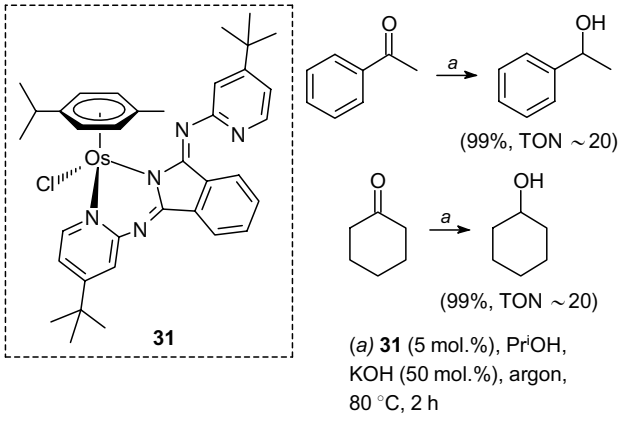


Figure 2. Plausible transition states for the hydrogen transfer reactions catalyzed by complexes bearing amino acid ligands, L-proline (*a*) and *N*-methyl-L-phenylalanine (*b*).[37]

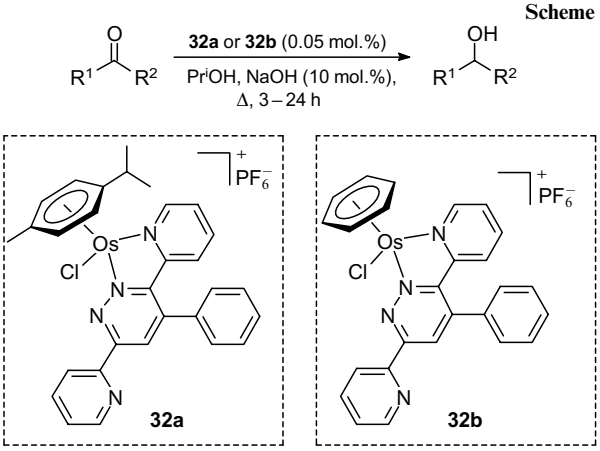
Scheme 25



In 2015, Gade and co-workers[38] prepared osmium complex **31** (Scheme 25), which was catalytically active in the transfer hydrogenation of ketones. In particular, this complex can catalyze the reaction of acetophenone and cyclohexanone giving the corresponding alcohols in quantitative yields.

In 2017, Friedrich and co-workers[39] synthesized a number of osmium arene complexes bearing various nitrogen-containing bidentate ligands and tested them in the transfer hydrogenation of ketones (Scheme 26). These complexes were very active in the catalytic reduction of cyclohexanone in isopropyl alcohol in the presence of a base. The TON values for these complexes were calculated based on the reported yields of cyclohexanol and were in the range from 1820 to 1960. The results of studying the substrate specificity of the most active complexes are presented in Table 7. Complex **32a** with a *p*-cymene ligand showed a slightly higher activity than its benzene analogue **32b**. The authors attributed this difference to the increased electron density that the cymene ligand can donate to the osmium atom. It is important to note that in the presence of an α-positioned substituent in cyclohexanone, the yield of the resulting alcohol (*e.g.*, 2-methylcyclohexanol) decreases almost twice as compared to that of unsubstituted cyclohexanone.

Scheme 26



In 2008, Esteruelas and co-workers[40] synthesized hydroxo complex **33** (Scheme 27), which does not require a base for activation in the hydrogen transfer process. Presumably, the reaction of this complex with isopropyl alco-

Scheme 27

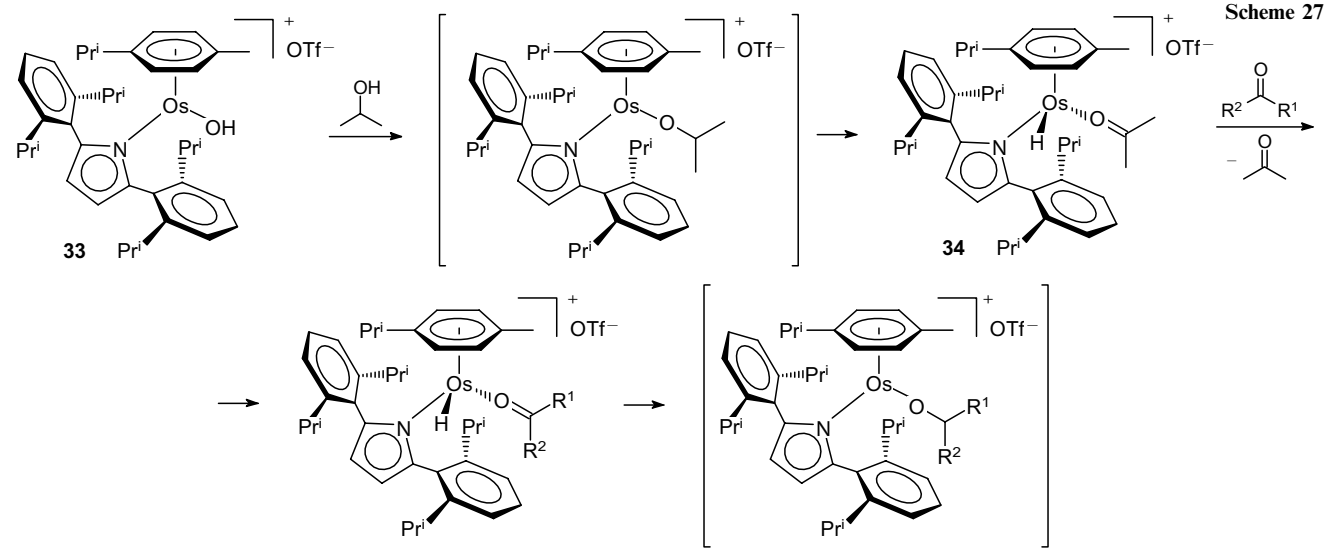
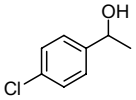
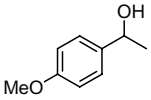
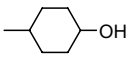


Table 7. Catalytic activity of Os compexes **32a**,**b** in the reduction of ketones (see Scheme 26).[39]

Product	Catalyst	Yield (%)	TON	TOF, h^{-1}
	**32a**	90	1800	287
	32b	87	1740	248
	**32a**	87	1740	866
	32b	85	1700	560
	**32a**	74	1480	149
	32b	77	1540	128
	**32a**	90	1800	594
	32b	86	1720	572
	**32a**	52	1040	87
	32b	52	1040	81
	**32a**	81	1620	80
	32b	76	1520	76
	**32a**	80	1600	104
	32b	89	1780	101
	**32a**	83	1660	75
	33b	80	1600	60

hol initially affords an isopropoxy derivative followed by its conversion into hydride **34**. Subsequently, acetone is replaced with aldehyde or ketone followed by a hydrogen transfer to the target carbonyl compound.

Complex **33** displayed a high catalytic activity in the reduction of aliphatic and aromatic aldehydes in isopropyl alcohol through a hydrogen transfer mechanism. However, this complex was found to be much less active in the reduction of acetophenone compared to other osmium complexes (Scheme 28, Table 8).

In 2011, when studying the mechanism of the reduction of ketones, Lough and Morris[41] prepared osmium complex **35** with N-heterocyclic carbene (Scheme 29). Complex **35**

Scheme 28

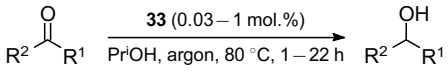
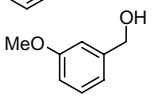
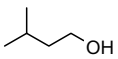
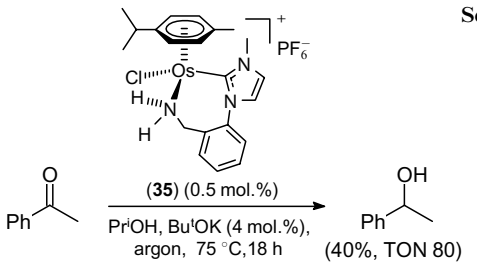


Table 8. Catalytic activity of Os compex **33** in the reduction of aldehydes and acetophenone (see Scheme 28).[40]

Product	Catalyst loading (mol.%)	Product yield (%)	TON	TOF, h^{-1}
	0.1	98	980	1360
	0.03	88	2933	950
	0.1	96	980	3530
	0.03	96	3200	2730
	0.1	98	980	3530
	0.03	96	3200	2730
	0.1	98	980	2300
	0.03	96	3200	1550
	1	72	72	12

Scheme 29

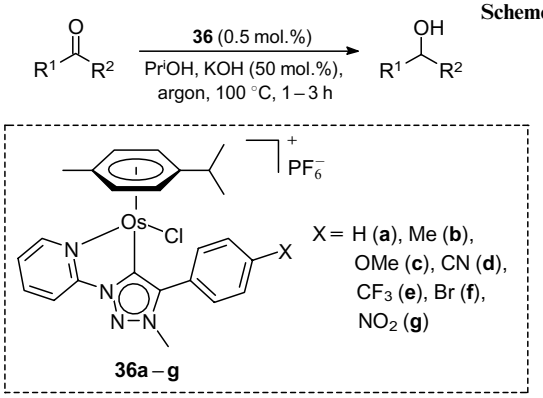


had a lower catalytic activity in hydrogen transfer reactions than related systems prepared previously, in 2008 (see Scheme 27)[40] and 2001 (see Scheme 21).[35] The authors explained such a low activity by the oxophilic nature of the metal resulting, upon activation with the Bu^tO^- anion,

in the formation of stable osmium(II) alkoxide. In the absence of potassium *tert*-butoxide, this complex was catalytically inactive in the hydrogen transfer reaction.

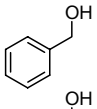
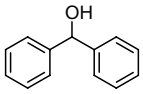
In 2015, Sarkar and co-workers [42] described a family of carbene complexes **36a–g**, containing various substituted triazoles, and studied the influence of the electronic effects of substituents in the carbene ligand on the catalytic activity of these complexes in hydrogen transfer reactions (Scheme 30, Table 9).

Scheme 30



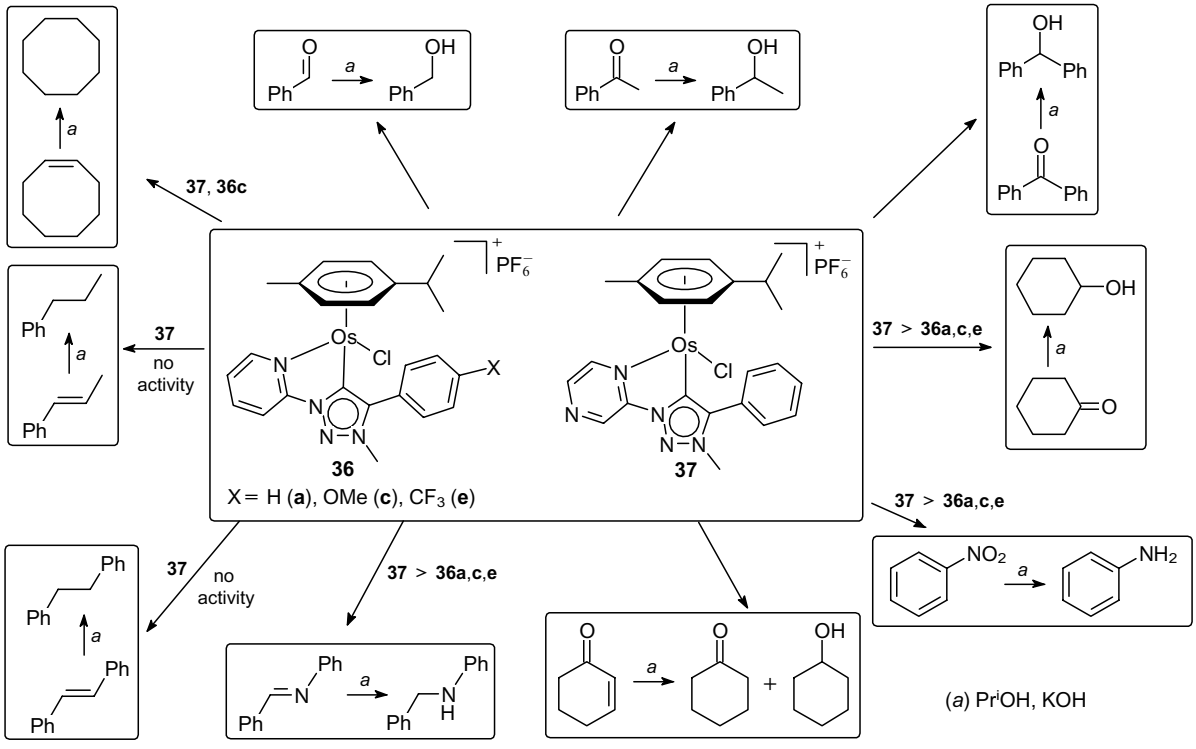
The authors showed that electron-withdrawing substituents dramatically reduce the catalytic activity of the complex in the reduction of benzaldehyde, acetophenone, cyclohexanone and benzophenone *via* a hydrogen transfer mechanism in isopropyl alcohol in the presence of KOH. Iridium complexes, reported in the same publication, are characterized by the opposite pattern. In the case of ruthenium analogues, the nature of a substituent in the ligand has no impact on the activity of the catalyst. It is important to note that the effect of electron-withdrawing substituents on the activity of the complex is most pronounced in the reduction of aromatic ketones, whereas the difference in the activity is not so noticeable for cyclohexanone and benzaldehyde. In the case of ketones, osmium complexes were less active in comparison to their ruthenium and iridium analogues.

Table 9. Catalytic activity of Os compexes **36** in the reduction of carbonyl compounds (see Scheme 30).[42]

Product	Catalyst	Yield (%)	TON
	**36a–g**	99	198
	36a,**c**,**e** (see [a])	99	9900
	**36a**	76	152
	36b	80	160
	36c	88	176
	36d	50	100
	36e	65	130
	36f	70	140
	36g	68	136
	**36a–c**	99	198
	36d	93	186
	36e	91	182
	36f	94	188
	36g	89	187
	36c (see [b])	99	760
	**36a**	68	136
	36b	71	142
	36c	88	176
	36d	31	62
	36e	25	50
	36f	27	54
	36g	20	40

Catalyst loading (mol.%): [a] 0.01, [b] 0.1 in other examples, 0.5.

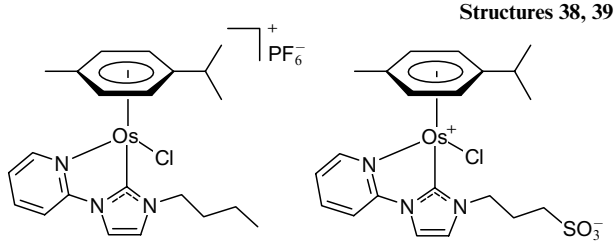
Scheme 31



In 2016, while continuing their research on osmium complexes with triazole-containing ligands, Sarkar and co-workers [43] not only expanded the family of such complexes but also demonstrated their efficiency in the reduction of various functionalities with multiple bonds (Scheme 31). Complex **37** performed better in the reduction of nitrobenzene, Schiff base and cyclohexanone than compounds **36a**,**c**,**e**. At the same time, complex **37** did not exhibit any noticeable catalytic activity in the reduction of methylstyrene and stilbene; however, its performance in the reduction of cyclooctene was comparable to that of the most active pyridine complex, namely, compound **36c**. Derivative **36e** showed lower catalytic activity in all reactions compared to its analogues **36a**,**c**, which is consistent with the findings related to the adverse effect of the electron-withdrawing substituents on the activity, made back in 2015.

In 2018, Kühn and co-workers [44] synthesized two osmium compounds (**38** and **39**) acive in hydrogen transfer reactions, when studying complexes with N-heterocyclic carbenes. Complex **38** showed a moderate activity as a catalyst for the reduction of acetophenone in isopropyl alcohol in the presence of KOH, making it possible to prepare 1-phenylethanol in 60% yield. Unlike its lipophilic analogue, water-soluble compound **39** was inactive in the reduction of acetophenone in a buffer solution of sodium formate and formic acid.

Structures 38, 39



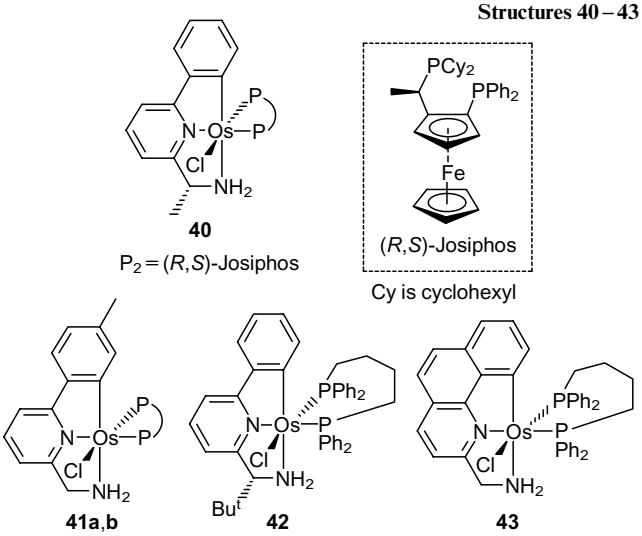
38 **39**

2.3. Catalysis by osmium pincer complexes and their analogues

In a study of osmium complexes, Baratta *et al.*[45,46] prepared a number of CNN-type pincer complexes **40**–**43**. The authors found that compounds **41** and **43** exhibit similar chemical behaviour under transfer hydrogenation conditions to afford complexes **44**–**49** (Schemes 32, 33).

