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High-resolution NMR studies of (diphosphine)(diene)rhodium complexes in the solid state

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Abstract

Well-resolved resonances are observed in the ^{31}P-CPMAS NMR spectra of (2S,4S)-2,4-bis(diphenylphosphino)pentane or (*S,S*)-BDPP (**1**) and its cationic complexes [(Rh{(*S,S*)-BDPP}(NBD)]BF$_4$ (**2a**), [Rh{(*S,S*)-BDPP}(NBD)]PF$_6$ (**2b**), [Rh{(*S,S*)-BDPP}-(NBD)]ClO$_4$ (**2c**) and [Rh{(*S,S*)-BDPP}(COD)]BF$_4$ (**3**). Packing forces split the single resonance observed for these systems in solution. The spectral parameters depend remarkably on the counterion in **2a**, **2b**, and **2c**. Complex **3** showed a splitting of every resonance due to the presence of two independent molecules in the unit cell. The complex [Rh{(*S,S*)-BDPP}(NBD)Cl] (**4**) showed two broad ^{31}P resonances which are ascribed to a number of closely related structures based on the expected trigonal bipyramidal geometry.

1. Introduction

The advantages of solid state NMR investigations compared to routine solution studies are manifold [1]. High-resolution solid state spectra often show a higher number of resonances than the solution spectra, which reflect minor differences in the atomic positions which are normally averaged in the liquid state by the molecular motions [2]. The correlation between the solid state coordination shifts (the difference of the solid state chemical shifts of free and coordinated donors) and the principal tensor components can provide useful insights into the bonding [3,4]. Furthermore, solid state NMR spectroscopy usually allows the derivation of structural information on compounds whose "frozen" structure cannot be attained in low temperature limiting spectra in solution.

The principal aim of this study was to compare solid state NMR spectra with solution spectra for some related (diphosphine)(diene)rhodium complexes [6–8], where the diphosphine is (2*S*,4*S*)-2,4-bis-(diphenylphosphino) pentane, (*S,S*)-BDPP, and the diene is norbornadiene (NBD) or cyclooctadiene (COD).

We have already reported the solution state stereochemistry and crystal structures of some of these homogeneous catalyst precursors [7]. In solution the cationic complexes (**2** and **3**) possess a time-averaged C_2 symmetry axis, and the "frozen" structures were not achieved even at 195 K.

2. Results and discussion

2.1. Spectrum of S,S-BDPP (1)

The solid contains only one molecule in the unit cell [5]. The asymmetric unit contains one molecule, and we would expect to observe two ^{31}P resonances in the ^{31}P-CPMAS spectrum as well as two methyl, two methyne, and a number of aromatic carbon resonances, but a single methylene resonance in the ^{13}C-CPMAS spectrum. This is actually observed (Table 1). The fact that the achiral analogues dppe (1,2-bis(diphenylphosphino)ethane) and dppp (1,3-bis(diphenylphosphino)-propane, show only one ^{31}P resonance in their ^{31}P-CPMAS spectra [9] may be the result of

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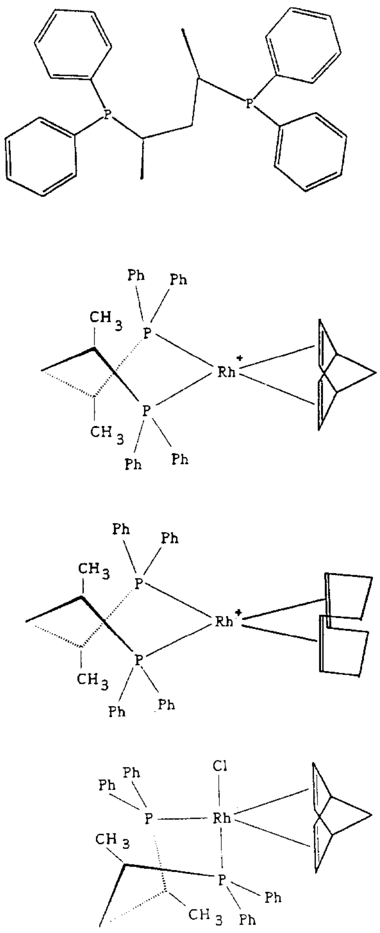

Fig. 1. Molecular structures of **1**, **2a,b,c**, **3** and **4**.

higher symmetry in the unit cell reducing the asymmetric unit to a half-molecule. The chemical shift difference (4.6 ppm) between the averaged value in the solid state and the solution value [7] is an indication that in solution there is a dynamic process involving conformations other than that found at the solid state. From the intensities of the spinning side-band manifold in low spinning speed experiments a chemical shift anisotropy (CSA) value of 53–55 ppm was evaluated, which is in the range of the values reported for organo-phosphines [10].

