Bis(phosphane oxide) Adducts of $Rh_2(MTPA)_4$ — Kinetics and Chirality Discrimination

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Dedicated to the memory of Prof. Dr. Dr.h.c.(H) Günther Snatzke (1928−1992)[‡]

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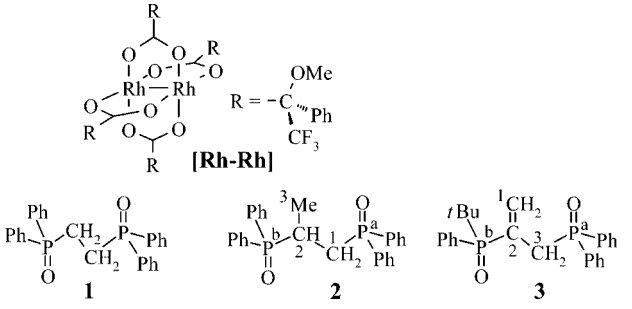
The symmetrical bis(phosphane oxide) **1** and its chiral derivatives **2** and **3** form a variety of adduct species with the dirhodium complex **[Rh–Rh]** which can be identified by low-temperature ^1H and ^{31}P NMR spectroscopy by using varying **[Rh–Rh]**:ligand ratios. The asymmetric bis(phosphane oxide) **3** shows a distinct preference for binding through the Ph_2P=O (P^a) as compared to the *t*Bu(Ph)P=O (P^b) functionality due to the bulky *tert*-butyl group. The chiral bis(phosphane oxides) **2** and **3** form complex mixtures of various adduct species. Nevertheless, it is possible to monitor enantiomeric compositions from various NMR signal duplications at 213 K and even at room temperature or slightly elevated temperatures.

Introduction

Dirhodium complexes as well as their phosphane adducts have been the focus of interest for many years.[1] They were first introduced as homogeneous catalysts in various reactions[2] and have even found medicinal applications.[3] We have shown that the enantiomers of chiral phosphane chalcogenides can easily be discriminated by adding an equimolar amount of the dirhodium complex $[Rh^{II}_2\{(R)\text{-}(+)\text{-MTPA}\}_4]$ (**[Rh−Rh]**, MTPA-H = methoxytrifluoromethylphenylacetic acid ≡ Mosher's acid; see Scheme 1) to their $CDCl_3$ solution and monitoring the diastereomeric dispersion Δν of their ^1H or ^{31}P NMR signals at room temperature ("dirhodium method" of chirality recognition).[4] However, we noticed that coalescence effects may broaden the NMR signals even at room temperature and that phosphane oxides seemed to have a different ligand behaviour from their sulfide and selenide analogues.[4c] Moreover, when we attempted to study some chiral bis(phosphane oxides) (Scheme 1) by variable-temperature NMR spectroscopy we found signals of complicated mixtures of free and ligated species.



Scheme 1. Structures of the dirhodium complex and the phosphanyl chalcogenides studied

Recently, Deubel has communicated a theoretical study based on density-functional theory (DFT) calculations of donor-acceptor interactions contributing to the binding energy in the adducts of dirhodium(II) tetraformate and a representative choice of strong and weak ligands (e.g., methylene carbene vs. benzene).[5] As a result, attractive contri-

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butions were shown to be a blend of electrostatic and HOMO−LUMO interactions, the former always dominating.[5] In a comparative study of the ligand properties of the triphenylphosphane chalcogenides $Ph_3P{=}X$ (X = Se, S, and O), and of methyldiphenylphosphane oxide, $Ph_2(CH_3)P{=}O$, we have recently found that, in contrast to phosphane selenides and sulfides, phosphane oxides bind primarily by an electrostatic attraction, and orbital interactions can be neglected.[6] Moreover, this binding energy is strongly sensitive to steric crowding around the P=O group.[6] For $Ph_3P{=}O$, the binding constant *K* is only about 1 (weak donor). In contrast, *K* is larger than 100 for $Ph_2(CH_3)P{=}O$ (strong donor); no free ligand molecules can be detected in the presence of an excess of rhodium sites in the latter case, for example in an equimolar mixture of **[Rh−Rh]** and $Ph_2(CH_3)P{=}O$.[6] Since bis(phosphane oxides) are considered to be useful ligands in homogeneous catalysis, we extended this work to the bis(phosphane oxides) **1**−**3** in order to explore how bifunctional phosphane oxide ligands behave under "dirhodium method" experimental conditions and whether or not chirality recognition is still possible. In addition, we wanted to see whether there is a binding competition between the two P=O groups in each of the asymmetric compounds **2** and **3**.

