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New Benzo[*h*]quinoline-Based Ligands and their Pincer Ru and Os Complexes for Efficient Catalytic Transfer Hydrogenation of Carbonyl Compounds

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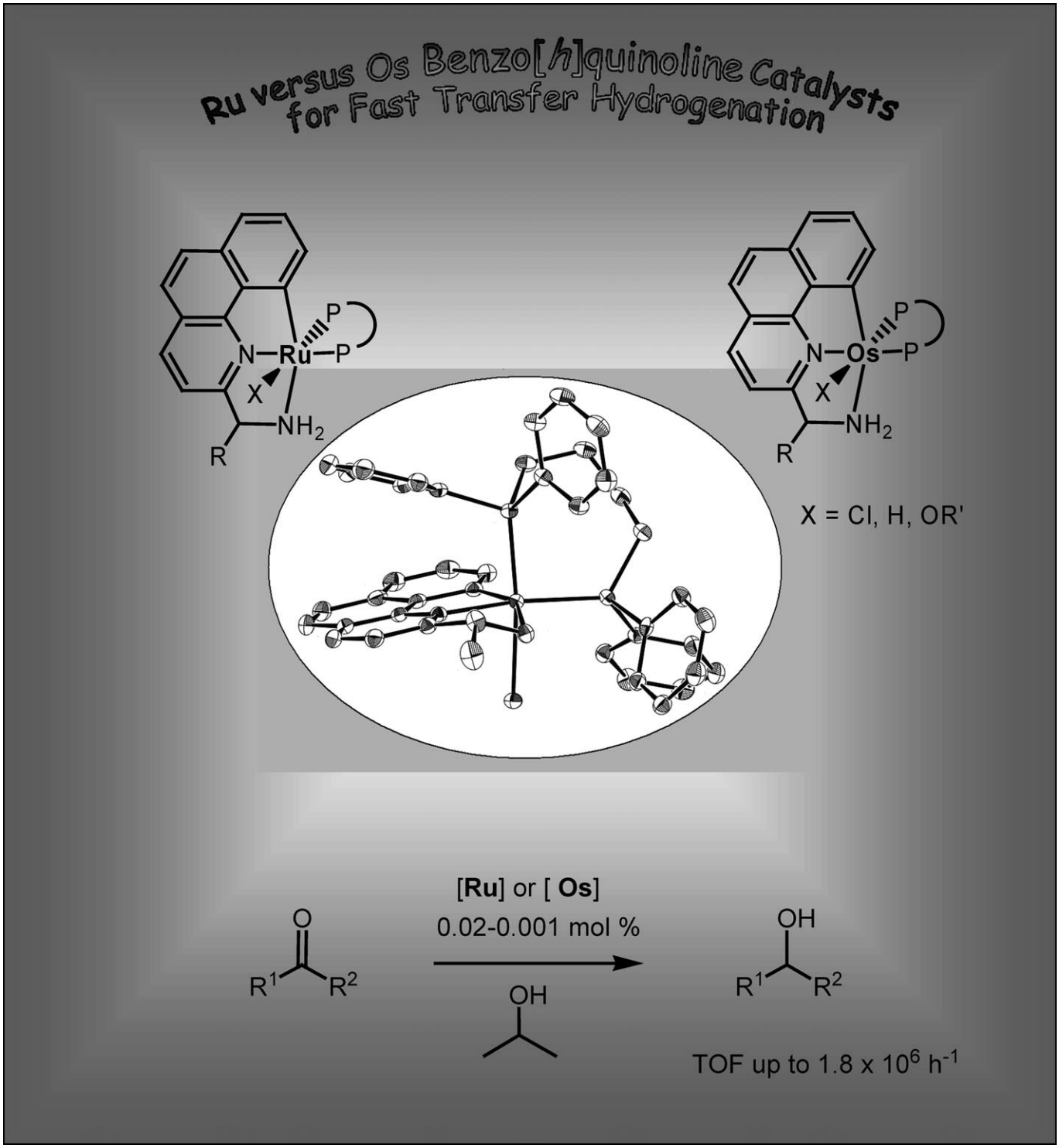

Abstract: New benzo[*h*]quinoline ligands (HCN′N) containing a $CHRNH_2$ (R = H (**a**), Me (**b**), *t*Bu (**c**)) function in the 2-position were prepared starting from benzo[*h*]quinoline *N*-oxide (in the case of ligand **a**) and 2-chlorobenzo[*h*]-quinoline (for ligands **b** and **c**). These compounds were used to prepare ruthenium and osmium complexes, which are excellent catalysts for the transfer hydrogenation (TH) of ketones. The reaction of **a** with $[RuCl_2(PPh_3)_3]$ in 2-propanol at reflux afforded the terdentate CN′N complex $[RuCl(CN'N)(PPh_3)_2]$ (**1**), whereas the complexes [RuCl(CN′N)(dppb)] (**2**–**4**; dppb = $Ph_2P(CH_2)_4PPh_2$) were obtained from $[RuCl_2(PPh_3)$(dppb)] with **a**–**c**, respectively. Employment of (*R*,*S*)-Josiphos, (*S*,*R*)-Josiphos*, (*S*,*S*)-Skewphos, and (*S*)-MeO-Biphep in combination with $[RuCl_2(PPh_3)_3]$ and ligand **a** gave the chiral derivatives [RuCl-(CN′N)(PP)] (**5**–**8**). The osmium complex [OsCl(CN′N)(dppb)] (**12**) was prepared by treatment of $[OsCl_2(PPh_3)_3]$ with dppb and ligand **a**. Reaction of the chloride **2** and **12** with NaO*i*Pr in 2-propanol/toluene afforded the hydride complexes [MH(CN′N)(dppb)] (M = Ru **10**, Os **14**), through elimination of acetone from [M(O*i*Pr)(CN′N)-(dppb)] (M = Ru **9**, Os **13**). The species **9** and **13** easily reacted with 4,4′-difluorobenzophenone, via **10** and **14**, respectively, affording the corresponding isolable alkoxides [M(OR)(CN′N)-(dppb)] (M = Ru **11**, Os **15**). The complexes $[MX(CN'N)(P_2)]$ (**1**–**15**) (M = Ru, Os; X = Cl, H, OR; P = PPh_3 and P_2 = diphosphane) are efficient catalysts for the TH of carbonyl compounds with 2-propanol in the presence of NaO*i*Pr (2 mol %). Turnover frequency (TOF) values up to $1.8\times10^6\ h^{-1}$ have been achieved using 0.02–0.001 mol % of catalyst. Much the same activity has been observed for the Ru−Cl, −H, −OR, and the Os−Cl derivatives, whereas the Os−H and Os−OR derivatives display significantly lower activity on account of their high oxygen sensitivity. The chiral Ru complexes **5**–**8** catalyze the asymmetric TH of methyl–aryl ketones with TOF $\approx10^5\ h^{-1}$ at 60 °C, up to 97 % enantiomeric excess (*ee*) and remarkably high productivity (0.005 mol % catalyst loading). High catalytic activity (TOF up to $2.2\times10^5\ h^{-1}$) and enantioselectivity (up to 98 % *ee*) have also been achieved with the in-situ-generated catalysts prepared from $[MCl_2(PPh_3)_3]$, (*S*,*R*)-Josiphos or (*S*,*R*)-Josiphos*, and the benzo[*h*]quinoline ligands **a**–**c**.

Keywords: asymmetric catalysis · hydrogen transfer · osmium · phosphane ligands · ruthenium

Introduction

Asymmetric reduction of prochiral ketones for the synthesis of optical active alcohols is one of the most researched areas in homogeneous catalysis. Among the catalytic methods available for the accomplishment of this transformation, enantioselective hydrogenation with molecular H_2 (HY)[1] and transfer hydrogenation (TH)[2] are continuously being developed and represent a current subject of industrial and academic research. Noyori and co-workers pioneered the research in both areas, leading to the development of the efficient catalytic systems [RuCl(η^6-arene)(H_2NCHPhCHPh-NTs)] and *trans*-[$RuCl_2$(PP)(1,2-diamine)] (PP = diphosphane) for the asymmetric TH and HY of ketones, respectively.[3] The use of ancillary ligands featuring an NH functionality is crucial for the achievement of excellent results both in terms of activity and enantioselectivity (bifunctional catalysis).[4] In this context our research group found that replacement of the diamine in [$RuCl_2$(PP)(1,2-diamine)] with the mixed bidentate nitrogen ligand 1-(pyridin-2-yl)methanamine (Pyme), or the 1-substituted analogous ligands (RPyme), affords the complexes *cis*-[$RuCl_2$(PP)(RPyme)] that are highly efficient catalysts for the asymmetric TH of ketones (Figure 1).[5]

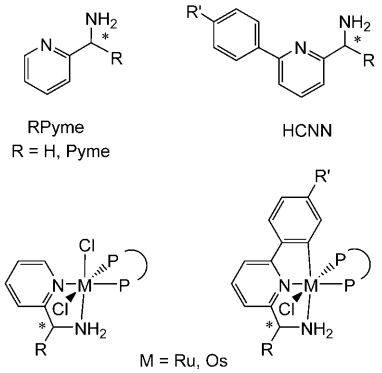

Figure 1. Pyme-type ligands and their Ru and Os complexes

Importantly, the same system has also been proven to efficiently catalyze the HY of several ketones, including bulky and poor reactive substrates, such as *tert*-alkyl ketones.[6] The remarkable acceleration effect of Pyme in TH has also

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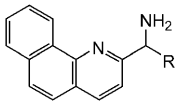
been documented by the high activity of cyclometalated phosphane and N-heterocyclic carbene ruthenium systems.[7] Subsequently, we reported on the pincer CNN ruthenium complexes [RuCl(CNN)(PP)], obtained from the ortho-metalation of the 1-[6-(4-methylphenyl)pyridin-2-yl]methanamine (HCNN) ligand, displaying sp^2 and sp^3 N donor atoms (Figure 1).[8] To the best of our knowledge, these complexes are the most active catalysts for the TH of ketones and aldehydes reported to date (turnover frequencies (TOF) up to $2.5\times10^6\ h^{-1}$), requiring a very low ruthenium loading (0.005–0.001 mol%). The pincer terdentate CNN ligand was designed to combine the Pyme motif with 2-phenylpyridine which is known to give easily CN ortho-metalated ruthenium species.[9] More recently, we have shown that Pyme and the terdentate CNN ligand give with osmium the related compounds $[OsCl_2(PP)(Pyme)]$[10] and [OsCl(CNN)(PP)].[11] Notably, these osmium complexes rapidly catalyze both the TH and HY of different ketones with activities that appear to rival those of the analogous ruthenium systems. These results expand the relatively low number of osmium catalytic systems capable to reduce carbonyl compounds with dihydrogen or hydrogen donors with both high activity and enantioselectivity.[12] The pincer complexes [MCl(CNN)(PP)] (M = Ru, Os) appear very attractive for practical applications, because the presence of a metal–carbon bond gives these compounds with a high degree of thermal stability, thus preventing their easy deactivation and leading to highly productive catalysts. With the advances accomplished in the decade, TH has emerged as powerful and versatile tool for the small and medium production of chiral alcohols[2a] complementary to the pressure HY process.

On account of the excellent catalytic performances of the Ru– and Os–diphosphane derivatives containing the terdentate CNN ligand, we decided to examine the coordination chemistry and the catalytic potential of a new class of CN′N complexes based on the 2-aminomethylbenzo[*h*]quinoline framework (shown here).

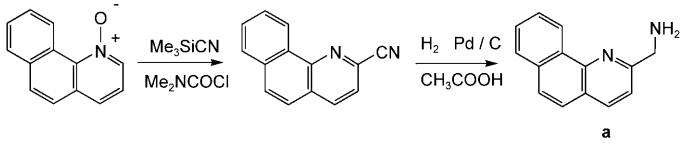


Simple ortho-metalated CN′ benzo[*h*]quinoline complexes of Ru and Os have extensively been described,[13] and some of them have been found to be relevant for photochemical and photophysical applications.[14] However, only one example of a terdentate CN′N benzo[*h*]quinoline complex with Ru has been reported, starting from the 2-(pyridin-2-yl)benzo[*h*]quinoline ligand.[15] For the CN′N ligands a higher conformational rigidity is expected, compared to those based on 2-phenylpyridine, due to the presence of the planar benzo[*h*]quinoline system. The great interest in the extension of the family of the pincer CNN ligands arises from the remarkable stability of their metal complexes, which allows the formation of long-living catalytically active species that can have great potential in organic synthesis. A chiral variant of these CN′N ligands can be obtained by incorporating a stereochemical center on the benzylic carbon atom of the CHR−NH_2 arm. In the recent years a number of studies on the successful use of cyclometalated ruthenium complexes containing either pincer NCN[16] and CNN[8] or bidentate CN[17] ligands for TH catalysts have been described.

