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# Benzo[*h*]quinoline Pincer Ruthenium and Osmium Catalysts for Hydrogenation of Ketones

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Chiral orthometalated osmium complexes [OsCl(CN′N)(PP)] {PP = (*S*,*R*)-Josiphos type diphosphane} based on 2-aminomethylbenzo[*h*]quinoline ligands (HCN′N) were prepared by reaction of $[OsCl_2(PPh_3)_3]$ with a Josiphos diphosphane and a HCN′N ligand in the presence of $NEt_3$. Ruthenium and osmium complexes [MX(CN′N)(PP)] {M = Ru, Os; X = Cl, $OCH(p\text{-}C_6H_4F)_2$; PP = dppb, (*S*,*R*)-Josiphos}, in the presence of KO*t*Bu, efficiently catalyze the chemoselective hydrogenation ($H_2$ = 5 atm) of aromatic and aliphatic ketones to secondary alcohols in methanol or methanol/ethanol mixtures, when a S/C ratio of 10000–50000 is used. With use of these chiral phosphanes, alkyl aryl ketones have been reduced with *ee* values up to 99 % and turnover frequencies (TOFs) up to $5.6 \times 10^4$ $h^{-1}$.

## Introduction

The catalytic asymmetric hydrogenation (AH) of the polar C=O bond with $H_2$ has been investigated extensively in the last decade and represents a core reaction for the synthesis of valuable chiral alcohols.[1] This transformation is usually performed with transition metal catalysts based on rhodium and iridium, and particular attention has been devoted to ruthenium. For the group 8 metals, osmium[2] has been employed sparingly, whereas iron[3] is beginning to attract attention on account of its environmental sustainability. Recently, we have isolated a new class of osmium complexes based on the 1-(pyridin-2-yl)methanamine motif, namely $[OsCl_2(diphosphane)(RPyme)]$[4] {RPyme = 1-substituted-1-(pyridin-2-yl)methanamine} and [OsCl(CNN)(diphosphane)],[5] prepared from the orthometalation of 1-(6-arylpyridin-2-yl)methanamine ligands (HCNN) (Figure 1). Surprisingly, these systems were found to be highly active catalysts in hydrogenation and also asymmetric transfer hydrogenation (ATH)[6] of carbonyl compounds, with reaction rates comparable to those of the analogous ruthenium complexes $[RuCl_2(diphosphane)(RPyme)]$[7] and [RuCl(CNN)(diphosphane)].[8]

In this regard, it is worth noting that on account of the stronger bonding, osmium compounds are thought to be more stable and less active catalysts[9] relative to those of ruthenium for the reduction of ketones. Although a few Os catalysts have been described for ATH,[10] no examples of AH catalysts based on osmium were reported before our recent work on [OsCl(CNN)(diphosphane)].[5] Pincer derivatives [MCl(CNN)(diphosphane)] (M = Ru, Os) appear very attractive for practical applications, because of the presence of a metal–carbon bond that affords compounds with a high degree of thermal stability, preventing easy deactivation and leading to highly productive catalysts. On account of the excellent catalytic performances of the CNN pincer Ru and Os complexes, we decided to examine the coordination chemistry and the catalytic potential of a new class of CN′N derivatives based on the 2-aminomethylbenzo[*h*]quinoline framework, which is characterized by a higher conformational rigidity relative to CNN ligands containing the 2-arylpyridine moiety. In this context, we have recently reported on the preparation of the terdentate complexes [MCl(CN′N)(diphosphane)] (**1**–**4**) (M = Ru, Os), which were found to promote the transfer hydrogenation of carbonyl compounds in basic 2-propanol with a high rate and low catalyst loading (Figure 2).[11]

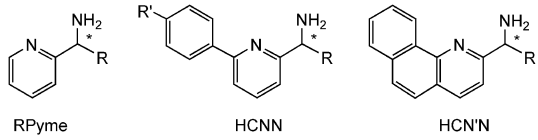


Figure 1. Ligands containing the 1-(pyridin-2-yl)methanamine motif.

