

Synthesis, Molecular Structure and Catalytic Activity of Six-Coordinate Chloro(hydrido)- and Dihydridoruthenium(II) and -osmium(II) Complexes with the Chiral Ligands $\text{P}i\text{Pr}_2\text{NH}(\text{Me})\text{Ph}$, (*S,S*)-Chiraphos and (*S,S*)-Diop

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Dedicated to Professor Albrecht Salzer on the occasion of his 60th birthday

Keywords: Chirality / Hydrido complexes / Osmium / Phosphane complexes / Ruthenium

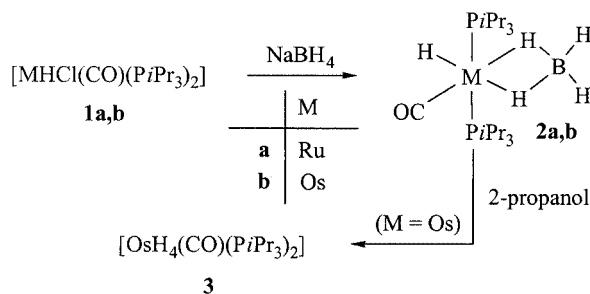
The five-coordinate compounds $[\text{MHCl}(\text{CO})(\text{P}i\text{Pr}_3)_2]$ (where **1a**: M = Ru; **1b**: M = Os) react with $\text{P}i\text{Pr}_2\text{R}^*$ [where $\text{R}^* = \text{CH}(\text{Me})\text{Ph}$] to give the octahedral complexes *mer*- $[\text{MHCl}(\text{CO})(\text{P}i\text{Pr}_2\text{R}^*)_3]$ (**6** and **7**). The lability of the phosphane *trans* to the hydride is illustrated by the replacement reactions with CO, $\text{P}(\text{OMe})_3$ and $\text{C}_2(\text{CO}_2\text{Me})_2$, which afford the substitution products $[\text{MHCl}(\text{CO})(\text{L})(\text{P}i\text{Pr}_2\text{R}^*)_2]$ (**8–12**) in high yields. The reactions of **1a** and **1b** with (*S,S*)-Chiraphos and (*S,S*)-Diop lead to one or two diastereoisomers of the chelate complexes $[\text{MHCl}(\text{CO})(\text{P}i\text{Pr}_3)(\text{Chiraphos})]$ (**15**, **16**) and $[\text{MHCl}(\text{CO})(\text{P}i\text{Pr}_3)(\text{Diop})]$ (**17**, **18**); the ratio of the diastereoisomers is dependent on the metal, the bidentate ligand and the reaction conditions. The racemate of $[\text{OsHCl}(\text{CO})(\text{P}i\text{Pr}_3)(\text{dppe})]$ (**14**) was obtained from **1b** and 1,2- $\text{C}_2\text{H}_4(\text{PPh}_2)_2$ (dppe). The hydrido(tetrahydroboranato) compounds $[\text{MH}(\kappa^2\text{-H}_2\text{BH}_2)(\text{CO})(\text{P}i\text{Pr}_3)_2]$ (where **2a**: M = Ru; **2b**: M = Os) also react with (*S,S*)-Chiraphos and (*S,S*)-Diop to

give either the mononuclear, octahedral, chelate complexes **19–21** or, for M = Os and (*S,S*)-Diop, the dinuclear compound $[\{\text{OsH}_2(\text{CO})(\text{P}i\text{Pr}_3)_2\}_2(\mu\text{-Diop})]$ (**22**). The molecular structure of **22** was determined crystallographically. Treatment of $[\text{OsH}_2\text{Cl}_2(\text{P}i\text{Pr}_3)_2]$ (**23**) with two equivalents of (*S,S*)-Chiraphos afforded stepwise $[\text{OsH}_2\text{Cl}_2(\text{P}i\text{Pr}_3)(\text{Chiraphos})]$ (**25**) and, after reductive elimination of HCl and displacement of $\text{P}i\text{Pr}_3$, *trans*- $[\text{OsHCl}(\text{Chiraphos})_2]$ (**24**). Both **24** and $[\text{OsH}_2(\text{Chiraphos})_2]$ (**27**), which was prepared from **24** and $\text{NaBH}_4/\text{MeOH}$, were transformed with HBF_4 in diethyl ether into the dihydrogen complexes $[\text{OsCl}(\text{H}_2)(\text{Chiraphos})_2]\text{BF}_4$ (**28**) and $[\text{OsH}(\text{H}_2)(\text{Chiraphos})_2]\text{BF}_4$ (**29**) in excellent yields. The catalytic activity of the chloro(hydrido)- and dihydridometal derivatives in the asymmetric transfer hydrogenation of acetophenone with 2-propanol was investigated. © Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2004

Introduction

In the context of our studies on the chemistry of the five-coordinate (hydrido)ruthenium(II) and (hydrido)osmium(II) complexes $[\text{MHCl}(\text{CO})(\text{P}i\text{Pr}_3)_2]$ (where **1a**: M = Ru; **1b**: M = Os),^[1] we reported that the osmium compound **1b**, under hydrogen, catalyzes the reduction of cyclohexene, 1,3- and 1,4-cyclohexadiene, styrene, and diphenyl- and phenylacetylene.^[2,3] Furthermore, in the presence of NaBH_4 , it also serves as a catalyst for hydrogen transfer from 2-propanol to cyclohexanone, acetophenone, benzylidenacetone, etc.^[4] It was shown that both **1a** and **1b** react with NaBH_4 to give the tetrahydroboranato compounds **2a** and **2b** (see Scheme 1), of which **2b**, upon treatment with 2-propanol,

decomposes to the tetrahydride **3**.^[5] Kinetic investigations suggest that in the hydrogen-transfer process catalyzed by **1b** and NaBH_4 , the coordinatively unsaturated dihydride $[\text{OsH}_2(\text{CO})(\text{P}i\text{Pr}_3)_2]$, which is generated from **3** by loss of H_2 , is the active catalytic species.^[6]



Scheme 1

As a continuation of our work on the reactivity of chloro(hydrido)-, hydrido(boranato)- and (dihydrido)ruthenium

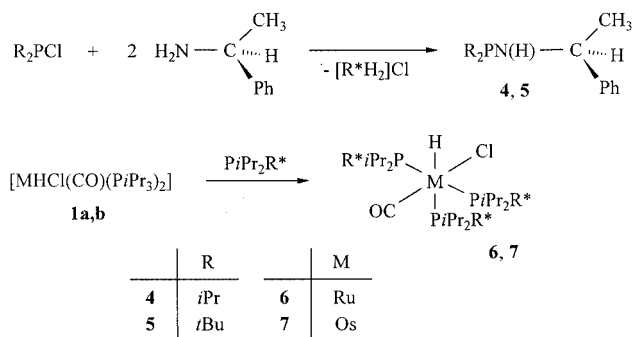
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and -osmium complexes we have now attempted to modify the coordination sphere by linking chiral mono- and bisphosphanes to the metal center. In this paper we describe the preparation and molecular structure of the compounds obtained and report some preliminary results concerning their catalytic activity in the asymmetric reduction of acetophenone by 2-propanol.

Results and Discussion

The preparation of the chiral aminophosphanes **4** and **5** (see Scheme 2) follows the route which was developed for the diphenylphosphanyl counterpart (*S*)-Ph₂PNHR* [R* = CH(Me)Ph] by Brunner et al.^[7] The reason for using isopropyl and *tert*-butyl substituents instead of phenyl at the phosphorus atom was that we wanted to make the phosphane comparable in size to *PtPr*₃ and *PtBu*₂Me, respectively. The reactions of R₂PCl and R*NH₂ were carried out in diethyl ether and gave, after removal of ammonium chloride, the chiral products in 64–72 % isolated yield. Both **4** and **5** are colorless, extremely air-sensitive liquids, the composition of which was confirmed by elemental analysis and mass spectrometry. The ¹H NMR spectrum of **5** displays two resonances for the *tert*-butyl protons, which is a consequence of a chiral center next to the phosphorus atom. For the same reason four signals, which are pairwise equivalent, appear in the ¹H NMR spectrum of **4** for the methyl protons of the isopropyl groups. They are doublets of doublets and become doublets with ³J_{H,H} = 6.4, 6.9 Hz in off resonance.



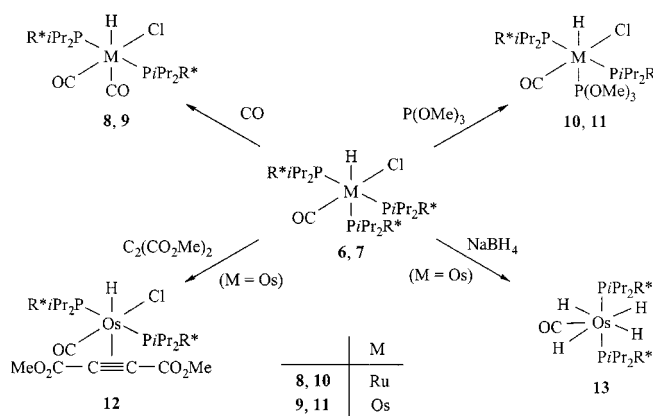
Scheme 2. [R* = NHCH(Me)Ph]

Attempts to prepare the five-coordinate complexes, [MHCl(CO)(PiPr₂R*)₂], (where M = Ru, Os) from ruthenium- and osmium trichloride, using the same methodology as that applied for the synthesis of **1a** and **1b**,^[1] failed. Under the reaction conditions (stirring the reaction mixtures of MCl₃·3H₂O and **4** or **5** in methanol or 2-propanol under reflux) partial cleavage of the P–N bond of the aminophosphane and decomposition of possibly formed metal-containing intermediates occurred.

The reactions of **1a** and **1b** with an excess of the less sterically demanding phosphane, **4**, proceeded by ligand exchange as well as by addition of a third phosphane mol-

ecule to the metal center. After recrystallization from benzene/methanol, the six-coordinate compounds **6** and **7** were isolated as white, moderately air-stable solids in 67–71 % yield (see Scheme 2). The starting materials are inert toward **5** which is reminiscent to the behavior of other (phosphane)ruthenium and -osmium complexes, such as [MCl₂(PPh₃)₃] (M = Ru, Os) toward *PtBu*₃.^[8] The most typical spectroscopic features of **6** and **7** are the two ³¹P NMR signals at δ = 89.4 and 75.4 ppm for **6** and at δ = 57.2 and 48.5 ppm for **7**, which, together with the splitting pattern, indicate that two of the aminophosphane ligands are stereochemically equivalent while the third is not. Thus, a *mer* configuration for the octahedral compounds can be assigned. In agreement with this proposal, the ¹H NMR spectrum of **7** displays a high-field resonance at δ = –8.77 ppm for the Os–H proton, which appears as a doublet of triplets due to P–H coupling with different ³¹P nuclei.

The results regarding the reactivity of **6** and **7** toward Lewis bases are summarized in Scheme 3. According to the strong *trans* influence of the hydride, the M–P bond in *trans* disposition was assumed to be rather labile and this was substantiated by the reactions of **6** and **7** with CO, P(OMe)₃ and C₂(CO₂Me)₂. Passing a slow stream of CO through a solution of **6** or **7** in benzene, after a short period of time, leads to a ligand exchange and affords the dicarbonyl complexes **8** and **9** in high yields. The white solids are thermally stable and for a few minutes can be handled in air. The IR spectra display two ν(CO)-stretching modes at 1970 and 1905 cm^{–1} (for **8**) and 1970 and 1910 cm^{–1} (for **9**), indicating that the two CO ligands are not stereochemically equivalent. The ¹H NMR spectra show a hydride signal at δ = –5.47 ppm (for **8**) and δ = –4.68 ppm (for **9**), which is split into a triplet due to P–H coupling.



