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Solid-State Structure of Binuclear Transition Metal Bisphosphine Complexes. Rotation-rate-dependent MAS Spectra of Dipolar and Scalar Coupled Four-Spin Systems of Dimeric Palladium(I) Complexes

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Summary. Straightforward ^{31}P MAS investigations were carried out in the solid state on a series of [$Pd_2X_2(dppm)_2$] ($X = Cl, Br, I$) complexes in order to study the effects that ring distortion, conformations, and crystal packing have on the solid-state spectra of these molecules and also to get experimental values for certain scalar couplings (*e.g.* two-bond *trans* P–Pd–P) normally not available from solution-state spectra.

The phosphorus nuclei in these structures form a tightly dipolar coupled four-spin system which cannot be treated by the averaged *Hamilton*ian theory. The presence of strong homonuclear dipolar couplings, especially under the so called "rotational resonance" conditions, was expected to add to the complexity of the spectra. It turned out that the molecules are asymmetric in solid state but the rotation-rate dependence of the spectra is simpler than expected. Whereas *trans* spin-pairs with small isotropic chemical shift differences show a *J*-recouping phenomenon at modest MAS frequencies, the strongly dipolar coupled *cis* pairs (outside of the real rotational resonance conditions) do not have a characteristic effect in the rotation range studied or the effect is beyond the spectral resolution (<250 Hz). At higher MAS frequencies under the assumption of "inhomogeneous" behaviour reliable values of the *trans* *J*-couplings are available from the spectra.

Keywords. NMR; ^{31}P MAS; Four-spin system; *J*-recoupling; Rotational resonance $\eta = 0$; Dimeric palladium(I) complexes.

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Introduction

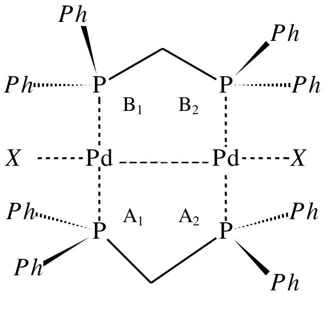
Many dinuclear d^8 Rh^I, Pt^{II}, Pd^{II}, *etc.*, species exhibit "A-frame" type structures or their non-bridged analogues with direct metal – metal bond [1]. The structural features of such complexes possessing an $M_2(dppm)_2$ unit (*dppm* = bis(diphenylphosphino)-methane) is well documented [2]. Crystallographic characterization of palladium(I) dimers including $[Pd_2Cl_2(dppm)_2]$ has been reported recently [3]. A single-crystal X-ray structure, though not complete, exists also for the bromo analogue $[Pd_2Br_2(dppm)_2]$ [4]. The reported structures are monoclinic and possess $P2_1/c$ space group, the $M_2P_4C_2$ rings have a *chair-like* conformation [3].

Given these facts, we carried out a detailed solid state NMR investigation on a series of $[Pd_2X_2(dppm)_2]$ (X = Cl, Br, I) complexes **1**–**3** in order to study the effects of ring twisting, asymmetry, conformation, and crystal packing on the solid-state spectra of these molecules, and also to get experimental values for certain scalar couplings (*e.g.* two-bond *trans* P–Pd–P) normally not available from solution-state spectra.

These structures are of interest also from the NMR point of view since the P atoms involved form a tightly dipolar coupled four-spin system. In the solid state the presence of strong dipolar couplings, especially under the so called "rotational resonance" conditions, is expected to add to the complexity of the spectra even if crystallographically equivalent P sites are present. At the same time, under such conditions simple MAS spectra can provide information on the magnitude and orientation of all anisotropic interactions (CSA, dipolar and *J*-coupling) present. However, anisotropy of *J*-coupling is generally ignored due to its small magnitude. Rotation-rate-dependent MAS spectra have already been reported for isolated two-spin systems, *e.g.* for ^{31}P–^{31}P pairs [5–11], for the ^{19}F–^{29}Si pair [12], and for the ^{13}C–^{13}C pair [13]. Several examples concerning isolated P-atoms pairs of Pd complexes have been collected and reported in a recent review by *Nelson* [14].

The theory for "weakly-coupled" (*i.e.* where the difference in isotropic shifts exceeds the dipolar coupling) two-spin systems has been elaborated by *Levitt* and others [15–16]. The phenomena were explained by the presence of chemical shielding-dipolar coupling cross-terms, CSA/DD, and it was predicted that the rotation-rate dependence should be quite general for dipolar coupled spin pairs.

In principle, MAS NMR in conjunction with numerical line shape simulations [17] of isolated spin systems of more than two dipolar coupled spins ($I = 1/2$) can provide quantitative information about the geometry of fragments concerned.



1 X = Cl

2 X = Br

3 X = I

Scheme 1

However, the complexity of the problem increases exponentially with the number of the involved spins due to the large number of parameters present in the numerous anisotropic interactions.

It has not been long ago when the first reports on more complicated spin systems, *e.g.* for a dipolar and scalar coupled four-spin system, appeared [18]. However, the phosphole tetramer studied could be finally treated as two isolated spin pairs related to each other by a C_2 axis since the dipolar and J-coupling constants between the directly bonded ^{31}P nuclei are much greater than the other P–P interactions. *Sebald et al.* reported recently [12] on the characterisation of $^{29}Si(^{19}F)_{2-3}$ systems and discussed the possibilities of the straightforward MAS NMR approach.

Softwares capable to carry out simulations and iterative fittings of parameters to the experimental spectra have been developed in the last years, in particular GAMMA [19] and SIMPSON [20] have found well-spread public usage. Possibilities and limitations of the iterative line shape fitting procedures have been studied in details more recently [21].

