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Reaction of a Rhodium−MiniPHOS Complex with Dihydrogen: NMR and Computational Study

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The rhodium−MiniPHOS complex $[Rh((R,R)\text{-}MeBu^tPCH_2PMeBu^t)_2]^+BF_4^-$ (**1**) is reversibly and stereoselectively hydrogenated at low temperatures to give one isomer of *cis*-dihydride **2a**. The second possible diastereomer, **2b**, is not observed experimentally. DFT calculations suggest that **2b** is 3.5 kcal mol^{-1} less stable than **2a**. The parameters of the equilibrium between **2a**, **1**, and H_2 determined by NMR are $\Delta H = -7.7 \pm 0.1$ kcal mol^{-1} and $\Delta S = -25 \pm 1$ cal mol^{-1} K^{-1}. Formation of the *trans*-dihydride **3** is observed at around −20 °C. Most probably **3** is formed by isomerization of **2a** or **2b**. This isomerization involves reversible dissociation of the Rh−P bond. Similar dissociation of the Rh−P bond in **2a** might make possible the substrate binding when **1** is used as a catalyst for asymmetric hydrogenation.

Introduction

Although the mechanism of asymmetric hydrogenation of C═C bonds catalyzed by Rh(I) diphosphine complexes was actively studied for about three decades,[1] a complete understanding of the stereoselection has not yet been achieved. In this respect the mechanistic studies of the newly designed effective catalytic systems are of significant interest.

It is generally accepted that a homogeneous catalyst acts through the coordination of a substrate, at least on one stage of the catalytic cycle. The usually assumed catalytic cycle of asymmetric hydrogenation of activated C═C bonds implies the bidentate coordination of a substrate, which is considered to be an important factor for the successful stereodifferentiation.[1] Such bidentate coordination is easily achieved by the reaction of a substrate with solvate complexes which are formed upon hydrogenation of the catalytic precursors.[2−4]

Recently, we have reported that rhodium complexes of the structure $[Rh(MiniPHOS)_2]^+X^-$ (MiniPHOS = (R,R)-MeRPCH$_2$PRMe; X = BF$_4$, PF$_6$) are active as catalysts for the asymmetric hydrogenation of dehydroamino acids and related compounds.[5] Although the catalytic activity of these complexes is lower compared to that of $[Rh(BisP^*)(nbd)]BF_4$ precatalysts (BisP* = (S,S)-RMePCH$_2$CH$_2$PMeR), which also contain P-chirogenic trialkyl diphosphines,[6−8] the use of Rh-MiniPHOS complexes gives very high enantioselectivities (up to 99.9% ee).[5] The structure of $[Rh((R,R)\text{-}MeBu^tPCH_2PMeBu^t)_2]PF_6$ was determined by X-ray analysis.[5] It apparently lacks vacant sites for the substrate coordination. Naturally, questions arise on the mechanism of substrate binding and on the intermediate species involved in the catalytic cycle. Previously, James et al. have shown that the cationic complex $[Rh(diop)_2]BF_4$ is a reasonably effective catalyst in the asymmetric hydrogenation.[9,10] The partial ligand dissociation in the dihydride $[RhH_2(diop)_2]BF_4$ has been suggested to provide a vacant site nessesary for the substrate binding.[9]

The dihydride $[RhH_2(diop)_2]BF_4$ and other dihydrides of general formula $[RhH_2(Ph_2P(CH_2)_nPPh_2)_2]^+X^-$ ($n \geq 3$) containing six- or seven-membered chelate rings are isolable compounds; however, attempts to detect similar compounds with $n = 2$, 1 have so far been unsuccessful.[9−11] Therefore, it seemed interesting to investigate the hydrogenation of a MiniPHOS−Rh complex, which contains strained four-membered chelate cycles. In this work we have studied the reaction of $[Rh(MeBu^tPCH_2PMeBu^t)_2]BF_4$ (**1**) with dihydrogen.

