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Cationic Rhodium-BINAP Complexes: Full Characterization of Solvate- and Arene-Bridged Dimeric Species

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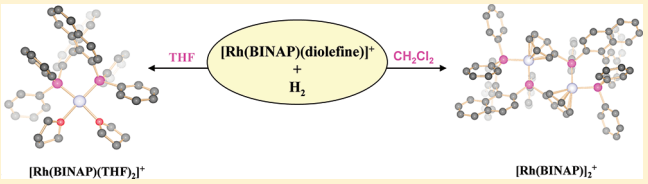
Supporting Information

ABSTRACT: In the asymmetric hydrogenation promoted by rhodium-diphosphine complexes in coordinating solvents such as methanol, the solvate complex is regarded as the catalytically active species. Here, we present for the first time the X-ray structures of rhodium-diphosphine solvate complexes [Rh((*S*)-BINAP)$(MeOH)_2$]BF_4, [Rh((*R*)-BINAP)$(acetone)_2$]BF_4, and [Rh((*S*)-BINAP)$(THF)_2$]BF_4. In noncoordinating solvents such as dichloromethane or dichlorethane hydrogenation of the diolefin in cationic precatalysts of the type [Rh(BINAP)(diolefin)]X (X = noncoordinating anion) results in the formation of the dimeric arene-bridged species $[Rh(BINAP)]_2(BF_4)_2$. The X-ray structure of the dinuclear species reveals that each BINAP acts as both a chelating and bridging ligand that coordinates a second unsaturated rhodium center through one of the phosphorus phenyl substituents.



INTRODUCTION

Commonly applied complexes in homogeneous catalysis are rhodium-diphosphine systems. Cationic complexes of the type [Rh(PP)(diolefin)]X (PP = chelating diphosphine, X = non-coordinating anion, e.g., BF_4^-, ClO_4^-, PF_6^-, diolefin = (*Z*,*Z*)-1,5-cyclooctadiene (cod), norbornadiene (nbd)) are used as catalyst precursors to promote, among others, asymmetric hydrogenation,[1] hydroformylation,[2] ring-opening of oxabicyclic alkenes,[3] C−C bond formation under hydrogenative conditions,[4] [2+2+2] cycloaddition of alkynes,[5] and the 1,4-addition of organoboronic acids.[6] Such complexes can be used as preformed catalyst precursors, many of which are commercially available, or prepared *in situ* through reaction of a diolefin complex such as $[Rh(cod)_2]X$ ("procatalyst") with a diphosphine ligand ("cocatalyst").[7] In the latter case main advantages are the easy handling and operational simplicity of routine applications and the possibility to vary the ligand to metal ratio.[8]

However, the application of the *in situ* procedure in the asymmetric hydrogenation of prochiral olefins can result in induction periods, due to which the hydrogenation rate increases in the beginning of the reaction.[9,10] On the other hand, if the solvate complex is used, which is formed by hydrogenation of the diolefin in the precatalyst *prior* to hydrogenation of the prochiral olefin, the reaction proceeds at the maximum rate from the very beginning. Investigations dealing with the determination of rate constants of diolefin hydrogenations, i.e., the transformation of the precatalyst into the active species, have been carried out in our group for a wide range of rhodium-diphosphine complexes.[9] Nonetheless, detailed investigations into the nature of the resulting solvate complexes are still scarce.

BINAP and its derivatives are recognized as "privileged ligands"[11] that have found widespread application in homogeneous catalysis.[12] Although the best results were obtained in combination with ruthenium,[13] BINAP-rhodium complexes have been successfully applied in a variety processes, e.g., C−C bond formation under hydrogenative conditions[4] or the [2+2+2] cycloaddition of alkynes.[5] A summary of published results obtained in asymmetric hydrogenation catalyzed by BINAP-rhodium complexes can be found in ref 14.

This work focuses on the characterization of several BINAP-rhodium solvate complexes as produced in coordinating solvents, including the first ever reported X-ray structures of this type of complexes, and of the arene-bridged dimers arising in noncoordinating solvents.