In the case of **1**–**3** complicated, if not intractable, spectra are expected because (i) the isotropic chemical shielding differences among the P atoms cannot be substantial, and (ii) dipolar coupling between the *cis* related P atoms is about the same (600–800 Hz) as the J-coupling between the *trans* related ones (300–600 Hz). Therefore magnitude and orientation of these interactions can also be encoded in the MAS line shapes. However, the success of decoding is questionable. In the following we will discuss what kind of information is available from such spectra.

Results and Discussion

Solution Phase NMR

In solution these complexes are known to be fluxional *via* a fast "swinging" process [22] and a butterfly-like ring "flipping" motion what makes the axial and equatorial methylene protons and phenyl rings equivalent in the ^{1}H spectrum [23, 24]. In agreement with these data our ^{13}C NMR measurements in CD_2Cl_2 at room temperature indicate the presence of eight identical phenyl rings in **1**. The spectra exhibit binominal-like quintets (the A part of an $AXX'X''X'''$ system, $A={}^{13}C$, $X=X'=X''=X'''={}^{31}P$) for all carbon atoms coupled at least to one phosphorus. In case of **1** simulations of these patterns for the *ipso*, *ortho*, and *meta* carbons of the aromatic ring resulted in *trans* and *cis* $^{2}J(P\cdots P)$ coupling values of about 450 ± 10 Hz and -130 ± 10 Hz. At 7.04 T the $^{31}P\{^{1}H\}$ NMR spectrum of **1** consists of a singlet at –1.1 ppm (−2.5 ppm has been reported earlier [25]), the signal does not show any broadening when cooling down the sample in CD_2Cl_2 to 189 K. Likewise, singlets have been observed in the $^{31}P\{^{1}H\}$ spectra for the bromo (**2**) and iodo (**3**) derivatives at −4.7 and –10.5 ppm [25].

Solid Phase ^{31}P MAS and CPMAS Studies

The MAS spectra, in agreement with the crystal structures, prove C_1 symmetry for the molecules studied. The spectra show the presence of two AB-like patterns.

While under appropriate conditions splitting of these patterns may serve as estimates for the *trans* P–Pd–P couplings, the much smaller *cis* P–C–P couplings are not resolved. The line widths are substantial (about 150–330 Hz). To explain this, beside the dispersion of the isotropic shifts, other reasons can also be envisaged. *E.g.* one can speculate that an interplay with the quadrupolar Pd or X nuclei may contribute. However, the fact that they are similar in all complexes, and thus seem to be independent of the quadrupolar moment of X, does not support this view. The line widths tend to narrow at higher rotation speeds so there must be some residual dipolar coupling effect too. Resolved satellites due to the ^{105}Pd nucleus were not

Table 1. Estimates[a] of isotropic chemical shifts (ppm), scalar *trans* P–Pd–P coupling values (Hz), estimates of the CSA (ppm), the asymmetry parameter, η, and the principal shielding tensor components[a] (ppm), shielding span and skew values[b], for the different phosphorus environments of **1–3**

	P_{A_1} ppm	P_{B_1} ppm	$^2J_{A_1B_1}$ Hz	P_{A_2} ppm		P_{B_2} ppm	$^2J_{A_2B_2}$ Hz
1 (X = Cl)							
δ_{iso}	6.7	3.7		−3[c]		−6[c]	
σ_{33}	−67.0	−76.0			−65.0		
σ_{22}	30.0	30.1			16.1		
σ_{11}	57.1	57.0	480		40.2		450
CSA	−79.3	−80.0			−62.6		
η	0.53	0.33			0.38		
span Ω/skew κ	124.1/0.54	133.0/0.6			105.2/0.54		
2 (X = Br[c])							
δ_{iso}	~6.75	~3.0			−6.4 (~A_2)		
σ_{33}	−67.8				−67.0		
σ_{22}	14.2				1.3		
σ_{11}	67.0		~455		46.7		~450 ± 20[d]
CSA	−72.3				−60.9		
η	0.73				0.746		
span Ω/skew κ	134.8/0.21				113.7/0.2		
3 (X = I[c])							
δ_{iso}	~4.5	~3.0		−1.0		−10.0	
σ_{33}	−77.4			−70.0		−67.5	
σ_{22}	14.2			1.4		−13.7	
σ_{11}	55.0		450	65.6		51.2	~450
CSA	−80.5			−69.0		61.2	
η	0.28			0.93		0.88	
span Ω/skew κ	132.4/0.24			135.6/0.06		118.7/0.9	

$P_{A_1B_1}$ and $P_{A_2B_2}$ denote the high- and low-frequency AB-like multiplets; [a] based on assumption of isolated spins (therefore the values given in the table are estimates only, especially at low rotation speeds) and calculated using the STARS program package of Varian which applies the *Haeberlen* shielding notation; [b] as defined by *Jameson et al.* [38]; [c] unfortunately the line separation obtained sometimes did not allow the determination of the principal shielding tensor components for all P atoms; data were obtained using average value for the two overlapping signals; the estimated standard deviations are about 8 ppm for the overlapping signals and 5 ppm for the rest; [d] separation of the first and third lines in Hz observed. However, some broadening at the bottom of the resonances due to residual dipolar effects [26] cannot be excluded. The estimates obtained for *trans* $^{2}J(\mathrm{P}\cdots\mathrm{P})$ values are in the range of 420–500 Hz, indicating a rather similar frame for 1–3.

The isotropic chemical shift difference of the assumed *trans* A and B atoms varied between 50 and 1200 Hz, *i.e.* in general they are larger than the dipolar coupling (~200 Hz) between them. For the *cis* pairs the isotropic chemical shift differences are in the same range but the dipolar couplings are much larger (~800 Hz). The spectral data of **1**–**3**, the estimates of principal components, and the asymmetry and anisotropy values of the shielding tensors are given in Table 1.