When treated with $NaOPr^i$ in isopropyl alcohol, complexes **41a** and **43** give an equilibrium mixture of alkoxide (**44** or **47**) and hydride (**45** or **48**). It was also demonstrated that the hydride intermediate can bind a new ketone (*e.g.*, 4,4′-difluorobenzoquinone) to give the corresponding alkoxide (**46** or **49**). Since complexes **41** and **43** have a similar

Structures 40–43



40

P_2 = (*R*,*S*)-Josiphos

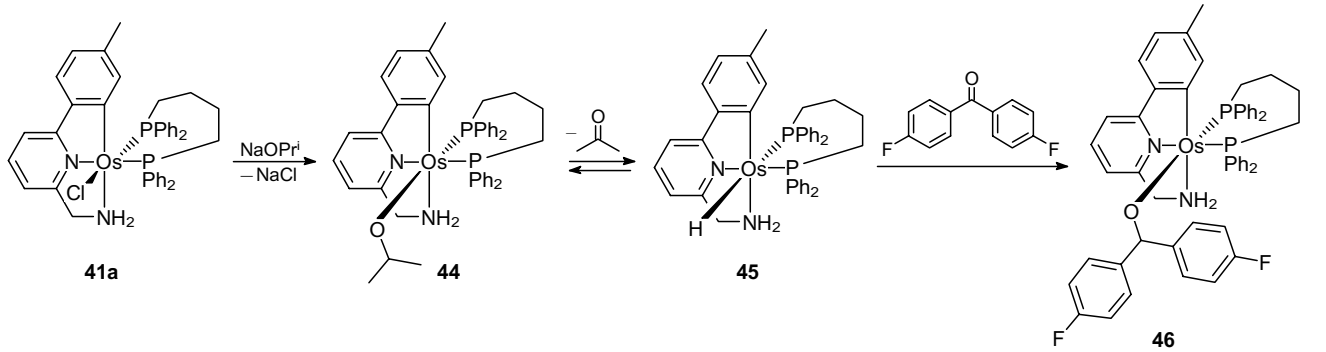
(*R*,*S*)-Josiphos

Cy is cyclohexyl

41a,**b** **42** **43**

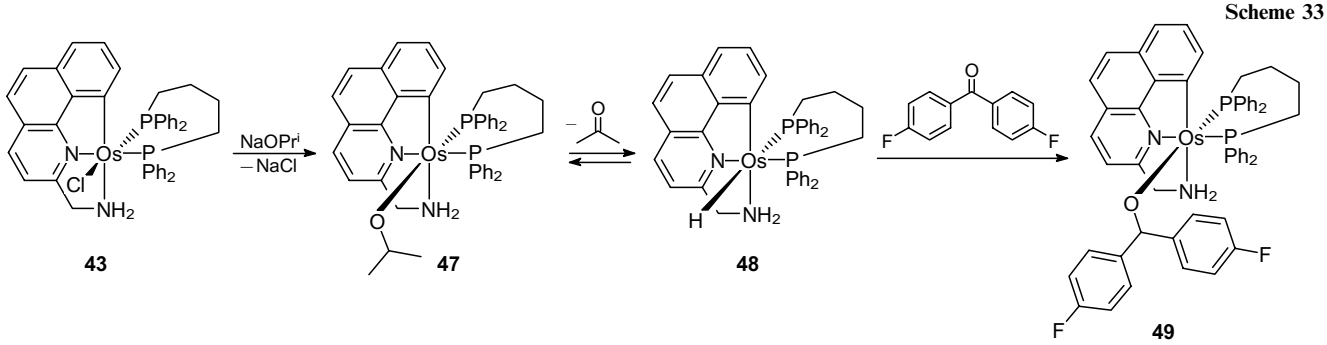
P_2 = dppb (**a**), (*R*,*S*)-Josiphos (**b**);
dppb is 1,4-bis(diphenylphosphino)butane

Scheme 32



41a **44** **45** **46**

Scheme 33



43 **47** **48** **49**

Scheme 34

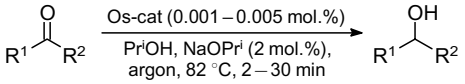
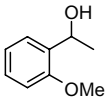
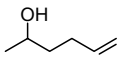


Table 10. Catalytic activity of Os compexes **41 – 43** in the reduction of ketones (see Scheme 34).[45, 46]

Product	Catalyst	Loading (mol.%)	Conversion (%)	TON	TOF, h^{-1}
	**43**	0.005	96	< 19 200	$< 1.3 \times 10^6$
	43	0.001	94	< 94 000	$< 4.3 \times 10^5$
	41a		97	< 97 000	$< 4.3 \times 10^5$
	41b		95 [a]	< 19 000	$< 1.7 \times 10^5$
	42		94 [b]	< 18 800	$< 1.2 \times 10^5$
	**43**		99	< 19 800	$< 1.8 \times 10^6$
	**43**		97	< 19 400	$< 3.0 \times 10^5$
	41a		95	< 19 000	$< 4.0 \times 10^5$
	**43**		98	< 19 600	$< 3.0 \times 10^5$
	41a		95	< 19 000	$< 6.0 \times 10^5$

[a] The *S* enantiomer was obtained with 83% *ee*; [b] Within 120 min, the *S* enantiomer, with 74% *ee*.

reactivity, it would be reasonable to expect that these complexes will show a similar catalytic activity. Indeed, the difference in the catalytic turnover frequency for these complexes in the reduction of ketone *via* a hydrogen transfer mechanism, differs by less than an order of magnitude (Scheme 34, Table 10).

It is noteworthy that complex **42** containing no optically active phosphine ligand could provide an acohol with a significant enantiomeric excess of 74% (see Table 10). The incorporation of optically active phosphine [(*R,S*)-Josiphos in relation to complex **40**] into the catalyst provides an access to the products with a higher *ee* value by the reduction of substituted acetophenones under these conditions (Scheme 35, Table 11).

Scheme 35

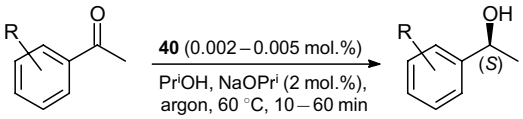
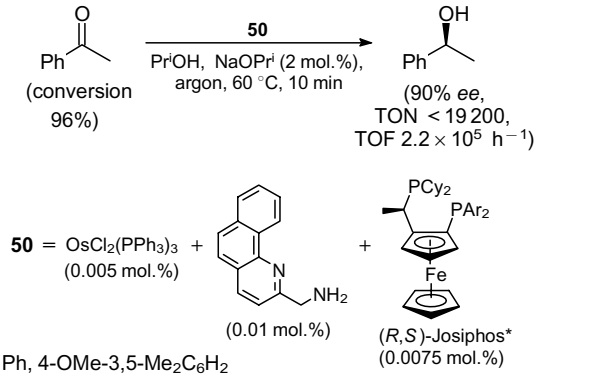


Table 11. Catalytic activity of Os compex **40** in the reduction of acetophenone derivatives (see Scheme 35).[45]

R	Conversion (%)	*ee* (%)	TON	TOF, h^{-1}
H	97	93	< 19 400	$< 1.7 \times 10^5$
2-Me	92	91	< 18 400	$< 4.0 \times 10^4$
2-Cl	96	90	< 19 200	$< 1.3 \times 10^5$
2-OMe	95	97	< 10 400	$< 1.9 \times 10^5$
3-OMe [a]	94	97	< 47 000	$< 4.0 \times 10^5$

[a] The catalyst loading is 0.002 mol.%.

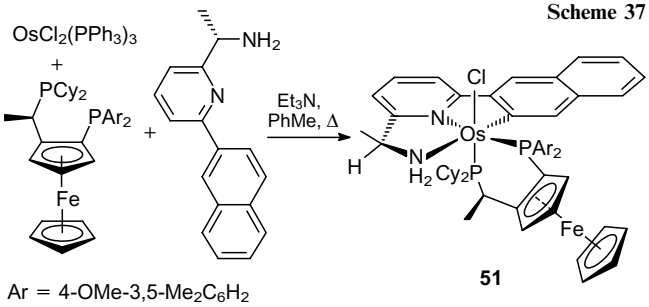
Scheme 36



Besides, Baratta *et al.*[45, 46] found that catalytic system **50** designed for the enantioselective transfer hydrogenation of ketones can be generated *in situ* from $OsCl_2(PPh_3)_3$ and two different ligands, (*R,S*)-Josiphos* and benzo[*h*]quinolin-2-ylmethylamine (Scheme 36). The authors $NaOPr^i$ used at a loading of 2 mol.% as a base for the activation of the catalyst.

In 2010, in continuation of their research on the expansion of a family of osmium pincer complexes, Baratta *et al.*[47] prepared a series of optically active HCNN ligands. It was found that the pincer complex, generated *in situ* from $OsCl_2(PPh_3)_3$ and (*R,S*)-Josiphos* in combiation with the ligand (*S*)-1-[6-(2-naphthyl)pyridin-2-yl]ethylamine in the presence of 2 mol.% of $NaOPr^i$ (Scheme 37), showed the highest productivity in the reduction of acetophenone *via* a hydrogen transfer mechanism.

Scheme 37



Based on these data, the authors prepared complex **51** and evaluated its catalytic activity towards a number of aromatic ketones (Scheme 38, Table 12). The developed approach made it possible for the first time to perform the osmium-catalyzed transfer hydrogenation of aromatic ketones containing electron-withdrawing substituents, such as the bis(trifluoromethyl) moiety and the pyridine ring.

In 2008, Baratta *et al.*[48] synthesized a number of complexes based on chelate N,N′-ligands showing high performance in the transfer hydrogenation reaction. Best results were observed for the catalytic system comprising a mixture of complexes **52a**,**b** in a 1 : 3 ratio (Scheme 39, Table 13). This system is produced by the reaction of the complex $OsCl_2(PPh_3)_3$ with the dppb ligand and 2-aminomethylpyridine.

The authors also succeeded in reducing a series of *ortho*-substituted acetophenones to (*S*)-alcohols with an enantiomeric excess of 94 – 96% using catalytic system **53** generated *in situ* from a mixture of $OsCl_2(PPh_3)_3$, (*R,S*)-Josiphos* and

Scheme 38

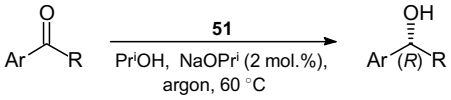


Table 12. Catalytic activity of Os compex **51** in the reduction of acetophenone derivatives (see Scheme 38).[47]

Ar	R	Loading (mol.%)	Conversion (%)	*ee* (%)	TON	TOF, h^{-1}
3,5-$(MeO)_2C_6H_3$	Me	0.002	97	97	< 48 500	$< 9.0 \times 10^5$
3,5-$(F_3C)_2C_6H_3$ (see [a])	Me	0.01	99	98	< 9900	$< 5.1 \times 10^4$
2-Py	Me	0.005	99	91	< 19 800	$< 5.1 \times 10^4$
3-Py [a]	Me	0.005	99	90	< 19 800	$< 7.6 \times 10^4$
4-Py [a]	Me	0.01	99	97	< 9900	$< 8.3 \times 10^4$
Ph	Et	0.005	93	99	< 18 600	$< 1.4 \times 10^4$

[a] The catalyst was generated *in situ*. Py is pyridyl.

Scheme 39

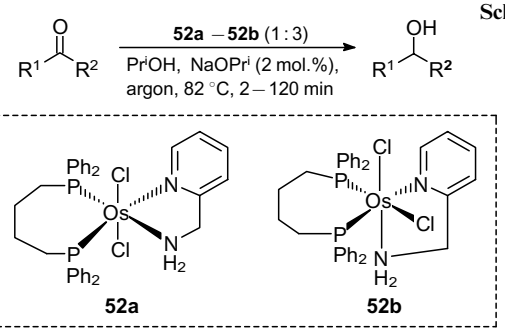
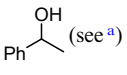
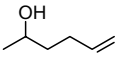
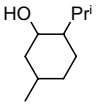


Table 13. Catalytic activity of a mixture of Os complexes **52a**,**b** in the reduction of ketones (see Scheme 39).[47]

Product	Conversion (%)	TON	TOF, h^{-1}
 (see [a])	98	< 98 000	$< 3.4 \times 10^5$
	96	< 1920	$< 3.2 \times 10^5$
	98	< 1960	$< 1.7 \times 10^4$
	93	< 1860	$< 8.0 \times 10^3$
	99	< 1980	$< 2.7 \times 10^4$

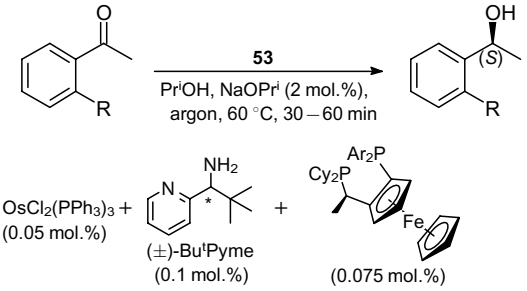
[a] The catalyst loading is 0.01 mol.%; in the other examples, 0.05 mol.%.

(±)-Bu^{t}Pyme in the presence of 2 mol.% NaOPr^i in isopropyl alcohol (Scheme 40).

In 2012, the same research team [49] proposed osmium complex **54** containing 1,1′-bis(diphenylphosphino)ferrocene as a readily available and versatile catalyst, which is active in a variety of reactions (Scheme 41).

The authors managed to reduce a series of aliphatic and aromatic aldehydes and ketones, some of which are presented in Table 14, *via* a hydrogen transfer mechanism (Scheme 42), with complex **54** being superior in activity to its ruthenium analogue.

Scheme 40

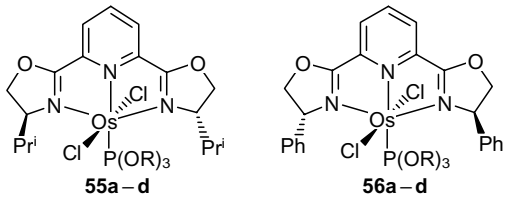


Ar = Ph, 4-OMe-3,5-$Me_2C_6H_2$

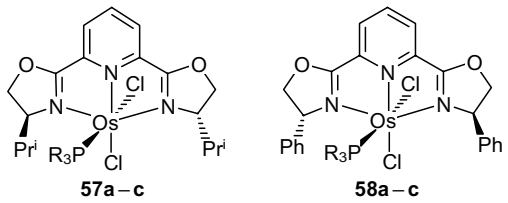
R	Conversion (%)	*ee* (%)	TON	TOF, h^{-1}
Cl	99	94	< 1980	$< 1.2 \times 10^4$
OMe	98	95	< 1960	$< 9.1 \times 10^3$
Me	99	96	< 1980	$< 8.6 \times 10^3$

In 2013, Gamasa and co-workers [50] prepared osmium complexes **55**–**58** with tridentate 2,6-bis(oxazolin-2-yl)pyridine (PYBOX) scaffolds for the enantioselective catalytic reduction of aromatic ketones.

Structures 55 – 58



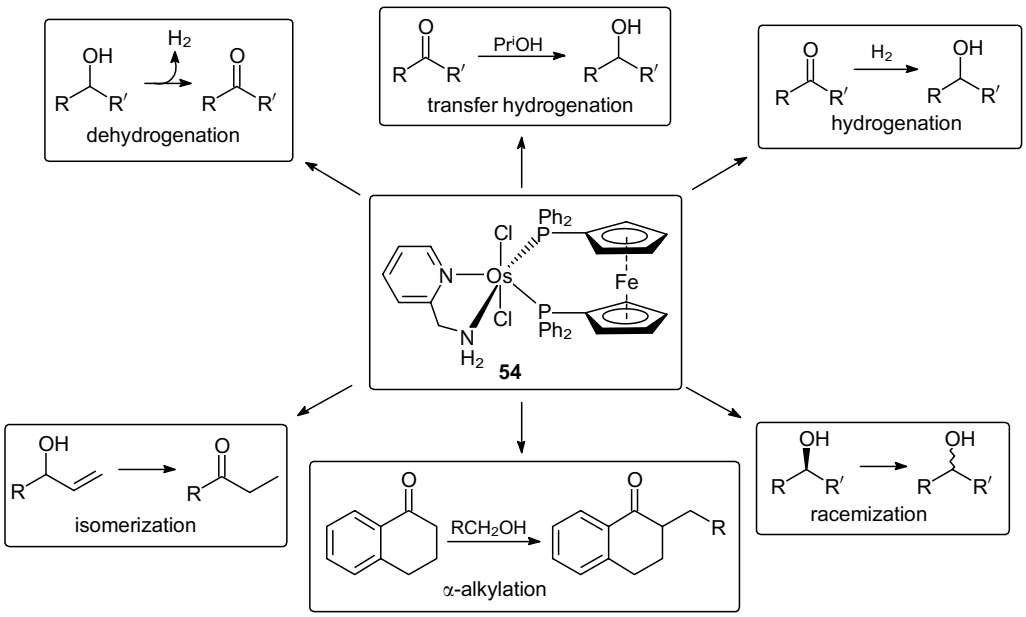
R = Me (**a**), Et (**b**), Pr^i (**c**), Ph (**d**)



R = Cy (**a**), Pr^i (**b**), Ph (**c**)

While optimizing the catalytic system, it was found that complexes **55a** and **57b**,**c**, bearing isopropyl-substituted PYBOX ligands, display a higher catalytic activity compared to phenyl-substituted complexes **56a** and **58b**,**c**. An opposite trend was observed for ruthenium analogues. Thus, the complexes with phenyl-substituted PYBOX ligands were the most active.[51] During the further optimization, it was elucidated that phosphite complexes (*e.g.*, **55a**) showed a higher activity compared to phosphine complexes **57b**–**d** c. The authors failed to compare the efficiency of the *cis* and *trans* isomers of the catalysts, since in the case of phosphines involved in ethylene-containing complex **59**, only complexes with the *cis*-configuration of the chloride ligands were produced (route *b* in Scheme 43), whereas the presence of phosphites, on the

Scheme 41



Scheme 42

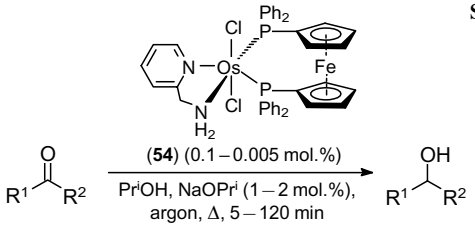
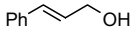
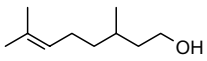
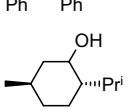
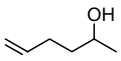


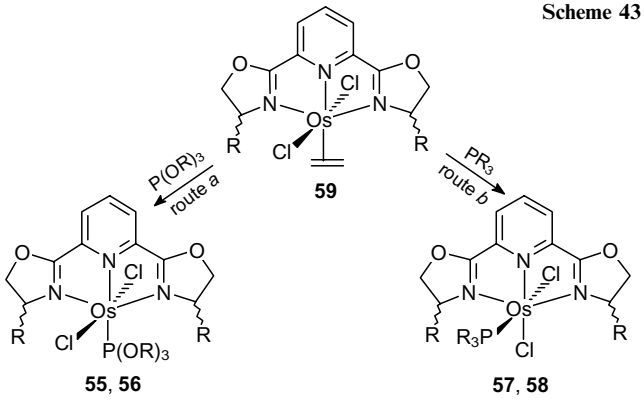
Table 14. Catalytic activity of Os compex **54** in the reduction of carbonyl compounds (see Scheme 42).[49]

Product	Conversion (%)	TON	TOF, h^{-1}
Reduction of aldehydes			
BnOH	98	< 19 600	$< 3.0 \times 10^5$
	90	< 1800	$< 8.9 \times 10^4$
	98	< 1960	$< 2.6 \times 10^3$
Reduction of ketones			
	98	< 19 600	$< 1.9 \times 10^5$
	91	< 1820	$< 4.7 \times 10^3$
	98	< 19 600	$< 7.8 \times 10^4$
	96	< 1920	$< 4.6 \times 10^4$
	98	< 1960	$< 4.3 \times 10^4$

contrary, led to complexes with the *trans*-configuration (see route *a*).