Table 1. ^1H, ^{13}C and ^{31}P NMR chemical shifts as well as $^{31}P,^1H$ and $^{31}P,^{13}C$ coupling constants (*J* in Hz) of the free ligands **1**−**3**, recorded at room temperature[a]

			^1H	^{13}C	^{31}P	$^nJ(^{31}P,^1H)$	$^nJ(^{31}P,^{13}C)$
1		CH_2	2.52	21.6	33.8	n.d.[b]	
		ipso	−	131.9		−	
		ortho	7.70	130.7			
		meta	7.45	128.7		n.d.	
		para	7.51	132.0		n.d.	
2[c]		CH_3	1.20	13.6	P^a: 32.5	^3J = 16.9	^2J = 3.2
						$^4J \approx 0$	^3J = 0.9
		$>CH_2$: H^a	2.48	28.8	P^b: 39.0	n.d.	^1J = 69.2
							^2J = 1.7
		$>CH_2$: H^b	2.56			n.d.	
		CH	2.99	26.9		n.d.	^1J = 70.5
							^2J = 4.0
	P^a	*ipso*	−	131.1/131.0		n.d.	$^1J \approx$ 97/96
		ortho	7.68−7.76	131.1/131.0		n.d.	^2J = 9.6/9.6
		meta	7.37−7.47	129.3/129.2		n.d.	^3J = 11.3/11.7
		para	7.47−7.58	131.9/131.8		n.d.	^4J = 2.8/2.8
	P^b	*ipso*	−	133.4/132.6		n.d.	^1J = 98.3/99.5
		ortho	7.68−7.76	131.5/131.5		n.d.	^2J = 8.6/8.9
		meta	7.37−7.47	129.1/129.1		n.d.	^3J = 11.9/11.4
		para	7.47−7.58	131.9/131.9		n.d.	^4J = 3.1/3.1
3[c]		C-2	−	132.9	P^a: 32.7	−	^1J = 80.6
							^2J = 7.8
		C(*t*Bu)	−	34.0	P^b: 42.9	−	^1J = 69.2
		$>CH_2$: H^a	3.40			^2J = 15.5	
				31.0		^3J = 8.5	^1J = 66.7
							^2J = 7.5
		$>CH_2$: H^b	3.57			^2J = 12.5	
						^3J = 8.5	
		$=CH_2$:[d] H^a	6.80			^3J = 39.8	
				132.3		^4J = 1.6	$^2J \approx$ 7.5
							$^3J \approx$ 7.5
		$=CH_2$:[d] H^b	6.04			^3J = 17.2	
						$^4J \approx 0$	
		CH_3	1.16	25.2		^3J = 14.9	$^2J \approx 0$
	P^a	*ipso*	−	132.6/131.8		−	^1J = 100.3/101.6
		ortho	7.72/7.83	131.0/130.9		^3J = 11.7/ 11.6	^2J = 8.3/8.0
		meta	7.29/7.46	128.3/128.6		n.d./n.d.	^3J = 12.1/11.9
		para	7.35/7.50	131.5/131.8		n.d./n.d.	^4J = 2.7/2.9
	P^b	*ipso*	−	129.2		−	^1J = 89.1
		ortho	7.62	131.9		^3J = 9.5	^2J = 8.2
		meta	7.37	128.1		n.d.	^3J = 10.9
		para	7.46	131.6		n.d.	^4J = 2.9

[a] For both P atoms of **2** and for P^a of **3** two entries exist for each aromatic ^1H and ^{13}C nucleus because the phenyl groups are diastereotopic. The first entry belongs to one phenyl group and the second entry to the other; a stereochemical differentiation is not possible. [b] n.d.: not detectable. [c] Compound **2**: $^3J(^{31}P^a,^{31}P^b)$ = 49.4 Hz; compound **3**: $^3J(^{31}P^a,^{31}P^b)$ = 18.2 Hz. [d] The protons of the methylene group (=CH_2) can be differentiated because of their $^3J(^{31}P,^1H)$-values to P^b: H^a is *trans* to P^b (^3J = 39.8 Hz), and H^b is *cis* (^3J = 17.2 Hz).

Results and Discussion

NMR Signal Assignment

The assignment of the NMR signals of the free ligands **1**−**3** (cf. Scheme 1) was straightforward in most cases when routine NMR methods such as DEPT, HMQC, HMBC and NOE techniques were applied. Thereby, all ^{1}H, ^{13}C and ^{31}P NMR signals could be identified; the unequivocal assignment of the ^{31}P signals of the two heterotopic phosphorus sites in **2** and **3** was achieved by $\{^{31}P\}$ ^{1}H-detected HMBC experiments correlating P^{b} with the methyl or the *tert*-butyl protons, respectively. In the case of **[Rh−Rh]** adducts the identification of the ligand signals was occasionally hampered by overlapping Mosher acid signals, particularly when aromatic signals were involved. All NMR signals of the free ligands **1**−**3**, as well their complexation shifts Δδ (in ppm), for 1:1 adducts at room temperature are collected in Table 1 and 2.