*$[Pd_2Cl_2(dppm)_2]$ (**1**)*

The crystal structure, as noted above, is monoclinic with space group $P2_1/c$. The eight-membered $Pd_2P_4C_2$ ring has a skewed "*extended-chair*" conformation [3]. Other relevant single-crystal X-ray data and the calculated dipolar coupling values are collected in Table 2. In the ^{31}P CPMAS different crystallisation products gave slightly different spectra. Two AB-like quartets (A_1B_1 and A_2B_2) are suspected in the spectrum, it is noteworthy that the two lower frequency transitions (assigned to the B spins) of both systems are definitely broader than the higher frequency ones (see Fig. 1).

We recorded spectra at different rotational frequencies, all of which, however, exceeded the separation between the estimated isotropic shift values (they are about 1300 and 1600 Hz for the B_1–B_2 and A_1–A_2 *cis* pairs) therefore no real ($n = 1$, 2, *etc.*) rotational resonance ($\Delta\omega_{\mathrm{iso}} = n * \omega_{\mathrm{R}}$) [15] was possible. In case of slower rotation, center bands and spinning side bands overlap. Nevertheless, the spectra at different rotation speeds showed some changes in the low speed range (Fig. 1) especially for the B_1–B_2 *cis* pair. Moreover, at a certain rotation rate their lowest frequency transitions are further split into doublets, but singlet signals are seen below and above these frequencies. Intensities of the outer transitions of the A_2B_2 pair decrease as the rotation rate is going up and they almost disappear

Table 2. Internuclear bond lengths, calculated dipolar couplings, and coordination plane angles, φ, data of complexes **1** and **2** (single-crystal X-ray data)

	$\mathrm{P}\cdots\mathrm{P}$ *cis* distances $P_{1,2}$ and $P_{3,4}$/Å	Calculated homonuclear dipolar P, P couplings[a], D_{PP}/Hz	$\mathrm{P}\cdots\mathrm{P}$ *trans* distances $P_{1,3}$ and $P_{2,4}$/Å	Calculated homonuclear dipolar P, P couplings[a], D_{PP}/Hz	Pd–Pd bond length/Å	Space group	Coord. angle, φ/°	Ref.
1	2.902 and 2.933	−806.9 and −781.6	4.581 and 4.594	−205.1 and −203.4	2.661	$P2_{1/c}$	38.7	[3]
2	n.r.	–	n.r.	–	2.699	$P2_{1/c}$	39.0	[4]

[a] $D_{\mathrm{PP}} = (\mu_o/4\pi)\ (h/2\pi)\gamma_p{}^2\langle r_{\mathrm{pp}}{}^{-3}\rangle$ (calculated by the SIMPSON routine); n.r. = not reported; Note that to be in agreement with the reported data the phosphorus numbering was taken over from the reported references

