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$Rh_2[(R)$-(+)-MTPA$]_4$ as an NMR auxiliary for the enantiodifferentiation of chiral secondary and tertiary phosphine–borane complexes

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Abstract—The direct chiral recognition of secondary and tertiary phosphine–borane complexes is made possible by applying the dirhodium method (NMR in the presence of $Rh_2[(R)$-(+)-MTPA$]_4$, **Rh***). Due to the acid lability of the phosphine–borane complexes, it is advisable to use deuterated benzene as solvent rather than deuterated chloroform. The decomposition of the phosphine–borane complexes and the resulting **Rh***–phosphine adducts are also studied.

1. Introduction

Phosphines and their Lewis base complexes are of widespread interest.[1] Chiral phosphines have been used as ligands for the preparation of a variety of transition metal complexes in homogenous catalysis reactions,[2,3] and borane (BH_3) has been introduced as a protecting group for phosphines.[4] Phosphine–borane complexes ligated to metal atoms were investigated in order to compare their properties with those of the corresponding hydrocarbon analogues,[5] and it has been shown that stable chromium, molybdenum and tungsten complexes with $BH_3{\cdot}PR_3$ (R = Me or Ph) can exist and involve an end-on (η^1) M–H–B linkage (M = Cr, Mo, W).[6] The complexation proceeds via a σ donation from a B–H bond into an antibonding metal orbital whereas π back donation from the metal into a σ* B–H bond orbital is negligible.[5,6]

To the best of our knowledge, no spectroscopic method exists for direct ee determination of *P*-stereogenic phosphine–boranes. So far, the enantiomeric purities of phosphine–boranes have only been determined by means of chiral HPLC or by chemical correlation with the corresponding known phosphine oxides via a stereoretentive deboranation/oxidation sequence.[7] The deboranation is easy for tertiary phosphine–boranes and provides stable phosphines to study. However, the latter correlation cannot be used for secondary phosphine–boranes because the secondary phosphines released are configurationally labile. Instead, low temperature alkylation of lithiated secondary phosphine–boranes has been used to correlate them with already known tertiary phosphine–boranes.[8]

This situation, and the fact that phosphine–borane complexes are sensitive to acid prompted us to explore whether or not BH_3 hydrogen atoms in phosphine–borane complexes may act as binding sites forming adducts with the chiral auxiliary **Rh*** ($Rh_2[(R)$-(+)-MTPA$]_4$) (**Rh***, MTPA-H ≡ methoxytrifluoromethylphenylacetic acid; Mosher's acid; Scheme 1).[9] This complex has proven to be an excellent reagent for enantiodifferentiation of soft Lewis base molecules.[10] It should be mentioned in this context that, very recently, we found that an analogous linkage (Rh–H–Si) is effective in the dirhodium experiment with a silane.[11]

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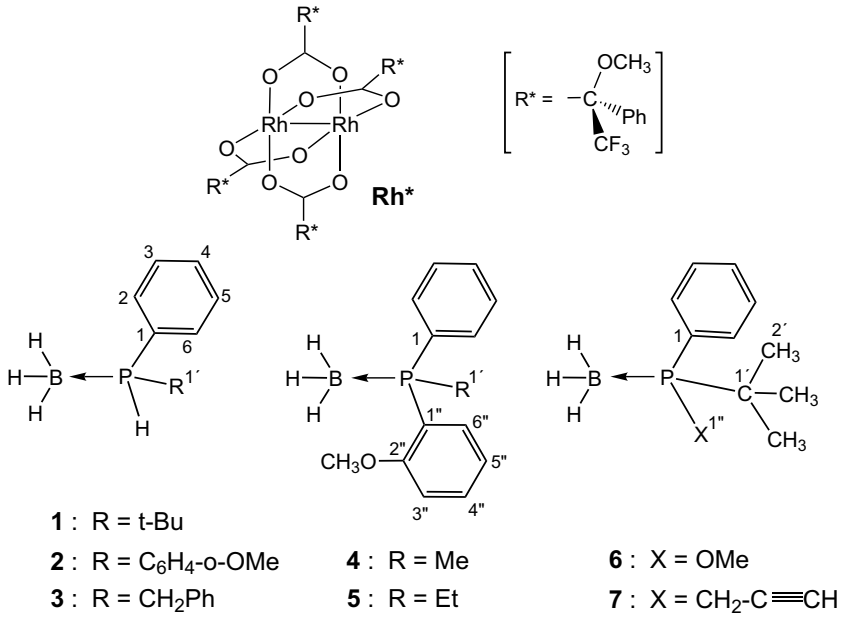


Scheme 1. Structures of the compounds investigated.

2. Results and discussion

2.1. Phosphine–borane complexes and their decomposition in the presence of Rh*

As usual in applying the dirhodium method,[10] all phosphine–borane complexes **1**–**7** were subjected to extensive NMR investigation prior to the addition of chiral auxiliary **Rh*** in order to extract all available NMR chemical shifts (Table 1); coupling constants of **1**–**7** are listed in Section 4.3. These parameters were compared with their respective counterparts obtained from the NMR spectra in the presence of an equimolar mixture of **Rh***. All ^{1}H and ^{13}C NMR signals of **1**–**7** were assigned unequivocally by applying two-dimensional NMR correlation spectroscopy (COSY, HMQC, and HMBC).[12] ^{11}B NMR spectra were recorded both with and without ^{1}H-decoupling and ^{31}P NMR only under ^{1}H-decoupling.