We report herein the synthesis of new 2-aminomethylbenzo[*h*]quinoline type ligands (HCN′N) and the isolation of the related complexes $[MX(CN'N)(P_2)]$ (M = Ru, Os, X = Cl, H, OR; P = PPh_3 or P_2 = diphosphane). The ruthenium and osmium compounds are highly efficient catalysts for the TH of ketones (TOF up to $1.8\times10^6\ h^{-1}$) at 0.02–0.001 mol% loading, in basic 2-propanol. Highly enantioselective TH has been achieved by employment of Josiphos ligands. Evidence has been provided that the species [MX(CN′N)(P_2)] (X = H and OR) are involved in the catalytic TH. The results presented here expand the number heterocyclic pincer ligands for highly active and productive metal based homogeneous catalysts.

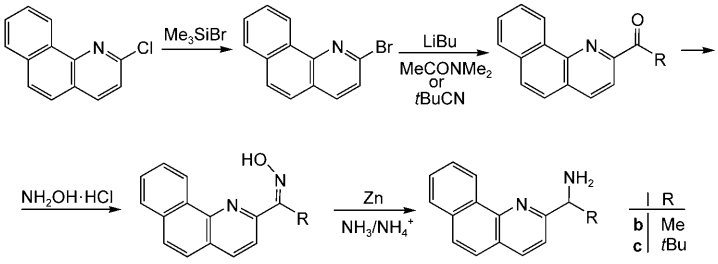
Results and Discussion

Synthesis of HCN′N benzo[*h*]quinoline ligands: The intermediate benzo[*h*]quinoline-2-carbonitrile was prepared by reaction of benzo[*h*]quinoline *N*-oxide[18] with trimethylsilylcyanide and dimethylcarbamyl chloride, according to the Fife's procedure for the regioselective cyanation of pyridine 1-oxides (Scheme 1).[19]



Scheme 1. Synthesis of the ligand **a**.

Catalytic hydrogenation (10% Pd/C; 2 atm of H_2) at room temperature of a solution of benzo[*h*]quinoline-2-carbonitrile in acetic acid afforded the 2-aminomethylbenzo[*h*]quinoline ligand **a** isolated in 90% yield. The substituted ligands **b** and **c**, containing a methyl and a *tert*-butyl group, respectively, bonded to the carbon atom connected to the NH_2 moiety, were synthesized following the route shown in Scheme 2.

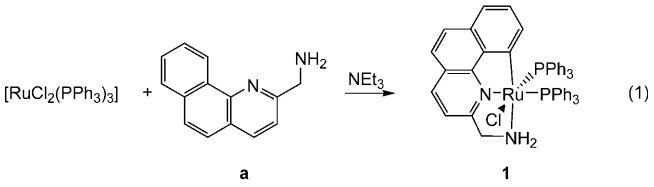


Scheme 2. Synthesis of the ligands **b** and **c**.

Treatment of 2-chlorobenzo[*h*]quinoline[18b] with bromotrimethylsilane gave 2-bromobenzo[*h*]quinoline (96% yield), according to the Schlosser method.[20] Addition of *n*-butyl-

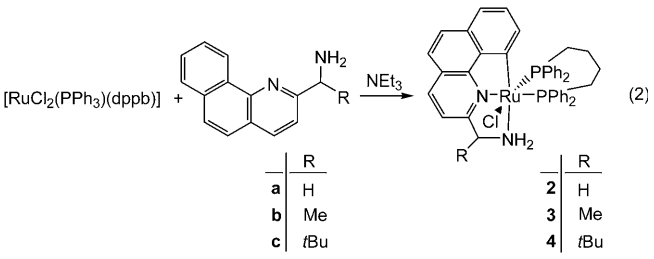
lithium at −78 °C and *N*,*N*-dimethylacetamide (R = Me) or pivalonitrile (R = *t*Bu) resulted in the formation of 1-(benzo[*h*]quinolin-2-yl)ethanone and 1-(benzo[*h*]quinolin-2-yl)-2,2-dimethylpropanone, respectively (77 and 80 % yield). By reaction with $NH_2OH{\cdot}HCl$ in ethanol, these ketones were converted into the corresponding oximes, which were reduced with Zn/ammonium acetate/NH_4OH to the amine ligands **b** and **c** in 77 and 48 % overall yield, based on the ketones.

Synthesis and characterization of [RuX(CN′N)(P_2)] (X = Cl, H, and OR) complexes: Reaction of $[RuCl_2(PPh_3)_3]$ with ligand **a** and the base NEt_3 in 2-propanol at reflux temperature (2 h) affords, by substitution of PPh_3 and HCl elimination, the thermally stable CN′N pincer complex **1** (74 % yield) [Eq. (1)].



a 1 (1)

The $^{31}P\{^1H\}$ NMR spectrum of **1** in CD_2Cl_2 shows two doublets at $\delta = 56.5$ and 50.5 ppm ($^2J(P,P) = 33.4$ Hz), for a *cis*-Ru(P_2) arrangement. The ^1H NMR doublet of doublets at $\delta = 8.32$ ppm ($J(H,H) = 6.3$, 1.7 Hz) has been attributed to the CH proton close to the ortho-metalated carbon atom and no signals at lower field were observed, consistent with the absence of the C–H proton in the 10-position of the benzo[*h*]quinoline ($\delta = 9.37$ ppm for **a** in CD_2Cl_2). The complexes **2**–**4** containing the diphosphane $Ph_2P(CH_2)_4PPh_2$ (dppb) have been prepared in 52–85 % yield by treatment of $[RuCl_2(PPh_3)(dppb)]$ with the ligands **a**–**c**, respectively, in the presence of NEt_3 [Eq. (2)].



	R
a	H
b	Me
c	*t*Bu

	R
2	H
3	Me
4	*t*Bu

(2)

The $^{31}P\{^1H\}$ NMR spectrum of **2** exhibits two doublets at $\delta = 57.3$ and 43.7 ppm ($^2J(P,P) = 38.2$ Hz), while the ^1H NMR signals of the two nonequivalent NCH_2 protons are at $\delta =$ 4.37 and 3.96 ppm and one NH_2 proton is at $\delta = 3.60$ ppm. In the $^{13}C\{^1H\}$ NMR spectrum the NCH_2 signal is downfield shifted at $\delta = 52.2$ ppm ($\Delta\delta = 5.9$ ppm) and coupled with one phosphorus atom ($^3J(C,P) = 2.8$ Hz), whereas the ortho-metalated carbon appears as a doublet of doublets at $\delta =$ 177.0 ppm, with $^2J(C,P) = 16.6$ and 8.3 Hz. The complexes **3** and **4** show related NMR spectra with the $^{13}C\{^1H\}$ NMR signals for the NCH group at $\delta = 58.5$ and 72.9 ppm, whereas those of the ortho-metalated carbon atoms are at $\delta = 179.1$ and 180.3 ppm, respectively. The molecular structure of **3** was confirmed by X-ray analysis carried out on a single crystal and the selected bond lengths and angles are reported in Table 1. The ruthenium center of **3** is in a pseudo-octahedral environment with the ortho-metalated ligand **b** bound to the metal in a terdentate fashion, forming two five-membered chelate rings (Figure 2).

Table 1. Selected bond lengths [Å] and angles [°] for **3**·2CH_2Cl_2.

Ru–Cl1	2.5035(6)	Ru–N1	2.244(2)
Ru–P1	2.2945(5)	Ru–N2	2.055(2)
Ru–P2	2.2512(6)	Ru–C1	2.072(2)
Cl1-Ru-P1	91.47(2)	P1-Ru-C1	107.34(6)
Cl1-Ru-P2	172.39(2)	P2-Ru-N1	103.41(6)
Cl1-Ru-N1	81.55(6)	P2-Ru-N2	92.04(5)
Cl1-Ru-N2	83.70(5)	P2-Ru-C1	86.12(6)
Cl1-Ru-C1	86.97(6)	N1-Ru-N2	74.30(6)
P1-Ru-P2	93.62(2)	N1-Ru-C1	153.42(7)
P1-Ru-N1	96.89(5)	N2-Ru-C1	80.69(7)
P1-Ru-N2	170.46(5)		

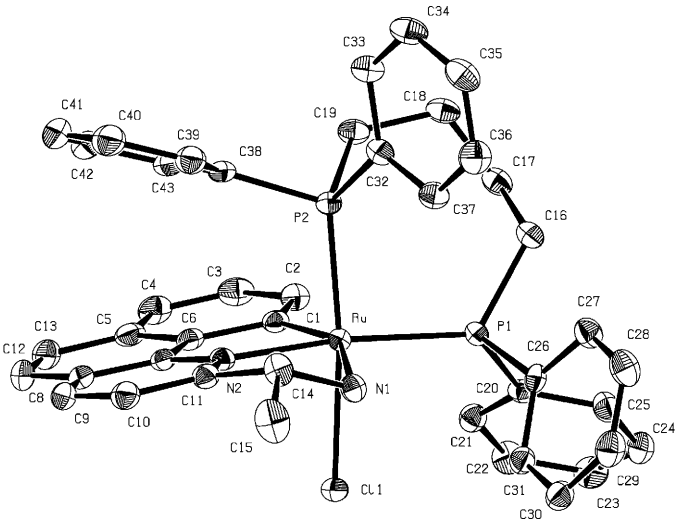


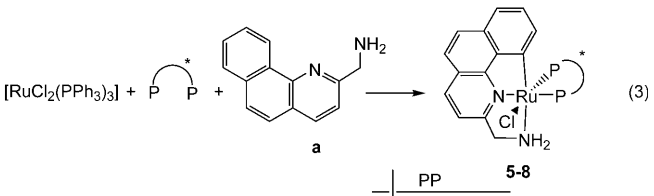
Figure 2. ORTEP style plot of compound **3** in the solid state. Thermal ellipsoids are drawn at the 50 % probability level. Hydrogen atoms are omitted for clarity.

The structure of **3** shows the Me group bound to the carbon atom that points to the side of the chloride, away from the phosphane phenyl groups, similarly to the related chiral pyridyl complex of the type [RuCl(CNN)(dppb)], bearing a *tert*-butyl group bonded to the $CHNH_2$ moiety.[8b] The Ru–N2 bond length of the benzo[*h*]quinoline *trans* to the phosphorus atom is significantly shorter (2.055(2) Å) than the Ru–N1 amino bond length (2.244(2) Å), in agreement with the geometrical constrains of the terdentate ligand showing narrow N2-Ru-C1 and N1-Ru-N2 bond

angles (80.69(7), 74.30(6)°) and the higher *trans* influence exerted by the aryl ligand (Table 1).

The amino nitrogen N1 and the $CHNH_2$ carbon are displaced by −0.556(3) and +0.108(3) Å, respectively, from the best-fit plane through the terdentate ligand. This arrangement leads one N−H bond to be almost parallel to the Ru−Cl1 bond (H-N1-Ru-Cl1 dihedral angle of about 1.2°, with a H···Cl1 distance of 2.57 Å), suggesting a possible intramolecular hydrogen-bond interaction.[21] In addition, there is a relatively short contact between the benzo[*h*]quinoline nitrogen atom and the *ipso*-carbon atom C38 of the phosphane phenyl (3.058(3) Å), indicating a stacking between the benzo[*h*]quinoline and one phenyl ring.

The chiral terdentate CN′N derivatives **5–8** were prepared by reaction of $[RuCl_2(PPh_3)_3]$ with the appropriate chiral diphosphane in toluene at 110 °C or dichloromethane at RT, followed by addition of the ligand **a** and NEt_3 in 2-propanol heated under reflux [Eq. (3)].

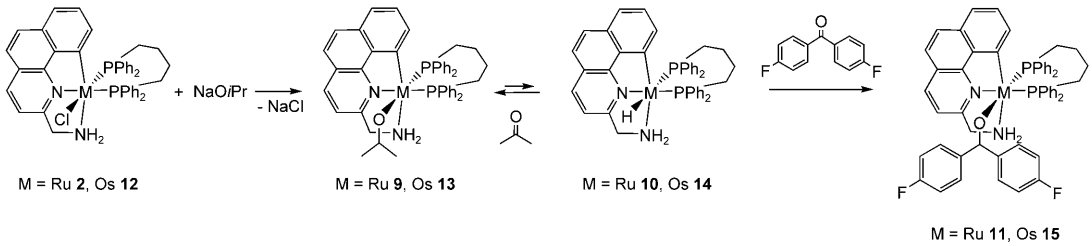


	PP (5-8)
5	(*R*,*S*)-Josiphos
6	(*S*,*R*)-Josiphos*
7	(*S*,*S*)-Skewphos
8	(*S*)-MeO-Biphep

With (*R*,*S*)-Josiphos the compound **5** was obtained as single stereoisomer and was isolated in 61 % yield. Employment of the bulkier diphosphane (*S*,*R*)-Josiphos*, which contains 4-OMe-3,5-$Me_2C_6H_2$ groups instead of Ph ones, led to **6** (55 % yield) as a mixture of two diastereoisomers in a 5:1 ratio, as inferred from $^{31}P\{^1H\}$ NMR spectroscopy.[22] Prolonged heating of this mixture inhibited the isolation of a single stereoisomer. Similarly to **6**, the derivative **7** was prepared using (*S*,*S*)-Skewphos and was isolated as mixture of two isomers (4:1 ratio), whereas **8** containing (*S*)-MeO-Biphep was obtained as a mixture of two stereoisomers in a 3:1 ratio.