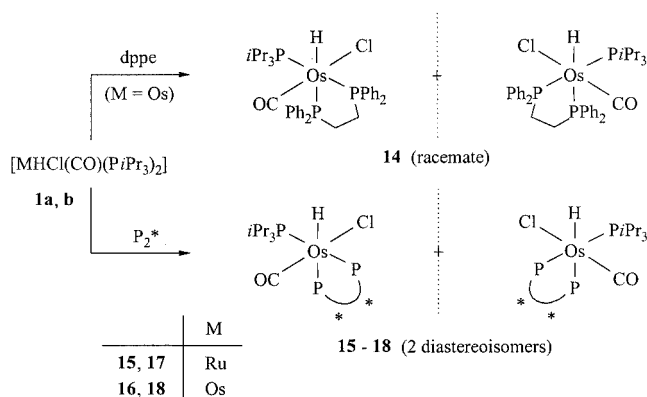
Scheme 3. [R* = NHCH(Me)Ph]

The preparation of the phosphite and alkyne derivatives **10–12** takes place under similar conditions (hexane, room temperature) as those used for the dicarbonyl complexes **8** and **9**. After evaporation of the solvent, compounds **10–12** were isolated as white, moderately air-stable solids, which readily dissolved in most common organic solvents (with the exception of methanol and hexane). The proposed

structure for **10–12** with the phosphite or alkyne ligand *trans* to the hydride is supported by the mass spectra in which, besides the peak for the molecular M^+ ion, a second peak corresponding to $M^+ - P(OMe)_3$ or $M^+ - C_2(CO_2Me)_2$ appears. Thus, the hydride ligand presumably labilizes the $M-PiPr_2R^*$ as well as the $M-P(OMe)_3$ and $M^+ - C_2(CO_2Me)_2$ bonds in the *trans* position. The ^{31}P NMR spectra of the phosphite complexes **10** and **11** are noteworthy insofar as they show the pattern of an ABX system, which means that the two aminophosphane ligands are magnetically nonequivalent. Since the metal atom in the octahedral complexes **10** and **11** is a prochiral center, the two phosphane units are diastereotopic and thus give rise to two resonances in the ^{31}P NMR spectra. Accordingly, the ^{31}P NMR spectrum of the alkyne compound **12** displays the pattern of an AB spin system with $\delta_{PA} = 65.7$ ppm and $\delta_{PB} = 61.8$ ppm. There are also two signals for the NH and two for the $NCHCH_3$ protons of the $PiPr_2R^*$ ligands in the 1H NMR spectrum of **12**, which is consistent with the proposed stereochemistry. We note that even under forcing conditions no insertion of the alkyne into the Os–H bond occurs, which is in contrast to the behavior of the bis(triisopropylphosphane) analogue $[OsHCl(CO)\{C_2(CO_2Me)_2\}(PiPr_3)_2]$ that rearranges in chloroform to give a product with a chelating vinyl ligand.^[3]

The reaction of **7** with $NaBH_4$ in benzene/methanol proceeds similarly to that of **1b** with the same reagents.^[4] We assume that in the initial step (see below the formation of **26**) the tetrahydroboranato compound, $[OsH(\kappa^2-H_2BH_2)(CO)(PiPr_2R^*)_2]$, is generated and rapidly reacts with methanol to give **13** (see Scheme 3). The (tetrahydrido)osmium(IV) complex, **13**, is a light yellow, extremely air-sensitive solid, the IR spectrum of which shows a strong $\nu(CO)$ band at 1890 cm^{-1} . The ^{31}P NMR spectrum of **13** displays a singlet at $\delta = 87.4$ ppm which is converted into a symmetrical quintet in off resonance. Since the 1H NMR spectrum shows a sharp triplet at $\delta = -8.76$ ppm, we assume that, similarly to the $PiPr_3$ counterpart, the seven-coordinate molecule, **13**, also possesses a fluxional structure at room temperature, which leads to the equivalence of the hydrido ligands on the NMR time scale. The $^2J_{P,H}$ coupling constants for the hydride signal of **13** and $[OsH_4(CO)(PiPr_3)_2]$ are nearly the same.

To compare the catalytic activity of the ruthenium and osmium complexes with two monodentate $PiPr_2R^*$ units on one side and a chiral bidentate bisphosphane on the other, the starting materials **1a** and **1b** were also treated with (*S,S*)-Chiraphos and (*S,S*)-Diop. As a test, prior to the reaction with the chiral bisphosphanes, the reaction of **1b** with 1,2- $C_2H_4(PPh_2)_2$ (dppe) was carried out and afforded the racemate of compound **14** in 80 % yield (see Scheme 4). Similarly to that of **10** and **11**, the ^{31}P NMR spectrum of **14** shows an ABX spin pattern which can be clearly resolved and was simulated with the program Laocoon. Typical features are the large coupling constant $^2J_{PA,PB}$ (250.6 Hz) for the *trans*-disposed ^{31}P nuclei and the small coupling constants $^2J_{PA,PX}$ (6.7 Hz) and $^2J_{PB,PX}$ (13.8 Hz) for the ^{31}P nuclei in *cis*-position.



Scheme 4. [**15, 16**: $P_2^* = (S,S)$ -Chiraphos; **17, 18**: $P_2^* = (S,S)$ -Diop]

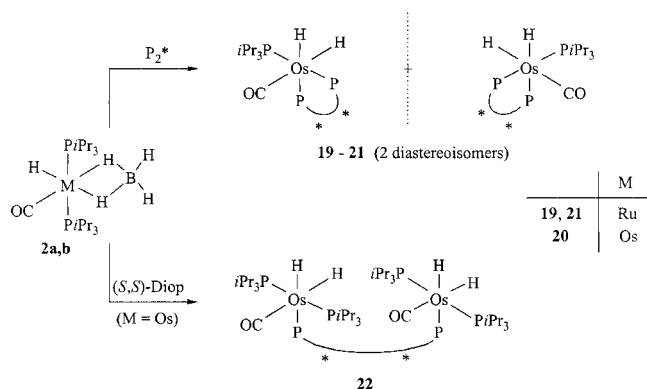
The chiral bisphosphanes (*S,S*)-Chiraphos and (*S,S*)-Diop behave analogously to dppe and under similar conditions (hexane, 24 h, reflux) give the chelate complexes **15–18** as white, moderately air-stable solids in 79–89 % isolated yield. Due to the presence of chiral centers at the metal and the chelating ligands, the formation of diastereoisomers should be expected and was confirmed for the Diop derivatives **17** and **18**. In contrast, the NMR spectra of the Chiraphos compounds **15** and **16** display only one set of signals, which probably means that only one diastereoisomer was generated. The high-field region of the 1H NMR spectra of **15** and **16** consists of a sharp doublet of doublets at $\delta = -6.61$ ppm (for **15**) and $\delta = -6.69$ ppm (for **16**) with two small and one large $^2J_{P,H}$ coupling constant. Owing to these numbers, there is no doubt that one of the phosphorus atoms is *trans* to the hydride. Although the ^{31}P NMR spectra of **15** and **16** are in agreement with an ABX spin system, they differ from the spectrum of **14** insofar as the outer lines of the AB part were not observed and, therefore, the values for δ_{PA} , δ_{PB} and $^2J_{PA,PB}$ could not be determined. With regard to the structure of **15** and **16**, we assume that the five-membered chelate ring possesses the δ -conformation, which for steric arguments should be preferred.^[9] We were unable to substantiate this by X-ray crystallography since all attempts to grow single crystals of **15** or **16** failed.

The reactions of **1a** and **1b** with (*S,S*)-Diop lead to two diastereoisomers, the ratio of which depends on the reaction conditions. For example, by refluxing a solution of **1b** and (*S,S*)-Diop in hexane for 24 h the two diastereoisomers **A** and **B** of compound **18** were obtained in a ratio of 3:2, whereas stirring the same mixture for five days gave the two species **A** and **B** in equal amounts. In the ruthenium case, an A/B ratio of 7:1 was found after refluxing the reaction mixture in hexane for 24 h, whereas only **A** was generated by carrying out the reaction at room temperature.

In contrast to the 1H NMR spectra of **15** and **16**, those of **17** and **18** are rather complicated and therefore no exact assignment for the resonances (for $\delta = 0–9$) could be made. For each of the diastereoisomers **A** and **B** the hydride signal is a doublet of doublets of doublets with similar coupling constants as observed for **15** and **16**. The ^{31}P NMR spectra

of **17** and **18** display the expected number of lines for ABX spin systems and thus the chemical shifts for the signals corresponding to P_A ($PiPr_3$), P_B and P_X (each PPh_2) could be exactly determined. The presence of the two diastereoisomers of **18** is also indicated by the IR spectrum, which shows two $\nu(CO)$ absorptions at 1905 and 1895 cm^{-1} with comparable intensities. We note that at room temperature, the diastereoisomers **A** and **B** of both **17** and **18** are stable and do not interconvert.

The preparation of the (dihydrido)ruthenium(II) and -osmium(II) complexes **19–22** followed the route that we already used to obtain compounds of the general composition $[MH_2(CO)(L)(PiPr_3)_2]$ ($L = PMe_3, P(OMe)_3$).^[4] Treatment of **2a** and **2b** with (*S,S*)-Chiraphos and of **2a** with (*S,S*)-Diop in methanol under reflux conditions affords, after recrystallization from CH_2Cl_2 /methanol, the chelate complexes **19–21** in 76–83 % isolated yield (see Scheme 5). In contrast to related dihydrido derivatives such as $[RuH_2(PMe_3)_4]$ or $[OsH_2(PMe_3)_4]$,^[10] compounds **19–21** are only slightly air sensitive and, apart from hexane and methanol, readily soluble in common organic solvents. While the ^{31}P NMR spectrum of **19** clearly indicates that only one diastereoisomer is formed, the spectrum of **20** displays two sets of resonances for two diastereoisomers, **A** and **B**, in an approximate ratio of 10:1. For both **19** and the dominating isomer of **20**, the pattern corresponding to an ABX spin system is observed with values for the coupling constants $^2J_{PA,PB}$, $^2J_{PA,PX}$ and $^2J_{PB,PX}$ that are similar to those of **15** and **16**. For compound **21**, a mixture of two diastereoisomers in a 3:2 ratio was obtained; they are configurationally stable at room temperature and do not interconvert. The 1H NMR spectra of **19** and **20** confirm the nonequivalence of the hydrido ligands and display two doublets of doublets of doublets at $\delta = -8.16$ and -8.76 ppm (for **19**) and $\delta = -9.32$ and -10.04 ppm (for **20**). In agreement with the size of the coupling constants, the signal for the lower chemical shift belongs to the hydride *trans* to CO and that for the higher chemical shift to the hydride *trans* to one of the PPh_2 groups. For the Diop compound, **21**, the two signals overlap and thus no correct δ values can be given.