2.2. [Rh{(S,S)-BDPP}(NBD)]BF$_4$ (2a), [Rh{(S,S)-BDPP}(NBD)]PF$_6$ (2b), [Rh{(S,S)-BDPP}(NBD)]ClO$_4$ (2c)

The three compounds show the expected number of resonances in both ^{31}P and ^{13}C-CPMAS spectra assuming that the asymmetric unit corresponds to one molecule [5]. This has been verified for **2c** only. However it is interesting that the three compounds (which show similar low resolution solution spectra) have quite different solid state NMR spectra (Fig. 2). The effect of counterion on the spectral pattern is in fact remarkable. The chemical shift separation between the two ^{31}P resonances is 2.7 ppm in **2c**, 9.3 ppm in **2a**, and very small in **2b**. Furthermore, the spectral differences between the three species are emphasised by the values of the individual tensor components (Table 1), which clearly show different dispositions of the phosphorus atoms in the two solids with respect to the

TABLE 1. ^{31}P-isotropic chemical shifts and one-bond Rh–P coupling constants in solution (CDCl$_3$) and in the solid state

Compound		Isotropic shifts				Shielding tensor			CSA
		δP_{liq}	J(Rh–P) liq	δP_{sol}	J(Rh–P) sol	σ_{11}	σ_{22}	σ_{33}	$\Delta\sigma$
1	P$_1$	−1.5	–	−2.8	–	−19.2	−12.0	39.8	55.4
	P$_2$	−1.5	–	−9.4	–	−20.2	3.5	44.9	53.3
2a	P$_1$	29.8	149.0	30.6	140	−46.5	40.3	97.3	99.8
	P$_2$	29.8	149.0	21.3	125	−34.6	13.2	85.2	95.9
2b	P$_1$	29.8	149.0	29.3	153	−112	−24.8	48.9	117.5
	P$_2$	29.8	149.0	27.6	153	−110	−23.1	50.5	117.3
2c	P$_1$	29.8	149.0	30.1	146	−106	−9.5	22.7	80.7
	P$_2$	29.8	149.0	27.4	152	−89.2	−33.9	40.9	102.5
3 [a]	P$_1$	29.8	149.0	37.1	134	−106	−37.3	32.6	104.5
	P$_2$	29.8	149.0	29.8	128	−99.0	−23.0	33.5	95.0
	P$_1$	29.8	149.0	26.2	159	−100.0	−16.1	38.1	96.4
	P$_2$	29.8	149.0	24.8	146	−96.7	−21.1	43.0	101.7
4 [c]	P$_1$	40.8	134.7	42.5	[c]	−107	−37.8	17.4	89.8
	P$_2$	8.4	130.0	7.1	[c]	−54.9	7.7	68.1	91.7

[a] The assignment of the ^{31}P resonances to the two molecules of compound 3 in the unit cell is only tentative. [b] The solution data were obtained in CD$_2$Cl$_2$ at 195 K. [c] The Rh–P couplings were not resolved because the linewidth was too broad.

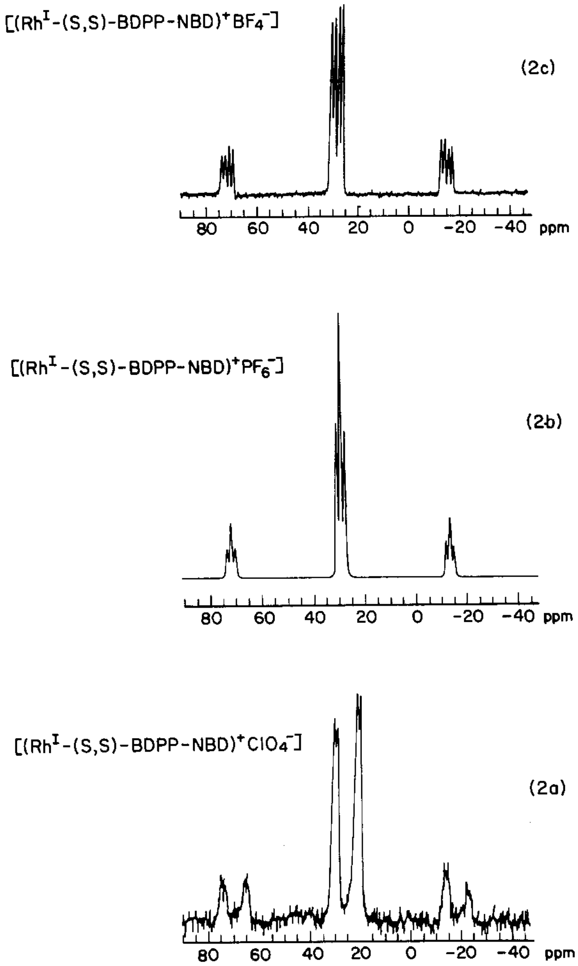

Fig. 2. ^{31}P-CPMAS NMR spectra of **2a, 2b** and **2c** at ambient temperature (spinning speed 3.5 KHz, spectral width 50 KHz, contact time 1 ms).

applied magnetic field. This is a consequence of the steric and electronic requirements of the counterions [11].

