OsXCl(phosphine)2(diamine) and OsXCl(diphosphine)(diamine) (X = Cl, H) Complexes for Ketone Hydrogenation

Final version

Organometallics

OsXCl(phosphine)$_2$(diamine) and OsXCl(diphosphine)(diamine) (X = Cl, H) Complexes for Ketone Hydrogenation

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Abstract

The osmium complex *trans*-[$OsCl_2(PPh_3)_2$(en)] (**2**) was prepared by reaction of [$OsCl_2(PPh_3)_3$] (**1a**) with ethylenediamine (en), whereas the diphosphine derivatives *trans*-[$OsCl_2$(dppf)(NN)] (NN = en, **3**; bn = 1,4-butanediamine, **4**) and *trans*-[$OsCl_2$(dpbp)(en)] (**5**) were obtained from **1a**, dppf or dpbp and the corresponding NN ligand in CH_2Cl_2 or toluene. An X-ray diffraction study has been provided for **3**. The isolation of the chiral derivatives *trans*-[$OsCl_2$(diphosphine)((*R*,*R*)-dpen)] (diphosphine = dppf, **6**; dpbp, **7**; (*R*,*R*)-skewphos, **8**) was achieved by reacting **1a** with the diphosphine and (*R*,*R*)-dpen in toluene. Treatment of the precursor [Os_2Cl_4(P(*m*-tolyl)$_3$)$_5$] (**1b**) with en afforded [$OsCl_2$(P(*m*-tolyl)$_3$)$_2$(en)] (**9**), while reaction of **1b** with dppb and *N*,*N*-dmen gave [$OsCl_2$(dppb)(*N*,*N*-dmen)] (**10**). The chiral derivatives [$OsCl_2$(diphosphine)(NN)] (**11**-**21**) (diphosphine = (*S*)-MeObiphep, (*R*)-MeObiphep, (*R*)-xylMeObiphep, (*R*)-binap, (*S*)-xylbinap), (*R*)-xylbinap, (*R*,*S*)-Josiphos*; NN = en, (*R*,*R*)-dpen, (*R*)-daipen, (*R*,*R*)-dppn) were prepared from **1b** and the corresponding diphosphine and NN ligands in toluene. The monohydride *trans*-[OsHCl(P(*m*-tolyl)$_3$)$_2$(en)] (**22**) was synthesized by reaction of **1b** with H_2 (1 atm) in the presence of NEt_3, followed by addition of en in toluene. Similarly, *trans*-[OsHCl(dppf)(en)] (**23**) was synthetized from **1a**, H_2 and NEt_3, followed by treatment with dppf and en. Complexes **2-5**, **9**, **10**, **22** and **23** efficiently catalyzed the hydrogenation of acetophenone with H_2 under low pressure (5 atm) at 60-70 °C in ethanol (1-2 mol% of NaOEt) with a ratio S/C = 5000-10000. The chiral derivatives **6-8** and **11-21** afforded the asymmetric hydrogenation of acetophenone with up to 90%

ee by combining bulky xylyl substituted MeObiphep or binap-type ligands with (*R*)-daipen or (*R,R*)-dpen ligands. Catalytic transfer hydrogenation of acetophenone was observed with **3**, **6** and **7** (S/C = 2000) in 2-propanol and in the presence of NaO*i*Pr (2 mol%) at 60-82 °C.

Introduction

The preparation of new efficient catalysts for the selective reduction of carbonyl compounds is a subject of high relevance for both academic research and industrial applications. Great attention is focused on the catalytic hydrogenation (HY)[1] with dihydrogen and transfer hydrogenation (TH)[2] with hydrogen donor compounds, such as 2-propanol and formic acid, for the preparation of alcohols under mild reaction conditions (i.e. low pressure and temperature, low catalysts loading) and by using environmentally friendly reactants and solvents, affording small amounts of side products (atom economy).[3] In this context, several catalysts have reached high performances in terms of productivity and stereoselectivity, which are relevant parameters for the efficient synthesis of intermediates and fine chemicals. Ruthenium, rhodium and iridium complexes are usually employed as homogeneous catalysts for the reduction of C=O containing compounds. In the last decade, following the studies on *trans*-[$RuCl_2$(diphosphine)(diamine)] complexes developed by Noyori,[4] several highly efficient ruthenium catalysts have been developed for HY and TH reactions. By contrast, osmium catalysts have received much less attention on account of the expected poor catalytic activity based on the slower ligand exchange kinetics with respect to ruthenium.[5] The complexes [$OsHX(CO)(PR_3)_n$] (X = Cl, H; n = 2, 3),[6a,b] [$OsH(CO)(NCMe)_2(PPh_3)_2$][BF_4],[6c] [(η^6-*p*-cymene)OsCl(NN)]PF_6,[7] are catalysts for ketone TH, while [$OsHCl(CO)(PPh_3)$(phosphine)$_2$] and [$OsHCl(CO)(PPh_3)$(diphosphine)] catalyze both the TH and HY of carbonyl compounds.[5a,8] Faller and Lavoie reported that the complexes generated *in situ* from [$OsCl_2(\eta^6$-*p*-cymene)$]_2$ and β-amino alcohols allow enantioselective TH of ketones.[9] Osmium-arene TsDPEN complexes (TsDPEN = *N*-(*p*-toluenesulfonyl)-1,2-diphenylethylenediamine), analogous to the Ru Noyori-type catalysts,[10] were reported by Wills and Sadler[11] and found to catalyze the ketone asymmetric TH reduction with a relatively high catalyst loading. In addition, the amido-hydride derivative [$OsH(HNCMe_2CMe_2NH_2)(PPh_3)_2$], described by Morris and isolated from [$OsHCl(H_2NCMe_2CMe_2NH_2)(PPh_3)_2$], catalyze the HY of ketones under mild reaction conditions.[12]

We have demonstrated that the osmium complexes [$OsCl_2(PPh_3)_2$(ampy)] and [$OsCl_2$(diphosphine)(ampy)] (ampy = 2-(aminomethyl)pyridine) efficiently catalyze both the HY and the TH of ketones (S/C = 10000-100000).[13] It is worth pointing out that the activity of the osmium complexes is comparable and in some cases is higher than that observed for the analogous ruthenium derivatives.[14] Interestingly, *trans*-[$OsCl_2$(dppf)(ampy)][15] bearing the dppf[16] diphosphine

is active in a number of C-H activation reactions, namely dehydrogenation and racemization of alcohols, isomerization of allylic alcohols to ketones and α-alkylation of ketones with alcohols. The related pincer derivatives [OsCl(CNN)(diphosphine)][17,18] (HCNN = 1-(6-arylpyridin-2-yl)methanamines, 2-aminomethylbenzo[*h*]quinolines) are extremely active in the HY and TH with very low catalysts loading, attaining asymmetrical reduction of ketones, and racemization and C-deuteration of alcohols.[19] We described also the isolation of diamine osmium derivatives [OsX_2(diphosphine)(diamine)][20] (X = Cl, OR), containing binap and MeObiphep[16] phosphines which catalyze the enantioselective HY of ketone, whereas *trans*-[$OsCl_2$(dppf)(en)][21] can promote the dehydrogenation of alcohols.

We report herein the straightforward synthesis and characterization of the class of osmium complexes [OsXCl(phosphine)$_2$(diamine)] and [OsXCl(diphosphine)(diamine)] (X = Cl, H) starting from the osmium precursors [$OsCl_2(PPh_3)_3$] (**1a**) and [$Os_2Cl_4(P(m\text{-tolyl})_3)_5$] (**1b**) and the suitable achiral or chiral ligands under Ar or H_2 atmosphere (Figure 1). These complexes display good to high catalytic activity in the (asymmetric) ketone HY and TH reactions under low hydrogen pressure and with low catalyst loading.

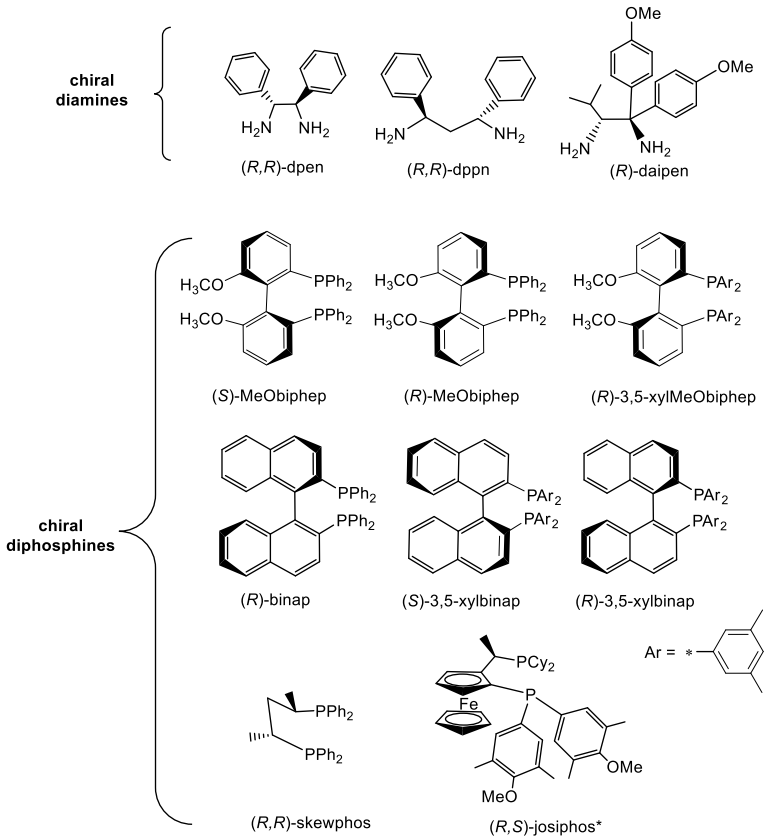
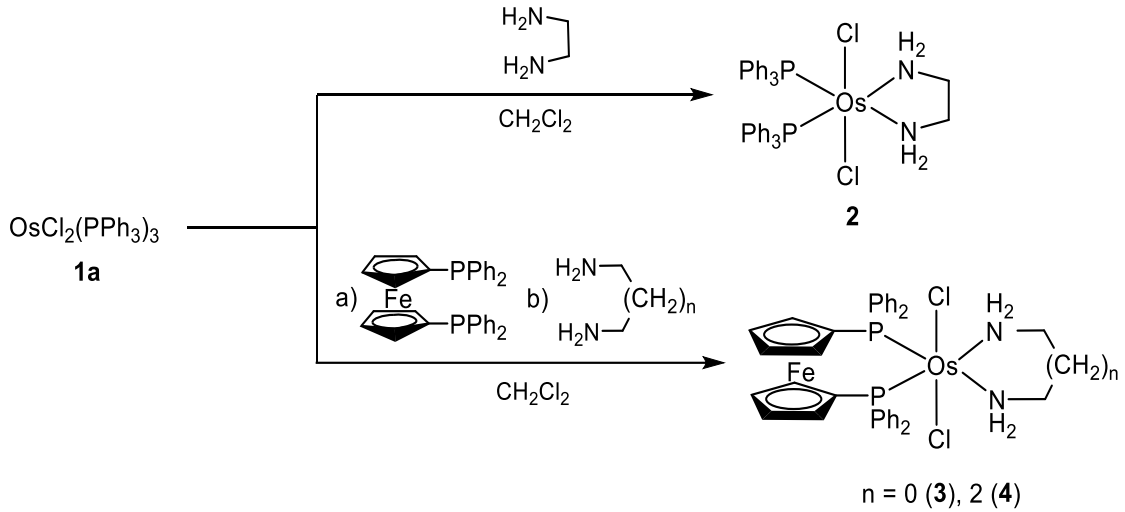


Figure 1. Chiral diamines and diphosphines

Results and Discussion

Synthesis of [$OsCl_2$(phosphine)$_2$(diamine)] and [$OsCl_2$(diphosphine)(diamine)] complexes from [$OsCl_2(PPh_3)_3$] (1a). Treatment of [$OsCl_2(PPh_3)_3$] (**1a**) with 1 equivalent of en[16] in CH_2Cl_2 at 40 °C (1 h) promptly afforded the compound *trans*-[$OsCl_2(PPh_3)_2$(en)] (**2**) isolated in 88% yield (Scheme 1).



Scheme 1. Synthesis of [$OsCl_2(PPh_3)_2$(en)] (**2**) and [$OsCl_2$(dppf)(diamine)] (**3, 4**)

The $^{31}P\{^1H\}$ NMR spectrum of **2** displays one signal at δ -11.3, consistent with a *trans* configuration of the two chloride atoms, similarly to the related ruthenium *trans*-[$RuCl_2(PPh_3)_2$(en)].[4] In the ^1H NMR spectrum the en ligand shows two broad signals at δ 3.42 and 2.67 for the CH_2 group and NH_2 groups respectively, whereas in the $^{13}C\{^1H\}$ NMR spectrum the CH_2 signal is at δ 44.2. The ferrocene derivatives **3** and **4** were prepared by reaction of **1a** with dppf in CH_2Cl_2, followed by addition of the corresponding diamine en or bn.[16] An X-ray diffraction experiment carried out for **3** shows that this complex crystallizes in a distorted octahedral geometry with the two *trans* chlorine atoms (Figure 2).

