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Rhodium(I) Complexes Containing β-Amino Alcohol and 1,2-Diamine Ligands: Syntheses, Structures, and Catalytic Applications

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The bridge-opening reaction of $[(\eta^4\text{-}C_8H_{12})_2Rh_2(\mu\text{-}Cl)_2]$ with chiral and achiral β-amino alcohol nucleophiles gave mononuclear complexes $[(\eta^4\text{-}C_8H_{12})RhCl\{HN(R)\cap OH\text{-}\kappa N\}]$ containing the amino alcohol ligands in N-monodentate coordination; HN(R)∩OH = ethanolamine (**4**), 2-amino-2-methyl-1-propanol (**5**), and either enantiomer of (*R*)-, (*S*)-2-amino-3-methyl-1-butanol (D-, L-valinol) [(*R*)-**6**, (*S*)-**6**], (*R*)-, (*S*)-2-pyrrolidinemethanol (D-, L-prolinol) [(*R*)-**7**, (*S*)-**7**], (1*S*,2*R*)-, (1*R*,2*S*)-2-amino-1-phenyl-1-propanol (D-, L-norephedrine) [(1*S*,2*R*)-**8**, (1*R*,2*S*)-**8**], and (1*S*,2*R*)-, (1*R*,2*S*)-*cis*-1-amino-2-indanol [(1*S*,2*R*)-**9**, (1*R*,2*S*)-**9**]. Coordination of the free hydroxy function of the N,O ligands was brought about by both dehydrochlorination, which furnished the neutral valinolato chelate complex $[(\eta^4\text{-}C_8H_{12})Rh\{(S)\text{-}H_2NCH(CHMe_2)CH_2O\text{-}\kappa N,\kappa O\}]$, (*S*)-**10**, and by precipitation of the metal-bound chloride with TlO_3SCF_3 to produce ionic chelate complexes $[(\eta^4\text{-}C_8H_{12})Rh\{HN(R)\cap OH\text{-}\kappa N,\kappa O\}]O_3SCF_3$; HN(R)∩OH = 2-amino-2-methyl-1-propanol (**11**), (*S*)-2-amino-3-methyl-1-butanol [(*S*)-**12**], (*S*)-2-pyrrolidinemethanol [(*S*)-**13**], (1*R*,2*S*)-2-amino-1-phenyl-1-propanol [(1*R*,2*S*)-**14**], and (1*R*,2*S*)-*cis*-1-amino-2-indanol [(1*R*,2*S*)-**15**]. Except for only two in situ characterized $[\{(R)\text{-binap}\}Rh(H_2N\cap OH\text{-}\kappa N,\kappa O)]^+$ cations, where H₂N∩OH = L-valinol or L-norephedrine, no compound containing the various N,O ligands in addition to mono- or bidentate phosphanes could be prepared. In contrast, the P_2/N_2-coordinated chelate complexes $[\{(R)\text{-binap}\}Rh(H_2N\cap NH_2)]BF_4$ with $H_2N\cap NH_2 = H_2NCMe_2CMe_2NH_2$ [(*R*)-(**16**)], (*R*,*R*)-$H_2NCH(Ph)CH(Ph)NH_2$ [(*R*),(*R*,*R*)-**17**], and (*R*,*R*)-1,2-$(H_2N)_2C_6H_{10}$ [(*R*),(*R*,*R*)-**18**] were easily obtained from $[(\eta^4\text{-}C_8H_{12})Rh\{(R)\text{-binap}\}]BF_4$ and 1,2-diamines. Oxidative addition of HCl to (*R*),(*R*,*R*)-**17** produced *trans*-$[\{(R)\text{-binap}\}Rh(H)(Cl)\{(R,R)\text{-}H_2NCH(Ph)CH(Ph)NH_2\}]BF_4$ [(*R*),(*R*,*R*)-**19**]. If activated by strong base (KOH), (*R*),(*R*,*R*)-**17** and (*R*),(*R*,*R*)-**19** acted as moderately active and enantioselective catalysts for the reduction of acetophenone by both direct and transfer hydrogenation: ee_{max}: 71% (*S*). The crystal structures of **4**, (*S*)-**6**, (*R*)-**7**, (1*R*,2*S*)-**8**, (*S*)-**10**, (1*R*,2*S*)-**14**, (1*R*,2*S*)-**15**, (*R*)-**16**, (*R*),(*R*,*R*)-**17**, and two alcohol/alcoholato addition compounds, $[(\eta^4\text{-}C_8H_{12})Rh(H_2NCMe_2CH_2O\text{-}\kappa N,\kappa O)][(\eta^4\text{-}C_8H_{12})Rh(H_2NCMe_2CH_2OH\text{-}\kappa N,\kappa O)][(\eta^4\text{-}C_8H_{12})RhCl_2]$ [**1·2**], and $[(\eta^4\text{-}C_8H_{12})Rh(H_2NCMe_2CH_2O\text{-}\kappa N,\kappa O)][(\eta^4\text{-}C_8H_{12})Rh(H_2NCMe_2CH_2OH\text{-}\kappa N,\kappa O)]Cl$ [**1·3**], were determined.

Introduction

Our recent activities have focused on the catalytic potential of iridium (and rhodium) complexes bearing various β-aminophosphanes derived from optically active amino alcohols in asymmetric C=O hydrogenation reactions.[1] Following these studies, we have turned our attention to coordination compounds of the two platinum metals containing the very same β-amino alcohols and some akin 1,2-diamines as ligands.

Whereas ruthenium(II) complexes with N,O- and N,N donors − in particular, *N*-methyl-1,2-diphenylethanolamine and 1,2-diphenylethylenediamine − are well known to serve as efficient catalysts for the asymmetric hydrogenation and transfer hydrogenation of ketones and imines,[2] virtually no systematic studies on amino alcohol compounds of rhodium or iridium in their +1 or +3 oxidation states have so far been reported. Noteworthy exceptions are (1) the (amino alcoholato)rhodium(III) chelate $[\{\eta^5\text{-}C_5Me_4\text{-}(1R,2S)\text{-}C_6H_4CH_2NHCH(Me)CH(Ph)O\text{-}\kappa N,\kappa O\}RhCl]$, which contains an *N*-benzyl-(L)-norephedrine component tethered to a tetramethylcyclopentadienyl ligand and has been used as a highly active catalyst for the asymmetric reduction of ketones,[3] and (2) the acetate salt of the $[(\eta^4\text{-}C_8H_{12})Rh\{(S)\text{-}H_2NCH(Ph)CH_2OH\text{-}\kappa N,\kappa O\}]^+$ cation published only recently in this journal.[4]

Furthermore, notwithstanding that cationic $[(\eta^4\text{-}C_8H_{12})M(diamine)]^+$ complexes, where M = Rh or Ir and diamine = ethylenediamine, *o*-phenylenediamine, 1,8-diaminonaphthalene, and the like, are well-documented,[5] we are not aware of any previously described diphosphane(diamine)-coordinated cations $[M(R_2P\cap PR_2)(H_2N\cap NH_2)]^+$ or $[M(X)(Y)(R_2P\cap PR_2)(H_2N\cap NH_2)]^+$ (X, Y = halide, hy-

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dride) which, at least from a structural point of view, bear a direct resemblance to the famous $[Ru(X)(Y)(R_2P\cap PR_2)(H_2N\cap NH_2)]$ hydrogenation catalysts. A limited number of examples coming closest to the so far unknown diphosphane(diamine) chelate compounds of the two metals include the dihydrides $[MH_2(PPh_3)_2(H_2NC_2H_4NH_2)]^+$ (M = Rh,[6] Ir[7]) along with only two in situ characterized Rh^{I} species, $[Rh\{(S)\text{-binap}\}(NEt_3)_2]^+$[8] and $[Rh(dppe)(NH_3)_2]^+$,[9] respectively.

Using the chlorido-bridged dimer $[(\eta^4\text{-}C_8H_{12})_2Rh_2(\mu\text{-}Cl)_2]$ as a common starting material, we have obtained a family of (cyclooctadiene)rhodium(I) complexes containing both chiral and achiral amino alcohols in κ*N*-monodentate and κ*N*,κ*O*-bidentate coordination. It is envisaged that such compounds and some related (diphosphane)diamine chelate complexes $[Rh\{(R)\text{-binap}\}(H_2N\cap NH_2)]^+$, both of which are the subject of this communication, can be useful for the construction of stereoselective catalysts,[10] and a first account of their application to homogeneous C=O hydrogenation is given in the following.

Results and Discussion

β-Amino Alcohol Complexes

Initial attempts were directed towards the synthesis of amino alcoholato derivatives of Rh^{I} by treating $[(\eta^4\text{-}C_8H_{12})_2Rh_2(\mu\text{-}Cl)_2]$ with solutions of the respective sodium alkoxides $H_2N\cap ONa$ in $H_2N\cap OH$/toluene. Although such experiments did produce amino alcoholato complexes as desired, their results remained inconclusive in that mixtures of the neutral and ionic chelates, $[(\eta^4\text{-}C_8H_{12})Rh(H_2N\cap O\text{-}\kappa N,\kappa O)]$ and $[(\eta^4\text{-}C_8H_{12})Rh(H_2N\cap OH\text{-}\kappa N,\kappa O)]^+$, were formed. Thus, the sodium salt of 2-amino-2-methyl-1-propanol reacted in $H_2NCMe_2CH_2OH$/toluene to give $[(\eta^4\text{-}C_8H_{12})Rh(H_2NCMe_2CH_2O\text{-}\kappa N,\kappa O)]$ (**1**) as the wanted target complex but also furnished the amino alcohol chelated salts $[(\eta^4\text{-}C_8H_{12})Rh(H_2NCMe_2CH_2OH\text{-}\kappa N,\kappa O)][(\eta^4\text{-}C_8H_{12})RhCl_2]$ (**2**) and $[(\eta^4\text{-}C_8H_{12})Rh(H_2NCMe_2CH_2OH\text{-}\kappa N,\kappa O)]Cl$ (**3**) as unwanted byproducts. Repeated crystallizations of such mixtures and subsequent single-crystal X-ray diffraction studies revealed that **1** and **2** cocrystallized from thf/*n*-pentane as the addition compound **1·2**·thf stabilized by multiple O–H···O, N–H···O, and N–H···Cl hydrogen bonding interactions, whereas **1** and **3** were separated from solution as the likewise hydrogen-bonded adduct **1·3**, if crystallized from toluene/*n*-hexane mixtures.

In the structure of **1·2**·thf, the two rhodium-alcohol(ato) constituents were located on crystallographically independent positions of a triclinic unit cell (space group $P\bar{1}$) and, hence, could be distinguished without difficulty (Figure 1). In contrast, the tetragonal unit cell of **1·3** (crystallizing in the space group $P\bar{4}2c$) was found to contain neutral $[(\eta^4\text{-}C_8H_{12})Rh(H_2NCMe_2CH_2O\text{-}\kappa N,\kappa O)]$ and cationic $[(\eta^4\text{-}C_8H_{12})Rh(H_2NCMe_2CH_2OH\text{-}\kappa N,\kappa O)]^+$ on symmetry-related sites such that the mixed composition of the compound was only evident from the presence of one chloride anion spread with quarter occupancies over special positions *a* and *b* of the cell (Figure 2). For the two structures, the rhodium–oxygen and rhodium–nitrogen bond lengths fall in the usual range.[11] The molecular parameters of the $[(\eta^4\text{-}C_8H_{12})RhCl_2]^-$ anion also deserve no further comment as they are very similar to those previously measured for the same ion in a number of related $[(\eta^4\text{-}C_8H_{12})RhL_2][(\eta^4\text{-}C_8H_{12})RhCl_2]$ complexes.[11]

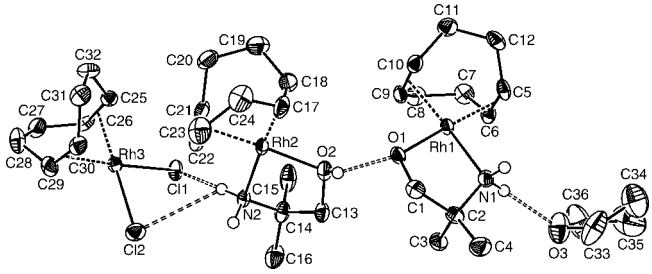


Figure 1. Molecular structure of the addition compound $[(\eta^4\text{-}C_8H_{12})Rh(H_2NCMe_2CH_2O\text{-}\kappa N,\kappa O)]\cdot[(\eta^4\text{-}C_8H_{12})Rh(H_2NCMe_2CH_2OH\text{-}\kappa N,\kappa O)][(\eta^4\text{-}C_8H_{12})RhCl_2]\cdot$thf (**1·2**·thf), which shows the multiple O–H···O, N–H···O, and N–H···Cl hydrogen bonding interactions (H atoms of the diolefin ligand are omitted for clarity). Selected bond lengths [Å] and angles [°]: Rh1–O1, 2.053(3); Rh1–N1, 2.093(4); Rh2–O2, 2.065(4); Rh2–N2, 2.098(4); Rh3–Cl1, 2.387(1); Rh3–Cl2, 2.372(2). O1–Rh1–N1, 81.2(1); O2–Rh2–N2, 80.4(1); Cl1–Rh3–Cl2, 89.47(5). Hydrogen-bonding interactions as D–H, H···A, D···A, D–H···A [Å °]: O2–H···O1, 0.82, 1.79, 2.417(5), 132.5; N1–H···O3, 0.92, 2.15, 3.015(6), 155.4; N2–H···Cl1, 0.92, 2.55, 3.447(4), 165.5; N2–H···Cl2, 0.92, 2.95, 3.422(5), 113.6; N1–H···Cl1_#1, 0.92, 2.40, 3.289(5), 163.3; N2–H···Cl2_#2, 0.92, 2.65, 3.353(4), 133.6. Symmetry transformations used to generate equivalent atoms: #1 = x, $y+1$, z; #2 = $-x+1$, $-y-1$, $-z$.