Nevertheless, the nature of substituents in the phosphine ligands was shown to have no significant influence on the reaction pathway. Under the optimized conditions, a number of aromatic ketones were successfully reduced, including

Scheme 43



acetophenone and its derivatives, and also methyl 2-naphthyl ketone, in high yields and with an enantiomeric excess from 54 to 94% using catalyst (*S*,*S*)-**55a** (Scheme 44, Table 15).[50] The use of acetophenone and its derivatives bearing substituents in the *meta* and *para* positions resulted in the formation of alcohols with the *R* configuration of the asymmetric centre, whereas the corresponding (*S*)-alcohols were produced from methyl 2-naphthyl ketone and *ortho*-substituted acetophenones.

In the follow-up study of complexes with tridentate PYBOX scaffolds subtituted with isopropyl groups, a number of novel osmium complexes **60** – **63** bearing N-heterocyclic ligands were prepared in 2018.[52]

The authors showed that similar ruthenium complexes bearing nitrogen-containing ligands are significantly inferior to osmium catalysts in activity in the enantioselective hydrogen transfer reaction.[52] During the optimization of the catalyst structure, it was found that complex **60a** with an unsaturated pyridine ligand had the highest catalytic performance among derivatives of this family, as demonstrated by a number of examples (Scheme 45, Table 16).

In 2013, Chattopadhyay and co-workers[53] synthesized osmium complex **64** bearing a tridentate NNO ligand (Scheme 46). This complex showed a catalytic activity in the reduction of ketones *via* a hydrogen transfer mechanism. It is important to note that the introduction of a

Scheme 44

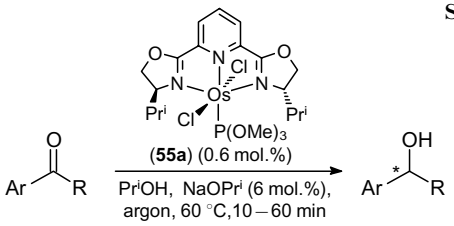
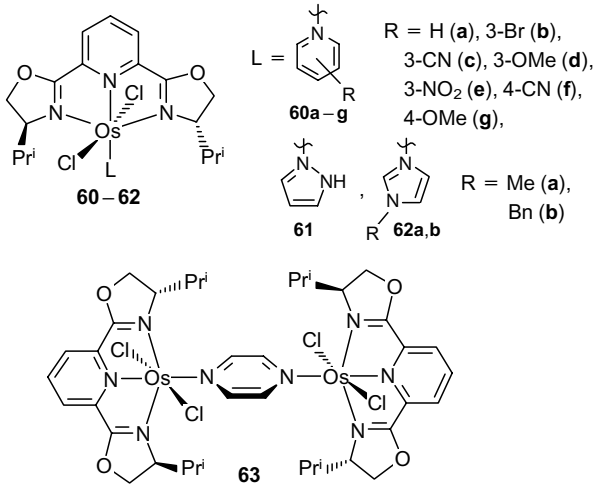


Table 15. Catalytic activity of Os compex **55a** in the reduction of alkyl aryl ketones (see Scheme 44).[50]

Ar	R	Conversion (%)	*ee* (%)	Configuration	TON
Ph	Me	98	94	*R*	< 163
Ph	Et	92	91	*R*	< 153
2-BrC_6H_4	Me	99	57	*S*	< 165
2-$MeOC_6H_4$	Me	99	74	*S*	< 165
3-$MeOC_6H_4$	Me	97	80	*R*	< 162
2-Naph [a]	Me	99	55	*S*	< 165
4-$MeOC_6H_4$	Et	97	94	*R*	< 162
4-$MeOC_6H_4$	Me	98	93	*R*	< 163
4-BrC_6H_4	Me	97	73	*R*	< 162
3-BrC_6H_4	Me	99	92	*R*	< 165

[a] Naph is naphthyl.

Structures 60 – 63



methoxy group at the 4-position of acetophenone reduced the yield of alcohol by a factor of 1.5.

3. Borrowing hydrogen reactions

The C – N and C – C bond formation is an important goal in chemistry. One way of addressing this problem is the use of the borrowing hydrogen or hydrogen autotransfer reaction, which has attracted great interest in the past years. This process got its name for the mechanism (Scheme 47). In the first step, the catalyst oxidizes the starting alcohol to give the corresponding carbonyl compound, then the nucleophile (NuH_2) attacks the carbonyl group followed by the formation of a multiple bond. In the final step, the reduction of this multiple bond by the catalyst is induced by the hydrogen borrowed in the first step during the oxidation of

Scheme 45

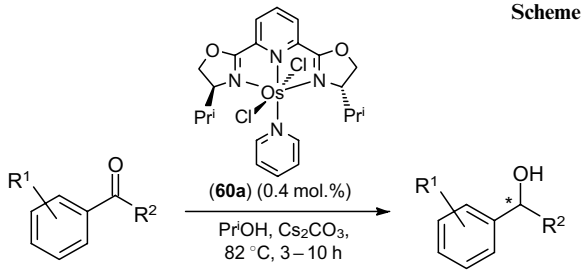
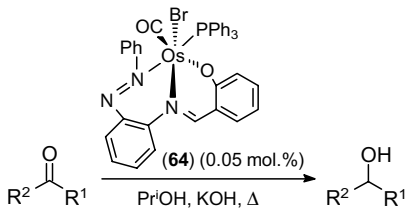


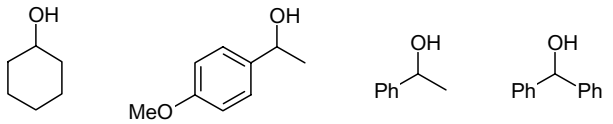
Table 16. Catalytic activity of Os compex **60a** in the reduction of acetophenone derivatives (see Scheme 45).[52]

R^1	R^2	Conversion (%)	*ee* (%)	Configuration	TON	TOF, h^{-1}
H	Me	93	63	*R*	< 233	< 110
4-Br	Me	95	55	*R*	< 238	< 50
3-Br	Me	97	63	*R*	< 243	< 80
2-OMe	Me	91	46	*S*	< 240	< 50
H	Pri	94	73	*R*	< 235	< 75
H	Et	97	68	*R*	< 243	< 95

Scheme 46



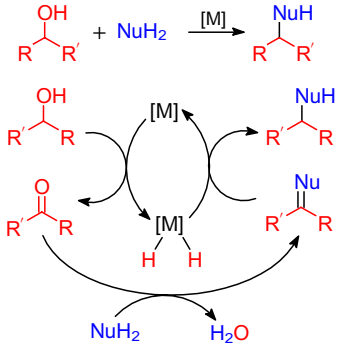
Examples of products



alcohol. Catalysts based on 3d metals [54] are widely used in these reactions, while the activity of osmium catalytic systems has been poorly studied.

As part of the above study of osmium complexes **16** – **20**, Gusev and co-workers [31, 32] showed that these compounds are catalytically active in the borrowing hydrogen reactions. Thus, the presence of complexes **16** and **20** made it possible to introduce methyl and ethyl groups into hexylamine, cyclohexylamine and aniline (Scheme 48, Table 17). It is

Scheme 47



Scheme 48

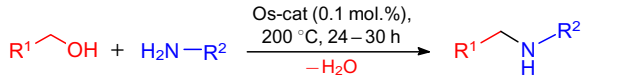
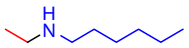
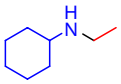
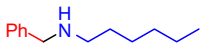
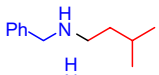
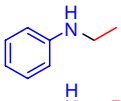
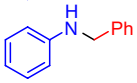
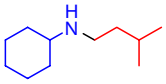


Table 17. Catalytic activity of Os compexes **16**–**20** in the borrowing hydrogen reaction (see Scheme 48).[31,32]

Product	Catalyst	Yield (%)	TON
	**16**	81	810
	**16**	92	920
	20 + Bu^{t}OK	92	920
	**18**	84	840
	**18**	74	740
	**16**	67	670
	**18**	37	370
	18 + Bu^{t}OK	47	470
	**16**	64	640
	20 + Bu^{t}OK	75	750
	17	68	680
	18	60	600
	**18**	68	680
	19	43	430

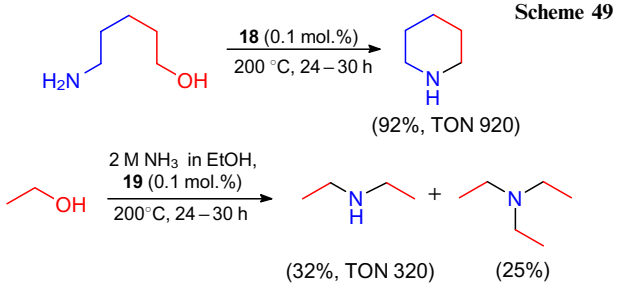
important to note that sodium *tert*-butoxide should be used to activate chloride complex **20**, whereas complex **16** works without any added base. The authors also demonstrated that catalysts **17** and **18** can be used for the alkylation of hexylamine, cyclohexylamine, benzylamine and aniline with methanol, ethanol, isoamyl and benzyl alcohols. Aniline enters these reactions with more difficulty than aliphatic amines.

Besides, the authors prepared piperidine from 5-aminopentanol in 92% yield, and also introduced several ethyl groups into ammonia to form a mixture of di- and triethylamines in 32 and 25% yields, respectively (Scheme 49).

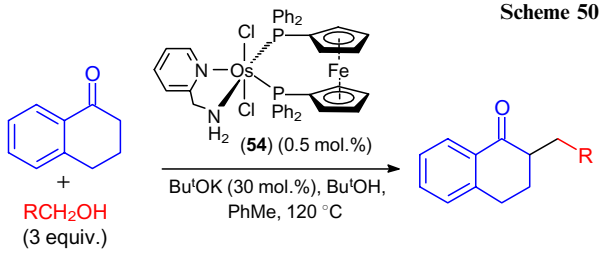
In 2012, it was demostrated that osmium complex **54** can promote the alkylation of α-tetralone with aliphatic alcohols (Scheme 50).[49] This is the first example of using osmium catalysis to create the C–C bond *via* α-alkylation of ketones.

Complex **54** showed a higher catalytic productivity compared to its ruthenium analogue, which had a maximum TOF value of 420 h^{-1} for these substrates.

Scheme 49



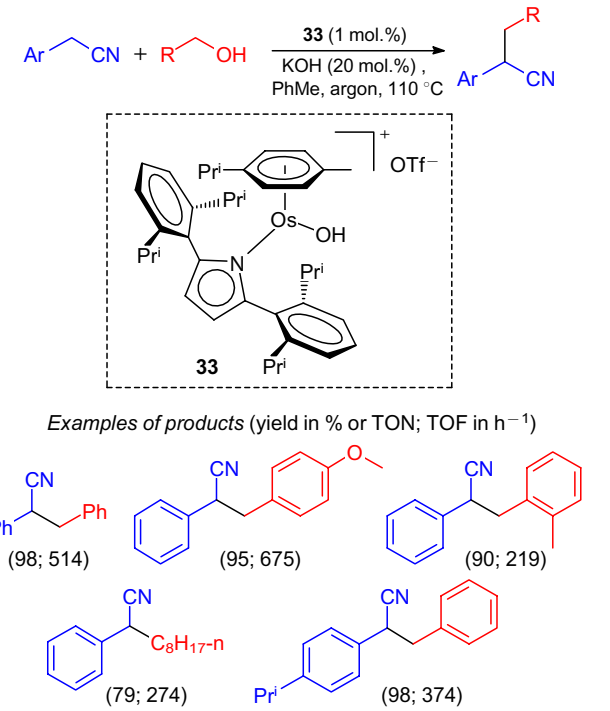
Scheme 50



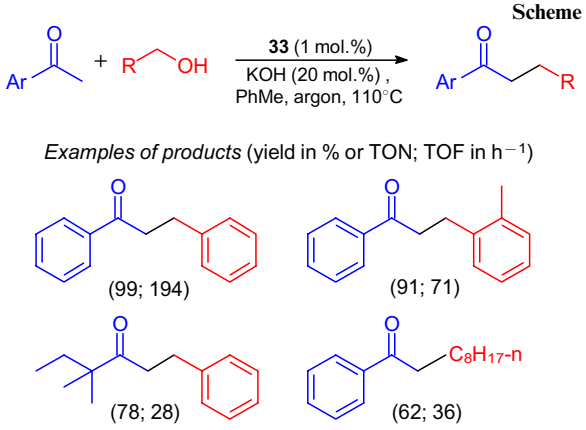
R	Conversion (%)	TON	TOF, h^{-1}
Me	93	< 186	< 520
Et	91	< 182	< 910
Pr^n	93	< 186	< 2800

In 2013, Esteruelas, Yus and co-workers[55] were the first to demonstrate the effectiveness of osmium complexes in the α-alkylation of nitriles with alcohols (Scheme 51). The process was catalyzed with pyrrole complex **33**, wich has

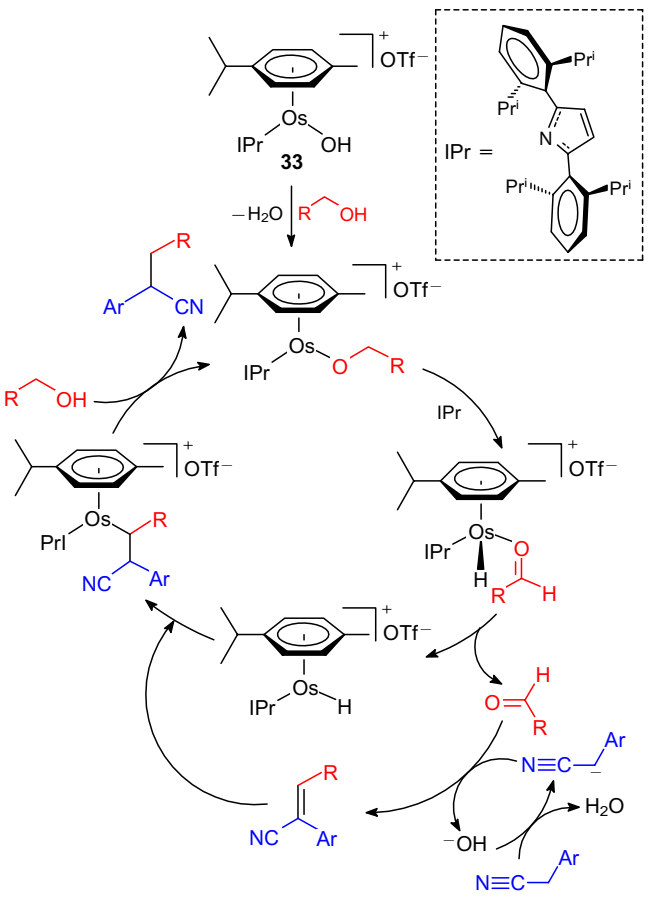
Scheme 51



Scheme 52



Scheme 53



also proved to be successful in α-alkylation of ketones (Scheme 52).

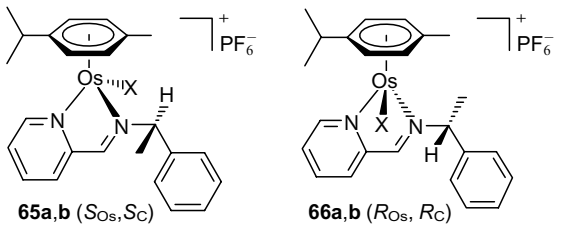
The authors proposed the mechanism of catalytic α-alkylation of nitriles, which is a classical pathway of the borrowing hydrogen (Scheme 53). One of the key steps is the dehydration of alcohol to give osmium hydrides.

4. Hydrogen transfer reactions in the presence of formates

In 2013, Sadler and co-workers[56] incorporated iminopyridine ligands into osmium complexes to study their anticancer activity.

Two complexes (**65b** and **66b**) were tested for catalytic activity in the reduction of imines with a mixture of triethylamine and formic acid (Scheme 54, Table 18). Formic acid serves as a hydrogen donor in this reaction. Remarkably, the *R* isomer of the product predominated regardless of the configuration of the catalyst chiral centres.

Structures 65, 66



X = Cl (**a**), I (**b**)

Scheme 54

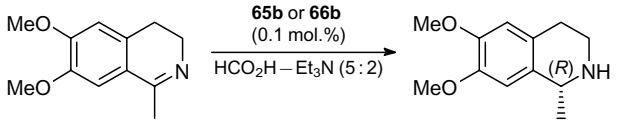


Table 18. Catalytic activity of Os compexes **65b** and **66b** in the reduction of the CN bond (see Scheme 54).[56]

Catalyst	Temperature, °C	Time, h	Conversion (%)	TON	*ee* (%)
65b	45	22	40	< 400	22
65b	60	18	76	< 760	22
66b	28	23	20	< 200	23

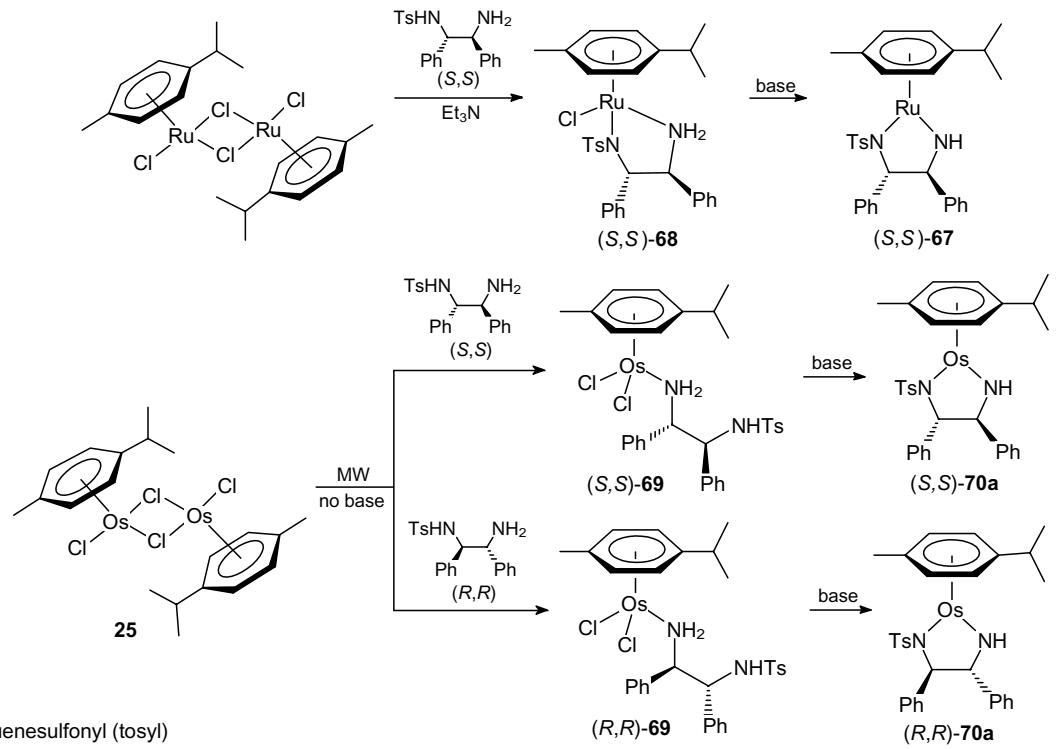
In 2015, Wills, Sadler and co-workers[57] pioneered in preparing the Noyori-type osmium complexes (Scheme 55) and carried out the enantioselective reduction of acetophenone and its derivatives to furnish the corresponding products with an enantiomeric excess of up to 98%. Initially, the authors attempted to use the procedure for the synthesis of a Noyori-type ruthenium catalyst (**67**) but encountered poor solubility of the starting osmium chloride complex in isopropyl alcohol and undesirable side reactions. This issue was resolved through the use of microwave irradiation (MW) to activate the reaction. However, instead of an analogue of ruthenium complex **68**, monodentate osmium complex **69** was obtained as an intermediate, which was transformed into the target 16-electron osmium derivative **70a** in the presence of a base (see Scheme 55). The authors mentioned that the synthesis and storage of this complex do not require an inert atmosphere.