Scheme 5. [**19**, **20**: $P_2^* = (S,S)$ -Chiraphos; **21**, **22**: $P_2^* = (S,S)$ -Diop]

Quite surprisingly, the reaction of **2b** with (*S,S*)-Diop affords, under the same conditions as those used for the preparation of **19–21**, the dinuclear complex **22**, instead of a mononuclear one (see Scheme 5) in 81 % yield. The result is reminiscent of the formation of the catalytically active ruthenium compound $[RuCl_2(Diop)]_2(\mu\text{-Diop})$, obtained by James et al. from $[RuCl_2(PPh_3)_3]$ and a 2.5-fold excess of Diop.^[11] Similarly to the 1H NMR spectra of **19** and **20**, the 1H NMR spectrum of **22** also shows two high-field signals at $\delta = -9.34$ and -11.56 ppm, which appear both as doublets of doublets of triplets, due to two different P–H and to one H–H coupling. For the hydride *trans* to the PPh_2 unit, two significantly different $^2J_{P,H}$ coupling constants result. The ^{31}P NMR spectrum of **22** is more simple than the spectra of **19–21** and displays one doublet for the ^{31}P nuclei of the two $PiPr_3$ ligands and one triplet for the ^{31}P nuclei of Diop.

The X-ray crystal structure analysis of **22** (see Figure 1) confirms the proposed structure, including the presence of the bridging Diop unit. The high quality of data allowed the location of the hydrides in the Fourier maps and their isotropic refinement. Taken the positions of these ligands into consideration, the coordination geometry around both metal centers is best described as distorted octahedral with bond angles that in some cases deviate significantly from the ideal 90° value. The most remarkable feature is the size of the angles $P(4)\text{--}Os\text{--}P(5)$ and $P(3)\text{--}Os\text{--}P(6)$ [$148.90(6)^\circ$ and $145.65(5)^\circ$], which is unusual and probably explained by steric hindrance between the isopropyl and phenyl groups. The chirality (*S,S*) of the Diop ligand was maintained. The bond lengths between osmium and the phos-

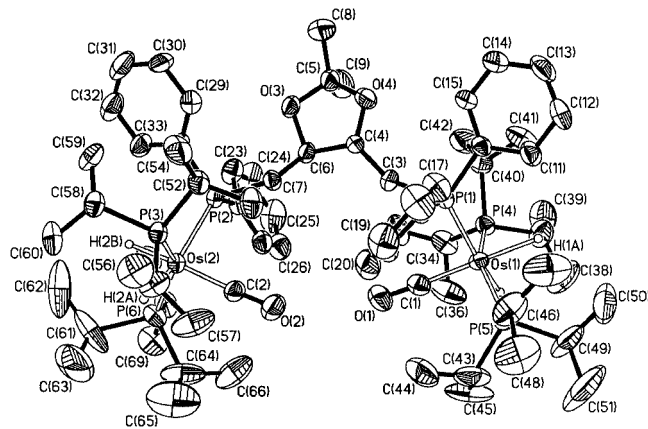
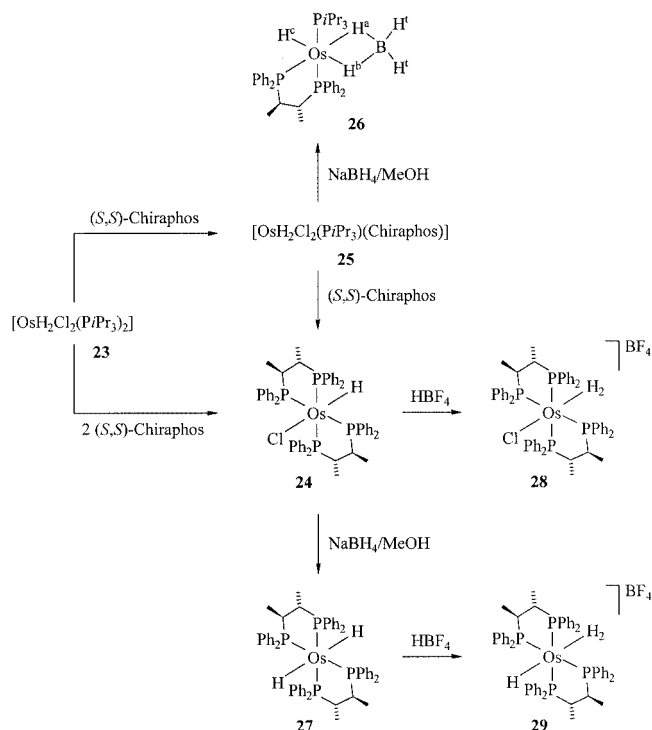


Figure 1. Molecular structure of compound **22**; selected bond lengths (Å) and angles ($^\circ$): Os(1)–P(1) 2.3725(13), Os(2)–P(2) 2.3711(4), Os(2)–P(3) 2.3431(16), Os(1)–P(4) 2.3412(15), Os(1)–P(5) 2.3457(15), Os(2)–P(6) 2.3640(15), Os(1)–C(1) 1.873(7), Os(2)–C(2) 1.852(6), C(1)–O(1) 1.197(7), C(2)–O(2) 1.191(7); P(1)–Os(1)–P(4) 101.27(5), P(1)–Os(1)–P(5) 106.24(6), P(1)–Os(1)–C(1) 88.51(19), P(4)–Os(1)–P(5) 148.90(6), P(4)–Os(1)–C(1) 97.9(2), P(5)–Os(1)–C(1) 97.0(2), P(2)–Os(2)–P(3) 101.59(5), P(2)–Os(2)–P(6) 109.33(5), P(2)–Os(2)–C(2) 91.31(18), P(3)–Os(2)–P(6) 145.65(5), P(3)–Os(2)–C(2) 96.42(18), P(6)–Os(2)–C(2) 97.44(18), P(1)–C(3)–C(4) 126.2(4), P(2)–C(7)–C(6) 120.2(4), C(3)–C(4)–C(6) 110.7(4), C(7)–C(6)–C(4) 114.4(4), C(3)–C(4)–O(4) 113.1(5), C(7)–C(6)–O(3) 111.6(4), C(4)–O(4)–C(5) 111.4(4), C(6)–O(3)–C(5) 106.4(4).

phorus atoms of the $\text{P}i\text{Pr}_3$ units are slightly shorter than in the five-coordinate vinyl complex $[\text{OsCl}(\text{CH}=\text{CHPh})(\text{CO})(\text{P}i\text{Pr}_3)_2]$,^[12] but somewhat longer than in the bis(triisopropylphosphane)osmium(IV) compound, $[\text{OsH}_2\text{Cl}_2(\text{P}i\text{Pr}_3)_2]$ (**23**) (see below).^[5] There is also a small difference in the distances $\text{Os}-\text{P}i\text{Pr}_3$ and $\text{Os}-\text{PPh}_2\text{X}$, which might be due to the different donor strength of the trialkylphosphane and alkylidylphosphane moieties.

The above-mentioned osmium(IV) compound, **23**, was also used as starting material for the reactions with (*S,S*)-Chiraphos (see Scheme 6). It was already known that the dichloro(dihydrido) complex reacts with CO and PMe_3 to give $[\text{OsCl}_2(\text{CO})_2(\text{P}i\text{Pr}_3)_2]$ and $[\text{OsCl}_2(\text{PMe}_3)_4]$ by reductive elimination of H_2 .^[5]



Scheme 6

The reaction of **23** with two equivalents of (*S,S*)-Chiraphos, however, does not lead to the elimination of H_2 but of HCl and affords the chloro(hydrido)osmium(II) compound **24** in 89 % isolated yield. If equimolar amounts of **23** and (*S,S*)-Chiraphos are reacted in hexane under reflux, a white, extremely air-sensitive solid, **25**, can be isolated and it slowly decomposes at room temperature, even under argon. The assumption that **25** is the substitution product of **23** is supported by the elemental analysis and, in particular, by the ^{31}P NMR spectrum, which displays the pattern of an ABX spin system. The ^1H NMR spectrum of **25** shows a broadened doublet of doublets of doublets in the high-field region, indicating that under these conditions the two hydrido ligands are magnetically equivalent on the NMR time scale. Since the three coupling constants $^2J_{\text{P-H}}$ are virtually the same, it is conceivable that the seven-coordinate

molecule is fluxional in solution, as has also been observed for the osmium tetrahydrides $[\text{OsH}_4(\text{PPh}_3)_3]$ and $[\text{OsH}_4(\text{PMe}_2\text{Ph})_3]$.^[13] Since, by lowering the temperature, the high-field resonance in the ^1H NMR spectrum of **25** becomes broader and the coupling constants become smaller, the possibility of an equilibrium between a classical OsH_2 and a nonclassical $\text{Os}(\text{H}_2)$ species was taken into consideration. Therefore, T_1 measurements were carried out at $+20^\circ\text{C}$, -20°C and -50°C resulting in T_1 values of 170, 110 and 100 ms, respectively. Since the T_1 minimum has not been found (for comparison see compounds **28** and **29**), the question that remains is whether a nonclassical octahedral osmium(II) complex, $[\text{OsCl}_2(\text{H}_2)(\text{P}i\text{Pr}_3)(\text{Chiraphos})]$, exists. If treated in 1,2-dichloroethane under reflux, compound **25** reacts with one equivalent of (*S,S*)-Chiraphos to give the bis(chelate) complex **24** in nearly quantitative yield. The ^1H NMR spectrum of **24** displays a complicated symmetrical multiplet for the hydrido ligand at $\delta = -20.27$ ppm; the chemical shift is similar to that of related chloro(hydrido)-metal derivatives with two chelating moieties.^[14]

The reaction of **25** with an excess of NaBH_4 in toluene/methanol does not lead to the (tetrahydrido)osmium(IV) complex $[\text{OsH}_4(\text{P}i\text{Pr}_3)(\text{Chiraphos})]$ (the counterpart of compound **3**) but gives the hydrido(tetrahydroboranato)osmium(II) derivative **26** instead. A mixture of two diastereoisomers **A** and **B**, formed in about equal quantities, is obtained. The white solid is exceedingly air-sensitive and thermally not very stable; slow decomposition occurs even in toluene solution. The ^1H NMR spectrum of **26** shows two sharp doublets of doublets of doublets in the high-field region which are assigned to the metal-bonded proton H^c (see Scheme 6) of the two diastereoisomers. Apart from these sharp signals four rather broadened resonances appear at $\delta = -7.81$, -8.55 , -9.42 and -10.10 ppm which probably belong to the bridging hydrides H^a and H^b . The broadening could be a consequence of the linkage of H^a and H^b to the boron nuclei. Since the spectrum does not change between -20°C and $+30^\circ\text{C}$, we assume that, in contrast to $[\text{OsH}(\kappa^2\text{-H}_2\text{BH}_2)(\text{CO})(\text{P}i\text{Pr}_3)_2]$, the fragment $\text{Os}(\kappa^2\text{-H}_2\text{BH}_2)$ of **26** is rigid in this temperature region and no exchange between the bridging and terminal hydrogens of the BH_4 moiety occurs. The situation is similar to that of the structurally related ruthenium compounds $[\text{RuH}(\kappa^2\text{-H}_2\text{BH}_2)(\text{PR}_3)_3]$ ($\text{PR}_3 = \text{PMePh}_2$, PMe_2Ph), for which a rigid structure has also been proposed.^[15,16]

The reaction of the chloro(hydrido) complex, **24**, with NaBH_4 and methanol in toluene does not yield a hydrido-(tetrahydroboranato) derivative such as **26** but leads to the formation of the dihydridoosmium(II) compound **27** in good yield. Since the ^{31}P NMR spectrum of **27** displays only a singlet at $\delta = 50.9$ ppm, there is no doubt that the four PPh_2 units are chemically and spectroscopically equivalent. Due to this fact, the two hydrides must be in *trans* disposition. This stereochemistry is also supported by the IR spectrum that shows a $\nu(\text{OsH})$ band at relatively low wavenumbers (1730 cm^{-1}). In the IR spectrum of the related complex *trans*- $[\text{OsH}_2(\text{dppe})_2]$, the $\nu(\text{OsH})$ stretching mode is observed at 1721 cm^{-1} .^[15] The ^1H NMR spectrum

of **27** displays a quintet in the high-field region at $\delta = -10.70$ ppm, which equally suggests that the phosphido moieties are equivalent.