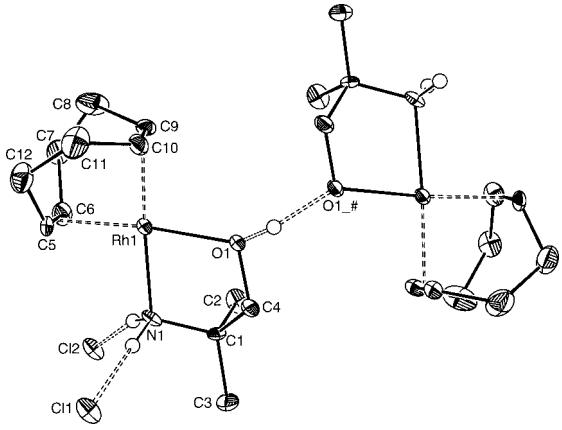
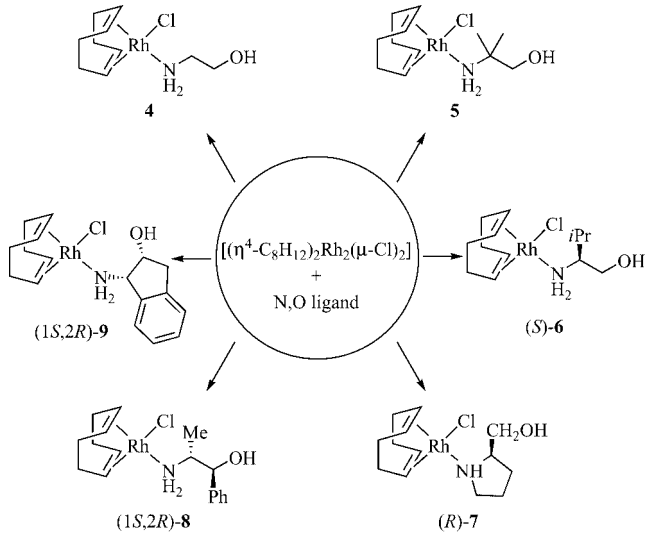


Figure 2. Molecular structure of the hydrogen-bonded amino alcohol/amino alcoholato adduct $[(\eta^4\text{-}C_8H_{12})Rh(H_2NCMe_2CH_2O\text{-}\kappa N,\kappa O)]\cdot[(\eta^4\text{-}C_8H_{12})Rh(H_2NCMe_2CH_2OH\text{-}\kappa N,\kappa O)]Cl$ (**1·3**), where the two complex moieties reside on symmetry-related positions and the chloride counterion is distributed with 1/4 occupancies over special sites *a* (0, 0, 3/4) and *b* (0, 1/2, 3/4) of space group $P\bar{4}2c$ (H atoms of the diolefin ligand are omitted for clarity). Selected bond lengths [Å] and angles [°]: Rh1–O1, 2.074(5); Rh1–N1, 2.112(5). O1–Rh1–N1, 81.0(2). Hydrogen-bonding interactions as D–H, H···A, D···A, D–H···A [Å °]: O1–H···O1_#, 0.85, 1.55, 2.396(9), 171.3; N1–H···Cl1, 0.92, 2.43, 3.339(5), 168.9; N1–H···Cl2, 0.92, 2.51, 3.418(5), 167.9. Symmetry transformation used to generate equivalent atoms: #1 = $-x+1$, y, $-z+1$.

The transformation of $[(\eta^4\text{-}C_8H_{12})_2Rh_2(\mu\text{-}Cl)_2]$ by the $H_2NCMe_2CH_2ONa/H_2NCMe_2CH_2OH$ mixture to give, in

addition to neutral alcoholato complex **1**, the ionic products $[(\eta^4\text{-}C_8H_{12})Rh(H_2NCMe_2CH_2OH\text{-}\kappa N,\kappa O)][(\eta^4\text{-}C_8H_{12})RhCl_2]$ (**2**) and $[(\eta^4\text{-}C_8H_{12})Rh(H_2NCMe_2CH_2OH\text{-}\kappa N,\kappa O)]Cl$ (**3**) is reminiscent of some bridge-cleaving reactions of the dimer with a number of aliphatic diamines described in earlier work, where either ion-pair complexes $[(\eta^4\text{-}C_8H_{12})Rh(diamine)][(\eta^4\text{-}C_8H_{12})RhCl_2]$ or chloride-containing products $[(\eta^4\text{-}C_8H_{12})Rh(diamine)Cl]$ were obtained. Different from **3**, however, the latter were formulated as neutral pentacoordinate rather than ionic tetracoordinate species.[5e]

From the above results it was inferred that better-defined products could arise from preparations that avoid the presence of alkoxide base in the initial reaction solutions. Hence, further experiments used the $[(\eta^4\text{-}C_8H_{12})_2Rh_2(\mu\text{-}Cl)_2]$ starting compound together with toluene dilutions of the pure amino alcohols. Under these conditions, smooth opening of the chloride bridges by the amine nucleophiles was observed to give high yields of mononuclear products $[(\eta^4\text{-}C_8H_{12})RhCl\{HN(R)\cap OH\text{-}\kappa N\}]$ (R = H, alkyl), **4**–**9**, containing the amino alcohol ligands in monodentate coordination: HN(R)∩OH = ethanolamine (**4**), 2-amino-2-methyl-1-propanol (**5**), as well as either enantiomer of (*R*)-, (*S*)-2-amino-3-methyl-1-butanol (D-, L-valinol) [(*R*)-**6**, (*S*)-**6**], (*R*)-, (*S*)-2-pyrrolidinemethanol (D,- L-prolinol) [(*R*)-**7**, (*S*)-**7**], (1*S*,2*R*)-, (1*R*,2*S*)-2-amino-1-phenyl-1-propanol (D-, L-norephedrine) [(1*S*,2*R*)-**8**, (1*R*,2*S*)-**8**], and (1*S*,2*R*)-, (1*R*,2*S*)-*cis*-1-amino-2-indanol [(1*S*,2*R*)-**9**, (1*R*,2*S*)-**9**], respectively (Scheme 1).



Scheme 1. Synthesis of κ*N*-monodentate amino alcohol complexes **4**–**9**; only one enantiomer of chiral molecules **6**–**9** is drawn.

Complexes **4**–**9** form relatively air-stable yellow crystals which are readily soluble in the more polar solvents, for example methanol, thf, $CHCl_3$, CH_2Cl_2, and the like. From such solutions, compounds **4**, (*S*)-**6**, (*R*)-**7**, and (1*R*,2*S*)-**8** (crystallizing as a solvate with the idealized composition $[(\eta^4\text{-}C_8H_{12})RhCl\{(1R,2S)\text{-}H_2NCH(Me)CH(Ph)CH_2OH\}]\cdot 1/4CH_2Cl_2\cdot 1/4thf$) were isolated as single-crystals and subjected to X-ray structure analyses (Figures 3, 4, 5, and 6. Whereas the asymmetric units of **4** and (*S*)-**6** comprised one complex molecule each, two crystallographically independent molecules with partially disordered pyrrolidine and cyclooctadiene rings were found in structures (*R*)-**7** and (1*R*,2*S*)-**8**. In the solid-state packing of the four compounds, the individual complexes are assembled through O–H···Cl and N–H···Cl hydrogen bonds from the dangling hydroxy group and the ligated amino groups to the chlorido ligands of neighboring molecules. Not unexpectedly, neither the Rh–Cl distances (2.381–2.398 Å) nor the Rh–NH_2 bond lengths (2.127–2.137 Å) displayed any significant differences.

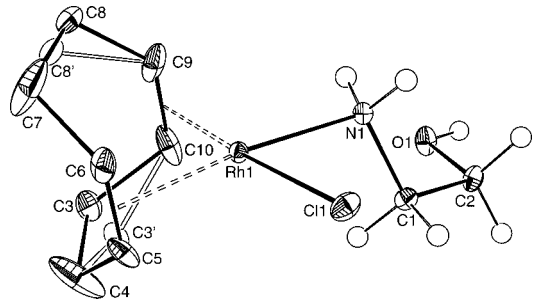


Figure 3. Molecular structure of $[(\eta^4\text{-}C_8H_{12})RhCl\text{-}(H_2NCH_2CH_2OH\text{-}\kappa N)]$ (**4**), which shows the twofold disorder of two methylene C atoms in the C_8H_{12} ring (H atoms of the diolefin ligand are omitted for clarity). Selected bond lengths [Å] and angles [°]: Rh1–Cl1, 2.3930(4); Rh1–N1, 2.128(2). Cl1–Rh1–N1, 88.38(4). Hydrogen-bonding interactions as D–H, H···A, D···A, D–H···A [Å [°]]: O1–H···Cl1_#1, 0.84, 2.39, 3.128(2), 147.5; N1–H···Cl1_#2, 0.92, 2.73, 3.623(2), 164.5; N1–H···O1_#3, 0.92, 2.19, 3.002(2), 147.3. Symmetry transformations used to generate equivalent atoms: #1 = $-x+2$, $y+1/2$, $-z+1/2$; #2 = x, $-y+11/2$, $z-1/2$; #3 = x, $-y+11/2$, $z+1/2$.

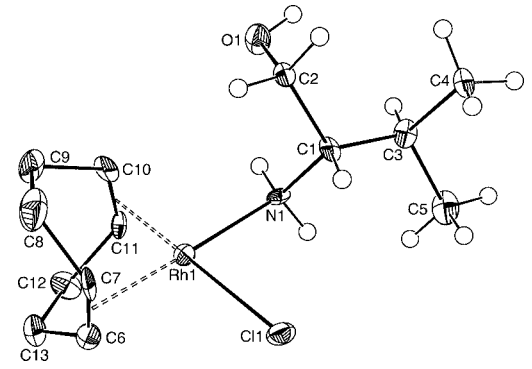


Figure 4. Molecular structure of $[(\eta^4\text{-}C_8H_{12})RhCl\{(S)\text{-}H_2NCH(CHMe_2)CH_2OH\text{-}\kappa N\}]$, (*S*)-**6** (H atoms of the diolefin ligand are omitted for clarity). Selected bond lengths [Å] and angles [°]: Rh1–Cl1, 2.395(3); Rh1–N1, 2.127(8). Cl1–Rh1–N1, 86.5(2). Hydrogen-bonding interactions as D–H, H···A, D···A, D–H···A [Å [°]]: O1–H···Cl1_#1, 0.84, 2.42, 3.250(8), 171.5; N1–H···Cl1_#2, 0.92, 2.57, 3.301(9), 137.2. Symmetry transformations used to generate equivalent atoms: #1 = $-x+1$, $y+1/2$, $-z$; #2 = $-x$, $y+1/2$, $-z$.

For converting the $[(\eta^4\text{-}C_8H_{12})RhCl\{HN(R)\cap OH\text{-}\kappa N\}]$ complexes into N,O-chelated derivatives, two obvious approaches can be taken into account: (1) removal of both the chlorido ligand and the OH proton by base to give neutral amino alcoholato products $[(\eta^4\text{-}C_8H_{12})Rh\{HN(R)\cap O\text{-}$

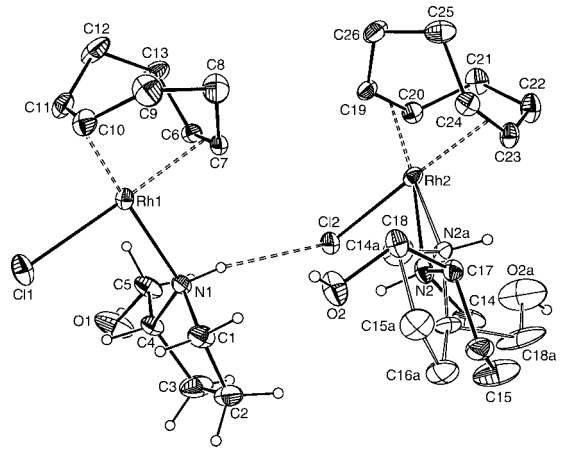


Figure 5. Structure of the two crystallographically independent hydrogen-bonded molecules of $[(\eta^4\text{-}C_8H_{12})RhCl\{(R)\text{-}HN(CH_2CH_2CH_2CH)CH_2OH\text{-}\kappa N\}]$, (*R*)-**7** (H atoms of the diolefins and the disordered D-prolinol ligand are omitted for clarity). Selected bond lengths [Å] and angles [°]: Rh1–Cl1, 2.381(2); Rh1–N1, 2.134(4); Rh2–Cl2, 2.397(2); Rh2–N2, 2.13(1); Rh2–N2A, 2.18(1). Cl1–Rh1–N1, 90.3(1); Cl2–Rh2–N2, 77.4(3); Cl2–Rh2–N2A, 95.4(3). Hydrogen-bonding interactions as D–H, H···A, D···A, D–H···A [Å [°]]: N1–H···Cl2, 0.92, 2.52, 3.432(4), 170.0; O1–H···Cl1_#1, 0.83, 2.24, 3.057(7), 167.8; O2–H···Cl2_#2, 0.83, 2.32, 3.13(1), 164.6; O2A–H···O1_#3, 0.83, 2.10, 2.51(2), 110.3; N2A–H···Cl1_#3, 0.92, 2.84, 3.72(1), 161.2. Symmetry transformations used to generate equivalent atoms: #1 = *x*, *y*+1, *z*; #2 = *x*, *y*–1, *z*; #3 = *x*–1, *y*, *z*.

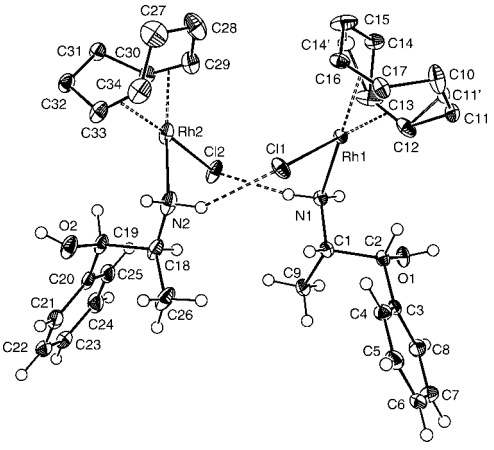
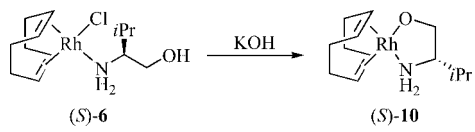


Figure 6. Structure of the two crystallographically independent hydrogen-bonded complex molecules (1*R*,2*S*)-**8** of $[(\eta^4\text{-}C_8H_{12})RhCl\{(1R,2S)\text{-}H_2NCH(Me)CH(Ph)OH\text{-}\kappa N\}]\cdot 1/4CH_2Cl_2\cdot 1/4thf$, which shows the twofold disorder of two methylene C atoms in one of the C_8H_{12} ligands (cyclooctadiene H atoms and solvate molecules are omitted for clarity). Selected bond lengths [Å] and angles [°]: Rh1–Cl1, 2.3912(4); Rh1–N1, 2.134(2); Rh2–Cl2, 2.3982(5); Rh2–N2, 2.137(2). Cl1–Rh1–N1, 88.16(5); Cl2–Rh2–N2, 88.54(5). Hydrogen-bonding interactions as D–H, H···A, D···A, D–H···A [Å [°]]: N1–H···Cl2, 0.92, 2.38, 3.281(2), 167.7; N2–H···Cl1, 0.92, 2.52, 3.338(2), 148.8; O1–H···Cl2_#1, 0.84, 2.28, 3.109(2), 171.8; O2–H···Cl1_#3, 0.84, 2.28, 3.111(2), 172.6; N1–H···ClCH$_2$Cl_#2, 0.92, 2.88, 3.703(3), 149.5; N2–H···ClH$_2$Cl_#3, 0.92, 2.83, 3.646(5), 148.8; N2–H···OC$_4$H$_8$_#3, 0.92, 2.34, 3.137(4), 144.5. Symmetry transformations used to generate equivalent atoms: #1 = -*x*+1, *y*–1/2, –*z*+1; #2 = –*x*+1, *y*+1/2, –*z*+1; #3 = –*x*+1, *y*+1/2, –*z*+2.