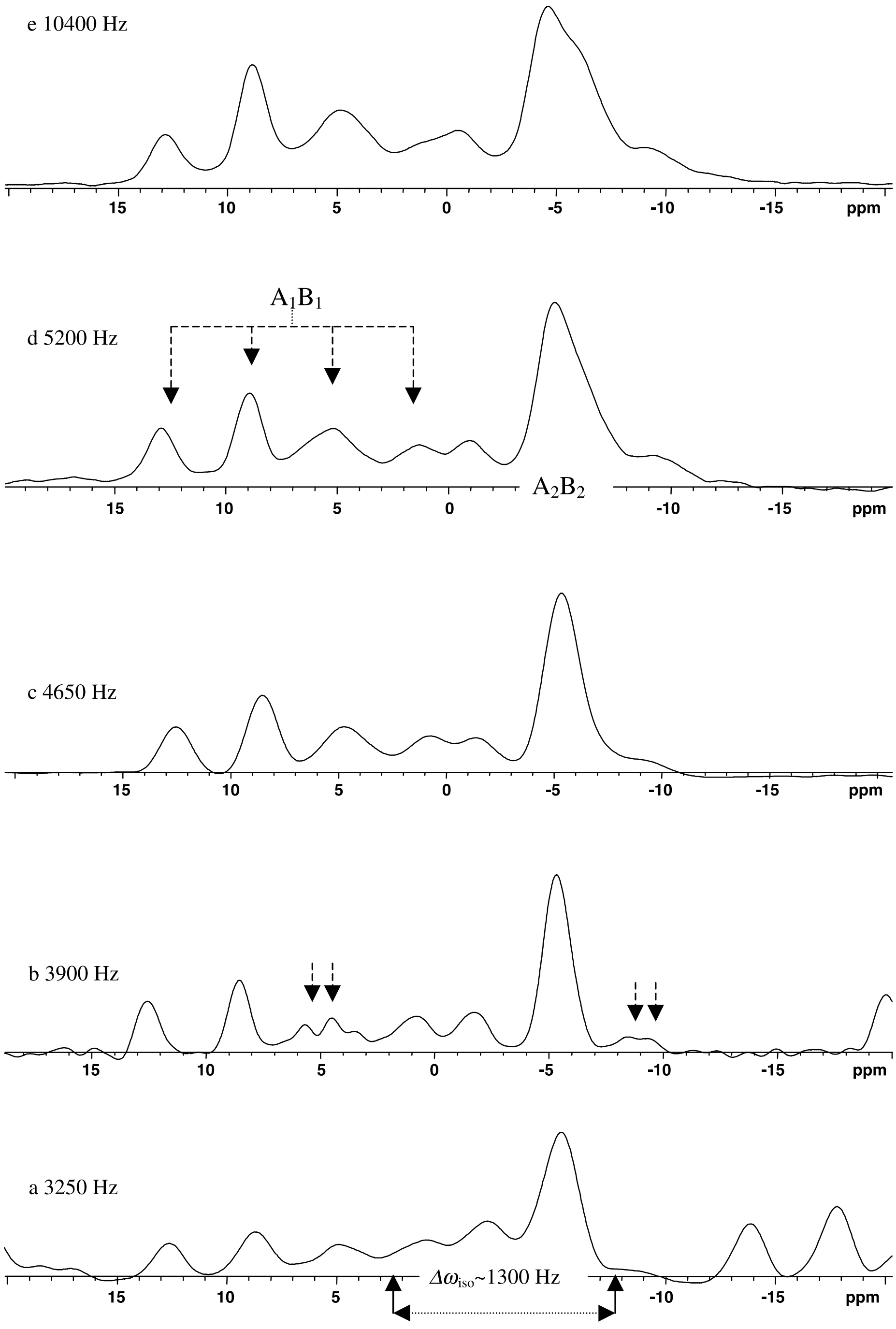


Fig. 1. Complex **1** (Pd_2Cl_2*dppm*$_2$): Rotation rate dependence of the ^{31}P MAS spectra (isotropic region only), estimated isotropic chemical shift difference of the *cis* B_1–B_2 pair, $\Delta\omega_{iso} \sim 1300$ Hz; MAS frequencies (a) 3250 Hz (b) 3900 Hz (c) 4650 Hz (d) 5200 Hz (e) 10400 Hz

above 8000 Hz. Line width of the inner overlapping transitions, however, is increasing from about 270 Hz to 380 Hz, and a shoulder indicates that most probably two phosphorus environments are present. At the same time line widths of the lower frequency nucleus (B_1) of the high-frequency spin-pair decrease slightly, the doublet splitting disappears. However the line separations do not change.

Such homogeneous [16] systems with large isotropic chemical shift difference relative to the dipolar coupling may behave "inhomogeneously" if away from real rotation resonance conditions [15]. If so, in the fast spinning region the lines observed should be split by *J*-coupling only, therefore their absolute values are available directly from the spectrum (see Table 1 for estimates of *J*-values based on this assumption). In this compound for the *trans* related P atoms the $\Delta\omega_{\mathrm{iso}}$ values are larger than the dipolar couplings (for A_1B_1, $\Delta\omega_{\mathrm{iso}} \approx 850\,\mathrm{Hz}$, for A_2B_2, $\Delta\omega_{\mathrm{iso}} \approx 360\,\mathrm{Hz}$ whereas the dipolar coupling among them is only about 200 Hz). The assignment of the *trans* and *cis* pairs is not straightforward. It is based on the magnitude of the observed *J*-recoupling effects in cases of **2** and **3** (see below).

Assignment of the resonances to the particular P atoms is even more difficult and is hardly possible without further information. The chemical shift differences are in the range of the steric effects (see Table 1) and distortions from the square-plane geometry can sufficiently explain them. In an earlier report on linear bimetallic bis(tri-*n*-butylphosphine)palladium complexes rather similar spectral appearances are seen for the *trans* AB pairs [27]. As mentioned above the X-ray structure shows an *extended-chair*-like conformation for the $Pd_2P_4C_2$ ring without any element of symmetry. The main reason for the observed asymmetry is the twisting of the coordination planes around the Pd–Pd bond. The dihedral angle, φ of these planes is 38–39° for the halogeno derivatives studied so far (see Table 2). A closer look at the crystal structure [28] reveals that if neglecting the phenyl rings the Pd_2P_4 core has an axis of symmetry, *i.e.* the P atoms are pair-wise nearly identical. A slightly different conformation of the five-membered rings and/or orientations of the phenyl rings fixed in the solid phase can be, at least partially, responsible for the loss of symmetry.

SIMPSON simulations [20] of the four-spin system based on estimated isotropic chemical shifts and reliable dipolar and *J*-coupling values failed to give satisfactory agreement between the experimental and calculated spectra. The dipolar coupling values were calculated from the X-ray structure and the *J*-values were taken from solution state spectra of appropriate model compounds (an asymmetric derivative, [Pd_2*X_2dppm,dppm-Me*] was used for this purpose [22]. Assumptions of mirror plane, inversion symmetry, or a C_2 axis between the shielding tensors of the AB pairs in the calculations had some but not sufficiently characteristic effect on the calculated line shapes. Fitting of the calculated spectra to the experimental ones was not attempted due to the high number of unknown parameters.

[$Pd_2Br_2(dppm)_2$] (**2**)

Partial crystal structure data have been reported long ago [4]. The structure is also monoclinic with space group $P2_1/c$, and, like the chloro complex, the $Pd_2P_4C_2$ ring has a *chair*-like conformation. The reported data are collected in Table 2.