Ruthenium derivative **3**, which contains the bulky (*S*,*R*)-Josiphos* ligand, has been proven to catalyze the ATH of ketones with both high enantioselectivity and productivity on account of the presence of the strongly coordinated CN′N tridentate and PP bidentate ligands. Since Ru and Os complexes of the bidentate RPyme and terdentate CNN ligands are efficient catalysts in ATH as well as AH, we

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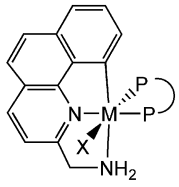
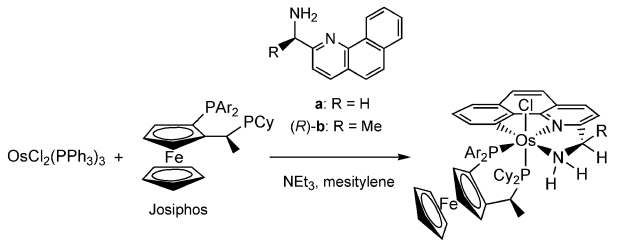



| | M | X | PP |
|---|---|---|---|
| 1 | Ru | Cl | dppb |
| 2 | Ru | OCH(*p*-$C_6H_4F$)$_2$ | dppb |
| 3 | Ru | Cl | (*S*,*R*)-Josiphos* |
| 4 | Os | Cl | dppb |

Figure 2. Ruthenium and osmium [MCl(CN′N)(diphosphane)] complexes.




| | diphosphane | Ar | R |
|---|---|---|---|
| 5 | (*S*, *R*) Josiphos | Ph | H |
| 6 | (*S*, *R*) Josiphos* | 4-OMe-3,5-$Me_2C_6H_2$ | Me |

(1)

decided to investigate whether complexes based on 2-aminomethylbenzo[*h*]quinoline could promote the AH of carbonyl compounds. It is worth noting that good AH catalysts are generally poorly active ATH catalysts and vice versa; the choice of solvent and pH of the reaction medium appears crucial.[12] A universal catalyst for both pressure AH and ATH of ketones is a desirable goal,[1,4–8,13] the former being preferred at commercial scale, whereas ATH is more convenient in a research laboratory.

We report herein a study of the reactivity of the terdentate 2-aminomethylbenzo[*h*]quinoline complexes [MCl(CN′N)(diphosphane)] (M = Ru, Os) in the pressure hydrogenation of carbonyl compounds. The synthesis of new chiral osmium derivatives with (*R*,*S*)-Josiphos diphosphanes is also reported. Ruthenium and osmium complexes of CN′N ligands were found to efficiently catalyze the chemoselective hydrogenation of aromatic and aliphatic ketones to secondary alcohols in methanol or methanol/ethanol mixtures and in the presence of KO*t*Bu with a S/C ratio of 10000–50000. With use of chiral (*R*,*S*)-Josiphos phosphanes, reduction of alkyl aryl ketones was achieved with *ee* values up 99% and turnover frequencies (TOFs) up to $5.6 \times 10^4$ h$^{-1}$. Complexes [MCl(CN′N)P$_2$] (M = Ru, Os) extend the relatively low number of efficient catalysts for both AH and ATH reactions.

## Results and Discussion

### Synthesis and Characterization of [OsCl(CN′N)(PP)] Complexes

Complexes **1**–**4** were prepared according to the previously described methods.[11] Treatment of [$OsCl_2(PPh_3)_3$] with 1.2 equiv. of the (*S*,*R*)-Josiphos diphosphane in mesitylene at 110 °C (2 h) gave a mixture of uncharacterized products, which slowly reacted with 2-aminomethylbenzo[*h*]quinoline **a** (1.4 equiv.) in the presence of $NEt_3$ to afford complex **5** (24 h at 140 °C) isolated in 67% yield [Equation (1)].