RESULTS AND DISCUSSION

The hydrogenation of [Rh(BINAP)(cod)]BF_4 or [Rh(BINAP)-(nbd)]BF_4 in methanol[9a,14] results in the solvate complex [Rh(BINAP)$(MeOH)_2$]BF_4 (**1**). From a concentrated solution of [Rh(BINAP)$(MeOH)_2$]BF_4 dark red prisms suitable for X-ray analysis were crystallized. Analysis of these highly air sensitive crystals isolated under a film of perfluorinated oil gave the structure of the methanol complex shown in Figure 1.

Although to the best of our knowledge only one similar solvate complex has been isolated before,[15] the X-ray structure of **1** represents the first ever reported one of a rhodium-diphosphine complex: this species is regarded as the active catalyst in asymmetric hydrogenation.[16] Two solvent molecules are coordinated to each rhodium center, in the same fashion as in $[Rh(DIPAMP)(MeOH)_2]^+$, as shown earlier by EXFAS.[17]

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Encouraged by this result, we tried to isolate single crystals of other solvate complexes and were indeed successful. Figure 2 shows the X-ray structures of solvate complexes [Rh((*S*)-BINAP)(THF)$_2$]BF$_4$ (**2**) and [Rh((*R*)-BINAP)(acetone)$_2$]-BF$_4$ (**3**).

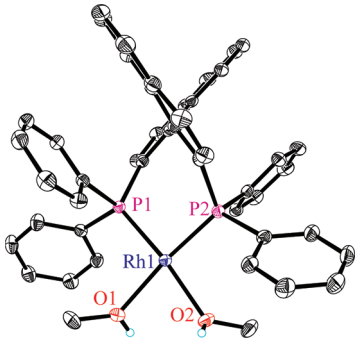

Figure 1. X-ray structure of [Rh((*S*)-BINAP)(MeOH)$_2$]BF$_4$ (**1**). The anion BF$_4^-$ and the hydrogen atoms of the ligand are omitted for clarity (ORTEP, 30% probability ellipsoids).

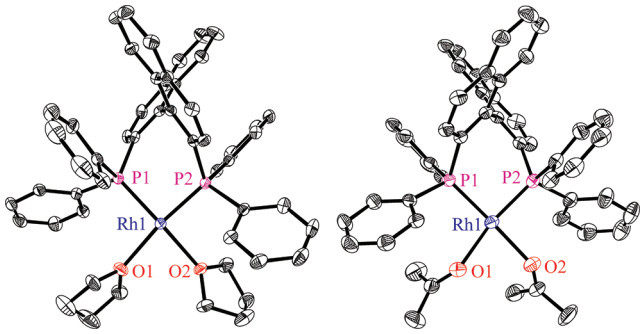

Figure 2. X-ray structures of [Rh((*S*)-BINAP)(THF)$_2$]BF$_4$ (**2**) (left) and [Rh((*R*)-BINAP)(acetone)$_2$]BF$_4$ (**3**) (right). The anions BF$_4^-$ and hydrogen atoms are omitted for clarity (ORTEP, 30% probability ellipsoids).

Crystallographic data of crystal structures **1**−**3** as well as of known diolefin complexes[14] are summarized in Table 1. The Rh−P distances are slightly shortened (by ca. 0.1 Å) in comparison with those found in the parent diolefin complexes [Rh(BINAP)(diolefin)]X (with diolefin = nbd, cod, X = BF$_4^-$, OTf$^-$, ClO$_4^-$), while the bite angles of the BINAP ligand lie between those observed in the nbd and cod complexes. Rh−O distances fall within the range of the corresponding Rh−C$_M$ distances (C$_M$ = centroid of the double bond), given in ref 14.

Solvate complexes **1**−**3** surprisingly show a deviation from the ideal square-planar coordination around the rhodium center as defined by the angle of the two planes P−Rh−P and O−Rh−O: an average tetrahedral distortion of ca. 10° is found. Such deviation had been observed before for a number of diolefin and catalyst substrate complexes.[1a,b,18] In [Rh((*R*)-BINAP)(acetone)$_2$]-BF$_4$ (**3**) the acetone molecules coordinate end-on through the O atoms as expected.