Results and Discussion

Low-Temperature Hydrogenation of 1. A deuteriomethanol solution of **1** was hydrogenated at −90 °C for 10−15 min (2−3 atm of H_2) and then immediately placed in a precooled probe of an NMR spectrometer. A doublet of broad multiplets at δ −10.8 was found in the hydride region of the ^{1}H NMR spectrum of the sample so obtained (Figure 1). This signal correlates with two multiplets at δ 11.1 and −15.6 in the ^{31}P NMR spectrum, which are coupled with each other, as follows from

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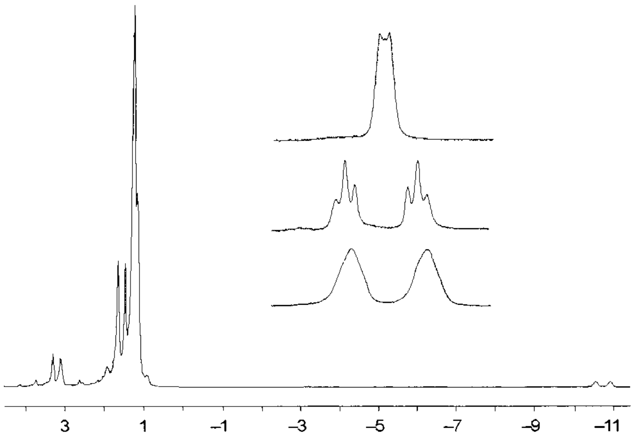
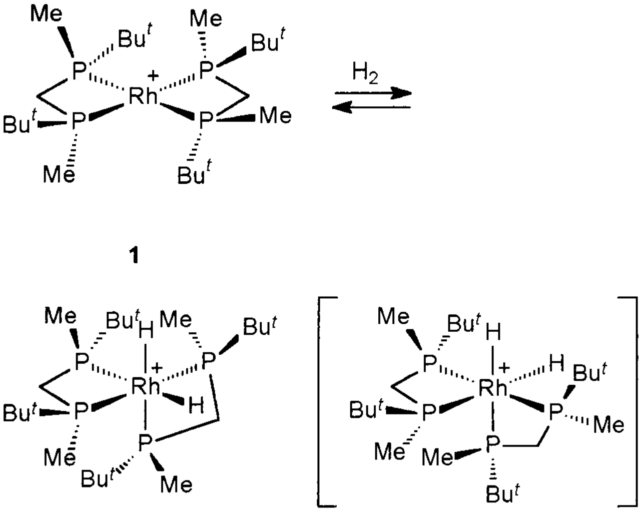


Figure 1. ^{1}H NMR spectrum (400 MHz, CD_3OD, 183 K) of the equilibrium mixture of **1** and **2a**. The inserts show the line shapes of the hydride signal of **2a** in the normal spectrum (bottom), in a spectrum with selective decoupling from ^{31}P with δ 11.1 (middle), and in a spectrum with selective decoupling from ^{31}P with δ −15.6 (top).

Scheme 1



1

2a

2b

the ^{31}P−^{31}P COSY experiment. Both multiplets appear as double triplets with a large Rh−P coupling (80 and 71 Hz, respectively) and two equivalent P−P couplings (35 Hz). On the basis of the spectral data we conclude that the hydrogenation product has the structure of *cis*-dihydride **2** (Scheme 1). The details of the ^{1}H−^{31}P and ^{1}H−^{103}Rh coupling patterns were confirmed by the ^{1}H-{^{31}P} NMR spectra, with selective decoupling from each multiplet (Figure 1, Table 1).

There are two possible diastereomers of dihydride **2** (Scheme 1). However, only one set of signals was detected in the ^{1}H and ^{31}P spectra. Different alkyl groups of the dihydride **2** resonate very closely in the ^{1}H NMR spectrum (Figure 1), and hence the experimental determination of its structure is extremely complicated. We therefore challenged this problem computationally.