Initially, we followed the standard dirhodium experimental procedure[10] and performed the experiments in such a way that an equimolar mixture of **Rh*** and a phosphine–borane complex was prepared in $CDCl_3$; then, the ^{1}H NMR measurements were executed. Here, however, we immediately observed a color change of the solution from the usual dark-green to dark-brown indicating decomposition; this molecular system was clearly not stable. It turned out that the **Rh***–phosphine–borane adducts (Scheme 2) could be identified, but their signals decayed within minutes after mixing if secondary phosphine–boranes were involved or within ca. 1 h for tertiary phosphine–boranes. A variety of signals evolved, and the solution contained a number of phosphoryl (P=O) compounds. The majority of the new signals appeared in the range of $\delta = +40$ to $+60$ ppm, which is typical for phosphoryl groups.[13–15] In addition, some ^{31}P signals appeared, which, according to their chemical shift ($\delta = -34$ to -32 ppm) and their multiplicities, correspond to 1:1 adducts of **Rh*** and phosphines.[16,17] It seemed that traces of acid present in $CDCl_3$ led to rapid decomposition. After changing the solvent from $CDCl_3$ to C_6D_6 under exclusion of molecular oxygen, the lifetimes of the adducts increased to 1 h and ca. 1 day, respectively.

As mentioned above, **Rh***–phosphine adduct signals appeared after some time (see above). The originally dark-green solution adopted some reddish coloration, which is typical for phosphine adducts and ^{103}Rh-^{31}P coupling constants can be read from the ^{31}P NMR signals.[10,16,17]

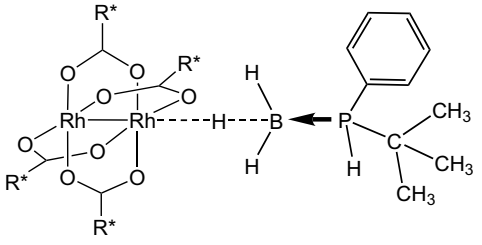
This is shown in Figure 1 displaying the ^{31}P NMR signals of the diastereomeric 1:1 **Rh*** adducts with the racemic tertiary phosphine produced from **7**. The signal multiplicities allow us to extract typical one- and two-bond ^{103}Rh, ^{31}P coupling constants (95.4 and 23.0 Hz, respectively) as well as a significant diastereomeric dispersion effect ($\Delta\nu = 46.3$ Hz). As expected, no 2:1 **Rh***–phosphine adducts are observed under the conditions used (equimolar ratio of **Rh*** and the phophine–borane). A semiquantitative interpretation allows us to state that two different reactions of the adduct of **Rh*** and a phosphine–borane complex (Rh–H–B–P; Scheme 2) may occur, namely (a) a fast oxidation of the phosphine to one or more phosphoryl species[13–15] if O_2 has not been removed and (b)—after consumption of the dissolved O_2—a much slower BH_3 removal producing **Rh***–phosphine adducts.[16,17] Apparently, the complex **Rh*** competes with 'BH_3' in adding to the phosphine, and finally stable **Rh***–phosphine adducts are the predominant products of the adduct formation equilibria. This process is acid-catalyzed.

Since the phosphine–boranes **1**–**7** were all recorded as racemic mixtures, it is currently not possible to determine whether or not a racemization of the configurationally

Table 1. ^{1}H, ^{11}B, ^{13}C, and ^{31}P chemical shifts of the phosphine–borane complexes **1**–**7**, recorded in C_6D_6 at 9.4 T[a]

	1	2	3		4	5	6	7
P–*H*	4.6	6.4	5.0	B–*H*	1.9	1.9	1.5	1.5
B–*H*	1.6	2.0	1.5	H-2/6	7.60	7.66	7.65	7.72
H-2/6	7.19	7.59	7.20	H-3/5	6.99	7.00	7.06	7.04
H-3/5	6.96	6.95	6.87	H-4	7.01	7.00	7.06	7.04
H-4	7.01	6.95	6.97	H-1′	1.68	2.10/2.37[b]	—	—
H-1′	—	—	2.68/2.88[b]	H-2′	—	1.07	1.00	0.91
H-2′	0.86	—	—	H-1″	—	—	—	2.51/2.55[b]
H-3′	—	6.33	6.62	H-3″	6.23	6.24	—	1.62
H-4′	—	7.01	6.97	H-4″	7.04	7.05	—	—
H-5′	—	6.70	6.97	H-5″	6.76	6.77	—	—
H-6′	—	7.90	6.97	H-6″	8.19	8.24	—	—
H-7′	—	—	6.62	O*CH*$_3$	2.90	2.93	3.35	—
O*CH*$_3$	—	3.00	—	C-1	132.4	131.7	130.2	126.2
C-1	125.8	127.9	125.7	C-2/6	131.5	132.0	132.3	133.8
C-2/6	134.3	133.1	133.4	C-3/5	128.4	128.4	128.3	128.3
C-3/5	128.6	128.7	128.7	C-4	130.2	130.2	131.4	131.3
C-4	131.4	130.9	131.5	C-1′	10.5	17.5	32.0	29.8
C-1′	28.1	115.5	32.1	C-2′	—	7.6	24.2	25.6
C-2′	26.3	160.7	133.8	C-1″	118.5	117.0	—	33.5
C-3′	—	110.8	129.5	C-2″	161.5	161.5	—	72.4
C-4′	—	133.6	128.6	C-3″	111.2	111.1	—	76.6
C-5′	—	121.4	127.0	C-4″	133.5	133.5	—	—
C-6′	—	135.3	128.6	C-5″	121.3	121.4	—	—
C-7′	—	—	129.5	C-6″	136.2	137.1	—	—
OCH$_3$	—	55.0	8.0	OCH$_3$	54.7	54.7	54.4	—
P	31.8	−13.8	8.0	P	10.9	20.5	128.7	36.2
B	−38.5	−36.2	−36.8	B	−33.0	−35.1	−39.4	−37.7