A better understanding of such effects would require a detailed comparison of their solid state structures but we have not yet been able to obtain suitable crystals of **2a** and **2b**.

As shown in Table 1 the CSA are almost double that of the free donor. Large CSA values suggest efficient relaxation for the ^{31}P resonances in solution especially at high magnetic fields (T_1 (^{31}P) at ambient temperature in $CDCl_3$ solution of **2a** changes from 4.3 s at 36.4 MHz to 2.6 s at 161.8 MHz). The Rh–P coupling constants are also sensitive probes of the change of the counterion. Within the six measured values there is a large range of 20%. This reflects a distortion of the square-planar stereochemistry around Rh. The largest difference between J(Rh–P) values is found in **2a**, which also shows the largest ^{31}P chemical shift separation.

2.3. [Rh{(S,S)BDPP}(COD)]BF$_4$ (3)

The solid state X-ray structures of **3** and **2** differ in two important features: (i) in **3** the BDPP has a skew conformation, whereas in **2c** it has a chair conformation; (ii) two unrelated molecules are present in the unit cell of **3** whereas **2c** contains only one molecule [6].

The latter feature is responsible for the splitting of each resonance in the high resolution ^{31}P-CPMAS spectrum (the two high field doublets overlap to give rise to a triplet pattern). In both molecules, the cyclooctadiene moiety is somewhat twisted away from C_2 symmetry, but this distortion is in the opposite sense in the two molecules. The presence of only one molecule in the unit cell of **2c** may be due to the rigidity of norbornadiene which cannot adopt any other conformation.

No ^{31}P resonances (Table 1) can be assigned on the basis of the available data. Although the average of the isotropic shifts is very close to the chemical shift found in solution, the individual values spread over a range of 12.3 ppm. In contrast, the average of the one-bond Rh–P coupling constants is significantly smaller (142 Hz) than the values (149 Hz) observed in $CDCl_3$. Moreover the differences between them spans a range of 31 Hz. This shows that dynamic processes in solution do not simply average out the minor structural differences among atomic positions (which are responsible for the number of resonances observed in the solid state spectra) but that they probably involve exchange with other conformations not present in the solid.

The calculated chemical shift anisotropies are about 100 ± 15 ppm for all four resonances, close to those of **2a, b** and **c**. However, from these data we cannot confirm the occurrence of a skew or chair conformation of the BDPP.

2.4. [Rh{(S,S)-BDPP}(NBD)Cl] (4)

The ^{31}P-CPMAS spectrum of **4** shows two resonances, at 42.5 and 7.1 ppm. The substantial difference between the ^{31}P chemical shifts (as well as the individual tensor components) is consistent with a trigonal-bipyramidal structure.

In contrast to **2a, 2b, 2c** and **3**, which all show well resolved signals (some minor broadening may be due to unresolved ^2J(P–P) couplings), the ^{31}P resonances of **4** are very broad (900 Hz). Since there is no reason to think that such a broadening is due to relaxation [11], it must be evidence of the occurrence of a dynamic process and/or of a spread of chemical shifts arising from a number of related structures. Since no sharpening of the ^{31}P resonances was observed as the temperature was raised to +60°C, we rule out the possibility that the broadening of the resonances arises from a dynamic process occurring at the solid state.

In summary, these results are fully consistent with those previously reported by Maciel *et al.* [9a] for a related series of Rh^{I} complexes. The stronger field and the higher spinning speed available to us have now eventually allowed us to obtain better resolved spectra.

3. Experimental details

BDPP and **2a, 2b, 2c, 3** and **4** were prepared by published procedures [6–8]. High resolution solid state ^{13}C and ^{31}P NMR were recorded on a JEOL GX 270/89 spectrometer equipped with a solid state accessory. The spectra were obtained under the condition of ^{1}H-^{31}P cross polarization, high power proton decoupling and magic angle spinning. Samples (typically 50–100 mg) were packed into zirconia rotors and spun at 2.5–4.5 kHz. If needed, the positions of the centrebands were located by varying the spinning speed. Shielding tensor components were derived by graphical analysis (Herzfeld-Berger method) [12] of the spinning sidebands using an iterative computer program based on the equations given by the Levenberg-Marquardt method [13]. The chemical shift anisotropy was calculated by the formula CSA $= \sigma_{33} - (\sigma_{22} + \sigma_{11})/2$. Chemical shifts ($\delta$ scale, high frequency positive) were referenced to external H_3PO_4 (85%) for ^{31}P.

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