κ*N*,κ*O*}]; (2) precipitation of the metal-bound chloride as, for example, AgCl or TlCl to afford cationic amino alcohol chelates $[(\eta^4\text{-}C_8H_{12})Rh\{HN(R)\cap OH\text{-}\kappa N,\kappa O\}]^+$.

Method (1) was probed by using $[(\eta^4\text{-}C_8H_{12})RhCl\{(S)\text{-}H_2NCH(CHMe_2)CH_2OH\text{-}\kappa N\}]$ [(*S*)-**6**] together with powdered KOH in CH_2Cl_2 (Scheme 2). This dehydrochlorination reaction furnished the "valinolato" chelate complex $[(\eta^4\text{-}C_8H_{12})Rh\{(S)\text{-}H_2NCH(CHMe_2)CH_2O\text{-}\kappa N,\kappa O\}]$ [(*S*)-**10**] which crystallized from the reaction solution in the (rare) triclinic space group *P*1 with one molecule of lattice water per formula unit. The water of crystallization served to assemble two molecules of (*S*)-**10**·H_2O in the unit cell by multiple N–H···OH_2 and O–H···O hydrogen bonds, as shown in Figure 7. The metal-to-nitrogen und metal-to-oxygen bond lengths as well as the O–Rh–N angles closely resemble those measured for $[(\eta^4\text{-}C_8H_{12})Rh(H_2NCMe_2\text{-}CH_2O\text{-}\kappa N,\kappa O)]$ (**1**) in its thf-solvated addition compound with $[(\eta^4\text{-}C_8H_{12})Rh(H_2NCMe_2CH_2OH\text{-}\kappa N,\kappa O)][(\eta^4\text{-}C_8H_{12})RhCl_2]$ (**2**).



Scheme 2. Formation of L-valinolato chelate complex (*S*)-**10** by dehydrochlorination of (*S*)-**6**.

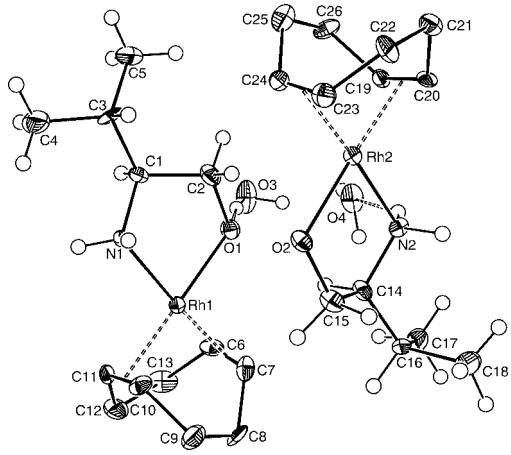
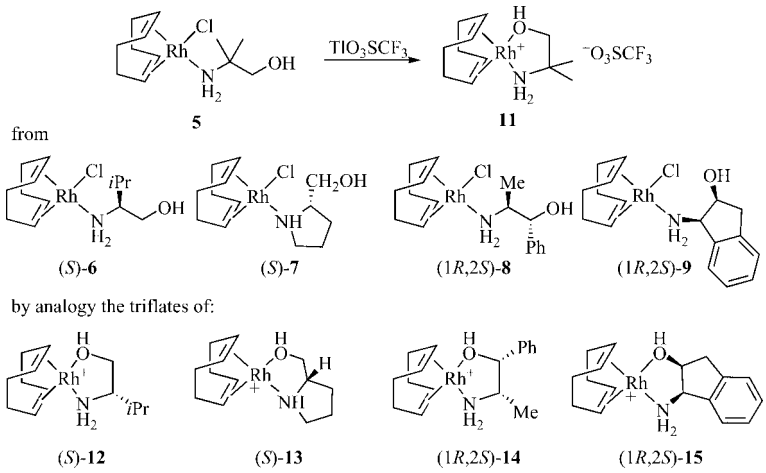


Figure 7. Structure of the two lattice water-containing molecules $[(\eta^4\text{-}C_8H_{12})Rh\{(S)\text{-}H_2NCH(CHMe_2)CH_2O\text{-}\kappa N,\kappa O\}]\cdot H_2O$ [(*S*)-**10**·H_2O] which fill the triclinic unit cell of space group *P*1 (cyclooctadiene H atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: Rh1–O1, 2.037(7); Rh1–N1, 2.102(7); Rh2–O2, 2.041(6); Rh2–N2, 2.126(8). O1–Rh1–N1, 82.9(3); O2–Rh2–N2, 81.4(3). Hydrogen-bonding interactions as D–H, H···A, D···A, D–H···A [Å [°]]: O3–H···O1, 0.85, 2.00, 2.83(1), 167.0; N2–H···O4, 0.92, 1.94, 2.77(1), 148.9; O3–H···O2_#1, 0.85, 1.95, 2.77(1), 162.2; O4–H···O2_#1, 0.85, 1.94, 2.69(1), 146.5; N1–H···O3_#2, 0.92, 2.00, 2.92(1), 171.6. Symmetry transformations used to generate equivalent atoms: #1 = *x*–1, *y*, *z*; #2 = *x*+1, *y*, *z*.

Attempts to induce chelation of the unligated hydroxy groups of complexes **4**–**9** by reaction with soluble silver salts such as $AgBF_4$ or AgO_3SCF_3 according to method (2) resulted in the deposition of elemental silver rather than silver chloride with concomitant decomposition of the com-



Scheme 3. Synthesis of triflate salts **11**–**15** containing chelated β-amino alcohol ligands.

pounds. Reduction of the Ag^+ ion is most likely caused by the free OH functions of the amino alcohols as may be judged from the standard electrode potentials for the equilibria "$Ag^+ + e^- = Ag$" ($E^0 = +0.799$ V) and, as a rough estimate, "$CH_3CHO + 2\ H^+ + 2\ e^- = C_2H_5OH$" ($E^0 = +0.192$ V).[12] Because of the low standard potential of the redox couple Tl^+/Tl ($E^0 = -0.336$ V), thallium(I) trifluoromethanesulfonate proved to be a more suitable chloride-precipitating reagent, which smoothly converted the [(η^4-C_8H_{12})RhCl{HN(R)∩OH-κ*N*}] complexes into the triflate salts [(η^4-C_8H_{12})Rh{HN(R)∩OH-κ*N*,κ*O*}]O_3SCF_3, where HN(R)∩OH-κ*N*,κ*O* stands for chelated 2-amino-2-methyl-1-propanol (**11**), (*S*)-2-amino-3-methyl-1-butanol (L-valinol) [(*S*)-**12**], (*S*)-2-pyrrolidinemethanol (L-prolinol), [(*S*)-**13**], (1*R*,2*S*)-2-amino-1-phenyl-1-propanol (L-norephedrine) [(1*R*,2*S*)-**14**], and (1*R*,2*S*)-*cis*-1-amino-2-indanol [(1*R*,2*S*)-**15**] (Scheme 3). As mentioned in the introductory section, the closely related (*S*)-2-amino-2-phenylethanol containing compound [(η^4-C_8H_{12})Rh{(*S*)-H_2NCH(Ph)-CH_2OH-κ*N*,κ*O*}]O_2CMe was only recently isolated from the bridge-cleaving reaction of the amino alcohol with the [(η^4-C_8H_{12})$_2$Rh$_2$(μ-O_2CMe)$_2$] dimer.[4]

Complexes (1*R*,2*S*)-**14** and (1*R*,2*S*)-**15** were fully characterized by single-crystal X-ray diffraction (Figures 8 and 9). In both structures, the complex cations and their counterions are linked by hydrogen-bonding interactions from the coordinated amino and hydroxy donors to the triflate anion acceptors. Relative to the metal-to-oxygen bond lengths measured for the two crystallographically independent molecules of alcoholato complex (*S*)-**10**, 2.037(7) and 2.041(6) Å, the Rh–O separations observed for (1*R*,2*S*)-**14**, 2.125(3) Å, and the two cations filling the asymmetric unit of (1*R*,2*S*)-**15**, 2.086(4) and 2.089(4) Å, tend to be slightly elongated, which thereby reflects the weaker bonding capabilities of neutral alcohol than those of anionic alkoxo donor groups.

In the ^{1}H NMR spectra of both the monodentate and the chelated amino alcohol complexes [(η^4-C_8H_{12})-RhCl{HN(R)∩OH-κ*N*}] (**4**–**9**) and [(η^4-C_8H_{12})Rh{HN(R)-∩OH-κ*N*,κ*O*}]O_3SCF_3 (**11**–**15**) measured at ambient temperature, largely unresolved broad multiplets, each accounting for four protons, are observed for the allylic CH_2 ($\delta \approx$ 1.6–1.8 and 2.3–2.5 ppm) and the olefinic CH groups ($\delta \approx$ 4.0–4.2 ppm) of the diene ligand. In the ^{13}C NMR spectra, the olefinic carbon atoms similarly give rise to very broad signals centered at $\delta \approx$ 77–83 ppm; the resonances of the methylene carbon atoms appear as either one or two singlets ($\delta \approx$ 29–32 ppm), which likewise show line broadening. From these NMR spectroscopic data it is apparent that a dynamic process occurs in solution, which averages the chemical nonequivalency of the CH=CH groups that are bound *trans* to N and Cl in **4**–**9** and *trans* to N and O in **11**–**15**, respectively.

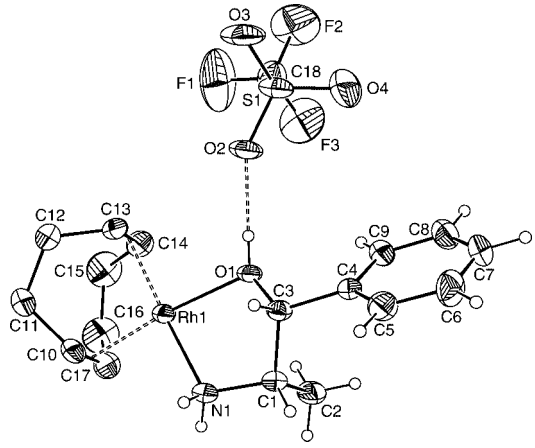


Figure 8. Structure of the ion pair [(η^4-C_8H_{12})Rh{(1*R*,2*S*)-H_2NCH(Me)CH(Ph)OH-κ*N*,κ*O*}]O_3SCF_3 [(1*R*,2*S*)-**14**] (cyclooctadiene H atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: Rh1–O1, 2.125(3); Rh1–N1, 2.112(4). O1–Rh1–N1, 78.8(1). Hydrogen-bonding interactions as D–H, H···A, D···A, D–H···A [Å [°]]: O1–H···O2, 0.82, 1.86, 2.672(5), 174.2; N1–H···O2_#1, 0.90, 2.20, 3.074(7), 164.2; N1–H···O3_#2, 0.90, 2.09, 2.968(6), 164.5. Symmetry transformations used to generate equivalent atoms: #1 = $x-1/2, -y+1/2, -z$; #2 = $x-1, y, z$.

This interconversion of the double bonds could not be frozen by lowering the temperature in the case of the monodentate amino alcohol complexes. Thus, the ^{13}C NMR

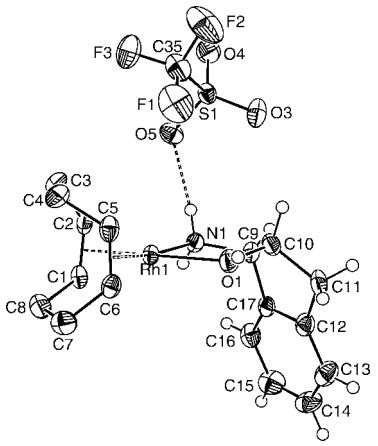


Figure 9. Structure of one of the two crystallographically independent ion pairs of $[(\eta^4\text{-}C_8H_{12})Rh\{(1R,2S)\text{-}H_2NCH[CH(OH)CH_2]\text{-}C_6H_4\text{-}\kappa N,\kappa O\}]O_3SCF_3$ [(1*R*,2*S*)-**15**] (cyclooctadiene H atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: Rh1–O1, 2.089(4); Rh1–N1, 2.109(4). O1–Rh1–N1, 79.6(2). Analogous parameters for ion pair 2: Rh2–O2, 2.086(4); Rh2–N2, 2.124(5). O2–Rh2–N2, 78.6(2). Hydrogen-bonding interactions as D–H, H···A, D···A, D–H···A [Å [°]]: N1–H···O5, 0.91, 2.09, 2.981(6), 165.7; N1–H···O6_#1, 0.91, 2.26, 3.001(6), 137.9; O1–H···O7_#2, 0.84, 1.82, 2.665(6), 175.4 (both from complex 1 to triflate 2); N2–H···O3_#3, 0.91, 2.27, 3.139(6), 159.0; N2–H···O4_#3, 0.91, 2.65, 3.158(6), 116.3; O2–H···O5_#4, 0.85, 1.81, 2.651(6), 171.6 (all from complex 2 to triflate 1). Symmetry transformations used to generate equivalent atoms: #1 = *x*, *y*, *z* + 1; #2 = –*x*, *y* + 1/2, –*z*; #3 = –*x*, *y* – 1/2, –*z* + 1; #4 = *x*, *y*, *z* – 1.

spectrum of $[(\eta^4\text{-}C_8H_{12})RhCl(H_2NCMe_2CH_2OH\text{-}\kappa N)]$, **5**, which displays two broad signals for the CH_2 and CH carbon atoms (δ = 30.6 and 77.1 ppm) in $[D_6]$DMSO at 30 °C, still showed considerable line-broadening for the cyclooctadiene resonances when recorded in $[D_4]$methanol at –25 °C: δ = 29.6, 30.7 (both CH_2), and 81.7 (CH) ppm. Conversely, it could be demonstrated for the chelated L-norephedrine compound $[(\eta^4\text{-}C_8H_{12})Rh\{(1R,2S)\text{-}H_2NCH(Me)CH(Ph)OH\text{-}\kappa N,\kappa O\}]O_3SCF_3$ [(1*R*,2*S*)-**14**] that a ^{13}C NMR spectrum consistent with a rigid C_1-symmetric structure of the cation can in fact be observed if a $[D_4]$methanol solution cooled to –35 °C is used. Both the methylene and the olefinic carbon atoms then resolve into four distinct signals, the former protons appear as singlets (δ = 30.31, 30.90, 32.11, and 32.45 ppm), and the latter protons resonate as ^{103}Rh-coupled doublets (δ = 73.41, 73.85, 84.32, and 84.51 ppm; $J_{Rh,C}$ = 11.7–16.9 Hz).