In the spectrum recorded at a rotation speed of 2750 Hz (see Fig. 2d) of the two AB-like quartets only the high-frequency one is resolved, though not completely. The low-frequency pair, A_2B_2, shows an unresolved four-line pattern

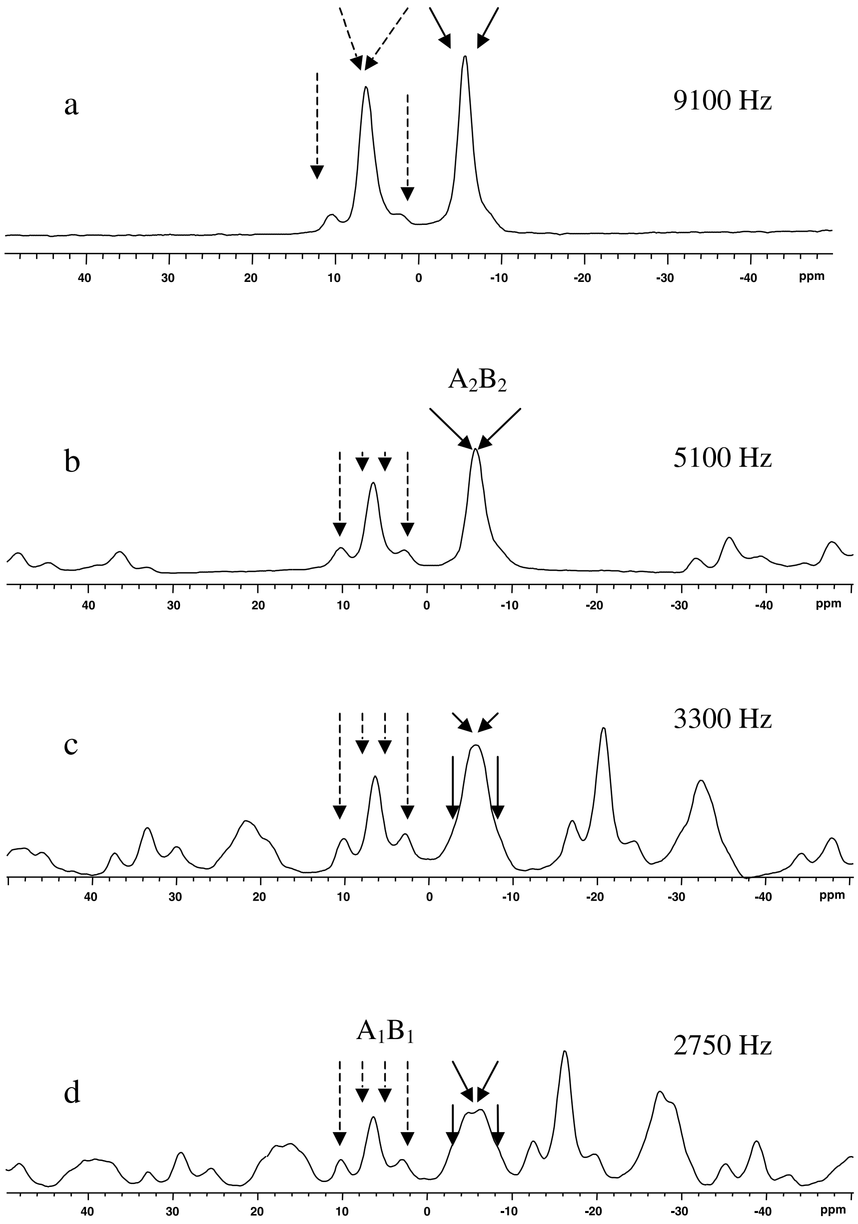


Fig. 2. Complex **2** (Pd_2Br_2*dppm*$_2$): ^{31}P MAS spectra; rotation rate dependence of the homonuclear *trans* spin pairs A_1B_1 and A_2B_2 (a) 9100 Hz (b) 5100 Hz (c) 3300 Hz and (d) 2750 Hz, $J_{A_2B_2} \sim 450$ Hz

($\Delta\omega_{\text{iso}} \approx 50$–100 Hz). As the rotation speeds up line widths of the inner transitions are decreasing gradually, above 5000 Hz they collapse to a singlet ($\Delta\nu_{1/2} \approx 150$ Hz), at the same time the outer weaker transitions disappear (see Fig. 2c–a). Unlike **1** the signal is symmetrical, as if there would be no chemical shift difference between the two nuclei ($\sim A_2$).

At lower rotation speeds the quartet of the low-frequency spin-pair (A_2B_2) is better resolved. The splitting of the inner transitions is about 180–200 Hz, whereas the separation of the 1–3 or 2–4 transitions is about 450 Hz what corresponds well to the expected J value of such *trans*-related pairs [29]. At the same time the high-frequency spin-pair (A_1B_1) with larger chemical shift difference ($\Delta\omega_{\text{iso}} \approx 480\,\text{Hz}$) does not show such a rotation-dependent phenomenon. It is also noteworthy that both spin-pairs behave as if they were isolated from the other, *i.e.* despite of the strong dipolar coupling among the *cis* P pairs, the high-order "cross" interaction among them, if away from rotational resonance conditions, is small [15]. The described behaviour seems to be a typical J-recoupling phenomenon of the "unusual" type similar to those of reported for isolated dipolar coupled spin-1/2 pairs [6, 7, 15, 16, 30]. Such J-recoupling patterns may arise even between chemically identical P atoms (as is well known, coupling between chemically identical spins in a two-spin system cannot be observed in isotropic liquids) if the nuclei are also J-coupled and the main axis of their chemical shielding tensors are non-coincident. Reported examples include $Na_4P_2O_7 \cdot 10H_2O$ [31, 32], $W(CO)_4P_2R_n$ [33], and $Pt(II)P_2Cl_2$ [5]. They were treated as a special case, *i.e.* an "n = 0 rotational resonance". Further instances are $Cd(NO_3)_2(PPh_3)_2$ [7] and $Hg(NO_3)_2(PPh_3)_2$ [6].