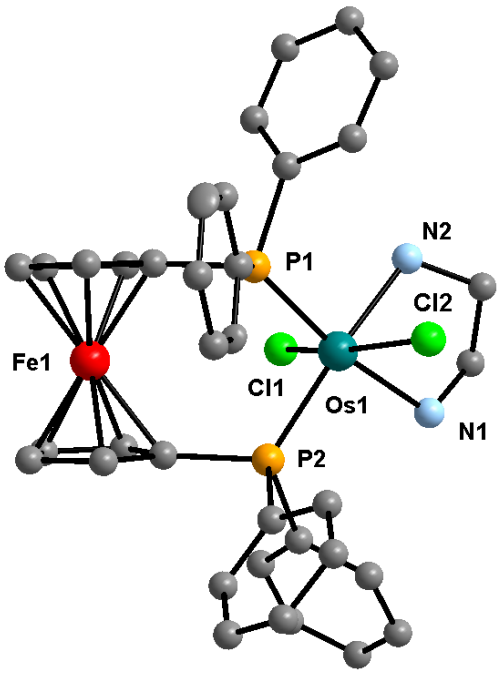


Figure 2. Diamond[22] ball and stick plot of compound **3** in the solid state

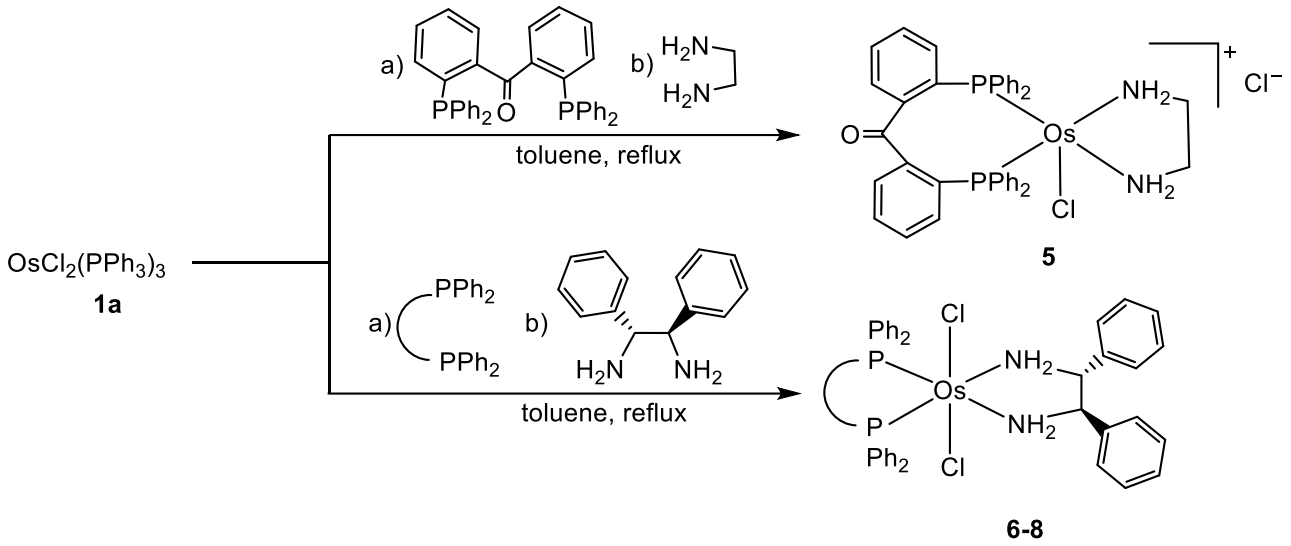
Although several diffraction studies on [$RuCl_2$(diphosphine)(diamine)] complexes were reported,[4,23] no data for the analogous osmium complexes [$OsCl_2$(diphosphine)(diamine)] were given. Complex **3** displays Os–Cl distances (2.4101(10), 2.4332(9) Å) and Os–N (2.190(3), 2.179(4) Å) slightly longer than the Ru–Cl (2.4030(10), 2.4279(10)) and Ru–N (2.167(3), 2.171(3) Å) distances observed in the related *trans*-[$RuCl_2$(dppf)(en)].[23a] Conversely, the Os–P (2.2773(10), 2.2804(11) Å) are slightly shorter than the corresponding Ru–P (2.2957(10), 2.2865(9) Å) with a Cl–M–Cl angle of 164.20(3) and 166.31(4) ° for Os and Ru, respectively (Table 1). In addition, the P-Os-P bite angle in **3** is 95.94(4) °, which is a value very close to that found for the P-Ru-P one in *trans*-[$RuCl_2$(dppf)(en)] (95.87(4) °). Complex **4** exhibits one singlet in the $^{31}P\{^1H\}$ NMR spectrum at δ -11.0 for a *trans* configuration, whereas in the ^1H NMR spectrum the diamine ligand displays three broad signals at δ 3.19, 2.77 and 1.59 for the NCH_2, NH_2 and central CH_2 groups, respectively. Finally, the $^{13}C\{^1H\}$ NMR spectrum shows two peaks at δ 41.6 and 28.9 for NCH_2 and CH_2 groups, consistent with the presence of a plane of symmetry entailing the $OsCl_2$ moiety. Reaction of **1a** in refluxing toluene with dpbp,[16] displaying a flexible and wide bite angle, followed by addition of en, afforded complex **5** in 84% yield (Scheme 2). The singlet at δ -1.6 of the $^{31}P\{^1H\}$ NMR spectrum is in agreement with a complex showing the P atoms *trans* to the N atoms, similarly to what reported for the analogous [$RuCl_2$(dpbp)(en)].[24] The ^1H NMR spectrum shows two broad signals at δ 3.68,

3.54 for the CH_2 groups and 2.95 for the NH_2 moieties, whereas in the $^{13}C\{^1H\}$ NMR spectrum the multiplet at δ 151.5 can be attributed to the carbonyl carbon of dpbp.

Table 1. Selected Bond Distances (Å) and Angles (°) of Complex *trans*-[$OsCl_2$(dppf)(en)] (3)

Os1-Cl1	2.4101(10)
Os1-Cl2	2.4332(9)
Os1-P1	2.2773(10)
Os1-P2	2.2804(11)
Os1-N1	2.190(3)
Os1-N2	2.179(4)
Cl1-Os1-Cl2	164.20(3)
Cl1-Os1-P1	97.17(3)
Cl1-Os1-P2	88.44(4)
Cl1-Os1-N1	83.10(9)
Cl1-Os1-N2	82.84(9)
Cl2-Os1-P1	90.63(3)
Cl2-Os1-P2	104.46(3)
Cl2-Os1-N1	86.78(9)
Cl2-Os1-N2	83.10(9)
P1-Os1-P2	95.94(4)
P1-Os1-N1	169.65(10)
P1-Os1-N2	92.58(9)
P2-Os1-N1	94.41(10)
P2-Os1-N2	168.50(10)

This upfield resonance with respect to free dpbp (δ 198),[24,25] is likely due to an interaction of the C=O moiety with the osmium center, via displacement of one chloride (see further part for **7**). The chiral derivatives **6** and **7** were obtained in 74-80% yield by treatment of **1a** in toluene with dppf and dpbp, respectively, followed by reaction with (*R*,*R*)-dpen[16] (Scheme 2 and Table 2).



Scheme 2. Synthesis of the non-chiral and chiral complexes [$OsCl_2$(diphosphine)(diamine)] (**5**-**8**) (see Table 2 and Figure 1)

Table 2. $^{31}P\{^1H\}$ NMR data of the complexes [$OsCl_2$(diphosphine)((*R*,*R*)-dpen)] (6-8)

Complex	Formula	δ($^{31}P\{^1H\}$)[a]
6	*trans*-[$OsCl_2$(dppf)((*R*,*R*)-dpen)]	-8.7 (s)
7	*trans*-[$OsCl_2$(dpbp)((*R*,*R*)-dpen)]	2.2 (d), - 2.5 (d) (^2J(P,P) = 5.0 Hz)
8	[$OsCl_2$((*R*,*R*)-skewphos)((*R*,*R*)-dpen)] *trans*/*cis* 2:1	*trans*: - 10.6 (s) *cis*: 0.5 (d), - 11.7 (d) (^2J(P,P) = 17.3 Hz)

[a] in C_6D_6, 20 °C.

The $^{31}P\{^1H\}$ NMR spectrum of the complex **6**, containing a C_2-symmetric diamine ligand, shows a singlet at δ -8.7 for a *trans* geometry. Conversely, the complex **7** displays two doublet at δ 2.2 and -2.5 with ^2J(P,P) = 5.0 Hz, in agreement with a C_1-symmetric complex. It is worth noting that the *tropos* benzophenone-type diphosphine dpbp shows a rapid interconversion between right and left-handed enantiomers in solution,[26a,b] as also reported for *ortho* substituted benzophenones[26c] (Figure 3).

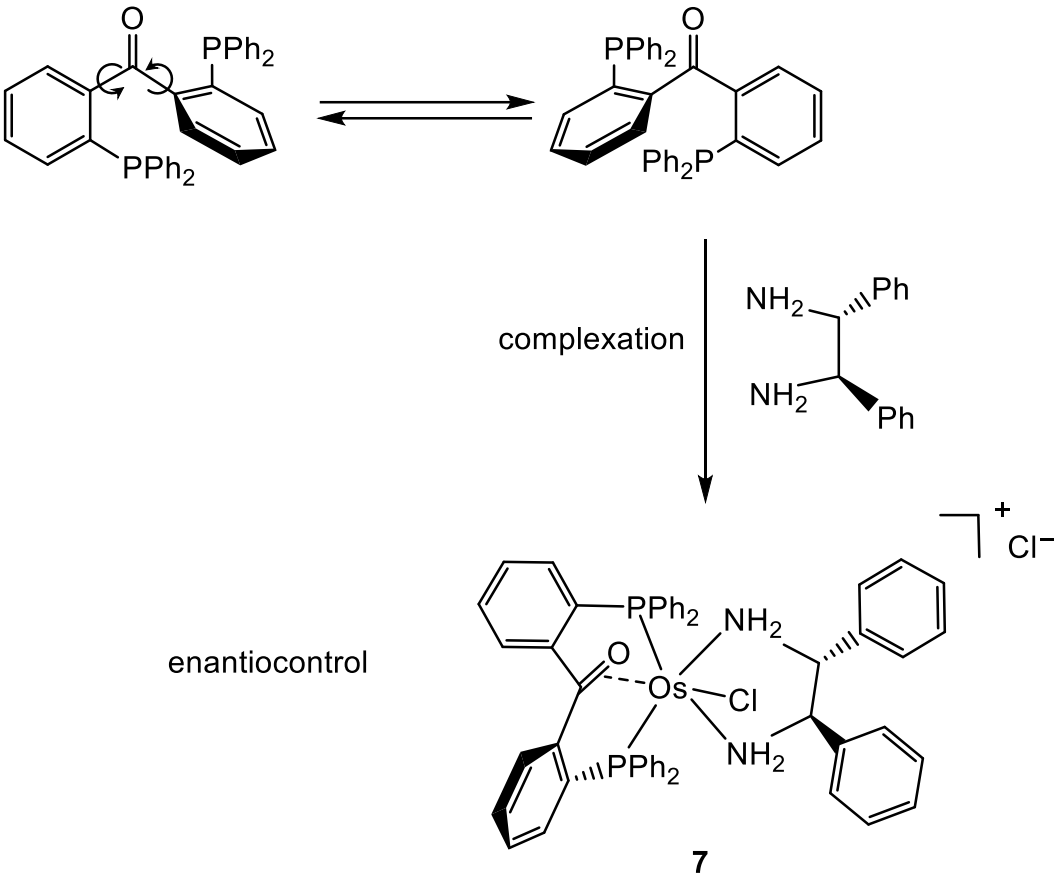
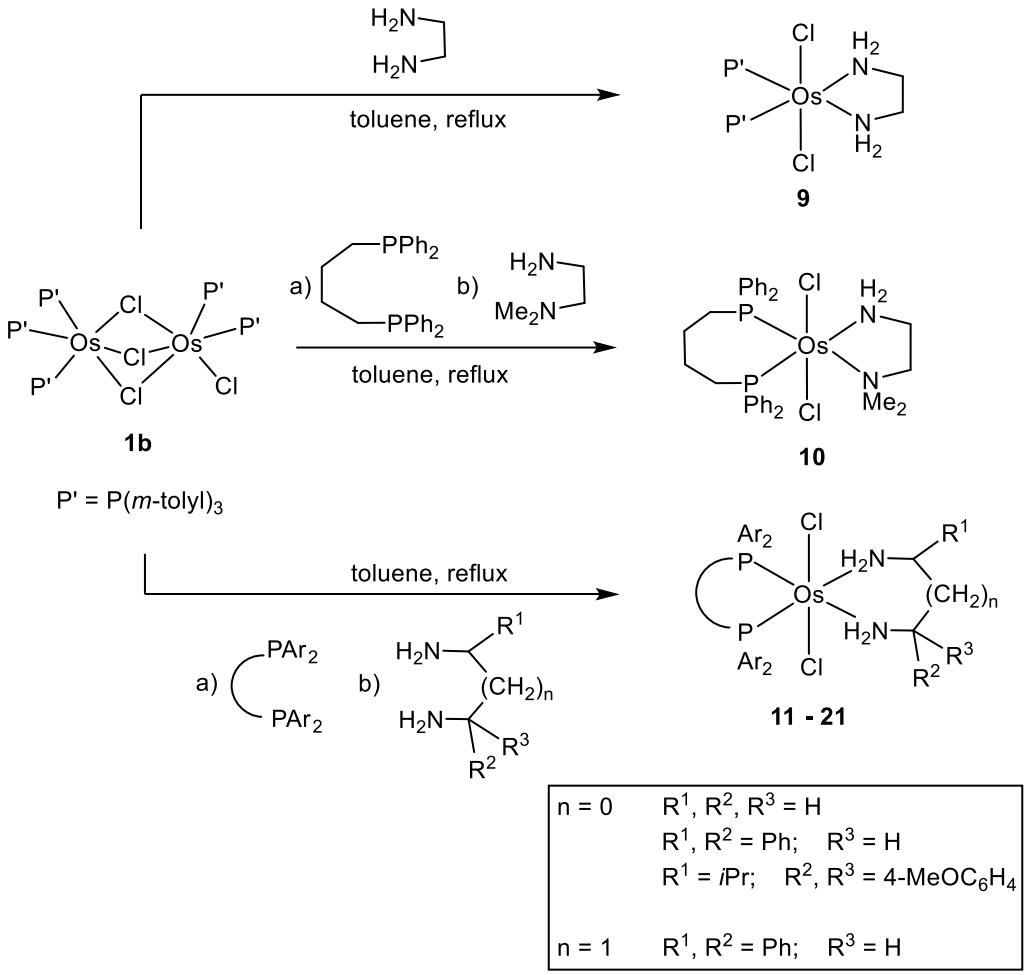