In the $^{31}P\{^1H\}$ NMR spectrum of complex **5**, there are two doublets at $\delta$ = 8.9 and –3.2 ppm [d, $^2J$(P,P) = 22.7 Hz], whereas the $^{13}C\{^1H\}$ NMR resonance at $\delta$ = 162.6 ppm is due to the carbon bound to osmium. Attempts to use $Na_2CO_3$ as weak base to favor orthometalation resulted in the formation of several products, including hydride species. In order to isolate catalysts displaying higher enantioselectivity, a chiral HCN′N ligand was employed in combination with a Josiphos ligand. According to our studies on Ru and Os complexes, which showed that (*S*,*R*)-Josiphos is correctly matched with the chiral RPyme and CNN ligands of *R* configuration, we prepared derivative **6** by reaction of [$OsCl_2(PPh_3)_3$] with the bulkier (*S*,*R*)-Josiphos* diphosphane and ligand (*R*)-**b**, obtained from 1-(benzo[*h*]quinolin-2-yl)ethanone via lipase-mediated kinetic resolution of the corresponding racemic secondary alcohol.[14] Complex **6** was obtained as a single stereoisomer, as confirmed by $^{31}P$ NMR spectroscopy, and isolated in 64% yield.

### Catalytic Results

Ruthenium complexes **1**–**3** and osmium complexes **4**–**6** were found to be active in the hydrogenation of C=O and C=N bonds with dihydrogen at low pressure (5 atm) in methanol or methanol/ethanol mixtures and in the presence of a strong base (Figure 3). By carrying out the reaction in methanol at 40 °C and in the presence of KO*t*Bu (base/Ru = 200), derivative **1** catalyzed the quantitative reduction of acetophenone **7a** into 1-phenylethanol in 30 min and afforded a TOF of $3.1 \times 10^4$ h$^{-1}$ (Table 1) with a substrate/Ru ratio of 10000.

This complex has been proven to be active also at a higher ketone/Ru ratio (S/C = 50000), indicating that the deactivation is retarded. Linear and cyclic dialkyl ketones such as **7h** and **7k** are promptly hydrogenated in 1 h, whereas the unsaturated ketone 5-hexen-2-one (**7j**) is chemoselectively reduced at the C=O bond, and no hydrogenation or isomerization of the C=C function was observed (TOF = $1.4 \times 10^4$ to $3.0 \times 10^4$ h$^{-1}$). Complex **1** was also found to be active in the reduction of imine **7m**, albeit with a significantly lower rate (TOF = $1.4 \times 10^3$ h$^{-1}$) relative to that of the carbonyl substrates, which are characterized by a stronger polarity of the C=X bond.[15] The isolated alkoxide **2** shows an activity in the hydrogenation of **7a**

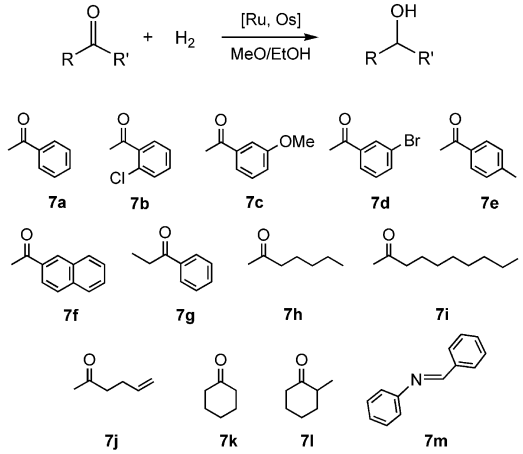



Figure 3. Hydrogenation of carbonyl compounds and imine **7** catalyzed by [MCl(CN′N)(diphosphane)] (M = Ru, Os) complexes.

