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Residual Dipolar Couplings in ^{31}P MAS Spectra of P*Ph*$_3$ Substituted Cobalt Complexes

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Summary. Residual dipolar couplings between ^{31}P–^{59}Co spin pairs were studied in ^{31}P MAS spectra of mono- and dinuclear cobalt-triphenylphosphine complexes. These spectra can provide important informations such as the scalar coupling between the dipolar phosphorus and the quadrupolar cobalt nuclei normally not available from solution phase studies. In case of complementary (NQR or X-ray) data even the relative orientation of the interacting shielding, dipolar, scalar couplings, and electric field gradient tensors or internuclear distances can be determined. Examples are shown both for well resolved and practically unresolved cases, factors which possibly control the spectral resolution are discussed in detail.

Keywords. Solid state NMR; Residual dipolar effects; Cobalt complexes; ^{31}P–^{59}Co pair; One-bond ^{31}P–^{59}Co couplings.

Introduction

Spin–spin interaction between spin-1/2 and quadrupolar nuclei has been the subject of several earlier [1–3] and more recent solid-state NMR studies [4]. The MAS experiment cannot average the dipolar interaction between such spin-pair to zero because the quadrupolar nucleus is not solely quantized by the applied external magnetic field, but also by the anisotropic quadrupolar interaction. The easiest way to look at the effect is to record the MAS spectrum of the spin-1/2 nucleus. Spin pairs, such as ^{13}C–^{14}N [5–8], ^{13}C–^{35,37}Cl [9–12], ^{31}P–^{63,65}Cu [13], ^{119}Sn–^{35,37}Cl [14], ^{31}P–^{35,37}Cl [15], ^{13}C–^{2}H [16, 17], and ^{31}P–^{59}Co [3, 18] have been studied so far.

Our main reason for this work was that the acquisition of MAS spectra allows for the measurements of scalar coupling between the spin-1/2 nucleus ^{31}P and a quadrupolar nucleus, which is not observed normally in liquid phase experiments. In organometallic chemistry the value of the one-bond indirect coupling between phosphorus and a metal is of crucial interest, *e.g.* from the stereochemical point of view. The information one can get from the ^{31}P MAS spectra may even include the

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orientation of the electric field gradient, EFG tensor, and the magnitude and sign of the quadrupolar coupling constant, and in some cases the asymmetry parameter too. However, in unfavourable conditions, occasionally only good estimates of isotropic shifts and coupling values are available.

We have studied in particular the characteristic of ^{31}P–^{59}Co ($I = 7/2$) spin-pair in mono- and dinuclear PPh_3 substituted Co complexes. A practical approach was taken, several examples will be shown for small and larger second-order quadrupolar shifts, for slow and fast cobalt relaxation rates, and for different coordination modes of the cobalt atoms to illustrate the effects and to help the understanding of factors which govern the spectral resolutions.

Results and Discussion

Theory

Using the first-order perturbation treatment [2, 3] first and second-order quadrupolar effects of an S nucleus transferred to MAS spectra of a spin 1/2 nucleus (I) can be calculated by Eqs. (1)–(5).

The first-order frequency shift, ${}^1\Delta\nu_m$ is given by Eq. (1)

$$ {}^1\Delta\nu_m = -mJ - mD'(1 - \cos^2\Omega) \tag{1} $$

with Ω the angle between the I, S internuclear vector and the external magnetic field, $\mathbf{B}_o$, D' is the effective dipolar coupling.

The second-order frequency shift, ${}^2\Delta\nu_m$ is given by Eq. (2)

$$ {}^2\Delta\nu_m = \left(\frac{3D'x}{20\nu_S}\right)\left(\frac{S(S+1) - 3m^2}{S(2S-1)}\right)(3\cos^2\beta^D - 1 + \eta\sin^2\beta^D\cos 2\alpha^D) \tag{2} $$

where m = magnetic quantum number, J = scalar coupling between I and S, ΔJ = anisotropy of scalar coupling, D = dipolar coupling between I and S, its effective value $D' = D - \Delta J/3$, χ = quadrupolar coupling = e^2Qq_{zz}/h, q_{zz} = the largest component of the electric field gradient, Q nuclear quadrupole moment, ν_S = S nucleus *Larmor* frequency, η = asymmetry of the electric field gradient, EFG. For the angles α^D and β^D see the illustration below.