In other coordinating solvents the hydrogenation of [Rh-(BINAP)(nbd)]BF$_4$ leads to the corresponding solvate complexes, too. Table S1 (Supporting Information) summarizes their NMR data and also lists the ^{103}Rh NMR chemical shifts of complexes **1**−**3**.

The formation of such solvate complex structures, however, cannot be translated into noncoordinating solvents. The NMR spectra of solutions obtained by dissolving isolated crystals of [Rh(BINAP)(MeOH)$_2$]BF$_4$ in CD$_2$Cl$_2$ or by direct hydrogenation of [Rh(BINAP)(nbd)]BF$_4$ in the same solvent are identical, yet very different from those recorded in MeOH-d_4. The experimental findings (i.e., high-field protons at 5.15 and 5.25 ppm in MeOH-d_4 and additionally diagnostic protons at 4.95 and 5.40 ppm in trifluoroethanol (TFE)) suggest the formation of a dimeric arene-bridged species, similar to others reported before,[19] although only for [Rh(DPPE)]$_2^{2+}$[20] and [Rh(DIPAMP)]$_2^{2+}$[21] have the structures been unambiguously assigned by X-ray analysis.

Table 1. Selected Distances [Å] and Angles [deg] for Solvate Complexes 1−3

complex	Rh−P	P−Rh−P	Rh−O	O−Rh−O	tetrahedral distortion
1	2.179(1)	90.9(1)	2.151(2)	76.2(1)	10.7(2)
	2.191(1)		2.169(2)		
2	2.177(1)	90.3(1)	2.165(2)	80.9(1)	11.7(1)
	2.179(1)		2.187(2)		
3	2.181(2)	91.4(1)	2.140(4)	78.7(2)	9.6(2)
	2.196(2)		2.161(4)		
			Rh−C$_M$[a]	C$_M$−Rh−C$_M$	
[Rh((*R*)-BINAP)-(cod)]BF$_4$[14]	2.318	89.6(1)	2.123−	83.3(1)	7.5(1)
	2.335(2)		2.145(4)		
[Rh((*R*)-BINAP)-(nbd)]BF$_4$[14]	2.308	91.7(1)	2.073−	68.1(1)	13.2(1)
	2.311(2)		2.084(6)		
[Rh((*R*)-BINAP)-(cod)]OTf[14]	2.304	88.7(1)	2.128−	84.2(1)	16.8(1)
	2.329(3)		2.130(5)		
[Rh((*R*)-BINAP)-(nbd)]OTf[14]	2.319	91.6(1)	2.084−	66.5(1)	0.3(1)
	2.325(2)		2.107(4)		
[Rh((*R*)-BINAP)-(nbd)]ClO$_4$[12a,b]	2.305	91.8(1)	2.096−	68.9(1)	14.9
	2.321(1)		2.113(5)		

[a] C$_M$ = centroid of the double bond.

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Although the complex $[Rh(BINAP)]_2^{2+}$ has been described in the literature before, its molecular structure was not proven,[12a,b] and difficulties in its synthesis were described.[19e,f]

Dark brown crystals were isolated from a solution of $[Rh((R)\text{-}BINAP)]_2(BF_4)_2$ (**4**) in dichloromethane that was layered with diethyl ether. Single crystals suitable for X-ray analysis were obtained by recrystallization from TFE; Figure 3 shows the X-ray structure of **4**.

In **4** each BINAP acts as a bridging ligand between two rhodium atoms, the second unsaturated rhodium center being coordinated through one of the phenyl rings of the ligand backbone, in the same fashion as in $[Rh(DPPE)]_2^{2+}$ and $[Rh(DIPAMP)]_2^{2+}$. In Table 2 characteristic crystallographic data are summarized together with data of analogous arene-bridged dinuclear rhodium diphosphine complexes.[22]

Average Rh−C(coordinated phenyl ring) distances are similar among the four complexes. In **4** the Rh−Rh distance is 4.498 Å and thus ca. 0.22 and 0.35 Å longer than in the corresponding bridged dimers of DPPE (4.277 Å) and DIPAMP (4.144 Å).[21] The bite angle of BINAP in **4** (88.5−89.5) does not differ notably from those of the parent cod complexes (Table 1).[14]

In **4**, upon coordination to the second rhodium center through one of their phenyl substituents, both phosphorus atoms P1 and P3 of axially chiral BINAP become chiral. The X-ray structure shows that both the BINAP molecules are of *R*-configuration.