Table 2. Complexation shifts in **1**−**3** in 1:1 adducts (in ppm); recorded at room temperature[a]

			Δδ(^{1}H)	Δδ(^{13}C)	Δδ(^{31}P)
1		CH_2	+0.29	[b]	+3.9
		ipso	−		
		ortho	+0.13		
		meta	−0.20		
		para	−0.10		
2		CH_3	+0.26	−0.5/−0.6[c]	
		$>CH_2$: H^a	+0.29	+0.2/+0.1[c]	
		$>CH_2$: H^b	+0.32		
		CH	+0.45	+0.1/−0.1[c]	
	P^a	*ipso*	−/−	n.d./n.d.	+5.6
		ortho	+0.17/+0.25	−0.1/+0.1	
		meta	−0.28/−0.24	−0.8/−0.7	
		para	n.d./−0.14	n.d./−0.3	
	P^b	*ipso*	−/−	n.d./n.d.	+4.6
		ortho	−0.04 /+0.08	−0.5/−0.5	
		meta	−0.26/−0.31	−0.6/−0.6	
		para	n.d./−0.17	n.d./−0.2	
3		C-2	−	0.0	
		C(*t*Bu)	−	+0.4/+0.3[c]	
		$>CH_2$: H^a	+0.24	−0.5	
		$>CH_2$: H^b	+0.46		
		$=CH_2$: H^a	+0.40	+2.1	
		$=CH_2$: H^b	−0.10		
		CH_3	+0.03	0.0/−0.1[c]	
	P^a	*ipso*	−/−	n.d./n.d.	+4.4
		ortho	+0.16/+0.08	+0.5/+0.4	
		meta	−0.30/−0.32	−0.2/−0.7	
		para	−0.17/−0.20	−0.4/−0.2	
	P^b	*ipso*	−	n.d.	+3.1
		ortho	+0.11	+0.4	
		meta	−0.18	+0.3	
		para	−0.09	−0.2	

[a] For both P atoms of **2** and for P^a of **3** two entries exist for each aromatic ^{1}H and ^{13}C nucleus because the phenyl groups are diastereotopic. The first entry belongs to one phenyl group and the second entry to the other; a stereochemical differentiation is not possible. [b] No ^{13}C NMR spectroscopic data were recorded for the **[Rh−Rh]-1** mixture because precipitation of solid material from the solution occurred after a few hours. [c] Signal duplication due to dispersion effects (see text).

Identification of the Various Adduct Species

1,2-Bis(diphenylphosphinoyl)ethane (**1**) contains two chemically equivalent P=O residues; each is connected to two phenyl rings and to the ethylene chain. Thus, one can expect that its complexing properties are similar to those of triphenylphosphane oxide and methyldiphenylphosphane oxide.[6]

The low-temperature (213 K) ^{31}P NMR spectra of **1** at various molar ratios (Figure 1) allow the identification of the adduct species involved (Scheme 2). Spectrum **a** (0.5:1) was recorded for a solution with an excess of rhodium sites, spectrum **b** (1:1) for a solution with equimolar amounts of both **[Rh−Rh]** and **1**, and spectra **c** and **d** with an excess of P=O sites. The ratios were chosen in such a way that the molar amount of **1** relative to that of **[Rh−Rh]** is doubled when going from one spectrum to the next (**a** to **b**, **b** to **c**, and **c** to **d**) so that the P=O content increases strongly from bottom to top.

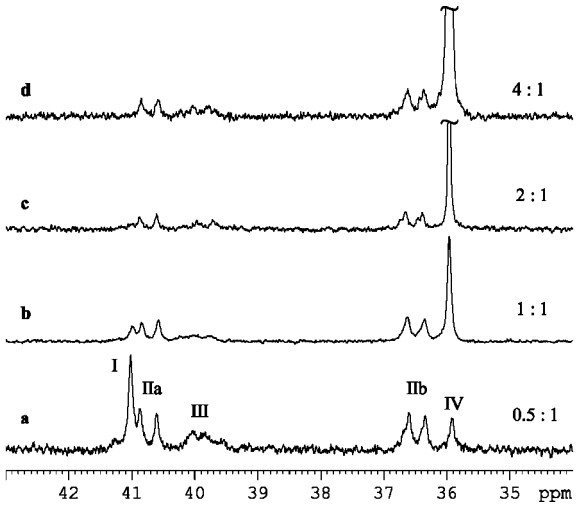
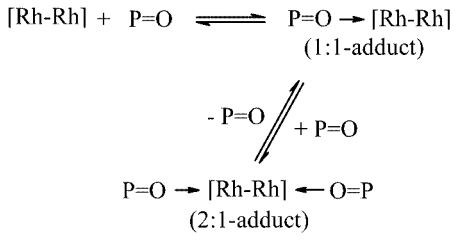


Figure 1. ^{31}P NMR spectra of **1** and **[Rh−Rh]**, recorded at 213 K; molar ratios are (a) 0.5:1, (b) 1:1, (c) 2:1 and (d) 4:1



Scheme 2. Equilibria between free components and the adducts[a]
[a] "P=O" symbolizes phosphane oxide groups

By comparing the ^{31}P NMR signals and their relative intensities in Figure 1, the following assignments can be deduced. There are two different signal groupings: one at δ = 39.5−41.5 ppm for ligated P=O sites (Rh···O=P) and another at δ = 36−37 ppm for free P=O sites. The free ligand of **1** corresponds to the signal at δ = 36.1 ppm (**IV**; Scheme 3) as proven by its strong intensity increase upon further addition of **1** (spectra **b**, **c** and **d**). The signal at δ =

41.2 ppm (singlet) belongs to a doubly complexed ligand molecule which is in a symmetrical environment and therefore does not show the typical doublet splitting due to the $^{31}P,^{31}P$ coupling in unsymmetric bis(phosphane oxides) or analogous adducts. Thus, this species is of type **I** (Scheme 3). The intensity of this peak is rather large in spectrum **a** (Rh site excess), low in spectrum **b** (1:1), and the signal vanishes totally in spectra **c** and **d** with their increasing P=O site excess.