Figure 3. Enantiocontrol of dpbp ligand promoted by (*R*,*R*)-dpen in complex **7**

The comparison of the ^{1}H NMR spectra of **6** and **7** shows that the signals of the NCH moieties of the (*R*,*R*)-dpen ligand appear as a single broad multiplet in **6** (δ 4.49), whereas **7** exhibits two broad triplets at δ 5.03 and 3.12 (^{2}J(H,H) = 12.4 Hz). Interestingly, in the latter compound the protons of one of the two NH_2 moieties are downshifted at δ 6.27 and 5.60, while those of the other NH_2 group appear as a broad multiplet at δ 3.75-3.45. By contrast, the NH_2 signals of **6** appear as two broad triplets at δ 4.17 and 3.69 with J(H,H) = 7.8 Hz. The ^{1}H NMR data of **7** suggest the presence of a hydrogen bond interaction between one NH_2 with the C=O group of the dpbp ligand, resulting in lowering of the symmetry of the complex. The ^{13}C{^{1}H} NMR spectrum of **6** shows one signal for the NCH of (*R*,*R*)-dpen ligand (δ 64.0), whereas **7** afforded two singlets at δ 66.8 and 63.3 for. It should be noted that similarly to the related ruthenium derivatives, the carbonyl group of **7** appears in the ^{13}C{^{1}H} NMR spectrum as a doublet of doublets at δ 153.1 (^{3}J(C,P) = 57.3, 25.3 Hz), strongly upfield shifted compared with the free dpbp, and suggesting an (C=O)-Os interaction as observed for **5**. The ^{13}C{^{1}H} NMR data agree with those found in the related Ni complexes containing dpbp, [NiCl(dpbp)] and [Ni(dpbp)(PPh_3)],[27] and with diphosphines-ketones [(dippe)Ni(η^2-O,C-ketone)].[28] Differently to **5**, a chiral control is promoted in **7** by the (*R*,*R*)-dpen ligand, leading to the formation of a single enantiomer. It is likely that upon complexation, the

benzophenone skeleton of the dpbp ligand adopts a chiral propeller conformation as reported for the related ruthenium complexes $[RuCl_2(dpbp)\{(R,R)\text{-dpen}\}]$[29] and $[RuCl(OTf)(dpbp)\{(S,S)\text{-dpen}\}]_2AgOTf$.[26a] In the ruthenium derivatives the change of the dpbp conformation is favored by a (C=O)-Ru interaction, observed in solid state and solution, leading to a cationic complex with Cl^- as counterion. Treatment of **1a** with (2*R*,4*R*)-skewphos[16] in refluxing toluene, followed by reaction with (*R*,*R*)-dpen, led to complex **8** isolated in 40% yield, as a mixture of the *trans* and *cis* diastereoisomers (*trans*/*cis* ratio 2:1) as shown in the $^{31}P\{^1H\}$ NMR spectrum. The singlet at δ -10.6 is due to the *trans* major isomer, whereas the two doublets at δ 0.54 and -11.7 (^2J(P,P) = 17.3 Hz) are attributable to the minor *cis* diastereoisomer. This pattern can be compared with the ruthenium complex *trans*-$[RuCl_2\{(S,S)\text{-Skewphos}\}\{(R,R)\text{-dpen}\}]$ which exhibits only a singlet (δ 55.0) in the $^{31}P\{^1H\}$ NMR spectrum at room temperature.[30]

Synthesis of $[OsCl_2(phosphine)_2(diamine)]$ and $[OsCl_2(diphosphine)(diamine)]$ complexes from $[Os_2Cl_4(P(m\text{-tolyl})_3)_5]$ (1b). Several phosphine - amine osmium complexes were easily obtained by reaction of the dinuclear compound $[Os_2Cl_4(P(m\text{-tolyl})_3\}_5]$ (**1b**), containing the bulky tri(*m*-tolyl)phosphine, with the suitable ligands. This precursor allows higher reactivity than $[OsCl_2(PPh_3)_3]$ (**1a**) and enables the isolation of $[OsCl_2(phosphine)_2(diamine)]$ and $[OsCl_2(phosphine)_2(diamine)]$ derivatives in pure form also using sterically hindered chiral diphosphines. The complex $[OsCl_2(P(m\text{-tolyl})_3)_2(en)]$ (**9**) was easily prepared from **1b** with one equivalent of en in refluxing toluene (75% yield %) (Scheme 3).



Scheme 3. Synthesis of $[OsCl_2(P(m\text{-tolyl})_3)_2(en)]$ (**9**) and $[OsCl_2(diphosphine)(diamine)]$ (**10-21**) (see Table 3 and Figure 1) from the precursor **1b**

The derivative **10**, containing a C4 backbone diphosphine ligand and a *N*,*N*-dimethylated diamine, was obtained in high yield (79%) by reaction of **1b** with dppb in refluxing toluene, followed by treatment with *N*,*N*-dmen.[16] The $^{31}P\{^1H\}$ NMR spectrum of **10** displays two close doublets at δ = -17.2 and -18.5 (^2J(P,P) = 13.1 Hz), whereas in the ^1H NMR spectrum the methylene moieties of the diphosphine appears at δ 3.28, 2.99 and 1.45-1.30, while the NCH_2 signals of the diamine ligand are at δ 2.79 and 1.95-1.76, superimposed to the peaks of the NH_2 amine group. In the $^{13}C\{^1H\}$ NMR spectrum, the signals of the CH_2 carbons of the dppb are at δ 30.7, 24.5, 24.2 and 20.4, while the methylene resonances of *N*,*N*-dmen are at δ 65.1 and 41.9.

The preparation of the chiral $[OsCl_2(diphosphine)(diamine)]$ complexes **11-21** entailed the reaction of the precursor **1b** with the chosen diphosphine (Figure 1) in refluxing toluene for 2-4 h. Addition of the diamine to the resulting reaction mixture at room temperature, followed by heating under reflux for 1 h, afforded the desired complex in good yield (48-65%) (Scheme 3, Table 3). Following this procedure, the derivatives **11-21** were obtained as single *trans* stereoisomers, except complex

15, containing (*R*)-xylMeObiphep and (*R*)-daipen,[16] which was isolated as a mixture of two stereoisomers in a 4:1 ratio. As evidenced in Table 3, the $^{31}P\{^{1}H\}$ NMR spectra of the compounds containing a C_2-symmetric diphosphine with a non-chiral or C_2-symmetric diamine display one singlet, in agreement with a *trans* geometry of the complexes.

For the (*R*)-daipen derivative **14**, **15**, **17** and **20** the ^{1}H NMR signals of the methyl isopropyl groups are highfield shielded (δ 0.57 - 0.01) compared to the free ligand,[31] while the $^{13}C\{^{1}H\}$ NMR methyl signals of the corresponding methyl carbons give two singlets at δ 22.6 - 16.1. The (*R*)-MeObiphep complexes **11**, **12** and **13** containing en or (*R,R*)-dpen lead to only one ^{1}H NMR resonance for the OMe groups at about δ 2.95, while the 5,5'-diphenyl signals appear as a triplet at δ 6.00-6.04. Conversely, in the complex **14**, obtained from (*R*)-MeObiphep and (*R*)-daipen, the methoxide groups appear as two singlets at δ 2.91 and 2.82, with the 5,5'-diphenyl protons as two doublets at δ 6.16 and 5.98, respectively. The $^{13}C\{^{1}H\}$ NMR spectra exhibit an analogous behavior with one methoxide signal for **11**, **12** and **13** in the range δ 54.1-54.4, whereas the spectrum of **14** shows two carbon singlets at δ 54.2 and 54.4. Finally, an enhanced effect of the differentiation of the ^{1}H and $^{13}C\{^{1}H\}$ NMR signals is observed when the bulky (*R*)-3,5-xylbinap[16] (complex **20**) was used in place of (*R*)-binap (complex **17**), in combination with (*R*)-daipen.

Table 3. $^{31}P\{^{1}H\}$ NMR data of the chiral complexes [$OsCl_2$(diphosphine)(diamine)] (11-21)

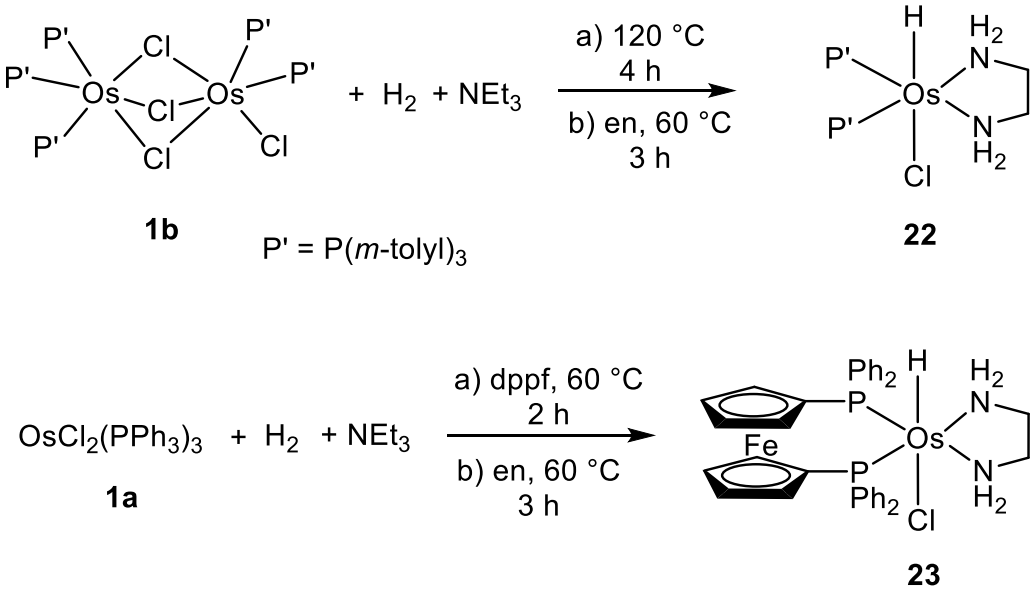
Complex	Formula	δ($^{31}P\{^{1}H\}$)[a]
11	*trans*-[$OsCl_2$((*S*)-MeObiphep)(en)]	- 12.4 (s)
12	*trans*-[$OsCl_2$((*S*)-MeObiphep)((*R,R*)-dpen)]	- 11.8 (s)
13	*trans*-[$OsCl_2$((*R*)-MeObiphep)((*R,R*)-dpen)]	- 11.6 (s)
14	*trans*-[$OsCl_2$((*R*)-MeObiphep)((*R*)-daipen)]	- 8.5 (d), - 11.5 (d) (^{2}J(P,P) = 16.0 Hz)
15	[$OsCl_2$((*R*)-xylMeObiphep)((*R*)-daipen)] (two diastereoisomers)	- 10.4 (d), - 13.8 (d) (^{2}J(P,P) = 16,5 Hz) - 10.8 (d), - 13.2 (d) (^{2}J(P,P) = 15.0 Hz)
16	*trans*-[$OsCl_2$((*R*)-binap)((*R,R*)-dpen)]	- 11.2 (s)
17	*trans*-[$OsCl_2$((*R*)-binap)((*R*)-daipen)]	- 9.8 (d), - 11.8 (d) (^{2}J(P,P) = 16,5 Hz)
18	*trans*-[$OsCl_2$((*S*)-xylbinap)((*R,R*)-dpen)]	- 13.3 (s)
19	*trans*-[$OsCl_2$((*S*)-xylbinap)((*R,R*)-dppn)]	- 13.1 (s)
20	*trans*-[$OsCl_2$((*R*)-xylbinap)((*R*)-daipen)]	- 13.1 (d), - 14.6 (d) (^{2}J(P,P) = 16,5 Hz)

21	*trans*-[$OsCl_2$((*R*,*S*)-Josiphos*)((*R*,*R*)-dpen)]	2.0 (d), - 11.6 (d) (^2J(P,P) = 22,0 Hz)

[a] in C_6D_6, 20 °C.

Synthesis of the monohydride [OsHCl(P(*m*-tolyl)$_3$)$_2$(en)] (22) and [OsHCl(dppf)(en)] (23) complexes. Ruthenium and osmium hydride complexes are key species involved in the reduction of carbonyl compounds to alcohols via HY and TH, and are generally formed from the metal chloride catalytic precursors by reaction with dihydrogen or alkali metal alkoxides.[32] The monohydride osmium derivatives bearing mono and diphosphine ligands were prepared from the precursors **1a** and **1b** with H_2 in the presence of the weak base NEt_3 and further addition of the suitable bidentate ligands (diphosphine, diamine).