To further modify the reactivity of the osmium(II) compounds with Chiraphos as ligands, **24** and **27** were transformed into the cationic $\text{OsCl}(\text{H}_2)$ and $\text{OsH}(\text{H}_2)$ derivatives **28** and **29**, respectively (see Scheme 6). The preparation took place with HBF_4 in diethyl ether at room temperature (for **28**) or at -78°C (for **29**) and gave the products as white solids in 71–83 % yield. Both **28** and **29** are air sensitive but can be stored under argon for days; they do not eliminate H_2 in THF, acetone or chloroform solutions. In the presence of N_2 , no ligand exchange to afford $[\text{OsX}(\text{N}_2)(\text{Chiraphos})_2]\text{BF}_4$ ($\text{X} = \text{Cl}, \text{H}$) occurs. The ^{31}P NMR spectra of **28** and **29** display in each case two triplets for the ^{31}P nuclei of the pairwise equivalent PPh_2 units with $^2J_{\text{P,P}}$ coupling constants that are similar to those of **24**. The ^1H NMR spectrum of **29** shows a broadened signal at $\delta = -6.45$ ppm and a sharp multiplet at $\delta = -8.63$ ppm with the relative intensities of 2:1. By decreasing the temperature, the broadened signal is shifted to the lower-field region, where free dihydrogen resonates. T_1 measurements of the broadened signal resulted in values of 70 ms at 20°C , 60 ms at 0°C , 50 ms at -20°C and 40 ms at -50°C . Although the minimum could not be exactly located in the given range of temperatures, a non-classical $\text{Os}(\text{H}_2)$ structure can be assumed. The $T_1(\text{min})$ value for the well-characterized complex $[\text{OsH}(\text{H}_2)(\text{dppe})_2]^+$ is 18 ms at -85°C .^[17] In contrast to this species, which is dynamic and where an equilibration between the OsH and the $\text{Os}(\text{H}_2)$ protons occurs at room temperature, a similar process could not be observed for **29**. Whether this difference is a result of steric effects, that is, of the larger size of (*S,S*)-Chiraphos compared with dppe, is open to speculation.

Since the preparation of optically active alcohols by catalytic asymmetric transfer hydrogenation of ketones is an important process in organic synthesis,^[18] we were prompted to explore the catalytic activity of some of the chiral ruthenium and osmium complexes prepared in this study. For this purpose, the reduction of acetophenone with 2-propanol was carried out in a mixture of 2-propanol/toluene (2:1) at 85°C under an argon atmosphere. The results are listed in Table 1. In analogous studies, where rhodium, iridium and ruthenium compounds containing chiral phosphane,^[19] amine,^[20] and Schiff-base ligands were used,^[21] the presence of KOH was necessary for the substitution of the halide by a coordinated isopropoxide group; the latter afforded a hydride-metal intermediate by β -elimination. However, for the Chiraphos and Diop complexes **15**–**18** the presence of KOH is not necessary; it does not lead to any significant improvement either in the rate of conversion or in the *ee* values. Although the *ee*'s in general are not very high, the chloro(hydrido) complexes **15** and **16** with Chiraphos as the chelating ligand are more active than the Diop counterparts **17** and **18** and, moreover, than the dihydrido compounds **19**–**22**. The (dihydrido)osmium(II) derivative **20** is not active at all. We note that for **16** and **17** the presence of KOH as cocatalyst changes the chirality of the product,

Table 1. Asymmetric hydrogen transfer from 2-propanol to acetophenone, catalyzed by (hydrido)ruthenium and -osmium complexes

Catalyst	Time	Conversion (%)	<i>ee</i> (%)	Configuration
7	16 h	70	3.5	<i>R</i> -(+)
15	23 h	91	22.6	<i>S</i> -(-)
15/KOH	22 h	85	25.3	<i>S</i> -(-)
16	7 days	85	20	<i>S</i> -(-)
16/KOH	22 h	62	17.4	<i>R</i> -(+)
17	7 h	92	15.4	<i>R</i> -(+)
17/KOH	6 h	85	10.4	<i>S</i> -(-)
18	18 h	94	3.5	<i>R</i> -(+)
18/KOH	40 h	35	1.2	<i>S</i> -(-)
19	16 h	92	6.3	<i>S</i> -(-)
20	not active			
21	24 h	75	3.8	<i>R</i> -(+)
22	45 h	63	1.4	<i>R</i> -(+)
24	not active			
27	not active			
29	not active			

which is not unexpected and in agreement with the general rule.^[22]

Conclusions

The work presented in this paper has shown that in five-coordinate ruthenium(II) and osmium(II) compounds $[\text{MHCl}(\text{CO})(\text{P}i\text{Pr}_3)_2]$ (**1a** and **1b**) either one or both triisopropylphosphane ligands can be replaced by an optically active monophosphane, such as $\text{P}i\text{Pr}_2\text{R}^*$, or by a chiral chelating bisphosphane such as (*S,S*)-Chiraphos or (*S,S*)-Diop. In the isolated octahedral complexes $[\text{MHCl}(\text{CO})(\text{P}i\text{Pr}_2\text{R}^*)_3]$ (**6**, **7**), the *M*–*P* bond *trans* to the hydride is quite labile and thus substitution products $[\text{MHCl}(\text{CO})(\text{L})(\text{P}i\text{Pr}_2\text{R}^*)_2]$ with *L* = CO, $\text{P}(\text{OMe})_3$ and $\text{C}_2(\text{CO}_2\text{Me})_2$ are readily obtained. The reactions of **1a** and **1b** and of the tetrahydroboranato derivatives **2a** and **2b** with (*S,S*)-Chiraphos and (*S,S*)-Diop afford a mixture of two diastereoisomers, the ratio of which depends on the metal, the chiral bisphosphane and the reaction conditions. For the Chiraphos complexes **15**, **16** and **19**, the formation of only one diastereoisomer was observed. With the osmium(IV) compound $[\text{OsH}_2\text{Cl}_2(\text{P}i\text{Pr}_3)_2]$ (**23**) and (*S,S*)-Chiraphos as starting materials, chloro(hydrido)- and (dihydrido)osmium(II) complexes can be prepared and, by treatment with HBF_4 in diethyl ether, transformed into the cationic dihydrogen derivatives **28** and **29**, respectively. Regarding the catalytic potential in the asymmetric transfer hydrogenation of acetophenone with 2-propanol as a hydrogen source, the osmium(II) complexes with two Chiraphos ligands are completely inactive. The catalytic activity of the related ruthenium(II) and osmium(II) compounds **15**–**21** with one chiral chelating ligand is also not very pronounced and could be due to the fact that they are coordinatively saturated, that is, they have an 18-electron count. Although the *trans* influence of the hydride ligand is rather strong, it is probably not strong enough to open the *trans*-disposed co-

ordination site by maintaining the chirality at the metal center. The introduction of optically active tridentate chelating ligands could possibly improve the optical yield but this has to be confirmed by further investigations.

Experimental Section

All operations were carried out under argon using Schlenk techniques. The starting materials **1a**, **1b**,^[1] **2a**, **2b**,^[4] and **23**^[5] were prepared as described in the literature. The chlorophosphanes $R_2P\text{Cl}$, the optically pure amine (*S*)- $H_2NCH(\text{Me})\text{Ph}$ and the chelating phosphanes are commercially available. NMR: Bruker AC 200 and Jeol FX 90 Q. IR: Perkin–Elmer 397 and 1320. Mass spectra: Varian CH 7 MAT (70 eV). Melting points determined by DTA. Abbreviations used: $R^* = (S)\text{-}NHCH(\text{Me})\text{Ph}$; s, singlet; d, doublet; t, triplet; q, quadruplet; quint, quintet; m, multiplet; vt, virtual triplet; br, broadened signal; $N = {}^3J_{\text{P,H}} + {}^5J_{\text{P,H}}$.

Preparation of (*S*)-*i*Pr₂PNHCH(Me)Ph (4**):** A solution of *i*Pr₂PCL (6.1 mL, 40.0 mmol) in diethyl ether (50 mL) was added dropwise to a solution of (*S*)- $H_2NCH(\text{Me})\text{Ph}$ (12.7 mL, 100.0 mmol) in diethyl ether (400 mL) at room temperature. The reaction mixture was stirred for 3 h at 25 °C and then filtered. The separated solid was washed three times with 20 mL portions of diethyl ether, and the combined filtrates were concentrated to about 15 mL in vacuo. The solution was poured into a column (height 5 cm) filled with finely divided SiO₂ and the product was eluted with 200 mL of diethyl ether. The solvent was evaporated in vacuo (20 mbar) and the residue maintained under high vacuum (0.01 mbar) at 70 °C to remove traces of the amine. A clear air-sensitive liquid was obtained; yield 6.8 g (72 %). MS: m/z (I_r) = 237 (10) [M^+]. IR: $\tilde{\nu} = 3370 \text{ v}(\text{NH}) \text{ cm}^{-1}$. ¹H NMR (90 MHz, CDCl₃): $\delta = 7.17$ (m, 5 H, C₆H₅), 4.01 (ddq, ${}^3J_{\text{H,H}} = {}^3J_{\text{H,H}} = {}^3J_{\text{P,H}} = 6.6 \text{ Hz}$, 1 H, NCH), 1.51 (m, 2 H, PCHCH₃), 1.35 (d, ${}^3J_{\text{H,H}} = 6.6 \text{ Hz}$, 3 H, NCHCH₃), 1.05, 1.04 (both m, 3 H each PCHCH₃; both d in off resonance, ${}^3J_{\text{H,H}} = 6.4 \text{ Hz}$), 0.91, 0.88 (both m, 3 H each, PCHCH₃, both d in off resonance, ${}^3J_{\text{H,H}} = 6.9 \text{ Hz}$) ppm; signal of NH proton not exactly located. ³¹P NMR (36.2 MHz, CDCl₃): $\delta = 60.3$ (s) ppm. C₁₄H₂₄NP (237.3): calcd. C 70.85, H 10.19, N 5.90; found C 69.93, H 10.09, N 5.71.

Preparation of (*S*)-*t*Bu₂PNHCH(Me)Ph (5**):** This compound was prepared as described for **4**, with *t*Bu₂PCL (4.5 mL, 25.0 mmol) and (*S*)- $H_2NCH(\text{Me})\text{Ph}$ (8.0 mL, 63.0 mmol) as starting materials. The reaction mixture was refluxed for 10 h and, after cooling to room temperature, worked up as described for **4**. Colorless air-sensitive liquid; yield 4.2 g (64 %). MS: m/z (I_r) = 265 (7; M^+). IR: $\tilde{\nu} = 3380 \text{ v}(\text{NH}) \text{ cm}^{-1}$. ¹H NMR (90 MHz, CDCl₃): $\delta = 7.29$ (m, 5 H, C₆H₅), 4.10 (ddq, ${}^3J_{\text{H,H}} = {}^3J_{\text{H,H}} = {}^3J_{\text{P,H}} = 6.6 \text{ Hz}$, 1 H, NCH), 1.45 (d, ${}^3J_{\text{H,H}} = 6.6 \text{ Hz}$, 3 H, NCHCH₃), 1.13, 0.96 (both d, ${}^3J_{\text{P,H}} = 14.6 \text{ Hz}$, 9 H each, PCCH₃) ppm, signal of the NH proton not exactly located. ³¹P NMR (36.2 MHz, CDCl₃): $\delta = 71.9$ (s) ppm. C₁₆H₂₈NP (265.4): calcd. C 72.42, H 10.63, N 5.28; found C 71.33, H 10.13, N 5.61.