I: Rh—Rh ← O=P-CH_2-CH_2-P=O → Rh—Rh

II: Rh—Rh ← O=P^a-CH_2-CH_2-P^b=O

III: ···CH_2-P=O → Rh—Rh ← O=P-CH_2-CH_2-P=O → Rh—Rh ← O=P-CH_2···

IV: O=P-CH_2-CH_2-P=O (free ligand)

Scheme 3. Adduct species of **1** and **[Rh−Rh]** identified by low-temperature ^{31}P NMR spectroscopy (see text and Figure 1); the Mosher acid residues in **[Rh−Rh]** and the phenyls at the phosphoryl groups have been omitted for clarity

The two doublets at δ = 40.7 and 36.5 ppm correspond to an unsymmetrically ligated molecule of type **II** (Scheme 3). The former doublet (signal **IIa**) is from the complexed end of **1** (P^a=O) and the latter (signal **IIb**) from the free one (P^b=O). The signal splitting is the vicinal $^3J_{^{31}P,^{31}P}$ coupling constant (53.5 Hz). Finally, there is a broad hump at δ = 39.7−40.5 ppm corresponding to Rh···O=P situations of type **III**; apparently, these are the ^{31}P NMR resonances of doubly complexed ligand molecules incorporated in oligomeric structures (Scheme 3).

This interpretation is supported by the ^1H NMR signals of the methoxy group of the Mosher acid residues of **[Rh−Rh]** at low-temperature, as displayed in Figure 2, taken from the same samples as used for Figure 1. Signal **A** (δ = 3.14 ppm) representing the free **[Rh−Rh]** complexes without any ligating **1** has an intensity of about 40% in the solution at 0.5:1 molar ratio, falling to about 25% at P=O site excess. The majority of dirhodium moieties (ca. 50%), however, are in the 1:1 adduct situation represented by signal **B** (δ = 3.03 ppm). There is hardly any change in the proportion of this adduct with increasing amounts of **1**. Finally, signal **C** (δ = 2.93 ppm) can be attributed primarily to a Mosher methoxy signal in the 2:1 adduct situation; its proportion varies from about 10% at a 0.5:1 ratio to about 20% at a 4:1 ratio. This proportion of the 2:1 adducts is surprisingly low, especially with high P=O site excess, and is a consequence of the low donor properties of **1** and the severe steric congestion around the P=O group, similar to Ph_3P=O.[6] Additionally, this small amount of 2:1 adducts may be associated with the observation that some insoluble material precipitated from the $CDCl_3$ solution after several hours. We suspect that this material is a copolymer of type **III** (Scheme 3).

It should be noted that the temperature dependence of the ^1H NMR spectrum proves that a small part of signal **C** in spectrum **a** belongs to the CH_2 signal, which is averaged

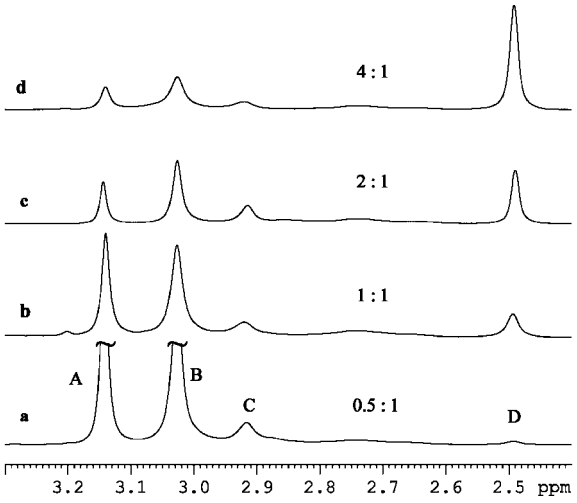


Figure 2. Sections of the ^1H NMR spectra of **1** and **[Rh−Rh]**, recorded at 213 K; molar ratios (a) 0.5:1, (b) 1:1, (c) 2:1 and (d) 4:1

at room temperature (δ = 2.77 ppm) but splits into two (δ = 2.93 and 2.52 ppm) at 213 K. The former part (δ = 2.93 ppm) belongs to Rh···O=P−CH_2 situations and the latter one (δ = 2.52 ppm) to free O=P−CH_2 groups (signal **D**); the relative proportion of signal **D** is strongly increased upon addition of larger amounts of **1** when going from spectrum **a** to spectrum **d** in Figure 2. The exchange barrier of the adduct formation can be estimated easily from the temperature dependence of the CH_2 and the methoxy protons ($\Delta G_c^{\ddagger}$ = 51.3 ± 1 kJ/mol). This value is somewhat higher than those of the monophosphane chalcogenides ($\Delta G_c^{\ddagger}$ = 46.4−48.0 ± 1 kJ/mol).[6]

All these spectra lead to the conclusion that the phosphane oxide group of **1** is only a weak donor; even under Rh site excess there is a substantial proportion of free P=O sites (P^b=O in **II** and **IV**; Scheme 3). Thus, the steric congestion in **1** must be higher than in $Me(Ph_2)P$=O and more similar to that of Ph_3P=O.[6] The majority of the molecules of **1** form adducts **II** and, eventually, oligomers **III** with their composition depending on the P=O site excess: oligomers become more and more dominant the higher the P=O content becomes.