The hydride [OsHCl(P(*m*-tolyl)$_3$)$_2$(en)] (**22**) was synthetized by reaction of **1b** with H_2 (1 atm) and 1.5 equiv. of NEt_3 in refluxing toluene for 4 h, possibly via the species [OsH_nCl(P(*m*-tolyl)$_3$)$_3$] (n = 1, 3) (see further part for **23**). Subsequent treatment with en (1.1 equiv.) under H_2 (1 atm) led to **22**, which was isolated in 57% yield (Scheme 4).

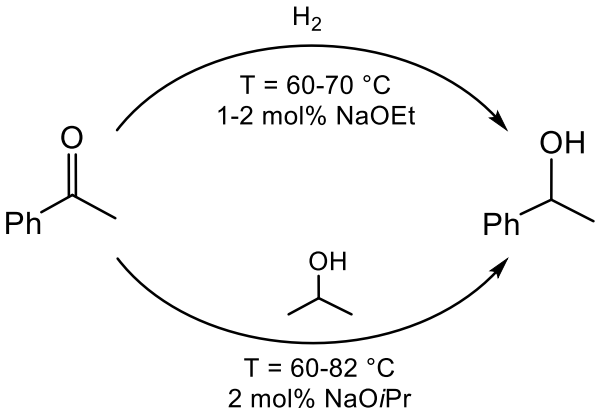


Scheme 4. Synthesis of the hydrides [OsHCl(P(*m*-tolyl)$_3$)$_2$(en)] (**22**) and [OsHCl(dppf)(en)] (**23**)

The geometry of **22** was definitively established by NMR measurements. The $^{31}P\{^1H\}$ NMR spectrum of **22** exhibits a singlet at δ 20.1, strongly shifted downfield[33] compared to the related dichloride **9** (δ - 11.4), while the ^1H NMR spectrum shows the Os-H resonance as a triplet at δ -20.9 (^2J(P,H) = 16.3 Hz), consistent with a *fac* $RuHP_2$ arrangement. In addition, the two CH_2 groups of en lead to a singlet at δ 45.5 in the $^{13}C\{^1H\}$ NMR spectrum, consistent with the presence of the en

trans to the two P atoms and *cis* to the hydride, in agreement with the data of the related ruthenium[34] and osmium[12] complexes. Compound [OsHCl(dppf)(en)] (**23**) was prepared by treatment of $[OsCl_2(PPh_3)_3]$ (**1a**) with 1.5 equivalents of NEt_3 under H_2 (1 atm) in toluene, affording the three-hydride complex $[OsH_3Cl(PPh_3)_3]$ which equilibrates with the mono-hydride $[OsHCl(PPh_3)_3]$, as described by Caulton.[35] Subsequent reactions with dppf and en under H_2 at 60 °C afforded the complex **23**, which was isolated in 63% yield. Similarly to **22**, complex **23** shows in the ^1H NMR spectrum a triplet at δ -20.8 (^2J(P,H) = 17.0 Hz) for the Os-H moiety and one $^{13}C\{^1H\}$ NMR signal at δ 45.3 for the two CH_2 groups of en, while the $^{31}P\{^1H\}$ NMR singlet is at δ 14.5, shifted downfield with respect to **3** (δ - 10.1).

Reduction of acetophenone via HY and TH catalyzed by Os complexes. The catalytic activity of the osmium(II) complexes of formula [OsXCl(phosphine)$_2$(diamine)] and [OsXCl(diphosphine)(diamine)] (X = Cl, H) was investigated in the conversion of the model substrate acetophenone into 1-phenylethanol via HY under low H_2 pressure (5 atm) in ethanol, and TH in 2-propanol in the presence of sodium alkoxides (Scheme 5).



Scheme 5. Hydrogenation and transfer hydrogenation of acetophenone

Table 4. HY of acetophenone (0.5 M) in the presence of the non-chiral osmium catalysts (2-5, 9, 10, 22 and 23) in ethanol (1 mol% of NaOEt, 5 atm H_2 pressure)

Complex	S/C	T (° C)	Time (h)	Conv. (%)[a]
2	5000	60	10.0	> 99
3[b]	10000	70	0.1	> 99
3[b]	200000	70	2.0	98
4[c]	5000	60	17.0	30
5[d]	5000	60	20.0	90
9	5000	60	17.0	87
10	10000	70	20.0	67
22	5000	60	17.0	32
23	10000	70	0.5	99

[a] The conversion was determined by GC analysis; [b] see note 20; [c] NaOEt = 2 mol%; [d] the reaction was performed in 2-propanol and with NaOEt = 2 mol%.

Acetophenone (0.5 M) was completely reduced by the complex **2** with a S/C ratio of 5000 within 10 h in the presence of 1 mol% NaOEt at 60 °C (Table 4). By employing **3**, containing the bidentate phosphine dppf, quantitative HY was achieved with a S/C ratio in the range between 5000 and 200000. A similar result was obtained with *trans*-[$OsCl_2$(dppf)(pn)], bearing the diamine pn[16] with C_3 backbone, indicating that dppf osmium complexes with en and pn diamine ligands are among the most active and fast HY systems.[6,8b,12,36] Lower catalytic activity (30% conv. in 17 h, S/C = 5000) has been observed at 60 °C with the derivative **4** that displays the 1,4-diamine ligand bn,[16] suggesting that the 7-membered dinitrogen chelate ring with osmium leads to a less stable catalytic active hydride species, as also observed for ruthenium complexes.[37] The employment of the complex **5**, where dppf is replaced with the tropos benzophenone-type diphosphine dpbp, led to 90% conversion in 20 h. The compound **9**, containing tri(*m*-tolyl)phosphine ligand and en, afforded the hydrogenation of acetophenone in 17 h at 60 °C at S/C of 5000 with 87% of conversion. The lower activity of **9** with respect to **2** can be ascribed to the easy displacement of P(*m*-tolyl)$_3$ on account of the higher cone angle. The low activity of the dppb complex **10**, bearing *N*,*N*-dmen (67% conv. in 20 h), is due to the presence of the NMe_2 moiety, which can easily give pyramidal inversion,[38] affording a complex of a lower stability,[39] hindering the approach of the substrate with

respect to the N-H group.[4,40] This study indicates that the diphosphine osmium derivatives show higher activity compared to the mono-phosphine catalysts which may undergo deactivation via phosphine dissociation. Furthermore, the monodentate phosphines complexes (**2** and **9**) can lead during catalysis to a mixture of hydride isomers (i.e. *fac* and *mer* $OsHP_2$ core) with different reactivity, resulting in a decreasing of the overall reaction rate and selectivity. The monohydride chloride **22** displayed a lower activity compared to the corresponding dichloride **9** (Table 4), which can be attributed to the higher air and moisture sensitivity of **22**. A similar behavior was observed for the hydride **23**, which leads to full conversion of acetophenone in 30 min (S/C = 10000), but with a rate lower with respect to the dichloride **3**.

The chiral complexes **6-8** and **11-20** promoted the enantioselective catalytic HY of acetophenone in ethanol at 60-70 °C under 5 atm of H_2 and in the presence of 1-2 mol% of NaOEt (S/C ratio up to 10000). Several of these compounds gave excellent results in terms of conversion and good enantioselectivity. The complexes **6**, **7** and **11** displaying chiral bidentate ligands in combination with a non chiral diamine or diphosphine afford poor enantioselectivity. Complex **6**, showing dppf and (*R*,*R*)-dpen gave (*S*)-1-phenylethanol with 52% *ee*, whereas **7** bearing dpbp with (*R*,*R*)-dpen afforded complete reduction affording racemic alcohol (Table 5).

Table 5. Enantioselective HY of acetophenone (0.5 M) in the presence 6-8 and 11-21 complexes in ethanol (2 mol% NaOEt, 5 atm H_2 pressure)

Complex	S/C	T (°C)	Time (h)	Conv. (%)[a]	ee (%)[a]
6	20000/1	70	3.0	39	52 *S*
7[b]	5000/1	70	4.0	92	*rac*
7[c]	5000/1	70	8.0	90	22 S
8	10000/1	70	1.0	97	88 S
8[d]	10000/1	70	1.0	99	89 S
11	10000/1	70	1.0	97	26 R
12	10000/1	70	0.5	97	*rac*
13	10000/1	70	0.5	96	53 S
14	10000/1	70	15.0	> 99	81 S
15	10000/1	70	15.0	> 99	90 S

16[e]	10000/1	60	0.5	> 99	89 S
17	10000/1	70	15.0	87	74 S
18[e]	10000/1	60	0.5	86	55 R
19	10000/1	70	1.0	80	82 R
20	10000/1	70	4.0	> 99	88 S
21	10000/1	70	1.0	> 99	87 S

[a] The conversion and *ee* were determined by GC analysis; [b] the reaction was carried out in 2-propanol; [c] 3-bromoacetophenone is used in place of acetophenone in 2-propanol; [d] generated *in situ*, see experimental part; [e] NaOEt = 1 mol%.

With 2-bromoacetophenone in the presence of **7** the (*S*)-alcohol was obtained with 22% *ee* (S/C = 5000). The comparison of the dbpb derivatives **5** and **7**, bearing en and (*R*,*R*)-dpen, respectively, show that the latter is more active, in line with the data reported for the analogous ruthenium complexes,[29] which was ascribed to the steric repulsion of the (*R*,*R*)-dpen phenyl groups with the dpbp ligand, facilitating the substrate approach. By contrast to **7**, the analogous dpbp ruthenium complexes,[25,26,29] afforded high *ee*. Complex **11** (S/C = 10000) containing the diamine en with the chiral (*S*)-MeObiphep displayed high rate (97% conv. in 1 h), but low *ee* (26%). The derivatives containing a chiral C_2-symmetric diphosphine, namely (*R*)-binap, (*R*)-MeObiphep and (*R*,*R*)-skewphos in combination with (*R*,*R*)-dpen or (*R*)-daipen, catalyzed the asymmetric HY of acetophenone to (*S*)-1-phenylethanol with up to 90% *ee*. Conversely, the use of phosphines of opposite configuration with (*R*,*R*)-dpen or (*R*)-daipen afforded the (*R*)-alcohol with low *ee.* Thus, the HY of MeCOPh with **8** (*trans*/*cis* = 2:1) quickly gave 97% conversion of (*S*)-alcohol with 88% *ee* (S/C = 10000, 1 h), suggesting the formation of one active hydride species in catalysis. It is worth noting that the *in situ* generated complex **8**, obtained from **1a**, (*R*,*R*)-skewphos and (*R*,*R*)-dpen, exhibited a similar activity (99% conv. and 89% *ee*). The (*S*)- and (*R*)-MeObiphep derivatives **12** and **13**, displaying the (*R*,*R*)-dpen, led to fast and complete HY of acetophenone (30 min), but with absent or poor enantioselectivity (53% *ee*) respectively, on account of the matching/mismatching effect of the chiral ligands. With **14**, bearing the bulkier (*R*)-daipen, instead of (*R*,*R*)-dpen, resulted in an increase of enantioselectivity (81% *ee*), but with a longer reaction time (15 h). Complex **15**, containing (*R*)-xylMeObiphep and (*R*)-daipen, fully hydrogenates acetophenone to (*S*)-1-phenylethanol with 90% *ee* in 15 h. Better results, were obtained by employing the derivative **16** (S/C = 10000), incorporating (*R*)-binap and (*R*,*R*)-dpen, which afforded quantitative conversion in 30 min (89% *ee*). Conversely, **17** displaying (*R*)-daipen in place of (*R*,*R*)-

dpen leads to a decrease of both rate and enantioselectivity (74% *ee*). The comparison of the catalytic activity of the (*S*)-xylbinap osmium derivatives **18** and **19**, bearing (*R*,*R*)-dpen and (*R*,*R*)-dppn, respectively, showed 86% conversion with 55% *ee* (30 min) and 89% conversion with 82% *ee* (1 h). Complex **18** (S/C = 5000) catalyzed the HY at 60 °C of α-tetralone to a racemic mixture of α-tetralol (99% conv. in 3 h). Interestingly, under the same catalytic conditions, 2-phenylcyclohexanone was quantitatively reduced with **18** in 1 h to (1*S*,2*S*)-2-phenylcyclohexanol with high diastereoselectivity (*cis*/*trans* = 98:2) and 83% *ee*. The use of **20** with acetophenone afforded (*S*)-1-penylethanol (> 99% conv. in 4 h) with 88% *ee*. Accordingly, employment of the bulkier (*R*)-daipen instead of (*R*,*R*)-dpen diamine, usually leads to an increase of enantioselectivity associated to a longer reaction time. A similar trend was observed for xylMeObiphep and xylbinap diphosphines, which generally give a better asymmetric induction with respect to the corresponding MeObiphep and binap ligands, (*R*)- or (*R*,*R*)-diphosphine with (*R*,*R*)- and (*R*)-diamines being the correct matching. Finally, compound **21** (S/C = 10000), containing the bulkier diphosphine (*S*,*R*)-Josiphos* and the (*R*,*R*)-dpen, catalyzes the complete conversion of MeCOPh to (*S*)-1-phenylethanol in 1 h at 70 °C and with 87% *ee* in the presence of 0.5 mol% NaOEt.

The osmium(II) complexes of formula *trans*-[$OsCl_2$(diphosphine)(diamine)] were also found active in the TH of acetophenone in basic 2-propanol (Scheme 5). The dppf complex **3** (S/C = 2000) catalyzed the quantitative TH of acetophenone (0.1 M) to 1-phenylethanol within 10 min in refluxing 2-propanol and in the presence of 2 mol% NaO*i*Pr (Table 6).

Table 6. TH of acetophenone (0.1 M) in the presence of the complexes 3, 6 and 7 (MeCOPh/Os/NaO*i*Pr = 2000/1/40)

Complex	T (°C)	Time (h)	Conv. (%)[a]	*ee* (%)[a]
3	82	0.1	99	-
6	60	1.0	99	48 S
6[b]	60	1.0	98	47 S
7	60	1.0	96	*rac*

[a] The conversion and *ee* were determined by GC analysis. [b] Hg poisoning test (Hg / **6** = 400).