We do not know the mechanism of the olefin site interchange of the coordinated diene in compounds **4**–**9** and **11**–**15** but note that analogous scrambling of two chemically nonequivalent CH=CH bonds was previously described for a number of related four-coordinate rhodium(I) compounds $[(\eta^4\text{-}C_8H_{12})RhCl(R_2P\cap E\text{-}\kappa P)]$ and $[(\eta^4\text{-}C_8H_{12})Rh\{R_2P\cap E\text{-}\kappa P,\kappa E)]^+$ containing different P,N and P,S chelate ligands bonded in a mono- or bidentate fashion.[13] For the chlorido complexes containing "dangling" donor groups similar to the free hydroxy functions of **4**–**9**, the exchange dynamics were accounted for in terms of a fast equilibrium between the square planar form of the molecule and small amounts of a pentacoordinate chelated isomer undergoing rapid pseudorotation.[13a] For the cationic chelate complexes that bear some structural resemblance to **11**–**15**, a mechanism involving breaking of the Rh–N or Rh–S linkage, followed by rotation around the Rh–P bond and rebuilding of the four-coordinate chelate structure was proposed as an alternative.[13b–13d] As a further alternative, the diene dynamics were ascribed to diolefin rotation proceeding by cleavage of one Rh–diene bond, rotation through 180° around the remaining metal–olefin bond, and recoordination of the free CH=CH group either *cis* or *trans* to one of the two different donors of the chelate ligand.[13e]

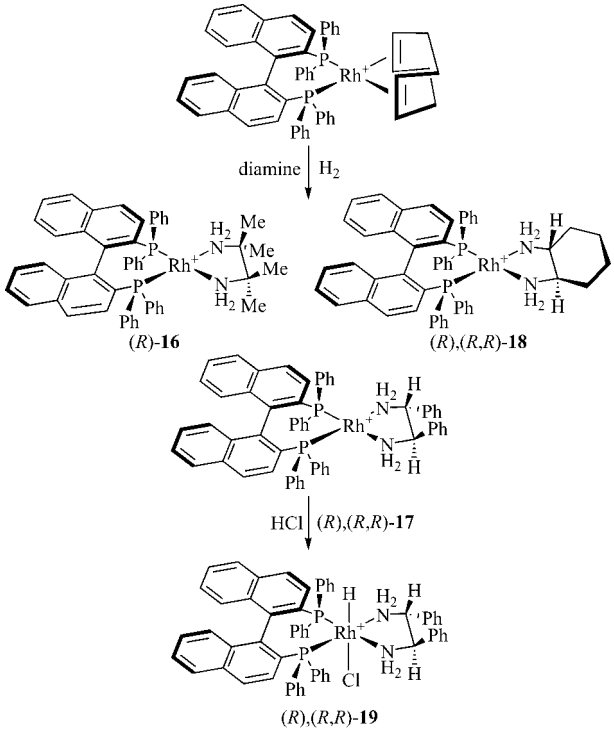
1,2-Diamine Complexes

For catalytic applications, it seemed desirable to substitute P donors, in particular chiral diphosphanes, for the cyclooctadiene ligand of the newly prepared complexes bearing the diverse amino alcohols in κ*N*-monodentate or κ*N*,κ*O*-bidentate coordination. Accordingly, numerous attempts were made to obtain phosphane-coordinated products by reaction of the amino alcohol compounds with both chiral and achiral mono- and ditertiary phosphanes or, vice versa, by combining phosphane-containing precursors such as $[(i\text{Pr}_3P)_2Rh_2(\mu\text{-}Cl)_2]$[14] and $[(\eta^4\text{-}C_8H_{12})Rh\{(R)\text{-binap}\}]BF_4$[15] with amino alcohol ligands. So far, all of these experiments failed in that reaction mixtures were produced from which only ill-defined or unwanted compounds could be isolated, some of which were already known. Thus, reactions of the dinuclear bis(triisopropylphosphane) complex with L-valinol or L-norephedrine in thf under a nitrogen atmosphere repeatedly furnished the well-known dinitrogen compound *trans*-$[(i\text{Pr}_3P)_2RhCl(N_2)]$[16] rather than any amino alcohol containing material, whereas both $[(i\text{Pr}_3P)_2Rh_2(\mu\text{-}Cl)_2]$ and $[(\eta^4\text{-}C_8H_{12})Rh\{(R)\text{-binap}\}]BF_4$ afforded mixtures of multifarious unidentified derivatives, if combined with a number of different amino alcohols in CH_2Cl_2 or thf under an atmosphere of argon or hydrogen. Largely unidentified products were also formed upon treatment of several $[(\eta^4\text{-}C_8H_{12})RhCl\{HN(R)\cap OH\text{-}\kappa N\}]$ or $[(\eta^4\text{-}C_8H_{12})Rh\{HN(R)\cap OH\text{-}\kappa N,\kappa O\}]O_3SCF_3$ precursors with a number of different mono- or bidentate phosphanes.

For the time being, only L-valinol and L-norephedrine chelate complexes (*S*)-**12** and (1*R*,2*S*)-**14** and the (*R*)-binap ligand reacted to give defined mixtures of products. ^{31}P and ^1H NMR spectroscopy disclosed the predominant presence (>90%; see Experimental Section) of each an (*R*)-binap-coordinated C_1-symmetric species assumed to be $[\{(R)\text{-binap}\}Rh\{(S)\text{-}H_2NCH(CHMe_2)CH_2OH\text{-}\kappa N,\kappa O\}]^+$ and $[\{(R)\text{-binap}\}Rh\{(1R,2S)\text{-}H_2NCH(Me)CH(Ph)OH\text{-}\kappa N,\kappa O\}]^+$, respectively, but all attempts to isolate these cations as pure compounds resulted in their degradation to unidentified materials.

In contrast to the largely unsuccessful reactions of β-amino alcohols with, for example, $[(\eta^4\text{-}C_8H_{12})Rh\{(R)\text{-binap}\}]BF_4$, 1,2-diamines such as 1,1′,2,2′-tetramethylethyl-

enediamine and (*R*,*R*)-1,2-diphenylethylenediamine, and (*R*,*R*)-1,2-diaminocyclohexane smoothly displaced the C_8H_{12} ligand from the metal giving the chelate complexes [{(*R*)-binap}Rh($H_2N\cap NH_2$)]BF_4, if allowed to interact with the diene(diphosphane) complex in thf under a hydrogen atmosphere; $H_2N\cap NH_2$ = $H_2NCMe_2CMe_2NH_2$ [(*R*)-(**16**)], (*R*,*R*)-$H_2NCH(Ph)CH(Ph)NH_2$ [(*R*),(*R*,*R*)-**17**], (*R*,*R*)-1,2-$(H_2N)_2C_6H_{10}$ [(*R*),(*R*,*R*)-**18**]. Further reaction of (*R*),(*R*,*R*)-**17** with hydrogen chloride afforded *trans*-[{(*R*)-binap}Rh(H)(Cl){(*R*,*R*)-$H_2NCH(Ph)CH(Ph)NH_2$}]BF_4 [(*R*),(*R*,*R*)-**19**], by oxidative addition (Scheme 4). From a structural point of view, the cation of the latter can be regarded as a blueprint of the neutral Ru^{II} complex *trans*-[{(*R*)-binap}Ru(H)(Cl){(*R*,*R*)-$H_2NCH(Ph)CH(Ph)NH_2$}], known to be an excellent catalyst precursor for the stereoselective hydrogenation of ketones and imines.[17a]



Scheme 4. Preparation of (*R*)-binap/1,2-diamine complexes (all as BF_4^- salts).

Single-crystals of (*R*)-**16** and (*R*),(*R*,*R*)-**17** containing solvent molecules of crystallization [i.e. (*R*)-**16**·1/2Me_2CO·1/4thf and (*R*),(*R*,*R*)-**17**·CH_2Cl_2] were obtained upon slow diffusion of diethyl ether into concentrated solutions of the two complexes in acetone/thf and dichloromethane, respectively. As anticipated, the X-ray structure analyses of the two compounds revealed the presence of N–H···F hydrogen-bonded [{(*R*)-binap}Rh($H_2N\cap NH_2$)]BF_4 ion pairs with the rhodium atoms in a close to planar coordination geometry (Figures 10 and 11). The metal-to-phosphane and metal-to-amine linkages measure 2.213(2)–2.223(2) Å and 2.147(7)–2.156(7) Å, respectively, which is slightly shorter than, but still comparable to, the Ru–P and Ru–N bond lengths previously reported for the octahedral molecules *trans*-[{(*R*)-binap}Ru(X)(Cl){(*R*,*R*)-$H_2NCH(Ph)CH(Ph)NH_2$}] (X = H[17a] or Cl[18]), where *d*(Ru–P) = 2.238–2.282 Å and *d*(Ru–N) = 2.164–2.198 Å.

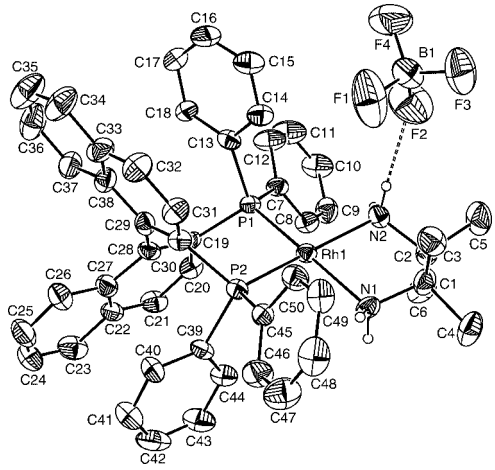


Figure 10. Structure of the ion pair [{(*R*)-binap}Rh($H_2NCMe_2CMe_2NH_2$)]BF_4 [(*R*)-**16**] as observed for the solid state of (*R*)-**16**·1/2Me_2CO·1/4thf (phenyl and methyl H atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: Rh1–P1, 2.223(2); Rh1–P2, 2.219(2); Rh1–N1, 2.155(6); Rh1–N2, 2.147(7). P1–Rh1–P2, 90.86(8); P1–Rh1–N1, 170.8(2); P1–Rh1–N2, 98.1(2); P2–Rh1–N1, 94.3(2); P2–Rh1–N2, 166.2(2); N1–Rh1–N2, 78.3(3). Hydrogen-bonding interactions as D–H, H···A, D···A, D–H···A [Å [°]]: N2–H···F2, 0.90, 2.26, 3.15(1), 171.1; N2–H···F3_#, 0.90, 2.23, 3.13(1), 176.7. Symmetry transformation used to generate equivalent atom: # = $-x$, $y-1/2$, $-z+1/2$.

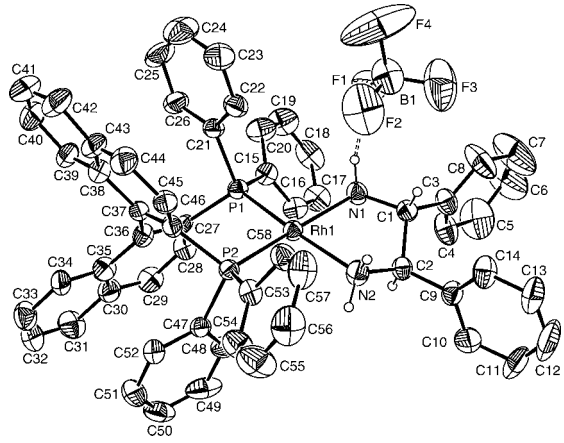


Figure 11. Structure of the ion pair [{(*R*)-binap}Rh{(*R*,*R*)-$H_2NCH(Ph)CH(Ph)NH_2$}]BF_4 [(*R*),(*R*,*R*)-**17**] as observed for the solid state of (*R*),(*R*,*R*)-**17**·CH_2Cl_2 (phenyl H atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: Rh1–P1, 2.219(2); Rh1–P2, 2.213(2); Rh1–N1, 2.147(7); Rh1–N2, 2.156(7). P1–Rh1–P2, 91.00(8); P1–Rh1–N1, 94.3(2); P1–Rh1–N2, 170.0(2); P2–Rh1–N1, 173.0(3); P2–Rh1–N2, 97.3(2); N1–Rh1–N2, 78.0(3). Hydrogen-bonding interaction as D–H, H···A, D···A, D–H···A [Å [°]]: N1–H···F1, 0.90, 2.05, 2.92(1), 163.2.

Catalytic C=O Hydrogenation

The close structural relationship of the ionic Rh^I and Rh^{III} complexes (*R*),(*R*,*R*)-**17** and (*R*),(*R*,*R*)-**19** to the neutral Ru^{II} ketone hydrogenation (pre)catalysts *trans*-[{(*R*)-

binap}Ru(X)(Cl){(*R*,*R*)-$H_2NCH(Ph)CH(Ph)NH_2$}] (X = H,[17a] Cl[18]) prompted us to also inspect the two rhodium compounds for their ability to form C=O hydrogenation catalysts. In these probing experiments, which were run in 2-propanol with acetophenone at a substrate-to-catalyst (*s*:*c*) ratio of 200:1 under the conditions summarized in Table 1, virtually no conversion to 1-phenylethanol was observed on attempted catalysis in the absence of an activating basic additive (Table 1, Entries 1 and 4). Only when combined with strong base (typically, 5 equiv. of KOH) did both complexes behave as relatively sluggish catalysts for the hydrogenation of the ketone functionality − irrespective of whether the reactions were carried out in the absence of hydrogen gas (Table 1, Entries 2 and 5) or under H_2 pressure (Table 1, Entries 3 and 6). These observations clearly demonstrate that neither the d^8 species [{(*R*)-binap}Rh{(*R*,*R*)-$H_2NCH(Ph)CH(Ph)NH_2$)]BF_4 nor its HCl adduct *trans*-[{(*R*)-binap}Rh(H)(Cl){(*R*,*R*)-$H_2NCH(Ph)CH(Ph)NH_2$)]BF_4 as such can act as catalysts for C=O hydrogenation, whereas the two base-modified systems are able to catalyze the transfer of H^+ and H^- equivalents both from the solvent and the gas molecule to the carbonyl dipole. Reduction of the substrate is slower in the absence than in the presence of hydrogen gas, which indicates that the two catalytic systems favor the direct hydrogenation by H_2 gas over the transfer of hydrogen from solvent molecules. The product alcohol was obtained in higher (albeit still modest) enantiomeric excess for the (*S*) enantiomer by transfer hydrogenation (64 and 71% *ee*) than by direct hydrogenation (30 and 33% *ee*).