In contrast to **1**, 1,2-bis(diphenylphosphinoyl)propane (**2**) is a *C*-chiral compound derived from **1** by formal methylation of one methylene carbon (cf. Scheme 1). Here, the two Ph_2P=O groups are heterotopic, and separate NMR signals are observable for each of them. In order to distinguish the two phosphoryl groups we use the superscript "a" for that Ph_2P=O group which is attached to CH_2 (C-1) and thereby structurally closest to **1**. The same procedure was applied to differentiate the two P=O groups in **3** (see below). The method of assigning the two phosphorus atoms to the two ^{31}P signals has already been described above.

The room-temperature ^{31}P NMR signals of **2** in the presence of **[Rh−Rh]** are broad humps showing averaged peaks. As can be seen in Figure 3, however, the low-temperature spectra (213 K) display a number of signals indicating the existence of several species, the concentrations of which de-

pend on the molar ratio of the components **2** and **[Rh−Rh]**. The ratio producing the lower spectrum was 2:1 — it was recorded under P=O site excess — whereas that in the top spectrum was 0.5:1 — Rh site excess. It should be noted that further spectra were taken from samples with 1:1 and 4:1 molar ratios. These are not displayed in Figure 3 but support the following conclusions.

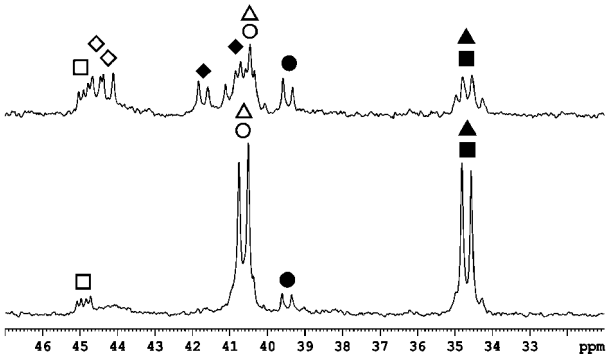


Figure 3. ^{31}P NMR spectra of **2** in the presence of various amounts of **[Rh−Rh]**, recorded at 213 K; top, molar ratio **2**:**[Rh−Rh]** 0.5:1, bottom 2:1; see Scheme 4 for the meaning of the symbols

The different ratio conditions enabled us to assign the peaks. Moreover, we recorded a ^{31}P,^{31}P COSY spectrum (not depicted) correlating the two heterotopic ^{31}P nuclei within each species. For sake of clarity we used the following icons for the ^{31}P signal assignment (Scheme 4): ▲/Δ for the free ligand OP^a∼P^{b}O, ●/○ for the adduct Rh···OP^a∼P^{b}O, ■/□ for the adduct OP^a∼P^{b}O···Rh and ◆/◇ for the adduct Rh···OP^a∼P^{b}O···Rh; filled icons refer to P^a and open ones to P^b (see also Scheme 4; "∼" depicts the carbon chain between the phosphorus atoms).

▲	OP^a ∼ P^{b}O	△
●	Rh → OP^a ∼ P^{b}O	○
■	OP^a ∼ P^{b}O ← Rh	□
◆	Rh → OP^a ∼ P^{b}O ← Rh	◇

Scheme 4. Assignment of the symbols to the phosphorus atoms in the Rh*-ligand species; filled icons refer to P^a and open ones to P^b, "∼" represents the carbon chain between the phosphorus atoms

It is obvious that the two doublet signals of the free ligand **2** (▲/Δ) are the largest ones in the bottom spectrum due to an excess of **2**. On the other hand, four small signals appear in the top spectrum that are not visible in the bottom spectrum; they were assigned to ″symmetrical″ adduct species (◆/◇). The fact that each of them appears twice can be attributed to the existence of two diastereomeric adducts (*R*)-**[Rh−Rh]**···[(*R*)-OP^a∼P^{b}O]···(*R*)-**[Rh−Rh]** and (*R*)-**[Rh−Rh]**···[(*S*)-OP^a∼P^{b}O]···(*R*)-**[Rh−Rh]**, an example of chirality recognition (**2** exists as a racemate). The signals of the "unsymmetrical" species (●/○ and ■/□) are visible in both spectra. Taking the relative intensities (●/○ vs. ■/□) into account and the fact that the signals of the free ligand **2** (▲/Δ) still exist under excess Rh site conditions, one can state that, like in **1**, both phosphoryl groups, P^a=O as well as P^b=O, of bis(phosphane oxide) **2** are weak donors, and that there is no significant selection between the two competing P=O groups.