We have used the approach of Landis et al.[12,13] recently applied to the theoretical studies of Rh−diphosphine complexes. The geometries were optimized using the B3LYP method, including Becke's three-parameter functional[14] and Lee, Yang, and Parr correlation energies.[15] Optimizations were made using the LANL2DZ basis set,[16−18] and the single-point energies of the optimized structures were recalculated using the more sophisticated basis sets and effective core potentials from the Stuttgart group[19,20] as implemented in the Gaussian-98W set of programs.[21] The calculations suggest that **2b** is 3.5 kcal mol^{-1} less stable than **2a** (Table 2). The probable reason for the relative instability of **2b** is a greater distortion of the octahedral environment of the rhodium atom acquired to avoid the close contacts of Bu^t groups in this isomer. Thus, in **2b** two

Table 1. Parameters of the ^{1}H, ^{13}C, and ^{31}P NMR Spectra of the Rhodium Complexes 1−3

	1[a]	**2a**[b]	**3**[c]
		^{1}H NMR[d]	
δ(hydride)		−10.8 $^2J_{P-H}$ = 146 Hz (trans) $^2J_{P-H}$ = $^1J_{Rh-H}$ = 20 Hz	−5.2 $^1J_{Rh-H}$ = $^2J_{P-H}$ = 17 Hz
$\delta(CH_3)$	1.5	1.6, 1.7	1.7
$\delta(3CH_3)$	1.2	1.1, 1.3	1.2
$\delta(CH_2)$	3.3	3.1 $^2J_{H-H}$ = 16 Hz[e]	3.3
		^{13}C NMR[d]	
$\delta(CH_3)$	12.4	14.7, 20.7	19.5
$\delta(3CH_3)$	26.7	25.0, 26.2	25.6
$\delta(C_{tert})$	32.0	29.1	30.1
$\delta(CH_2)$	39.6	35.8	37.5
		^{31}P NMR	
δ(P)	−23.9 $^1J_{P-Rh}$ = 111 Hz	11.1, −15.6 $^1J_{P-Rh}$ = 83, 71 Hz $^2J_{P-P}$ = 35 Hz	−4.5 $^1J_{P-Rh}$ = 80 Hz

[a] At 298 K. [b] At 183 K. [c] At 273 K. [d] All signals in the ^{1}H and ^{13}C spectra are multiplets. [e] The value of this coupling was found from a spectrum with selective decoupling of both phosphorus atoms.

Table 2. Computed Energies[a] of the Isomers 2a and 2b

species	abs energy B3LYP/ LANL2DZ[b]	rel energy B3LYP/ LANL2DZ	abs energy B3LYP/ SDD,[b]	rel energy B3LYP/ SD
2a	−1 006.120 739	0	−2 346.561 365	0
2b	−1 006.116 051	2.9	−2 346.555 884	3.4

[a] Absolute energies are given in au and relative energies in kcal mol^{-1}. [b] At 298 K.