Preparation of *mer*-[RuHCl(CO)(PiPr₂R*)₃] (6**):** A solution of **1a** (500 mg, 1.05 mmol) in benzene (30 mL) was treated dropwise with **4** (1.20 g, 5.05 mmol) and stirred for 2 h at room temperature. The solution was then concentrated to ca. 2 mL in vacuo and methanol (10 mL) was added. The volatile materials were evaporated in vacuo and a white solid precipitated. The solid was filtered, washed three times with 5 mL portions of methanol and dried; yield 617 mg (67 %); m.p. 86 °C (decomp). MS: m/z (I_r) = 612 (1; M^+

– CO–**4**). IR (KBr): $\tilde{\nu} = 3345, 3285, 3230 \text{ v}(\text{NH})$, 1985 $\text{v}(\text{RuH})$, 1890 $\text{v}(\text{CO}) \text{ cm}^{-1}$. ¹H NMR (90 MHz, C₆D₆): $\delta = 7.26$ (m, 15 H, C₆H₅), 4.19 (m, 3 H, NCH), 2.30 (m, 6 H, PCHCH₃), 1.21 (br m, 45 H, NCHCH₃ and PCHCH₃) ppm; signals for RuH and NH protons not exactly located. ³¹P NMR (36.2 MHz, C₆D₆): $\delta = 89.4$ (d, ${}^2J_{\text{P,P}} = 13.2 \text{ Hz}$, two PiPr₂R* in equatorial position), 75.4 (br, PiPr₂R* in axial position) ppm. C₄₃H₇₃ClN₃OP₃Ru (877.5): calcd. C 58.86, H 8.39, N 4.79; found C 59.03, H 8.42, N 4.61.

Preparation of *mer*-[OsHCl(CO)(PiPr₂R*)₃] (7**):** A solution of **1b** (200 mg, 0.35 mmol) in benzene (30 mL) was treated dropwise with **4** (410 mg, 1.73 mmol) and stirred at room temperature until the color of the starting materials disappeared. The solution was then concentrated to ca. 2 mL in vacuo and methanol (10 mL) was added. A white microcrystalline solid precipitated and was filtered, washed three times with 5 mL portions of methanol and dried; yield 240 mg (71 %); m.p. 101 °C (decomp). MS: m/z (I_r) = 730 (1; M^+ – **4**). IR (KBr): $\tilde{\nu} = 3345, 3290, 3245 \text{ v}(\text{NH})$, 2075 $\text{v}(\text{OsH})$, 1885 $\text{v}(\text{CO}) \text{ cm}^{-1}$. ¹H NMR (90 MHz, C₆D₆): $\delta = 7.23$ (m, 15 H, C₆H₅), 4.30 (m, 3 H, NCH), 2.49 (m, 6 H, PCHCH₃), 1.25 (br m, 45 H, NCHCH₃ and PCHCH₃), –8.77 (dt, ${}^2J_{\text{P,H}^{\text{cis}}} = 28.5$, ${}^2J_{\text{P,H}^{\text{trans}}} = 88.6 \text{ Hz}$, 1 H, OsH) ppm; signal for NH proton not exactly located. ³¹P NMR (36.2 MHz, C₆D₆): $\delta = 57.2$ (d, ${}^2J_{\text{P,P}} = 13.9 \text{ Hz}$, two PiPr₂R* in equatorial position), 48.5 (t, ${}^2J_{\text{P,P}} = 13.9 \text{ Hz}$, PiPr₂R* in axial position) ppm. C₄₃H₇₃ClN₃OsP₃ (966.7): calcd. C 53.43, H 6.61, N 4.35; found C 53.15, H 7.44, N 4.18.

Preparation of [RuHCl(CO)₂(PiPr₂R*)₂] (8**):** A slow stream of carbon monoxide was passed for 2 min through a solution of **6** (200 mg, 0.23 mmol) in benzene (10 mL) at room temperature. After the solution was stirred for 30 min at 25 °C, the solvent was evaporated in vacuo, the oily residue was suspended in 5 mL of methanol and the suspension stored at –78 °C. A white solid precipitated and was filtered, washed twice with 3 mL portions of methanol (0 °C) and dried; yield 121 mg (78 %); m.p. 133 °C (decomp). MS: m/z (I_r) = 639 (1; M^+ – CO), 611 (1; M^+ – 2 CO). IR (KBr): $\tilde{\nu} = 3365, 3290 \text{ v}(\text{NH})$, 1970, 1905 $\text{v}(\text{CO}) \text{ cm}^{-1}$. ¹H NMR (90 MHz, C₆D₆): $\delta = 7.14$ (m, 10 H, C₆H₅), 4.16 (m, 2 H, NCH), 2.10 (m, 4 H, PCHCH₃), 1.09 (br m, 30 H, NCHCH₃ and PCHCH₃), –5.47 (t, ${}^2J_{\text{P,H}} = 20.3 \text{ Hz}$, 1 H, RuH) ppm; signal for NH proton not exactly located. ³¹P NMR (36.2 MHz, C₆D₆): $\delta = 94.6$ (s; d in off resonance) ppm. C₃₀H₄₉ClN₂O₂P₂Ru (668.2): calcd. C 53.93, H 7.39, N 4.19; found 53.80, H 7.40, N 3.94.

Preparation of [OsHCl(CO)₂(PiPr₂R*)₂] (9**):** This compound was prepared as described for **8**, using **7** (250 mg, 0.26 mmol) and CO as starting materials. White solid; yield 196 mg (83 %), m.p. 132 °C (decomp). MS: m/z (I_r) = 757 (1; M^+), 729 (1; M^+ – CO). IR (KBr): $\tilde{\nu} = 3380, 3290 \text{ v}(\text{NH})$, 2040 $\text{v}(\text{OsH})$, 1970, 1915 $\text{v}(\text{CO}) \text{ cm}^{-1}$. ¹H NMR (90 MHz, C₆D₆): $\delta = 7.18$ (m, 10 H, C₆H₅), 4.02 (m, 2 H, NCH), 2.16 (m, 4 H, PCHCH₃), 1.35 (br m, 30 H, NCHCH₃ and PCHCH₃), –4.68 (t, ${}^2J_{\text{P,H}} = 20.7 \text{ Hz}$, 1 H, RuH) ppm; signal for NH proton not exactly located. ³¹P NMR (36.2 MHz, C₆D₆): $\delta = 62.5$ (s; d in off resonance) ppm. C₃₀H₄₉ClN₂O₂OsP₂ (757.3): calcd. C 47.59, H 6.52, N 3.69; found C 48.06, H 6.88, N 3.66.

Preparation of [RuHCl(CO){P(OMe)₃}(PiPr₂R*)₂] (10**):** A solution of **6** (220 mg, 0.25 mmol) in hexane (10 mL) was treated with trimethylphosphite (60 μL , 0.51 mmol) and stirred for 30 min at room temperature. The solvent was evaporated in vacuo and a white solid began to precipitate. After the solution was stored at –20 °C for 6 h, the white solid was filtered, washed three times with 3 mL portions of hexane (–20 °C) and dried; yield 130 mg (69 %); m.p. 108

$^{\circ}\text{C}$ (decomp). MS: m/z (I_r) = 764 (1) [M^+], 640 (4; $\text{M}^+ - \text{P}(\text{OMe})_3$). IR (KBr): $\tilde{\nu}$ = 3340, 3290 $\nu(\text{NH})$, 2000 $\nu(\text{RuH})$, 1910 $\nu(\text{CO})$ cm^{-1} . ^1H NMR (90 MHz, C_6D_6): δ = 7.28 (m, 10 H, C_6H_5), 4.03 (m, 2 H, NCH), 3.61 [d, $^3J_{\text{P,H}} = 9.6$ Hz, 9 H, $\text{P}(\text{OMe})_3$], 2.29 (m, 4 H, PCHCH_3), 1.19 (br m, 30 H, NCHCH₃ and PCHCH_3), -6.86 (dt, $^2J_{\text{P,Hcis}} = 25.3$, $^2J_{\text{P,Htrans}} = 193.1$ Hz, 1 H, RuH) ppm; signal for NH proton not exactly located. ^{31}P NMR (36.2 MHz, C_6D_6): ABX spin system; AB part consists of four signals at δ = 93.5, 93.3, 92.7, 92.5 ppm and corresponds to two PiPr_2R^* ligands; X part consists of three signals at δ = 133.3, 132.7, 132.0 ppm and corresponds to the $\text{P}(\text{OMe})_3$ ligand. $\text{C}_{32}\text{H}_{58}\text{ClN}_2\text{O}_4\text{P}_3\text{Ru}$ (764.3): calcd. C 40.29, H 7.65, N 3.67; found C 50.53, H 7.91, N 3.43.

Preparation of $[\text{OsHCl}(\text{CO})\{\text{P}(\text{OMe})_3\}(\text{PiPr}_2\text{R}^*)_2]$ (11): This compound was prepared as described for **10**, with **7** (250 mg, 0.26 mmol) and trimethylphosphite (62 μL , 0.52 mmol) as starting materials. White solid; yield 160 mg (72 %); m.p. 111 $^{\circ}\text{C}$ (decomp). MS: m/z (I_r) = 854 (1; M^+), 730 [5; $\text{M}^+ - \text{P}(\text{OMe})_3$]. IR (KBr): $\tilde{\nu}$ = 3345, 3270 $\nu(\text{NH})$, 2080 $\nu(\text{OsH})$, 1890 $\nu(\text{CO})$ cm^{-1} . ^1H NMR (90 MHz, C_6D_6): δ = 7.30 (m, 10 H, C_6H_5), 4.20 (m, 2 H, NCH), 3.59 [d, $^3J_{\text{P,H}} = 10.0$ Hz, 9 H, $\text{P}(\text{OMe})_3$], 2.41 (m, 4 H, PCHCH_3), 1.17 (br m, 30 H, NCHCH₃ and PCHCH_3), -6.89 (dt, $^2J_{\text{P,Hcis}} = 25.1$, $^2J_{\text{P,Htrans}} = 151.7$ Hz, 1 H, RuH) ppm; signal for NH proton not exactly located. ^{31}P NMR (36.2 MHz, C_6D_6): ABX spin system; AB part consists of four signals at δ = 61.6, 61.5, 61.4, 60.9 ppm and corresponds to two PiPr_2R^* ligands; X part consists of three signals at δ = 101.6, 101.0, 100.4 ppm and corresponds to the $\text{P}(\text{OMe})_3$ ligand. $\text{C}_{32}\text{H}_{58}\text{ClN}_2\text{O}_4\text{OsP}_3$ (853.4): calcd. C 45.04, H 6.85, N 3.28; found C 45.19, H 6.88, N 3.33.