It is known that the MAS experiment averages out the first order effect but only scales down the second-order one. Conditions under which the equation for ${}^2\Delta\nu_m$ is valid:

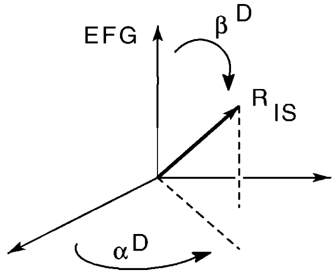
1. First-order perturbation theory can be applied on the S states, *i.e.* the *Zeeman* interaction is much stronger than the quadrupole one [2]:

$$ R_{qz} = \frac{x}{4S(2S-1)\nu_S} \ll 1 \tag{3} $$

2. The **J** tensor is axially symmetric and its main axis is aligned with the internuclear vector, r_{IS} (see Scheme 1).

Furthermore, if the EFG tensor **q** has axial symmetry too, *i.e.* $\eta = 0$, and is aligned with $\mathbf{r}_{IS}$ then we may define the second-order shift, Δ as follows:

$$ \Delta = \frac{3}{10}\frac{\chi D'}{\nu_S} \qquad \eta = \frac{q_{yy} - q_{xx}}{q_{zz}} \tag{4} $$



Scheme 1. Co-ordinates of an internuclear distance, R_{IS} in the electric field gradient frame of reference, and its descriptions by the β^D and α^D angles

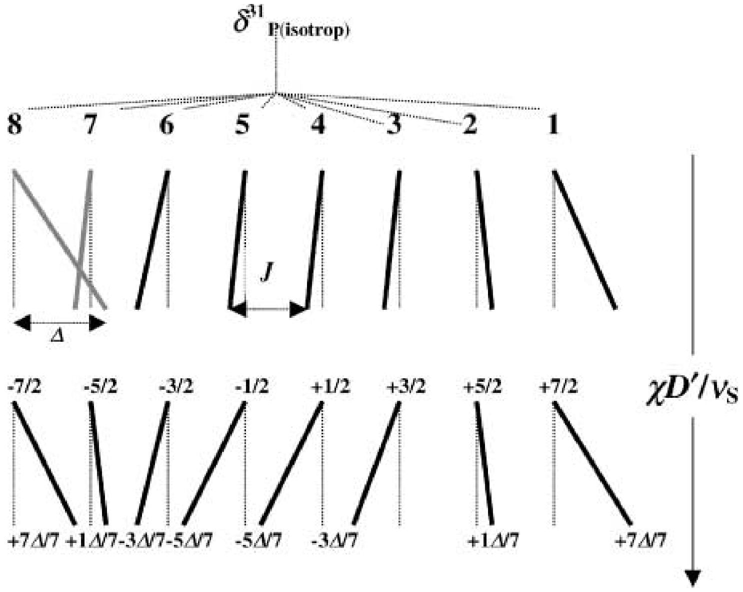
where as usual $|q_{zz}| \geq |q_{xx}| \geq |q_{yy}|$ (q_x, q_y and q_z are the unit vectors directed along the three axis of the EFG principal axis system).

Using Δ one can calculate positions of all I transitions ($\pm m$) by Eq. (5).

$$\Delta\nu_m + mJ = -\left[\frac{S(S+1) - 3m^2}{S(2S-1)}\right]\Delta \tag{5}$$

Provided the resolution is good enough to see all the $\pm m$ transitions, or at least most of them one can get J_{iso} by inspection of the spectrum, Δ can also be calculated by simple rules. To have a better overview an illustration for the $I(^{31}\text{P})$–$S(^{59}\text{Co})$ case, *i.e.* for a 1/2–7/2 spin pair, is given below (see Scheme 2). It is obvious that the higher the applied magnetic field is, the better is the chance for well resolved transitions.