[a] For coupling constants, see Section 4.3.
[b] Diastereotopic protons, no stereochemical assignment.



Scheme 2. Proposed adduct structure of **Rh*** and **1**.

unstable secondary phosphines has occurred during the BH_3 extrusion.

2.2. Adducts of Rh* and the phosphine–borane complexes 1–7—chiral recognition

All NMR data of secondary phosphine–borane complexes **1**–**3** obtained from the modified dirhodium experiment (in C_6D_6 under O_2 exclusion) are shown in Table 2. It can be seen that among all couplings constants (see Section 4.3) it is only the one-bond $^{31}P,^{1}H$ coupling, which is significantly changed by **Rh*** adduct formation: $\Delta^{1}J(^{31}P,^{1}H) = +12.7$ Hz (**1**) and -2.9 Hz (**3**); the corresponding value for **2** could not be determined safely due to signal overlap. It should be noted that, in contrast to the NMR signals in the free H_3B–PR_3 complexes, the $^{1}J(^{11}B,^{1}H)$ coupling is not detectable in the **Rh*** adducts due to a severe increase in ^{1}H and ^{11}B line widths.

The chemical shifts, however, display significant changes allowing an interpretation in terms of adduct formation and chiral recognition. Figure 2 shows a section of the ^{1}H NMR spectrum of **1** in the absence (bottom) and presence (top) of an equimolar amount of **Rh*** in C_6D_6. In both spectra, doublets [$^{1}J(^{31}P,^{1}H)$] are with quartet fine-splitting due to the three-bond coupling with the borane protons. This $^{3}J(^{1}H$–^{31}P–^{11}B–$^{1}H)$ coupling is the proof that an intact **Rh***–**1** adduct (Fig. 2) exists.

The complexation shifts and the diastereomeric dispersion effects of the adducts formed by **Rh*** and the tertiary phosphine–borane complexes **4**–**7** behave in a similar manner compared to the secondary phosphine analogues (Table 3).

The binding sites are the borane hydrogens, which is obvious from significant deshieldings of the ^{1}H nuclei: $\Delta\delta = +0.79$ for **1**, $+0.83$ for **2**, and $+0.91$ ppm for **3**. Likewise, the ^{11}B nuclei are deshielded: $\Delta\delta = +2.4$ for **1**, $+2.3$ for **3**, and $+2.6$ for **3**. Even the ^{31}P nuclei experience a strong effect, although in the diamagnetic direction: $\Delta\delta = -6.1$ for **1**, -3.9 for **2**, and -3.7 ppm for **3** (Table 2). Strong changes in $^{1}J(^{31}P,^{1}H)$ values from 362.3 Hz in the free **1** to 375.0 Hz in the **Rh*** adduct provide further evidence. The corresponding values for **3** are: 370.4 to 367.6 Hz, respectively; those of **2** could not be identified safely due to signal overlap. The other ^{1}H complexation shifts ($\Delta\delta$) are deshielding to a moderate or weak extent, and no major effects are observed for the ^{13}C nuclei as well.