The employment of the derivatives **6** and **7**, bearing dppf and dpbp in combination with (*R*,*R*)-dpen, respectively, gave complete conversion of acetophenone to (*S*)-alcohol at 60 °C in 1 h, but with poor enantioselectivity (48% *ee*) and absent enantioselectivity, respectively, which are data similar to those observed in the HY in ethanol (Table 5). Addition of Hg does not affect the TH of

acetophenone with **6**, suggesting that the catalysis takes place under homogeneous conditions (Table 6 and experimental section).[41]

As regards the mechanism of the HY and TH reactions, it is likely that the dichloride and hydrido chloride compounds containing the Os-N-H function [OsXCl(phosphine)$_2$(diamine)] and [OsXCl(diphosphine)(diamine)] (X = Cl, H) react with sodium alkoxides affording Os-alkoxide *vs* Os-amide complexes by chloride displacement. In the presence of H_2 and *i*PrOH these species afford the catalytically active osmium dihydride complexes in the HY and TH transformations, respectively.[12] The subsequent reduction of the substrate to the alcohol product occurs through a concerted Os-H hydride and N-H proton transfer (outer sphere), affording the Os-amide species which close the cycle, as proposed for the related ruthenium complexes.[37,42]

Concluding Remarks

In summary, we have described the straightforward preparation of the class of osmium complexes [OsXCl(phosphine)$_2$(diamine)] and [OsXCl(diphosphine)(diamine)] (X = Cl, H), which were isolated in high yield. The dichloride derivatives have been obtained from the [$OsCl_2(PPh_3)_3$] (**1a**) and [Os_2Cl_4(P(*m*-tolyl)$_3$)$_5$] (**1b**) precursors and the diphosphine and diamine ligands, while the monohydride compounds have been synthesized from **1a** and **1b** by reaction with H_2 in the presence of NEt_3, followed by treatment with the suitable bidentate ligands. For *trans*-[$OsCl_2$(dppf)(en)] (**3**) an X-ray study has been provided. The dichloride and monohydride complexes have been found active in the catalytic reduction of acetophenone via hydrogenation using H_2 under low pressure (5 atm) at 60-70 °C in basic ethanol and with a S/C ratio in the range from 5000 to 10000. Asymmetric hydrogenation (up to 90% *ee*) has been achieved with the osmium complexes containing C_2-symmetry and Josiphos diphosphines combined with (*R*)-daipen or (*R*,*R*)-dpen. These osmium complexes were also found active in the transfer hydrogenation in basic 2-propanol. Studies are ongoing to broaden the application of these catalysts, which are a valid complement to the analogous Ru complexes, in the asymmetric carbonyl reduction and explore their potential in other catalytic transformations.

Experimental Section

All reactions were carried out under an argon atmosphere using standard Schlenk techniques. The solvents were carefully dried by standard methods and distilled under argon before use. The diphosphines, diamines and all other chemicals were purchased from Aldrich and used without further purification. The compounds [$OsCl_2(PPh_3)_3$][43] (**1a)**, [Os_2Cl_4(P(*m*-tolyl)$_3$)$_5$][20] (**1b**) were

prepared according to the literature procedures. NMR measurements were recorded on a Bruker AC 200 spectrometer and the chemical shifts, in ppm, are relative to TMS for ^{1}H and $^{13}C\{^{1}H\}$, and 85% H_3PO_4 for $^{31}P\{^{1}H\}$. Elemental analysis (C, H, N) was carried out with a Carlo Erba 1106 elemental analyzer, whereas the GC analyses were performed with a Varian GP-3380 gas chromatograph equipped with a MEGADEX-ETTBDMS-β chiral column of 25 m length, column pressure 5 psi, hydrogen as carrier gas and flame ionization detector (FID). The injector and detector temperature was 250 °C, with initial T = 95 °C ramped to 140 °C at 3 °C/min^{-1} and then to 210 °C at 20 °C/min^{-1}, for a total of 20 min of analysis. The t_R of acetophenone was 7.03 min, while the t_R of (*R*)- and (*S*)-1-phenylethanol were 9.93 min and 10.15 min, respectively.

Synthesis of *trans*-[$OsCl_2(PPh_3)_2$(en)] (**2**). Complex **1a** (150 mg, 0.143 mmol) and en (9.6 µL, 0.143 mmol) were dissolved in dichloromethane (3.0 mL) and the solution was heated at 40 °C for 1 h. The resulting solution was concentrated (1.5 mL) and diethyl ether was added (4 mL) to afford a yellow precipitate, which was washed with diethyl ether (2x3 mL) and dried under reduced pressure. Yield: 106 mg (88%). Anal. Calcd (%) for $C_{38}H_{38}Cl_2N_2OsP_2$: C 53.96, H 4.53, N 3.31; found: C 53.83, H 4.43, N 3.41. ^{1}H NMR (200.1 MHz, CD_2Cl_2, 20 °C): δ 7.46-7.08 (m, 30H; Ph), 3.42 (broad s, 4H; CH_2), 2.67 (broad s, 4H; NH_2). $^{13}C\{^{1}H\}$ NMR (50.3 MHz, CD_2Cl_2, 20 °C): δ 138.2 (dd, ^{1}J(C,P) = 49.2 Hz, ^{3}J(C,P) = 4.6 Hz; ipso Ph), 134.9 (t, ^{2}J(C,P) = 4.7 Hz; Ph), 129.0 (t, ^{4}J(C,P) = 1.0 Hz; Ph), 127.5 (pseudo t, ^{3}J(C,P) = 4.5 Hz; Ph), 44.2 (s; CH_2). $^{31}P\{^{1}H\}$ NMR (81.0 MHz, CD_2Cl_2, 20 °C): δ - 11.7 (s).

Synthesis of *trans*-[$OsCl_2$(dppf)(en)] (**3**). Complex **3** was prepared following a slightly modified described procedure for **3**.[20] [$OsCl_2(PPh_3)_3$] (**1a**) (500 mg, 0.477 mmol) and dppf (290 mg, 0.523 mmol) were dissolved in dichloromethane (10 mL) and the solution was heated under reflux for 2 h. En (47 µL, 0.490 mmol) was added and the resulting solution was heated under reflux for 0.5 h, and then concentrated to 5 mL. Addition of heptane (10 mL) afforded a yellow solid, which was filtered, washed with heptane (2x6 mL) and dried under reduced pressure. Yield: 380 mg (91%).

Synthesis of *trans*-[$OsCl_2$(dppf)(bn)] (**4**). Complex **1a** (150 mg, 0.143 mmol) and dppf (87 mg, 0.157 mmol) were dissolved in dichloromethane (3.0 mL) and the solution was heated under reflux for 3 h. Bn (14 µL, 0.143 mmol) was added at room temperature and the mixture heated to 40 °C for 1 h. The solution was concentrated (1.5 mL) and then pentane (4 mL) was added affording a yellow precipitate, which was filtered off, washed with pentane (2x3 mL) and dried under reduced pressure. Yield: 106 mg (82%). Anal. Calcd (%) for $C_{38}H_{40}Cl_2FeN_2OsP_2$: C 50.61, H 4.46, N 3.10; found: C 50.74, H 4.42, N 3.00. ^{1}H NMR (200.1 MHz, CD_2Cl_2, 20 °C): δ 7.73-7.28 (m, 20H; Ph),

4.57 (m, 4H; C_5H_4), 4.15 (s, 4H; C_5H_4), 3.19 (broad s, 4H; NCH_2), 2.77 (broad s, 4H; NH_2), 1.59 (broad m, 4H; CH_2). $^{13}C\{^1H\}$ NMR (50.3 MHz, CD_2Cl_2, 20 °C): δ 139.1 (dd, ^1J(C,P) = 53.0 Hz, ^3J(C,P) = 9.6 Hz; ipso Ph), 135.0 (t, ^2J(C,P) = 4.8 Hz; Ph), 129.3 (t, ^4J(C,P) = 0.9 Hz; Ph), 127.4 (pseudo t, ^3J(C,P) = 4.5 Hz; Ph), 88.1 (dd, ^1J(C,P) = 62.5 Hz, ^3J(C,P) = 5.9 Hz; ipso C_5H_4), 76.2 (t, ^2J(C,P) = 3.9 Hz; C_5H_4), 70.5 (t, ^3J(C,P) = 2.9 Hz; C_5H_4), 41.6 (s; NCH_2), 28.9 (s; CH_2). $^{31}P\{^1H\}$ NMR (81.0 MHz, CD_2Cl_2, 20 °C): δ - 11.0 (s).

Synthesis of *trans*-[$OsCl_2$(dpbp)(en)] (5). Complex **1a** (50 mg, 0.048 mmol) and dpbp (32 mg, 0.058 mmol) were dissolved in toluene (2.0 mL). The solution was stirred at 110 °C for 2 h. En (26 mg, 0.124 mmol) was added at room temperature, followed by stirring of the reaction mixture for 3 h at 110 °C. The resulting suspension was concentrated (0.5 mL) and pentane (4 mL) was added. The yellow precipitate obtained was filtered off, washed with pentane (2x3 mL) and dried overnight under reduced pressure. Yield: 35 mg (84%). Anal. Calcd (%) for $C_{39}H_{36}Cl_2N_2OOsP_2$: C 53.73, H 4.16, N 3.21; found: C 53.83, H 4.20, N 3.18. ^1H NMR (200.1 MHz, CD_2Cl_2, 20 °C): δ 7.99 (d, ^3J(H,H) = 6.6 Hz, 2H; aromatic protons), 7.57 (t, ^3J(H,H) = 7.4 Hz, 2H; aromatic protons), 7.38-6.88 (m, 24H; aromatic protons), 3.68 (broad s, 2H; CH_2), 3.54 (broad s, 2H; CH_2), 2.95 (broad s, 4H; NH_2). $^{13}C\{^1H\}$ NMR (50.3 MHz, CD_2Cl_2, 20 °C): δ 151.5 (m; *C*O), 143.2-128.3 (m; aromatic carbon atoms), 46.0 (s; CH_2). $^{31}P\{^1H\}$ NMR (81.0 MHz, CD_2Cl_2, 20 °C): δ - 1.6 (s).

Synthesis of *trans*-[$OsCl_2$(dppf)((*R*,*R*)-dpen)] (6). Complex **1a** (150 mg, 0.143 mmol) and dppf (87 mg, 0.157 mmol) were dissolved in toluene (3.0 mL) and the solution was heated at 70 °C for 2 h. The ligand (*R*,*R*)-dpen (33 mg, 0.157 mmol) was added at room temperature and the mixture was heated to 100 °C for 1 h. The solution was concentrated (1.5 mL) and by addition of pentane (4 mL), the precipitation of a yellow solid was observed. The precipitate was filtered off, washed with pentane (2x3 mL) and dried under reduced pressure. Yield: 109 mg (74%). Anal. Calcd (%) for $C_{48}H_{44}Cl_2FeN_2OsP_2$: C 56.09, H 4.32, N 2.73; found: C 56.12, H 4.24, N 2.60. ^1H NMR (200.1 MHz, C_6D_6, 20 °C): δ 8.20 (m, 4H; aromatic protons), 8.10 (m, 4H; aromatic protons), 7.42-6.68 (m, 22H; aromatic protons); 5.06 (m 2H; C_5H_4), 4.95 (m, 2H; C_5H_4), 4.49 (br m, 2H; NCH), 4.17 (br t, *J*(H,H) = 7.8 Hz, 2H; NH_2), 3.96 (m, 4H; C_5H_4), 3.69 (br d, *J*(H,H) = 7.8 Hz, 2H; NH_2); $^{13}C\{^1H\}$ NMR (50.3 MHz, C_6D_6, 20 °C): δ 141.0 (dd, ^1J(C,P) = 53.6 Hz, ^3J(C,P) = 8.9 Hz; ipso Ph), 140.5 (dd, ^1J(C,P) = 30.4 Hz, ^3J(C,P) = 9.2 Hz; ipso Ph), 139.3 (s; ipso Ph), 135.1-127.0 (m; aromatic carbon atoms), 90.7 (dd, ^1J(C,P) = 61.1 Hz, ^3J(C,P) = 5.8 Hz; ipso C_5H_4), 76.8 (t, ^2J(C,P) = 3.9 Hz; C_5H_4), 76.6 (t, ^2J(C,P) = 3.7 Hz; C_5H_4), 70.3 (t, ^3J(C,P) = 2.8 Hz; C_5H_4), 70.2 (t, ^3J(C,P) = 2.8 Hz; C_5H_4), 64.0 (s; NCH); $^{31}P\{^1H\}$ NMR (81.0 MHz, C_6D_6, 20 °C): δ -8.7 (s).