In the case of dipolar coupled P atoms a doublet splitting, D, of signals of the interacting nuclei, different from the isotropic chemical shift difference, $\Delta\omega_{\text{iso}}$, was observed at spinning frequencies lower than the anisotropies involved. High-order correction terms to the average *Hamilton*ian were found to be responsible [8]. The suspected chemical shift/dipolar coupling, CSA/DD, cross-terms are functions containing the principal components of the CSA tensors (K), the dipolar coupling tensor (F) and the relative orientation of the chemical shift tensor with respect to the dipolar vector (G). The functions are rather complex but all are proportional with the product of the instantaneous chemical shift difference, $\Delta\nu$, of the two nuclei and the homonuclear dipolar coupling, R, between them. At the same time they are inversely proportional to the $2n^{\text{th}}$ or $(2n+1)^{\text{th}}$ power of the rotational speed, ω_R (Eq. (1)).

$$D = \left[(\delta - G)^2 + (\omega_J - F)^2 + K^2\right]^{\frac{1}{2}} \quad e.g.\ G = \sum_{n=0}^{+\infty} \frac{g_{2n}}{\omega_R^{2n}} \tag{1}$$

where $g_{2n} \propto (\Delta\nu)R^{2n}$ $n = 0, 1, 2, \ldots$

In Eq. (1) [8] δ denotes the isotropic chemical shift difference and ω_J is the scalar coupling between the two spins. This equation is also valid for crystallographically equivalent nuclei, *i.e.*, if $\Delta\omega_{\text{iso}} = \delta = 0$. As mentioned above for "inhomogeneous systems" [15] only at spinning speeds much higher than all anisotropic interactions do MAS spectra correspond to solution spectra.

Concerning the AB-like patterns of the *trans* related P atom pairs (A_1B_1 and A_2B_2) it is noteworthy, that the rate-dependence is always present for pairs with small isotropic chemical shift difference (<200 Hz) indicating that this is an "n = 0 rotational resonance" effect indeed. We have no reason to assume identity of the isotropic shifts, rather we are facing here similar shift values not sufficiently resolved due to the line broadening.

To confirm this we carried out spectral simulations for a simple two-spin model system with the SIMPSON package (see Fig. 3). In the case of small or zero isotropic chemical shift difference of the *trans* related spins (using the data from Table 1 and assuming a C_2 axis between the shielding tensors of the P atoms) the

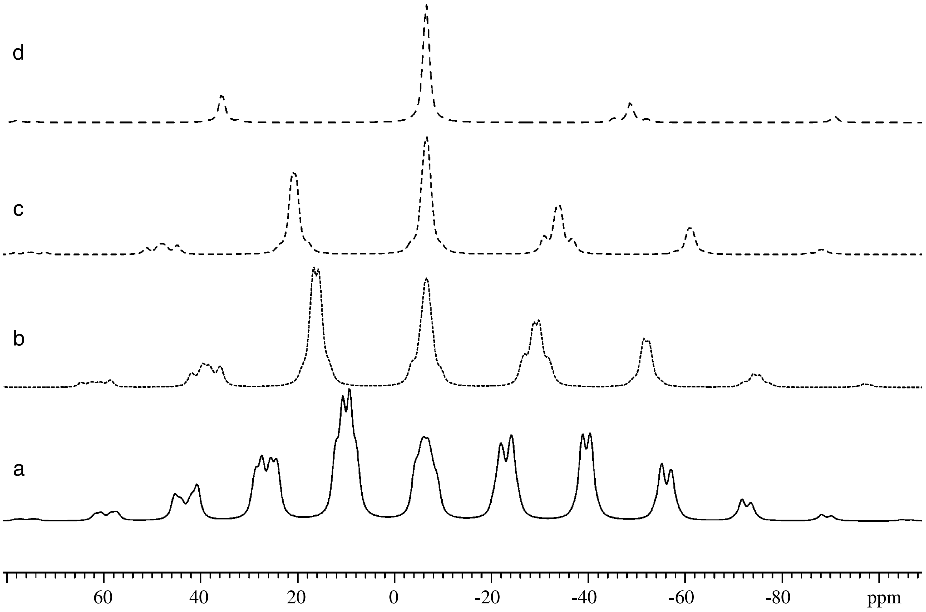


Fig. 3. SIMPSON simulations of MAS spectra of a *trans* related P spin-pair at different rotation frequencies, $\omega_{Rr}/2\pi =$ (a) - - - - 2000 Hz, (b) ······· 2750 Hz, (c) ——— 3300 Hz, and (d) - - - - - - - 5100 Hz, the input data were those shown in Table 1 for the $P_{A_2}P_{B_2}$ ($\sim A_2$) pair of **2**; based on known intermolecular distances a dipolar coupling of -200 Hz was assumed; the *Euler* angles used related the two ^{31}P shielding tensors by a C_2-axis; the difference of the isotropic chemical shifts $\Delta\omega_{iso}$ was set to zero; $J_{PPtrans} = -450$ Hz

calculated spectra agree quite well with the relevant part ($P_{A_2}P_{B_2}$) of spectra of **2** (compare with Fig. 2).

*[Pd$_2$I$_2$(dppm)$_2$] (**3**)*

Two AB-like quartets are clearly distinguishable in the spectra recorded at different rotation speeds (for spectra obtained between 4000 and 10800 Hz see Fig. 4). In fact the low-frequency system, A_2B_2, is almost of first-order with a chemical shift difference of about 8–9 ppm ($\Delta\omega_{iso} \approx 970$–$1090$ Hz) and does not show significant changes with the rotation speed. Note, however, that the line widths of its high-frequency transitions are somewhat broader than the low-frequency ones.