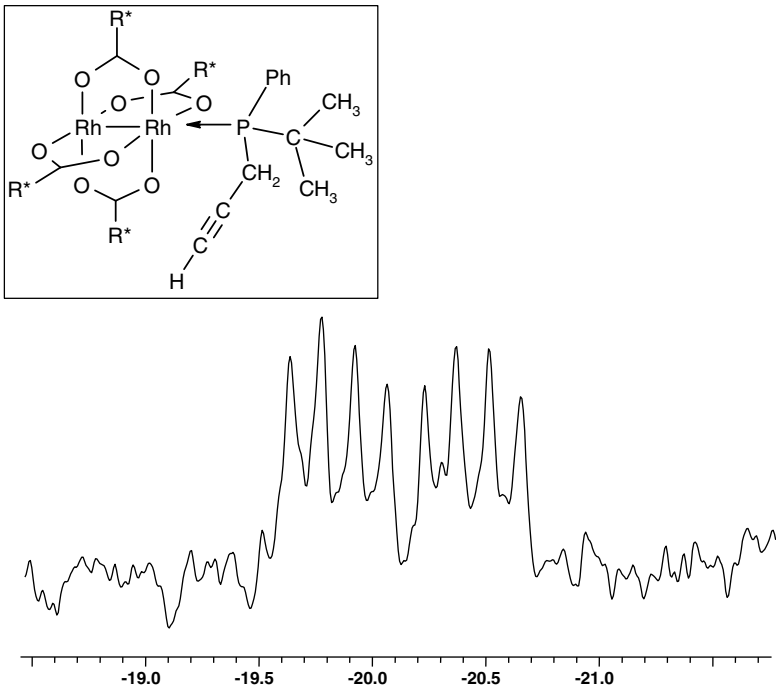


Figure 1. ^{31}P NMR signals of the diastereomeric 1:1 **Rh*** adducts with the racemic tertiary phosphine produced from **7** by BH_3 extrusion in C_6D_6; $^1J(^{103}Rh,^{31}P) = 95.4$ Hz, $^2J(^{103}Rh,^{31}P) = 23.0$ Hz, $\Delta\nu = 46.3$ Hz.

Table 2. Complexations shifts ($\Delta\delta$, in ppm) and diamagnetic dispersion effects ($\Delta\nu$, in Hz) for the ^1H, ^{11}B, ^{13}C, and ^{31}P NMR signals of the phosphine–borane complexes **1**–**3** in the presence of an equimolar amount of **Rh*** recorded in C_6D_6 at 9.4 T

	1		**2**		**3**	
	$\Delta\delta$	$\Delta\nu$	$\Delta\delta$	$\Delta\nu$	$\Delta\delta$	$\Delta\nu$
P–*H*	+0.1	12	+0.02	br[a]	+0.2	br[a]
B–*H*	+0.8	br[a]	+0.8	br[a]	+0.9	br[a]
H-2/6	n.d.[b]		+0.06	0–1	n.d.[b]	
H-3/5	n.d.[b]		+0.01	0–1	0	0–1
H-4	n.d.[b]		+0.01	0–1	n.d.[b]	
H-1′	—		—		−0.15/−0.14	br[a]
H-2′	4	4	—		—	
H-3′	—		+0.01	3	+0.05	0–1
H-4′	—		−0.04	0–1	n.d.[b]	
H-5′	—		+0.02	0–1	n.d.[b]	
H-6′	—		+0.15	14	n.d.[b]	
H-7′	—		—		+0.05	0–1
O*CH*$_3$	—		0	6	—	
C-1	+0.5	2	n.d.[b]		n.d.[b]	
C-2/6	+0.1	0–1	0	0–1	0	0–1
C-3/5	+0.1	3	+0.1	0–1	0	0–1
C-4	+0.3	3	0	0–1	n.d.[b]	
C-1′	+0.4	0–1	0	0–1	+0.6	0–1
C-2′	−0.2	0	+0.2	1	−0.1	0–1
C-3′	—		+0.1	2	−0.1	0
C-4′	—		−0.2	0–1	n.d.[b]	
C-5′	—		−0.1	0–1	+0.1	0–1
C-6′	—		−0.1	3	n.d.[b]	
C-7′	—		—		−0.1	0
O*C*H$_3$	—		−0.3	3	—	
P	−6.1	br[a]	−3.9	br[a]	−3.7	br[a]
B	+2.4	br[a]	+2.3	br[a]	+2.6	br[a]

[a] Signals too broad for detailed analysis.
[b] Signals not detectable due to signal overlap.

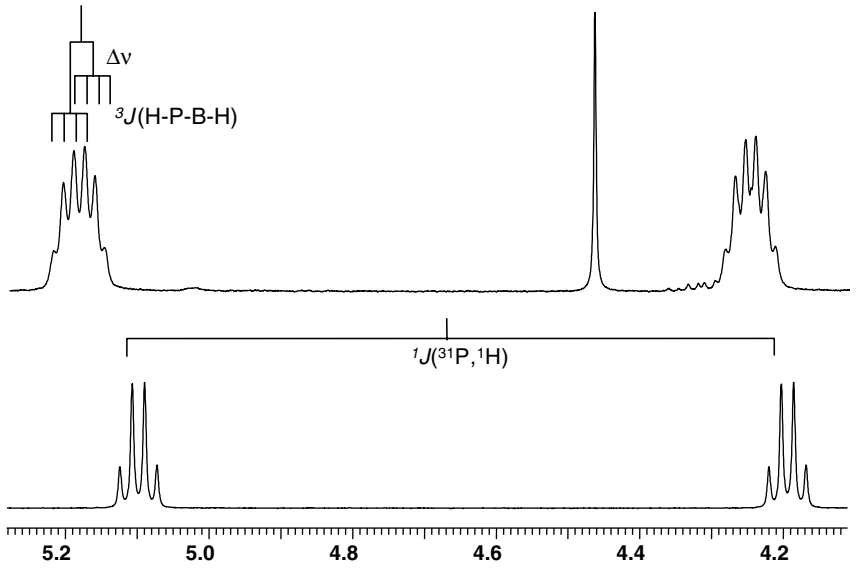


Figure 2. ^{1}H NMR signals of the P–H proton of **1** in the absence (bottom) and the presence (top) of an equimolar amount of **Rh*** in C_6D_6; $^{1}J(^{31}P,^{1}H) = 362.3$ and 375.0 Hz, respectively; $^{3}J(H–P–B–H) = 6.1$ Hz; $\Delta\nu = 12$ Hz.