Synthesis of *trans*-[$OsCl_2$(dpbp)((*R*,*R*)-dpen)] (7). Complex **1a** (100 mg, 0.095 mmol) and dpbp (63 mg, 0.114 mmol) were dissolved in toluene (2.0 mL) and the mixture was stirred at 110

°C for 2 h. The ligand (*R*,*R*)-dpen (26 mg, 0.124 mmol) was added at room temperature and the solution was stirred at 110 °C for 3 h. By concentration of the solution (0.5 mL) and by subsequent addition of pentane (4 mL) a precipitate was formed, which was filtered off, washed with pentane (2x3 mL) and dried overnight under reduced pressure. Yield: 78 mg (80%). Anal. Calcd (%) for $C_{51}H_{44}Cl_2N_2OOsP_2$: C 59.82, H 4.33, N 2.74; found: C 59.74, H 4.40, N 2.64. ^{1}H NMR (200.1 MHz, C_6D_6, 20 °C): δ 8.44 (d, ^3J(H,H) = 7.0 Hz, 1H; aromatic proton), 8.36 (d, ^3J(H,H) = 7.5 Hz, 1H; aromatic proton), 7.89 (pseudo t, ^3J(H,H) = 9.0 Hz, 2H; aromatic protons), 7.70-6.42 (m, 34H; aromatic protons), 6.27 (broad s, 1H; NH_2), 5.60 (broad s, 1H; NH), 5.03 (broad t, J(H,H) = 12.4 Hz, 1H; NCH), 3.75-3.45 (m, 2H; NH_2) 3.12 (broad t, J(H,H) = 12.4 Hz, 1H; NCH). ^{13}C{^{1}H} NMR (50.3 MHz, C_6D_6, 20 °C): δ 153.1 (dd, ^3J(CP) = 57.3, 25.3 Hz; *C*O), 140.0-128.0 (m; aromatic carbon atoms), 66.8 (s; CH), 63.3 (s; CH). ^{31}P{^{1}H} NMR (81.0 MHz, C_6D_6, 20 °C): δ 2.2 (d, ^2J(P,P) = 5.0 Hz), - 2.5 (d, ^2J(P,P) = 5.0 Hz).

Synthesis of *trans*-[OsCl$_2$((*R*,*R*)-skewphos)((*R*,*R*)-dpen)] (8). Complex **1a** (200 mg, 0.191 mmol) and (2*R*,4*R*)-skewphos (101 mg, 0.229 mmol) were dissolved in toluene (1.5 mL) and the mixture was heated under reflux at 120 °C for 4 h. The ligand (*R*,*R*)-dpen (45 mg, 0.210 mmol) was added at room temperature and the solution was refluxed for 45 min. The solvent was evaporated and by addition of ethyl ether (3 mL) the formation of a yellow precipitate was observed, which was filtered off and washed with ethyl ether (3x2 mL). The residue was dried under reduced pressure affording a brown oil. This oil was treated with heptane (2 mL) affording a yellow precipitate. The solid was filtered off, washed with heptane (2x3 mL) and dried under reduced pressure. Yield: 70 mg (40%). Anal. Calcd (%) for $C_{43}H_{46}Cl_2N_2OsP_2$: C 56.51, H 5.07, N 3.07; found: C 56.31, H 4.97, N 3.16. The product was obtained as a mixture of two diastereoisomers (*trans*/*cis* = 2:1). ^{1}H NMR (200.1 MHz, C_6D_6, 20 °C): δ 7.86-6.72 (m; aromatic protons), 4.53-3.10 (m; NCH, NH_2, PCH), 2.20-0.70 (m; CH_2, CH_3). ^{13}C{^{1}H} NMR (50.3 MHz, C_6D_6, 20 °C for the major isomer): δ 139.8-126.5 (m; aromatic carbon atoms), 63.9 (s; NCH), 38.3 (s; CH_2), 18.9 (s; CH_3). ^{31}P{^{1}H} NMR (81.0 MHz, C_6D_6, 20 °C): δ 0.54 (d, ^2J(P,P) = 17.3 Hz; minor isomer), - 10.6 (s), - 11.7 (d, ^2J(P,P) = 17.3 Hz; minor isomer).

Synthesis of *trans*-[OsCl$_2$(P(*m*-tolyl)$_3$)$_2$(en)] (**9**). Complex **1b** (100 mg, 0.049 mmol) and en (6.5 µL, 0.097 mmol) were dissolved in toluene (1 mL) and the mixture was heated at 120 °C for 2 h. The solvent was evaporated, heptane (5 mL) was added and the resulting mixture was again evaporated. Further addition of heptane (5 mL) afforded a yellow precipitate, which was washed with heptane (2x3 mL) and dried under reduced pressure. Yield: 68 mg (75%). Anal. Calcd (%) for $C_{44}H_{50}Cl_2N_2OsP_2$: C 56.83, H 5.42, N 3.01; found: C 56.60, H 5.35, N 3.03. ^{1}H NMR (200.1 MHz, C_6D_6, 20 °C): δ 7.83 (pseudo d, ^3J(H,H) = 9.3 Hz, 6H; aromatic protons), 7.68 (pseudo t, ^3J(H,H) =

8.1 Hz, 6H; aromatic protons), 7.00 (td, ^3J(H,H) = 7.7 Hz, ^3J(H,H) = 1.6 Hz, 6H; aromatic protons), 6.86 (pseudo d, ^3J(H,H) = 7.4 Hz, 6H; aromatic protons), 3.26 (broad s, 4H; CH_2), 2.00 (s, 18H; CH_3), 1.90 (broad s, 4H; NH_2). $^{13}C\{^1H\}$ NMR (50.3 MHz, C_6D_6, 20 °C): δ 138.9 (dd, ^1J(C,P) = 49.1 Hz, ^3J(C,P) = 5.0 Hz; ipso aromatic carbon), 136.8 (t, ^3J(C,P) = 4.7 Hz; ipso aromatic carbon), 136.3 (t, ^2J(C,P) = 5.2 Hz; aromatic carbon), 132.4 (t, ^2J(C,P) = 4.2 Hz; aromatic carbon), 129.6 (s; aromatic carbon), 127.3 (t, ^3J(C,P) = 4.5 Hz; aromatic carbon), 43.4 (s; CH_2), 21.6 (s; CH_3). $^{31}P\{^1H\}$ NMR (81.0 MHz, C_6D_6, 20 °C): δ - 11.4 (s).

Synthesis of *trans*-[$OsCl_2$(dppb)(*N*,*N*-dmen)] (10). Complex **1b** (100 mg, 0.049 mmol) and dppb (46 mg, 0.108 mmol) were dissolved in toluene (1 mL) and the mixture was heated under reflux at 120 °C for 2 h. *N*,*N*-dmen (11 µL, 0.098 mmol) was added at room temperature and the solution was heated under reflux at 120 °C for 1 h. The solvent was evaporated, heptane (5 mL) was added and the resulting mixture was again evaporated. Heptane (5 mL) was added to the residue causing the formation of a yellow precipitate. The obtained solid was filtered off, washed with heptane (2x3 mL), and dried under reduced pressure. Yield: 60 mg (79%). Anal. Calcd (%) for $C_{32}H_{40}Cl_2N_2OsP_2$: C 49.55, H 5.20, N 3.61; found: C 49.73, H 5.12, N 3.42. ^1H NMR (200.1 MHz, C_6D_6, 20 °C): δ 8.05 (broad t, ^3J(H,H) = 7.6 Hz, 4H; aromatic protons), 7.68 (broad t, ^3J(H,H) = 6.7 Hz, 4H; aromatic protons), 7.25-6.92 (m, 12H; aromatic protons), 3.28 (m, 2H; PCH_2), 2.99 (broad t, ^3J(H,H) = 9.7 Hz, 2H; PCH_2), 2.79 (s, 2H; NCH_2), 2.35 (s, 6H; CH_3), 1.95-1.76 (m, 4H; NCH_2, NH_2), 1.45-1.30 (m, 4H, CH_2). $^{13}C\{^1H\}$ NMR (50.3 MHz, C_6D_6, 20 °C): δ 141.3 (d, ^1J(C,P) = 37.5 Hz; aromatic ipso carbon atom), 139.5 (d, ^1J(C,P) = 46.7 Hz; aromatic ipso carbon atom), 134.5 (d, ^2J(C,P) = 8.2 Hz; aromatic carbon atom), 133.9 (d, ^2J(C,P) = 7.5 Hz; aromatic carbon atom), 128.8-127.4 (m; aromatic carbon atoms), 65.1 (s; *C*H_2NMe_2), 49.8 (s; CH_3), 41.9 (t, ^3J(C,P) = 1.5 Hz; CH_2NH_2), 30.7 (d, ^1J(C,P) = 31.2 Hz; PCH_2), 24.5 (d, ^1J(C,P) = 32.5 Hz; PCH_2), 24.2 (s; PCH_2*C*H_2), 20.4 (d, ^2J(C,P) = 5.8 Hz; PCH_2*C*H_2). $^{31}P\{^1H\}$ NMR (81.0 MHz, C_6D_6, 20 °C): δ - 17.2 (d, ^2J(P,P) = 13.1 Hz), - 18.5 (d, ^2J(P,P) = 13.1 Hz).

Synthesis of *trans*-[$OsCl_2$((*S*)-MeObiphep)(en)] (11). Complex **1b** (100 mg, 0.049 mmol) and (*S*)-MeObiphep (34 mg, 0.059 mmol) were dissolved in toluene (1 mL) and the mixture was heated at 120 °C for 3 h. To this solution was added en (2.4 µL, 0.036 mmol), and then heated at 120 °C for 1 h. The resulting mixture was concentrated (0.5 mL) and heptane (5 mL) was added. The yellow precipitate was filtered off, washed with heptane (3x5 mL) at 60 °C and dried under reduced pressure. Yield: 60 mg (65%). Anal. Calcd (%) for $C_{40}H_{40}Cl_2N_2O_2OsP_2$: C 53.16, H 4.46, N 3.10; found: C 53.35, H 4.52, N 3.06. ^1H NMR (200.1 MHz, C_6D_6, 20 °C): δ 8.25-8.12 (m, 8H; aromatic protons), 7.65-6.76 (m, 16H; aromatic protons), 6.00 (d, ^3J(H,H) = 8.0 Hz, 2H; aromatic protons), 3.17 (broad d, 2H; CH_2), 2.95 (s, 6H; OMe), 2.71 (m, 2H; CH_2), 1.91 (broad s, 4H; NH_2). $^{13}C\{^1H\}$

NMR (50.3 MHz, C_6D_6, 20 °C): δ 140.7-109.9 (m; aromatic carbon atoms), 54.1 (s; OMe), 43.2 (s; NCH_2). $^{31}P\{^1H\}$ NMR (81.0 MHz, C_6D_6, 20 °C): δ - 12.4 (s).

Synthesis of *trans*-[$OsCl_2$((*S*)-MeObiphep)((*R*,*R*)-dpen)] (12). Complex **1b** (100 mg, 0.049 mmol) and (*S*)-MeObiphep (63 mg, 0.108 mmol) were dissolved in toluene (1 mL) and the mixture was heated under reflux at 120 °C for 4 h. The ligand (*R*,*R*)-dpen (23 mg, 0.108 mmol) was added at room temperature and the solution was heated at 120 °C for 1 h. The solution was concentrated (0.5 mL) and by addition of heptane (5 mL), the formation of a yellow precipitate was observed. The solid was filtered off, washed with heptane (2x3 mL) and dried under reduced pressure. Yield: 64 mg (62%). Anal. Calcd (%) for $C_{52}H_{48}Cl_2N_2O_2OsP_2$: C 59.14, H 4.58, N 2.65; found: C 59.33, H 4.73, N 2.47. ^1H NMR (200.1 MHz, C_6D_6, 20 °C): δ 8.30 (m, 8H; aromatic protons), 7.80-6.64 (m, 26H; aromatic protons), 6.02 (t, ^3J(H,H) = 9.2 Hz, 2H; aromatic protons), 4.81 (broad m, 2H; NH_2), 4.68 (broad m, 2H; NCH), 3.75 (broad d, J(H,H) = 10.1 Hz, 2H; NH_2), 2.95 (s, 6H; OMe). $^{13}C\{^1H\}$ NMR (50.3 MHz, C_6D_6, 20 °C): δ 158.0 (t, ^3J(C,P) = 5.4 Hz, *C*OMe), 139.6-110.1 (m; aromatic carbon atoms), 64.1 (s; NCH), 54.1 (s; OMe). $^{31}P\{^1H\}$ NMR (81.0 MHz, C_6D_6, 20 °C): δ - 11.8 (s).

Synthesis of *trans*-[$OsCl_2$((*R*)-MeObiphep)((*R*,*R*)-dpen)] (13). Complex **13** was prepared by following the procedure used for the synthesis of **12**, with (*R*)-MeObiphep in place of (*S*)-MeObiphep**.** Yield: 66 mg (64%). Anal. Calcd (%) for $C_{52}H_{48}Cl_2N_2O_2OsP_2$: C 59.14, H 4.58, N 2.65; found: C 59.30, H 4.58, N 2.49. ^1H NMR (200.1 MHz, C_6D_6, 20 °C): δ 8.33 (m, 4H; aromatic protons), 8.21 (t, ^3J(H,H) = 7.2 Hz, 4H; aromatic protons), 7.80-6.64 (m, 26H; aromatic protons), 6.04 (t, ^3J(H,H) = 8.1 Hz, 2H; aromatic protons), 4.54 (broad m, 2H; CH), 4.17 (broad s, 4H; NH_2), 2.94 (s, 6H; OMe). $^{13}C\{^1H\}$ NMR (50.3 MHz, C_6D_6, 20 °C): δ 158.1 (t, ^3J(C,P) = 5.3 Hz, *C*OMe), 142.0-110.1 (m; aromatic carbon atoms), 63.9 (s; NCH), 54.4 (s; OMe). $^{31}P\{^1H\}$ NMR (81.0 MHz, C_6D_6, 20 °C): δ - 11.6 (s).