To isolate hydride ruthenium complexes, which are key species involved in the catalytic TH reactions, we have studied the reactivity of complex **2** with sodium isopropoxide in 2-propanol (alkoxide route). Treatment of **2** with NaO*i*Pr (1.1 equiv) in 2-propanol/toluene mixture (1:1 in volume) at 40 °C (1 h) affords a dark red solution with formation of the intermediate alkoxide **9** (Scheme 3).

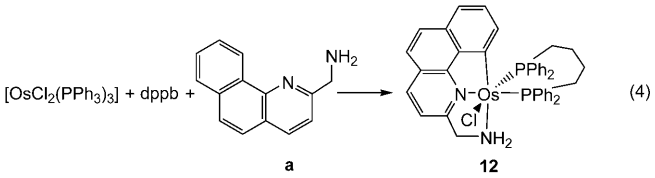
The $^{31}P\{^1H\}$ NMR spectrum of this solution shows two doublets at $\delta = 54.0$ and 47.6 ppm ($^2J(P,P) = 34.1$ Hz; C_6D_6 as inside lock), which are values close to those of the related [Ru(O*i*Pr)(CNN)(dppb)] in 2-propanol.[23] Evaporation of the solvent leads to the hydride complex **10**, through a reversible elimination of acetone in agreement with the previous studies on CNN ruthenium complexes. A better conversion into the orange hydride **10**, which was isolated in 83 % yield, has been achieved by stirring the alkoxide solution under dihydrogen for 1 h and by further elimination of the solvent. The ^1H NMR signal for the hydride appears as a doublet of doublets at $\delta = -5.40$ ppm with $^2J(H,P) = 90.0$ and 26.2 Hz, similarly to those of [RuH(CNN)(dppb)] and in agreement with the values reported for ruthenium hydride complexes with phosphorus atoms *trans* and *cis* to the hydride.[24] In the $^{31}P\{^1H\}$ NMR spectrum the two doublets are at $\delta = 66.6$ and 35.0 ppm with a small phosphorus–phosphorus coupling constant ($^2J(P,P) = 16.7$ Hz). The low value of the Ru−H stretching absorption band (1742 cm^{-1}) is consistent with the presence of a *trans*-phosphorus atom,[25] in addition to a possible RuH···HN hydrogen-bonding interaction. The intermediate CN′N isopropoxide **9**, which equilibrates with the hydride **10**, promptly reacts with ketones affording the corresponding alkoxides, by elimination of acetone, as previously observed for the CNN analogue.[23] Thus, the fluoro-substituted alkoxide **11** can easily be prepared by reaction of the in-situ-prepared **9** with 4,4′-difluorobenzophenone in a 2-propanol/toluene mixture at RT (75 % yield), through the hydride **10** (Scheme 3). The $^{31}P\{^1H\}$ NMR of **11** in C_6D_6 exhibits two doublets at $\delta = 57.0$ and 40.3 ppm with a $^2J(P,P) = 34.3$ Hz close to that of **9**. The alkoxide moiety OCH leads to a ^1H NMR doublet at $\delta =$ 4.46 ppm with a $^4J(H,P) = 3.3$ Hz, whereas the $^{13}C\{^1H\}$ NMR signal is at $\delta = 79.9$ ppm, shifted downfield compared to the free alcohol ($\delta = 74.5$ ppm). The $^{19}F\{^1H\}$ NMR spectrum of **11** shows two singlets at $\delta = -119.6$ and −120.3 ppm for two nonequivalent C_6H_4F groups and these signals disappear by addition of 4,4′-difluorobenzhydrol, affording a broad peak close to that of free alcohol at $\delta = -116.2$ ppm, indicating that a rapid alkoxide alcohol exchange occurs on the NMR chemical-shift time scale.[23] It is worth noting that **11** is obtained without the isolation of the hydride and by exploiting



Scheme 3. Formation of Ru and Os hydride and alkoxide complexes.

the higher redox potential of the diaryl ketone, relative to acetone.[26]

Synthesis and characterization of [OsX(CN′N)(dppb)] (X = Cl, H, and OR) complexes: The thermally stable pincer CN′N osmium complex **12** has easily been prepared in quantitative yield by treatment of $[OsCl_2(PPh_3)_3]$ with dppb in dichloromethane at RT and by further reaction with the ligand **a** in the presence of NEt_3 in 2-propanol at reflux temperature (3 h) [Eq. (4)].

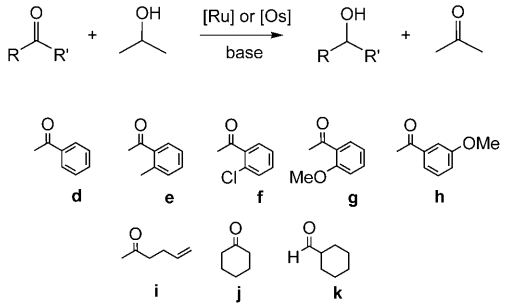


(4)

The $^{31}P\{^1H\}$ NMR spectrum of **12** in CD_2Cl_2 shows a pattern for an AB system with the two signals at $\delta = 0.9$ and 0.8 ppm ($^2J(P,P) = 13.7$ Hz). The $^{13}C\{^1H\}$ NMR signal of CH_2N is at $\delta = 54.6$ ppm, shifted downfield compared to **2**, whereas the ortho-metalated carbon atom appears as a pseudo triplet at $\delta = 157.2$ ppm ($^2J(C,P) = 6.5$ Hz), significantly upfield shifted with respect to **2**.

The osmium complex **12** reacts with sodium isopropoxide (1.2 equiv) in 2-propanol/toluene (1:1 in volume) at 35 °C (3 h) affording a dark red solution containing the alkoxide **13** and the hydride **14** in 5:1 molar ratio, respectively (Scheme 3). The $^{31}P\{^1H\}$ NMR data of **13** ($\delta = 6.0$ and -0.5 ppm with $^2J(P,P) = 9.8$ Hz) resemble those of the analogous complex [Os(O*i*Pr)(CNN)(dppb)] in 2-propanol.[11] For osmium, the equilibrium between the isopropoxide **13** and the hydride **14** is shifted more to the hydride, with respect to the corresponding ruthenium complexes **9** versus **10**, and this is consistent with a stronger M–H versus M–OR bonding for Os compared to Ru. The oxygen-sensitive hydride–osmium complex **14** was easily obtained in 74% yield by evaporation of the alcohol media and elimination of acetone.[27] The Os–H ^1H NMR signal of **14** is at $\delta = -5.14$ ppm (dd, $^2J(H,P) = 73.9$, 23.9 Hz) close to that of the ruthenium **10**, whereas the $^{31}P\{^1H\}$ NMR spectrum exhibits two doublets at $\delta = 19.9$ and 5.4 ppm with a small $^2J(P,P) = 3.7$ Hz. The mixture **13**/**14**, obtained from **12** and NaO*i*Pr, rapidly and quantitatively reacts with 4,4′-difluorobenzophenone, affording the osmium alkoxide **15**, which was isolated in 72% yield (Scheme 3). This complex gives two ^{31}P NMR doublets at $\delta = 1.8$ and -0.8 ppm with a $^2J(P,P) = 8.2$ Hz, whereas the ^1H and $^{13}C\{^1H\}$ NMR signals for the OsOCH moiety are at $\delta = 4.61$ and 79.7 ppm, respectively, close to those of **11**. The $^{19}F\{^1H\}$ NMR spectrum of **15** shows two singlets at $\delta = -119.4$ and -120.1 ppm and similarly to the behavior observed for **11**, addition of 4,4′-difluorobenzhydrol results in a fast exchange between the coordinated alkoxide and alcohol on the NMR timescale.

Catalytic results: The ruthenium and osmium chloride, hydride, and alkoxide complexes $[MX(CN'N)(P_2)]$ (**1**–**15**) are efficient catalysts for the TH of carbonyl compounds with 2-propanol in the presence of NaO*i*Pr (2 mol%; Scheme 4). Complex **1** (0.02 mol%) containing PPh_3 catalyzes the reduction of acetophenone (**d**) in 15 min with turnover frquency (TOF) of 7.0×10^4 h^{-1} (Table 2).



Scheme 4. TH of carbonyl compounds catalyzed by $[MX(CN'N)P_2]$ (M = Ru, Os; X = Cl, H, OR) complexes (0.02–0.001 mol%).

Table 2. Catalytic TH of carbonyl compounds (0.1 M) to the corresponding alcohols with $[MX(CN'N)P_2]$ (M = Ru, Os; X = Cl, H, OR) and NaO*i*Pr (2 mol%) in 2-propanol at 82 °C.

Complex	Loading [mol%]	Substrate	Conv. [%][a]	*t* [min]	TOF [h^{-1}][b]
1	0.02	**d**	94	15	7.0×10^4
2	0.005	**d**	97	2	1.2×10^6
2[c]	0.005	**d**	97	10	2.7×10^5
2	0.005	**f**	99	2	1.8×10^6
2	0.005	**h**	97	2	1.8×10^6
2	0.005	**i**	99	5	1.1×10^6
2	0.005	**j**	97	2	1.2×10^6
2[d]	0.01	**k**	>99	5	2.0×10^5
3	0.005	**d**	98	5	8.3×10^5
4	0.005	**d**	98	5	1.1×10^6
10	0.005	**d**	97	2	1.3×10^6
11	0.005	**d**	98	2	1.4×10^6
12	0.005	**d**	96	5	1.3×10^6
12	0.001	**d**	94	30	4.3×10^5
12	0.005	**g**	99	2	1.8×10^6
12	0.005	**i**	97	10	3.0×10^5
12	0.005	**j**	98	5	7.0×10^5
14	0.005	**d**	97	5	6.1×10^5
15	0.005	**d**	99	5	8.1×10^5

[a] The conversion was determined by GC analysis. [b] Turnover frequency (moles of ketone converted to alcohol per mole of catalyst per hour) at 50% conversion. [c] Reaction at 60 °C. [d] K_2CO_3 5 mol%.

Interestingly, the complex **2** bearing the diphosphane dppb promotes the quantitative conversion of **d** into 1-phenylethanol in 2 min, with a lower amount of catalyst (0.005 mol%) and affording a TOF value of 1.2×10^6 h^{-1}. This rate is slightly higher than that observed for the reduction of **d** with the analogous CNN pyridine derivative [Ru(CNN)(dppb)] (1.1×10^6 h^{-1}).[8a] With complex **2**, 2′-chloroacetophenone (**f**) and 3′-methoxyacetophenone (**h**) are quickly reduced to alcohols in 2 min with remarkably high rate (TOF = 1.8×10^6 h^{-1}). Chemoselective carbonyl TH of the

aliphatic substrate 5-hexen-2-one (**i**) has been achieved in 5 min (TOF = 1.1×10^6 h^{-1}), whereas cyclohexanone (**j**) was reduced with TOF = 1.2×10^6 h^{-1}. Complex **2** (0.01 mol%) also rapidly catalyzes the complete reduction of the aldehyde **k** with K_2CO_3 (5 mol%) as a weak base (TOF = 2.0×10^5 h^{-1}) and no aldol condensation or catalyst deactivation (i.e. through decarbonylation) reactions have been observed.[8c] High catalytic activity is also observed for the derivatives **3** and **4** containing the CHR−NH_2 (R = Me and *t*Bu) arm instead of CH_2−NH_2. Recently, Milstein and co-workers reported a pincer PNN ruthenium complex which catalyzes alcohol dehydrogenation.[28] Interestingly, the CH_2 bonded to the 2-position of the pyridine ligand undergoes easy C-H cleavage with reversible dearomatization–aromatization of the pyridine core. It is worth pointing out that also the hydride **10** and the alkoxide **11** in the presence of base efficiently catalyze the fast TH of **d** with TOF = 1.3×10^6 and 1.4×10^6 h^{-1}, which are slightly higher values compared to the chloride precursor **2**. This suggests that under catalytic conditions the isolable Ru−Cl, −H, and −OR complexes (**2**, **10**, and **11**) quickly lead to the catalytically active **9**/**10** system, through fast ligand substitution and ketone insertion into Ru−H bond reactions.[23] As regards osmium, it is interestingly to note that the complex **12** catalyzes the TH of **d** with a rate (TOF = 1.3×10^6 h^{-1}) slightly higher than that of the analogous ruthenium complex **2**, in agreement with our recent studies on pincer CNN pyridine complexes.[11] In addition, **12** displays also high productivity in the TH, affording the conversion of **d** into 1-phenylethanol in 30 min at 0.001 mol% of catalyst (Table 2). A serious drawback of the commonly used TH catalysts is their easy deactivation that requires a catalyst loading higher than 0.01 mol%, thus limiting the TH protocol for industrial applications. As for the ruthenium systems, **12** catalyzes the rapid and chemoselective TH of aryl and alkyl ketones, namely **g**, **i**, and **j** with TOF up to 1.8×10^6 h^{-1}. It is worth noting that the hydride **14** and the alkoxide **15** afforded the reduction of **d** with a rate (TOF = 6.1×10^5 and 8.1×10^5 h^{-1}) lower than that of the chloride **12**. By contrast to ruthenium, high catalytic performance with osmium is achieved by in-situ-formation of the Os−H and Os−OR species, on account of their higher oxygen sensitivity respect to the Ru analogues.