Preparation of $[\text{OsHCl}(\text{CO})\{\text{C}_2(\text{CO}_2\text{Me})_2\}(\text{PiPr}_2\text{R}^*)_2]$ (12): This compound was prepared as described for **10**, with **7** (200 mg, 0.21 mmol) and $\text{C}_2(\text{CO}_2\text{Me})_2$ (30 μL , 0.25 mmol) as starting materials. White solid; yield 145 mg (80 %); m.p. 76 $^{\circ}\text{C}$ (decomp). MS: m/z (I_r) = 872 (1; M^+), 730 [7; $\text{M}^+ - \text{C}_2(\text{CO}_2\text{Me})_2$]. IR (KBr): $\tilde{\nu}$ = 3270 $\nu(\text{NH})$, 2100 $\nu(\text{OsH})$, 1930 $\nu(\text{CO})$, 1790 $\nu(\text{C}\equiv\text{C})$, 1695 $\nu(\text{C}=\text{O})$ cm^{-1} . ^1H NMR (90 MHz, C_6D_6): δ = 7.29 (m, 10 H, C_6H_5), 5.02 (dd, $^2J_{\text{P,H}} = ^2J_{\text{H,H}} = 9.2$ Hz, 1 H, NH), 4.72 (dd, $^2J_{\text{P,H}} = ^2J_{\text{H,H}} = 10.6$ Hz, 1 H, NH), 4.25 (m, 2 H, NCH), 3.58 (s, 6 H, CO_2CH_3), 2.59 (m, 4 H, PCHCH_3), 1.56, 1.49 (both d, $^2J_{\text{H,H}} = 6.8$ Hz, 3 H, each, NCHCH₃), 1.01 (m, 24 H, PCHCH_3), -3.49 (t, $^2J_{\text{P,H}} = 31.8$ Hz, 1 H, OsH) ppm. ^{31}P NMR (36.2 MHz, C_6D_6): AB spin system; $\delta_{\text{PA}} = 65.7$, $\delta_{\text{PB}} = 61.8$ ppm, $^2J_{\text{PA,PB}} = 132.2$ Hz; d in off resonance. $\text{C}_{35}\text{H}_{55}\text{ClN}_2\text{O}_5\text{OsP}_2$ (871.4): calcd. C 48.24, H 6.36, N 3.21; found C 48.63, H 6.51, N 3.08.

Preparation of $[\text{OsH}_4(\text{CO})(\text{PiPr}_2\text{R}^*)_2]$ (13): A solution of **7** (300 mg, 0.31 mmol) in benzene (10 mL) was first treated with NaBH_4 (150 mg, 3.95 mmol) and subsequently dropwise with methanol (1 mL). The solution was filtered and the filtrate concentrated to ca. 0.5 mL in vacuo. The residue was extracted twice with 8 mL portions of hexane and the combined extracts were dried in vacuo. The oily residue was suspended in 6 mL of methanol and the suspension stored for 12 h at -78 $^{\circ}\text{C}$. A light yellow, extremely air-sensitive solid precipitated and was filtered, washed twice with 3 mL portions of methanol (-20 $^{\circ}\text{C}$) and dried; yield 108 mg (51 %). IR (C_6H_6): $\tilde{\nu}$ = 3250 $\nu(\text{NH})$, 2030, 1965 $\nu(\text{OsH})$, 1890 $\nu(\text{CO})$ cm^{-1} . ^1H NMR (90 MHz, C_6D_6): δ = 7.20 (m, 10 H, C_6H_5), 4.46 (m, 2 H, NCH), 1.50 (m, 4 H, PCHCH_3), 1.19 (d, $^2J_{\text{H,H}} = 6.8$ Hz, 6 H, NCHCH₃), 0.82 (m, 24 H, PCHCH_3), -8.76 (t, $^2J_{\text{P,H}} = 9.8$ Hz, 4 H, OsH₄) ppm; the signal for the NH protons not exactly located. ^{31}P NMR (36.2 MHz, C_6D_6): δ = 87.4 (s; quint in off resonance) ppm.

Preparation of $[\text{OsHCl}(\text{CO})(\text{PiPr}_3)(\text{dppe})]$ (14): A solution of **1b** (125 mg, 0.22 mmol) in hexane (15 mL) was treated with dppe

(95 mg, 0.24 mmol) and stirred for 24 h under reflux. A white solid precipitated and once the reaction mixture was cooled to room temperature, it was filtered and then washed three times with 8 mL portions of hexane. Recrystallization from benzene/hexane (1:3) gave white air-stable crystals; yield 143 mg (80 %). IR (Nujol): $\tilde{\nu}$ = 2065 $\nu(\text{OsH})$, 1895 $\nu(\text{CO})$ cm^{-1} . ^1H NMR (90 MHz, C_6D_6): δ = 7.47 (m, 10 H, C_6H_5), 3.01 (m, 4 H, PCH_2), 2.53 (m, 3 H, PCHCH_3), 1.21, 0.99 (both dvt, $N = 12.0$, $^3J_{\text{H,H}} = 7.1$ Hz, 9 H each, PCHCH_3), -6.93 (ddd, $2 \times ^2J_{\text{P,Hcis}} = 17.3$, $^2J_{\text{P,Htrans}} = 93.2$ Hz, 1 H, OsH) ppm. ^{31}P NMR (36.2 MHz, C_6D_6): ABX spin system; $\delta_{\text{PA}} = 39.6$ ppm, $\delta_{\text{PB}} = 29.4$ ppm, $^2J_{\text{PA,PB}} = 250.6$ Hz; $\delta_{\text{PX}} = 13.8$ ppm, $^2J_{\text{PA,PX}} = 6.7$ Hz, $^2J_{\text{PB,PX}} = 13.8$ Hz. $\text{C}_{36}\text{H}_{46}\text{ClOOP}_3$ (813.3): calcd. C 53.16, H 5.70; found C 52.91, H 5.61.

Preparation of $[\text{RuHCl}(\text{CO})(\text{PiPr}_3)(\text{Chiraphos})]$ (15): This compound was prepared as described for **14**, with **1a** (150 mg, 0.31 mmol) and (*S,S*)-Chiraphos (135 mg, 0.32 mmol) as starting materials. White solid; yield 233 mg (79 %); m.p. 150 $^{\circ}\text{C}$ (decomp). IR (Nujol): $\tilde{\nu}$ = 1920 $\nu(\text{CO})$ cm^{-1} . ^1H NMR (90 MHz, C_6D_6): δ = 7.71 (m, 20 H, C_6H_5), 3.91, 2.13 (both m, 1 H each, Ph_2PCH), 2.43 (m, 3 H, PCHCH_3), 1.18, 0.91 (both m, 9 H each, PCHCH_3 ; both d in off resonance, $^3J_{\text{H,H}} = 7.1$ Hz), -6.61 (ddd, $^2J_{\text{P,Hcis}} = 17.9$ and 22.2, $^2J_{\text{P,Htrans}} = 113.1$ Hz, 1 H, RuH) ppm; signals for Ph_2CHCH_3 protons partly covered by signals of PCHCH_3 protons. ^{31}P NMR (36.2 MHz, C_6D_6): ABX spin system; AB part consists of four signals at δ = 54.5, 54.0, 53.8, 53.5 ppm and corresponds to the ^{31}P nuclei of Chiraphos; X part also consists of four signals at δ = 42.6, 42.3, 42.2, 41.9 ppm and corresponds to the ^{31}P nuclei of the PiPr_3 ligand. $\text{C}_{38}\text{H}_{50}\text{ClOP}_3\text{Ru}$ (752.3): calcd. C 60.67, H 7.00; found C 60.45, H 6.70.

Preparation of $[\text{OsHCl}(\text{CO})(\text{PiPr}_3)(\text{Chiraphos})]$ (16): This compound was prepared as described for **14**, with **1b** (150 mg, 0.26 mmol) and (*S,S*)-Chiraphos (115 mg, 0.27 mmol) as starting materials. White solid; yield 180 mg (82 %); m.p. 197 $^{\circ}\text{C}$ (decomp). IR (Nujol): $\tilde{\nu}$ = 2030 $\nu(\text{OsH})$, 1920 $\nu(\text{CO})$ cm^{-1} . ^1H NMR (90 MHz, C_6D_6): δ = 7.78 (m, 20 H, C_6H_5), 3.67, 2.11 (both m, 1 H each, Ph_2PCH), 2.43 (m, 3 H, PCHCH_3), 1.14, 0.94 (both m, 9 H each, PCHCH_3 ; both d in off resonance, $^3J_{\text{H,H}} = 6.8$ Hz), -6.69 (ddd, $2 \times ^2J_{\text{P,Hcis}} = 19.1$, $^2J_{\text{P,Htrans}} = 113.3$ Hz, 1 H, OsH) ppm; signals for Ph_2CHCH_3 protons partly covered by signals of PCHCH_3 protons. ^{31}P NMR (36.2 MHz, C_6D_6): ABX spin system; AB part consists of three signals at δ = 24.4, 24.2, 24.1 ppm and corresponds to the ^{31}P nuclei of Chiraphos; X part consists of four signals at δ = 20.4, 20.3, 20.2, 20.0 ppm and corresponds to the ^{31}P nuclei of the PiPr_3 ligand. $\text{C}_{38}\text{H}_{50}\text{ClOOP}_3$ (841.4): calcd. C 54.25, H 5.99; found C 54.14, H 5.93.

Preparation of $[\text{RuHCl}(\text{CO})(\text{PiPr}_3)(\text{Diop})]$ (17): (a) A solution of **1a** (125 mg, 0.26 mmol) in hexane (15 mL) was treated with (*S,S*)-Diop (140 mg, 0.28 mmol) and stirred for 24 h under reflux. After the reaction mixture was cooled to room temperature, the white solid was filtered, washed three times with 8 mL portions of hexane, then with 5 mL of methanol and dried; yield 174 mg (81 %). Owing to the NMR spectra, two diastereoisomers **A** and **B** in the ratio of 7:1 were formed and could not be separated by fractional crystallization or column chromatography. (b) Analogously **1a** (180 mg, 0.37 mmol) was reacted with (*S,S*)-Diop (190 mg, 0.38 mmol) in hexane (15 mL) for 5 days under reflux. Under these conditions, only diastereoisomer **A** was obtained as a white solid; yield 250 mg (82 %); m.p. 143 $^{\circ}\text{C}$ (decomp). IR (Nujol): $\tilde{\nu}$ = 2000 $\nu(\text{RuH})$, 1920 $\nu(\text{CO})$ cm^{-1} . ^1H NMR (90 MHz, C_6D_6) diastereomer **A**: δ = -6.14 (ddd, $^2J_{\text{P,Hcis}} = 16.3$ and 27.1, $^2J_{\text{P,Htrans}} = 109.1$ Hz, 1 H, RuH) ppm; diastereomer **B**: δ = -6.71 (ddd,

$^2J_{\text{P,Hcis}} = 17.7$ and 26.1 , $^2J_{\text{P,Htrans}} = 116.1$ Hz, 1 H, RuH) ppm; all other signals for $\delta = 0-9$ ppm overlap and cannot be exactly assigned. ^{31}P NMR (36.2 MHz, C_6D_6) diastereomer **A**: ABX spin system; $\delta_{\text{PA}} = 50.2$, $\delta_{\text{PB}} = 21.2$ ppm, $^2J_{\text{PA,PB}} = 267.2$ Hz; $\delta_{\text{PX}} = 7.1$ ppm, $^2J_{\text{PA,PX}} = 18.0$, $^2J_{\text{PB,PX}} = 11.2$ Hz; diastereomer **B**: ABX spin system; $\delta_{\text{PA}} = 52.8$, $\delta_{\text{PB}} = 23.1$ ppm, $^2J_{\text{PA,PB}} = 267.4$ Hz; $\delta_{\text{PX}} = -3.5$, $^2J_{\text{PA,PX}} = 17.6$, $^2J_{\text{PB,PX}} = 11.6$ Hz. $\text{C}_{41}\text{H}_{54}\text{ClO}_3\text{P}_3\text{Ru}$ (824.3): calcd. C 59.74, H 6.60; found C 59.91, H 6.79.