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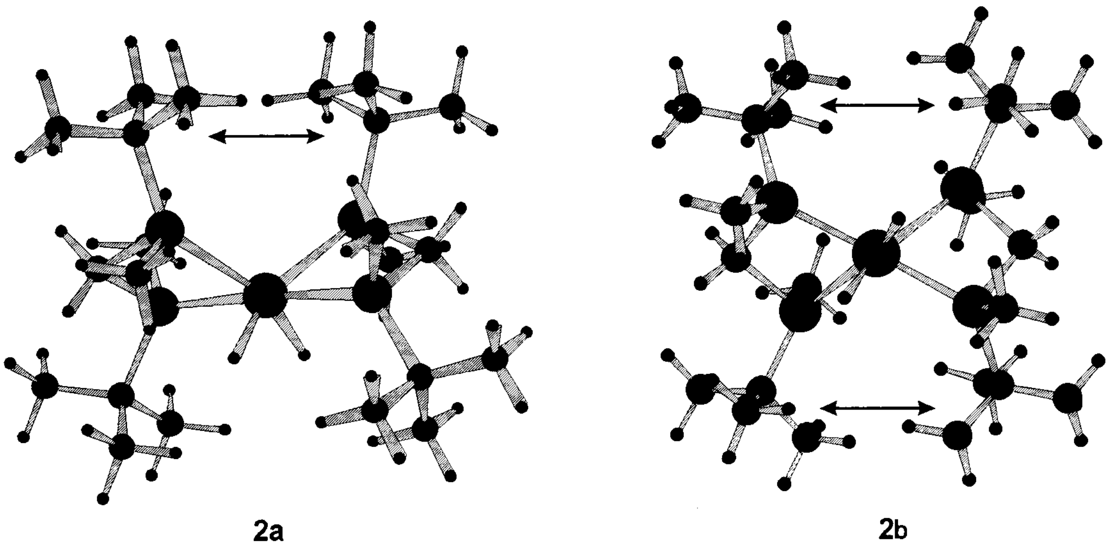

Figure 2. Geometry-optimized structures (DFT) of **2a** and **2b**. The arrows show close contacts of Bu^t groups.

close contacts of the nearby Bu^t groups are found, whereas only one similar close contact is observed in the structure of **2a**, since one pair of the Bu^t groups in **2a** is separated by the hydride ligands (Figure 2).

In the ^{31}P−^{31}P EXSY spectrum of the equilibrium mixture of **1** and **2a** taken at −50 °C (mixing time 1 s) intensive cross-peaks of equal intensity are observed between the signal of **1** and each of the multiplets of **2a** (Figure 3). Therefore, the equilibrium between **1** and **2a** is relatively fast at this temperature. The cross-peak of smaller intensity observed between two multiplets of **2a** is explained by exchange of the positions of the phosphorus atoms in **2a** which occurs via consequent elimination−hydrogenation (Figure 3).

The thermodynamic parameters of the equilibrium between **1**, **2a**, and H_2 were found from the integral intensities in the ^{1}H and ^{31}P NMR spectra in the temperature interval −80 to −30 °C. The equilibrium concentrations of **1** and **2a** at each temperature were calculated from the known starting concentration of **1** and the relative integral intensities of the signals of **1** and **2a** in the ^{31}P NMR spectrum. In turn, the concentration of H_2 in solution was calculated from the ratio [**2**]/[H_2] obtained from the ^{1}H NMR spectrum. The slope of the linear dependence of ln K vs $1/T$ (Figure 4) attests to the following thermodynamic parameters: $\Delta H = -7.7 \pm 0.1$ kcal mol^{-1}; $\Delta S = -25 \pm 1$ cal mol^{-1} K^{-1}.

Dihydrides similar to **2** of the general formula $[RhH_2(Ph_2P(CH_2)_nPPh_2)_2]^+X^-$ were previously reported for $n \geq 3$.[9−11] The attempts to generate such dihydrides with $n = 1$, 2 were, however, unsuccessful. Apparently the relative stability of **2a** is stipulated for the electron-rich character of the MiniPHOS ligand, which increases the affinity of **1** to dihydrogen.[12,22]

Formation of the *trans*-Dihydride 3. If the hydrogenation of **1** was carried out for 30 min at −20 °C, the additional hydride rhodium complex **3** was detected together with **2a**. Complex **3** gives in the ^{1}H NMR spectrum a doublet of quintets at δ −5.30 (Figure 5) and a doublet at δ −4.8 in the ^{31}P{^{1}H} NMR spectrum. Selective decoupling from phosphorus transforms the hydride multiplet in the ^{1}H NMR to a doublet with $^1J_{Rh-H} = 20$ Hz. Thus, the spectral data are consistent with the *trans*-dihydride structure of the complex **3** (Scheme 2).