Asymmetric TH of methyl aryl ketones has been achieved using CN′N ruthenium complexes containing chiral diphosphanes. Since **2** has been proven to be highly active for the reduction of **d** also at 60 °C (TOF = 2.7×10^5 h^{-1}, Table 2), the chiral Ru complexes were tested at this temperature in order to achieve higher enantiomeric excess (*ee*). The derivatives **5**–**8** (0.005 mol%) afforded complete reduction of **d** in 30–40 min with TOF up to 1.9×10^5 h^{-1} at 60 °C (Table 3).

By employment of **5** containing (*R*,*S*)-Josiphos, (*R*)-1-phenylethanol was obtained with 86% *ee*, whereas use of **6**, with the bulkier (*S*,*R*)-Josiphos*, led to an increase of the enantioselectivity (96% *ee* of (*S*)-alcohol). The complexes **7** and **8** with (*S*,*S*)-Skewphos and (*S*)-MeO-Biphep, repsectively afforded (*S*)- and (*R*)-1-phenylethanol, respectively, with moderate and poor enantioselectivity (73 and 26% *ee*, respectively). With **5**, the ketone **f** was reduced to the (*R*)-alcohol with 89% *ee*, whereas with **6** the substrates 2′-methylacetophenone **e** and **f** were converted into the corresponding (*S*)-alcohols with TOF up to 1.2×10^5 h^{-1} and high enantioselectivity (94 and 97% *ee*). Recently, we have reported that efficient ruthenium catalysts for asymmetric TH can be prepared by a combination of a chiral Josiphos with a racemic mixture of RPyme through a diastereoselective reaction, thus avoiding the necessity of using both ligands in enantiopure form.[5b] According to this strategy, the in-situ-generated catalyst, obtained by refluxing a 2-propanol solution of [$RuCl_2(PPh_3)_3$] with (*S*,*R*)-Josiphos* (1 h) and a racemic mixture of the Me-substituted ligand **b** (1 h), promotes the reduction of **d** to (*S*)-1-phenylethanol with high rate (TOF = 1.7×10^5 h^{-1}) and 90% *ee* at 0.005 mol% of catalyst loading (Table 3). By using the *t*Bu ligand **c** the (*S*)-alcohol is formed with 93% *ee*, whereas the substrates **f** and **g** were converted to (*S*)-alcohols with 98 and 97% *ee*, respectively (TOF up to 1.1×10^5 h^{-1}). We want to point out that the in-situ-generated species display much the same rate as the isolated complexes [RuCl(CN′N)(P_2)] and high enantioselectivity can be achieved through the combination of alkyl-substituted benzo[*h*]quinolines with bulky Josiphos ligands. As regards osmium, the species prepared in-situ from [$OsCl_2(PPh_3)_3$], (*S*,*R*)-Josiphos, and ligand **a**, afforded the reduction of **d** to (*S*)-alcohol with 80% *ee* and higher rate (TOF = 2.1×10^5 h^{-1} at 60 °C), compared to ruthenium. Furthermore, the use of the bulky (*S*,*R*)-Josiphos* resulted in an increase

Table 3. Enantioselective catalytic TH of ketones (0.1 M) with **5**–**8** and the system [$MCl_2(PPh_3)_3$]/PP/HCN′N (M = Ru, Os), in the presence of NaO*i*Pr (2 mol%) at 60 °C using 0.005 mol% of catalyst.

Complex	PP	HCN′N	Ketone	Conv. [%][a]	*t* [min]	TOF [h^{-1}][b]	*ee* [%][a]
5			**d**	97	30	1.3×10^5	86 *R*
5			**f**	97	60	6.4×10^4	89 *R*
6			**d**	98	40	1.0×10^5	96 *S*
6			**e**	96	60	6.0×10^4	94 *S*
6			**f**	98	40	1.2×10^5	97 *S*
7			**d**	95	30	1.1×10^5	73 *S*
8			**d**	97	30	1.9×10^5	26 *R*
[$RuCl_2(PPh_3)_3$][c]	(*S*,*R*)-Josiphos*	**b**	**d**	98	30	1.7×10^5	90 *S*
[$RuCl_2(PPh_3)_3$][d]	(*S*,*R*)-Josiphos*	**c**	**d**	98	30	1.2×10^5	93 *S*
[$RuCl_2(PPh_3)_3$][d]	(*S*,*R*)-Josiphos*	**c**	**f**	99	30	1.1×10^5	98 *S*
[$RuCl_2(PPh_3)_3$][d]	(*S*,*R*)-Josiphos*	**c**	**g**	95	30	1.0×10^5	97 *S*
[$OsCl_2(PPh_3)_3$][e]	(*S*,*R*)-Josiphos	**a**	**d**	96	10	2.1×10^5	80 *S*
[$OsCl_2(PPh_3)_3$][e]	(*S*,*R*)-Josiphos*	**a**	**d**	96	10	2.2×10^5	90 *S*

[a] The conversion and *ee* were determined by GC analysis. [b] Turnover frequency (moles of ketone converted to alcohol per mole of catalyst per hour) at 50% conversion. [c] [Ru]/PP/**b** = 1:1.5:3. [d] [Ru]/PP/**c** = 1:1.5:3. [e] [Os]/PP/**a** = 1:1.5:2.

of the enantioselectivity (90% *ee* of (*S*)-alcohol). On account of the robustness of the CN′N/diphosphane framework, these chiral ruthenium and osmium systems display remarkable high rate (TOF $\approx 10^5\ h^{-1}$ at 60°C) at low loading (0.005 mol%), thus representing a significant progress in the designing of more efficient catalysts for the asymmetric TH of ketones. Moreover, the benzo[*h*]quinoline complexes **2** and **12** have been proven to be catalytically active also in the hydrogenation of ketones at low H_2 pressure in alcohol media and these results will be published in the due course.

The TH of ketones catalyzed by transition-metal complexes is generally conceived to occur via metal-hydride species that deliver the hydride ligand to the substrate, affording a metal–alkoxide complex (inner sphere mechanism) or a metal–amide species when a NH_2 functionality is present (outer-sphere mechanism). Recently, we have suggested that with terdentate CNN ruthenium complexes, the Ru–alkoxides are key species of the catalytic TH and the role of the NH_2 linkage is to favor a hydrogen-bonding network involving the alkoxide and the alcohol.[23,29] According to the present studies, which show that in basic alcohol the Ru and Os chloride precursors **2** and **12** give M−OR (M = Ru, Os) in equilibrium with the M−H complexes, we believe that these species containing the NH_2 functionality are involved in TH.[30] Thus, [MH(CN′N)(P_2)] is a key species that provides the alkoxide [M(OR)(CN′N)(P_2)] by reaction with the incoming ketone. Protonation with 2-propanol gives the alcohol product and [M(O*i*Pr)(CN′N)(P_2)] which equilibrates with [MH(CN′N)(P_2)], closing the cycle. The high catalytic activity of these pincer complexes can be ascribed to the M−NH_2 linkage, which is involved in hydrogen-bonding interactions with the ketone and alcohol, and to the flat benzo[*h*]quinoline system that appears crucial for the easy access of the substrate to the metal center. In addition, high productivity is achieved by the combination of the diphosphane with the robust pincer CN′N frame.

Conclusion

In summary, we have reported on the preparation of novel 2-aminomethylbenzo[*h*]quinoline type ligands (HCN′N) that easily react with ruthenium and osmium precursors, affording the terdentate complexes [MCl(CN′N)(P_2)] (M = Ru, Os). These species are found to promote the transfer hydrogenation (TH) of carbonyl compounds in basic 2-propanol with high rate (TOF up to $1.8\times10^6\ h^{-1}$) and low loading (as little as 0.001 mol%), which are among the best performances for a TH catalyst reported to date. Interestingly, with this novel class of ligands the ruthenium and osmium complexes display similar high activity and productivity. The derivatives containing chiral diphosphanes (e.g., Josiphos) have proven to catalyze the TH of ketones with both high enantioselectivity (up to 98% *ee*) and productivity (0.005 mol% loading). This last point is particularly relevant for promoting asymmetric TH as a valuable method for the synthesis of alcohols, in alternative to dihydrogen under pressure. Experiments carried out with the chloride complexes in basic alcohol showed the formation of the hydride derivatives [MH(CN′N)(dppb)] which reversibly react with ketones leading to the alkoxide species [M(OR)(CN′N)(dppb)]. These studies suggest that the catalytic TH mediated by Ru and Os complexes with CN′N benzo[*h*]quinoline involves the formation of M−H and M−OR species containing the NH_2 functionality. Work is in progress to extend the application of these complexes in other catalytic reactions, including asymmetric hydrogenation of prochiral ketones, and to develop new homogeneous catalysts based on benzo[*h*]quinoline ligands.

Experimental Section

General: All reactions were carried out under an argon atmosphere using standard Schlenk techniques. The solvents and the ketones were carefully dried by standard methods and distilled under argon before use. The diphosphane ligands and all other chemicals were purchased from Aldrich and Strem and used without further purification. Benzo[*h*]quinoline *N*-oxide,[18a] 2-chlorobenzo[*h*]quinoline,[18b] the complexes [MCl_2-(PPh_3)$_3$] (M = Ru,[31] Os[32]) and [$RuCl_2$(PPh_3)(dppb)][33] were prepared according to literature procedure. NMR measurements were recorded on a Bruker AC 200 spectrometer and the chemical shifts, in ppm, are relative to TMS for ^1H and $^{13}C\{^1H\}$, whereas $CFCl_3$ was used for $^{19}F\{^1H\}$ 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 GP-3380 gas chromatograph equipped with a MEGADEX-ETTBDMS-β chiral column.

Benzo[*h*]quinoline-2-carbonitrile: Dimethylcarbamyl chloride (1.44 g, 13.5 mmol) was added dropwise to a solution of benzo[*h*]quinoline *N*-oxide (2.63 g, 13.5 mmol) and trimethylsilylcyanide (1.59 g, 14.8 mmol) in CH_2Cl_2 (100 mL). The solution was stirred at room temperature for 3 d and then heated under reflux for 18 h. A 10% Na_2CO_3 aqueous solution was added and stirring continued for 15 min. The organic phase was separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic phase was dried over anhydrous Na_2SO_4 and the solvent was evaporated. The residue was taken up with diethyl ether and the formed solid was filtered to give benzo[*h*]quinoline-2-carbonitrile. Yield: 2.07 g (75%); m.p. 161–162°C; ^1H NMR (200.1 MHz, $CDCl_3$, 20°C): $\delta = 9.27$ (m, 1H), 8.27 (d, $J(H,H) = 8.4$ Hz, 1H), 7.94 (m, 2H), 7.87–7.74 (m, 3H), 7.70 ppm (d, $J(H,H) = 9.0$ Hz, 1H); $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$, 20°C): $\delta = 147.0$, 136.5, 133.7, 131.6, 131.0, 130.5, 129.4, 128.0, 127.9, 127.7, 124.7, 124.6, 124.3, 118.0 ppm (CN); elemental analysis calcd (%) for $C_{14}H_8N_2$: C 82.33, H 3.95, N 13.72; found: C 82.14, H 3.98, N 13.75.

2-Aminomethylbenzo[*h*]quinoline (a): A solution of benzo[*h*]quinoline-2-carbonitrile (2.04 g, 10.0 mmol) in acetic acid (120 mL) was hydrogenated in a Parr apparatus at 2 atm of dihydrogen at room temperature in the presence of 10% palladium on carbon (0.40 g). The dihydrogen absorption ceased after the uptake of two equivalents of H_2 (about 4 h). The reaction mixture was then filtered and the organic solution was evaporated under reduced pressure. The oil residue was taken up in diethyl ether and the resulting solution was washed up to alkaline pH with a 10% aqueous solution of NaOH. The organic phase was dried over Na_2SO_4, the solvent was evaporated, and the residue was purified by flash chromatography (MeOH) to give **a** as a reddish low melting point solid. Yield: 1.87 g (90%); ^1H NMR (200.1 MHz, $CDCl_3$, 20°C): $\delta = 9.58$ (d, $J(H,H) = 7.4$ Hz, 1H; aromatic proton), 8.11–7.71 (m, 7H; aromatic protons), 4.37 (s, 2H; CH_2), 2.90 ppm (s, 2H; NH_2); $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$, 20°C): $\delta = 158.5$ (s; N*C*CH$_2$), 143.9 (s; N*C*C), 134.4–118.2 (m; aromatic carbon atoms), 46.3 ppm (s; CH_2); elemental analysis calcd (%) for $C_{14}H_{12}N_2$: C 80.74, H 5.81, N 13.45; found: C 80.55, H 5.91, N 13.66.