For the interpretation of NMR patterns first the spectra in CD_2Cl_2 were analyzed, showing two species in a ratio of 9:1. In the ^{31}P NMR spectrum the higher concentrated species exhibits two signal sets. The low-field signal set (46.6 ppm) is split into two multiplets, whereas the high-field signals (42.5 ppm) represent two doublets, Figure 4.

In the ^1H NMR spectrum diagnostic high-field-shifted protons are visible (5.2 and 5.1 ppm), which belong to the phenyl rings coordinated to a rhodium atom. The $^1H-^1H$ COSY NMR measurement confirms the phenyl−phenyl bridged structure found in the solid state, Figure 5.

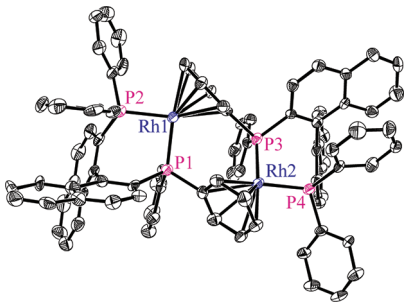

Figure 3. X-ray structure of $[Rh((R)\text{-}BINAP)]_2(BF_4)_2$ (**4**). The anions BF_4^- and hydrogen atoms are omitted for clarity (ORTEP, 30% probability ellipsoids). Selected distances [Å] and angles [deg]: Rh−Rh 4.498(3), Rh−P 2.231−2.246(3), P−Rh−P 88.5−89.5(1), Rh−C 2.269−2.379(9).

By recording the $^1H-^1H$ COSY NMR spectrum in CF_3CD_2OD, the structure of the less concentrated species could be likewise described as a phenyl−phenyl bridged dimer, Figure S9 (Supporting Information). The correlation of the proton signals is very similar to that found for the more abundant dimer; therefore the two species are most probably diastereomers.

Accordingly, the chemical shifts of the two supposedly diastereomeric species do not differ much on the ^{103}Rh NMR scale (−382 and −345 ppm), Figure S10.

The stability of dimers $[Rh(DIPAMP)]_2(BF_4)_2$ and $[Rh(BINAP)]_2(BF_4)_2$ relative to the corresponding solvate complexes in MeOH can be easily assessed by NMR: while $[Rh(DIPAMP)]_2(BF_4)_2$ coexists in equilibrium with the solvate complex $[Rh(DIPAMP)(MeOH)_2]BF_4$,[21] the equilibrium between solvate complex and dimer in the case of BINAP is entirely on the side of the solvate complex $[Rh(BINAP)(MeOH)_2]BF_4$.[23]

CONCLUSION

Solvate complexes as the catalytically active species in asymmetric hydrogenation have been characterized for the first time by X-ray analysis using $[Rh(BINAP)(solvent)]^+$ as an example, with MeOH, THF, and acetone as coordinating solvents. In nonpolar solvents, such as dichloromethane and dichloroethane, but also in trifluoroethanol, the hydrogenation of the cationic precursor $[Rh(BINAP)(nbd)]BF_4$ results in the formation of phenyl−phenyl bridged dimers $[Rh(BINAP)]_2(BF_4)_2$, which were characterized both in the solid (X-ray analysis) and in solution (NMR).

EXPERIMENTAL SECTION

All manipulations were carried out using standard Schlenk techniques under argon.