Synthesis of *trans*-[$OsCl_2$((*R*)-MeObiphep)((*R*)-daipen)] (14). Complex **14** was prepared following the procedure used for **12**, with (*R*)-MeObiphep in place of (*S*)-MeObiphep, and (*R*)-daipen (34 mg, 0.108 mmol) instead of (*R*,*R*)-dpen. Yield: 70 mg (62%). Anal. Calcd (%) for $C_{57}H_{58}Cl_2N_2O_4OsP_2$: C 59.11, H 5.05, N 2.42; found: C 59.24, H 4.93, N 2.44. ^1H NMR (200.1 MHz, C_6D_6, 20 °C): δ 8.19 (m, 8H; aromatic protons), 7.77 (t, ^3J(H,H) = 8.3 Hz, 2H; aromatic protons), 7.64-6.65 (m, 22H; aromatic protons), 6.16 (d, ^3J(H,H) = 8.5 Hz, 1H; a*r*omatic proton), 5.98 (d, ^3J(H,H) = 8.7 Hz, 1H; aromatic proton), 5.16 (broad d, J(H,H) = 11.7 Hz, 2H; NH_2 and CHN), 4.88 (broad d, J(H,H) = 10.6 Hz, 1H; NH_2), 3.78 (broad t, J(H,H) = 12.4 Hz, 1H; NH_2), 3.34 (s, 3H; OMe), 3.25 (m, 1H; NH_2), 3.21 (s, 3H; OMe), 2.91 (s, 3H; OMe), 2.82 (s, 3H; OMe), 1.77 (m 1H; C*H*Me), 0.57 (d, ^3J(H,H) = 6.8 Hz, 3H; CH*Me*), 0.01 (d, ^3J(H,H) = 6.8 Hz, 3H; CH*Me*). $^{13}C\{^1H\}$ NMR (50.3 MHz, C_6D_6, 20 °C): δ 159.3 (s; *C*OMe), 159.2 (s; *C*OMe), 158.3 (d, ^3J(C,P) =

11.4 Hz, *C*OMe), 158.0 (d, ^3J(C,P) = 11.6 Hz, *C*OMe), 136.7-110.1 (m; aromatic carbon atoms), 69.3 (s; N*C*Ar), 64.4 (s; N*C*H), 54.8 (s; OMe), 54.7 (s; OMe), 54.4 (s; OMe), 54.2 (s; OMe), 28.6 (s; *C*HMe$_2$), 22.6 (s; CH*Me*), 16.1 (s; CH*Me*). ^{31}P{^{1}H} NMR (81.0 MHz, C_6D_6, 20 °C): δ - 8.5 (d, ^2J(P,P) = 16.0 Hz), - 11.5 (d, ^2J(P,P) = 16.0 Hz).

Synthesis of [OsCl$_2$((*R*)-xylMeObiphep)((*R*)-daipen)] (15). Complex **15** was prepared following the procedure used for **12**, with (*R*)-xylMeObiphep (88 mg, 0.127 mmol) in place of (*S*)-MeObiphep, and (*R*)-daipen (34 mg, 0.108 mmol) instead of (*R*,*R*)-dpen. The solution was heated at 100 °C for 45 min. after the addition of the diamine. Yield: 79 mg (63%). Anal. Calcd (%) for $C_{65}H_{74}Cl_2N_2O_4OsP_2$: C 61.46, H 5.87, N 2.21; found: C 61.54, H 5.79, N 2.29. The product was obtained as a mixture of two diastereoisomers (ratio = 4:1). ^{31}P{^{1}H} NMR (81.0 MHz, C_6D_6, 20 °C): δ - 10.4 (d, ^2J(P,P) = 16.5 Hz), - 10.8 (d, ^2J(P,P) = 15.0 Hz; minor isomer), - 13.2 (d, ^2J(P,P) = 15.0 Hz; minor isomer), - 13.8 (d, ^2J(P,P) = 16.5 Hz).

Synthesis of *trans*-[OsCl$_2$((*R*)-binap)((*R*,*R*)-dpen)] (16). Complex **16** was prepared following the procedure used for **12**, with (*R*)-binap (67 mg, 0.127 mmol) in place of (*S*)-MeObiphep. Yield: 63 mg (59%). Anal. Calcd (%) for $C_{58}H_{48}Cl_2N_2OsP_2$: C 63.56, H 4.41, N 2.56; found: C 63.47, H 4.35, N 2.54. ^{1}H NMR (200.1 MHz, C_6D_6, 20 °C): δ 8.66 (t, ^3J(H,H) = 8.4 Hz, 2H; aromatic protons), 8.23 (t, ^3J(H,H) = 8.1 Hz, 6H; aromatic protons), 8.09 (t, ^3J(H,H) = 9.4 Hz, 6H; aromatic protons), 7.72 (d, ^3J(H,H) = 8.5 Hz, 4H; aromatic protons), 7.40 (d, ^3J(H,H) = 8.3 Hz, 4H; aromatic protons), 7.11-6.34 (m, 20H; aromatic protons), 4.49 (broad m, 2H; CH), 3.85 (broad d, *J*(H,H) = 9.2 Hz, 2H; NH$_2$), 3.67 (broad t, *J*(H,H) = 9.0 Hz, 2H; NH$_2$). ^{13}C{^{1}H} NMR (50.3 MHz, C_6D_6, 20 °C): δ 139.4-124.8 (m, aromatic carbon atoms), 63.8 (s; NCH). ^{31}P{^{1}H} NMR (81.0 MHz, C_6D_6,, 20 °C): δ - 11.2 (s).

Synthesis of *trans*-[OsCl$_2$((*R*)-binap)((*R*)-daipen)] (17). Complex **17** was prepared following the procedure used for **12**, with (*R*)-binap (67 mg, 0.127 mmol) in place of (*S*)-MeObiphep, and (*R*)-daipen (34 mg, 0.108 mmol) instead of (*R*,*R*)-dpen. Yield: 69 mg (59%). Anal. Calcd (%) for $C_{63}H_{58}Cl_2N_2O_2OsP_2$: C 63.15, H 4.88, N 2.34; found: C 63.28, H 4.89, N 2.45. ^{1}H NMR (200.1 MHz, C_6D_6, 20 °C): δ 8.64 (t, ^3J(H,H) = 8.0 Hz, 1H; aromatic proton), 8.39-6.35 (m, 39H; aromatic protons), 4.99 (broad m, 2H; NH$_2$ and CHN), 4.43 (broad d, *J*(H,H) = 10.8 Hz, 1H; NH$_2$), 3.61 (broad t, *J*(H,H) = 13.8 Hz, 1H; NH$_2$), 3.35 (s, 3H; OMe), 3.25 (m, 1H; NH$_2$), 3.19 (s, 3H; OMe), 1.74 (m 1H; C*H*Me), 0.52 (d, ^3J(H,H) = 6.8 Hz, 3H; CH*Me*), 0.02 (d, ^3J(H,H) = 7.5 Hz, 3H; CH*Me*). ^{13}C{^{1}H} NMR (50.3 MHz, C_6D_6, 20 °C): δ 159.3 (s; *C*OMe), 159.2 (s; *C*OMe), 136.3-113.6 (m; aromatic carbon atoms), 69.3 (s; N*C*Ar), 64.7 (s; N*C*H), 54.9 (s; OMe), 54.7 (s; OMe), 28.6 (s; *C*HMe), 22.6 (s; CH*Me*), 16.1 (s; CH*Me*). ^{31}P{^{1}H} NMR (81.0 MHz, C_6D_6, 20 °C): δ - 9.81 (d, ^2J(P,P) = 16.5 Hz), - 11.8 (d, ^2J(P,P) = 16.5 Hz).

Synthesis of *trans*-[$OsCl_2$((*S*)-xylbinap)((*R*,*R*)-dpen)] (18). Complex **18** was prepared following the procedure used for **12**, with (*S*)-xylbinap (79 mg, 0.108 mmol) in place of (*S*)-MeObiphep. Alter the usual work-up, the product was purified through silica gel (toluene) to remove traces of tri(*m*-tolyl)phosphine. Yield: 60 mg (51%). Anal. Calcd (%) for $C_{66}H_{64}Cl_2N_2OsP_2$: C 65.61, H 5.34, N 2.32; found: C 65.52, H 5.22, N 2.43. ^{1}H NMR (200.1 MHz, C_6D_6, 20 °C): δ 8.90 (t, ^3J(H,H) = 8.0 Hz, 2H; aromatic protons), 8.20 (d, ^3J(H,H) = 8.4 Hz, 4H; aromatic protons), 7.83-6.48 (m, 26H; aromatic protons), 5.91 (s, 2H; aromatic protons), 4.66 (broad m, 2H; NCH), 4.58 (broad m, 2H; NH_2), 3.49 (broad m, 2H; NH_2), 2.04 (s, 12H; CMe), 1.81 (s, 12H; CMe). ^{13}C{^{1}H} NMR (50.3 MHz, C_6D_6, 20 °C): δ 135.2-123.3 (m; aromatic carbon atoms), 63.8 (s; NCH), 21.5 (s; C*Me*), 21.3 (s; C*Me*). ^{31}P{^{1}H} NMR (81.0 MHz, C_6D_6, 20 °C): δ - 13.3 (s).

Synthesis of *trans*-[$OsCl_2$((*S*)-xylbinap)((*R*,*R*)-dppn)] (19). Complex **19** was prepared following the procedure used for **18**, with (*R*,*R*)-dppn (24 mg, 0.106 mmol) in place of (*R*,*R*)-dpen. Alter the usual work-up, the product was purified through silica gel (toluene) to remove traces of tri(*m*-tolyl)phosphine. Yield: 59 mg (49%). Anal. Calcd (%) for $C_{67}H_{66}Cl_2N_2OsP_2$: C 65.84, H 5.44, N 2.29; found: C 65.74, H 5.57, N 2.37. ^{1}H NMR (200.1 MHz, C_6D_6, 20 °C): δ 9.01 (t, ^3J(H,H) = 8.1 Hz, 2H; aromatic protons), 8.03 (d, ^3J(H,H) = 7.1 Hz, 4H; aromatic protons), 7.89-6.31 (m, 26H; aromatic protons), 5.88 (s, 2H; aromatic protons), 4.77 (broad m, 2H; NCH), 3.44-3.24 (broad m, 4H; NH_2), 2.01-1.77 (m, 26H; CMe). ^{13}C{^{1}H} NMR (50.3 MHz, C_6D_6, 20 °C): δ 135.2-123.3 (m; aromatic carbon atoms), 50.2 (s; NCH), 39.8 (s; CH_2), 21.4 (s; C*Me*), 21.1 (s; C*Me*). ^{31}P{^{1}H} NMR (81.0 MHz, C_6D_6, 20 °C): δ - 13.1 (s).

Synthesis of *trans*-[$OsCl_2$((*R*)-xylbinap)((*R*)-daipen)] (20). Complex **20** was prepared following the procedure used for **12**, with (*R*)-xylbinap (86 mg, 0.118 mmol) in place of (*S*)-MeObiphep, and (*R*)-daipen (34 mg, 0.108 mmol) instead of (*R*,*R*)-dpen. Yield: 75 mg (58%). Anal. Calcd (%) for $C_{71}H_{74}Cl_2N_2O_2OsP_2$: C 65.08, H 5.69, N 2.14; found: C 65.21, H 5.83, N 2.09. ^{1}H NMR (200.1 MHz, C_6D_6, 20 °C): δ 8.93 (t, ^3J(H,H) = 8.3 Hz, 1H; aromatic proton), 8.74 (t, ^3J(H,H) = 7.9 Hz, 1H; aromatic proton), 8.17-6.31 (m, 28H; aromatic protons), 5.93 (d, ^3J(H,H) = 12.2 Hz, 2H; aromatic protons), 4.95 (broad m, 2H; NH_2 and CHN), 4.28 (broad d, J(H,H) = 8.8 Hz, 1H; NH_2), 3.61 (broad m, 1H; NH_2), 3.36 (s, 3H; OMe), 3.29 (m, 1H; NH_2), 3.19 (s, 3H; OMe), 2.13 (s, 6H; C*Me*), 2.00 (s, 6H; C*Me*), 1.77 (s, 6H; C*Me*), 1.76 (s, 6H; C*Me*), 1.66 (m 1H; C*H*Me), 0.51 (d, ^3J(H,H) = 6.8 Hz, 3H; CH*Me*), 0.02 (d, ^3J(H,H) = 6.5 Hz, 3H; CH*Me*). ^{13}C{^{1}H} NMR (50.3 MHz, C_6D_6, 20°C): δ 159.2 (s; *C*OMe), 136.3-113.4 (m; aromatic carbon atoms), 69.3 (s; N*C*Ar), 64.5 (s; NCH), 54.8 (s; OMe), 54.6 (s; OMe), 28.4 (s; *C*HMe), 22.6 (s; CH*Me*), 21.5 (s; C*Me*), 21.2 (s; C*Me*), 15.9 (s; CH*Me*). ^{31}P{^{1}H} NMR (81.0 MHz, C_6D_6, 20 °C): δ - 13.1 (d, ^2J(P,P) = 16.5 Hz), - 14.6 (d, ^2J(P,P) = 16.5 Hz).