Preparation of $[\text{OsHCl}(\text{CO})(\text{PiPr}_3)(\text{Diop})]$ (18**):** This compound was prepared as described for **17**, with (a) **1b** (130 mg, 0.23 mmol) and (*S,S*)-Diop (123 mg, 0.25 mmol) or (b) **1b** (215 mg, 0.37 mmol) and (*S,S*)-Diop (195 mg, 0.39 mmol) as starting materials. White solid; yield 187 mg (89 %) for (a) and 307 mg (91 %) for (b). Owing to the NMR spectra, following route "a" the ratio of the two diastereomers **A** and **B** was 3:2 and following route "b" the ratio was 1:1. IR (Nujol): $\tilde{\nu} = 2055$ $\nu(\text{OsH})$, 1905 and 1895 $\nu(\text{CO})$ cm^{-1} . ^1H NMR (90 MHz, C_6D_6) diastereomer **A**: $\delta = -6.09$ (ddd, $^2J_{\text{P,Hcis}} = 18.4$ and 24.1 , $^2J_{\text{P,Htrans}} = 88.3$ Hz, 1 H, OsH) ppm; diastereomer **B**: $\delta = -6.74$ (ddd, $^2J_{\text{P,Hcis}} = 19.9$ and 28.2 , $^2J_{\text{P,Htrans}} = 96.2$ Hz, 1 H, OsH) ppm; all other signals for $\delta = 0-9$ ppm strongly overlap and cannot be assigned to one of the diastereomers. ^{31}P NMR (36.2 MHz, C_6D_6) diastereomer **A**: ABX spin system; $\delta_{\text{PA}} = 17.8$, $\delta_{\text{PB}} = -12.3$ ppm, $^2J_{\text{PA,PB}} = 243.2$ Hz; $\delta_{\text{PX}} = -18.9$ ppm, $^2J_{\text{PA,PX}} = 15.2$, $^2J_{\text{PB,PX}} = 3.8$ Hz; diastereomer **B**: ABX spin system; $\delta_{\text{PA}} = 19.6$, $\delta_{\text{PB}} = -9.0$ ppm, $^2J_{\text{PA,PB}} = 242.1$ Hz; $\delta_{\text{PX}} = -29.2$ ppm, $^2J_{\text{PA,PX}} = 17.5$, $^2J_{\text{PB,PX}} = 4.1$ Hz. $\text{C}_{41}\text{H}_{54}\text{ClO}_3\text{OsP}_3$ (913.5): calcd. C 53.91, H 6.02; found C 53.99, H 6.18.

Preparation of $[\text{RuH}_2(\text{CO})(\text{PiPr}_3)(\text{Chiraphos})]$ (19**):** A solution of **2a** (145 mg, 0.31 mmol) in methanol (15 mL) was treated with (*S,S*)-Chiraphos (140 mg, 0.33 mmol) and stirred for 24 h under reflux. After the solution was cooled to room temperature, it was concentrated to ca. 5 mL in vacuo. A white solid precipitated and was filtered, washed three times with 5 mL portions of methanol and dried. Recrystallization from dichloromethane/methanol (1:3) gave white, moderately air-sensitive crystals; yield 170 mg (76 %). IR (Nujol): $\tilde{\nu} = 1940$ $\nu(\text{RuH})$, 1930 $\nu(\text{CO})$ cm^{-1} . ^1H NMR (200 MHz, C_6D_6): $\delta = 7.68$ (m, 20 H, C_6H_5), 2.20, 1.83 (both m, 1 H each, Ph_2PCH), 1.79 (m, 3 H, PCHCH_3), 1.28 (dd, $^3J_{\text{P,H}} = 13.5$, $^3J_{\text{H,H}} = 7.0$ Hz, 9 H, PCHCH_3), 0.98 (dd, $^3J_{\text{P,H}} = 11.6$, $^3J_{\text{H,H}} = 7.0$ Hz, 9 H, PCHCH_3), -8.15 (dddd, $2 \times ^2J_{\text{P,Hcis}} = 20.2$, $1 \times ^2J_{\text{P,Hcis}} = 30.4$, $^2J_{\text{H,H}} = 4.1$ Hz, 1 H, RuH *trans* to CO), -8.76 (dddd, $2 \times ^2J_{\text{P,Hcis}} = 18.9$, $^2J_{\text{P,Htrans}} = 77.4$, $^2J_{\text{H,H}} = 4.1$ Hz, 1 H, RuH *trans* to PPh_2) ppm; signals for $\text{Ph}_2\text{PCHCH}_3$ protons partly covered by signals for PiPr_3 protons. ^{31}P NMR (81.0 MHz, C_6D_6): ABX spin system; $\delta_{\text{PA}} = 84.3$, $\delta_{\text{PB}} = 77.7$ ppm, $^2J_{\text{PA,PB}} = 216.2$ Hz; $\delta_{\text{PX}} = 68.1$ ppm, $^2J_{\text{PA,PX}} = 13.4$, $^2J_{\text{PB,PX}} = 17.4$ Hz. $\text{C}_{38}\text{H}_{51}\text{OP}_3\text{Ru}$ (717.8): calcd. C 63.58, H 7.16; found C 63.62, H 7.48.

Preparation of $[\text{OsH}_2(\text{CO})(\text{PiPr}_3)(\text{Chiraphos})]$ (20**):** This compound was prepared as described for **19**, with **2b** (150 mg, 0.27 mmol) and (*S,S*)-Chiraphos (125 mg, 0.29 mmol) as starting materials. White solid; yield 181 mg (83 %). Owing to the NMR spectra, one diastereomer was mainly obtained. The amount of the second isomer (data not given) was less than 10 %. IR (Nujol): $\tilde{\nu} = 1950$ $\nu(\text{OsH})$, 1860 $\nu(\text{CO})$ cm^{-1} . ^1H NMR (200 MHz, C_6D_6): $\delta = 7.64$ (m, 20 H, C_6H_5), 2.25, 1.95 (both m, 1 H each, Ph_2PCH), 2.43 (m, 3 H, PCHCH_3), 1.26 (dd, $^3J_{\text{P,H}} = 13.4$, $^3J_{\text{H,H}} = 6.9$ Hz, 9 H, PCHCH_3), 0.95 (dd, $^3J_{\text{P,H}} = 11.5$, $^3J_{\text{H,H}} = 6.9$ Hz, 9 H, PCHCH_3), -9.32 (dddd, $3 \times ^2J_{\text{P,Hcis}} = 21.4$, $^2J_{\text{H,H}} = 4.2$ Hz, 1 H, OsH *trans* to CO), -10.04 (dddd, $2 \times ^2J_{\text{P,Hcis}} = 21.4$, $^2J_{\text{P,Htrans}} = 62.1$, $^2J_{\text{H,H}} = 4.2$ Hz, 1 H, OsH *trans* to PPh_2) ppm; signals for $\text{Ph}_2\text{PCHCH}_3$ protons partly covered by signals for PiPr_3 protons. ^{31}P NMR (81.0 MHz, C_6D_6): ABX spin system; $\delta_{\text{PA}} = 48.5$, $\delta_{\text{PB}} =$

40.9 ppm, $^2J_{\text{PA,PB}} = 207.0$ Hz; $\delta_{\text{PX}} = 35.9$ (br) ppm, $^2J_{\text{PB,PX}} = 13.9$ Hz. $\text{C}_{38}\text{H}_{51}\text{OOS}_2\text{P}_3$ (807.0): calcd. C 56.56, H 6.37; found C 57.19, H 6.84.

Preparation of $[\text{RuH}_2(\text{CO})(\text{PiPr}_3)(\text{Diop})]$ (21**):** This compound was prepared as described for **19**, with **2a** (130 mg, 0.28 mmol) and (*S,S*)-Diop (150 mg, 0.30 mmol) as starting materials. White solid; yield 170 mg (77 %). Owing to the ^{31}P NMR spectrum, two diastereomers **A** and **B** in the ratio of 3:2 were obtained. IR (Nujol): $\tilde{\nu} = 1945$ $\nu(\text{RuH})$, 1860 $\nu(\text{CO})$ cm^{-1} . ^{31}P NMR (81.0 MHz, C_6D_6) diastereomer **A**: ABX spin system; $\delta_{\text{PA}} = 73.9$, $\delta_{\text{PB}} = 42.4$ ppm, $^2J_{\text{PA,PB}} = 212.1$ Hz; $\delta_{\text{PX}} = 27.5$ (br) ppm, $^2J_{\text{PA,PX}} = 18.0$, $^2J_{\text{PB,PX}} = -15.6$ Hz; diastereomer **B**: ABX spin system; $\delta_{\text{PA}} = 72.0$, $\delta_{\text{PB}} = 44.2$ ppm, $^2J_{\text{PA,PB}} = 209.8$ Hz; $\delta_{\text{PX}} = 22.7$ (br) ppm, $^2J_{\text{PA,PX}} = -6.1$, $^2J_{\text{PB,PX}} = 39.1$ Hz. $\text{C}_{41}\text{H}_{55}\text{OP}_3\text{Ru}$ (789.9): calcd. C 62.35, H 7.02; found C 62.20, H 7.13.

Preparation of $[\{\text{OsH}_2(\text{CO})(\text{PiPr}_3)_2(\mu\text{-Diop})\}]$ (22**):** This compound was prepared as described for **19**, with **2b** (155 mg, 0.28 mmol) and (*S,S*)-Diop (160 mg, 0.32 mmol) as starting materials. White solid; yield 183 mg (81 %). IR (Nujol): $\tilde{\nu} = 1930$ $\nu(\text{OsH})$, 1835 $\nu(\text{CO})$ cm^{-1} . ^1H NMR (200 MHz, C_6D_6): $\delta = -9.34$ (ddt, $2 \times ^2J_{\text{P,Hcis}} = 24.3$, $^3J_{\text{H,H}} = 5.0$ Hz, 2 H, OsH *trans* to CO), -11.56 (ddt, $2 \times ^2J_{\text{P,Hcis}} = 30.4$, $^2J_{\text{P,Htrans}} = 61.8$, $^2J_{\text{H,H}} = 5.0$ Hz, 2 H, OsH *trans* to PPh_2) ppm; all other signals for $\delta = 0-9$ ppm strongly overlap and cannot be assigned. ^{31}P NMR (36.2 MHz, C_6D_6): $\delta = 30.4$ (d, $^2J_{\text{P,P}} = 11.2$ Hz, PiPr_3), -2.8 (t, $^2J_{\text{P,P}} = 11.2$ Hz, Diop) ppm. $\text{C}_{69}\text{H}_{120}\text{O}_4\text{Os}_2\text{P}_6$ (1580.0): calcd. C 52.45, H 7.65; found C 51.91, H 7.13.

Preparation of *trans*- $[\text{OsHCl}(\text{Chiraphos})_2]$ (24**):** A solution of **23** (300 mg, 0.51 mmol) in dichloromethane (20 mL) was treated with (*S,S*)-Chiraphos (470 mg, 1.10 mmol) and stirred for 24 h under reflux. After the solution was cooled to room temperature, the solvent was evaporated in vacuo and the oily residue suspended in methanol (10 mL). The suspension was stored for 2 h and led to the precipitation of a pale yellow solid. This was separated from the mother liquor, washed twice with 5 mL portions of methanol and 5 mL portions of hexane and dried; yield 490 mg (89 %). IR (Nujol): $\tilde{\nu} = 2085$ $\nu(\text{OsH})$ cm^{-1} . ^1H NMR (200 MHz, C_6D_6): $\delta = 7.36$ (m, 40 H, C_6H_5), 3.31, 1.85 (both m, 2 H each, Ph_2PCH), 0.88, 0.52 (both dvt, $N = 12.0$, $^3J_{\text{H,H}} = 6.1$ Hz, 6 H each, Ph_2CHCH_3), -20.27 (m, 1 H, OsH) ppm. ^{31}P NMR (81.0 MHz, C_6D_6): $\delta = 42.3$, 16.8 (both t, $^2J_{\text{P,P}} = 21.0$ Hz) ppm. $\text{C}_{56}\text{H}_{57}\text{ClOsP}_4$ (1079.6): calcd. C 62.30, H 5.32; found C 62.35, H 5.75.