Under the classical conditions of the hydrogen transfer reaction, as well as in the presence of molecular hydrogen, the authors did not observe the desired Os–H bond formation in the osmium complex **70a** (Scheme 56, route *a*). However, in the presence of a mixture of formic acid and triethylamine, the formation of osmium hydrides **71** was confirmed by NMR spectroscopy (see Scheme 56, route *b*).

The authors further tested osmium complexes **69** and **70a** as catalysts for the reduction of ketones (Scheme 57). When using the *S*,*S*-configured complexes, *S* enantiomers of alcohols were obtained as the major products, except for α-chloroacetophenone, which produced an (*R*)-alcohol. A similar stereoselectivity was also observed for the *R*,*R*-configured complexes. It is important to point out that both osmium complexes showed high activity.

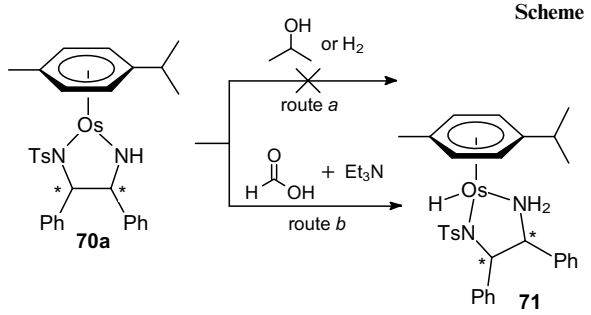
Sadler and co-workers[57–59] studied the effect of different substituents on the catalytic activity of osmium arene complexes based on diphenylethylenediamine. These complexes exhibited high activity in the enantioselective reduction of acetophenone in the presence of formic acid and triethylamine, which exceeded that of related second-generation Noyori pre-catalyst **68** (Scheme 58). It was found that the change of the substituent in the ligand from the tosyl group (complex **70a**) to any other sulfonyl group (**70b–e**) decreases the turnover frequency of the catalytic system (TOF values). On the contrary, replacing the cymene ligand (**70a**) with biphenyl (**72a**) increases the turnover frequency, but the incorporation of one more benzene ring (**73a**) into the catalyst structure already lowers the TOF value (Table 19).[59] As in the previous case, the use of the *S*,*S*-configured complex results in the formation of the

Scheme 55

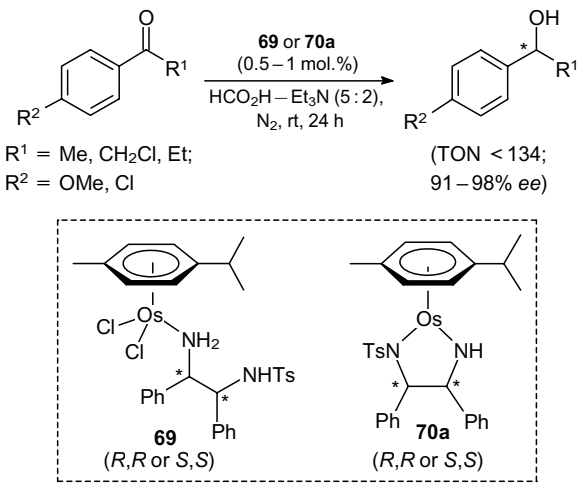


Ts is *p*-toluenesulfonyl (tosyl)

Scheme 56



Scheme 57



S enantiomer of 1-methylbenzyl alcohol, while the *R* enantiomer is formed in the presence of the *R*,*R*-configured complex.

The same authors found that the highest performance in the reduction of acetophenone with a mixture of formic acid and triethylamine was observed for complexes **70f** and **72b** bearing a *tert*-butylated sulfonyl substituent. An increase in the catalytic activity in the presence of the *tert*-butyl moiety in diphenylethylenediamine can be due to the hindered rotation of an arene ligand, which stabilizes the pericyclic transition state, thereby promoting the asymmetric hydrogen transfer.

Scheme 58

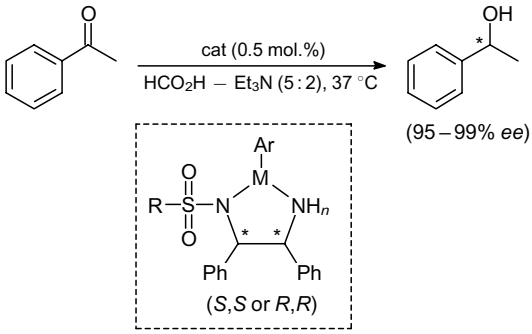
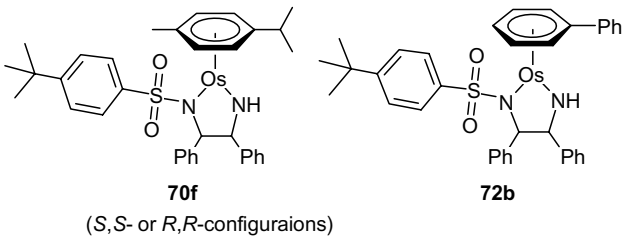


Table 19. Catalytic activity of ruthenium and osmium complexes in the reduction of acetophenone in the presence of formic acid and triethylamine (see Scheme 58).[59]

Catalyst	M	R	*n*	Ar	TOF_{max}, h^{-1}
68	Ru(Cl)	4-MeC_6H_4	2	*p*-Cymene	$< 23 \pm 1$
70a	Os	4-MeC_6H_4	1	*p*-Cymene	$< 63.9 \pm 0.3$
70b	Os	4-$O_2NC_6H_4$	1	*p*-Cymene	$< 61 \pm 2$
70c	Os	4-FC_6H_4	1	*p*-Cymene	$< 40 \pm 2$
70d	Os	Ph	1	*p*-Cymene	$< 58 \pm 1$
70e	Os	Me	1	*p*-Cymene	$< 58 \pm 2$
72a	Os	4-MeC_6H_4	1	Biphenyl	$< 78 \pm 1$
73a	Os	4-MeC_6H_4	1	*m*-Terphenyl	$< 43 \pm 2$

Structures 70f, 72b



70f **72b**

(*S*,*S*- or *R*,*R*-configuraions)

Scheme 59

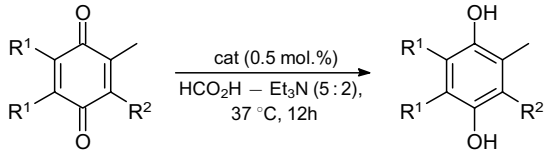


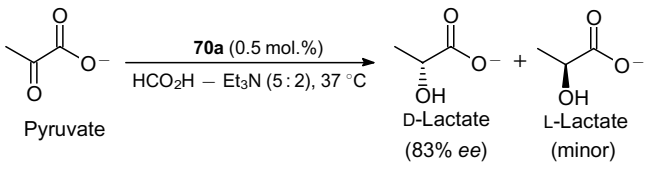
Table 20. Catalytic activity of ruthenium and osmium complexes in the reduction of quinones in the presence of formic acid and triethylamine (see Scheme 59).[58]

Catalyst	Metal	Yield (%)	TON	TOF_{max}, h^{-1}
Reduction of tetramethylquinone ($R^1 = R^2 = Me$)				
68	Ru(Cl)	98	< 196	< 48.1 ± 0.4
70f	Os	99	< 198	< 67.9 ± 0.6
72b	Os	97	< 194	< 55.5 ± 0.3
Reduction of 2-methylnaphthoquinone ($R^1 – R^1$ = benzo, R^2 = H)				
68	Ru(Cl)	93	< 186	< 36.5 ± 0.5
70f	Os	87	< 174	< 94 ± 2
72b	Os	97	< 194	< 145 ± 3

The authors were able to show that these complexes can catalyze the reduction of quinones (Scheme 59, Table 20). It is noteworthy that in this case osmium complexes were superior in activity to their ruthenium conterparts.

Besides, complex **70a** showed a satisfactory enantioselectivity (83% *ee*) in the reduction of pyruvate, which is a key intermediate in metabolic pathways, to lactate both in aqueous systems and in cells (Scheme 60).[59]

Scheme 60



Therefore, osmium complexes are of interest as anticancer agents due to their ability to generate reductive stress in cells. Coverdale *et al.*[59] suggested the putative structure of the transition state in the reduction of pyruvate (Fig. 3).

In 2019, based on density functional theory (DFT) calculations, Wang and Yang[60] proposed a mechanism for the asymmetric reduction of pyruvic acid *via* the hydride

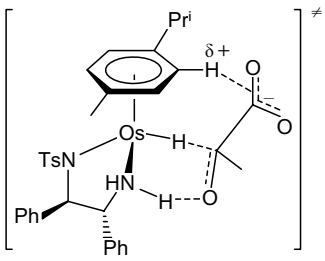


Figure 3. Putative transition state in the reduction of pyruvate to lactate under the action of an osmium complex **70a**.[59]

transfer catalyzed by chiral osmium complexes, using formic acid as a hydrogen source (Scheme 61). In the first step, pyruvate approaches hydride **74**, derived from osmium complex **70a**, from its *Re* or *Si* face to give the corresponding intermediates $\mathbf{75_R}$ and $\mathbf{75_S}$. This is followed by the hydrogen transfer from the osmium ion to pyruvate to afford structures $\mathbf{76_R}$ and $\mathbf{76_S}$. Further, under the action of formic acid, the starting hydride **74** is reduced through the formation of intermediates **77** and **78**. Complex **79** can also be produced from intermediate **77**.

The authors showed that the formation of D-lactate is 1.6 kcal mol^{-1} more favourable than the formation of the L-form, which matches well with the observed enantiomeric excess of 83%.

5. Miscellaneous reactions under hydrogen transfer conditions

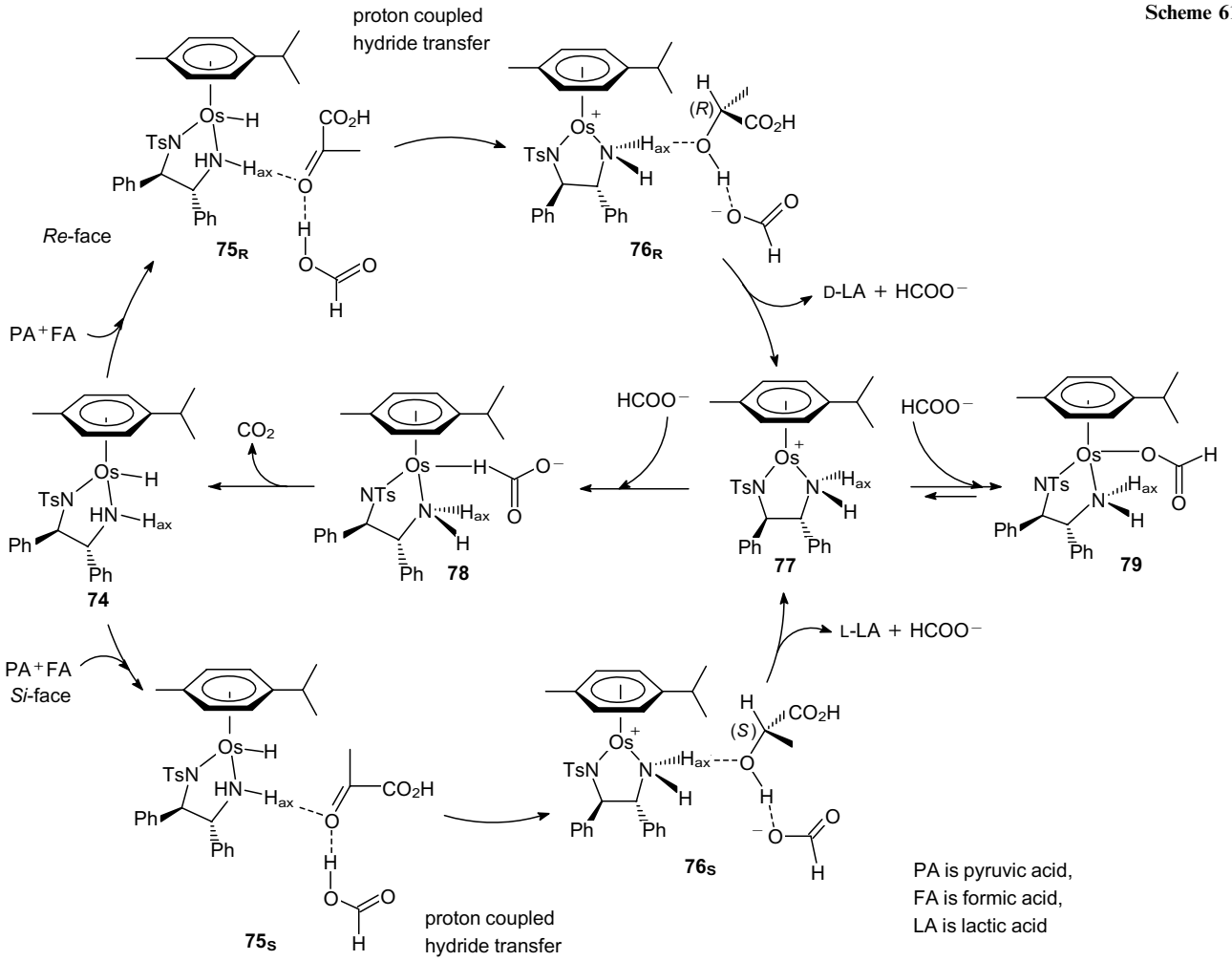
In 2015, Krische and co-workers[61] proposed a new strategy for the vinylation of activated secondary alcohols with enol carboxylates under hydrogen transfer conditions (Scheme 62). This method worked well for a wide range of substrates (17 examples).

The authors proposed a mechanism for this reaction, wherein the hydrogen atom is transferred from the reactant (alcohol) to the osmium atom to give ketone, which is involved in the osmacycle. In the final step, the hydride hydrogen, transferred to the osmium, is involved in the reductive elimination accompanied by the regeneration of the parent [Os^0] complex (see Scheme 63, by the example of vinylation of ethyl 2-hydroxy-2-phenylacetate).

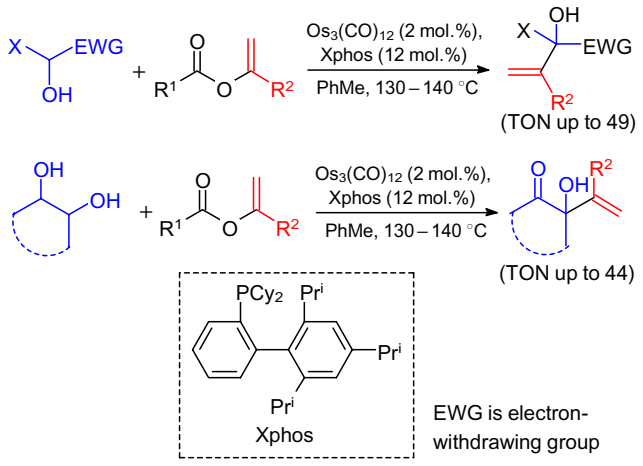
A year later, continuing the study of the catalytic properties of osmium carbonyl, the same research team demonstrated the possibility of alkylation of diols, ketols and esters bearing an α-positioned hydroxy group with terminal alkenes in the presence of 10 mol.% adamantane-1-carboxylic acid (see Scheme 64 by the example of ethylene).[62]

According to the proposed mechanism, the acid promotes the coordination of the reactant to the osmium atom (Scheme 65, as exemplified by the reaction of ethyl 2-oxo-2-phenylacetate with oct-1-ene). The advantage of osmuim lies in its enhanced ability to undergo back π-donation, which greatly facilitates the oxidative addition on this metal. The authors emphasize that ruthenium carbonyl is catalytically inactive under similar conditions.