Table 1. Hydrogenation of ketones and compound **7m** (0.5 M) in the presence of **1**, **2**, and **4** in MeOH, under 5 atm $H_2$. Substrate/Ru/KO*t*Bu = 10000:1:200; substrate/Os/KO*t*Bu = 10000:1:5.

| Complex | Ketone | *T* [°C] | Time [min] | Conversion [%][a] | TOF [$h^{-1}$][b] |
|---|---|---|---|---|---|
| **1** | **7a** | 40 | 30 | >99 | $3.1\times10^4$ |
| **1**[c] | **7a** | 40 | 6 h | 95 | $1.3\times10^4$ |
| **1** | **7h** | 40 | 60 | >99 | $3.0\times10^4$ |
| **1** | **7j** | 40 | 60 | 95 | $1.4\times10^4$ |
| **1** | **7k** | 40 | 60 | >99 | $1.9\times10^4$ |
| **1**[d] | **7m** | 40 | 10 h | 93 | $1.4\times10^3$ |
| **2** | **7a** | 40 | 30 | 98 | $2.9\times10^4$ |
| **4** | **7a** | 70 | 30 | 99 | $3.2\times10^4$ |
| **4** | **7g** | 70 | 30 | >99 | $2.7\times10^4$ |
| **4** | **7i** | 70 | 30 | 99 | $2.8\times10^4$ |
| **4** | **7k** | 70 | 30 | >99 | $2.8\times10^4$ |
| **4** | **7l** | 70 | 3 h | >99 | $5.4\times10^3$ |

[a] Conversion and *ee* values were determined by GC and NMR spectroscopic analyses. [b] Turnover frequency [mol of substrate converted to alcohol (amine) per mol of catalyst per hour] at 50% conversion. [c] Ketone/**1**/KO*t*Bu = 50000:1:1000. [d] Imine/**1**/KO*t*Bu = 5000:1:100.

(TOF = $2.9\times10^4$ $h^{-1}$) similar to that of chloride **1**, suggesting that in methanol catalytic precursors **1** and **2** undergo easy displacement of the anionic ligands with the formation of the catalytically active Ru–H species. Osmium complex **4** catalyzes the quantitative hydrogenation of alkyl aryl ketones **7a** and **7g** at 70 °C in 30 min (5 atm $H_2$) with a low amount of base (KO*t*Bu/Os = 5), affording a TOF up to $3.2\times10^4$ $h^{-1}$. In addition, linear ketone **7i** and cyclic ketones **7k** and **7l** were efficiently hydrogenated under these catalytic conditions (TOF = $5.4\times10^3$ to $2.8\times10^4$ $h^{-1}$). The significantly lower amount of KO*t*Bu employed with Os complex **4** relative to that used with Ru derivative **1** (base/Ru = 200) may be relevant for the hydrogenation of carbonyl compounds sensitive to strong bases. Furthermore, the stronger bonding of osmium relative to ruthenium allows operation at higher temperature without catalyst deactivation.

Asymmetric hydrogenation of **7a** has been achieved with **3** (S/Ru = 10000) in the presence of KO*t*Bu (base/Ru = 200) at 40 °C, affording quantitative formation of (*S*)-1-phenylethanol with 92% *ee* in 30 min (TOF = $4.3\times10^4$ $h^{-1}$) in a methanol/ethanol mixture (7:3 by volume) (Table 2). Hydrogenation of **7a** in MeOH or EtOH resulted in lower enantioselectivity, in line with the studies on the chiral CNN Ru complexes.[8e] Methyl aryl ketones **7b**–**7e** have quickly been reduced (TOF up to $5.5\times10^4$ $h^{-1}$) to the corresponding *S*-alcohols with 90–94% *ee*. 2-Acetonaphthone (**7f**) and ethyl phenyl ketone (**7g**) were also promptly converted to alcohols with TOF values up to $5.6\times10^4$ $h^{-1}$ and *ee* values of 93 and 99%, respectively. Aliphatic ketone **7h** was quantitatively hydrogenated to alcohol, but with poor enantioselectivity (42% *ee*).