Synthesis of *trans*-[OsCl$_2$((*R*,*S*)-Josiphos*)((*R*,*R*)-dpen)] (21). Complex **21** was prepared following the procedure used for **12**, with (*R*,*S*)-Josiphos* (76 mg, 0.107 mmol) in place of (*S*)-MeObiphep. Yield: 56 mg (48%). Anal. Calcd (%) for $C_{56}H_{72}Cl_2FeN_2O_2OsP_2$: C 56.80, H 6.13, N 2.37; found: C 56.92, H 6.06, N 2.29. ^{1}H NMR (200.1 MHz, C_6D_6, 20 °C): δ 8.44-6.73 (m, 14H; aromatic protons), 5.07-3.96 (broad m, 10H; CH, NH_2, PCH, C_5H_3), 3.88 (s, 5H; C_5H_5), 3.31 (s, 3H; OMe), 3.29 (s, 3H; OMe), 2.32 (s, 6H; CMe), 2.24 (s, 6H; CMe), 2.15-0.90 (m, 25H; CH_2, Me). ^{13}C{^{1}H} NMR (50.3 MHz, C_6D_6, 20 °C): δ 158.4 (d, ^4J(C,P) = 2.2 Hz; *C*OMe), 157.5 (d, ^4J(C,P) = 2.3 Hz; *C*OMe), 140.4 (d, *J*(C,P) = 1.6 Hz; ipso Ph), 140.2 (d, *J*(C,P) = 1.7 Hz; ipso Ph), 138.3 (d, ^3J(C,P) = 1.7 Hz; aromatic *C*Me), 138.1 (d, ^3J(C,P) = 2.7 Hz; aromatic *C*Me), 135.2-127.2 (m; aromatic carbon atoms), 95.8 (dd, ^1J(C,P) = 18.7 Hz, ^3J(C,P) = 4.2 Hz; ipso C_5H_3), 72.5 (s; FeC_5H_3), 70.6 (s; FeC_5H_5), 69.2 (d, *J*(C,P) = 7.7 Hz; FeC_5H_3), 67.0 (d, *J*(C,P) = 6.0 Hz; FeC_5H_3), 64.0 (s; N*C*H), 63.3 (s; N*C*H), 59.2 (s; OMe), 59.1 (s; OMe), 42.4 (d, ^1J(C,P) = 25.2 Hz; PCH of Cy), 39.5 (d, ^1J(C,P) = 19.5 Hz; PCH of Cy), 31.8 (d; ^1J(C,P) = 22.1 Hz; P*C*Me), 31.7-27.2 (m; CH_2 of Cy), 21.3 (s; Me), 16.6 (d, ^2J(C,P) = 8.5 Hz; PC*Me*). ^{31}P{^{1}H} NMR (81.0 MHz, C_6D_6, 20 °C): δ 2.0 (d, ^2J(P,P) = 22.0 Hz), - 11.6 (d, ^2J(P,P) = 22.0 Hz).

Synthesis of *trans*-[OsHCl(P(*m*-tolyl)$_3$)$_2$(en)] (22). Complex **1b** (100 mg, 0.049 mmol) was dissolved in toluene (20 mL) and NEt_3 (20 μL, 0.143 mmol) wad added under H_2 (1 atm). The solution was heated at 120 °C for 4 h. En (4.9 μL, 0.073 mmol) was added at room temperature and the solution was heated at 60 °C for 3 h under H_2. The resulting solution was concentrated (0.5 mL) and addition of diethyl ether (4 mL) afforded the precipitation of NEt_4Cl, which was fine-filtered and washed with diethyl ether (2x3 mL) and toluene (1x2 mL). The filtrate was concentrated (1 mL) and by addition of heptane (4 mL) gave the precipitation of a yellow product, which was filtered off, washed with heptane (3x5 mL) at 60 °C and dried under reduced pressure. Yield: 50 mg (57%). Anal. Calcd (%) for $C_{44}H_{51}ClN_2OsP_2$: C 59.02, H 5.74, N 3.13; found: C 59.23, H 5.88, N 3.21. ^{1}H NMR (200.1 MHz, C_6D_6, 20 °C): δ 7.93-6.72 (m, 24H; Ph), 2.79 (broad s, 2H; CH_2), 2.58 (broad s, 2H; CH_2), 2.06-1.90 (m, 20H; CH_3, NH_2), 1.56 (broad s, 2H; NH_2), - 20.9 (t, ^2J(P,H) = 16.3 Hz, 1H; OsH). ^{13}C{^{1}H} NMR (50.3 MHz, C_6D_6, 20 °C): δ 138.3-125.8 (m; aromatic carbon atoms), 45.5 (s; NCH_2), 21.5 (s; CH_3). ^{31}P{^{1}H} NMR (81.0 MHz, C_6D_6, 20 °C): δ 20.1 (s).

Synthesis of *trans*-[OsHCl(dppf)(en)] (23). Complex **1a** (100 mg, 0.095 mmol) was dissolved in toluene (20 mL) and NEt_3 (20 μL, 0143 mmol) wad added under H_2 (1 atm). Dppf (63 mg, 0.114 mmol) was added and the solution was heated at 60 °C for 2 h under H_2. After the addiction of en (7.6 μL, 0.114 mmol) at room temperature, the solution was heated at 60 °C for 3 h under H_2. The resulting mixture was concentrated (0.5 mL) and addition of diethyl ether (4 mL) afforded the precipitation of NEt_4Cl, which was fine-filtered and washed with diethyl ether (2x3 mL) and

toluene (1x2 mL). The filtrate was concentrated (1 mL) and by addition of heptane (4 mL) gave the precipitation of a green product, which was filtered, washed with heptane (3x5 mL) at 60 °C and dried under reduced pressure. Yield: 50 mg (63%). Anal. Calcd (%) for $C_{36}H_{37}ClFeN_2OsP_2$: C 51.41, H 4.43, N 3.33; found: C 51.48, H 4.51, N 3.39. ^{1}H NMR (200.1 MHz, C_6D_6, 20 °C): δ 8.43-6.76 (m, 20H; Ph), 4.76 (s, 2H; C_5H_4), 4.35 (s, 2H; C_5H_4), 4.07 (s, 2H; C_5H_4), 3.85 (s, 2H; C_5H_4), 2.60 (broad s, 2H; CH_2), 2.25 (broad s, 2H; CH_2), 1.93 (broad s, 2H; NH_2), 1.41 (broad s, 2H; NH_2), - 20.8 (t, ^2J(P,H) = 17.0 Hz, 1H; OsH). ^{13}C{^{1}H} NMR (50.3 MHz, C_6D_{26}, 20 °C): δ 136.7-125.6 (m; aromatic carbon atoms), 71.0 (s; C_5H_4), 70.3 (s; C_5H_4), 45.3 (s; CH_2). ^{31}P{^{1}H} NMR (81.0 MHz, C_6D_6, 20 °C): δ 14.5 (s).

Typical procedure for the catalytic reduction of acetophenone by hydrogenation. The catalyst solution was prepared by dissolving the osmium complex (1.7 μmol) in ethanol (2 mL). Acetophenone (4.30 mmol), NaOEt solution (0.25 M, 0.17 mL, 0.043 mmol) and the osmium solution (0.5 mL, 0.43 μmol) were added to ethanol (total volume 8.6 mL). The resulting solution was transferred into a thermostated reactor at 60-70 °C, and dihydrogen was introduced at a pressure of 5 atm (substrate/Os = 10000, 1 mol% NaOEt, 0.5 M substrate). Samples were withdrawn from the reactor at regular time intervals (2, 5, 10, 20, 30 min, and longer reaction times) in accordance with the S/C ratio. The solution was quickly quenched by the addition of diethyl ether (1:1 v/v), filtered over a short silica pad, and submitted to GC analysis.

Typical procedure for the enantioselective catalytic reduction of acetophenone by hydrogenation. The catalyst solution was prepared by dissolving the osmium complexes (1.7 μmol) in ethanol (2 ml). Acetophenone (0.5 mL, 4.30 mmol), NaOEt solution (0.25 M, 0.17 mL, 0.043 mmol) and the osmium solution (0.5 mL, 0.43 μmol) were added to ethanol (7.4 mL, total volume 8.6 mL). The resulting solution was transferred into a thermostated reactor at 60-70 °C, and dihydrogen was introduced at a pressure of 5 atm (substrate/Os = 10000, 1 mol% NaOEt, 0.5 M substrate). The samples were withdrawn from the reactor at regular time intervals (2, 5, 10, 20, 30 min, and longer reaction times) in accordance with the S/C ratio. The solution was quickly quenched by the addition of diethyl ether (1:1 v/v), filtered over a short silica pad, and submitted to GC analysis.

Typical procedure for the enantioselective catalytic reduction of ketones by hydrogenation. The process of ketone hydrogenation catalyzed by the complex **18** was analogous to that described above for the acetophenone reduction. The reaction was conducted in ethanol at 60 °C and 5 atm H_2 pressure (S/C ratio = 10000, NaOEt = 1 mol%).

Enantioselective catalytic reduction of acetophenone by hydrogenation in the presence of the *in situ* prepared complexes 8 and 21. The catalyst solution was prepared by dissolving the

osmium precursors **1a** or **1b** (2.5 μmol) and the chiral diphosphines (3.1 μmol) in toluene (0.5 ml), and then by refluxing the mixture for 3-4 hours. (*R,R*)-dpen (0.7 mg, 3.3 μmol) was then added and the solution was kept at 100 °C for 1-2 hours. Finally, ethanol (2.5 ml) was added. Acetophenone (0.5 mL, 4.30 mmol), NaOEt solution (0.25 M, 0.34 mL, 0.085 mmol), and the osmium solution (0.5 mL, 0.43 μmol) were added to ethanol (7.2 mL, total volume 8.6 mL). The resulting solution was transferred into a thermostated reactor at 70 °C, and dihydrogen was introduced at a pressure of 5 atm. The hydrogen addition was considered as the start time of the reaction. The acetophenone/catalyst/NaOEt molar ratios were 10000/1/200 and the substrate concentration was 0.5 M.

Typical procedure for the catalytic transfer hydrogenation of acetophenone. The osmium catalyst solution used for TH was prepared by dissolving the complex **3**, **6** or **7** (2.1 μmol) in 2 mL of 2-propanol. A 0.1 M solution of NaO*i*Pr (0.4 mL, 0.04 mmol) in 2-propanol and the catalyst solution (1 mL, 1.05 μmol) were added to acetophenone (240 μL, 2.06 mmol) in 2-propanol (18.6 mL). The resulting mixture was heated at 60 °C or under reflux. The reaction was sampled by removing an aliquot of the reaction mixture, which was quenched by addition of diethyl ether (1:1 v/v), filtered over a short silica pad, and submitted to GC analysis. The complex addition was considered as the start time of the reaction. The acetophenone/catalyst/NaO*i*Pr molar ratio was 2000/1/40 and the substrate concentration was 0.1 M.

Hg poisoning test for 6. The transfer hydrogenation of PhCOMe with complex **6** was performed following the procedure described in the previous paragraph for the catalytic transfer hydrogenation of acetophenone, in the presence of Hg (Hg / **6** = 400).

Single-crystal X-ray structure determination of compound 3.

Crystal data and details of the structure determination are presented in the Supporting Information (S65). A suitable single crystal for the X-ray diffraction study was grown from CH_2Cl_2. An orange fragment was fixed on the top of a glass fiber with perfluorinated ether and transferred to the diffractometer. Preliminary examination and data collection were carried out on an area detecting system (BRUKER AXS, Kappa APEX II) at the window of a rotating anode (BRUKER AXS, FR591) and graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The unit cell parameters were obtained by full-matrix least-squares refinement of 38621 reflections. Data collection were performed at 173 K (OXFORD CRYOSYSTEMS) within a θ-range of $1.34° < \theta < 25.35°$. The data set was measured in rotation scan modus with 15 runs with $\Delta\varphi/\Delta\omega = 0.50°$. A total number of 38621 intensities were integrated. Raw data were corrected for Lorentz, polarization, and, arising from the scaling procedure, latent decay and absorption effects. After merging $R_{int} = 0.037$) a sum of 6749 (all data) and 6720 [$I > 2\sigma(I)$], respectively, remained and all data were used. The structures were

solved by a combination of direct methods and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic displacement parameters. In the difference map(s) calculated from the model containing all non-hydrogen atoms, not all of the hydrogen positions could be determined from the highest peaks. For this reason, the hydrogen atoms were placed in calculated positions (d_{C-H} = 95, 99 pm, d_{N-H} = 92 pm). Isotropic displacement parameters were calculated from the parent carbon/nitrogen atom ($U_H = 1.2\ U_C$, $U_H = 1.2\ U_N$). The hydrogen atoms were included in the structure factor calculations but not refined. Full-matrix least-squares refinements with 451 parameters were carried out by minimizing $\Sigma w(F_o^2\text{-}F_c^2)^2$ with the SHELXL-97[44] weighting scheme and stopped at shift/err < 0.001. The final residual electron density maps showed no remarkable features. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from *International Tables for Crystallography.*[45] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1565971 **(3)**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Supporting Information. NMR data of the isolated complexes and X-ray structure of **3**. This material is available free of charge via the Internet at http://pubs.acs.org

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Notes

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(16) en = ethylenediamine; bn = 1,4-butanediamine; *N*,*N*-dmen = *N*,*N*-dimethyl-ethylenediamine; dpen = 1,2-diphenylethylenediamine; dppn = 1,3-diphenylpropanediamine; daipen = 1,1-dianisyl-2-isopropyl-1,2-ethylenediamine; dppf = 1,1′-bis(diphenylphosphino)ferrocene; dpbp = 2,2′-bis(diphenylphosphino)benzophenone; skewphos = 2,4-bis(diphenylphosphine)pentane; dppb = 1,4-bis(diphenylphosphino)butane; binap = (1,1'-binaphthalene)-2,2'-diylbis(1,1-diphenylphosphane); xylbinap = (1,1'-binaphthalene)-2,2'-diylbis[1,1-bis(3,5-dimethylphenyl)phosphane]; MeObiphep = [6,6'-dimethoxy(1,1'-biphenyl)-2,2'-diyl]bis(1,1-diphenylphosphane); xylMeObiphep = [6,6'-dimethoxy(1,1'-biphenyl)-2,2'-diyl]bis[1,1-bis(3,5-dimethylphenyl)phosphane; Josiphos* = 1-{2-[bis(3,5-dimethyl-4-methoxyphenyl)phosphine]ferrocenyl}ethyldicyclohexylphosphine.

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