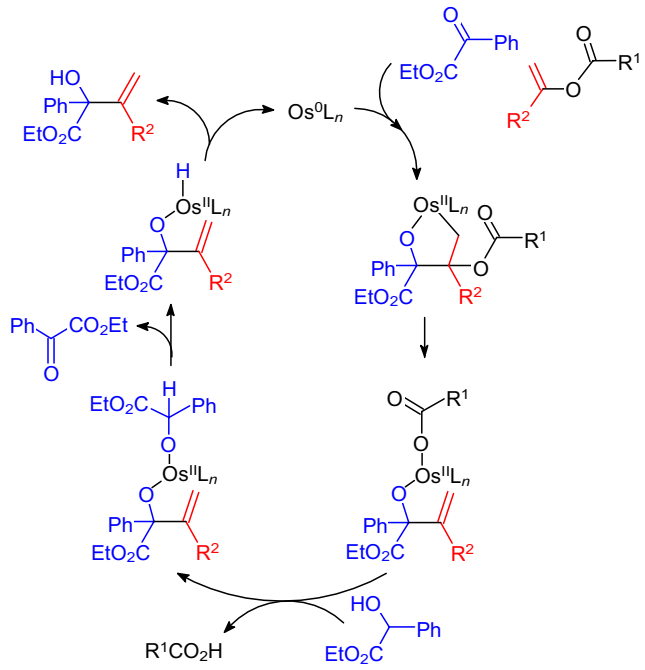
Scheme 61



Scheme 62



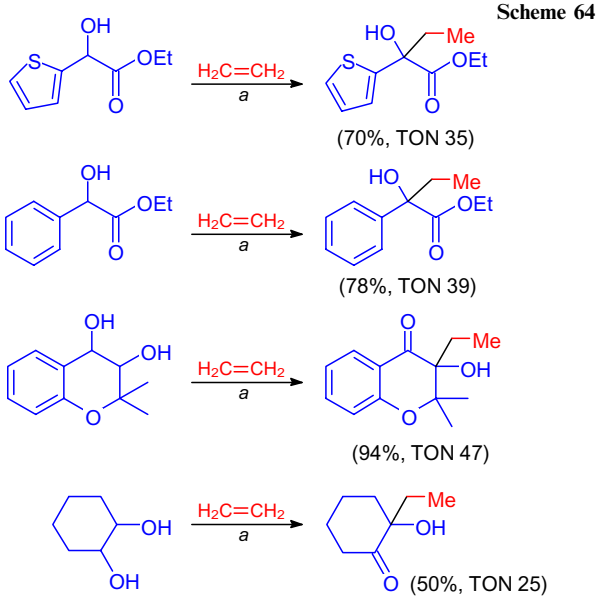
Scheme 63



6. Reductive dimerization reaction

In 2007, Sridevi and Leong[63] carried out the dimerization of 9-bromofluorene in the presence of $Os_3(CO)_{12}$ in refluxing toluene (Scheme 66). Among other osmium compounds, $OsCl_3$ was also tested as a catalyst, but this salt showed a low activity. The authors suggested that this reaction follows the radical mechanism. It should be noted that $FeCl_3$ proved to be the most active catalyst.

Scheme 64



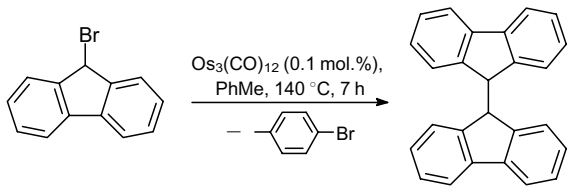
(*a*) $Os_3(CO)_{12}$ (2 mol.%), Xphos (12 mol.%), 1-$AdCO_2H$ (10 mol.%), PhMe, 130 – 140°C; Ad is 1-adamantyl

7. Hydrogenation reactions

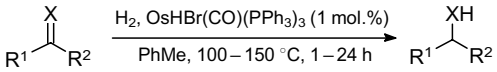
In 1965, Vaska[64] found that the complex $OsHCl(CO)(Ph_3P)_3$ can catalyze the hydrogenation of acetylene to ethylene and ethane (the publication provides no details). In 1973, Leigh and co-workers[65] reported the hydrogenation of cycloocta-1,5-diene to cyclooctene (1 atm H_2, refluxing toluene) catalyzed by the complex $OsH_4(PEtPh_2)_3$. Three years lates, Muetterties and co-workers[66] carried out the hydrogenation of CO to methane (2 atm H_2, toluene, 140 °C) using $Os_3(CO)_{12}$.

In 1985, Sánchez-Delgado *et al.*[21] studied the catalytic activity of the complex $OsHBr(CO)(Ph_3P)_3$ in the hydrogenation of aliphatic and aromatic aldehydes and ketones (Scheme 67, Table 21). This complex exhibited high selectivity in the hydrogenation of C=C bonds in α,β-unsaturated carbonyl compounds, *e.g.*, cyclohex-2-enone.

Scheme 66



Scheme 67



X = O, $CAlk_2$

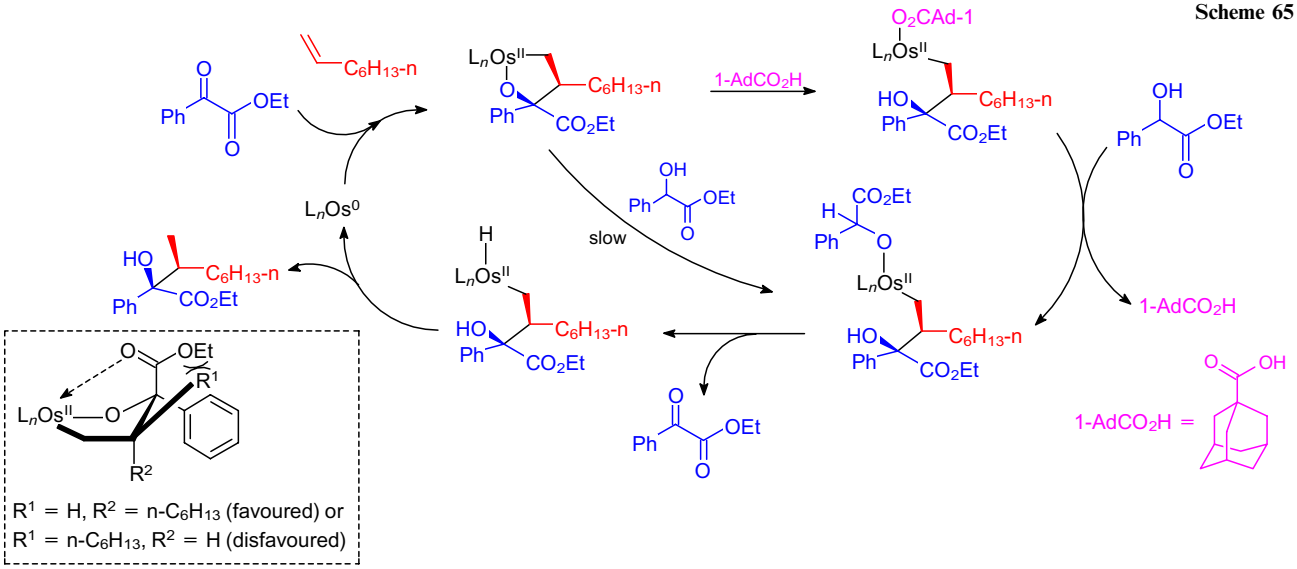
Table 21. Catalytic activity of the complex $OsHBr(CO)(Ph_3P)_3$ in hydrogenation reactions (see Scheme 67).[21]

Product	H_2 pressure, atm	Temperature, °C	Time, h	TON
	1	100	24	80
	68	150	3	15
	30	150	1.7	100
	1	100	24	85

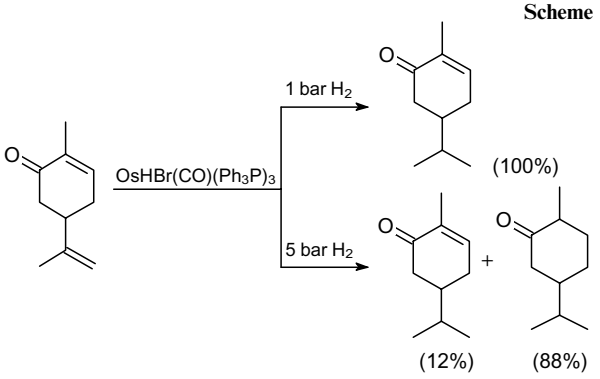
In addition, the authors showed that when using this catalytic system, L-carvone can give, depending on the pressure, hydrogenation products of one or two C=C bonds, with the carbonyl moiety of L-carvone remaining intact (Scheme 68).

Subsequently, the same research team studied the catalytic activity of osmium complexes in the hydrogenation of aliphatic and aromatic saturated and unsaturated carbonyl compounds. The rate constants were determined for the complexes $OsHCl(CO)(Ph_3P)_3$, $OsHBr(CO)(Ph_3P)_3$,

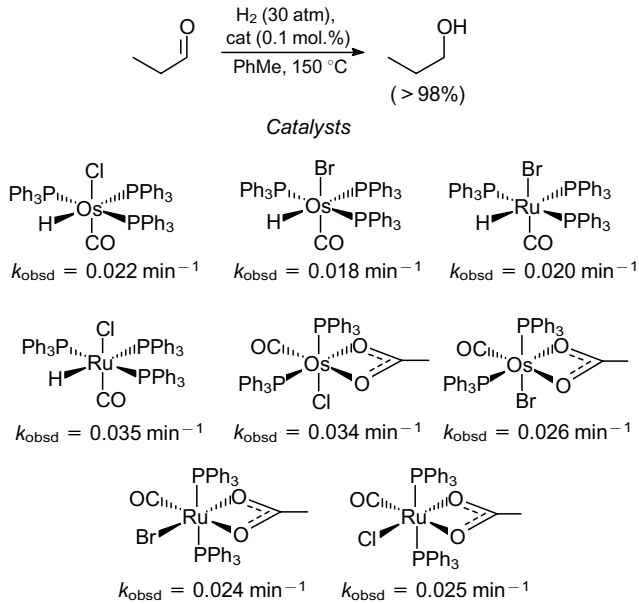
Scheme 65



Scheme 68



Scheme 69

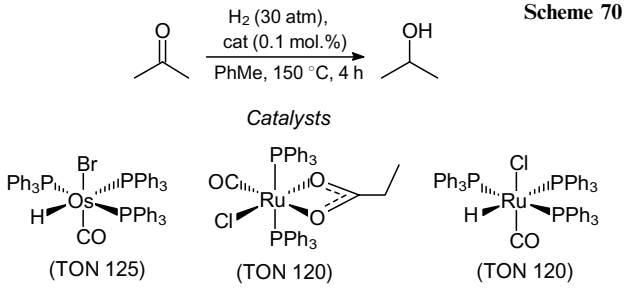


k_{obsd} is the observed rate constant

$Os(CO)Cl(OAc)(Ph_3P)_2$, $Os(CO)Br(OAc)(Ph_3P)_2$ (Scheme 69).[67]

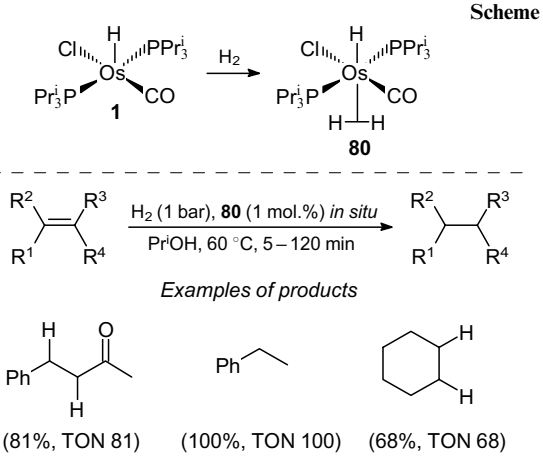
The acetate complexes $Os(CO)Hal(OAc)(Ph_3P)_2$ proved to be more active than the compounds $OsHHal(CO)(Ph_3P)_3$, whereas the reverse situation was observed for ruthenium derivatives. In general, the activity of osmium complexes in the reduction of both aldehydes and ketones was not inferior to that of their ruthenium analogues (Scheme 70). In particular, in the hydrogenation of acetone, the turnover frequency of the osmium complex even slightly exceeded this value for the ruthenium analogue.

Scheme 70



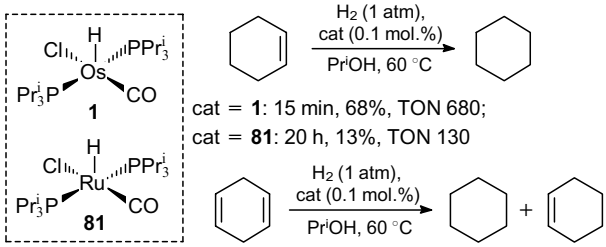
In 1988, Oro, Werner and co-workers[68] prepared catalytically active complex **80** with molecular hydrogen containing an $Os(\eta^2\text{-}H_2)$ structural unit (Scheme 71). Complex **80** efficiently catalyzes the hydrogenation of carbon–carbon double bonds including those in α,β-unsaturated carbonyl compounds.

Scheme 71



A year later, the same research team[25] found that the complex $OsHCl(CO)(PPr^i_3)_2$ (**1**) far exceeds the activity of its ruthenium analogue **81** in the hydrogenation of cyclohexene and cyclohexadienes (Scheme 72).

Scheme 72



Subsequently, Sánchez-Delgado *et al.*[69] developed a number of catalytic systems for the hydrogenation of cinnamaldehyde. It was found that both different osmium hydrides and complexes derived *in situ* from simple osmium salts (*e.g.*, $Na_2OsCl_6 \cdot 6H_2O$, $OsCl_3 \cdot 3H_2O$) and various phosphine ligands [PPh_3, diphenyl(*m*-sulfonatophenyl)-phosphine (TPPMS) and tris(*m*-sulfonatophenyl)phosphine (TPPTS)], in toluene or water–toluene mixtures, display similar moderate activity (Scheme 73, Table 22).

In 2004, Rosales *et al.*[70] carried out the hydrogenation of cyclohexanone catalyzed by the complex salt $[OsH(CO)(NCMe)_2(PPh_3)_2]BF_4$ (**82**), and studied the mechanism of this reaction (Scheme 74). The catalytic cycle begins with the replacement of one acetonitrile molecule with a ketone molecule in the ligand environment of osmium. Then a hydride migration occurs from the osmium atom to the carbonyl carbon atom followed by the oxidative addition of molecular oxygen to the osmium atom to form two hydride bonds. Next, a coordinated hydrogen atom migrates to the oxygen atom. In the final step of the

Scheme 73

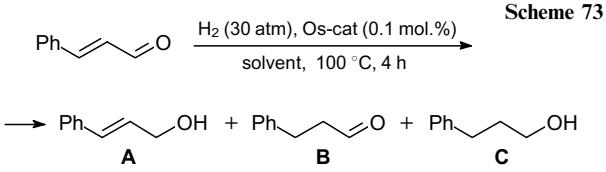
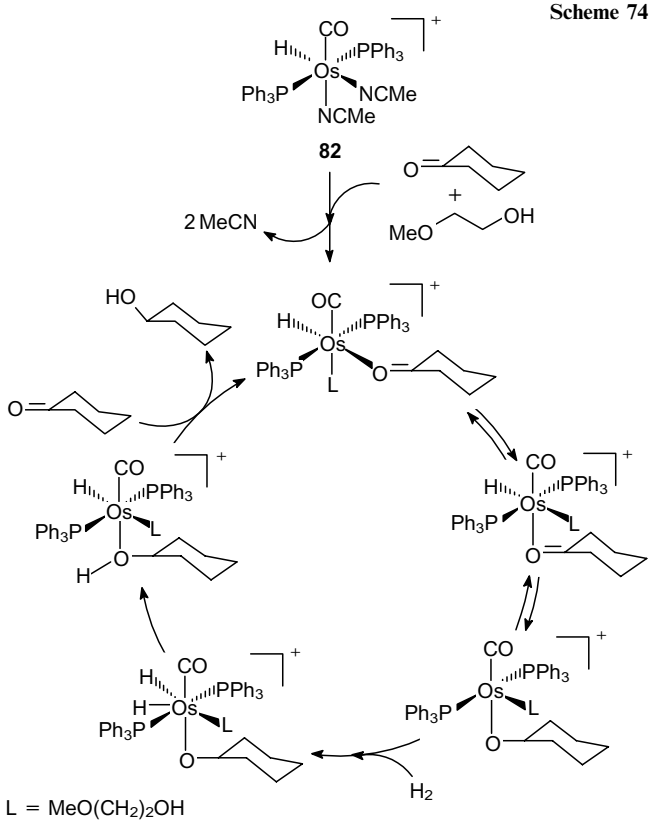


Table 22. Catalytic activity of osmium complexes in the hydrogenation of cinnamaldehyde (see Scheme 73).[69]

Complex	Auxiliary ligand	Solvent	Yield (%) (TON)		
			A	B	C
$OsCl_3 \cdot 3\,H_2O$	PPh_3	PhMe	76 (760)	3	13
$Na_2OsCl_6 \cdot 6\,H_2O$	PPh_3	PhMe	49 (490)	29	10
$OsHCl(CO)(PPh_3)_3$	—	PhMe	19	4	21 (210)
$OsCl_3 \cdot 3\,H_2O$	TPPMS	PhMe, H_2O	36 (360)	4	2
$Na_2OsCl_6 \cdot 6\,H_2O$	TPPMS	PhMe, H_2O	33 (330)	6	8
$OsHCl(CO)(TPPMS)_2$ (see [a])	—	PhMe, H_2O	35 (350)	10	7

[a] The conversion of the substrate is 58%.

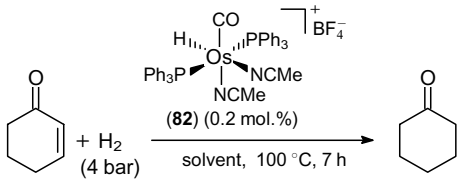
Scheme 74



catalytic cycle, the resulting alcohol molecule is replaced with a molecule of the starting carbonyl compound.

Complex **82** was found to be highly selective in the reduction of C=C bonds in α,β-unsaturated carbonyl compounds. Thus, the carbonyl functionality in cyclohex-2-enone remains intact until the C=C bond is reduced (Scheme 75). The authors suggested that such selectivity can

Scheme 75

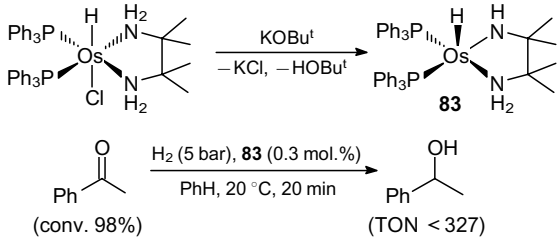


solvent = PhMe (65%, TON 325), $MeO(CH_2)_2OH$ (60%, TON 300)

be due to the increased ability of the osmium complex to coordinate over the carbon double bond in a manner similar to classical Wilkinson s rhodium catalysts.