It is useful to notice that the innermost lines ($m = \pm 1/2$) will always shift in the opposite direction from the outermost lines (for $m = \pm S$ the expression in the square bracket will be -1). General rule for the sense of the second-order shift: if Δ is positive (the "crowding" of peaks occurs to low frequencies) then either χ is



Scheme 2

negative with D and D' of the same sign, or χ is positive while D and D' are of the opposite sign.

Several informations are available from the spectra. First of all the one-bond scalar coupling value between the dipolar (I) and the quadrupolar (S) nucleus $^1J(I,S)$. Furthermore from the second-order shift, Δ, if the quadrupole coupling constant, χ is known (*e.g.* from NQR studies), D' may be derived. If $|\Delta J| \ll |3D|$ (this is very often assumed with good reason) then D is given, leading to a value for r_{IS} (internuclear distance). If r_{IS} is known (*e.g.* from diffraction studies) ΔJ may be derived. Or reversibly, if D' is known (or if D is known and ΔJ can be ignored) the quadrupole coupling, χ may be derived.

Under favourable conditions (first-order perturbation theory applies, J and q tensors have axial symmetry, the dipolar and scalar coupling main axes coincide) scalar and dipolar couplings or the sum of them (note that normally J_{iso} is not available from solution spectra) can be obtained for the spin-pair involved. However, no information can be gained if (a) the relaxation of the quadrupolar nucleus is fast, *i.e.* "self-decoupling" occurs or (b) any solid-state motion averages the mediating dipolar term to zero.

So far we have considered effects on the spacing of transitions of first-order J multiplets. However, even the intensities within the center band or those of within the spinning sidebands can be effected. This may arise from the interplay of the chemical shielding, dipolar, and scalar coupling tensors [19]. Since at room temperature the population should be practically equal for each $2I+1$ transitions the summation of the total spinning sideband intensity corresponding to a specific quantum number should be the same for all other quantum numbers [19]. It means that recording the spectra besides spinning speeds larger than the actual shielding anisotropy should result in equal intensities for all transitions. It also means that deviations from the 1:1:1:1:1:1:1:1 intensity ratio (in case of an isolated cobalt–phosphorus spin pair) are characteristic for the relative orientation of the shielding and dipolar tensors.

Study of Behaviour of $^{31}P(I=1/2)$–$^{59}Co(I=7/2)$ *Pairs*

Concerning this pair already several reports have been published in literature. *Gobetto et al.* reported on the ^{31}P MAS spectra of bi- and tetranuclear cobalt clusters [3], *Nelson et al.* reported more recently on a series of cobaloximes [18, 20, 21].

Mononuclear Complexes with Trigonal-Bipyramidal Structure, General Formula R–C(O)Co(CO)$_3$P*Ph*$_3$ [22]

For these molecules at 6.33 T or higher we can safely assume the validity of the first-order perturbation theory since even for quadrupole coupling constants of about 200 MHz the ratio between the quadrupole and *Zeeman* interaction, R_{qz} is only about 0.033. The axial symmetry of the dipolar coupling tensor and its co-linearity with the internuclear vector is generally assumed, other necessary conditions such as the axial symmetry of the $\mathbf{J}$ tensor and its co-linearity with the $r_{\text{Co–P}}$ bond are perhaps also met for the one-bond couplings. However, this is not necessarily the case for the symmetry and alignment of the EFG and shielding tensors of the