This interpretation is supported by the low-temperature (213 K) ^{1}H NMR spectrum in the ligand methyl group region recorded under **2**:**[Rh−Rh]** = 0.5:1 molar ratio conditions (Rh site excess; Figure 4). It shows signals of the various species whereas at room temperature the averaged signal is a doublet of doublets due to the $^3J_{^1H,^1H}$ (7.0 Hz) and $^3J_{^{31}P,^1H}$ (16.8 Hz) couplings (not depicted). The assignment shown was proven unequivocally by a {^{31}P} ^{1}H-detected HMBC spectrum (not depicted) correlating the methyl protons with the P^b atoms in each species. The integration shows that only about 30% of all ligand molecules are complexed to rhodium on both sides (◇); the content of free ligand molecules (Δ) cannot be derived safely due to signal overlap but there is no doubt that a considerable amount of it exists. Moreover, the amount of the species with only one complexed phosphoryl (○ for Rh···OP^a∼P^{b}O and □ for OP^a∼P^{b}O···Rh) is roughly similar so that the complexation constants of both phosphoryl groups must be similar as well; the methyl group has, indeed, no significant directing effect for an adduct formation preference of P^a vs. P^b (or vice versa).

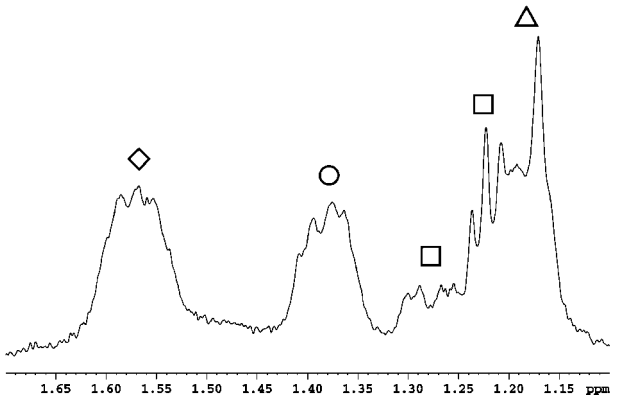


Figure 4. Methyl ^{1}H NMR signal of **2** in the presence of two molar equivalents of **[Rh−Rh]**, recorded at 213 K

Three factors make the ^{1}H NMR signals appear as broad multiplets instead of doublets of doublets: (a) the existence of different species regarding the 1:1 and 2:1 adduct situations of the Rh−Rh fragments, (b) high-order spin systems (ABX) because the methylene protons are diastereotopic, and (c) diastereomeric dispersion effects (compare the two signals marked by "□").

Whereas the bis(phosphane oxide) **2** has a chiral carbon center, 2-(*tert*-butylphenylphosphinoyl)-3-(diphenylphosphinoyl)propene (**3**) is *P*-chiral (P^b). In analogy to **2**, the two ^{31}P NMR signals of **3** were unambiguously assigned by a {^{31}P} ^{1}H-detected HMBC experiment at room temperature. Figure 5 shows the ^{31}P NMR spectra of **3** in the presence of three different molar equivalents of **[Rh−Rh]**, recorded at 213 K. The assignment of the various species was performed in analogy to those of **2** and is given in Figure 5 by icons similar to those used for **2** in Scheme 4. The signals

of P^a appear at δ = 35−39 ppm (filled icons) and those of P^b at δ = 44−49.5 ppm (open icons).

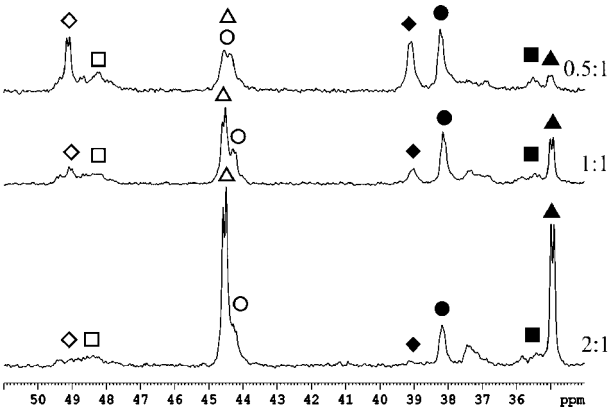


Figure 5. ^{31}P NMR spectrum of **3** in the presence of various amounts of **[Rh−Rh]**, recorded at 213 K; top: 0.5:1 molar ratio (**3**:**[Rh−Rh]**), middle: 1:1, bottom: 2:1; the icons used for the assignment of the various species of **3** have the same meaning as for **2** (see Scheme 4)

The basic difference in the complexing behaviour of the bis(phosphane oxides) **2** and **3** lies in the relative concentrations of the monoligated species Rh···OP^a∼P^bO (●/○) and OP^a∼P^bO···Rh (■/□). ^{31}P NMR signal integrations show that the ratio of the former relative to the latter is about 1.4 (**3**:**[Rh−Rh]** = 2:1, P=O site excess; Figure 5, bottom), about 1.7 (1:1; middle) and about 2.5 (0.5:1, Rh site excess; Figure 5, top). This clearly reflects the steric effects during complexation and reveals that the *tert*-butyl group at P^b creates a larger steric congestion during adduct formation and thereby repels approaching **[Rh−Rh]** molecules much more than the second phenyl group at P^a. Figure 6 shows the ^1H NMR signals of the *tert*-butyl group attached to P^b; some of these signals are multiplets for the same reasons as those described for the methyl protons of **2** (see above). The signal group at δ ≈ 1 ppm appears to be two overlapping doublets of the Rh···OP^a∼P^bO species, apparently another case of chirality recognition (see below).