2-Bromobenzo[*h*]quinoline: A mixture of 2-chlorobenzo[*h*]quinoline (2.43 g, 11.4 mmol), bromotrimethylsilane (3.00 mL, 22.8 mmol) and propionitrile (12 mL) was heated under reflux for 110 h. The reaction mixture was then poured into a 10% NaOH aqueous solution containing ice. The organic phase was separated and the aqueous layer was extracted with diethyl ether (3×15 mL). The combined organic phase was dried over anhydrous Na_2SO_4 and the solvent was evaporated. The residue was purified by chromatography (petroleum ether/ethyl acetate = 9:1) to give 2-bromobenzo[*h*]quinoline as a yellow solid. Yield: 2.82 g (96%); m.p. 113–114 °C; ^{1}H NMR (200.1 MHz, $CDCl_3$, 20 °C): δ = 9.35–9.15 (m, 1H), 7.96 (d, J(H,H) = 8.4 Hz, 1H), 7.92–7.84 (m, 1H), 7.81 (d, J(H,H) = 8.4 Hz, 1H), 7.74–7.67 (m, 2H), 7.61 ppm (dd, ^3J(H,H) = 8.4 Hz, ^4J(H,H) = 1.5 Hz, 2H); ^{13}C{^{1}H} NMR (50.3 MHz, $CDCl_3$, 20 °C): δ = 147.1, 140.7, 138.0, 133.7, 130.4, 128.7, 128.2, 127.7, 127.3, 126.1, 125.1, 124.7, 124.5 ppm; elemental analysis calcd (%) for $C_{13}H_8BrN$: C 60.49, H 3.12, N 5.43; found: C 60.33, H 3.25, N 5.38.

1-(Benzo[*h*]quinolin-2-yl)ethanone: A solution of 2-bromobenzo[*h*]quinoline (1.52 g, 5.89 mmol) in THF (36 mL) was cooled at −78 °C. After 10 min a 2.5 M solution of *n*-butyllithium in *n*-hexane (6.19 mmol, 2.47 mL) was added dropwise. The resulting deep red solution was stirred at this temperature for 1 h and then *N*,*N*-dimethylacetamide (6.48 mmol, 0.60 mL) was added dropwise. The solution was further stirred for 1 h at −78 °C and then allowed to warm slowly at room temperature. A 1 M solution of HCl was added (7.4 mL), the organic phase was separated and the aqueous phase was extracted with diethyl ether (2×15 mL). The combined organic phase was dried over Na_2SO_4, the solvent was evaporated, and the residue was purified by flash chromatography (petroleum ether/ethyl acetate = 95:5) to give 1-(benzo[*h*]quinolin-2-yl)ethanone as a yellow solid. Yield: 1.00 g (77%); m.p. 113–115 °C; ^{1}H NMR (200.1 MHz, $CDCl_3$, 20 °C): δ = 9.08 (dd, ^3J(H,H) = 8.1 Hz, ^4J(H,H) = 1.5 Hz, 1H), 8.02 (d, J(H,H) = 8.1 Hz, 1H), 7.92 (d, J(H,H) = 8.1 Hz, 1H), 7.80–7.70 (m, 1H), 7.69–7.55 (m, 3H), 7.39 (d, J(H,H) = 9.0 Hz, 1H), 2.83 ppm (s, 3H; CH_3); ^{13}C{^{1}H} NMR (50.3 MHz, $CDCl_3$, 20 °C): δ = 200.2 (CO), 151.0, 144.8, 135.9, 133.3, 131.1, 129.5, 128.2, 127.8, 127.6, 127.1, 124.5, 124.1, 118.3, 25.4 ppm (CH_3); elemental analysis calcd (%) for $C_{15}H_{11}NO$: C 81.43, H 5.01, N 6.33; found: C 81.16, H 4.92, N 6.40.

(Benzo[*h*]quinolin-2-yl)methyl ketoxime: A solution of 1-(benzo[*h*]quinolin-2-yl)ethanone (2.62 g, 11.85 mmol) and hydroxylamine hydrochloride (1.52 g, 21.88 mmol) in 96% ethanol (100 mL) was stirred for 30 h at room temperature. The reaction was monitored by TLC (petroleum ether/ethyl acetate = 9:1). The solvent was removed under reduced pressure and the residue was taken up with CH_2Cl_2 and a saturated solution of $NaHCO_3$. The resulting mixture was vigorously stirred for 30 min, the organic phase was separated, and the aqueous phase extracted with CH_2Cl_2 (2×20 mL). The combined organic phase was dried over Na_2SO_4 and the solvent was evaporated to give (benzo[*h*]quinolin-2-yl)methyl ketoxime as a yellow solid that was used in the next step without further purification. Yield: 2.7 g (96%); m.p. 200–202 °C; elemental analysis calcd (%) for $C_{15}H_{12}N_2O$: C 76.25, H 5.12, N 11.86; found: C 76.44, H 5.15, N 11.89.

1-(Benzo[*h*]quinolin-2-yl)ethanamine (b): A solution of (benzo[*h*]quinolin-2-yl)methyl ketoxime (2.6 g, 11.0 mmol) and ammonium acetate (1.05 g, 13.6 mmol) in 30% NH_3/H_2O/96% EtOH (39.5:26.3:26.3 mL) was stirred for 30 min at room temperature. Zinc powder (3.95 g, 60.4 mmol) was added portionwise over a period of 2 h at room temperature and then the reaction mixture was heated under reflux for 3 h. The grey precipitate was filtered under reduced pressure and the solvent was evaporated to give a residue that was alkalized with 10% NaOH, and extracted with diethyl ether (3×30 mL). The combined organic phase was dried over Na_2SO_4, the solvent was evaporated, and the residue was purified by flash chromatography by using MeOH as the eluant to give **b** as an orange liquid. Yield: 1.88 g (77%); ^{1}H NMR (200.1 MHz, $CDCl_3$, 20 °C): δ = 9.36 (d, J(H,H) = 8.1 Hz, 1H), 8.08 (d, J(H,H) = 8.1 Hz, 1H), 7.88 (d, J(H,H) = 8.1 Hz, 1H), 7.80–7.59 (m, 4H), 7.47 (d, J(H,H) = 8.1 Hz, 1H), 4.37 (q, ^3J(H,H) = 6.6 Hz, 1H; C*H*CH_3), 2.26 (s, 2H; NH_2), 1.56 ppm (d, ^3J(H,H) = 6.6 Hz, 3H; CH_3); ^{13}C{^{1}H} NMR (50.3 MHz, $CDCl_3$, 20 °C): δ = 164.2, 145.5, 136.3, 133.6, 131.3, 127.9, 127.7 127.0, 126.7, 125.1, 124.9, 124.3, 119.0, 52.8 (*C*CH_3), 24.8 ppm (CH_3); elemental analysis calcd (%) for $C_{15}H_{14}N_2$: C 81.05, H 6.35, N 12.60; found: C 81.24, H 6.38, N 12.58.

1-(Benzo[*h*]quinolin-2-yl)-2,2-dimethylpropanone: A solution of 2-bromobenzo[*h*]quinoline (1.52 g, 5.89 mmol) in THF (36 mL) was cooled at −78 °C. After 10 min a 2.5 M solution of *n*-butyllithium in *n*-hexane (2.47 mL, 6.19 mmol) was added dropwise. The resulting deep red solution was stirred at this temperature for 1 h and then pivalonitrile (0.78 mL, 7.07 mmol) in THF (5 mL) was added dropwise. The obtained purple solution was further stirred for 1 h at −78 °C and then was allowed to warm slowly at room temperature. A 1 M solution of H_2SO_4 was added (25 mL) and the mixture was heated under reflux for 3 h. After cooling to room temperature the organic phase was separated and the aqueous phase extracted with diethyl ether (3×15 mL). The combined organic phase was washed with a diluted NaOH solution and dried over Na_2SO_4. The solvent was evaporated and the residue was purified by flash chromatography (petroleum ether/ethyl acetate = 9:1) to give 1-(benzo[*h*]quinolin-2-yl)-2,2-dimethylpropanone as a yellow solid. Yield: 1.24 g (80%); m.p. 88–90 °C; ^{1}H NMR (200.1 MHz, $CDCl_3$, 20 °C): δ = 9.20 (d, J(H,H) = 7.8 Hz, 1H), 8.13 (s, 2H), 7.84 (d, J(H,H) = 7.8 Hz, 1H), 7.80–7.73 (m, 2H), 7.73–7.62 (m, 1H), 7.56 (d, J(H,H) = 9.0 Hz, 1H), 1.67 ppm (s, 9H; CH_3); ^{13}C{^{1}H} NMR (50.3 MHz, $CDCl_3$, 20 °C): δ = 206.7 (CO), 152.1, 144.5, 136.3, 133.7, 131.8, 129.5, 128.4, 127.9, 127.5, 124.9, 124.5, 121.2, 44.3 (*C*Me_3), 28.0 ppm (CH_3); elemental analysis calcd (%) for $C_{18}H_{17}NO$: C 82.10, H 6.51, N 5.32; found: C 82.26, H 6.67, N 5.17.

(Benzo[*h*]quinolin-2-yl)-*tert*-butyl ketoxime: A mixture of 1-(benzo[*h*]quinolin-2-yl)-2,2-dimethylpropanone (1.30 g, 4.94 mmol) and hydroxylamine hydrochloride (0.63 g, 9.13 mmol) in 96% ethanol (45 mL) was stirred at room temperature for 36 h (a white precipitate was formed after 30 min). The reaction was monitored by TLC (petroleum ether/ethyl acetate = 9:1). The solvent was removed under reduced pressure and the residue was taken up with CH_2Cl_2 and with a saturated solution of $NaHCO_3$. The resulting mixture was vigorously stirred for 30 min, the organic phase was separated and the aqueous phase extracted with CH_2Cl_2 (2×20 mL). The combined organic phase was dried over Na_2SO_4 and the solvent was evaporated to give (benzo[*h*]quinolin-2-yl)-*tert*-butyl ketoxime as a slightly brown powder (quite insoluble in almost common solvents) that was used in the next step without further purification. Yield: 0.69 g (50%); m.p. 234–236 °C; elemental analysis calcd (%) for $C_{18}H_{18}N_2O$: C 77.67, H 6.52, N 10.06, found: C 77.55, H 6.55, N 10.02.

1-(Benzo[*h*]quinolin-2-yl)-2,2-dimethylpropanamine (c): A solution of (benzo[*h*]quinolin-2-yl)-*tert*-butyl ketoxime (1.3 g, 4.68 mmol) and ammonium acetate (0.447 g, 5.80 mmol) in 30% NH_3/H_2O/96% EtOH (16.8:11.2:11.2 mL) was stirred for 30 min at room temperature. Zinc powder (1.68 g, 25.7 mmol) was added portionwise over a period of 2 h at room temperature and then the reaction mixture was heated under reflux for 4 h. After cooling, the mixture was acidified up to pH 1 by adding of 36% HCl. The resulting clean solution was concentrated under reduced pressure. The amine was liberated with a 50% aqueous solution of KOH and extracted with diethyl ether (4×25 mL). The combined organic phase was dried over Na_2SO_4, the solvent was evaporated, and the residue was purified by flash chromatography with MeOH as the eluant to give **c** as an orange liquid. Yield: 0.59 g (48%); ^{1}H NMR (200.1 MHz, $CDCl_3$, 20 °C): δ = 9.31 (d, J(H,H) = 8.1 Hz, 1H), 7.98 (d, J(H,H) = 8.1 Hz, 1H), 7.84 (d, J(H,H) = 7.5 Hz, 1H), 7.76–7.55 (m, 4H), 7.34 (d, J(H,H) = 8.1 Hz, 1H), 3.88 (s, 1H; CHN), 2.65 (s, 2H; NH_2), 0.99 ppm (s, 9H; CH_3); ^{13}C{^{1}H} NMR (50.3 MHz, $CDCl_3$, 20 °C): δ = 161.1, 145.1, 134.8, 133.4, 131.4, 127.8, 127.5, 126.8, 126.6, 125.0, 124.8, 124.3, 122.2, 65.8 (CHN), 35.5 (*C*Me_3), 26.5 ppm (CH_3); elemental analysis calcd (%) for $C_{18}H_{20}N_2$: C 81.78, H 7.63, N 10.60, found: C 81.66, H 7.67, N 10.63.