Table 2. Asymmetric hydrogenation of ketones (0.5 M) to alcohols in the presence of complexes **3**, **5**, **6**, and the $[OsCl_2(PPh_3)_3]$/(*S*,*R*)-Josiphos*/benzo[*h*]quinoline system. Ketone/complex/KO*t*Bu = 10000:1:200, $H_2$ pressure = 5 atm, solvent = MeOH/EtOH mixture (7:3 by volume).

| Complex | Ketone | *T* [°C] | Time [min] | Conv. [%][a] | TOF [$h^{-1}$][b] | *ee* [%][a] |
|---|---|---|---|---|---|---|
| **3** | **7a** | 40 | 30 | >99 | $4.3\times10^4$ | 92 *S* |
| **3** | **7b** | 40 | 60 | 95 | $1.6\times10^4$ | 90 *S* |
| **3** | **7c** | 40 | 60 | >99 | $1.6\times10^4$ | 94 *S* |
| **3** | **7d** | 40 | 10 | >99 | $5.5\times10^4$ | 91 *S* |
| **3** | **7e** | 40 | 60 | 96 | $3.1\times10^4$ | 92 *S* |
| **3** | **7f** | 40 | 30 | 95 | $5.6\times10^4$ | 93 *S* |
| **3** | **7g** | 40 | 60 | 97 | $2.0\times10^4$ | 99 *S* |
| **3** | **7h** | 40 | 60 | >99 | $1.8\times10^4$ | 42 *S* |
| **5** | **7a** | 70 | 30 | >99 | $2.0\times10^4$ | 86 S |
| **6** | **7a** | 70 | 60 | 97 | $1.4\times10^4$ | 92 S |
| in situ[c] | **7a** | 70 | 30 | >99 | $2.4\times10^4$ | 90 *S* |
| in situ[c] | **7c** | 70 | 30 | >99 | $2.2\times10^4$ | 91 *S* |
| in situ[c] | **7f** | 70 | 30 | >99 | $1.6\times10^4$ | 94 *S* |
| in situ[c] | **7g** | 70 | 60 | >99 | $1.3\times10^4$ | 99 *S* |

[a] The conversion and *ee* were determined by GC analysis. [b] Turnover frequency (mol of ketone converted to alcohol per mol of catalyst per hour) at 50% conversion. [c] $[OsCl_2(PPh_3)_3]$/(*S*,*R*)-Josiphos*/benzo[*h*]quinoline = 1:1.5:2.

Chiral osmium complexes **5** and **6** have been proven to hydrogenate **7a** at 70 °C with 86 and 92% *ee*, respectively, and at a good rate (TOF up to $2.0\times10^4$ $h^{-1}$) in the same MeOH/EtOH mixture and with a KO*t*Bu/Os ratio of 200. Similar performances have been reached with the Os/Josiphos/benzo[*h*]quinoline system prepared in situ, without isolation of the corresponding pincer complex.

As a matter of fact, treatment of $[OsCl_2(PPh_3)_3]$ with the bulky phosphane (*S*,*R*)-Josiphos* in MeOH/EtOH at reflux temperature (3 h), followed by the addition of **a** (1 h), led to a chiral Os system that catalyzed the AH of **7a** in 30 min, affording the *S*-alcohol with 90% *ee* and TOF = $2.4\times10^4$ $h^{-1}$ (Table 2). These values are slightly higher than those obtained with the isolated complex **5**, which contains the less bulky (*S*,*R*)-Josiphos, indicating that efficient chiral pincer osmium catalysts can also be conveniently prepared in situ, without the necessity of isolating the complexes. By employment of the in situ generated (*S*,*R*)-Josiphos* osmium catalyst, ketones **7c**, **7f**, and **7g** were quickly reduced to the corresponding *S*-alcohols with 91–99% *ee* (TOF = $1.3\times10^4$ to $2.2\times10^4$ $h^{-1}$). The mechanism of the catalytic hydrogenation, mediated by the Ru and Os pincer complexes, entails the reaction of the catalytic precursor with