trans-Dihydride **3** is stable for a long time if kept below −20 °C. At higher temperatures it decomposes, yielding **1** ($t_{1/2}$ at 20 °C is 4 min). It is clear that **3** cannot form by direct oxidative addition of dihydrogen to **1**. We suggest that *trans*-dihydride **3** is produced by isomerization of either **2a** or **2b** at relatively high temperatures (Scheme 2). Fast mutual interconversions of *cis*- and *trans*-dihydrides were reported for the complexes $[FeH_2(P(OEt)_3)_4]$ and $[FeH_2(PhP(OEt)_2)_4]$;[23] however, the rhodium *trans*-hydride complexes $[RhH_2(PMe_3)_4]^+$ and $[RhH_2(PPhMe_2)_4]^+$ were found to be structurally rigid, even at +90 °C.[24] We suppose that the isomerization of **2a** to **3** proceeds via reversible dissociation of the strained four-membered chelate cycle, reorganization of the ligands by either double Berry pseudorotation[22,25] or turnstile rotation,[22] and recoordination of the phosphorus (Scheme 2). Once formed, *trans*-dihydride **3** is relatively kinetically stable, since the direct reductive elimination of H_2 is impossible, and the rate of its decomposition is regulated by the rate of interconversion of **2a** and **3**. This rate is relatively slow, since no dynamic effects are observed for the ^{1}H and ^{31}P NMR signals of **3** up to 20 °C.

Thus, the interconversion of *cis*- and *trans*- dihydrides **2a** and **3** may be regarded as the evidence of the possibility of reversible dissociation of Rh−P bonds in **2a**. We suggest that a similar dissociation may take place in the catalytic cycle of asymmetric hydrogenation catalyzed by **1**, opening the vacant site for the coordination of the substrate. However, our attempts to detect the substrate binding were unsuccessful. Prolonged storage of the mixture of **1** and methyl (*Z*)-α-acetamidocinnamate (**4**) at room temperature does not give rise to any new products. No reaction of the dihydrides **2a**

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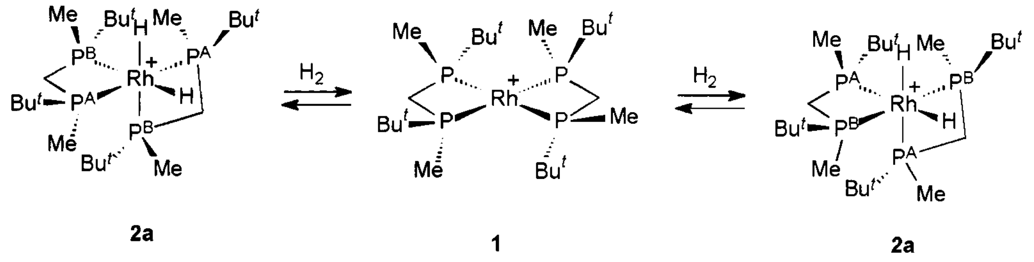