Table 1. Hydrogenation of acetophenone in the presence of (*R*),(*R*,*R*)-**17** and (*R*),(*R*,*R*)-**19** as precatalysts.[a]

No.	Complex/base (equiv. rel. to C_{Rh})	$p(H_2)$ [bar]	*t* [h]	% PhCH(OH)Me	% *ee* (config.)
1	(*R*),(*R*,*R*)-**17**/none	10	20		
2	(*R*),(*R*,*R*)-**17**/KOH (5)		5	57	71 (*S*)
3	(*R*),(*R*,*R*)-**17**/KOH (5)	10	2.5	100	33 (*S*)
4	(*R*),(*R*,*R*)-**19**/none	10	20		
5	(*R*),(*R*,*R*)-**19**/KOH (5)		5	30	64 (*S*)
6	(*R*),(*R*,*R*)-**19**/KOH (5)	10	2.5	75	30 (*S*)

[a] Acetophenone (2.0 mmol) together with (*R*),(*R*,*R*)-**17** or (*R*),(*R*,*R*)-**19** (0.01 mmol), plus added base, in 2-propanol (3 mL) at 50 °C.

Recent results of Rautenstrauch, Morris et al. have shown that the established Ru^{II}-based ketone hydrogenation precatalyst *trans*-[{(*S*)-tolbinap}$RuCl_2${(*S*,*S*)-$H_2NCH(Ph)CH(Ph)NH_2$}] (tolbinap = the di-*p*-tolyl analogue of binap) and its (*R*),(*R*,*R*) enantiomer also display catalytic activity for ketone transfer hydrogenation, if modified by strong alkaline base (usually KO*t*Bu) in 2-propanol.[17b] Relative to rhodium precatalysts (*R*),(*R*,*R*)-**17** and (*R*),(*R*,*R*)-**19**, the ruthenium complexes form much more active systems and work very fast at *s*:*c* = 10^5–10^6 under the conditions of direct hydrogenation and with a reduced rate, but still much faster than both (*R*),(*R*,*R*)-**17** and (*R*),(*R*,*R*)-**19**, at *s*:*c* = 10^4–10^5 under transfer hydrogenation conditions. With acetophenone as the substrate ketone, the (*R*),(*R*,*R*) forms of both the ruthenium and the rhodium catalysts favor the formation of the product alcohol as the (*S*) enantiomer. In direct hydrogenation, distinctly higher *ee*'s are achieved with the Ru systems than the Rh systems (≈80% versus ≈30%), although the latter give somewhat better optical yields than the former if allowed to operate on the pathway of transfer hydrogenation (64–71% versus 42–62%).

Conclusions

This work shows that β-amino alcohols behave as N-monodentate ligands towards the dirhodium complex [(η^4-C_8H_{12})$_2$$Rh_2$(μ-Cl)$_2$] to form [($\eta^4$-$C_8H_{12}$)RhCl{HN(R)∩OH-κ*N*}] by nucleophilic cleavage of the chlorido bridges. Coordination of the free hydroxy function of the N,O ligands can be brought about either by dehydrochlorination to furnish alcoholato chelates [(η^4-C_8H_{12})Rh(H_2N∩O-κ*N*,κ*O*)] or by precipitation of the metal-bound chloride as TlCl, which converts the neutral [(η^4-C_8H_{12})RhCl{HN(R)∩OH-κ*N*}] compounds into cationic [(η^4-C_8H_{12})Rh{HN(R)∩OH-κ*N*,κ*O*}]$^+$ amino alcohol chelate complexes. Whereas the exploratory studies aimed at the coordination of the amino alcohols to phosphane-containing rhodium compounds remain largely inconclusive, similar complexes could easily be made from [(η^4-C_8H_{12})Rh{(*R*)-binap}]BF_4 and 1,2-diamine ligands. If activated by strong base, the resulting products [{(*R*)-binap}Rh(H_2N∩NH_2)]BF_4 can act as moderately active and selective catalysts for the reduction of acetophenone by both direct and transfer hydrogenation, as was demonstrated for [{(*R*)-binap}Rh{(*R*,*R*)-$H_2NCH(Ph)CH(Ph)NH_2$)]BF_4 and its HCl adduct *trans*-[{(*R*)-binap}Rh(H)(Cl){(*R*,*R*)-$H_2NCH(Ph)CH(Ph)NH_2$)]BF_4.

Experimental Section

General: All manipulations were performed under a nitrogen or argon atmosphere, except for the preparation of the 1,2-diamine complexes [{(*R*)-binap}Rh(H_2N∩NH_2)]BF_4 (**16**–**18**) from [(η^4-C_8H_{12})Rh{(*R*)-binap}]BF_4, which were carried out under a hydrogen atmosphere. Solvents were distilled from the appropriate drying agents prior to use. IR spectra were obtained with a Mattson Polaris spectrometer. ^{1}H, ^{13}C, and ^{31}P NMR were obtained with Bruker DPX 300 or Bruker DRX 400 spectrometers with $SiMe_4$ as the internal standard or with H_3PO_4 as the external standard (downfield positive) at ambient temperature, unless stated otherwise ("m" = deceptively simple multiplet). HPLC were obtained with a Thermoquest P 4000 (UV detector) apparatus. The amino alcohols, as well as the diphosphane and diamine ligands (*R*)-2,2′-bis(diphenylphosphanyl)-1,1′-binaphthyl, (*R*,*R*)-1,2-diphenylethylenediamine, and (*R*,*R*)-1,2-diaminocyclohexane, were used as obtained commercially. 1,1′,2,2′-Tetramethylethylenediamine,[19] [(η^4-C_8H_{12})$_2$$Rh_2$(μ-Cl)$_2$],[20] [($\eta^2$-$C_8H_{14}$)$_4$$Rh_2$(μ-Cl)$_2$],[21] and [($\eta^4$-$C_8H_{12}$)Rh{(*R*)-binap}]$BF_4$[15] were prepared according to published procedures or slight modifications thereof.

Monodentate Amino Alcohol Complexes [(η⁴-C_8H_{12})RhCl{HN-(R)∩OH-κ*N*}] (4–9): Toluene solutions (5–10 mL) of [(η⁴-C_8H_{12})$_2$-Rh_2(μ-Cl)$_2$] (0.20–0.70 mmol) were treated with the respective amino alcohol (2.1–2.5 equiv.) for 1 h at ambient conditions. Slow addition of *n*-pentane (50 mL) caused the products to separate from the mixtures as yellow microcrystals, which were separated by filtration, washed with *n*-pentane (3 × 10 mL), and dried under vacuum.

[(η⁴-C_8H_{12})RhCl($H_2NCH_2CH_2OH$-κ*N*)] (4): From [(η⁴-C_8H_{12})$_2$-Rh_2(μ-Cl)$_2$] (250 mg, 0.51 mmol) and ethanolamine (66 mg, 1.08 mmol) in toluene (10 mL). Yield: 260 mg (85%). ^{1}H NMR (300.1 MHz, $CDCl_3$): δ = 1.64, 2.30 (both m, 4 H each, both diene CH_2), 2.5 (br., 2 H, NH_2), 2.67, 3.80 (both t, *J* = 4.95 Hz, 2 H each, NCH_2CH_2O), 4.0 (br., 4 H, diene CH) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 31.60 (s, diene CH_2), 46.80 (s, NCH_2), 62.90 (s, CH_2O), 79.7 (br., diene CH) ppm. $C_{10}H_{19}ClNORh$ (307.62): calcd. C 39.04, H 6.23, N 4.55; found C 39.25, H 6.26, N 4.56.

[(η⁴-C_8H_{12})RhCl($H_2NCMe_2CH_2OH$-κ*N*)] (5): From [(η⁴-C_8H_{12})$_2$-Rh_2(μ-Cl)$_2$] (152 mg, 0.31 mmol) and 2-amino-2-methyl-1-propanol (57 mg, 0.64 mmol) in toluene (5 mL). Yield: 190 mg (91%). ^{1}H NMR (300.1 MHz, [D_6]DMSO): δ = 1.11 (s, 6 H, CH_3), 1.69, 2.29 (both m, 4 H each, both diene CH_2), 3.18 (s, CH_2O), 4.0 (br., 4 H, diene CH), 5.2 (br., 2 H, NH_2) ppm. ^{1}H NMR (400.1 MHz, CD_3OD, –25 °C): δ = 1.30 (s, 6 H, CH_3), 1.81, 2.40 (both m, 4 H each, both diene CH_2), 3.41 (br., CH_2O), 3.8, 4.2 (both br., 2 H each, both diene CH) ppm. ^{13}C NMR (75.5 MHz, [D_6]DMSO): δ = 25.13 (s, CH_3), 30.6 (br., diene CH_2), 55.04 (s, N*C*Me_2), 71.62 (s, CH_2O), 77.1 (br., diene CH) ppm. ^{13}C NMR (100.6 MHz, CD_3OD, –25 °C): δ = 24.13 (s, CH_3), 29.6, 30.7 (both br, both diene CH_2), 56.92 (s, N*C*Me_2), 70.3 (br., diene CH), 76.12 (s, CH_2O), 81.7 (br., diene CH) ppm. $C_{12}H_{23}ClNORh$ (335.68): calcd. C 42.94, H 6.91, N 4.17; found C 43.89, H 6.85, N 4.76.

[(η⁴-C_8H_{12})RhCl{(*R*)-$H_2NCH(CHMe_2)CH_2OH$-κ*N*}] [(*R*)-6 and Enantiomer (*S*)-6]: From [(η⁴-C_8H_{12})$_2$$Rh_2$(μ-Cl)$_2$] (200 mg, 0.41 mmol) and (*R*)- or (*S*)-2-amino-3-methyl-1-butanol (D-, L-valinol) (104 mg, 1.03 mmol) in toluene (10 mL). Yield: 275 mg (96%). ^{1}H NMR (300.1 MHz, CD_2Cl_2): δ = 0.86 (d, *J* = 6.78 Hz, 6 H, CH_3), 1.68–1.80 (m, 5 H, C*H*Me_2 partially superimposed by 4 diene CH_2), 2.3–2.5 (br. m, 7 H, NCH and NH_2, partially superimposed by 4 diene CH_2), 3.61 (dd, ^2J = 12.06 Hz, ^3J = 4.50 Hz, 1 H, 1 CH_2O), 4.00 (br., 4 H, diene CH), 4.21 (dd, ^2J = 12.06 Hz, ^3J = 2.64 Hz, 1 H, 1 CH_2O) ppm. ^{1}H NMR (400.1 MHz, [D_8]thf): δ = 0.83, 0.88 (both d, *J* = 6.60, 6.84 Hz, 3 H each, both CH_3), 1.63 (m, 4 H, diene CH_2, partially superimposed by solvent), 1.82 ("dq", *J* = 6.60, 6.84 Hz, 1 H, C*H*Me_2), 2.26 (m, 4 H, diene CH_2), 2.49 (m, 1 H, NCH), 2.9 (br., 2 H, NH_2), 3.51 (dd, ^2J = 11.24 Hz, ^3J = 4.88 Hz, 1 H, 1 CH_2O), 3.94 (m, 3 H, 2 diene CH superimposing 1 CH_2O), 3.97 (m, 2 H, diene CH) ppm. ^{1}H NMR (400.1 MHz, [D_8]thf, –25 °C): δ = 0.80, 0.85 (both d, *J* = 6.60, 6.84 Hz, 3 H each, both CH_3), 1.62 (m, 4 H, diene CH_2, partially superimposed by solvent), 1.81 ("dq", *J* = 6.60, 6.84 Hz, 1 H, C*H*Me_2, 2.21 (m, 4 H, diene CH_2), 2.56 (br., 1 H, NCH), 2.78, 2.93 (both br, 1 H each, NH_2), 3.59 (m, 1 H, 1 CH_2O), 3.8–4.1(br. m, 5 H, 4 diene CH superimposing 1 CH_2O) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 18.71, 18.89 (both s, both CH_3), 30.44, 30.56 (both s, diene CH_2 and *C*HMe_2), 61.14 (s, NCH), 62.61 (s, CH_2O), 78.7 (br., diene CH) ppm. $C_{13}H_{25}ClNORh$ (349.70): calcd. C 44.65, H 7.21, N 4.01; found C 45.22, H 7.24, N 4.35.

[(η⁴-C_8H_{12})RhCl{(*R*)-HN($CH_2CH_2CH_2CH$)CH_2OH-κ*N*}] [(*R*)-7 and Enantiomer (*S*)-7]: From [(η⁴-C_8H_{12})$_2$$Rh_2$(μ-Cl)$_2$] (220 mg, 0.45 mmol) and (*R*)- or (*S*)-2-pyrrolidinemethanol (D-, L-prolinol) (99 mg, 0.98 mmol) in toluene (10 mL). Yield: 280 mg (89%). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 25.25, 26.81 (both s, prolinol C*C*H_2*C*H_2C), 30.80, 31.45 (both s, both diene CH_2), 49.84 (s, NCH_2), 61.65 (s, NCH), 68.38 (s, CH_2O), 83.0 (br., diene CH) ppm. $C_{13}H_{23}ClNORh$ (347.68): calcd. C 44.91, H 6.67, N 4.03; found C 45.28, H 6.66, N 4.33.