dihydrogen in the presence of potassium alkoxide in alcohol, leading to the displacement of the anionic ligand (chloride or alkoxide) and the formation of the hydride complex [MH(CN′N)(diphosphane)],[11] which is the key species involved in the ketone reduction, according to the mechanism proposed for $RuH/NH_2$ systems.[12,16] The high productivity of the Ru and Os complexes suggests that the pincer CN′N ligands, like the related CNN ligands, do not undergo M–C hydrogenolysis with dihydrogen in basic media and that the base is involved in the heterolytic splitting of dihydrogen.

Complexes of Ru (and also Os) based on benzo[*h*]quinoline show much the same enantioselectivity in the AH of ketones in methanol/ethanol and ATH of ketones in 2-propanol. Ruthenium complex **3** catalyzed the reduction of **7a** to *S*-alcohol with 92 vs. 96[11]% *ee* in AH and ATH, whereas Os derivative **5** and the corresponding $[OsCl_2(PPh_3)_3]$/(*S*,*R*)-Josiphos*/benzo[*h*]quinoline system[11] led to 86 and 80% *ee*, respectively. On the basis of these results and those obtained with CNN pincer complexes, it is reasonable to assume that the asymmetric reduction occurs on the same metal–hydride complex [MH(CN′N)(Josiphos)] (M = Ru, Os) in both reactions. However, the small difference in the enantioselectivity may be ascribed to the active role of the alcohol solvent,[17] which can lead to hydrogen bonding with the ketone, thus affecting activity and enantioselectivity.

The comparison of the activity of Ru CN′N pincer complexes based on benzo[*h*]quinoline with that of related CNN derivatives,[8e] obtained from 1-(6-arylpyridin-2-yl)methanamine with the same diphosphane, shows that the former complexes catalyze the AH of **7a** with slightly higher enantioselectivity (e.g. 92 vs. 88% for **3** and [RuCl(CNN){(*S*,*R*)-Josiphos*}]), with use of a more protic solvent mixture (MeOH/EtOH vs. EtOH) and with a lower amount of base. Also with Os, CN′N complexes displayed a better enantioselectivity relative to those of CNN: derivative **5** led to (*S*)-1-phenylethanol with 86% *ee*, whereas [OsCl(CNN){(*S*,*R*)-Josiphos}][5] gave 80% *ee*. Apparently, the more rigid benzo[*h*]quinoline system having an extended delocalized polynuclear ring may be responsible for the higher enantioselectivity with respect to complexes based on the 2-phenylpyridine moiety.

## Conclusions

In summary, we have found that the highly active transfer hydrogenation catalysts [MCl(CN′N)(diphosphane)] (M = Ru, Os) also display high catalytic activity in the hydrogenation of ketones with dihydrogen, thus extending the number of efficient systems for both types of reactions. The presence of the terdentate CN′N ligand allows slow deactivation of both Ru and Os catalysts, suggesting that no M–C hydrogenolysis may occur. The use of Os allowed the catalytic hydrogenation to be performed with a lower amount of base and at higher temperature. High enantioselectivity was achieved with Ru and also Os complexes of suitable chiral diphosphane and CN′N ligands. With Josiphos diphosphanes, similar values of enantioselectivity were observed in both asymmetric hydrogenation and transfer hydrogenation of methyl aryl ketones. Studies are under way to provide further insights into the mechanism of hydrogenation and to extend the use of chiral pincer complexes in asymmetric catalysis.