The difference in adduct formation energies of the two P=O groups is also evident when comparing the intensities of the *tert*-butyl ^1H NMR signal (○ vs. □; Figure 6).

Chirality Recognition

Dispersion effects, Δν, due to the existence of diastereomeric adducts have been identified in some low-temperature ^1H NMR spectra (see previous section). They are difficult to detect at room temperature because most NMR signals are severely broadened by coalescence effects. However, some atoms in the aliphatic part of the two chiral bis(phosphane oxides) **2** and **3** offer the possibility of enantiomeric discrimination. In the case of the racemic **2**, the ^{13}C NMR signals are split: $\Delta\nu(CH_3)$ = 11.1 Hz, $\Delta\nu(CH_2)$ = 18.2 Hz and $\Delta\nu(CH)$ = 9.9 Hz. The time-averaged *tert*-butyl signal in the ^1H NMR spectrum of **3** (ratio **3**:**[Rh−Rh]** = 2:1) recorded at elevated temperature (330 K; Figure 7) displays a signal dispersion of 4.9 Hz (recorded at 11.74 T).

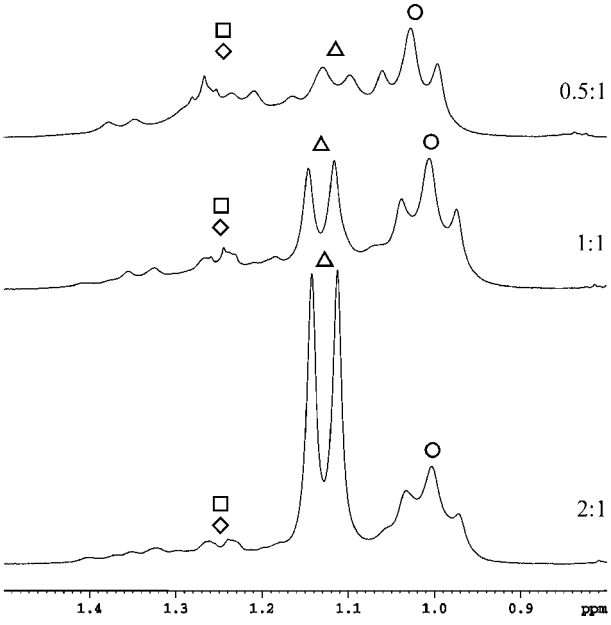


Figure 6. ^1H NMR signals of the *tert*-butyl group of **3**, recorded at 213 K; top: 1:2 molar ratio (**3**:**[Rh−Rh]**), middle: 1:1, bottom: 2:1; the icons used for the assignment of the various species of **3** have the same meaning as for **2** (see Scheme 4)

Moreover, the carbon signals of the *tert*-butyl group (recorded at 300 K) are duplicated as well: $\Delta\nu(CH_3)$ = 2.5 Hz and $\Delta\nu[C(t\text{Bu})]$ = 6.5 Hz. Interestingly, these diastereomeric dispersions occur preferably at the phosphane oxide group of **3** (P^b) that is clearly the weaker donor and, time-averaged, is further away from the Rh sites. Apparently, the branched structure of **3** guarantees that free P^b=O moieties cannot easily escape such interactions so that they come into closer spatial contact with the Mosher acid residues.

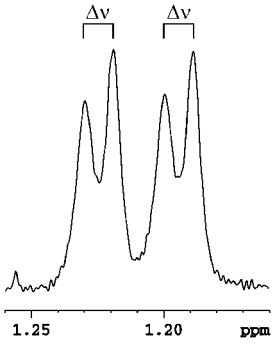


Figure 7. ^1H NMR signal of the *tert*-butyl group of **3** in the presence of an equimolar amount of **[Rh−Rh]**, recorded at 330 K, resolution enhanced; Δν = 4.9 Hz and $^3J_{^{31}P,^1H)}$ = 15.1 Hz

Conclusion

The bidentate 1,2-bis(diphenylphosphinoyl)ethane derivatives **1**−**3** are weak donors in adducts to the dirhodium complex **[Rh−Rh]**. Consequently, all conceivable species exist: free ligands, 1:1 adducts, 2:1 adducts and various iso-

mers and oligomers thereof. Their relative concentrations strongly depend on the molar ratio of **[Rh−Rh]** and the ligands so that an identification by low-temperature ^{31}P NMR spectroscopy is possible. Enantiomers can easily be resolved in the case of chiral bidentate ligands **2** and **3**.