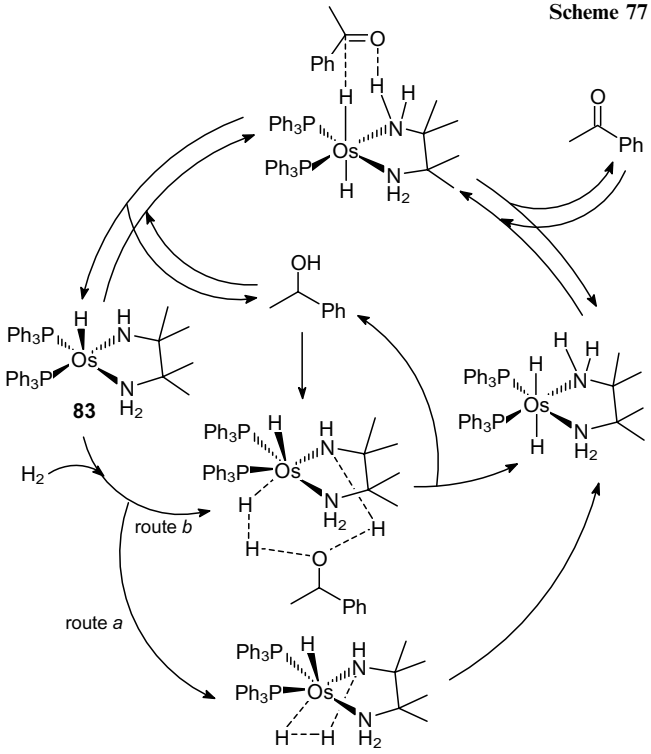
In 2005, Clapham and Morris [71] prepared osmium amide complex **83** (Scheme 76), capable of catalyzing the hydrogenation of acetophenone under mild conditions in a short period of time.

Scheme 76



Only a decade later, the mechanism for the hydrogenation using this complex was proposed (Scheme 77).[72] When studying the kinetics of the hydrogenation, the authors observed differences in the behaviour of osmium complex **83** and the related similar ruthenium complex. Thus, the hydrogenation of acetophenone catalyzed by the former compound involved an induction period, during which the

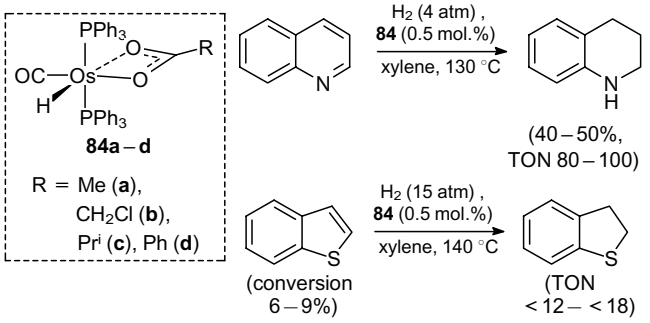
Scheme 77



target alcohol formed very slowly. However, once the alcohol is formed, the reaction is greatly accelerated. The authors explain this fact by the strength of the amide bond in complex **83**, the weakening of which is critical for splitting the hydrogen molecule (see Scheme 77, route *a*). The resulting alcohol contributes to the weakening of the bonding between atoms in the hydrogen molecule, thereby facilitating the formation of the hydride (route *b*). Therefore, this process is autocatalytic. In the course of the study, the authors also demonstrated that complex **83** can be active in the hydrogen transfer reaction. Thus, under reduced pressure, the target alcohol is dehydrogenated back to the starting acetophenone.

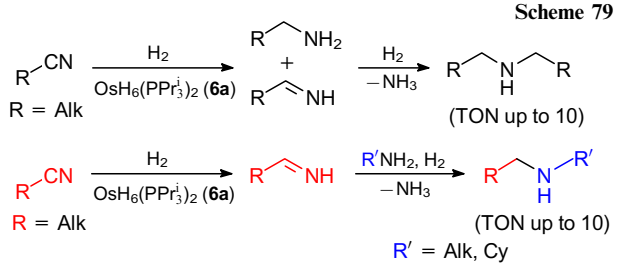
In 2008, Rosales *et al.*[73] found that a number of ruthenium and osmium carboxylate complexes can act as catalysts for the hydrogenation of quinoline and benzothiophene to 1,2,3,4-tetrahydroquinoline and 2,3-dihydrobenzothiophene, respectively (Scheme 78). In these reactions, osmium complexes **84a**–**d** showed a lower catalytic activity than their ruthenium conterparts.

Scheme 78



In 2020, Esteruelas and co-workers[74] developed an osmium-based catalytic system for the production of secondary amines from nitriles (Scheme 79). In particular, using the complex $OsH_6(PPr^i_3)_2$ (**6a**), the authors succeeded in performing this reaction with a wide range of nitriles and amines giving products in good to high yields (70–99%).

Scheme 79



In 2008, as part of their previous studies of the catalytic properties of osmium complexes, Baratta *et al.*[48] showed that the complexes active in hydrogen transfer reactions can also catalyze hydrogenation with molecular hydrogen. The best performance was observed for the catalytic system comprising a 1 : 3 mixture of complexes **52a** and **52b** (Scheme 80, Table 23). This system enabled the hydrogenation of acetophenone, *tert*-butyl phenyl ketone and a number of aliphatic cyclic and acyclic ketones to the corresponding alcohols with high conversion values.

Moreover, using osmium complex **40** as a catalyst, the authors managed to carry out the reaction in an enantioselective fashion and produce a series of *S*-configured alcohols from acetophenone derivatives with an enantiomeric excess of 86–98% (Scheme 81, Table 24).[45]

Scheme 80

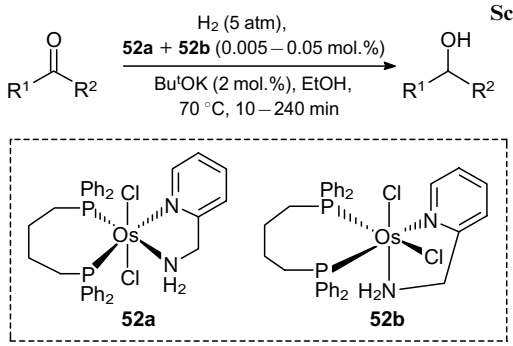


Table 23. Catalytic activity of a mixture of osmium complexes **52a** and **52b** in the hydrogenation of ketones (see Scheme 80).[48]

R^1	R^2	Conversion (%)	TON	TOF, h^{-1}
Ph	Me	99	< 19 800	$< 1.3 \times 10^4$
Ph	Bu^t	97	< 9700	$< 1.1 \times 10^4$
Bu^t	Me	97	< 9700	$< 1.1 \times 10^4$
$CH(Me)(CH_2)_4$		99	< 9900	$< 7.0 \times 10^3$
$CH_2{=}CH(CH_2)_2$	Me	99	< 9900	$< 1.4 \times 10^4$

Scheme 81

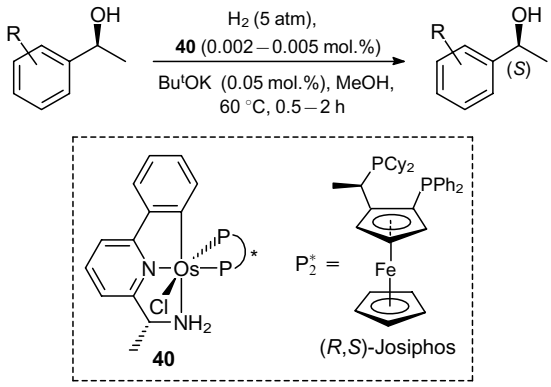


Table 24. Catalytic activity of osmium complex **40** in the hydrogenation of acetophenone derivatives (see Scheme 81).[45]

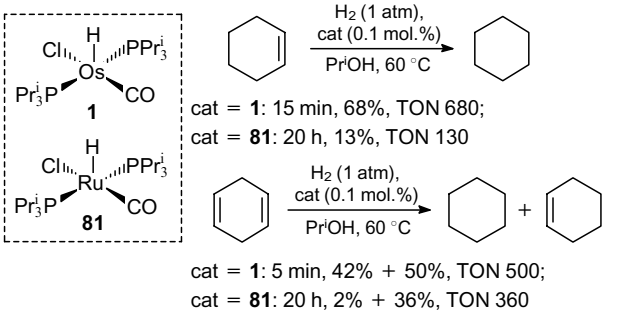
R	Conversion (%)	*ee* (%)	TON	TOF, h^{-1}
H	99	86	< 19 800	$< 1.2 \times 10^4$
2-OMe	99	93	< 19 800	$< 2.2 \times 10^4$
3-OMe	99	98	< 19 800	$< 2.0 \times 10^4$
3-Cl[a]	98	98	< 49 000	$< 3.0 \times 10^4$

[a] The reaction was carried out at 70 °C.

Special attention should be given to diamine complexes of the $[OsX_2(diphosphine)(diamine)]$ type, which demonstrate high catalytic activity in the hydrogenation of ketones and aldehydes.[75] In the hydrogenation of carbonyl compounds, osmium complex **85** turned out to be the most active (Scheme 82).

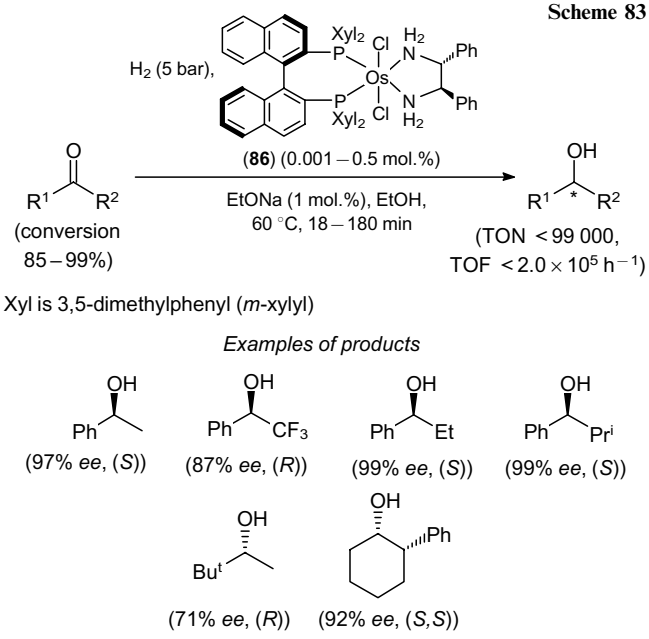
This complex can catalyze the hydrogenation of aromatic and aliphatic aldehydes and ketones to yield the target alcohols with an almost complete conversion of the

Scheme 82



substrates. Among the catalysts bearing optically active ligands, the best performance was observed for complex **86** containing a binaphthyl-based phosphine ligand (Scheme 83). The enantioselective hydrogenation of aromatic and aliphatic ketones using the catalysis by complex **86** delivers products with enantiomeric excess from 71 to 99%.

Scheme 83



In 2018, the range of diamine complexes, having the general formula [$OsHal_2$(diphosphine)(diamine)], was significantly expanded. Like the previously prepared complexes of this type,[75] these complexes showed extremely high catalytic activity and, in some cases, high stereoselectivity in the hydrogenation of ketones.[76] The highest enantiomeric excess (90%) for the reduction product was reached using diphosphine (*R*,*S*)-Josiphos*.

Osmium complex **54** bearing the 1,1′-bis(diphenylphosphino)ferrocenyl ligand, which was previously found to be highly active in hydrogen transfer reactions, also turned out to be an effective catalyst for the hydrogenation of carbonyl compounds with molecular hydrogen (Scheme 84, Table 25).[49] It should be noted that catalytic systems based on compound **54** require higher temperature in the hydrogenation reactions than those containing its ruthenium analogue.

In 2010, in continuation of their research on osmium complexes, Baratta *et al.*[77] prepared a number of optically

Scheme 84

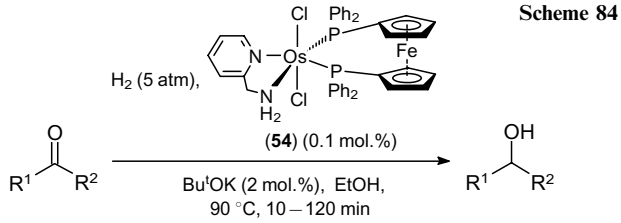
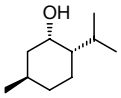
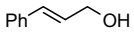
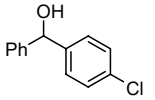


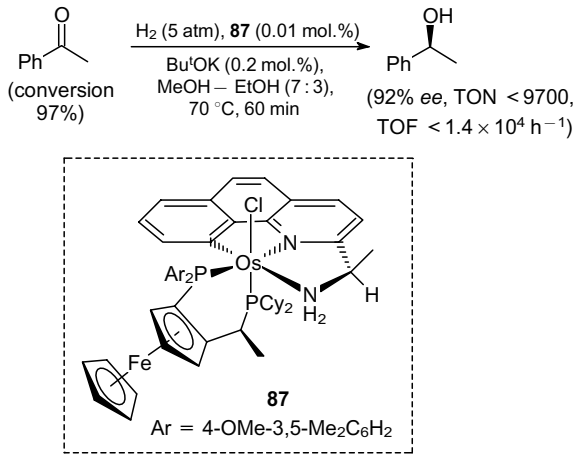
Table 25. Catalytic activity of osmium complex **54** in the hydrogenation of carbonyl compounds (see Scheme 84).[49]

Product	Conversion (%)	TON	TOF, h^{-1}
	98	< 980	$< 1.0 \times 10^4$
	90 [a]	< 900	$< 3.7 \times 103^4$
	91 [b]	< 910	$< 1.0 \times 10^3$
	90	< 900	$< 4.6 \times 10^3$
	97	< 970	$< 4.6 \times 10^3$

[a] The diastereomeric ratio (*dr*) is 2 : 1; [b] the reacton time is 8 h.

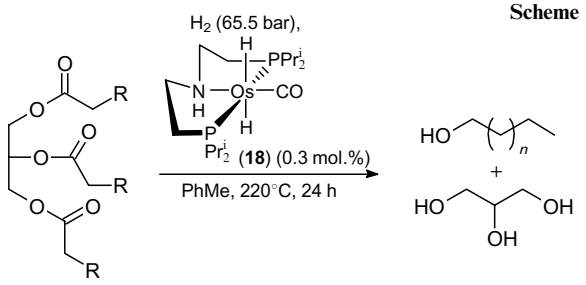
active HCNN complexes, which were employed as catalysts in the hydrogenation of ketones. For instance, complex **87** provides the reduction of acetophenone to (*S*)-alcohol with 92% enantiomeric excess (Scheme 85). Optically inactive complexes of this group can catalyze the hydrogenation of aromatic and aliphatic ketones to provide complete conversion of the substrates. Moreover, complexes such as compound **87** can show high catalytic activity even when generated *in situ*.

Scheme 85



In 2012, Gusev and co-workers[78] demonstrated the efficiency of complexes **17** and **18** (Scheme 86) in the hydrogenation of esters bearing long-chain aliphatic substituents, including fatty acid triglycerides, to alcohols. Importantly, in the case of unsaturated esters, both complexes effectively catalyze the hydrogenation of C=C bonds; however, they

Scheme 86

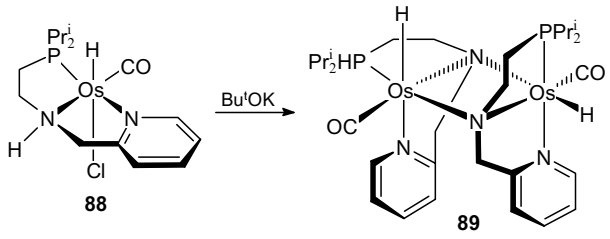


RCH_2CO_2H is oleic, linoliec, palmitic or stearic acid;
n = 13 (cetyl alcohol) or 15 (stearyl alcohol)

became almost inactive in the hydrogenation of an ester functionality.

Continuing the search for robust catalysts for the hydrogenation of esters, Gusev and co-workers[79] expanded the family of osmium pincer complexes. The authors found that when treated with potassium *tert*-butoxide, complex **88** yields dimer **89** (Scheme 87).

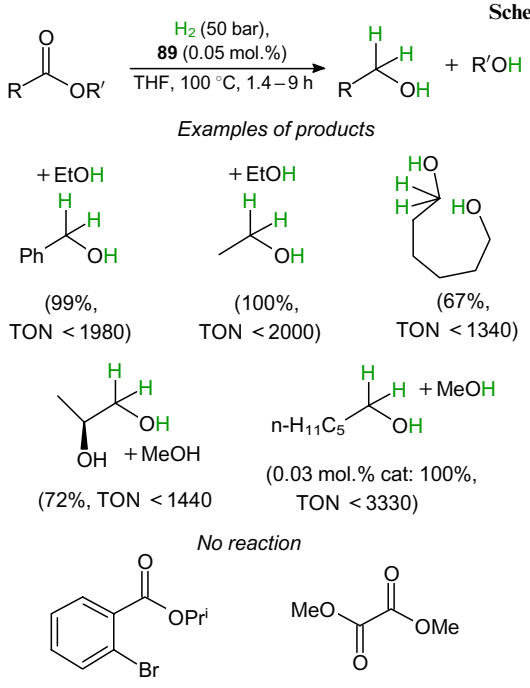
Scheme 87



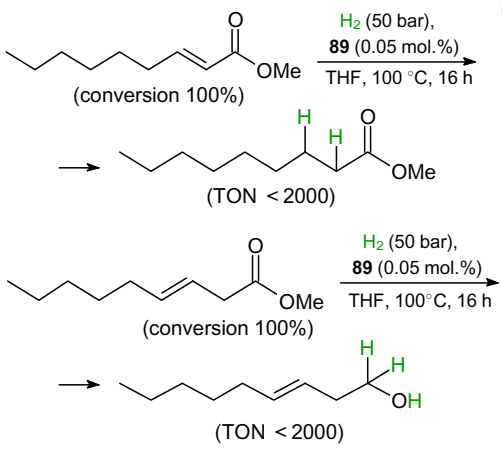
It turned out that complex **89** displays a high catalytic activity in the hydrogenation of esters, although it is inferior to its ruthenium analogue (Scheme 88).

It should also be noted that when catalyzed with this complex, in the case of α,β-unsaturated ester, only the double bond is reduced, while the ester functionality

Scheme 88



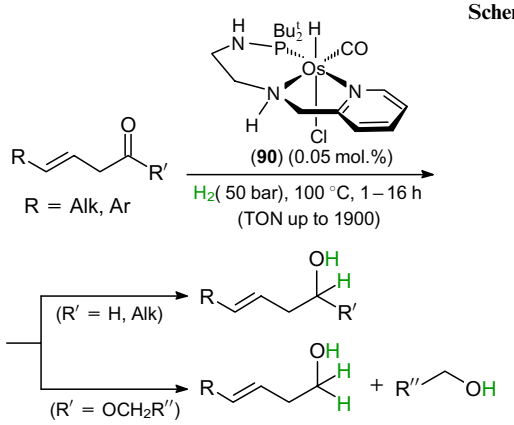
Scheme 89



remains intacts, whereas in the presence of an isolated double bond, only the ester moiety is reduced (Scheme 89).