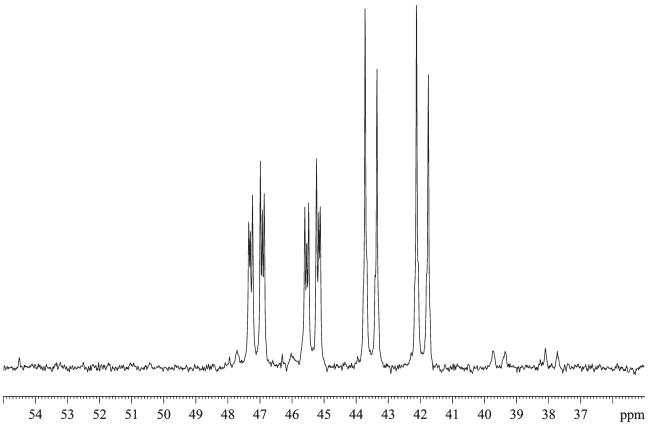

Figure 4. $^{31}P\{^1H\}$ NMR spectrum of **4** in CD_2Cl_2. Low-field signals of the lower concentrated species are overlapped by signals of the higher concentrated species.

Table 2. Crystallographic Data of Arene Bridged Dimeric Diphosphine Complexes

complex	Rh−Rh [Å]	Rh−P [Å]	P−Rh−P [deg]	Rh−C [Å]
$[Rh((R)\text{-}BINAP)]_2(BF_4)_2$ (**4**)	4.498(2)	2.231−2.246(3)	88.5, 89.5(1)	2.269−2.379(9)
$[Rh(DPPE)]_2(BF_4)_2 \cdot CF_3CH_2OH$[20]	4.275(1)	2.230, 2.240(2)[a]	[b]	2.285−2.368
$[Rh(DPPE)]_2(BF_4)_2$[21]	4.277(1)	2.218, 2.222(2)[a]	84.2(1)[a]	2.266−2.358(5)
$[Rh((S,S)\text{-}DIPAMP)]_2(BF_4)_2$[21]	4.144(1)	2.221, 2.228(2)[a]	84.2(1)[a]	2.258−2.346(8)

[a] Half of the molecule had been generated from a symmetric operation. [b] Value was not reported.

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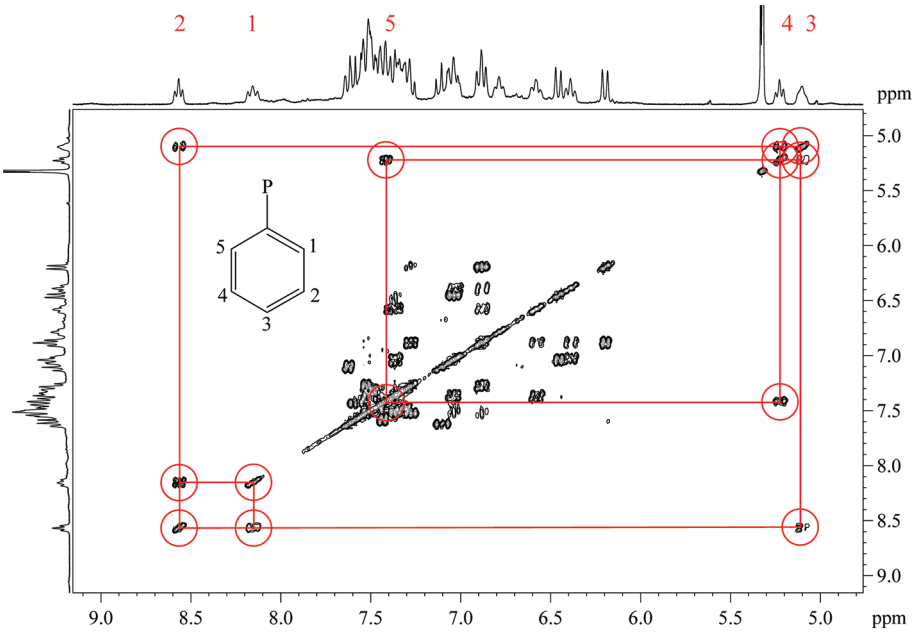

Figure 5. Details of the $^{1}H-^{1}H$ COSY NMR spectrum of **4** in CD_2Cl_2. The protons of the arene bridge of the more abundant diastereomer are encircled.