## Experimental Section

**General:** All reactions were carried out under an argon atmosphere with standard Schlenk techniques. The solvents and ketones were carefully dried by standard methods and distilled under argon before use. The Josiphos diphosphanes were purchased from Aldrich, whereas ligands **a**,[11] **b**,[14] and complexes $[OsCl_2(PPh_3)_3]$[18] and **1**–**4**[11] were prepared according to literature procedures. NMR spectroscopic measurements were recorded with a Bruker AC 200 spectrometer, and chemical shifts (in ppm) are relative to TMS for $^1H$ and $^{13}C\{^1H\}$ and 85% $H_3PO_4$ for $^{31}P\{^1H\}$. Elemental analyses (C, H, N) were carried out with a Carlo Erba 1106 elemental analyzer, whereas the GC analyses were performed with a Varian G*P*-3380 gas chromatograph equipped with a MEGADEX-ETTBDMS-β chiral column.

**Compound 5:** $[OsCl_2(PPh_3)_3]$ (100 mg, 0.095 mmol) and (*S*,*R*)-Josiphos·$C_2H_5OH$ (73 mg, 0.117 mmol) were treated with mesitylene (2 mL), and the suspension was stirred at 110 °C for 2 h. Ligand **a** (28 mg, 0.134 mmol) and triethylamine (133 μL, 0.954 mmol) were added to the suspension. The mixture was stirred at 140 °C for 24 h. The solution was concentrated to 0.5 mL, and addition of pentane afforded a dark brown precipitate, which was filtered, washed with pentane (3 × 5 mL), and dried under reduced pressure. The solid was extracted with diethyl ether (3 × 5 mL), and the solution was concentrated. Addition of pentane gave a brown precipitate, which was washed with *n*-heptane at 60 °C (3 × 5 mL) and dried under reduced pressure. Yield: 65 mg (67%). $^1H$ NMR (200.1 MHz, $C_6D_6$, 20 °C): $\delta$ = 8.58–8.45 (m, 2 H, aromatic protons), 7.83 [t, $^3J$(H,H) = 7.0 Hz, 1 H, aromatic proton], 7.71 [d, $^3J$(H,H) = 8.4 Hz, 1 H, aromatic proton], 7.60–6.75 (m, 12 H, aromatic protons), 6.73 [d, $^3J$(H,H) = 6.2 Hz, 1 H, aromatic proton], 4.91 (m, 1 H, $CH_2N$), 4.60 (m, 1 H, PCH), 4.37–3.96 (m, 4 H, $CH_2N$, $C_5H_3$), 3.84 (s, 5H, $C_5H_5$), 3.55 (s, 1 H, $NH_2$), 2.49–0.84 (m, 26 H, $CH_3$, Cy, $NH_2$) ppm; $^{13}C\{^1H\}$ NMR (50.3 MHz, $C_6D_6$, 20 °C): $\delta$ = 162.6 (m; OsC), 157.9 (s; aromatic carbon), 156.9 (s; aromatic carbon), 148.9–116.0 (m; aromatic carbons), 98.0 [d, $J$(C,P) = 17.4 Hz; *ipso*-$C_5H_3$], 74.1 (s, $C_5H_3$), 71.6 (s. $C_5H_3$), 70.5 (s. $C_5H_5$), 67.9 [d, $J$(C,P) = 3.7 Hz; $FeC_5H_3$], 54.5 (s; $CH_2N$), 40.6 [d, $J$(C,P) = 22.7 Hz; CH of Cy], 38.0 [d, $J$(C,P) = 22.9 Hz; CH of Cy], 31.6–26.7 (m; $CH_2$ of Cy, P*C*Me), 16.1 [d, $J$(C,P) = 6.4 Hz; PC*Me*] ppm; $^{31}P\{^1H\}$ NMR (81.0 MHz, $C_6D_6$, 20 °C): $\delta$ = 8.9 [d, $^2J$(P,P) = 22.7 Hz], –3.2 [d, $^2J$(P,P) = 22.7 Hz] ppm. $C_{50}H_{55}ClFeN_2OsP_2$ (1027.45): calcd. C 58.45, H 5.40, N 2.73; found C 59.03, H 5.50, N 2.80.