Synthesis of 1: The ligand **a** (36 mg, 0.173 mmol) and NEt_3 (0.22 mL, 0.158 mmol) were added to $[RuCl_2(PPh_3)_3]$ (0.150 g, 0.156 mmol) in 2-propanol (2 mL) and the mixture was heated under reflux for 2 h. The resulting solution was concentrated (1 mL) and addition of pentane (2 mL) afforded an orange precipitate. The product was filtered, washed with pentane (3×5 mL), and dried under reduced pressure. Yield: 100 mg (74%); ^{1}H NMR (200.1 MHz, CD_2Cl_2, 20 °C): δ = 8.32 (dd, ^3J(H,H) = 6.3, ^4J(H,H) = 1.7 Hz, 1H; CHCRu), 7.77–6.66 (m, 36H; aromatic protons), 4.30 (dd, ^2J(H,H) = 16.1, ^3J(H,H) = 3.8 Hz, 1H; CH_2N), 3.83–3.55 (m, 2H;

CH_2N, NH_2), 1.96 ppm (s, 1H; NH_2); $^{31}P\{^1H\}$ NMR (81.0 MHz, CD_2Cl_2, 20°C): $\delta = 56.5$ (d, $^2J(P,P) = 33.4$ Hz), 50.5 ppm (d, $^2J(P,P) = 33.4$ Hz); elemental analysis calcd (%) for $C_{50}H_{41}ClN_2P_2Ru$: C 69.16, H 4.76, N 3.23; found: C 69.35, H 4.85, N 3.34.

Synthesis of 2: The ligand **a** (232 mg, 1.11 mmol) and NEt_3 (1.55 mL, 11.1 mmol) were added to $[RuCl_2(PPh_3)(dppb)]$ (800 mg, 0.929 mmol) in 2-propanol (15 mL). The mixture was heated under reflux for 2 h, obtaining an orange precipitate which was filtered, washed with methanol (3× 10 mL), and dried under reduced pressure. Yield: 608 mg (85%); ^1H NMR (200.1 MHz, CD_2Cl_2, 20°C): $\delta = 8.19$ (pseudo t, $J(H,H) = 7.6$ Hz, 2H; aromatic protons), 7.99 (d, $J(H,H) = 7.0$ Hz, 1H; aromatic proton), 7.82 (pseudo t, $J(H,H) = 8.0$ Hz, 2H; aromatic protons), 7.64 (d, $J(H,H) = 8.5$ Hz, 2H; aromatic protons), 7.52–7.20 (m, 14H; aromatic protons), 6.98 (d, $J(H,H) = 8.2$ Hz, 1H; aromatic proton), 6.45 (t, $J(H,H) = 7.3$ Hz, 1H; aromatic proton), 6.16 (pseudo t, $J(H,H) = 7.8$ Hz, 2H; aromatic protons), 5.47 (t, $J(H,H) = 8.1$ Hz, 2H; aromatic protons), 4.37 (dd, $^2J(H,H) = 16.3$, $^3J(H,H) = 5.4$ Hz, 1H; NCH_2), 3.96 (ddd, $J(H,H) = 16.4$, 11.0, 5.0 Hz, 1H; NCH_2), 3.60 (m, 1H; NH_2), 3.01 (m, 2H; CH_2), 2.35–1.00 ppm (m, 7H; CH_2 and NH_2); $^{13}C\{^1H\}$ NMR (50.3 MHz, $CDCl_3$, 20°C): $\delta = 177.0$ (dd; $^2J(C,P) = 16.6$, 8.3 Hz; CRu), 154.3 (s; N*C*C), 152.3 (d, $^3J(C,P) = 1.0$ Hz; NCCH_2), 146.2–115.5 (m; aromatic carbon atoms), 52.2 (d, $^3J(C,P) = 2.8$ Hz; NCH_2), 33.1 (dd, $^1J(C,P) = 24.8$ Hz, $^4J(C,P) = 1.8$ Hz; PCH_2), 29.9 (d, $^1J(C,P) = 31.9$ Hz; PCH_2), 26.5 (d, $^2J(C,P) = 1.3$ Hz; PCH_2CH_2), 21.5 ppm (dd, $^2J(C,P) = 2.5$, $^3J(C,P) = 2.0$ Hz; CH_2; PCH_2CH_2); $^{31}P\{^1H\}$ NMR (81.0 MHz, CD_2Cl_2, 20°C): $\delta = 57.3$ (d, $^2J(P,P) = 38.2$ Hz), 43.7 ppm (d, $^2J(P,P) = 38.2$ Hz); elemental analysis calcd (%) for $C_{42}H_{39}ClN_2P_2Ru$: C 65.49, H 5.10, N 3.64; found: C 65.18, H 5.23, N 3.47.

Synthesis of 3: The ligand **b** (39 mg, 0.175 mmol) and NEt_3 (0.16 mL, 1.15 mmol) were added to $[RuCl_2(PPh_3)(dppb)]$ (100 mg, 0.116 mmol) in 2-propanol (2 mL). The mixture was heated under reflux for 3 h, giving an orange precipitate which was filtered, washed with pentane (4×3 mL), and dried under reduced pressure. The solid was dissolved in CH_2Cl_2 (0.5 mL), kept at −20°C for 18 h, affording the precipitation of triethylammonium chloride which was eliminated by filtration. The resulting solution was concentrated (1 mL) and addition of pentane (2 mL) gave an orange precipitate which was filtered, washed with pentane (2 mL), and dried under reduced pressure. Yield: 60 mg (66%); ^1H NMR (200.1 MHz, CD_2Cl_2, 20°C): $\delta = 8.18$ (pseudo t, $J(H,H) = 8.0$ Hz, 2H; aromatic protons), 8.01 (d, $J(H,H) = 7.0$ Hz, 1H; aromatic proton), 7.82 (pseudo t, $J(H,H) = 8.4$ Hz, 2H; aromatic protons), 7.68 (d, $J(H,H) = 5.4$ Hz, 1H; aromatic proton), 7.65 (d, $J(H,H) = 6.0$ Hz, 1H; aromatic proton), 7.49–7.22 (m, 14H; aromatic protons), 6.98 (d, $J(H,H) = 8.4$ Hz, 1H; aromatic proton), 6.45 (t, $J(H,H) = 7.4$ Hz, 1H; aromatic proton), 6.16 (pseudo t, $J(H,H) = 8.2$ Hz, 2H; aromatic protons), 5.45 (t, $J(H,H) = 8.4$ Hz, 2H; aromatic protons), 4.37 (m, 1H; NC*H*Me), 3.55 (t, $J(H,H) = 11.4$ Hz, 1H; NH_2), 3.20–2.85 (m, 3H; CH_2), 2.40–1.70 (m, 6H; CH_2 and NH_2), 1.58 ppm (d, $^3J(H,H) = 6.7$ Hz, 3H; $CHCH_3$); $^{13}C\{^1H\}$ NMR (50.3 MHz, CD_2Cl_2, 20°C): $\delta = 179.1$ (dd, $^2J(C,P) = 16.3$, 8.4 Hz; CRu), 157.8–116.5 (m; aromatic carbon atoms), 58.5 (d, $^3J(C,P) = 2.6$ Hz; N*C*HMe), 33.3 (dd, $^1J(C,P) = 24.9$ Hz, $^4J(C,P) = 2.2$ Hz; PCH_2), 30.5 (d, $^1J(C,P) = 32.1$ Hz; PCH_2), 26.8 (d, $^2J(C,P) = 2.0$ Hz; PCH_2CH_2), 23.4 (s; CH*C*H_3), 22.0 ppm (m; PCH_2CH_2); $^{31}P\{^1H\}$ NMR (81.0 MHz, CD_2Cl_2, 20°C): $\delta = 57.3$ (d, $^2J(P,P) = 38.3$ Hz), 43.6 ppm (d, $^2J(P,P) = 38.3$ Hz); elemental analysis calcd (%) for $C_{43}H_{41}ClN_2P_2Ru$: C 65.85, H 5.27, N 3.57; found: C 66.10, H 5.40, N 3.74.

Synthesis of 4: Compound **4** was prepared in a way similar to that described for **3**, using the ligand **c** in place of **b** and heating the $[RuCl_2(PPh_3)(dppb)]$/**c**/NEt_3 mixture under reflux for 5 h. Yield: 50 mg (52%); ^1H NMR (200.1 MHz, CD_2Cl_2, 20°C): $\delta = 8.08$ (pseudo t, $J(H,H) = 9.5$ Hz, 2H; aromatic protons), 7.98 (d, $J(H,H) = 6.9$ Hz, 1H; aromatic proton), 7.71 (pseudo t, $J(H,H) = 8.4$ Hz, 2H; aromatic protons), 7.53 (d, $J(H,H) = 8.7$ Hz, 1H; aromatic proton), 7.51 (d, $J(H,H) = 8.5$ Hz, 1H; aromatic proton), 7.39–7.19 (m, 14H; aromatic protons), 7.11 (d, $J(H,H) = 8.8$ Hz, 1H; aromatic proton), 6.33 (pseudo t, $J(H,H) = 8.0$ Hz, 1H; aromatic proton), 6.03 (pseudo t, $J(H,H) = 8.0$ Hz, 2H; aromatic protons), 5.32 (t, $J(H,H) = 8.4$ Hz, 2H; aromatic protons), 3.60–3.36 (m, 2H; NC*H*tBu and NH_2), 3.09–2.84 (m, 3H; CH_2), 2.24–1.40 (m, 6H; CH_2 and NH_2), 0.91 ppm (s, 9H; *t*Bu); $^{13}C\{^1H\}$ NMR (50.3 MHz, CD_2Cl_2, 20°C): $\delta = 180.3$ (dd, $^2J(C,P) = 16.7$, 8.1 Hz; CRu), 155.5–118.8 (m; aromatic carbon atoms), 72.9 (d, $^3J(C,P) = 2.9$ Hz; NC*H*tBu), 35.3 (s; *C*$(CH_3)_3$), 33.4 (dd, $^1J(C,P) = 24.7$ Hz, $^4J(C,P) = 1.9$ Hz; PCH_2), 30.4 (d, $^1J(C,P) = 32.2$ Hz; PCH_2), 27.5 (s; C(*C*$H_3)_3$), 27.0 (d, $^2J(C,P) = 1.7$ Hz; PCH_2CH_2), 21.8 ppm (d, $^2J(C,P) = 3.1$ Hz; PCH_2CH_2); $^{31}P\{^1H\}$ NMR (81.0 MHz, CD_2Cl_2, 20°C): $\delta = 57.1$ (d, $^2J(P,P) = 38.6$ Hz), 44.5 ppm (d, $^2J(P,P) = 38.6$ Hz); elemental analysis calcd (%) for $C_{46}H_{47}ClN_2P_2Ru$: C 66.86, H 5.73, N 3.39; found: C 67.10, H 5.70, N 3.19.

Synthesis of 5: Toluene (2 mL) was added to $[RuCl_2(PPh_3)_3]$ (0.150 g, 0.156 mmol) and (*R*,*S*)-Josiphos·C_2H_5OH (120 mg, 0.187 mmol) and the suspension was heated under reflux for 1 h. The solvent was removed under reduced pressure and the residue was treated with 2-propanol (2 mL), the ligand **a** (36 mg, 0.172 mmol), and NEt_3 (0.22 mL, 1.58 mmol). The mixture was heated under reflux for 2 h and then cooled to room temperature. Addition of pentane (5 mL) afforded a precipitate which was filtered, washed with pentane (4×3 mL), and dried under reduced pressure. The solid was dissolved in CH_2Cl_2 (0.5 mL), kept at −20°C for 18 h, to afford the precipitation of triethylammonium chloride which was eliminated by filtration. The solution was concentrated (1 mL) and addition of pentane (2 mL) afforded an orange precipitate which was filtered, washed with pentane (2×2 mL), and dried under reduced pressure. Yield: 90 mg (61%); ^1H NMR (200.1 MHz, CD_2Cl_2, 20°C): $\delta = 8.33$ (d, $J(H,H) = 7.0$ Hz, 1H; aromatic proton), 8.22–7.16 (m, 16H; aromatic protons), 4.70–4.35 (m, 4H; C_5H_3, PCH), 4.24–4.10 (m, 2H; NCH_2), 3.79 (s, 5H; C_5H_5), 3.45 (m, 1H; NH_2), 2.95–0.60 ppm (m, 26H; CH, CH_2, CH_3, NH_2); $^{13}C\{^1H\}$ NMR (50.3 MHz, CD_2Cl_2, 20°C): $\delta = 158.0$–117.0 (m; aromatic carbon atoms), 97.6 (m; ipso-C_5H_3), 74.4 (s; C_5H_3), 72.5 (m; ipso-C_5H_3), 70.8 (s; C_5H_5), 70.3 (d, $J(C,P) = 4.3$ Hz; C_5H_3), 68.9 (d, $J(C,P) = 4.8$ Hz; C_5H_3), 53.0 (d, $^3J(C,P) = 1.8$ Hz; NCH_2), 40.4 (d, $^1J(C,P) = 15.8$ Hz; CH of Cy), 38.0 (d, $^1J(C,P) = 17.5$ Hz; CH of Cy), 31.8–23.1 (m; CH_2 of Cy), 29.6 (d, $^1J(C,P) = 3.5$ Hz; P*C*HCH$_3$), 15.9 ppm (d, $^2J(C,P) = 6.8$ Hz; PCH*C*H$_3$); $^{31}P\{^1H\}$ NMR (81.0 MHz, $CDCl_3$, 20°C): $\delta = 68.8$ (d, $^2J(P,P) = 42.0$ Hz), 43.4 ppm (d, $^2J(P,P) = 42.0$ Hz); elemental analysis calcd (%) for $C_{50}H_{55}ClFeN_2P_2Ru$: C 64.00, H 5.91, N 2.99; found: C 64.30, H 6.02, N 3.05.