Table 3. Complexations shifts ($\Delta\delta$, in ppm) and diamagnetic dispersion effects ($\Delta\nu$, in Hz) for the ^{1}H, ^{11}B, ^{13}C, and ^{31}P NMR signals of the phosphine–borane complexes **4**–**7** in the presence of an equimolar amount of **Rh***, recorded in C_6D_6 at 9.4 T

	4		**5**		**6**		**7**	
	$\Delta\delta$	$\Delta\nu$	$\Delta\delta$	$\Delta\nu$	$\Delta\delta$	$\Delta\nu$	$\Delta\delta$	$\Delta\nu$
B–*H*	+0.9	br[a]	+0.9	br[a]	+1.0	br[a]	+0.8	br[a]
H-2/6	+0.09	0–1	+0.06	3	+0.09	0–1	+0.03	0–1
H-3/5	−0.08	0–1	−0.03	0–1	+0.01	0–1	+0.06	n.d.[b]
H-4	−0.05	0–1	−0.03	0–1	+0.01	0–1	+0.06	n.d.[b]
H-1′	+0.16	5	+0.18/+0.1	3/6		—		—
H-2′		—	+0.07	2	+0.06	3	+0.08	7
H-1″		—		—		—	−0.53/−0.23	0–1
H-3″	−0.01	0	−0.01	1		—	+0.08	0–1
H-4″	−0.03	0–1	−0.01	1		—		—
H-5″	+0.03	0–1	+0.04	5		—		—
H-6″	+0.13	16	+0.13	2		—		—
O*C*H$_3$	+0.01	2	−0.01	3	+0.12	15		—
C-1		n.d.[c]		n.d.[c]		n.d.[c]		n.d.[c]
C-2/6	+0.1	10	+0.0	5	+0.1	0		n.d.[c]
C-3/5	+0.1	3	+0.2	3	+0.2	0–1		n.d.[b]
C-4	+0.3	5	+0.4	3	+0.4	1	+0.2	2
C-1′	−0.7	18	−0.1	11	+0.3	0–1	+0.4	3
C-2′		—	−0.1	1	−0.2	3		n.d.[c]
C-1″	−1.4	6		n.d.[c]		—	+0.2	0–1
C-2″	+0.1	1	+0.1	1		—	+0.1	6
C-3″	+0.1	0–1	+0.0	2		—	−0.1	0–1
C-4″	+0.3	0–1	+0.3	1		—		—
C-5″	+0.3	2	+0.4	1		—		—
C-6″	−0.1	3	+0.1	14		—		—
O*C*H$_3$	0	1	−0.1	0	+0.6	1		—
P	−3.8	br[a]	−4.4	br[a]	−6.6	br[a]	−5.8	br[a]
B	+4.1	br[a]	+3.7	br[a]	+3.4	br[a]	+1.8	br[a]

[a] Signals too broad for detailed analysis.
[b] Signals not detectable due to signal overlap.
[c] Signals not discernable safely from noise level.

No chemical non-equivalence among the BH_3 protons in the adduct **Rh***–**1** was observed; this was also the case for the other complexes as well. As mentioned above, however, only one of those hydrogen forms a bond to the metal atom so that a 2:1 non-equivalence should result. The explanation for this contradiction is the fact that—as expected—the adducts are kinetically unstable and NMR signals are time-averaged.[10]

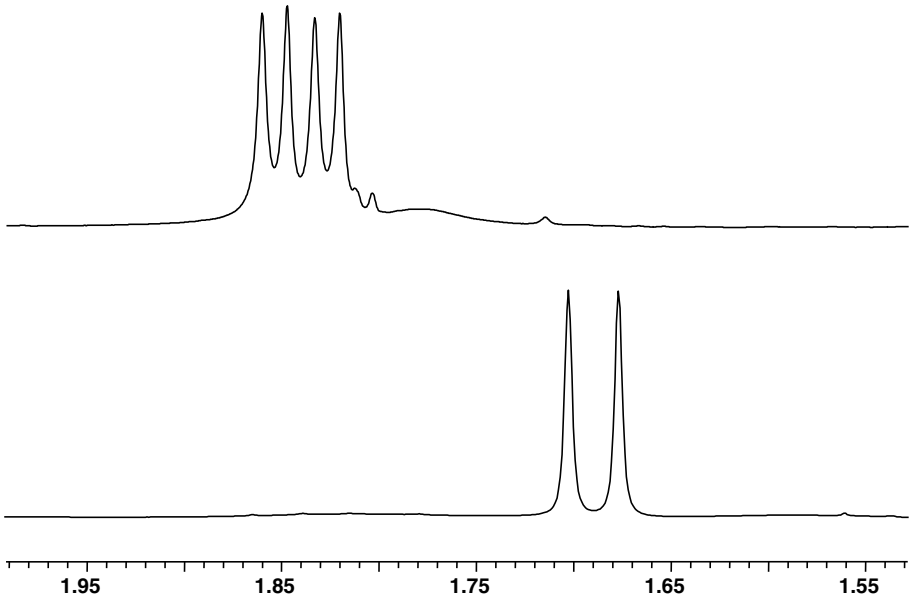


Figure 3. ^{1}H NMR signal of the methyl group (H-1′) of **4** in the absence (bottom) and the presence (top) of an equimolar amount of **Rh*** in C_6D_6; $\Delta\nu = 5$ Hz; ^{2}J(P,H-1′) = 10.2 Hz. Both doublets are of equal intensity (racemate).