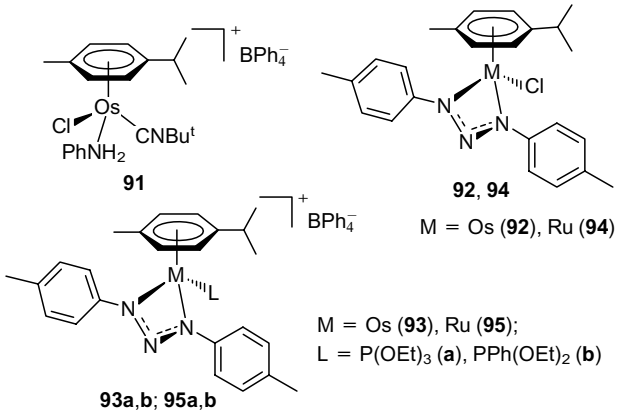
Derivative **90**, related to compound **88** and containing an additional NH functionality in the pincer ligand, showed high selectivity in the reduction of aldehydes, ketones and esters, since it did not affect the carbon–carbon double bond (Scheme 90).[80]

Scheme 90



In 2010, Albertin *et al.*[81] synthesized osmium derivative **91** and also a number of complexes of osmium (**92**, **93**) and ruthenium (**94**, **95**), which, in addition to the (η^6-cymene)Os moiety, included 1,3-triazene ligands.

Structures 91 – 95



The authors compared the catalytic performance of the resulting complexes in the hydrogenation reactions. Ruthenium complexes **94**, **95** were found to be superior to their osmium analogues in activity in the hydrogenation of α,β-unsaturated carbonyl compounds. Thus, ruthenium complexes **95a**,**b** allow for the hydrogenation of cyclohex-2-enone at lower temperatures as compared to their osmium analogues **93a**,**b** (Scheme 91, Table 26).

Scheme 91

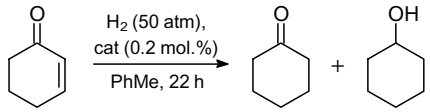
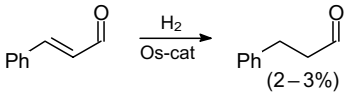


Table 26. Comparison of the catalytic activity of osmium and ruthenium complexes in the hydrogenation of cyclohex-2-enone (see Scheme 91).[81]

Catalyst	Metal	Temperature, °C	Yield (%) (TON)	
			cyclohexanone	cyclohexanol
91	Os	100	0	100 (500)
		80	64 (320)	12
92	Os	100	81 (405)	19
		80	10 (50)	0
94	Ru	80	22 (110)	8
93a	Os	100	58 (290)	42
93b	Os	100	61 (305)	39
95a	Ru	60	85 (425)	6
		80	24	76 (380)
95b	Ru	60	82 (410)	5
		80	27	73 (365)

In the hydrogenation of cinnamaldehyde, none of the tested osmium complexes showed any catalytic activity (Scheme 92), while the ruthenium derivatives provided the conversion of the substrate up to 90%.

Scheme 92

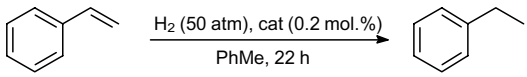


The authors believe that the low catalytic activity of osmium complexes in the hydrogenation of cinnamaldehyde is due to the steric crowding of these complexes. During this study, it was also demonstrated that the activity of ruthenium and osmium catalysts does not change much when the triethyl phosphite ligand is replaced with diethylphenyl phosphonite.

Among osmium compounds, complexes **91** and **92** were the most active in the hydrogenation of alkenes. Such catalysts, for example, enabled the quantitative reduction of styrene to ethylbenzene (Scheme 93) at low catalyst loading (0.2 mol.%). Despite the low productivity, osmium complexes proved to be more stable than their ruthenium analogues, allowing their regeneration after the completion of the reaction.[81]

In 2013, Phillips and co-workers[82] for the first time prepared osmium β-diketiminato complexes **96** and **97**.

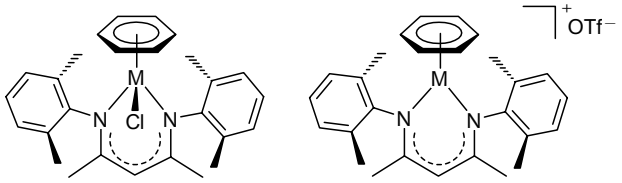
Scheme 93



Catalyst	Temperature, °C	Yield (%)	TON
91	80	100	500
92	100	100	500
93a	80	95	475
93b	100	84	420

When studying their catalytic activity in the olefin hydrogenation, complexes **96** and **97** were found to be far superior to their ruthenium analogues **98** and **99**. The only exception was the most sterically crowded alkene, 1-methylcyclohexene, which was reduced in an acceptable yield (41%) only using ruthenium complex **99** (Scheme 94, Table 27). It is also noteworthy that in the case of limonene in the presence of catalyst **96**, it was possible to selectively

Structures 96 – 99



96, **98** **97**, **99**

M = Os (**96**, **97**), Ru (**98**, **99**)

Scheme 94

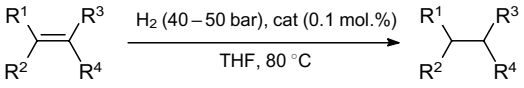
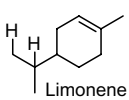


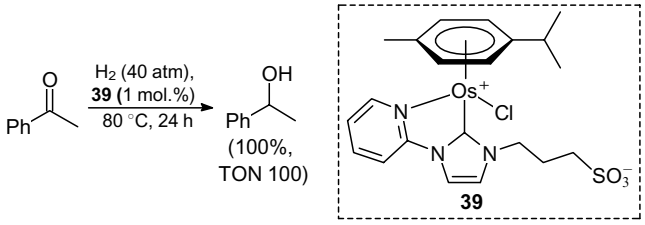
Table 27. Catalytic activity of osmium (**96**, **97**) and ruthenium (**98**, **99**) complexes in olefin hydrogenation (see Scheme 94).[82]

Product	Catalyst	Metal	Time, h	Conversion (%)	TOF, h^{-1}
	**96**	Os	0.5	92	< 1842
	98	Ru	0.5	66	< 1326
	97	Os	0.5	62	< 1246
	99	Ru	1.0	84	< 836
	**96**	Os	0.5	55	< 1060
	98	Ru	0.5	42	< 840
	97	Os	0.5	75	< 1492
	99	Ru	0.5	64	< 1276
	**96**	Os	1.0	7	< 66
	98	Ru	1.0	7	< 69
	97	Os	1.0	6	< 60
	99	Ru	1.0	41	< 406
	**96**	Os	1.5	97	< 647
	98	Ru	1.0	8	< 64
	97	Os	1.0	50	< 334
	99	Ru	1.0	20	< 195

reduce only the terminal double bond without affecting the endocyclic one.

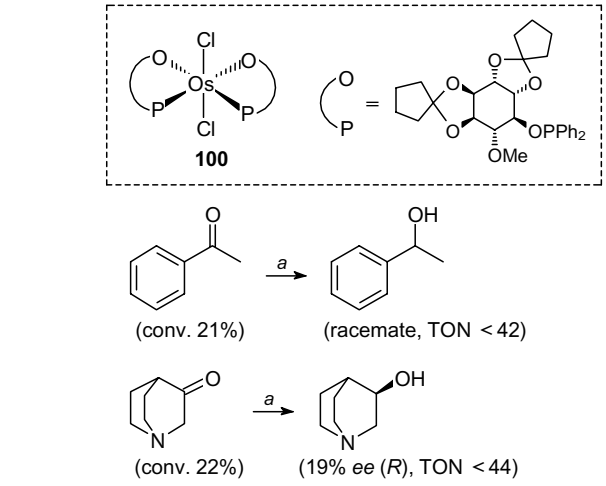
Subsequently, in studies on the development of water-soluble catalysts for hydrogen transfer reactions, Kühn and co-workers [44] showed that osmium complex **39** also has high activity in the hydrogenation of acetophenone (Scheme 95). However, related rhodium complexes bearing a pentamethylcyclopentadienyl (Cp*) moiety proved to be more active.

Scheme 95



In 2014, Wright and co-workers [83] described a wide range of ruthenium complexes with monophosphinite ligands and one osmium complex (**100**). The latter compound showed a lower catalytic performance in the hydrogenation of acetophenone and quinuclidin-3-one than its ruthenium analogues (Scheme 96).

Scheme 96



(*a*) H_2 (69 atm), **100** (0.5 mol.%), Bu^{t}OK (2 mol.%), PhMe – Pr^{i}OH (1 : 1), 60 °C, 3 h

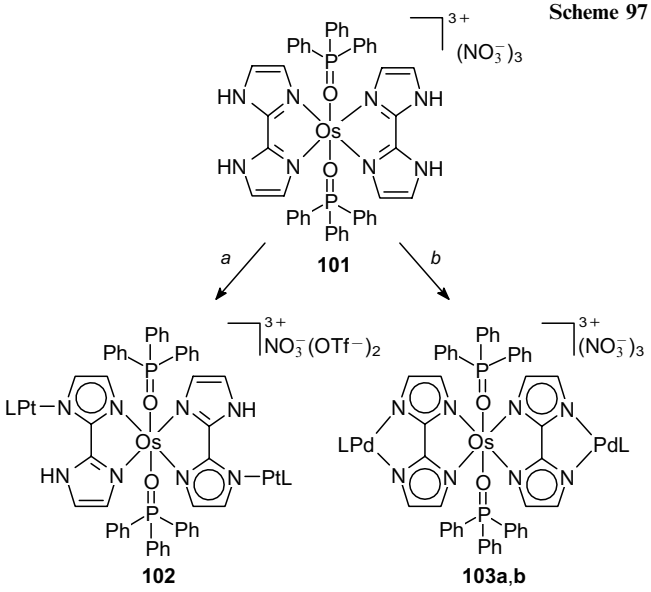
In 2003, Comba and co-workers [84] used derivative **101** to prepare heteronuclear osmium complexes **102** and **103** with other platinum group metal complexes (Scheme 97).

The authors found that [(COD)Pd]-containing complex **103a** showed the highest activity in the hydrogenation of alkenes (Scheme 98).

It is noteworthy that the hydrogenation of hex-1-ene is also accompanied by isomerization with the double bond shifting inside the carbon chain (Scheme 99).

According to the proposed mechanism, the hydrogenation occurs at the palladium atom, whereas osmium only stablilzes the catalytic centre, thereby preventing the formation of palladium metal.[84]

Scheme 97

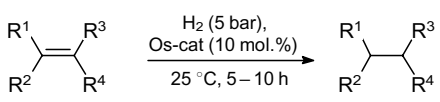


L = $C_6H_3(CH_2NMe_2\text{-}2,6)_2$

(*a*) 1) KOH (2 equiv.), 2) $PtL(OTf)_2$ (2 equiv.);
(*b*) $PdL(NO_3)_2$ (2 equiv.), KOH (4 equiv.)

L = COD (**a**), en (**b**); COD is cycloocta-1,5-diene, en is ethylenediamine

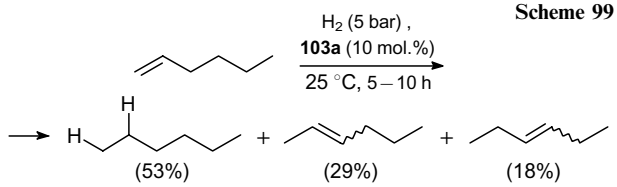
Scheme 98



Examples of products

Catalyst	yield (%)	TON	yield (%)	TON
101	11	1	0	–
102	7	0.7	3	0.3
103a	53	5	36	3.6
103b	15	1.5	10	1

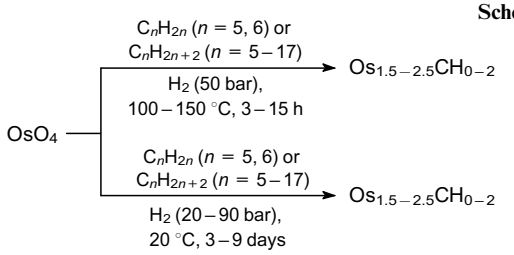
Scheme 99



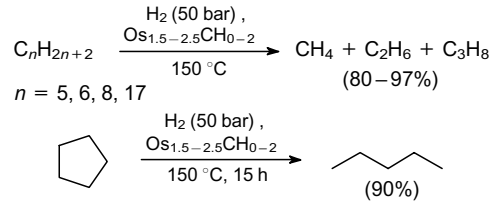
In 1989, Vol'pin and co-workers [85] developed a catalytic system for the hydrogenolysis of alkanes and cycloalkanes (Scheme 100). The catalysts were prepared by the reduction of OsO_4 with hydrogen (50 bar) in alkanes (C_5-C_{17}) and cycloalkanes (C_5-C_6) at 100 – 150 °C for 3 – 15 h or at 20 °C for 3 – 9 days at a hydrogen pressure of 20 – 90 bar. The authors found that the catalysts are particles of the composition of $Os_{1.5-2.5}CH_{0-2}$ with a size of 10 – 40 Å and a specific surface area of 34 – 46 $m^2\ g^{-1}$.

The hydrogenolysis occurs under drastic conditions: at a temperature of 150 °C and a hydrogen pressure of 50 bar (Scheme 101).

Scheme 100



Scheme 101



It should be noted that the reduction of OsO_4 with hydrogen in the presence of diisobutylaluminium hydride (DIBAl-H) produces a less active catalyst. The authors also demonstrated that an active catalyst can be prepared by the reduction in water; on the contrary, the use of acetic acid led to an inactive catalyst. The prepared catalysts can be stored only under a hydrogen atmosphere, otherwise they undergo irreversible poisoning.

The idea of using nanoparticles as hydrogenation catalysts was further developed by Feldmann *et al.*[86] using bimetallic $NiOs_4$ nanoparticles. Despite a decrease in the activity of $NiOs_4$ particles in the hydrogenation of cinnamaldehyde as compared to individual Ni and Os particles, this alloy has increased selectivity in the reduction of 1,2-diphenylacetylene to (*Z*)-stilbene: the *Z* : *E* isomer ratio (in %) is 85 : 5, the remaining 10% is 1,2-diphenylethane.

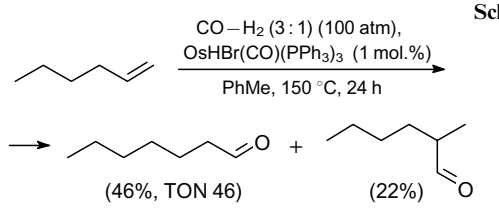
8. Hydroformylation reactions

The hydroformylation is an important atom-economical approach to the synthesis of aldehydes from alkenes using carbon monoxide and hydrogen. The most effective systems for the hydroformylation were obtained based on cobalt and rhodium.[87] Osmium compounds remain understudied catalysts for such reactions.

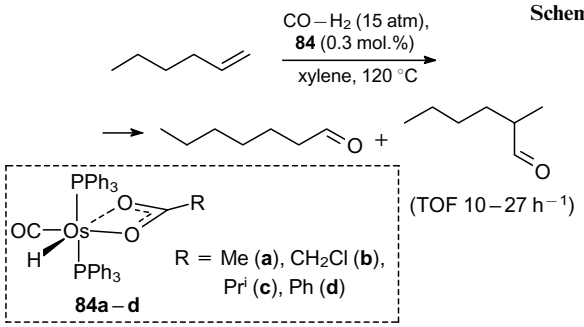
Nevertheless, in 1985 Sánchez-Delgado *et al.*[21] showed on the example of hex-1-ene that the osmium phosphine complex $OsHBr(CO)(Ph_3P)_3$ can catalyze the hydroformylation reaction. The authors managed to obtain heptanal in moderate yield with an admixture of isomeric 2-methylhexanal (Scheme 102).

Osmium carboxylate complexes **84a–d** obtained by Rosales *et al.*[73] also show a catalytic activity in the hydroformylation of hex-1-ene (Scheme 103). The ratio of normal to iso aldehydes under the said conditions was 0.8–1.6.

Scheme 102



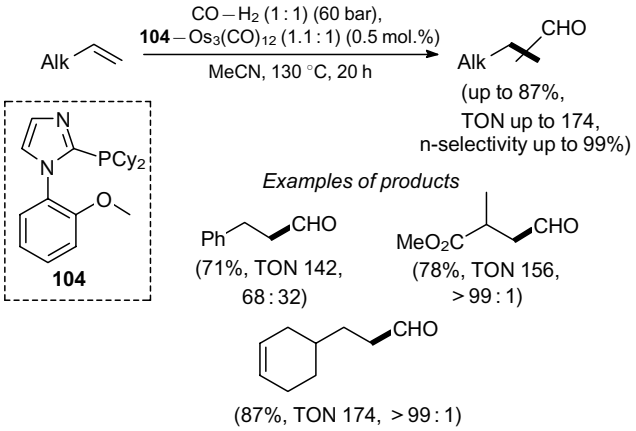
Scheme 103



However, these complexes proved to be less effective than their ruthenium analogues.

Beller and co-workers[87] have been much more successful in using osmium complexes in the hydroformylation of alkenes. It was found that osmium carbonyl $Os_3(CO)_{12}$, along with various imidazolyl-substituted phosphine ligands (*e.g.*, **104**), allows the selective synthesis of linear aldehydes in high yields (Scheme 104; in addition to the yield and TON value, the ratio of normal to iso aldehydes are given in parentheses below the product formulae). Not only simple but also functionalized alkenes can be used in this reaction.

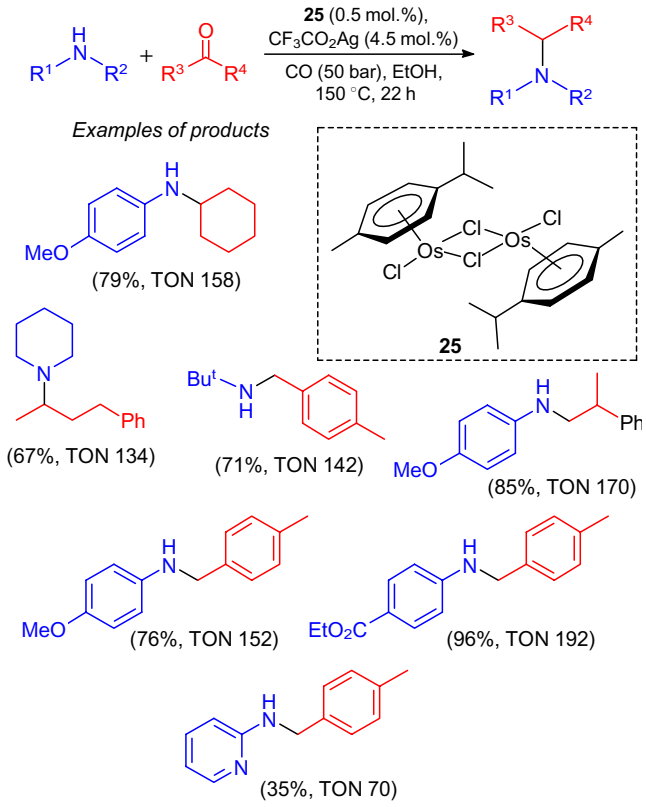
Scheme 104



9. Reductive amination without an external hydrogen source

The authors of the present review developed the osmium-catalyzed reductive amination without an external hydrogen source using carbon monoxide as a reducing agent (Scheme 105).[88] It was possible to perform this reaction of a number of aliphatic and aromatic aldehydes and ketones with aromatic and aliphatic amines; the yields ranged from satisfactory to high. The readily available complex $[(\eta^6\text{-cymene})OsCl_2]_2$ (**25**), which should be activated by a silver salt, served as a catalyst. It was found that one of the proposed mechanisms includes the intermediate formation of hemiaminal, and its coordination to the osmium complex is stabilized by an intramolecular hydrogen bonding. Osmium compexes proved to be more active catalysts as compared to iridium derivatives. However, they were inferior to the rhodium and ruthenium complexes, which is explained by the formation of a more stable and hence less active compound in the case of metals of the third transition series.