Experimental Section

Substances: The synthesis of **[Rh−Rh]** has been communicated by us previously.[7] 1,2-Bis(diphenylphosphinoyl)ethane (**1**)[8] was prepared from the respective commercially available bisphosphane by oxidation with H_2O_2 in water.

1,2-Bis(diphenylphosphinoyl)propane (2): Diphenylphosphane oxide (1.19 g, 5.9 mmol) and diphenyl(propadienyl)phosphane oxide[9] (1.43 g, 5.9 mmol) were dissolved in toluene (25 mL), and the resulting solution was heated to reflux for 3 days. Evaporation of the solvent and recrystallization of the solid residue from toluene/diethyl ether (10:1) gave 1.84 g of 2,3-bis(diphenylphosphinoyl)propene as white crystals. Yield 70%; m.p. 132−133 °C. IR (KBr): $\tilde{\nu}$ = 1482, 1437, 1397, 1261, 1199 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 3.39 (br. d, J = 12.7 Hz, 1 H), 3.46 (br. d, J = 12.2 Hz, 1 H), 5.49 (dd, J = 20.5, 2.5 Hz, 1 H), 6.64 (dd, J = 41.6, 1.7 Hz), 7.21−7.89 (m, 20 H) ppm. ^{31}P NMR ($CDCl_3$): δ = 30.5 (d, J = 24 Hz), 32.6 (d, J = 24 Hz) ppm. $C_{27}H_{24}O_2P_2$ (442.4) calcd. C 72.96, H 5.84; found C 72.51, H 5.96.

Pd/C (20%; 0.096 g) was added to a solution of 2,3-bis(diphenylphosphinoyl)propene (0.2 g, 0.45 mmol) in 10 mL of methanol, and the resulting mixture was stirred at room temperature under a hydrogen atmosphere (balloon) for 2 days. The catalyst was then removed by filtering the reaction mixture through a thin bed of celite, and the methanol was evaporated to dryness. Recrystallization of the solid residue from toluene/hexane gave 0.175 g of **2**. Yield 87%; m.p. 128−131 °C. EI-HRMS: $C_{27}H_{26}O_2P_2$ [M^+] calcd. 444.1408; found 444.1399. See Table 2 for ^1H, ^{13}C and ^{31}P NMR spectroscopic data.

2-(*tert*-Butylphenylphosphinoyl)-3-(diphenylphosphinoyl)propene (3): *tert*-Butylphenylphosphane oxide (0.38 g, 2.1 mmol) was added to a solution of diphenyl(propadienyl)phosphane oxide[9] (0.51 g, 2.1 mmol) in 15 mL of toluene and the resulting solution was heated to 110 °C for 2 days. Evaporation of the solvent and recrystallization of the solid residue from diethyl ether/hexane (20:1) gave 0.51 g of **3**. Yield 57%; m.p. 84−86 °C. IR (KBr): $\tilde{\nu}$ = 1484, 1474, 1462, 1439, 1277, 1258, 1214, 1184 cm^{-1}. $C_{25}H_{28}O_2P_2$ (422.4) calcd. C 71.08, H 6.68; found C 70.71, H 6.80. See Table 2 for ^1H, ^{13}C and ^{31}P NMR spectroscopic data.

NMR Spectroscopy: Room-temperature ^1H (400.1 MHz), $^{13}C\{^1H\}$ (100.6 MHz), and $^{31}P\{^1H\}$ (161.9 MHz), NMR measurements were performed on a Bruker Avance DPX-400 spectrometer (9.4 T). Chemical shift standards were internal tetramethylsilane (δ = 0 ppm) for ^1H and ^{13}C, and external aqueous H_3PO_4 for ^{31}P (δ = 0 ppm). Signal assignments were assisted by NOE-difference, COSY, HMQC and HMBC (standard Bruker software) as well as by inspecting couplings to ^{31}P. Digital resolutions were 0.14 Hz/point in the ^1H, 0.24 Hz/point in the ^{13}C, and 0.22 Hz/point in the ^{31}P NMR spectra. One drop of [D_6]acetone was added to each NMR sample before measurement in order to increase the solubility of **[Rh−Rh]**.[10]

Variable-temperature ^1H (500.1 MHz) and $^{31}P\{^1H\}$ NMR (202.4 MHz) spectra were recorded in the presence of **[Rh−Rh]** on a Bruker Avance DRX-500 spectrometer (11.74 T). Temperatures varied from 213 to 330 K (333 K in the case of **1**) and were read from the instrument panel; no further measurements for more precise temperature determinations were taken.

$\{^{31}P\}$ ^1H-detected HMBC experiments were recorded at 213 K; relaxation delay 1.5 s, number of scans 32, delay optimized for long-range couplings (8 Hz); spectral width δ = 30−50 (^{31}P) and δ = 0−9 (^1H). Gradient-edited ^{31}P,^{31}P COSY spectra were recorded at 213 K; relaxation delay 4.0 s, number of scans 32, spectral width δ = 31−52 (^{31}P).

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