This time the high-frequency quartet, A_1B_1, shows characteristic rate-dependent changes. It is not surprising anymore since the isotropic chemical shift difference is small here ($\Delta\omega_{iso} \approx 200$ Hz). At 6000 Hz and below four transitions are observed. The separation of the first and third transition is again about 450 Hz (remember this is the expectation value of the $^2J_{PPtrans}$ coupling). The inner transitions collapse to a symmetrical singlet above 7500 Hz. All these indicates that we are facing again with a "simple unusual" AB system as described by *Wasylishen* [6]. Although, like **2**, the *cis* related P atoms must be strongly dipolar coupled (see Table 2 for the relevant PP distances), no rotational recouping phenomenon is observed among them since the required conditions are not fulfilled. The spectrum recorded at 11 T is identical except that signals are somewhat

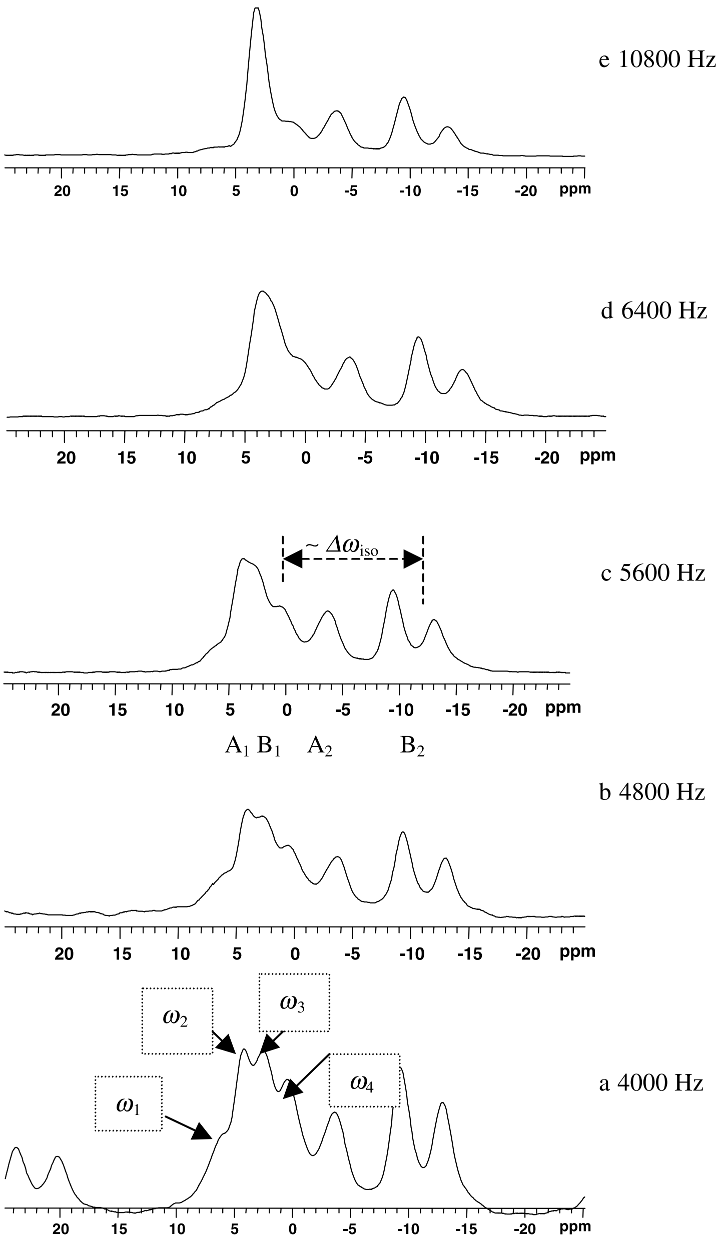


Fig. 4. Complex **3** (Pd_2I_2*dppm*$_2$): ^{31}P MAS spectra recorded at increasing rotational rates; the estimated isotropic chemical shift difference of the B_1B_2 *cis* spin pair, $\delta\omega_{iso}$, is 1600 Hz; $\omega_1 - \omega_3 = 450$ Hz, $\omega_1 - \omega_3 = 230$ Hz, $J_{A_1B_1} \sim 450$ Hz

broader. If one considers the whole spinning sideband manifold of the high-frequency AB quartets (Fig. 5) it is noteworthy that the relative intensities of the peaks within each spinning side band are not symmetric about their center. Nevertheless, the sum of all sidebands at any given rotation rate perhaps gives rise to a symmetric pattern, *i.e.* the transition probabilities are equal as expected. Such phenomena have already been reported and used to illustrate the effect of dipolar