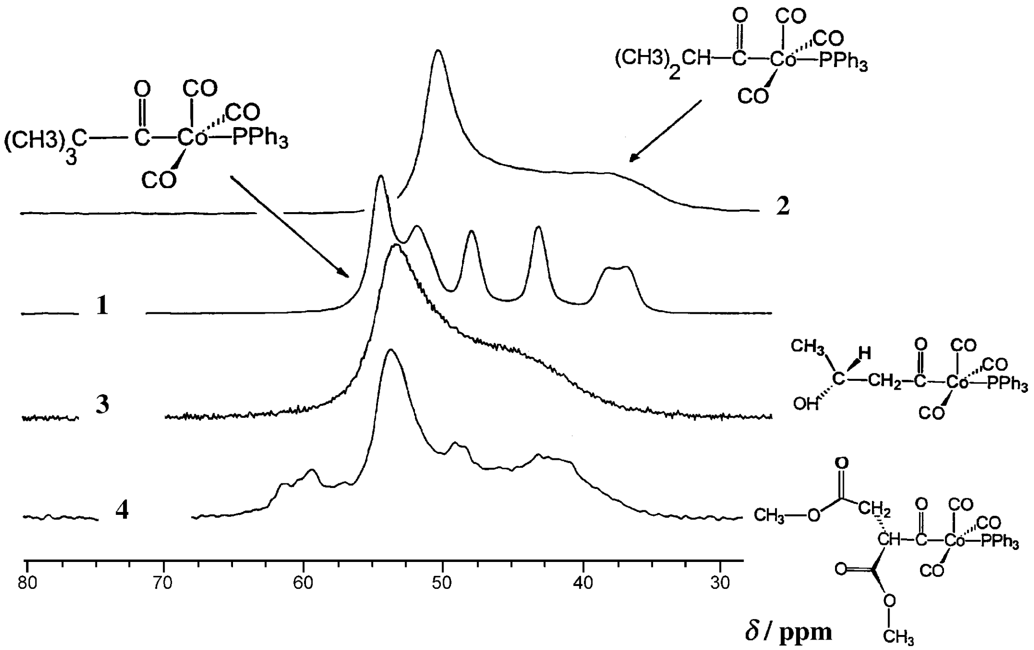


Fig. 1. ^{31}P MAS spectra of **1**–**4** (centerbands only). Spinning speeds were 5180, 3450, 5150, and 5250 Hz for **1**, **2**, **3**, and **4**, recorded at 109.2 MHz (6.33 T)

Co nucleus. The examples shown above (see Fig. 1) range from the moderately resolved (**2**, $R = -CH(CH_3)_2$) to the completely unresolved (**3**, $R = -CH_2-CH(CH_3)-OH$) cases.

Compound **1** ($R = t$.butyl): The isotropic chemical shift is 50.8 ppm, in the solid phase it is 49.6 ppm. Deconvolution of the experimental spectrum resulted in ten lines instead of the expected eight (see Fig. 2), a possible indication that the assumed axial symmetry of the quadrupole tensor is not complete. Nevertheless, values obtained for the second-order quadrupolar shift (− 342 Hz) and for the one-bond ^{31}P–^{29}Co scalar coupling (− 242 Hz) are quite reasonable. The negative sign of Δ comes from the observation that the transitions get closer to each other at high frequencies (peaks 6, 7 and 8 overlap). Anisotropy of the phosphorus shielding, $\Delta\sigma$ is about − 170 ppm (thorough this article we use the *Haeberlen* notation [23], principal components and anisotropies of chemical shielding tensors were calculated from the spinning sideband manifold by the *Herzfeld–Berger* method [24]).

Compound **2** ($R =$ isopropyl): A *J*-coupled fine structure is not resolved, not even in distorted form. The isotropic chemical shift is 49.9 ppm in $CDCl_3$ whereas in the solid phase it is 48.6 ppm. Anisotropy of the phosphorus is about − 175 ppm.

Concerning the possible reasons for the substantial difference between the MAS spectra of **1** and **2**, all other things being very similar, one reasonable explanation might be a difference in the asymmetries of the cobalt EFG tensors due to the different *R* groups. This can lead to fast cobalt relaxation even in solid state what may cause a "self-decoupling" phenomenon [2]. Notice that while in **1** the *R* group has a threefold axis in **2** this is not so.