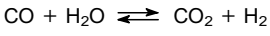
Scheme 105



10. Water-gas shift reaction

Water-gas shift reaction (WGSR) (Scheme 106) is of interest not only for industry but also for organic chemistry, allowing for reduction processes.[89]

Scheme 106



Despite extensive research on this reaction, osmium catalytic systems are scarce, and the synthetic potential of such systems is largely unexplored.

In 1977, Pettit and co-workers[90] showed that osmium carbonyl compounds [$Os_3(CO)_{12}$, $H_2Os_3(CO)_{10}$ and $H_4Os_4(CO)_{12}$] are catalytically active in the hydroformylation of propene using the water-gas shift reaction, which provided hydrogen necessary for this transformation. Interestingly, in the case of $Os_3(CO)_{12}$, the reaction did not stop in the step of isobutyraldehyde formation, but led to the reduction of aldehyde to alcohol (the ratio of aldehyde to alcohol was 6.6 : 1). At the same time, the complexes $H_2Os_3(CO)_{10}$ and $H_4Os_4(CO)_{12}$, although being less active, exhibited higher selectivity — the ratio of aldehyde to alcohol reached ~300 : 1 (Scheme 107). The catalysts used in this process, the ratios of the catalyst to the amounts of the newly formed butyraldehyde and the released hydrogen, the amounts of normal and iso aldehydes and the amounts of aldehydes and alcohol are given in Table 28.

Subsequently, King *et al.*[91] found that $Os_3(CO)_{12}$ is an active homogeneous catalyst for the water-gas shift reaction. This complex was virtually impervious to the action of sulfides, in contrast to $Fe(CO)_5$, whose catalytic activity disappeared in the presence of sulfide ions in the system (Scheme 108).

Scheme 107

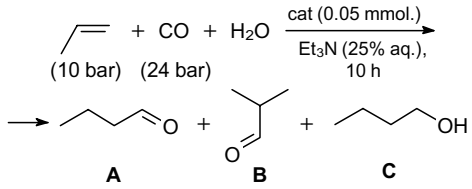
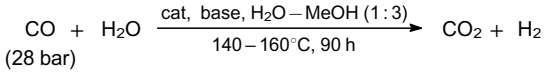


Table 28. Catalytic activity of osmium and ruthenium complexes in the hydroformylation of propene (see Scheme 107).[90]

Catalyst	Temperature, °C	(A + B) : cat, mol	A : B	(A + B) : C, mol	WGSR, H_2 : cat, mol
$H_4Ru_4(CO)_{12}$	100	79	11	37	3400
$Os_3(CO)_{12}$	180	13	1.9	6.6	270
$H_2Os_3(CO)_{10}$	180	6	1.2	~300	270
$H_4Os_4(CO)_{12}$	180	9	1.4	~300	400

Scheme 108



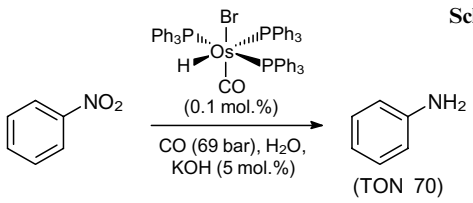
Complex	Base	Reaction rate, mol H_2 per day (mol of catalyst)$^{-1}$
$Os_3(CO)_{12}$	KOH	210
$Os_3(CO)_{12}$	Na_2S	200
$Fe(CO)_5$	KOH	650
$Fe(CO)_5$	Na_2S	0

Since it is known[91] that many feed gaseous mixtures for the water-gas shift reaction may contain sulfur-containing impurities, an industrial catalyst system should have high sulfur tolerance. In 1981, Ganzerla *et al.*[92] found that zeolite-supported $Os_3(CO)_{12}$ reacts on heating with hydroxy groups of the support to give a variety of compounds, which are active in the water-gas shift reaction. Therefore, the activity of the catalyst depends on the thermal treatment used. When using NaOH, the hydrido carbonyl anion $[H_3Os_4(CO)_{10}]^-$ is formed, and this anion is trapped in the zeolite framework and also is an active catalyst for the water-gas shift reaction.[93]

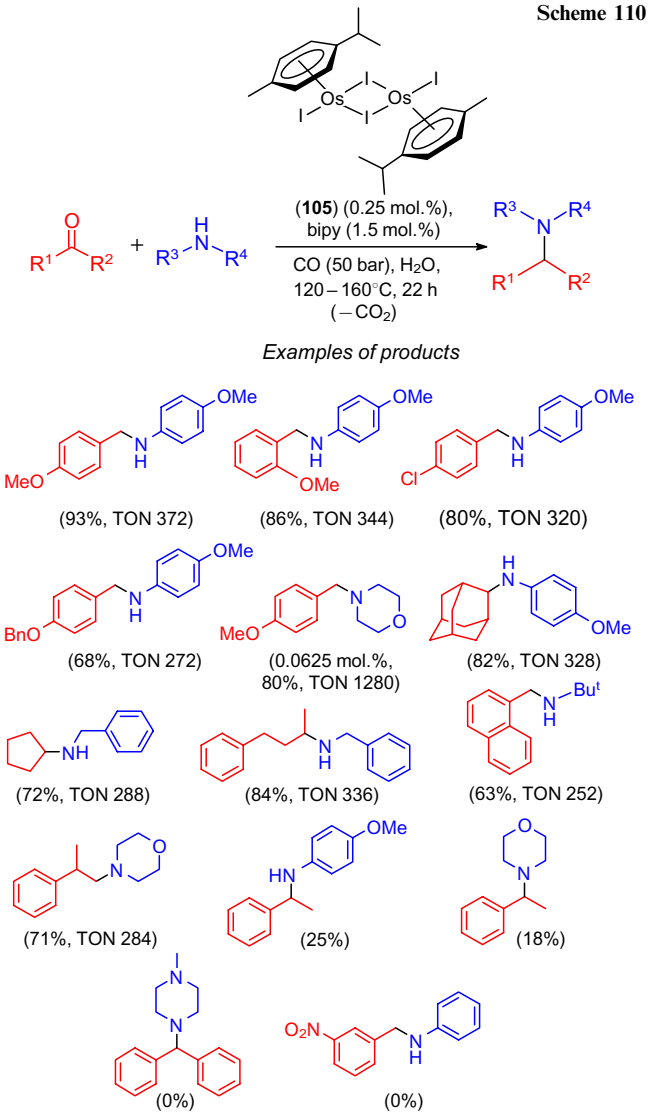
By using the water-gas shift reaction, Oramas and Sánchez-Delgado[94] found that the complex $OsHBr(CO)(PPh_3)_3$ is able to reduce nitrobenzene to aniline (Scheme 109). However, in this process, the osmium complex is significantly inferior to ruthenium analogues.

In 2021, the authors of this review developed a method for the osmium-catalyzed reductive amination using the water-gas shift reaction (Scheme 110). Iodide $[(\eta^6\text{-cymene})OsI_2]_2$ (**105**) was proposed as a catalyst, which

Scheme 109



Scheme 110

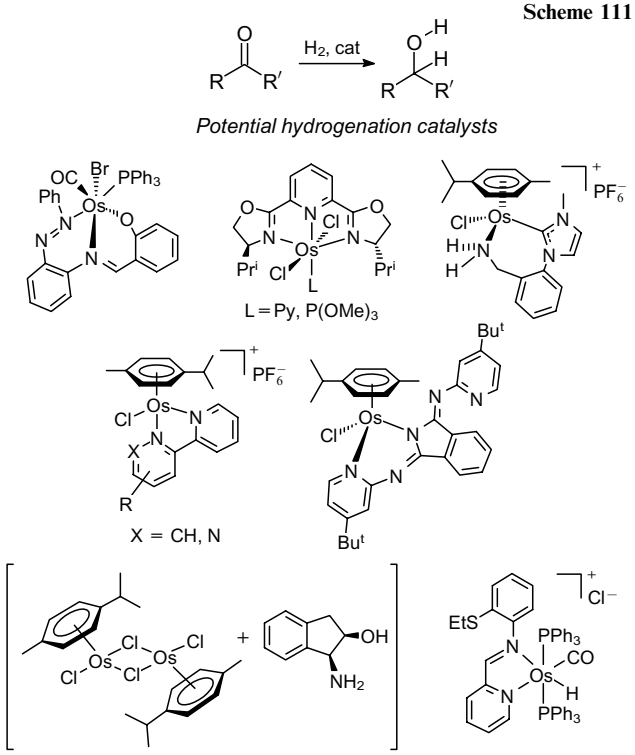


proved to be more active than the related chloride. Also, it was found that the addition of N,N′-ligands, such as 2,2′-bipyridine (bipy) and 1,10′-phenanthroline, significantly improves the activity of the catalytic system. This process tolerates a wide range of functionalities (*e.g.*, Cl, BnN, BnO) in the substrate; moreover, various aliphatic ketones and even sterically hindered adamantan-2-one enter this reaction. However, under these conditions, aromatic ketones, such as benzophenone and acetophenone, showed poor reactivity, and it was not possible to subject the compounds bearing nitro and cyano groups to this reaction.

11. Conclusion

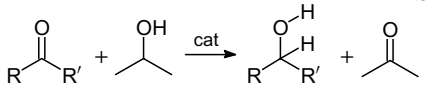
The present review considers various reductive catalytic systems based on osmium compounds. An analysis of the literature in this field revealed a number of general features. Osmium complexes bearing nitrogen-containing ligands can be superior to their ruthenium analogues in hydrogenation and hydrogen transfer reactions and also in certain other processes, *e.g.*, in reductive amination using the water-gas shift reaction. This has been successfully demonstrated by the research teams led by Gusev, Sadler, Baratta, Gamasa and others. The most active catalysts for the described processes are summarized in Table 29. The advantage of osmium complexes in reduction reactions in relation to derivatives of earlier transition elements may be due to the high affinity of this metal for the formation of hydride complexes. This may also be the cause why osmium complexes, which show a catalytic activity in the hydrogen transfer reaction and related transformations, are able to effectively catalyze hydrogenation reactions with molecular hydrogen (Scheme 111). Both reactions occur through similar intermediates containing Os–H bonds.

Scheme 111



Conversely, catalysts that are active in the hydrogenation may be active in the hydrogen transfer (Scheme 112).

Scheme 112



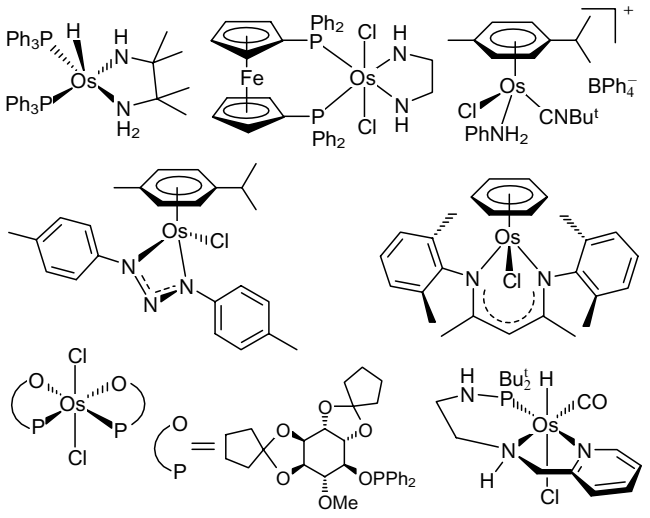
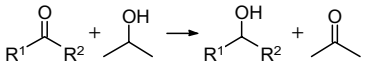
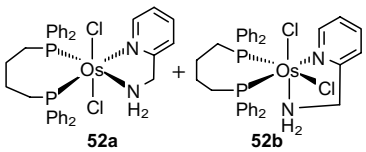
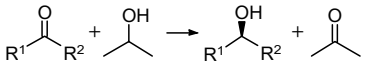
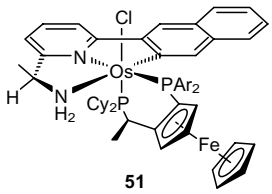
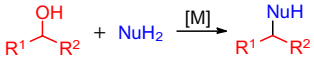
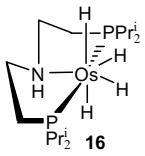
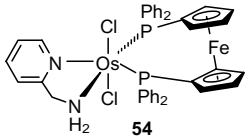
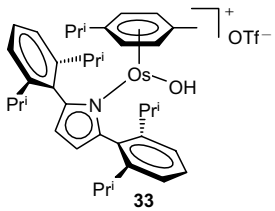
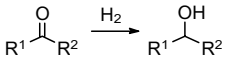
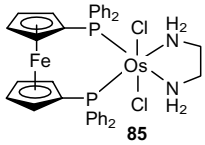
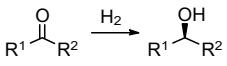
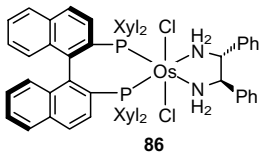
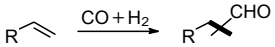
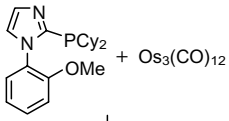
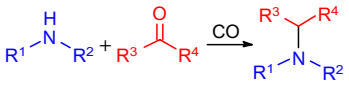
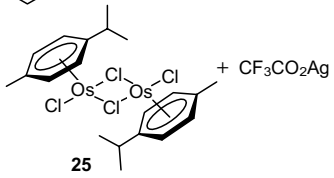
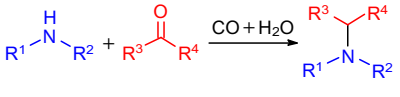
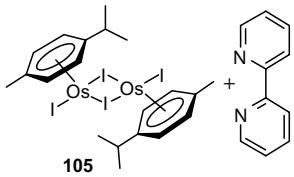


Table 29. Most active osmium catalysts for various reactions.

Name of the reaction	Reaction scheme	Catalyst structure	Maximum values	Ref.
Hydrogen transfer		 **52a** **52b**	TON < 98 000, TOF $< 3.4 \times 10^5$ h^{-1}	48
Hydrogen transfer (enantioselective variant)		 **51** (Ar = 4-OMe-3,5-$Me_2C_6H_2$)	97% *ee*, TON < 48 500, TOF $< 9.0 \times 10^5$ h^{-1}	47
Borrowing hydrogen		 **16**	$NuH_2 = RNH_2$: TON 920	31
		 **54**	$NuH_2 = R^3C(O)CH_2R^4$: TON < 186	49
		 **33**	$NuH_2 = ArCH_2CN$: TON 99	55
Hydrogenation		 **85**	TON < 196 000, TOF $< 3.0 \times 10^5$ h^{-1}	75
Hydrogenation (enantioselective variant)		 **86**	99% *ee*, TON < 99 000, TOF $< 2.0 \times 10^5$ h^{-1}	75
Hydroformylation			TON 174	87
Reductive amination		 **25**	TON 192	88
Water-gas shift reaction		 **105**	TON 1280	95

Among chiral ligands, the tandem of P,P,N,N-ligands and N,O-ligands (*e.g.*, amino alcohols) are the most effective for these transformations. The least promising chiral ligands are carboxylates (RCO_2^-) and N,O-ligands (*e.g.*, amino acids).

Another advantage of osmium systems over related ruthenium complexes is the convenience of their use due to their high stability. This was clearly demonstrated by Sadler s group.[49, 50] In particular, 16-electron Noyori-type osmium complexes were found to be air-stable, and their synthesis and further use in catalysis do not require an inert atmosphere, while in the case of ruthenium it was necessary to use a more stable Noyori-type second generation 18-electron pre-catalyst. Moreover, osmium hydrides have increased stability, thus allowing the fixation of key intermediates in various reduction reactions. Further research in this field is expected to provide a better understanding of the mechanisms for various reduction reactions and also may enable the development of new effective catalysts based on other metals.

One of the main factors hampering the development of osmium-catalyzed reductive transformations is high toxicity of osmium tetroxide. However, there is no information[96] about the toxicity of other osmium compounds, even such simple compounds as halides. Therefore, assumptions about the toxicity of osmium compounds should not prevent the study of the chemistry of these compounds. A major actual drawback of osmium complexes is the high strength of the bonds formed by this metal, which complicates both the synthesis of the complexes *per se* and their application in catalysis. Along with iridium derivatives, osmium complexes are still much less frequently used in catalysis compared to rhodium and ruthenium analogues. Nevertheless, the material of this review clearly demonstrates that osmium complexes have good prospects as catalysts for reduction reactions proceeding through the formation of metal hydrides.

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12. List of acronyms

Ad — adamantyl,
bipy — 2,2′-bipyridine,
COD — cycloocta-1,5-diene,
Cy — cyclohexyl,
DFT — density functional theory,
DIBAl-H — diisobutylaluminium hydride,
dppb — 1,4-bis(diphenylphosphino)butane,
ee — enantiomeric excess,
en — ethylenediamine,
EWG — electron-withdrawing group,
FA — formic acid,
LA — lactic acid,
MW — microwave irradiation,
Naph — naphthyl,
PA — pyruvic acid,
Py — pyridyl,
rt — room temperature,
TOF — turnover frequency,
TON — turnover number,
TPPMS — diphenyl(*m*-sulfonatophenyl)phosphine,
TPPTS — tris(*m*-sulfonatophenyl)phosphine,
Ts — *p*-toluenesulfonyl (tosyl),
WGSR — water-gas shift reaction,
Xyl — 3,5-dimethylphenyl (*m*-xylyl),
k_{obsd} — observed rate constant.

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