Diastereomeric dispersion effects are visible at the signals of some hydrogen and carbon atoms, which are further away from the binding site protruding into the sphere of anisotropic influences exerted by the Mosher acid residues, a typical behavior of ligand nuclei (Figs. 3 and 4).[10] As a result, differentiation of the enantiomeric complexes **1** can be easily performed. Benzyl derivative **3** proved an exception in that no significant ^{1}H and ^{13}C signal dispersion could be safely identified. Accidentally compensating influences from the four Mosher acid residues may be the reason.

3. Conclusion

It has been shown that the dirhodium method for enantiodifferentiation of Lewis basic ligands can be applied successfully to borane complexes of secondary and tertiary phosphines. The complexes are sensitive to oxygen and to traces of acid, which give rise to a fast and efficient extrusion of B_2H_6. Nevertheless, **Rh*** adducts of those complexes are stable during the period of time required for NMR experiments if protic acids are absent.

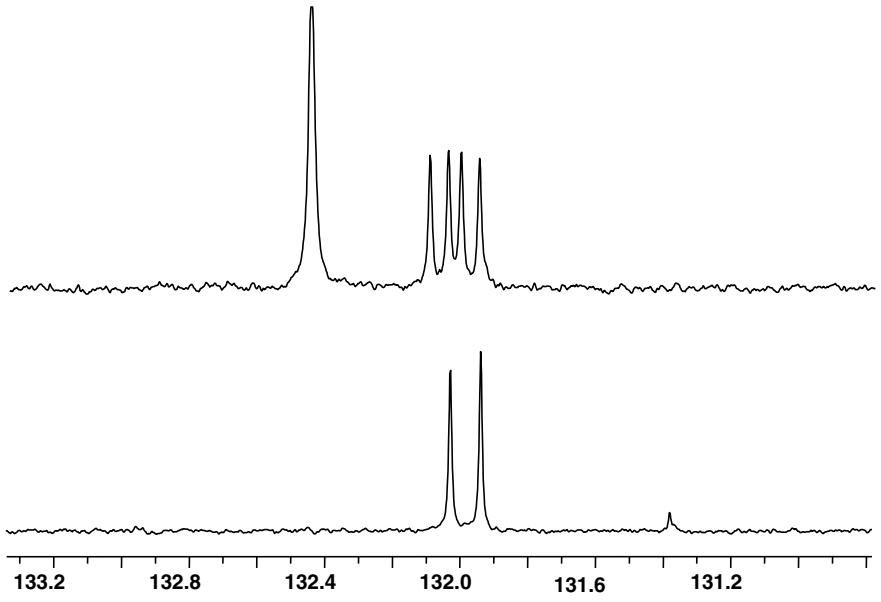


Figure 4. ^{13}C NMR signals of *ortho* carbon C-2/6 of **5** in the absence (bottom) and the presence (top) of an equimolar amount of **Rh*** in C_6D_6; $\Delta\nu = 5$ Hz; ^{2}J(P,C-2/6) = 8.9 Hz. The ^{13}C signal at $\delta = 132.4$ ppm in the upper spectrum belongs to the Mosher acid residues. Both doublets are of equal intensity (racemate).

Complexation shifts clearly indicate that the hydride atoms attached to boron are the complexation sites. Nearly all phosphine–borane adducts studied provide dispersed ^{1}H and ^{13}C signals. The only exception is benzyl derivative **3**.

As a consequence of the sensitivity of phosphine–borane–**Rh*** adducts to oxygen and acid, some precautions have to be taken into account:

(a) Molecular oxygen has to be excluded since it rapidly converts the phosphines in the adducts into phospine oxides.
(b) Traces of acid lead to an efficient and fast extrusion of B_2H_6 so that **Rh***–phosphine adducts are formed. This reaction offers another option for chiral recognition by ^{31}P NMR. However, it is not yet clear whether this reaction involves phosphorus inversion, which would lead to racemization. As a result, we recommend to modify the standard dirhodium method protocol[10] by careful oxygen exclusion and the use of C_6D_6 as solvent.

4. Experimental

4.1. Compounds

The synthesis of the NMR auxiliary **Rh*** has already been reported.[9] Phosphine–boranes **1**–**3** were prepared from the corresponding secondary phosphine oxides as described previously.[18] Phosphine–boranes **4**, **5**, and **7** were obtained from **2** and **1**, respectively, by the known deprotonation–alkylation procedure.[7] Compound **6** was synthesized by the O-methylation of *tert*-butylphenylphosphinous acid-borane.[19] All phosphine–borane complexes investigated here were racemates.

4.2. NMR spectroscopy

^{1}H (400.1 MHz), ^{11}B (128.3 MHz), ^{13}C (100.6 MHz), and ^{31}P (161.9 MHz) NMR spectroscopies were performed on a Bruker DPX-400 spectrometer (9.4 T) at room temperature. Standards were internal tetramethylsilane ($\delta = 0$ ppm) for ^{1}H and ^{13}C, external BF_3 etherate ($\delta = 0$ ppm) for ^{11}B and external aqueous H_3PO_4 ($\delta = 0$ ppm) for ^{31}P. Digital resolutions were 0.14 Hz/point in the ^{1}H, 0.2 Hz/point in the ^{11}B, 0.24 Hz/point in the ^{13}C, and 0.22 Hz/point in the ^{31}P.