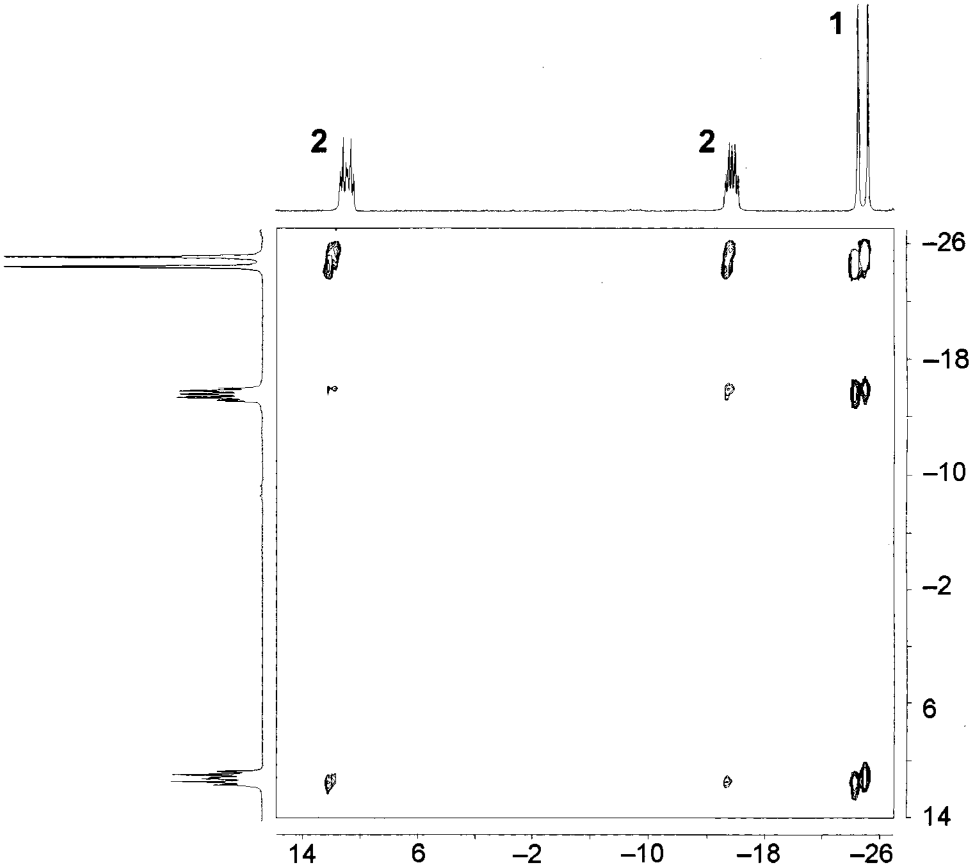


Figure 3. $^{31}P-^{31}P$ EXSY spectrum of the equilibrium mixture of **1** and **2a** (162 MHz, CD_3OD, 253 K, mixing time 1 s).

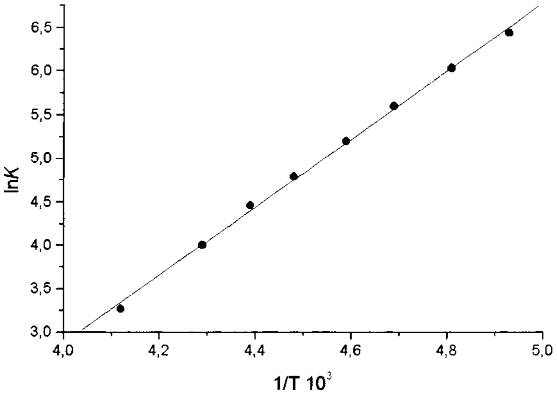


Figure 4. Dependence of ln K vs inverse temperature for the equilibrium between **1**, **2a**, and H_2.