[Rh((*R*)-BINAP)(nbd)]BF_4 and [Rh((*S*)-BINAP)(nbd)]BF_4 were synthesized according to ref 14. BINAP was supplied by Suzhou LAC Co. Ltd. (www.suzhoulac.com) and used as received.

Diethyl ether and THF were distilled from sodium benzophenone ketyl immediately prior to use. MeOH was distilled from Mg turnings prior to use; CD_3OD from $LiAlH_4$. CH_2Cl_2 and CD_2Cl_2 were distilled from P_4O_{10}; dichloroethane and $ClCD_2CD_2Cl$ from CaH_2. CF_3CD_2OD and THF-d_8 were stored and distilled from activated molecular sieves and subsequently frozen and evaporated (3×) to remove remaining traces of oxygen.

NMR spectra were recorded on a Bruker ARX-400 spectrometer (400 MHz for ^{1}H) at 297−298 K. Chemical shifts are reported in parts per million (ppm) referenced to the deuterated solvent for ^{1}H NMR. For chemical shifts in ^{31}P NMR spectra (in ppm), 85% H_3PO_4 was used as an external standard. ^{103}Rh NMR chemical shifts (in ppm) were determined in $^{31}P-^{103}Rh$ HMQC measurements (under proton decoupling). The reference frequency was determined individually for each sample with $\Xi(^{103}Rh) = 3.16$ MHz.

Crystal data and details of the structure solution are summarized in Table S2 (Supporting Information). Diffraction data were collected on a STOE-IPDS II diffractometer using graphite -monochromated Mo Kα radiation. The structures were solved by direct methods (SHELXS-97)[24] and refined by full matrix least-squares techniques against F^2 (SHELXL-97).[24] XP (Siemens Analytical X-ray Instruments, Inc.) was used for structure representations.

The non-hydrogen atoms, except the partially occupied atoms of the solvents and anions, were refined anisotropically. The hydrogen atoms were placed into theoretical positions (except the hydrogen atoms of the OH group from the coordinated methanol in [Rh((*S*)-BINAP)$(MeOH)_2$]BF_4·5MeOH) and were refined by using the riding model. The weighting schemes used in the last cycles of refinement are $w = 1/[\sigma^2(F_o^2) + (0.00.0471P)^2 + 0.0000P]$ for [Rh((*S*)-BINAP)$(MeOH)_2$]BF_4·5MeOH, $w = 1/[\sigma^2(F_o^2) + (0.0348P)^2 + 0.1294P]$ for [Rh((*S*)-BINAP)$(THF)_2$]BF_4·thf, $w = 1/[\sigma^2(F_o^2) + (0.0884P)^2 + 0.0000P]$ for [Rh((*R*)-BINAP)$(acetone)_2$]BF_4·1/2 acetone·1/2 diethyl ether, and $w = 1/[\sigma^2(F_o^2) + (0.0120P)^2 + 0.0000P]$ for [Rh((*R*)-BINAP)]$_2(BF_4)_2$.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-842944 for [Rh((*S*)-BINAP)$(MeOH)_2$]BF_4·5MeOH, CCDC-842946 for [Rh((*S*)-BINAP)$(THF)_2$]BF_4·thf, CCDC-842947 for [Rh((*R*)-BINAP)$(acetone)_2$]BF_4·1/2 acetone·1/2 diethyl ether, and CCDC-842945 for [Rh((*R*)-BINAP)]$_2(BF_4)_2$.

Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB21EZ, UK (fax: int. code + (1223) 336-033; e-mail: deposit@ccdc.cam.ac.uk.

Hydrogenation of [Rh(BINAP)(nbd)]BF_4 in polar solvents leads to the corresponding solvate complexes [Rh(BINAP)$(solvent)_2$]BF_4; see Table S1 for ^{31}P NMR data and Supporting Information for spectra.