The standard dirhodium experiment[10] was modified for the optimization of the phosphine–borane–**Rh*** adduct life-times. **Rh*** and an equimolar amount of the phosphine–borane adducts were dissolved in 0.7 ml C_6D_6 under prevention of air oxygen uptake. Typically, 48.6 mg of **Rh*** (0.043 mM concentration) was employed. No acetone-d_6 was added for assisting **Rh*** solubility[20] in order to avoid competition of acetone molecules with ligands **1**–**7** in the adduct formation. NMR samples should be prepared immediately prior to recording the NMR spectra in order to avoid decomposition reactions of the phosphine–borane–**Rh*** adducts.

For a faster preparation of phosphine–**Rh*** adducts, a trace amount of a protic acid (e.g., some trifluoroacetic acid vapor) can be added. Alternatively, the solution can be warmed up to 50 °C for a couple of minutes.

4.3. Coupling constants

All coupling constants reported in this section were obtained from measurement in C_6D_6, if not otherwise noted.

$^{1}H,^{1}H$ coupling constants within the organic residues are in the expected ranges.[21,22]

Coupling constants involving ^{11}B (in Hz). Compound **1**: $^{1}J(^{31}P,^{11}B) = 43.0$ [$^{1}J(^{31}P,^{10}B) = 550$–$600$, in $CDCl_3$], $^{1}J(^{11}B,^{1}H) = 99.5$; compound **2**: $^{1}J(^{31}P,^{11}B) = 45.0$, $^{1}J(^{11}B,^{1}H) = 100.0$; compound **3**: $^{1}J(^{31}P,^{11}B) = 41$–$42$, $^{1}J(^{11}B,^{1}H) = 99$–100; compound **4**: $^{1}J(^{31}P,^{11}B) \approx 55$, $^{1}J(^{11}B,^{1}H) = 98$–99; compound **5**: $^{1}J(^{31}P,^{11}B) \approx 60$, $^{1}J(^{11}B,^{1}H) = 97.9$; compound **6**: $^{1}J(^{31}P,^{11}B) = 62.0$, $^{1}J(^{11}B,^{1}H) = 97.0$; compound **7**: $^{1}J(^{31}P,^{11}B) = 50.9$, $^{1}J(^{11}B,^{1}H) = 98.2$.