Synthesis of 6: CH_2Cl_2 (2 mL) was added to $[RuCl_2(PPh_3)_3]$ (0.150 g, 0.156 mmol) and (*S*,*R*)-Josiphos* (133 mg, 0.187 mmol) and the mixture was stirred for 1 h at room temperature. The solvent was removed under reduced pressure and the residue was treated with 2-propanol (1 mL), heptane (1 mL), the ligand **a** (36 mg, 0.172 mmol), and NEt_3 (0.22 mL, 1.58 mmol). The suspension was heated under reflux overnight and after filtration the solvent was removed. The residue was treated with heptane (2 mL) and the solution was heated under reflux for 2 h, concentrated (1 mL), and addition of pentane (1 mL) led to a precipitate, which was filtered and dried under reduced pressure. The solid was dissolved in CH_2Cl_2 (0.5 mL), kept at −20°C for 18 h to afford the precipitation of the residual NEt_3HCl, which was filtered. The resulting solution was concentrated (1 mL) and addition of pentane (2 mL) led to an orange precipitate, which was filtered, washed with pentane (2×2 mL), and dried under reduced pressure. Yield: 90 mg (55%) as mixture of two diastereoisomers in 5:1 ratio; ^1H NMR (200.1 MHz, CD_2Cl_2, 20°C): $\delta = 8.37$–6.60 (m; aromatic protons), 5.02–4.01 (m; PCH, C_5H_3, CH_2NH_2), 3.74–3.70 (m; OMe, C_5H_5), 2.57 (s; CH_3), 2.20 (s; CH_3), 2.18 (s; CH_3), 1.84–0.78 ppm (m; CH_3, Cy, NH_2); $^{13}C\{^1H\}$ NMR (50.3 MHz, CD_2Cl_2, 20°C): $\delta = 182.8$ (m; CRu), 161.3–116.4 (m; aromatic carbons), 97.5 (dd, $J(C,P) = 21.2$, 3.9 Hz; ipso-C_5H_3), 74.3–70.5 (s; C_5H_3, C_5H_5), 70.3 (s; OCH_3), 70.2 (s; C_5H_3), 68.3 (d, $J(C,P) = 4.1$ Hz; C_5H_3), 68.0 (d, $J(C,P) = 4.2$ Hz; C_5H_3), 53.4 (br s; NCH_2), 38.0 (d, $^1J(C,P) = 20.3$ Hz; CH of Cy), 37.2 (d, $^1J(C,P) = 18.3$ Hz; CH of Cy), 32.5–26.2 (m; P*C*HMe, CH_2 of Cy), 16.7 (s, Me), 16.6 (s, Me), 16.2 (s, Me), 15.5 ppm (d, $^2J(C,P) = 6.1$ Hz; P*CMe*); $^{31}P\{^1H\}$ NMR (81.0 MHz, CD_2Cl_2, 20°C): $\delta = 67.3$ (d, $^2J(P,P) = 41.9$ Hz; major complex), 60.1 (d, $^2J(P,P) = 40.0$ Hz), 40.9 (d, $^2J(P,P) = 40.0$ Hz), 38.5 ppm (d, $^2J(P,P) = 41.9$ Hz; major complex); elemental analysis calcd (%) for $C_{56}H_{67}ClFeN_2O_2P_2Ru$: C 63.79, H 6.40, N 2.66; found: C 64.02, H 6.60, N 2.86.

Synthesis of 7: Toluene (3 mL) was added to $[RuCl_2(PPh_3)_3]$ (0.150 g, 0.156 mmol) and (*S*,*S*)-Skewphos (89 mg, 0.202 mmol) and the mixture

was heated under reflux for 2 h, following the procedure described for **5**. Yield: 70 mg (57%) as mixture of two diastereoisomers in 4:1 ratio; ^{1}H NMR (200.1 MHz, CD_2Cl_2, 20°C): δ = 8.31–5.80 (m; aromatic protons), 6.44 (t, J(H,H) = 8.6 Hz; aromatic proton), 6.14 (t, J(H,H) = 6.4 Hz; aromatic proton), 5.84 (t, J(H,H) = 8.0 Hz; aromatic proton), 4.42 (s), 4.20 (d, J(H,H) = 3.4 Hz), 3.68 (br s), 3.37 (m), 3.03 (m), 2.78 (br s), 2.36 (pseudo q, J(H,H) = 13.5 Hz; C*H*CH$_2$), 2.00–1.40 (m), 1.35 (t, J(H,H) = 7.4 Hz), 1.29 (dd, ^3J(H,H) = 14.5, ^2J(H,P) = 7.3 Hz; CH$_3$), 0.91 (br m, CHC*H*$_2$), 0.76 (br s), 0.55 ppm (dd, ^3J(H,H) = 11.4, ^2J(H,P) = 6.9 Hz; CH$_3$); ^{13}C{^{1}H} NMR (50.3 MHz, CD_2Cl_2, 20°C): δ = 178.5 (m; CRu), 159.3–116.2 (m; aromatic carbon atoms), 51.3 (d, ^3J(C,P) = 1.5 Hz; NCH$_2$), 37.9 (m; C*H*CH$_2$), 33.0 (m; PCH), 32.6 (m; PCH), 19.5 (d, ^2J(C,P) = 6.1 Hz; PCH*C*H$_3$), 17.5 ppm (dd, ^2J(C,P) = 6.5, ^4J(C,P) = 3.0 Hz; PCH*C*H$_3$); ^{31}P{^{1}H} NMR (81.0 MHz, CD_2Cl_2, 20°C): δ = 66.2 (d, ^2J(P,P) = 46.2 Hz; major complex), 64.4 (d, ^2J(P,P) = 48.7 Hz), 53.3 (d, ^2J(P,P) = 48.7 Hz), 47.8 ppm (d, ^2J(P,P) = 46.2 Hz; major complex); elemental analysis calcd (%) for $C_{43}H_{41}ClN_2P_2Ru$: C 65.85, H 5.27, N 3.57; found: C 66.06, H 5.37, N 3.63.

Synthesis of 8: Toluene (2 mL) was added to [$RuCl_2(PPh_3)_3$] (0.150 g, 0.156 mmol) and (*S*)-MeO-Biphep (136 mg, 0.233 mmol) and the mixture was heated under reflux for 2 h, following the procedure described for **5**. Yield: 95 mg (66%) as mixture of two diastereoisomers in 3:1 ratio; ^{1}H NMR (200.1 MHz, $CDCl_3$, 20°C): δ = 8.45 (d, J(H,H) = 7.0 Hz; aromatic protons), 8.07–5.52 (m; aromatic protons), 4.43 (dd, ^2J(H,H) = 15.8, ^3J(H,H) = 5.4 Hz, 1H; NCH$_2$, major complex), 4.25 (m, 1H; NCH$_2$, major complex), 3.88 (s; OCH$_3$, major complex), 3.74 (s; OCH$_3$, minor complex), 3.39 (s; OCH$_3$, major complex), 3.28 (s; OCH$_3$, minor complex), 2.05 ppm (t, 1H, J(H,H) = 7.3 Hz; NH$_2$); ^{13}C{^{1}H} NMR (50.3 MHz, $CDCl_3$, 20°C): δ = 177.8 (m; CRu), 164.8–110.6 (m; aromatic carbon atoms), 55.8 (s, OCH$_3$), 55.7 (s, OCH$_3$), 54.9 (s, OCH$_3$), 54.6 (s, OCH$_3$), 52.2 ppm (d, ^3J(C,P) = 1.7 Hz; NCH$_2$); ^{31}P{^{1}H} NMR (81.0 MHz, CD_2Cl_2, 20°C): δ = 60.3 (d, ^2J(P,P) = 40.5 Hz), 51.9 (d, ^2J(P,P) = 40.5 Hz), 50.3 (d, ^2J(P,P) = 35.5 Hz; major complex), 49.8 ppm (d, ^2J(P,P) = 35.5 Hz; major complex); elemental analysis calcd (%) for $C_{52}H_{43}ClN_2O_2P_2Ru$: C 67.42; H 4.68; N 3.02; found: C 67.73, H 4.80, N 3.12.

Synthesis of 10: A 0.1 M solution of NaO*i*Pr (2.9 mL, 0.290 mmol) in 2-propanol was added to a suspension of complex **2** (150 mg, 0.195 mmol) in toluene (2.9 mL). The mixture was stirred at 60°C for 1 h. The resulting dark red solution was concentrated to half volume, stirred at RT for 1 h and after addition of toluene (3 mL), kept at −20°C for 18 h to afford the precipitation of NaCl, which was filtered on celite (fine frit). The solution was stirred under H_2 (1 atm) at RT for 1 h, and the solvent was eliminated obtaining a bright orange product, which was dried under reduced pressure. Yield: 119 mg (83%); ^{1}H NMR (200.1 MHz, C_6D_6, 20°C): δ = 8.58 (t, J(H,H) = 8.2 Hz, 2H; aromatic protons), 8.40–6.80 (m, 18H; aromatic protons), 6.37 (d, J(H,H) = 6.8 Hz, 1H; aromatic proton), 6.27 (d, J(H,H) = 7.7 Hz, 2H; aromatic protons), 6.14 (m, 2H; aromatic protons), 5.50 (t, J(H,H) = 6.5 Hz, 2H; aromatic protons), 3.20–1.45 (m, 12H; CH$_2$ and NH$_2$), −5.40 ppm (dd, ^2J(H,P) = 90.0, 26.2 Hz, 1H; Ru-H); ^{31}P{^{1}H} NMR (81.0 MHz, C_6D_6, 20°C): δ = 66.6 (d, ^2J(P,P) = 16.7 Hz), 35.0 ppm (d, ^2J(P,P) = 16.7 Hz); IR (Nujol): ν = 1742 cm^{-1} (Ru-H); elemental analysis calcd (%) for $C_{42}H_{40}N_2P_2Ru$: C 68.56, H 5.48, N 3.81; found: C 68.20, H 5.44, N 3.45.

Synthesis of 11: A 0.1 M solution of NaO*i*Pr (3.9 mL, 0.390 mmol) in 2-propanol was added to a suspension of complex **2** (200 mg, 0.260 mmol) in toluene (3.9 mL). The mixture was stirred at 60°C for 2 h, and at RT for an additional 1 h. The resulting dark red solution was kept at −20°C for 4 h to afford the precipitation of NaCl, which was filtered on celite (fine frit). 4,4′-Difluorobenzophenone (68.0 mg, 0.312 mmol) was added and the solution was stirred at RT for 30 min. The solvent was eliminated, toluene (2 mL) was added, and the mixture was kept at −20°C for 2 h, filtered on celite, and the solution was concentrated (1 mL). Addition of pentane afforded the precipitation of a red-orange product which was dried under reduced pressure. Yield: 186 mg (75%); ^{1}H NMR (200.1 MHz, C_6D_6, 20°C): δ = 8.15 (m, 2H; aromatic protons), 8.03 (t, J(H,H) = 7.60 Hz, 2H; aromatic protons), 7.66–6.25 (m, 26H; aromatic protons), 6.02 (t, J(H,H) = 7.8 Hz, 2H; aromatic protons), 5.86 (d, J(H,H) = 8.0 Hz, 1H; aromatic proton), 5.41 (t, J(H,H) = 8.2 Hz, 2H; aromatic protons), 5.28 (br s, 1H; NH$_2$), 4.46 (d, ^4J(H,P) = 3.3 Hz, 1H; OCH), 3.24–2.65 (m, 4H; CH$_2$, NH$_2$), 2.35–0.80 ppm (m, 7H; CH$_2$, NH$_2$); ^{13}C{^{1}H} NMR (50.3 MHz, C_6D_6, 20°C): δ = 183.4 (dd, ^2J(C,P) = 15.0, 8.5 Hz; CRu), 161.1 (d, ^1J(C,F) = 240.6 Hz; C-F), 160.6 (d, ^1J(C,F) = 240.2 Hz; C-F), 156.0–113.4 (m; aromatic carbon atoms), 79.9 (s, OCH), 52.0 (d, ^3J(C,P) = 2.5 Hz; NCH$_2$), 31.3 (d, ^1J(C,P) = 28.3 Hz; PCH$_2$), 30.7 (d, ^1J(C,P) = 29.5 Hz; PCH$_2$), 26.8 (s; PCH$_2$C*H*$_2$), 22.3 ppm (d, ^2J(C,P) = 2.3 Hz; PCH$_2$C*H*$_2$); ^{31}P{^{1}H} NMR (81.0 MHz, C_6D_6, 20°C): δ = 57.0 (d, ^2J(P,P) = 34.3 Hz), 40.3 ppm (d, ^2J(P,P) = 34.3 Hz); ^{19}F{^{1}H} NMR (188.3 MHz, C_6D_6, 20°C, $CFCl_3$): δ = −119.6, −120.3 ppm; elemental analysis calcd (%) for $C_{55}H_{48}F_2N_2OP_2Ru$: C 69.24, H 5.07, N 2.94; found: C 69.16, H 5.29, N 2.93.