[(η⁴-C_8H_{12})RhCl{(1*S*,2*R*)-$H_2NCH(Me)CH(Ph)OH$-κ*N*}] [(1*S*,2*R*)-8 and Enantiomer (1*R*,2*S*)-8]: From [(η⁴-C_8H_{12})$_2$$Rh_2$(μ-Cl)$_2$] (346 mg, 0.70 mmol) and (1*S*,2*R*)- or (1*R*,2*S*)-2-amino-1-phenyl-1-propanol (D-, L-norephedrine) (230 mg, 1.52 mmol) in toluene (10 mL). Yield: 510 mg (92%). ^{1}H NMR (300.1 MHz, CD_2Cl_2): δ = 0.97 (d, *J* = 6.39 Hz, 3 H, CH_3), 1.83 (m, 4 H, diene CH_2), 2.47 (m, 5 H, NCH, partially superimposed by 4 diene CH_2), 3.19 (m, 1 H, CHO), 4.1 (br., 4 H, diene CH), 5.7 (br., 2 H, NH_2), 7.31–7.42 (m, 5 H, C_6H_5) ppm. ^{13}C NMR (75.5 MHz, CD_2Cl_2): δ = 16.87 (s, CH_3), 31.50 (s, diene CH_2), 56.21 (s, NCH), 76.30 (s, CHO), 80.0 (br., diene CH), 126.68, 128.14, 129.05, 141.79 (all s, all C_6H_5) ppm. $C_{17}H_{25}ClNORh$ (397.74): calcd. C 51.34, H 6.34, N 3.52; found C 51.49, H 6.35, N 3.80.

[(η⁴-C_8H_{12})RhCl{(1*S*,2*R*)-$H_2NCH[CH(OH)CH_2]C_6H_4$-κ*N*}] [(1*S*,2*R*)-9 and Enantiomer (1*R*,2*S*)-9]: From [(η⁴-C_8H_{12})$_2$$Rh_2$(μ-Cl)$_2$] (148 mg, 0.30 mmol) and (1*S*,2*R*)- or (1*R*,2*S*)-*cis*-1-amino-2-indanol (94 mg, 0.63 mmol) in toluene (5 mL). Yield: 225 mg (94%). ^{1}H NMR (300.1 MHz, CD_2Cl_2): δ = 1.82, 2.57 (both m, 4 H each, both diene CH_2), 2.97 (dd, ^2J = 16.40 Hz, ^3J = 3.21 Hz, 1 H, 1 C*H*$_2$CH), 3.17 (dd, ^2J = 16.40 Hz, ^3J = 5.67 Hz, 1 H, 1 C*H*$_2$CH), 4.1 (br., 4 H, diene CH), 4.40 (d, *J* = 3.21 Hz, 1 H, CHN), 4.79 (m, 1 H, CHO), 7.31 (m, 3 H, phenylene H), 7.70 (m, 1 H, phenylene H) ppm. ^{13}C NMR (75.5 MHz, CD_2Cl_2): δ = 31.51, 31.58 (both s, both diene CH_2), 39.41 (s, *C*H_2CH), 61.88 (s, NCH), 73.85 (CHO), 80.3 (br., diene CH), 126.29, 126.13, 127.64, 129.25, 141.69, 141.89 (all s, all C_6H_4) ppm. $C_{17}H_{23}ClNORh$ (395.73): calcd. C 51.60, H 5.86, N 3.54; found C 51.54, H 6.13, N 3.91.

[(η⁴-C_8H_{12})Rh{(*S*)-$H_2NCH(CHMe_2)CH_2O$-κ*N*,κ*O*}]·H_2O, (*S*)-10·H_2O: Powdered potassium hydroxide (300 mg, 5.35 mmol) was added to a solution of [(η⁴-C_8H_{12})RhCl{(*S*)-$H_2NCH(CHMe_2)$-CH_2OH-κ*N*}], [(*S*)-**6**; (105 mg, 0.30 mmol] in dichloromethane (5 mL). The mixture was stirred for 16 h at room temperature and excess KOH was removed by filtration. Orange crystals identified as (*S*)-**9**·H_2O by X-ray structure determination (see below) were deposited from the filtrate upon standing for several days at ambient conditions.

Chelated Amino Alcohol Complexes [(η⁴-C_8H_{12})Rh{HN(R)∩OH-κ*N*,κ*O*}]O_3SCF_3 (11–15): Solid thallium trifluoromethanesulfonate was added in 10–20% excess to stirred solutions of the required monodentate amino alcohol complex [(η⁴-C_8H_{12})RhCl(HN-(R)∩OH-κ*N*)] (0.25–0.40 mmol) in dichloromethane (5–10 mL). After stirring for 30 min at room temperature, the precipitated thallium chloride was filtered off and the products were isolated as yellow powders by removing all volatile material from the filtrates.

[(η⁴-C_8H_{12})Rh($H_2NCMe_2CH_2OH$-κ*N*,κ*O*)]O_3SCF_3 (11): From **5** (99 mg, 0.29 mmol) and TlO_3SCF_3 (125 mg, 0.35 mmol) in CH_2Cl_2 (5 mL). Yield: 115 mg (88%). ^{1}H NMR (300.1 MHz, CD_3OD): δ = 1.33 (s, 6 H, CH_3), 1.84, 1.86 (both m, 4 H each, both diene CH_2), 3.47 (s, 2 H, CH_2O), 4.1 (br., 4 H, diene CH) ppm. ^{13}C NMR (75.5 MHz, CD_3OD): δ = 25.57 (s, CH_3), 31.7 (br., diene CH_2), 57.13 (s, N*C*Me_2), 76.15 (s, CH_2O), 82.0 (br., diene CH), 122.21 (q, $^1J_{F,C}$ = 318.6 Hz, CF_3) ppm. $C_{13}H_{23}F_3NO_4RhS$ (449.29): calcd. C 34.75, H 5.16, N 3.12, S 7.12; found C 34.14, H 5.34, N 3.12, S 6.87.

[(η⁴-C_8H_{12})Rh{(*S*)-$H_2NCH(CHMe_2)CH_2OH$-κ*N*,κ*O*}]O_3SCF_3 [(*S*)-12]: From (*S*)-**6** (108 mg, 0.31 mmol) and TlO_3SCF_3 (105 mg,

0.30 mmol) in CH_2Cl_2 (5 mL). Yield: 130 mg (90%). ^{1}H NMR (300.1 MHz, $CDCl_3$): δ = 0.89, 0.93 (both d, J = 6.78 Hz each, 3 H each, both CH_3), 1.68–1.84 (m, 5 H, 4 diene CH_2 superimposing 1 C*H*Me$_2$), 2.36 (m, 4 H, diene CH_2), 2.5 (br., 1 H, NCH), 2.9, 3.0 (both br, 1 H each, NH_2), 3.55 ("t", ^2J + ^3J = 10.35 Hz, 1 H, 1 CH_2O), 3.79 (dd, ^2J = 10.56 Hz, ^3J = 3.76 Hz, 1 H, 1 CH_2O), 4.1 (br., 4 H, diene CH) ppm. ^{1}H NMR (400.1 MHz, [D$_8$]thf): δ = 0.83, 0.87 (both d, J = 6.60, 6.84 Hz, 3 H each, both CH_3), 1.73 (m, 5 H, 4 diene CH_2 superimposing 1 C*H*Me$_2$), 2.31 (m, 4 H, diene CH_2), 2.5 (br., 1 H, NCH), 3.3, 3.6 (both br., 1 H each, NH_2), 3.50 (m, 1 H, 1 CH_2O, partially superimposed by solvent), 3.74 (dd, ^2J = 10.40, ^3J = 4.16 Hz, 1 H, 1 CH_2O), 4.06, 4.13 (both m, 2 H each, both diene CH) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 19.48, 19.74 (both s, both CH_3), 30.04, 30.44, 30.82 (all s, diene CH_2 and *C*HMe$_2$), 61.50 (s, NCH), 68.35 (s, CH_2O), 79.0 (br., diene CH), 120.54 (q, $^1J_{F,C}$ = 319.2 Hz, CF_3) ppm. $C_{14}H_{25}F_3NO_4RhS$ (463.32): calcd. C 36.29, H 5.44, N 3.02, S 6.92; found C 36.98, H 5.72, N 3.09, S 6.67.

[(η^4-C$_8$H$_{12}$)Rh{(*S*)-HN(CH$_2$CH$_2$CH$_2$CH)CH$_2$OH-κ*N*,κ*O*}]-O$_3$SCF$_3$ [(*S*)-13]: From (*S*)-**7** (86 mg, 0.25 mmol) and TlO_3SCF_3 (131 mg, 0.37 mmol) in CH_2Cl_2 (5 mL). Yield: 98 mg (85%). ^{1}H NMR (400.1 MHz, CD_3OD): δ = 1.59, 1.79 (both m, 1 and 3 H, prolinol CCH_2CH_2C), 1.95 (m, 4 H, diene CH_2), 2.40, 2.52 (both m, 2 H each, both diene CH_2), 2.89 (br. m, 2 H, NCH_2), 3.68 (br. m, 1 H, NCH), 3.51, 3.71 (both m, 1 H each, CH_2O), 4.08, 4.21 (both m, 2 H each, both diene CH) ppm. ^{13}C NMR (100.6 MHz, CD_3OD): δ = 23.37, 24.70 (both s, prolinol C*C*H$_2$*C*H$_2$C), 29.40, 30.32 (both s, both diene CH_2), 46.66 (s, NCH_2), 61.98 (s, NCH), 67.81 (s, CH_2O), 78.4 (br., diene CH), 120.48 (q, $^1J_{F,C}$ = 318.9 Hz, CF_3) ppm. $C_{14}H_{23}F_3NO_4RhS$ (461.30): calcd. C 36.45, H 5.03, N 3.04, S 6.95; found C 35.69, H 4.91, N 2.89, S 6.10.

[(η^4-C$_8$H$_{12}$)Rh{(1*R*,2*S*)-H$_2$NCH(Me)CH(Ph)OH-κ*N*,κ*O*}]O$_3$SCF$_3$ [(1*R*,2*S*)-14]: From (1*R*,1*S*)-**8** (150 mg, 0.38 mmol) and TlO_3SCF_3 (160 mg, 0.45 mmol) in CH_2Cl_2 (5 mL). Yield: 182 mg (94%). ^{1}H NMR (400.1 MHz, CD_3OD): δ = 1.08 (d, J = 6.80 Hz, 3 H, CH_3), 1.93, 2.53 (both m, 4 H each, both diene CH_2), 3.25 (m, 1 H, NCH), 4.2 (br., 4 H, diene CH), 4.99 (d, J = 3.92 Hz, 1 H, CHO), 7.40–7.66 (m, 5 H, C_6H_5) ppm. ^{1}H NMR (400.1 MHz, CD_3OD, –35 °C): δ = 1.03 (d, J = 6.36 Hz, 3 H, CH_3), 1.94, 2.54 (both m, 4 H each, both diene CH_2), 3.18 (m, 1 H, NCH), 4.0, 4.1 (both br, 1 H each, 2 diene CH), 4.4 (br., 2 H, 2 diene CH), 5.00 (d, J = 3.68 Hz, 1 H, CHO), 7.44–7.74 (m, 5 H, C_6H_5) ppm. ^{13}C NMR (100.6 MHz, CD_3OD): δ = 15.62 (s, CH_3), 31.18, 31.48 (both s, both diene CH_2), 55.07 (s, NCH), 68.84 (s, CHO), 79.2 (br., diene CH), 121.89 (q, $^1J_{F,C}$ = 320.0 Hz, CF_3), 127.78, 129.60, 138.06 (all s, C_6H_5) ppm. ^{13}C NMR (100.6 MHz, CD_3OD, –35 °C): δ = 15.94 (s, CH_3), 30.31, 30.90, 32.11, 32.45 (all s, all diene CH_2), 54.94 (s, NCH), 68.94 (s, CHO), 73.41, 73.85, 84.32, 84.51 (all d, $J_{Rh,C}$ = 13.20, 16.87, 11.73, 14.67 Hz, all diene CH), 121.69 (q, $^1J_{F,C}$ = 317.0 Hz, CF_3), 127.08, 127.94, 129.68, 138.06 (all s, C_6H_5) ppm. $C_{18}H_{25}F_3NO_4RhS$ (511.36): calcd. C 42.28, H 4.93, N 2.74, S 6.27; found C 42.23, H 5.13, N 2.93, S 5.96.

[(η^4-C$_8$H$_{12}$)Rh{(1*R*,2*S*)-H$_2$NCH[CH(OH)CH$_2$]C$_6$H$_4$-κ*N*,κ*O*}]-O$_3$SCF$_3$ [(1*R*,2*S*)-15]: From (1*R*,1*S*)-**9** (94 mg, 0.24 mmol) and TlO_3SCF_3 (100 mg, 0.28 mmol) in of CH_2Cl_2(10 mL). Yield: 120 mg (98%). ^{1}H NMR (300.1 MHz, CD_3OD): δ = 1.78, 2.31 (both m, 4 H each, both diene CH_2), 3.03 (dd, ^2J = 16.74, ^3J = 3.00 Hz, 1 H, 1 C*H*$_2$CH), 3.18 (dd, ^2J = 16.74, ^3J = 4.89 Hz, 1 H, 1 C*H*$_2$CH), 4.00, 4.14 (both br. m, 2 H each, both diene CH), 4.33 (d, J = 4.50 Hz, 1 H, CHN), 4.76 (m, 1 H, CHO), 7.32–7.45 (m, 4 H, phenylene H) ppm. ^{13}C NMR (75.5 MHz, CD_3OD): δ = 30.40 (s, diene CH_2), 40.36 (s, *C*H$_2$CH), 63.36 (s, NCH), 79.0 (br., diene CH), 83.66 (CHO), 122.22 (q, $^1J_{F,C}$ = 318.5 Hz, CF_3), 125.64, 126.93, 128.56, 128.94, 130.47, 141.30 (all s, all C_6H_4) ppm. $C_{18}H_{23}F_3NO_4RhS$ (509.34): calcd. C 42.45, H 4.55, N 2.75, S 6.29; found C 41.66, H 4.44, N 2.71, S 6.27.

1,2-Diamine Complexes [{(*R*)-binap}Rh(H$_2$N∩NH$_2$)]BF$_4$ (16–18): A thf solution (8 mL) of [(η^4-C_8H_{12})Rh{(*R*)-binap}]BF_4 (0.10–0.15 mmol) was combined with the required 1,2-diamine ligand in a 1:1 stoichiometry and allowed to react for 24 h at room temperature under an atmosphere of hydrogen. Evaporation of the solvent to a residual volume of ca. 2 mL followed by the slow addition of diethyl ether (15 mL) induced the precipitation of the product as a crystalline solid which was washed with diethyl ether (5 mL) and dried under vacuum.