**Compound 6:** Complex **6** was prepared as described for **5** by using (*S*,*R*)-Josiphos* (82 mg, 0.115 mmol) instead of (*S*,*R*)-Josiphos·$C_2H_5OH$ and (*R*)-**b** (42 mg, 0.189 mmol) instead of **a**. Yield: 70 mg (64%). $^1H$ NMR (200.1 MHz, $CD_2Cl_2$, 20 °C): $\delta$ = 9.34 (m, 1 H, aromatic proton), 8.39–6.56 (m, 10 H, aromatic proton), 4.71 (m, 1 H, PCH), 4.53–4.38 (m, 3H. $C_5H_3$), 3.79 [q, $^3J$(H,H) = 4.5 Hz, 1 H, CHN], 3.75 (s, 6 H, OMe), 3.70 (s, 5H. $C_5H_5$), 3.45 (broad s 1 H, $NH_2$), 2.40–0.72 (m, 41 H, Me, Cy, $NH_2$) ppm. $^{13}C\{^1H\}$ NMR (50.3 MHz, $CD_2Cl_2$, 20 °C): $\delta$ = 158.0 (m;

OsC), 157.9 (s; aromatic carbon), 141.5–123.2 (m; aromatic carbons), 74.1 (s. $C_5H_3$), 70.7 (s. $C_5H_3$), 70.3 (s. $C_5H_5$), 68.9 [d, $J$(C,P) = 5.8 Hz. $C_5H_3$], 60.0–59.8 (m; CHN, OMe), 45.6 [d, $J$(C,P) = 11.3 Hz; CH of Cy], 31.3–26.5 (m; $CH_2$ of Cy, P*C*Me), 21.3 (s; NC*Me*), 16.6–16.3 (m; Me, PC*Me*) ppm. $^{31}P\{^1H\}$ NMR (81.0 MHz, $CD_2Cl_2$, 20 °C): $\delta$ = 3.4 [d, $^2J$(P,P) = 24.3 Hz], –8.6 [d, $^2J$(P,P) = 24.3 Hz] ppm. $C_{57}H_{69}ClFeN_2O_2OsP_2$ (1157.63): calcd. C 59.14, H 6.01, N 2.42; found C 60.02, H 6.08, N 2.50.

**Procedure for the Catalytic Hydrogenation of Ketones:** The ruthenium or osmium complex (1.72 μmol) was dissolved in MeOH (2 mL) or MeOH/EtOH mixture (2 mL, 7:3 by volume). The ketone (4.3 mmol), KO*t*Bu (9.6 mg, 0.086 mmol), and the solution containing the complex (0.5 mL, 0.43 μmol) were added to the MeOH or MeOH/EtOH mixture (to a final volume of 8.6 mL). The resulting solution was transferred into a thermostatted reactor at 40 °C (for the Ru complex) or 70 °C (for the Os complex), and the reduction was performed by introducing dihydrogen at a pressure of 5 atm (substrate/catalyst/base = 10000:1:200, ketone 0.5 M).

**Procedure for the Catalytic Hydrogenation of Ketones with the In Situ Prepared Catalyst:** The osmium complex $[OsCl_2(PPh_3)_3]$ (1.8 mg, 1.7 μmol) and (*S*,*R*)-Josiphos* (1.8 mg, 2.5 μmol) were dissolved in MeOH/EtOH mixture (2 mL, 7:3 by volume) and refluxed for 3 h. Ligand **a** (0.7 mg, 3.4 μmol) was added, and the mixture was refluxed for another 1 h. The ketone (4.3 mmol), KO*t*Bu (9.6 mg, 0.086 mmol), and the solution containing the complex (0.5 mL, 0.43 μmol) were added to the MeOH or MeOH/EtOH mixture (to a final volume of 8.6 mL). The resulting solution was transferred into a thermostatted reactor at 70 °C, and the reduction was performed by introducing dihydrogen at a pressure of 5 atm (substrate/Os/base = 10000:1:200, ketone 0.5 M).

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