Preparation of $[\text{OsH}_2\text{Cl}_2(\text{PiPr}_3)(\text{Chiraphos})]$ (25**):** A suspension of **23** (160 mg, 0.27 mmol) in hexane (20 mL) was treated with (*S,S*)-Chiraphos (117 mg, 0.27 mmol) and stirred for 10 h under reflux. After the solution was cooled to room temperature, the yellow-brown solid was filtered, washed twice with 5 mL portions of hexane and recrystallized from benzene/hexane (1:3); yield 174 mg (76 %). ^1H NMR (200 MHz, C_6D_6): $\delta = 7.50$ (m, 20 H, C_6H_5), 4.02, 2.47 (both m, 5 H, PCH), 1.08 (br m, 24 H, PCHCH_3 and $\text{Ph}_2\text{PCHCH}_3$), -10.28 (ddd, $3 \times ^2J_{\text{P,H}} = 15.1$ Hz, 2 H, OsH_2) ppm; $T_1 = 170$ ms (20 °C), 110 ms (−20 °C), 100 ms (−50 °C). ^{31}P NMR (36.2 MHz, C_6D_6): ABX spin system; $\delta_{\text{PA}} = 1.4$, $\delta_{\text{PB}} = 12.3$ ppm, $^2J_{\text{PA,PB}} = 288.7$ Hz; $\delta_{\text{PX}} = 31.2$ ppm, $^2J_{\text{PA,PX}} = 6.2$, $^2J_{\text{PB,PX}} = 17.2$ Hz. $\text{C}_{37}\text{H}_{51}\text{Cl}_2\text{OsP}_3$ (848.9): calcd. C 52.26, H 6.05; found C 52.26, H 5.97.

Preparation of $[\text{OsH}(\kappa^2\text{-H}_2\text{BH}_2)(\text{PiPr}_3)(\text{Chiraphos})]$ (26**):** A solution of **25** (150 mg, 0.18 mmol) in toluene (10 mL) was first treated with NaBH_4 (65 mg, 1.70 mmol) and then dropwise with 1 mL of methanol. After the evaporation of gas (H_2) had stopped, the solution was stirred for 15 min at room temperature and then filtered.

The filtrate was concentrated to ca. 5 mL in vacuo and methanol (8 mL) was added. A white solid precipitated and was filtered, washed twice with 2 mL portions of methanol (0 °C) and dried; yield 97 mg (68 %). Owing to the NMR spectroscopic data, a mixture of the two diastereoisomers in about equal amounts was obtained. Attempts to separate the two diastereoisomers by fractional crystallization from benzene/methanol failed. IR (Nujol): $\tilde{\nu}$ = 2450, 2380 br $\nu(\text{BH})$, 2070 $\nu(\text{OsH})$ cm^{-1} . ^1H NMR (200 MHz, C_6D_6): δ = −7.81, −8.55 (both br, 1 H each, H^a of isomer A or B), −9.42, −10.10 (both br, 1 H each, H^b of isomer A or B), −16.71 (ddd, $2 \times {}^2J_{\text{P,Hcis}}$ = 16.0, $1 \times {}^2J_{\text{P,Hcis}}$ = 31.0 Hz, 1 H, H^c of isomer A or B), −17.40 (ddd, $3 \times {}^2J_{\text{P,Hcis}}$ = 23.0 Hz, 1 H, H^c of isomer A or B) ppm; signal of H^t not observed; all other signals for δ = 0–9 ppm overlap and cannot be assigned; for assignment of H^a , H^b , H^c , H^t see Scheme 6. $\text{C}_{37}\text{H}_{54}\text{BOsP}_3$ (792.8): calcd. C 56.06, H 6.87; found C 56.39, H 7.38.

Preparation of *trans*-[OsH₂(Chiraphos)₂] (27): This compound was prepared as described for **26**, with **24** (180 mg, 0.17 mmol), NaBH_4 (65 mg, 1.70 mmol) and methanol (1 mL) as starting materials. White solid; yield 109 mg (61 %). IR (Nujol): $\tilde{\nu}$ = 1730 br $\nu(\text{OsH})$ cm^{-1} . ^1H NMR (200 MHz, C_6D_6): δ = 7.73 (m, 40 H, C_6H_5), 2.25 (br, 4 H, Ph_2PCH), 0.96 (br, 12 H, $\text{Ph}_2\text{PCHCH}_3$), −10.70 (quint, ${}^2J_{\text{P,H}}$ = 16.2 Hz, 2 H, OsH_2) ppm. ^{31}P NMR (81.0 MHz, C_6D_6): δ = 50.9 (s) ppm. $\text{C}_{56}\text{H}_{58}\text{OsP}_4$ (1045.2) calcd. C 64.35, H 5.56; found C 63.95, H 5.62.

Preparation of *trans*-[OsCl(H₂)(Chiraphos)₂]BF₄ (28): A suspension of **24** (90 mg, 0.08 mmol) in diethyl ether (10 mL) was treated with a solution of HBF_4 in diethyl ether (15 μL , 0.11 mmol) and stirred for 20 min at room temperature. The mother liquor was decanted, the precipitate was dissolved in dichloromethane (5 mL) and the solution was filtered. The filtrate was concentrated to ca. 1 mL in vacuo and diethyl ether (10 mL) was added. A white solid precipitated and was filtered, washed twice with 5 mL portions of diethyl ether (0 °C) and dried; yield 80 mg (83 %). ^1H NMR (200 MHz, CDCl_3): δ = 7.25 (m, 40 H, C_6H_5), 3.09, 1.81 (both m, 2 H each, Ph_2PCH), 0.89, 0.37 (both dvt, N = 12.0, ${}^3J_{\text{H,H}}$ = 6.1 Hz, 6 H each, $\text{Ph}_2\text{PCHCH}_3$), −11.62, (br, 2 H, OsH_2) ppm; T_1 = 110 ms (20 °C). ^{31}P NMR (81.0 MHz, CDCl_3): δ = 34.9, 2.0 (both t, ${}^2J_{\text{P,P}}$ = 17.3 Hz) ppm. $\text{C}_{56}\text{H}_{58}\text{BClF}_4\text{OsP}_4$ (1167.4): calcd. C 57.62, H 5.01; found C 57.24, H 5.16.

Preparation of *trans*-[OsH(H₂)(Chiraphos)₂]BF₄ (29): A solution of HBF_4 in diethyl ether (25 μL , 0.18 mmol) was added dropwise to a suspension of **27** (140 mg, 0.13 mmol) in diethyl ether (10 mL) under an H_2 atmosphere at −78 °C. After the solution was warmed to room temperature, it was stirred for 10 min and then filtered. The white solid was washed twice with 2 mL portions of diethyl ether (0 °C) and then recrystallized from dichloromethane/diethyl ether (1:5); yield 107 mg (71 %). IR (Nujol): $\tilde{\nu}$ = 2010 $\nu(\text{OsH})$ cm^{-1} . ^1H NMR (200 MHz, CDCl_3): δ = 7.63 (m, 40 H, C_6H_5), 2.24, 2.13 (both m, 2 H each, Ph_2PCH), 0.98 (br m, 12 H, $\text{Ph}_2\text{PCHCH}_3$), −6.45, (br, 2 H, OsH_2), −8.63 (m, 1 H, OsH) ppm; T_1 = 70 ms (20 °C), 60 ms (0 °C), 50 ms (−20 °C), 40 ms (−50 °C). ^{31}P NMR (81.0 MHz, CDCl_3): δ = 42.0, 36.0 (both t, ${}^2J_{\text{P,P}}$ = 19.0 Hz). $\text{C}_{56}\text{H}_{59}\text{BF}_4\text{OsP}_4$ (1133.0): calcd. C 59.37, H 5.25; found C 59.33, H 5.15.

Hydrogen-Transfer Reactions: The catalytic reactions were carried out under an argon atmosphere in a mixture of 2-propanol/toluene (2:1), with magnetic stirring, in a 50 mL round-bottomed flask fitted with a condenser and provided with a serum cap. In a typical procedure, a solution of the catalyst (0.1 mmol) in 12.5 mL of toluene and 12.5 mL of 2-propanol was stirred for 1 h at 85 °C, and

then a solution of acetophenone (10 mmol) in 12.5 mL of 2-propanol was injected. The progress of the reaction was monitored by a Perkin–Elmer 8900 gas chromatograph with a flame ionization detector and an FFAP on Chromosorb GHP 80/100 mesh column (3.6 $\times$ 1/8 in.) at 160 °C. The solvents were evaporated in vacuo, and the remaining mixture (alcohol and ketone) was isolated by distillation at reduced pressure. The *ee* was calculated from its optical rotation in ethanol solution, using a value of $[\alpha]_D^{25} = +42.9$ (undil.)^[23] for the (*R*)-(+)-1-phenylethanol isomer, and corrected to the composition of the distillate. Optical rotations were measured with a Perkin–Elmer 241 polarimeter. For reactions carried out in the presence of KOH as cocatalyst, a 0.1 M solution of KOH (3 mL) in 2-propanol was added to the solution of the catalyst.

X-ray Structure Determination of Compound 22: Single crystals of **22** were grown by slow diffusion of hexane into a solution of **22** in 1,2-dichloroethane at room temperature. Crystal data (from 62 reflections, $2.4^\circ < \theta < 18.36^\circ$): monoclinic, space group $P2_1$ (No. 4); a = 11.2952(6), b = 29.521(3), c = 11.7201(6) Å, β = 106.771(5)°; V = 3741.8 Å³, Z = 2; $D_{\text{calcd.}}$ = 1.402 g cm^{−3}; $\mu(\text{Mo-K}_\alpha)$ = 3.563 mm^{−1}; crystal size 0.42 $\times$ 0.35 $\times$ 0.31 mm; Siemens-Stoe AED-2 diffractometer, Mo-K α radiation (0.71073 Å), graphite monochromator; T = 293(2) K; $\omega/2\theta$ -scan, max. 2θ = 44.96°; 10271 reflections measured, 9707 independent (R_{int} = 0.016), 9461 with $I > 2\sigma(I)$. Intensity data were corrected for Lorentz, polarization and absorption effects.^[24] The structure was solved by direct methods (SHELXS-97).^[25] Atomic coordinates and anisotropic thermal parameters of the non-hydrogen atoms were refined by full-matrix least-square methods using SHELXL-97.^[26] The hydride ligands H(1A), H(1B), H(2A) and H(2B) were found after proper refinement of the whole structure including a weighting scheme. They were included in the refinement as free isotropic atoms with a common thermal parameter. The positions of all other hydrogen atoms were calculated according to ideal geometry and refined by the riding method. Conventional R = 0.0208 [for 9461 reflections with $I > 2\sigma(I)$], and weighted wR_2 = 0.0508 for all 9707 located reflections; reflection/parameter ratio 12.6; absolute structure Flack parameter −0.017(4); residual electron density +0.487/−0.487 e Å^{−3}.

CCDC-225188 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-0333; E-mail: deposit@ccdc.cam.ac.uk].

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