[{(*R*)-binap}Rh(H$_2$NCMe$_2$CMe$_2$NH$_2$)]BF$_4$ [(*R*)-16]: From [(η^4-C_8H_{12})Rh{(*R*)-binap}]BF_4 (110 mg, 0.12 mmol) and 1,1′,2,2′-tetramethylethylenediamine (14 mg, 0.12 mmol). Yield: 82 mg (74%), red needles. ^{1}H NMR (300.1 MHz, [D$_6$]acetone): δ = 1.04, 1.15 (both s, 6 H each, both CH_3), 1.34, 4.17 (both br. d, ^2J = 12.9 Hz, 2 H each, both NH_2), 6.27–7.74 (m, 32 H, aryl H) ppm. ^{13}C NMR (75.5 MHz, CD_2Cl_2): δ = 25.86, 26.18 (both s, both CH_3), 60.81 (s, *C*Me$_2$), 125.65–138.79 (m, aryl C) ppm. ^{31}P NMR (121.5 MHz, [D$_6$]acetone): δ = 61.43 (d, $^1J_{Rh,P}$ = 173.9 Hz) ppm. $C_{50}H_{48}BF_4N_2P_2Rh$ (928.59): calcd. C 64.67, H 5.22, N 3.02; found C 64.75, H 5.69, N 2.75.

[{(*R*)-binap}Rh{(*R*,*R*)-H$_2$NCH(Ph)CH(Ph)NH$_2$}]BF$_4$ [(*R*),(*R*,*R*)-17]: From [(η^4-C_8H_{12})Rh{(*R*)-binap}]BF_4 (120 mg, 0.13 mmol) and (*R*,*R*)-1,2-diphenylethylenediamine (28 mg, 0.13 mmol). Yield: 100 mg (75%), dark red needles. ^{1}H NMR (300.1 MHz, CD_3CN): δ = 2.40, 3.27, 4.24 (all m, 2 H each, CHN and NH_2), 6.48–7.95 (m, 42 H, aryl H) ppm. ^{13}C NMR (75.5 MHz, CD_2Cl_2): δ = 63.35 (s, CHN), 124.52–138.14 (m, aryl C) ppm. ^{31}P NMR (121.5 MHz, CD_2Cl_2): δ = 62.36 (d, $^1J_{Rh,P}$ = 175.7 Hz) ppm. $C_{58}H_{48}BF_4N_2P_2Rh$ (1024.69): calcd. C 67.99, H 4.73, N 2.74; found C 67.39, H 4.92, N 2.79.

[{(*R*)-binap}Rh{(*R*,*R*)-1,2-(H$_2$N)$_2$C$_6$H$_{10}$}]BF$_4$ [(*R*),(*R*,*R*)-18]: From [(η^4-C_8H_{12})Rh{(*R*)-binap}]BF_4 (120 mg, 0.13 mmol) and (*R*,*R*)-1,2-diaminocyclohexane (15 mg, 0.13 mmol). Yield: 71 mg (59%), orange crystals. ^{1}H NMR (300.1 MHz, CD_3CN): δ = 0.92, 1.04, 1.46, 1.53 (all m, 2 H each, all CH_2), 1.66, 2.22, 3.20 (all m, 2 H each, CHN and NH_2), 6.41–7.96 (m, 32 H, aryl H) ppm. ^{13}C NMR (75.5 MHz, CD_3CN): δ = 23.88, 34.10 (both s, both CH_2), 58.72 (s, CHN), 125.41–133.87 (m, aryl C) ppm. ^{31}P NMR (121.5 MHz, CD_3CN): δ = 61.84 (d, $^1J_{Rh,P}$ = 173.9 Hz) ppm. $C_{50}H_{46}BF_4N_2P_2Rh$ (926.22): calcd. C 64.78, H 5.01, N 3.02; found C 63.95, H 5.40, N 2.98.

[{(*R*)-binap}Rh(H)(Cl){(*R*,*R*)-H$_2$NCH(Ph)CH(Ph)NH$_2$}]BF$_4$ [(*R*),(*R*,*R*)-19]: Dropwise addition of a saturated solution of hydrogen chloride in diethyl ether (2.5 mL) to (*R*),(*R*,*R*)-**17** (85 mg, 0.08 mmol) in thf (10 mL) caused an immediate change in color from dark red to bright yellow. The resulting mixture was stirred for 30 min at ambient conditions and then reduced in volume to 2 mL. Dilution with *n*-pentane (10 mL) gave the product as an off-white precipitate which was collected by filtration, washed with *n*-pentane (2 × 4 mL), and dried under vacuum. Yield: 61 mg (72%). ^{1}H NMR (300.1 MHz, CD_2Cl_2): δ = –14.06 ("dt", $^1J_{Rh,H}$ = 20.86 Hz, $\Sigma^2J_{P,H}$ = 39.01 Hz, 1 H, RhH), 2.54, 2.76, 3.34, 4.43 (all m, 6 H, CHN and NH_2), 6.20–8.16 (m, 42 H, aryl H) ppm. ^{31}P NMR (121.5 MHz, CD_2Cl_2): δ = 44.23 (dd, $^1J_{Rh,P}$ = 122.1 Hz, $^2J_{P,P}$ = 35.1 Hz), 57.32 (dd, $^1J_{Rh,P}$ = 120.2 Hz) ppm. $C_{58}H_{49}BClF_4N_2P_2Rh$ (1060.21): calcd. C 65.65, H 4.67, N 2.64; found C 65.27, H 4.53, N 2.58.

Reaction of $[(\eta^4\text{-}C_8H_{12})_2Rh_2(\mu\text{-}Cl)_2]$ with $H_2NCMe_2CH_2ONa$/$H_2NCMe_2CH_2OH$: A solution of $[(\eta^4\text{-}C_8H_{12})_2Rh_2(\mu\text{-}Cl)_2]$ (50 mg, 0.10 mmol) in toluene (3 mL) was treated with a solution of $H_2NCMe_2CH_2ONa$ in 2-amino-2-methyl-1-propanol (1.1 M, 0.2 mL), prepared by dissolving the required amount of sodium metal in that amino alcohol. Stirring at room temperature for several minutes produced a yellow precipitate which was collected by filtration. Slow diffusion of *n*-pentane into a saturated thf solution of the solid afforded the addition compound $[(\eta^4\text{-}C_8H_{12})Rh(H_2NCMe_2CH_2O\text{-}\kappa N,\kappa O)]\cdot[(\eta^4\text{-}C_8H_{12})Rh(H_2NCMe_2CH_2OH\text{-}\kappa N,\kappa O)][(\eta^4\text{-}C_8H_{12})RhCl_2]\cdot$thf (**1·2·**thf), while recrystallization of the crude product from a toluene/*n*-hexane mixture resulted in the isolation of the adduct $[(\eta^4\text{-}C_8H_{12})Rh(H_2NCMe_2CH_2O\text{-}\kappa N,\kappa O)]\cdot[(\eta^4\text{-}C_8H_{12})Rh(H_2NCMe_2CH_2OH\text{-}\kappa N,\kappa O)]Cl$ (**1·3**), as shown by X-ray structure analyses (see below).

Formation of *trans*-$[(i\text{Pr}_3\text{P})_2RhCl(N_2)]$: L-Valinol was added in slight excess to the solution formed by mixing $[(\eta^2\text{-}C_8H_{14})_4Rh_2(\mu\text{-}Cl)_2]$ (103 mg, 0.14 mmol) in thf (5 mL)with $Pi\text{Pr}_3$ (0.11 mL, ca. 4 equiv.) under a nitrogen atmosphere at room temperature. Gentle warming of the solution resulted in an immediate change in color from dark red to orange. All volatile materials were then removed, and the remaining orange solid was redissolved in CH_2Cl_2. Slow evaporation of the solvent induced the deposition of orange crystals which X-ray crystallography showed to be *trans*-$[(i\text{Pr}_3\text{P})_2RhCl(N_2)]$ (see below). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 49.52 (d, $^1J_{Rh,P}$ = 120.3 Hz); ref.[15b]: δ = 41.8 (d, $^1J_{Rh,P}$ = 122.5 Hz) in [D$_8$]toluene. No identifiable products were formed when the reaction was carried out under an atmosphere of argon or hydrogen.

Reaction of $[(\eta^4\text{-}C_8H_{12})Rh(H_2N\cap OH\text{-}\kappa N,\kappa O\})]O_3SCF_3$ Chelate Complexes (*S*)-12 and (1*R*,2*S*)-14 with (*R*)-binap: (*a*) A solution of L-valinol complex (*S*)-**12** (55 mg, 0.12 mmol) in thf (5 mL) was treated with an equimolar quantity of (*R*)-binap (74 mg). The color of the mixture changed immediately from yellow to red–orange. After stirring for 3 h at ambient temperature, the solvent was removed to leave an orange powder (109 mg), the ^{31}P NMR spectrum of which revealed the presence of an (*R*)-binap-coordinated C_1-symmetric species, assumed to originate from the $[\{(R)\text{-binap}\}Rh\{(S)\text{-}H_2NCH(CHMe_2)CH_2OH\text{-}\kappa N,\kappa O\}]^+$ cation. ^{31}P NMR (121.5 MHz, [D$_8$]thf): δ = 47.58 (dd, $^1J_{Rh,P}$ = 172.7 Hz, $^2J_{P,P}$ = 62.4 Hz), 55.71 (dd, $^1J_{Rh,P}$ = 207.2 Hz); comparative ^{31}P NMR spectroscopic data (CD_2Cl_2) for an in situ generated cationic complex formulated as $[\{(R)\text{-binap}\}Rh\{(S)\text{-nobin}\}]^+$ (SbF_6^- salt; nobin = 2′-amino-1,1′-binaphth-2-ol): δ = 39.4 (dd, $^1J_{Rh,P}$ = 203.6 Hz, $^2J_{P,P}$ = 89.3 Hz), 40.1 (dd, $^1J_{Rh,P}$ = 201.5 Hz) ppm.[10] The product also contained traces of uncoordinated (*R*)-binap (δ = –14.19 ppm) in addition to minor quantities (ca. 6%) of oxidized forms of the ligand, that is, (*R*)-binap(O) (δ = –13.76, 26.84 ppm) and (*R*)-binap(O)$_2$ (δ = 29.39 ppm); ref.[22] δ = –14.3, 28.1 ppm for binap(O) and δ = 29.3 ppm for binap(O)$_2$. Only inferior amounts (ca. 4%) of the $[(\eta^4\text{-}C_8H_{12})Rh\{(R)\text{-binap}\}]^+$ cation resulting from substitution of the amino alcohol rather than the diolefin were detected by ^{31}P NMR spectroscopic analysis: δ = 26.71 (d, $^1J_{Rh,P}$ = 147.1 Hz) ppm; comparative data for authentic $[(\eta^4\text{-}C_8H_{12})Rh\{(R)\text{-binap}\}]BF_4$ (121.5 MHz, $CDCl_3$): δ = 26.65 (d, $^1J_{Rh,P}$ = 144.8 Hz) ppm. The predominant replacement of the diene ligand by the diphosphane was also evident from the ^{1}H NMR spectrum (300.1 MHz,

Table 2. Crystal data and structure refinement for compounds **1·2·**thf, **1·3**, **4**, (*S*)-**6**, and (*R*)-**7**.

Compound	**1·2·**thf	**1·3**	**4**	(*S*)-**6**	(*R*)-**7**
Empirical formula	$C_{36}H_{65}Cl_2N_2O_3Rh_3$	$C_{24}H_{45}ClN_2O_2Rh_2$	$C_{10}H_{19}ClNORh$	$C_{13}H_{25}ClNORh$	$C_{13}H_{23}ClNORh$
M [g mol^{-1}]	953.53	634.89	307.62	349.70	347.68
Crystal size [mm]	0.50 × 0.28 × 0.08	0.48 × 0.27 × 0.23	0.23 × 0.18 × 0.17	0.41 × 0.35 × 0.20	0.32 × 0.17 × 0.13
T [°C]	–150 ± 2	–150 ± 2	–173 ± 2	–150 ± 2	–60 ± 2
Crystal system	triclinic	tetragonal	monoclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{4}2c$	$P2_1/c$	$P2_1$	$P2_1$
a [Å]	11.643(5)	11.220(2)	14.1313(3)	7.202(2)	11.220(2)
b [Å]	12.877(8)	11.220(2)	9.0605(5)	9.354(3)	7.267(1)
c [Å]	15.343(2)	21.023(8)	8.9213(4)	11.046(3)	17.461(3)
α [°]	102.85(2)	90	90	90	90
β [°]	101.60(2)	90	92.405(3)	100.53(2)	90.99(2)
γ [°]	111.12(4)	90	90	90	90
V [Å^3]	1989.6(17)	2646.6(12)	1141.25(8)	731.6(4)	1423.5(4)
Z	2	4	4	2	4
$D_{calcd.}$ [g cm^{-3}]	1.592	1.593	1.790	1.587	1.622
F(000)	976	1304	624	360	712
μ [mm^{-1}]	1.399	1.370	1.699	1.335	1.372
θ range [°]	1.97 to 25.17	1.94 to 26.27	3.66 to 28.70	1.88 to 25.15	1.17 to 26.97
h; k; l range	–13, 12; 0, 15; –18, 17	–13, 13; 0, 10; 0, 25	–19, 19; –12, 12; –12, 12	–8, 8; –11, 11; –13, 13	0, 14; –9, 9; –22, 22
Reflections collected	7491	5115	25405	3030	6500
Unique reflections	7148 ($R_{int.}$ = 0.0272)	2685 ($R_{int.}$ = 0.0630)	2929 ($R_{int.}$ = 0.0206)	2625 ($R_{int.}$ = 0.0521)	6183 ($R_{int.}$ = 0.0423)
Complete to θ_{max} [%]	100.0	99.7	99.8	100.0	99.7
Intensities $I > 2\sigma(I)$	5747	2018	2779	2147	5630
T_{min}/T_{max}	0.668/0.894	0.578/0.731	0.670/0.749	0.652/0.763	0.739/0.835
Parameters refined	435	146	146	157	374
wR_2 (all data)	0.1032	0.1290	0.0394	0.1353	0.0980
R_1 [$I > 2\sigma(I)$]	0.0410	0.0466	0.0170	0.0547	0.0371
GoF on F^2	1.043	1.081	1.102	1.096	1.039
ρ_{max}/ρ_{min} [e Å^{-3}]	1.17/–0.87	1.27/–0.68	0.59/- 0.57	1.16/–1.30	0.76/–0.62
Flack parameter x[29]		0.41(9)[a]		0.01(10)	0.01(5)

[a] Racemic twin.