Synthesis of 12: CH_2Cl_2 (5 mL) was added to [$OsCl_2(PPh_3)_3$] (200 mg, 0.191 mmol) and dppb (98 mg, 0.230 mmol), and the green solution was stirred at RT for 2 h. The solvent was removed under reduced pressure and the residue was suspended in 2-propanol (5 mL). Addition of the ligand **a** (48 mg, 0.230 mmol) and NEt_3 (0.32 mL, 2.30 mmol) afforded a mixture which was heated under reflux for 3 h, leading to a red precipitate. After filtration the product was washed with 2-propanol (3×10 mL) and pentane (2×10 mL) and dried under reduced pressure at 45°C. Yield: 144 mg (88%); ^{1}H NMR (200.1 MHz, CD_2Cl_2, 20°C): δ = 8.13 (pseudo t, J(H,H) = 7.5 Hz, 2H; aromatic protons), 7.93 (d, J(H,H) = 6.9 Hz, 1H; aromatic proton), 7.76 (t, J(H,H) = 7.5 Hz, 2H; aromatic protons), 7.64–7.20 (m, 16H; aromatic protons), 6.98 (d, J(H,H) = 8.1 Hz, 1H; aromatic proton), 6.44 (t, J(H,H) = 7.3 Hz, 1H; aromatic proton), 6.17 (pseudo t, J(H,H) = 7.8 Hz, 2H; aromatic protons), 5.49 (t, J(H,H) = 7.9 Hz, 2H; aromatic protons), 4.50 (d, J(H,H) = 20.7 Hz, 1H; NCH$_2$), 4.00 (m, 2H; NH$_2$ and NCH$_2$), 3.53 (m, 1H; CH$_2$), 3.30–2.65 (m, 2H; CH$_2$ and NH$_2$), 2.42–1.48 ppm (m, 6H; CH$_2$); ^{13}C{^{1}H} NMR (50.3 MHz, CD_2Cl_2, 20°C): δ = 157.2 (t; ^2J(C,P) = 6.5 Hz; C-Os), 155.6 (s; N*C*C), 154.5 (s; NCCH$_2$), 147.7–115.8 (m; aromatic carbon atoms), 54.6 (s; NCH$_2$), 35.2 (dd, ^1J(C,P) = 36.5 Hz, ^4J(C,P) = 4.3 Hz; PCH$_2$), 30.2 (dd, ^1J(C,P) = 42.2 Hz, ^4J(C,P) = 5.2 Hz; PCH$_2$), 26.7 (s; PCH$_2$C*H*$_2$), 21.2 ppm (pseudo t, J(C,P) = 2.0 Hz; PCH$_2$C*H*$_2$); ^{31}P{^{1}H} NMR (81.0 MHz, CD_2Cl_2, 20°C): δ = 0.9 (d, ^2J(P,P) = 13.7 Hz), 0.8 ppm (d, ^2J(P,P) = 13.7 Hz); ^{31}P{^{1}H} NMR (81.0 MHz, C_6D_6, 20°C): δ = 1.7 (d, ^2J(P,P) = 12.9 Hz), 0.5 ppm (d, ^2J(P,P) = 12.9 Hz); elemental analysis calcd (%) for $C_{42}H_{39}ClN_2OsP_2$: C 58.70, H 4.57, N 3.26; found: C 58.42, H 4.74, N 3.27.

Synthesis of 14: A 0.1 M solution of NaO*i*Pr (1.3 mL, 0.130 mmol) in 2-propanol was added to a suspension of complex **12** (100 mg, 0.116 mmol) in toluene (1.3 mL), and the mixture was stirred at 35°C for 3 h. The resulting dark red solution was kept at −20°C for 4 h to afford the precipitation of NaCl, which was filtered on celite (fine frit). The solvent was eliminated at low pressure and the solid was extracted with pentane (1 mL), affording a brown product which was dried under reduced pressure. Yield: 71 mg (74%); ^{1}H NMR (200.1 MHz, C_6D_6, 20°C): δ = 8.53 (t, J(H,H) = 8.5 Hz, 2H; aromatic protons), 8.31 (d, J(H,H) = 7.9 Hz, 1H; aromatic proton), 8.05–6.62 (m, 18H; aromatic protons), 6.40 (t, J(H,H) = 8.2 Hz, 1H; aromatic proton), 6.25–6.05 (m, 3H; aromatic protons), 5.49 (t, J(H,H) = 7.6 Hz, 2H; aromatic protons), 4.0 (t, J(H,H) = 6.9 Hz, 1H; NCH$_2$), 3.66–0.70 (m, 11H; CH$_2$, NH$_2$), −5.14 ppm (dd, ^2J(H,P) = 73.9, 23.9 Hz, 1H; OsH); ^{31}P{^{1}H} NMR (81.0 MHz, C_6D_6, 20°C): δ = 19.9 (d, ^2J(P,P) = 3.7 Hz), 5.4 ppm (d, ^2J(P,P) = 3.7 Hz); elemental analysis calcd (%) for $C_{42}H_{40}N_2OsP_2$: C 61.15, H 4.89, N 3.40; found: C 60.85, H 5.02, N 3.13.

Synthesis of 15: A 0.1 M solution of NaO*i*Pr (1.6 mL, 0.160 mmol) in 2-propanol was added to a suspension of complex **12** (123 mg, 0.143 mmol) in toluene (1.6 mL), and the mixture was stirred at 35°C for 3 h. The resulting dark red solution was kept at −20°C for 4 h to afford the precipitation of NaCl, which was filtered on celite (fine frit). 4,4′-Difluorobenzophenone (35 mg, 0.160 mmol) was added and the mixture was stirred at RT for 1 h. The solvent was eliminated, toluene (2 mL) was added and the mixture was kept at −20°C for 2 h and filtered on celite; the resulting solution was concentrated. Addition of pentane (5 mL) afforded the precipitation of a dark-yellow product, which was filtered and dried under reduced pressure. Yield: 107 mg (72%); ^{1}H NMR (200.1 MHz, C_6D_6, 20°C): δ = 8.18 (t, J(H,H) = 7.5 Hz, 1H; aromatic proton), 8.07 (d, J(H,H) = 8.3 Hz, 1H; aromatic proton), 7.93 (t, J(H,H) = 7.6 Hz, 2H; aro-

matic protons), 7.66–6.21 (m, 26H; aromatic protons), 6.04 (dt, J(H,H) = 7.6, 1.8 Hz, 2H; aromatic protons), 5.83 (d, J(H,H) = 8.2 Hz, 1H; aromatic proton), 5.42 (t, J(H,H) = 7.9 Hz, 2H; aromatic protons), 5.28 (brs, 1H; NH_2), 4.61 (m, 1H; OCH), 3.48 (m, 1H; NCH_2), 3.26 (s, 2H; CH_2 and NH_2), 2.91 (pseudot, J(H,H) = 13.2 Hz, 1H; NCH_2), 2.42 (m, 1H; CH_2), 2.25 (m, 2H; CH_2), 1.94–0.77 ppm (m, 4H; CH_2); $^{13}C\{^1H\}$ NMR (50.3 MHz, C_6D_6, 20°C): δ = 162.4 (brd, ^1J(C,F) = 245 Hz; C-F), 162.0 (dd, ^2J(C,P) = 7.9, 3.7 Hz; C-Os), 156.4 (s; C*C*N), 155.1 (s; N*C*CH_2), 147.9–113.0 (m; aromatic carbon atoms), 79.7 (brs; OCH), 54.0 (d, ^3J(C,P) = 2.2 Hz; NCH_2), 33.7 (d, ^2J(C,P) = 33.2 Hz; PCH_2), 30.8 (d, ^2J(C,P) = 34.4 Hz; PCH_2), 26.7 (s; CH_2), 21.6 ppm (s; CH_2); $^{31}P\{^1H\}$ NMR (81.0 MHz, C_6D_6, 20°C): δ = 1.8 (d, ^2J(P,P) = 8.2 Hz), −0.8 ppm (d, ^2J(P,P) = 8.2 Hz); $^{19}F\{^1H\}$ NMR (188.3 MHz, C_6D_6, 20°C): δ = −119.4, −120.1 ppm; elemental analysis calcd (%) for $C_{55}H_{48}F_2N_2OOsP_2$: C 63.33, H 4.64, N 2.69; found: C 62.84, H 4.72, N 2.62.

Typical procedure for the catalytic TH of ketones: The complex (2.5 μmol) was dissolved in 2-propanol (5 mL). The ketone (2.0 mmol) was dissolved in 2-propanol (final volume 19.4 mL) and the solution was heated under argon. By addition of NaO*i*Pr in 2-propanol (0.1 M, 400 μL, 40 μmol) and a solution of the catalyst in 2-propanol (200 μL), the reduction of the ketone starts immediately and the yield was determined by GC (complex 0.005 mol%, NaO*i*Pr 2 mol%, ketone 0.1 M).

Typical procedure for the catalytic TH of ketones with the in-situ-prepared catalyst: A solution of $[MCl_2(PPh_3)_3]$ (M = Ru, Os; 2.5 μmol) and the diphosphane (3.8 μmol) in 2-propanol (5 mL) was heated under reflux for 1 h and, after addition of the HCN′N ligand (5.0 μmol of **a** or 7.5 μmol of **b**, **c**), for an additional 1 h. The ketone (2.00 mmol) was dissolved in 2-propanol (final volume: 19.4 mL) and the solution was heated at 60°C. Addition of NaO*i*Pr in 2-propanol (0.1 M, 400 μL, 40 μmol) and the solution of the complex in 2-propanol (200 μL), affords the reduction of the ketone (complex 0.005 mol%, NaO*i*Pr 2 mol%, ketone 0.1 M).

Single-crystal X-ray structure determination of compound 3: Crystal data and details of the structure determination: formula: $C_{43}H_{41}ClN_2P_2Ru{\cdot}2\,CH_2Cl_2$; M_r = 954.09; crystal color and shape: orange fragment, crystal dimensions = 0.28 × 0.43 × 0.61 mm; crystal system: triclinic; space group $P\bar{1}$ (no. 2); a = 10.8227(2), b = 12.1648(2), c = 17.3533(3) Å; α = 96.0103(13), β = 91.1186(12), γ = 112.3160(14)°; V = 2097.57(7) Å^3; Z = 2; $\mu(Mo_{K\alpha})$ = 0.804 mm^{-1}; ρ_{calcd} = 1.511 g cm^{-3}; θ range = 3.02–25.32°; data collected: 38733; independent data [$I_o > 2\sigma(I_o)$/all data/R_{int}]: 6940/7635/0.014; data/restraints/parameters: 7635/0/679; $R1$ [$I_o > 2\sigma(I_o)$/all data]: 0.0244/0.0287; $wR2$ [$I_o > 2\sigma(I_o)$/all data]: 0.0542/0.0572; GOF = 1.084; $\Delta\rho_{max/min}$: 0.88/−0.71 e Å^{-3}. Suitable single crystals for the X-ray diffraction study were grown from dichloromethane. A clear orange fragment was stored under perfluorinated ether, transferred in a Lindemann capillary, fixed, and sealed. Preliminary examination and data collection was carried out on an area detecting system with graphite-monochromated $Mo_{K\alpha}$ radiation (λ = 0.71073 Å, OXFORD DIFFRACTION, Xcalibur, κ-CCD, sealed tube, Enhance X-ray Source, SPELLMAN, DF3). The unit cell parameters were obtained by full-matrix least-squares refinements during the scaling procedure. Data collection was performed at low temperature (T = 153 K, OXFORD CRYOSYSTEMS cooling device). The crystal was measured with nine data sets in rotation scan modus ($\delta\pi/\delta\omega$ = 1.00°; dx = 50). Intensities were integrated and the raw data were corrected for Lorentz, polarization, and, arising from the scaling procedure for latent decay and absorption effects. The structure was solved by a combination of direct methods and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen positions could be located in the final Fourier maps and were allowed to refine freely. A disorder [0.52(3):0.48(3)] of one of the two solvent molecules could be resolved clearly. Those hydrogen atoms were placed in ideal positions and refied using a riding model. Small extinction effects were corrected with the SHELXL-97 procedure with ε = 0.0048(3). Full-matrix least-squares refinements were carried out by minimizing $Ew(F_2^0 - F_2^c)^2$ with the SHELXL-97 weighting scheme and stopped at shift/err < 0.002. 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 the International Tables for Crystallography.[34] CCDC-687367 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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