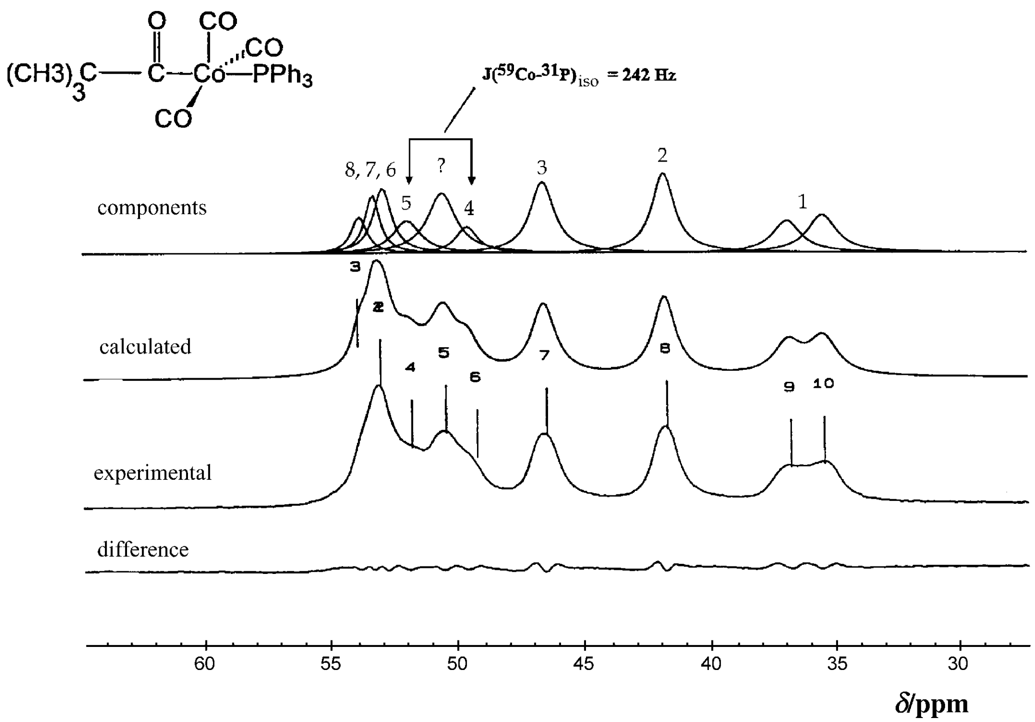


Fig. 2. Deconvolution of ^{31}P MAS spectrum (5180 Hz) of **1** (centerbands only)

Compound **3** ($R = –CH_2–CH(CH_3)–OH$): The isotropic chemical shift is 49.8 ppm, in solid phase it is very close to this. The *J*-coupling pattern is not resolved here, therefore no estimate for the second-order quadrupolar shift and for the one-bond ^{31}P–^{29}Co scalar coupling could be obtained. Anisotropy of the phosphorus chemical shielding is about -165 ppm.

Compound **4** ($R = –CH(COOCH_3)–CH_2–COOCH_3$ (see Fig. 1)): The isotropic chemical shift is 49.6 ppm, in solid phase it is 49.6 ppm. The observed pattern is not resolved, deconvolution of the experimental spectrum was not possible. It is also possible that more than one crystallographically different molecule is present. Anisotropy of the phosphorus chemical shielding is about -170 ppm.

Although it is not sufficiently proved, it is likely that small changes of the EFG tensor orientation or its deviation from the axial symmetry are responsible for the substantial changes observed in the spectra of compounds **1**–**4**. At the same time the phosphorus shielding anisotropies and tensor components are only slightly affected.

Compound **5** ($CH_2{=}CH–CH_2–Co(CO)_2PPh_3$ [25]): The isotropic chemical shift is 67.0 ppm, in solid phase it is 68.8 ppm. This is the least informative case experienced so far. No second-order shift was observed. An indication that either fast cobalt relaxation leads to self-decoupling from the ^{31}P nucleus or solid phase motions are averaging out the residual dipolar couplings. The former is more likely. The observed line width is fairly large (about 605 Hz). Anisotropy of the phosphorus chemical shielding calculated from the spinning sideband manifold is about -97 ppm, the shielding asymmetry is large ($\eta = 0.87$).