[D_8]thf) showing free cyclooctadiene (δ = 2.22 and 5.39 ppm) together with coordinated L-valinol: δ = 0.54, 0.75 (both d, J = 6.60, 6.78 Hz, 3 H each, both CH_3), 1.98 ("dq", J = 6.60, 6.78 Hz, 1 H, C*H*Me$_2$), 2.48 (br. m, 3 H, NCH and NH_2 superimposed), 3.38 (m, 1 H, 1 CH_2O), 3.76 (dd, ^2J = 9.98 Hz, ^3J = 3.48 Hz, 1 H, CH_2O); comparative data for free L-valinol: δ = 0.71, 0.72 (both d, J = 6.78 Hz each, 3 H each, both CH_3), 1.41 ("dq", J = 6.78 Hz, 1 H C*H*Me$_2$), 2.36 (m, 1 H, NCH), 2.4 (br., 2 H, NH_2), 3.11 (m, 1 H, 1 CH_2O), 3.42 (dd, ^2J = 10.53, ^3J = 3.75 Hz, 1 H, CH_2O). (*b*) The unwanted formation of the binap(O), binap(O)$_2$, and [(η^4-C_8H_{12})-Rh{(*R*)-binap}]$^+$ byproducts could be suppressed by using a slight deficiency of the diphosphane as shown by the reaction of the L-norephedrine chelate complex (1*R*,2*S*)-**14** (129 mg, 0.25$_2$ mmol) with the (*R*)-binap ligand (156 mg, 0.25$_0$ mmol) in dichloromethane (4 mL). ^{31}P NMR spectroscopic data (121.5 MHz, CD_2Cl_2) attributed to the [{(*R*)-binap}Rh{(1*R*,2*S*)-H_2NCH(Me)CH(Ph)OH-κ*N*,κ*O*}]$^+$ cation: δ = 47.39 (dd, $^1J_{Rh,P}$ = 173.8 Hz, $^2J_{P,P}$ = 60.1 Hz, 55.70 (dd, $^1J_{Rh,P}$ = 204.2 Hz) ppm. So far, all attempts to isolate the suspected (*R*)-binap/amino alcohol complexes as pure compounds resulted in their decomposition to unidentified products.

General Procedure for Catalytic C=O Hydrogenation: A 10-mL Schlenk tube equipped with a small magnetic stirring bar was charged with the catalyst complex dissolved in 2-propanol (typically 0.01 mmol in 3.0 mL). The required equivalent of potassium hydroxide (if any; see Table 1) and acetophenone (2.0 mmol) were added, the mixture was stirred for 10 min at ambient conditions, and the tube was inserted into an argon-filled stainless steel autoclave. The autoclave was sealed and, in direct hydrogenation experiments, vented several times with H_2 (Messer-Griesheim; 99.999%), subsequently pressurized to 10 bar and kept at 50 °C with stirring. Transfer hydrogenation experiments were carried out under an atmosphere of argon. At the end of the reaction, the pressure was vented, the solvent removed under vacuum, and the residue was diluted with *n*-pentane to precipitate the catalyst as a red oil. The pentane solution was decanted and chromatographed on silica gel (diethyl ether/*n*-pentane, 1:1). Volatile material was distilled off, and the mixture of products was analyzed by ^{1}H NMR spectroscopy. Conversions and product compositions were determined on the basis of the integrations of the PhC(O)C*H*$_3$ and PhCH(OH)C*H*$_3$ signals. Enantiomeric excesses were measured by HPLC by using a Daicel Chiralcel OD column.

X-ray Structure Determinations: Single-crystals of the addition compounds **1·2**·thf and **1·3** were obtained by crystallizing the precipitates formed upon treatment of [(η^4-C_8H_{12})$_2$Rh$_2$(μ-Cl)$_2$] with H_2NCMe$_2$CH$_2$ONa/H_2NCMe$_2$CH$_2$OH from thf/*n*-pentane and toluene/*n*-hexane, respectively. Crystals suitable for X-ray work of **4**, (*S*)-**6**, (*R*)-**7**, (1*R*,2*S*)-**14**, and (1*R*,2*S*)-**15** were grown from dichloromethane. Crystal growth of (1*R*,2*S*)-**8** from thf/CH_2Cl_2 and (*R*)-**16** from diethyl ether/acetone/thf afforded solvent-containing specimens having the idealized compositions (1*R*,2*S*)-**8**·1/4CH_2Cl_2·1/4thf and (*R*)-**16**·1/2Me$_2$CO·1/4thf (see below). Crystals of (*S*)-**10**·H_2O grew from the mother liquor of the reaction between (*S*)-**6** and powdered KOH in CH_2Cl_2; those of (*R*),(*R*,*R*)-**17**·CH_2Cl_2 were deposited upon slow diffusion of diethyl ether into a concentrated dichloromethane solution of the complex. Diffraction measurements were made with an Enraf–Nonius CAD-4 MACH 3 diffractometer (compounds **1·2**·thf, **1·3**, (*S*)-**6**, (*S*)-**10**·H_2O, (1*R*,2*S*)-**15**, (*R*)-**7**, (1*R*,2*S*)-**14**, (*R*)-**16**·1/2Me$_2$CO·1/4thf, and (*R*),(*R*,*R*)-

Table 3. Crystal data and structure refinement for compounds (1*R*,2*S*)-**8**·1/4CH_2Cl_2·1/4thf,[a] (*S*)-**10**·H_2O, (1*R*,2*S*)-**14**, (1*R*,2*S*)-**15**, and (*R*)-**16**·1/2Me$_2$CO·1/4thf.

Compound	(1*R*,2*S*)-**8**·1/4CH_2Cl_2·1/4thf	(*S*)-**10**·H_2O	(1*R*,2*S*)-**14**	(1*R*,2*S*)-**15**	(*R*)-**16**·1/2Me$_2$CO·1/4thf
Empirical formula	$C_{36.611}H_{55.222}Cl_{2.926}N_2O_{2.537}Rh_2$[b]	$C_{13}H_{26}NO_2Rh$	$C_{18}H_{25}F_3NO_4RhS$	$C_{18}H_{23}F_3NO_4RhS$	$C_{52.50}H_{53}BF_4N_2O_{0.75}P_2Rh$
M [g mol^{-1}]	873.62	331.26	511.36	509.34	957.63
Crystal size [mm]	0.23 × 0.18 × 0.16	0.38 × 0.25 × 0.19	0.50 × 0.33 × 0.28	0.45 × 0.40 × 0.35	0.43 × 0.35 × 0.10
T [°C]	–173 ± 2	–150 ± 2	+20 ± 2	–70 ± 2	+20 ± 2
Crystal system	monoclinic	triclinic	orthorhombic	monoclinic	orthorhombic
Space group	$P2_1$	$P\bar{1}$	$P2_12_12_1$	$P2_1$	$P2_12_12_1$
a [Å]	10.9864(3)	7.288(2)	10.3321(9)	10.7614(7)	11.448(2)
b [Å]	14.2188(13)	10.139(1)	10.3563(9)	16.7785(13)	15.002(2)
c [Å]	12.3624(4)	10.521(1)	21.9557(18)	11.5551(13)	30.887(4)
α [°]	90	91.59(1)	90	90	90
β [°]	105.747(2)	107.27(2)	90	108.621(8)	90
γ [°]	90	103.52(3)	90	90	90
V [Å^3]	1858.7(2)	717.8(2)	2135.3(3)	1977.2(3)	5305.1(14)
Z	2	2	4	4	4
$D_{calcd.}$ [g cm^{-3}]	1.561	1.533	1.591	1.711	1.222
F(000)	898	344	1040	1032	2016
μ [mm^{-1}]	1.135	1.181	0.946	1.021	0.432
θ range [°]	3.44 to 28.70	2.04 to 26.17	2.04 to 25.48	1.86 to 24.06	2.33 to 25.16
h; k; l range	–14, 13; –19, 19; –16, 16	0, 9; –12, 12; –13, 12	–12, 9; 0, 12; –24, 0	–12, 11; –19, 0; 0, 13	–13, 13; –17, 17; –36, 36
Reflections collected	40881	3114	4037	3422	10486
Unique reflections	9540 ($R_{int.}$ = 0.0213)	3114	3769 ($R_{int.}$ = 0.0248)	3249 ($R_{int.}$ = 0.0155)	9451 ($R_{int.}$ = 0.0378)
Complete to θ_{max} [%]	99.3	100.0	100.0	99.9	99.1
Intensities $I > 2\sigma(I)$	9232	3082	3161	3114	6569
T_{min}/T_{max}	0.727/0.830	0.655/0.798	0.668/0.763	0.665/0.699	0.794/0.958
Parameters refined	473	314	257	511	601
wR_2 (all data)	0.0421	0.0648	0.0861	0.0593	0.1951
R_1 [$I > 2\sigma(I)$]	0.0187	0.0223	0.0371	0.0232	0.0731
GoF on F^2	1.137	1.143	1.097	1.044	1.034
ρ_{max}/ρ_{min} [e Å^{-3}]	0.52/–0.67	0.99/–0.60	0.57/–0.48	0.53/- 0.52	1.05/–0.69
Flack parameter x[29]	–0.010(14)	0.01(5)	0.03(5)	0.01(3)	–0.05(5)

[a] Formula idealized for integer number of atoms in unit cell (see text). [b] Empirical formula given for the hydrogen-bonded dimeric unit (see Figure 6) including the solvent of crystallization.

17·CH_2Cl_2) and a Bruker-Nonius Kappa CCD instrument (compounds **4** and (1*R*,2*S*)-**8**·1/4CH_2Cl_2·1/4thf), by using Mo-K_α radiation (λ = 0.71073 Å); data corrected for absorption either semiempirically from equivalents[23] (**4** and (1*R*,2*S*)-**8**·1/4CH_2Cl_2·1/4thf) or by ψ-scans.[24]

The structures were solved by direct methods and subsequently refined by full-matrix least-squares procedures on F^2 with allowance for anisotropic thermal motion of all non-hydrogen atoms employing both the SHELXTL NT 6.12[25] and the WinGX[26a] packages with some of the relevant programs (SIR-97,[27] SHELXL-97,[28] ORTEP-3[26b]) implemented therein. Crystals of **1·3** showed racemic twinning which was refined to give a twin component ratio close to 1:1. The split occupancies for the disordered cyclooctadiene carbon atoms in structure **4** (Figure 3) refined to 0.55 and 0.45, those of (1*R*,2*S*)-**8**·1/4CH_2Cl_2·1/4thf (Figure 6) to 0.74 and 0.26, and those of the atoms belonging to the disordered D-prolinol ligand in structure (*R*)-**7** (Figure 5) to 0.73 and 0.27. The residual electron density remaining after refinement of the structural model resulting for complex (*R*)-**16** was modeled by assuming the presence of solvent of crystallization (acetone and thf) with site occupancies fixed to 0.5 for the acetone and 0.25 for the thf molecule: (*R*)-**16**·1/2Me_2CO·1/4thf. Similarly, the final ΔF maps of the structure analysis of (1*R*,2*S*)-**8** indicated that in the crystal under study two different solvent molecules (CH_2Cl_2 and thf) shared a single crystallographic site with occupancies refining to 0.23 for the CH_2Cl_2 and 0.27 for the thf of crystallization, that is, close to (1*R*,2*S*)-**8**·1/4CH_2Cl_2·1/4thf. Further details of the X-ray structure determinations and results of the structure refinements are provided in Tables 2 3, and 4. For comparison with previously published data,[16b] the results of the structure determination carried out for the already known dinitrogen complex *trans*-[(iPr$_3$P)$_2$RhCl(N_2)] have also been included in Table 4.

Table 4. Crystal data and structure refinement for compounds (*R*),(*R*,*R*)-**17**·CH_2Cl_2 and *trans*-[(iPr$_3$P)$_2$RhCl(N_2)].

Compound	(*R*),(*R*,*R*)-**17**·CH_2Cl_2	*trans*-[(iPr$_3$P)$_2$RhCl(N_2)]
Empirical formula	$C_{59}H_{50}BCl_2F_4N_2P_2RhS$	$C_{18}H_{42}ClN_2P_2Rh$
M [g mol^{-1}]	511.36	486.84
Crystal size [mm]	0.40 × 0.31 × 0.30	0.22 × 0.12 × 0.09
T [°C]	+20 ± 2	–70 ± 2
Crystal system	orthorhombic	monoclinic
Space group	$P2_12_12_1$	$P2_1/c$ [$P2_1/c$][a]
a [Å]	11.355(1)	8.105(2) [8.062(2)][a]
b [Å]	15.545(1)	8.887(3) [8.883(2)][a]
c [Å]	31.979(3)	16.551(8) [16.431(4)][a]
α [°]	90	90
β [°]	90	93.07(5) [92.45(1)][a]
γ [°]	90	90
V [Å^3]	5644.7(8)	1189.1(8)
Z	4	2[b]
$D_{calcd.}$ [g cm^{-3}]	1.306	1.360 [1.375][a]
F(000)	2272	512
μ [mm^{-1}]	0.505	0.969
θ range [°]	1.90 to 25.16	2.46 to 27.04
h; k; l range	0, 13; 0, 18; 0, 38	–10, 10; 0, 11; –21, 21
Reflections collected	5595	2779
Unique reflections	5595	2599 ($R_{int.}$ = 0.0226)
Complete to θ_{max} [%]	99.4	99.7
Intensities $I > 2\sigma(I)$	4286	2089
T_{min}/T_{max}	0.756/0.856	0.892/0.915
Parameters refined	667	124
wR_2 (all data)	0.1661	0.0720
R_1 [$I > 2\sigma(I)$]	0.0609	0.0294 [0.024][a]
GoF on F^2	1.055	1.014
ρ_{max}/ρ_{min} [e Å^{-3}]	0.77/–0.56	0.51/–0.30
Flack parameter x[29]	0.15(6)	

[a] Crystal and refinement data obtained at –160 °C[16b] given in brackets. [b] Cl and N_2 ligands disordered about center of symmetry.

CCDC-631170 (for **1·2**·thf), -631171 (for **1·3**), -631172 (for **4**), -631173 [for (*S*)-**6**], -631174 [for (*R*)-**7**], -631175 [for (1*R*,2*S*)-**8**·1/4CH_2Cl_2·1/4thf], -631176 [for (*S*)-**10**·H_2O], -631177 [for (1*R*,2*S*)-**14**], -631178 [for (1*R*,2*S*)-**15**], -631179 [for (*R*)-**16**·1/2Me_2CO·1/4thf], -631180 [for (*R*),(*R*,*R*)-**17**·CH_2Cl_2], and -631181 [for *trans*-[(iPr$_3$P)$_2$RhCl(N_2)] contain 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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