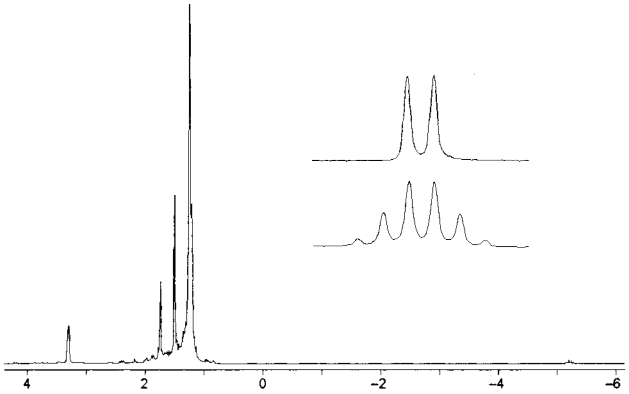
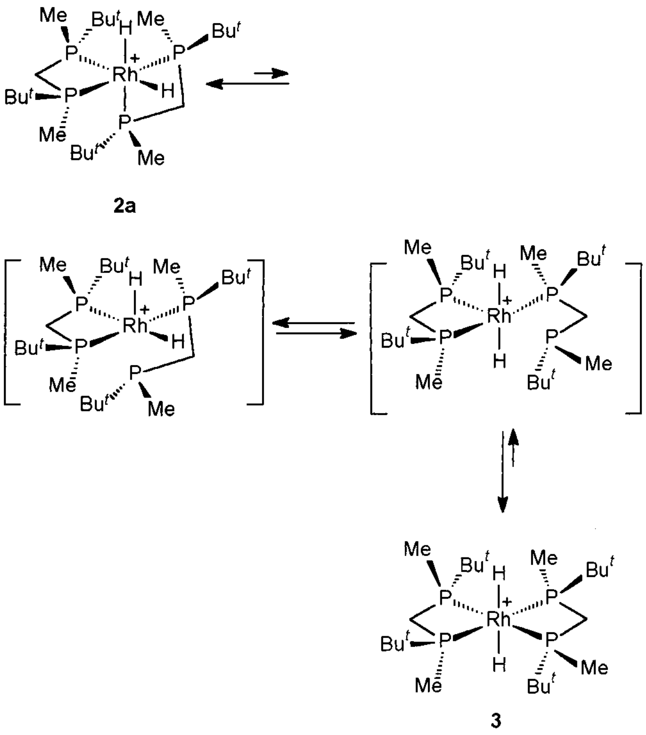


Figure 5. ^1H NMR spectrum (400 MHz, CD_3OD, 273 K) of the mixture of **1** and **3** (signals of **2a** are merged into the background at this temperature). The inserts show the appearance of the multiplet in the normal spectrum (bottom) and with selective decoupling from phosphorus (top).

and **3** with **4** was observed at temperatures below 0 °C. When the mixture of **1**, **2**, and **3** was treated with the substrate **4** at temperatures higher than 0 °C, the hydrogenation product was produced without any detectable intermediates. Apparently, the dissociation of the Rh−P bond is a rate-limiting stage of the catalytic cycle, and all subsequent transformations proceed much faster, not allowing the detection of the intermediates.

Scheme 2



The available experimental data give no indication whether this dissociation is complete and the $[RhH_2(MiniPHOS)S_2]^+$ is produced or only one vacant site becomes available, as was previously suggested by James for catalytic hydrogenation using $[Rh(diop)_2]BF_4$.[9] It is noteworthy that in the calculated structures of **2a** and **2b**, the lengths of both P−Rh bonds trans to the hydride ligands are notably longer than other two P−Rh bonds (2.6 and 2.4 Å, respectively). On the other hand, all four Rh−P bonds in **1** (X-ray data for the hexafluorophosphate salt)[5] are almost equal in length (2.31−2.35 Å). This fact suggests a third possible scenario, viz. the dissociation of both P−Rh bonds trans to the hydrides, and chelating coordination of the substrate to the Rh complex with two pendant diphosphine ligands.

In conclusion, we have found that the rhodium complex $[Rh(MiniPHOS)_2]BF_4$ (**1**) is reversibly and stereoselectively hydrogenated, producing the *cis*-dihydride $[RhH_2(MiniPHOS)_2]BF_4$ (**2a**), which rearranges to the *trans*-dihydride **3** at temperatures around −20 °C. This rearrangement suggests that the diphosphine may be more loosely bound in **2a** compared to **1**, and the coordination of the substrate in the catalytic cycle of asymmetric hydrogenation catalyzed by **1** occurs after the hydrogenation step, similarly to the hydrogenations catalyzed by Wilkinson catalyst.[1,26]

Experimental Section

General Procedures. All reactions and manipulations were performed under a dry argon atmosphere using standard Schlenk-type techniques. Solvents were purified appropriately before use. Synthesis of (*R*,*R*)-1,1-bis(*tert*-butylmethylphosphino)methane−borane was described previously.[6] NMR experiments were carried out on JEOL LA-400 and JEOL LA-500 spectrometers. Methanol-d_4 of the grade "100%" (99.6% D) packed in sealed ampules (Cambridge Isotope Laboratories, Inc.) and 99.9999% H_2 have been used for the mechanistic studies.