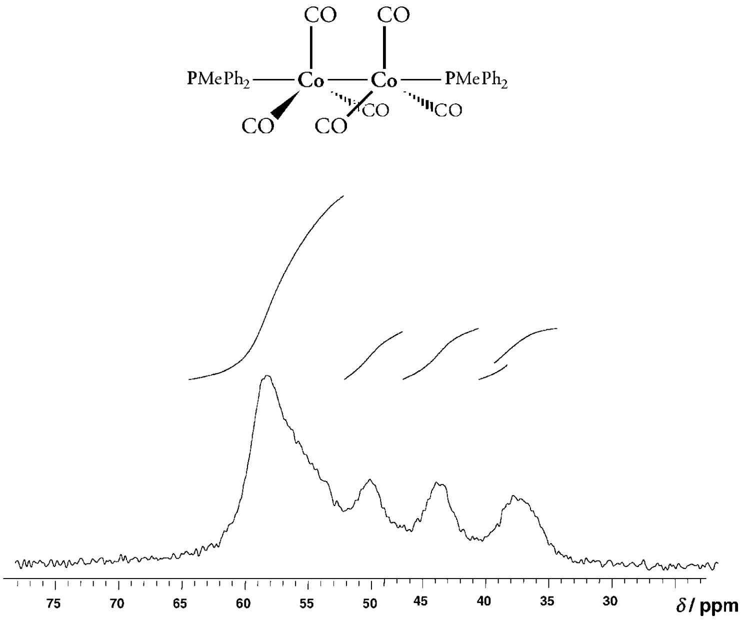


Fig. 3. ^{31}P MAS spectra of **6** (centerbands only). Spinning speed was 8360 Hz, recorded at 121.42 MHz (7.04 T)

Dinuclear Linear Complexes with Co–Co Bond: Ph_2MeP–Co(CO)$_3$–Co(CO)$_3$–P$MePh_2$ (**6**) [26] *vs.* Ph_3P–Co(CO)$_3$–Co(CO)$_3$–PPh_3 (**7**)

The ^{31}P MAS spectrum of **6** is shown in Fig. 3. Due to the heavy overlap of lines which occurs to high frequencies the center transitions are not completely resolved. Nevertheless, a good estimate of J (-395 ± 15 Hz) and the second-order shift, Δ (-440 ± 15 Hz) could be obtained from the spectrum.

Compound **7** (a close analogue to **6**) was thoroughly studied earlier [3], even the value of the quadrupole coupling, χ has been reported (146.8 MHz) and NQR data showed that it has axial symmetry [27]. At 121.4 MHz the phosphorus frequency ν_{Co} is 70.842 MHz therefore R_{qz} is only about 0.024. The P–Co–Co–P direction was thought to be a threefold symmetry axis (X-ray data exist for the (n-butyl)$_3$P analogue [28]. Therefore the co-axiality of tensors was assumed. This is not necessarily the case for **6** where only a C_2 axis can be assumed at best.

Based on arguments used above to explain the observed differences between the spectra of **1** and **2** one would expect different MAS spectra for these compounds too, however this is not the case. In fact the MAS spectra are rather similar. For **6** and **7** the second-order shifts, Δ the isotropic chemical shifts, δ_P and the one-bond scalar couplings, J_{iso}, are -517 Hz, 65.1 ppm, 359 Hz and -440 ± 15 Hz, 52.2 ppm, and 395 ± 15 Hz. This is also a warning that because of the possible interplay of several effects one has to be cautious when trying to interpret spectral changes.