Single crystals of [Rh(BINAP)$(MeOH)_2$]BF_4 (**1**) and [Rh(BINAP)-$(acetone)_2$]BF_4 (**3**), suitable for X-ray analysis, were obtained by hydrogenation (ca. 3 min) of 0.04 mmol of [Rh(BINAP)(nbd)]BF_4 in 1 mL of the corresponding solvent and subsequent removal of hydrogen gas from the solution by application of three freeze−thaw cycles. [Rh(BINAP)$(THF)_2$]BF_4 (**2**) was generated by hydrogenation (ca. 3 min) of 0.005 mmol of [Rh(BINAP)(nbd)]BF_4 in 1 mL of THF. After removal of hydrogen gas, the resulting solution was layered with diethyl ether. In all cases the solutions were allowed to stand overnight, during which time single crystals precipitated.

[Rh(BINAP)$(MeOH)_2$]BF_4 (1). ^{1}H NMR (CD_3OD): 8.06−7.99 (4H, m); 7.79 (4H, br s); 7.59−7.53 (10H, m); 7.40−7.28 (4H, m); 7.02−6.97 (2H, m); 6.82−6.70 (6H, m); 6.51−6.48 (2H, m); 4.87 (CH_3OH, s); 3.32 (CH_3OH) (spectrum contains signals of norbornane). ^{31}P NMR (CD_3OD): 55.1 (J_{P-Rh} = 205.8 Hz). ^{103}Rh NMR (CD_3OD): 327 (Ξ = 3.161033 MHz).

[Rh(BINAP)$(THF)_2$]BF_4 (2). The complex is poorly soluble in THF-d_8, and a minor species is also detected in solution (δ 47.7 ppm, J_{P-Rh} = 200 Hz). Therefore, ^{1}H NMR data are not available. ^{31}P NMR (THF-d_8): 54.2 (d, J_{P-Rh} = 207.5 Hz). ^{103}Rh NMR (THF-d_8): 350 (Ξ = 3.161106 MHz).

[Rh(BINAP)$(acetone)_2$]BF_4 (3). ^{1}H NMR (acetone-d_6): 7.89−7.84 (8H, m); 7.74−7.71 (2H, m); 7.66−7.60 (4H, m); 7.54−7.51 (6H, m); 7.36−7.32 (2H, m); 7.02−6.98 (2H, m); 6.81−6.74 (6H, m); 6.44−6.41 (2H, m); 2.04 (($CH_3)_2CO$, s) (spectrum contains signals of norbornane). ^{31}P NMR (acetone-d_6): 53.4 (d, J_{P-Rh} = 200.9 Hz). ^{103}Rh NMR (acetone-d_6): 365 (Ξ = 3.161153 MHz).

[Rh(BINAP)(BF_4)]$_2$ (4). [Rh(BINAP)(nbd)]BF_4 (0.04 mmol) was hydrogenated in 3 mL of MeOH. The resulting solution of [Rh(BINAP)$(MeOH)_2$]BF_4 was concentrated *in vacuo*, and the precipitate was redissolved in 1 mL of dichloromethane and layered with 5 mL of diethyl ether. Dark brown crystals precipitated within an hour. The mother liquor was removed via syringe; the crystals were washed with diethyl ether twice and dried *in vacuo*. Single crystals suitable for X-ray analysis were gained from recrystallization with trifluoroethanol.

^{1}H NMR (CD_2Cl_2): 8.60−8.55 (2H, m); 8.19−8.14 (2H, m); 7.65−7.26 (34H, m); 7.14−7.01 (8H, m); 6.91−6.86 (4H, m); 6.81−6.77 (2H, m); 6.61−6.55 (2H, m); 6.47−6.45 (2H, m); 6.42−6.36 (2H, m); 6.21−6.18 (2H, m); 5.25−5.20 (2H, m); 5.13−5.09 (2H, m). ^{31}P NMR (CD_2Cl_2): 42.5 (J_{P-Rh} = 194 Hz; J_{P-P} = 45 Hz); 46.6 (J_{P-Rh} = 212 Hz; J_{P-P} = 45 Hz); approximate values as the spectrum is of higher order. ^{103}Rh NMR (CD_2Cl_2): −394 (Ξ = 3.158755 MHz).

■ ASSOCIATED CONTENT

Supporting Information. NMR spectra and X-ray diffraction data for complexes **1**−**4** including tables of positional and isotropic thermal parameters and anisotropic thermal parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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