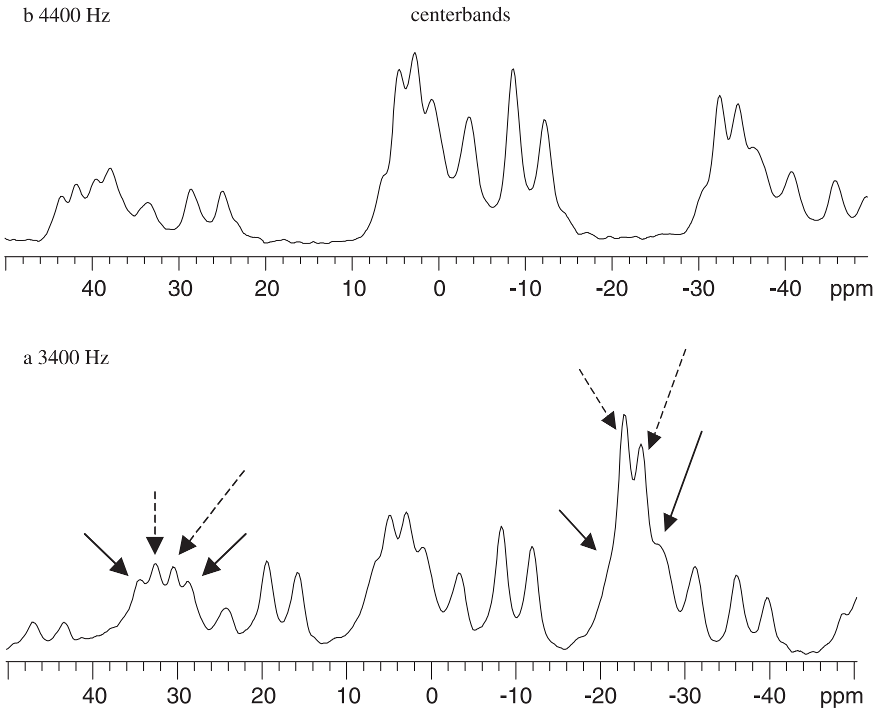


Fig. 5. Complex **3** (Pd_2I_2*dppm*$_2$): ^{31}P MAS spectra recorded at (a) 3400 Hz and (b) 4400 Hz; beside the isotropic region the signals of the first sidebands are also shown; transitions of the -1 and $+1$ sidebands are different in intensity as indicated by arrows

interactions on MAS spectra by *Harris* [34], *Zalewski* [35], and *Szalontai* [36]. We take this as an indication that in this molecule there is an interplay between the ^{31}P shielding tensors and the P–P dipolar coupling tensors depending in their relative orientation. Similar but smaller deviations from symmetry have been observed in the intensities of the sideband-transitions of the slow-spinning spectra of **1** and **2**.

Conclusion

The ^{31}P MAS spectra indicate that the Pd(I) dimeric complexes studied are asymmetric in solid state in agreement with the single-crystal X-ray results. Even small deviations of the shielding tensor components of the P atoms or in the orientation of their main axis cause significant changes in their isotropic shifts. According to the X-ray data, all Pd and P atoms have an individual environment. The steric requirement of the eight phenyl groups and the repulsion of the filled d orbitals on the Pd centers induce non-uniform distortions of the bond lengths and bond angles and make the P nuclei non-equivalent. As proved by X-ray data the $Pd_2P_4C_2$ molecular frames are distorted mainly due to a twist around the Pd–Pd bond. This twist is thought to be the main reason for the different P environments.

The spectra are simpler than expected for such tightly coupled four-spin systems, though it is tempting to interpret them by the theory developed for isolated two-spin pairs, this may be an oversimplification. The two-spin like behaviour of the MAS spectra of **1**, **2**, and **3** can be explained by the "inhomogeneous" nature of the system when away from real rotational resonance conditions [15]. It is also quite possible, however, that the relatively broad lines suppress the fine structure of the signals. Several *trans* spin-pairs with small isotropic chemical shift differences show *J*-recoupling phenomena at modest MAS frequencies. The higher order term contributions to the average *Hamilton*ian should be significant at these rotation rates.

Of the compounds studied so far **1** shows the most complex MAS spectrum. The doublet splitting of the low-frequency signals of the *cis* related phosphorus atoms disappears at 5000 Hz and above. When concerning the possible reasons one has to be cautious. Neither the internuclear distances between these strongly dipolar-coupled P atoms are very different, nor are their instantaneous chemical shift differences very large.

Simulations of the four-spin systems carried out so far failed, therefore no information concerning the relative orientation of the shielding tensors is available from the spectra. From the unequal intensity distribution of the spinning side bands we have, however, a clear indication for an interplay of the ^{31}P shielding tensors with the ^{31}P–^{31}P dipolar coupling tensors.

Experimental

Complexes **1**–**3** were synthesized according to previously reported procedures [37, 23]. The crystals were small but sufficiently homogeneous in size distribution. The solid-state NMR experiments were performed on a Varian UNITY 300 NMR spectrometer equipped with a room temperature double-bearing Doty XC5 probe. The ^{31}P resonance frequency, $\omega_o/2\pi$, was -121.4 MHz. Spectra were recorded with high-power (~100–120 W) proton decoupling. Sample spinning speeds were typically varied between 3000 and 11000 ± 10 Hz. Reliable rotation below 1500 Hz is not possible on this probe. Samples (80–100 mg) were used in 5 mm o.d. zirkonia or Si_3N_4 rotors. The number of scans varied between 32 and 128. Both MAS (with recycling delays of 12–15 s) and CPMAS spectra (with contact times of 0.7–1.2 ms and recycling delays of 6 s) were recorded and gave practically identical results. The ^{31}P 90° pulse width was about 3.6 µs. For referencing purposes polycrystalline PPh_3 was applied ($\delta = -6$ ppm relative to H_3PO_4) by the substitution method. The 11 T ^{31}P MAS spectrum ($\omega_o/2\pi$ was -202.5 MHz) was recorded on a Bruker Avance DRX500 using 4 mm rotors. The STARS program package (v.2.) of Varian Inc., and the *Haeberlen* convention ($|\sigma_{33} - \sigma_{\mathrm{iso}}| > |\sigma_{11} - \sigma_{\mathrm{iso}}| > |\sigma_{22} - \sigma_{\mathrm{iso}}|$, $\eta = \sigma_{22} - \sigma_{11}/(\sigma_{33} - \sigma_{\mathrm{iso}})$) was used to get estimates of the shielding tensor components, shielding anisotropy values, and asymmetry parameters, but span and skew values are also reported according to *Jameson* [38]. The SIMPSON software package [20] was applied to simulate the experimental MAS spectra or parts of them. This package is based on the γ-COMPUTE approach [19] and uses the REPULSION [39] scheme for powder averaging. Shielding notation was used. For simulations the main axis of the principal axis system (PAS) of the homonuclear dipolar coupling tensor has been assumed to coincide with the crystal axis system (CAS) of the molecules. In general *Euler* angles [40] relate the PAS and CAS systems.

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