(*R*,*R*)-1,1-Bis(*tert*-butylmethylphosphino)methane. Trifluoromethanesulfonic acid (840 μL, 9.5 mmol) was slowly added to a stirred, cooled (0 °C) solution of (*R*,*R*)-1,1-bis(*tert*-butylmethylphosphino)methane−borane (471 mg, 1.9 mmol). After 30 min the ice bath was removed and the reaction mixture was stirred at room temperature until the disappearance of bisphosphine−borane (TLC monitoring). The solvent was removed in vacuo. A solution of KOH (1.07 g, 19 mmol) in 8 mL of $EtOH-H_2O$ (10:1) was slowly added with stirring to the resulting pasty oil. The reaction mixture was stirred at 50 °C for 2 h, cooled to room temperature, and extracted three times with ether. The combined extracts were dried over Na_2SO_4, and the solution was passed through a column of basic alumina (30 g). The solvent was removed in vacuo, producing practically pure diphosphine. ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ 1.04 (m, 18H, 6 CH_3), 1.08 (m, 6H, 2 CH_3), 1.26 (m, 2H);^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ 9.19 (2CH_3, m), 22.09 (CH_2, m), 27.92 (6CH_3, m), 32.27 (C_{tert}, m), ^{31}P NMR (202 MHz, $CDCl_3$, 25 °C): δ −19.78.

$[(R,R)\text{-}(MeBu^tPCH_2PMeBu^t)_2Rh]^+BF_4^-$ (1). A solution of (*R*,*R*)-1,1-bis(*tert*-butylmethylphosphino)ethane (396 mg, 1.8 mmol) obtained in the previous experiment in freshly distilled THF (10 mL) was added to a stirred suspension of $[Rh(nbd)_2]BF_4$ (311 mg, 0.9 mmol) in THF (15 mL). The suspension gradually turned to an almost clear solution over 2 h. It was filtered, and the solvent was removed in vacuo. The residual solid was washed with hexane to give 380 mg (67%) of complex **1** as a yellow powder. The NMR spectra of the complex **1** are given in Table 1.

***cis*-$[(MeBu^tPCH_2PMeBu^t)_2RhH_2]^+BF_4^-$ (2a).** A solution of complex **1** in methanol-d_4 was cooled to −90 °C, and 2 atm of H_2 was admitted. The sample was kept under these conditions for 5 min with intensive manual shaking. Then the sample was placed in the precooled probe of the NMR spectrometer. For the NMR spectra, see Table 1.

***trans*-$[(R,R)\text{-}(MeBu^tPCH_2PMeBu^t)_2RhH_2]^+BF_4^-$ (3).** A solution of complex **1** in methanol-d_4 was cooled to 0 °C, and 2 atm of H_2 was admitted. The sample was kept under these conditions for 40 min with intensive manual shaking. Then the sample was placed in the precooled probe of the NMR spectrometer. For the NMR spectra, see Table 1.

Computational Methods. DFT calculations were performed on a Dell Perfomance PC workstation with two 933 MHz processors and 1 Gb of memory using the software package Gaussian-98W.[21] Becke's three-parameter exchange-correlation functional[14] was used, including the nonlocal gradient corrections described by Lee, Yang, and Parr[15] as implemented in the Gaussian-98W program package.[21] Geometries were optimized using the LANL2DZ basis set,[16−18] and the stationary points were recalculated on the B3LYP/SDD level.[19,20]

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