Other coupling constants involving ^{31}P (in Hz). Compound **1**: $^{1}J(^{31}P,^{1}H) = 362.3$, $^{3}J(^{31}P,$H-2/6$) = 9$–11, $^{4}J(^{31}P,$H-3/5$) = 2$–3, $^{5}J(^{31}P,$H-4$) = 1$–2, $^{3}J(^{31}P,$H-2′$) = 14.5$, $^{1}J(^{31}P,$C-1$) = 49.9$, $^{2}J(^{31}P,$C-2/6$) = 7.7$, $^{3}J(^{31}P,$C-3/5$) = 9.4$, $^{4}J(^{31}P,$C-4$) = 2.5$, $^{1}J(^{31}P,$C-1′$) = 32.1$, $^{2}J(^{31}P,$C-2′$) = 3.0$; compound **2**: $^{1}J(^{31}P,^{1}H) = 390.2$, $^{3}J(^{31}P,$H-2/6$) = 9$–11, $^{4}J(^{31}P,$H-3/5$) = 2$–3, $^{5}J(^{31}P,$H-4$) = 1$–2, $^{4}J(^{31}P,$H-3′$) = 3.5$, $^{5}J(^{31}P,$H-4′$) = 1$–2, $^{4}J(^{31}P,$H-5′$) = 1.7$, $^{3}J(^{31}P,$H-6′$) = 13.5$, $^{1}J(^{31}P,$C-1$) = 57.8$, $^{2}J(^{31}P,$C-2/6$) = 9.9$, $^{3}J(^{31}P,$C-3/5$) = 10.4$, $^{4}J(^{31}P,$C-4$) = 2.5$, $^{1}J(^{31}P,$C-1′$) = 54.5$, $^{2}J(^{31}P,$C-2′$) = 1.2$, $^{3}J(^{31}P,$C-3′$) = 4.2$, $^{4}J(^{31}P,$C-4′$) = 2.2$, $^{3}J(^{31}P,$C-5′$) = 12.1$, $^{2}J(^{31}P,$C-6′$) = 13.8$, compound **3**: $^{1}J(^{31}P,^{1}H) = 370.4$, $^{3}J(^{31}P,$H-2/6$) = 9$–11, $^{4}J(^{31}P,$H-3/5$) = 2$–3, $^{5}J(^{31}P,$H-4$) = 1$–2, $^{2}J(^{31}P,$H-1′$) = 14.5$, $^{4}J(^{31}P,$H-3′/7′$) = 3$–4, $^{5}J(^{31}P,$H-4′/6′$) = 1$–2, $^{6}J(^{31}P,$H-5′$) = 0$–1, $^{1}J(^{31}P,$C-1$) = 52.9$, $^{2}J(^{31}P,$C-2/6$) = 8.4$, $^{3}J(^{31}P,$C-3/5$) = 6.0$, $^{4}J(^{31}P,$C-4$) = 2.7$, $^{1}J(^{31}P,$C-1′$) = 30.4$, $^{2}J(^{31}P,$C-2′$) = 8.2$, $^{3}J(^{31}P,$C-3′/7′$) = 4.5$, $^{4}J(^{31}P,$C-4′/6′$) = 1.3$, $^{5}J(^{31}P,$C-5′$) = 2.9$, compound **4**: $^{3}J(^{31}P,$H-2/6$) = 9$–12, $^{4}J(^{31}P,$H-3/5$) = 2$–3, $^{5}J(^{31}P,$H-4$) = 1$–2, $^{2}J(^{31}P,$H-1′$) = 10.2$, $^{4}J(^{31}P,$H-3″$) = 3.3$, $^{5}J(^{31}P,$H-4″$) = 1$–2, $^{4}J(^{31}P,$H-5″$) = 2.0$, $^{3}J(^{31}P,$H-6″$)$ 14–15, $^{1}J(^{31}P,$C-1$) = 57.5$, $^{2}J(^{31}P,$C-2/6$) = 9.7$, $^{3}J(^{31}P,$C-3/5$) = 10.2$, $^{4}J(^{31}P,$C-4$) = 2.6$, $^{1}J(^{31}P,$C-1′$) = 42.3$, $^{1}J(^{31}P,$C-1″$) = 52.2$, $^{2}J(^{31}P,$C-2″$) = 1.8$, $^{3}J(^{31}P,$C-3″$) = 3.8$, $^{4}J(^{31}P,$C-4″$) = 2.0$, $^{3}J(^{31}P,$C-5″$) = 12.1$, $^{2}J(^{31}P,$C-6″$) = 14.6$; compound **5**: $^{3}J(^{31}P,$H-2/6$) = 9$–12, $^{4}J(^{31}P,$H-3/5$) = 2$–3, $^{5}J(^{31}P,$H-4$) = 1$–2, $^{2}J(^{31}P,$H-1′$) = 9.0/14.2$, $^{3}J(^{31}P,$H-2′$) = 18.2$, $^{4}J(^{31}P,$H-3″$) = 3.2$, $^{5}J(^{31}P,$H-4″$) = 1.7$, $^{4}J(^{31}P,$H-5″$) = 2.0$, $^{3}J(^{31}P,$H-6″$)$ 13.2, $^{1}J(^{31}P,$C-1$) = 56.2$, $^{2}J(^{31}P,$C-2/6$) = 8.9$, $^{3}J(^{31}P,$C-3/5$) = 9.8$, $^{4}J(^{31}P,$C-4$) = 2.5$, $^{1}J(^{31}P,$C-1′$) = 39.3$, $^{1}J(^{31}P,$C-1″$) = 50.4$, $^{2}J(^{31}P,$C-2″$) = 1.3$, $^{3}J(^{31}P,$C-3″$) = 4.0$, $^{4}J(^{31}P,$C-4″$) = 2.3$, $^{3}J(^{31}P,$C-5″$) = 11.9$, $^{2}J(^{31}P,$C-6″$) = 14.2$; compound **6**: $^{3}J(^{31}P,$H-2/6$) = 9$–12, $^{4}J(^{31}P,$H-3/5$) = 2$–3, $^{5}J(^{31}P,$H-4$) = 1$–2, $^{3}J(^{31}P,$H-2′$) = 14.3$, $^{3}J(^{31}P,$OC*H*$) = 11.1$, $^{1}J(^{31}P,$C-1$) = 48.4$, $^{2}J(^{31}P,$C-2/6$) = 9.7$, $^{3}J(^{31}P,$C-3/5$) = 9.7$, $^{4}J(^{31}P,$C-4$) = 3.2$, $^{1}J(^{31}P,$C-1′$) = 43.1$, $^{2}J(^{31}P,$C-2′$) = 3.1$, $^{2}J(^{31}P,$OC*H*$) = 4.0$; compound **7**: $^{3}J(^{31}P,$H-2/6$) = 9$–12, $^{4}J(^{31}P,$H-3/5$) = 2$–3, $^{5}J(^{31}P,$H-4$) = 1$–2, $^{3}J(^{31}P,$H-2′$) = 13.9$, $^{2}J(^{31}P,$H-1″$) = 10.6$, $^{4}J(^{31}P,$H-3″$) = 4.4$,

$^{1}J(^{31}P,C\text{-}1) = 47.3$, $^{2}J(^{31}P,C\text{-}2/6) = 8.3$, $^{3}J(^{31}P,C\text{-}3/5) = 9.5$, $^{4}J(^{31}P,C\text{-}4) = 2.4$, $^{1}J(^{31}P,C\text{-}1') = 29.1$, $^{2}J(^{31}P,C\text{-}2') = 2.4$, $^{1}J(^{31}P,C\text{-}1'') = 33.5$, $^{2}J(^{31}P,C\text{-}2'') = 6.6$, $^{3}J(^{31}P,C\text{-}3'') = 7.8$.

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