Dinuclear Complexes with Six-Coordinated (Octahedral) Cobalt Atoms

Compound **8**: $Co_2(CO)_2(PPh_3)_2(1{,}3\text{-}\eta\text{-}S_2CSMe)(\mu\text{-}1{,}2\text{-}\eta\text{-}SCSMe)$. The X-ray data indicate two nearly identical P atoms with an overall C_s symmetry of the molecule

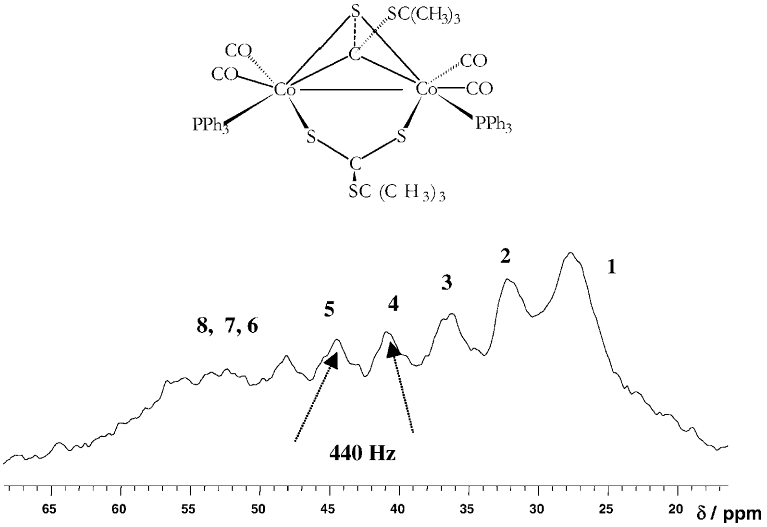


Fig. 4. ^{31}P MAS spectra of **8** (centerbands only). Spinning speed was 5700 Hz, recorded at 121.42 MHz (7.04 T). Nuclear distances from X-ray data: Co–P = 2.232 Å (both), Co–Co = 2.430 Å; the Co–Co–P angles are 154.3 and 158.6 degrees [29]

[29]. The isotropic chemical shift is 38.4 ppm in CD_2Cl_2, whereas in solid phase it is 40.2 ppm. Both Co–P distances are 2.232 Å. The Co–Co–P angles are not identical (154.3 and 158.6 degrees). The ^{31}P MAS spectrum is relatively well resolved (see Fig. 4). Two only slightly different phosphorus environments are suspected, however, only eight lines, though somewhat broadened, are observed. Use of the Co–P distance enable us to calculate D and by assuming that $\Delta J/3$ is much smaller than D, *i.e.* $D' \approx D$, we have an estimate for the quadrupole coupling constant (55.5 MHz). We obtained for J_{iso} and for Δ -440 Hz and -245 Hz.

Compound **9**: $Co_2(CO)_5(PPh_3)_2CHCOOCH_2CH_3$ [30]. X-ray data are not yet available. The isotropic chemical shift is 38.4 ppm in CD_2Cl_2, whereas in solid phase it is 40.2 ppm. The ^{31}P MAS spectrum is relatively well resolved (Fig. 5), two phosphorus environments are present. However, only ten lines are observed. From the distance of the innermost transitions we obtained -449 Hz for **J**, which is rather close to that of compound **8**. Using this value we calculated -75 Hz for the second-order shift, a small value compared to that of **8** ($\Delta = -245$ Hz).

As mentioned already, the interaction between the shielding, σ the dipolar, **D** and scalar coupling, **J** tensors can produce an uneven intensity distribution of the J-coupled multiplet [19]. For compound **9** at low spinning speed (4000 Hz) the central band shows a decrease of multiplet peak intensity in the high-frequency direction. However, by increasing the rotational speed, this is changing gradually, at intermediate frequencies (5800–6000 Hz) the intensities tend to equalize. At a higher rotational frequency (10300 Hz) all spinning sidebands exhibit the reverse trend, *i.e.* the intensities decrease in the low-frequency direction (see Fig. 5 for the changes in the 4000–10300 Hz range). While it is clear that in this molecule the main axis of the dipolar tensor should deviate from that of the shielding tensor, the reason for the complete reversal of the trend is far from being clear.

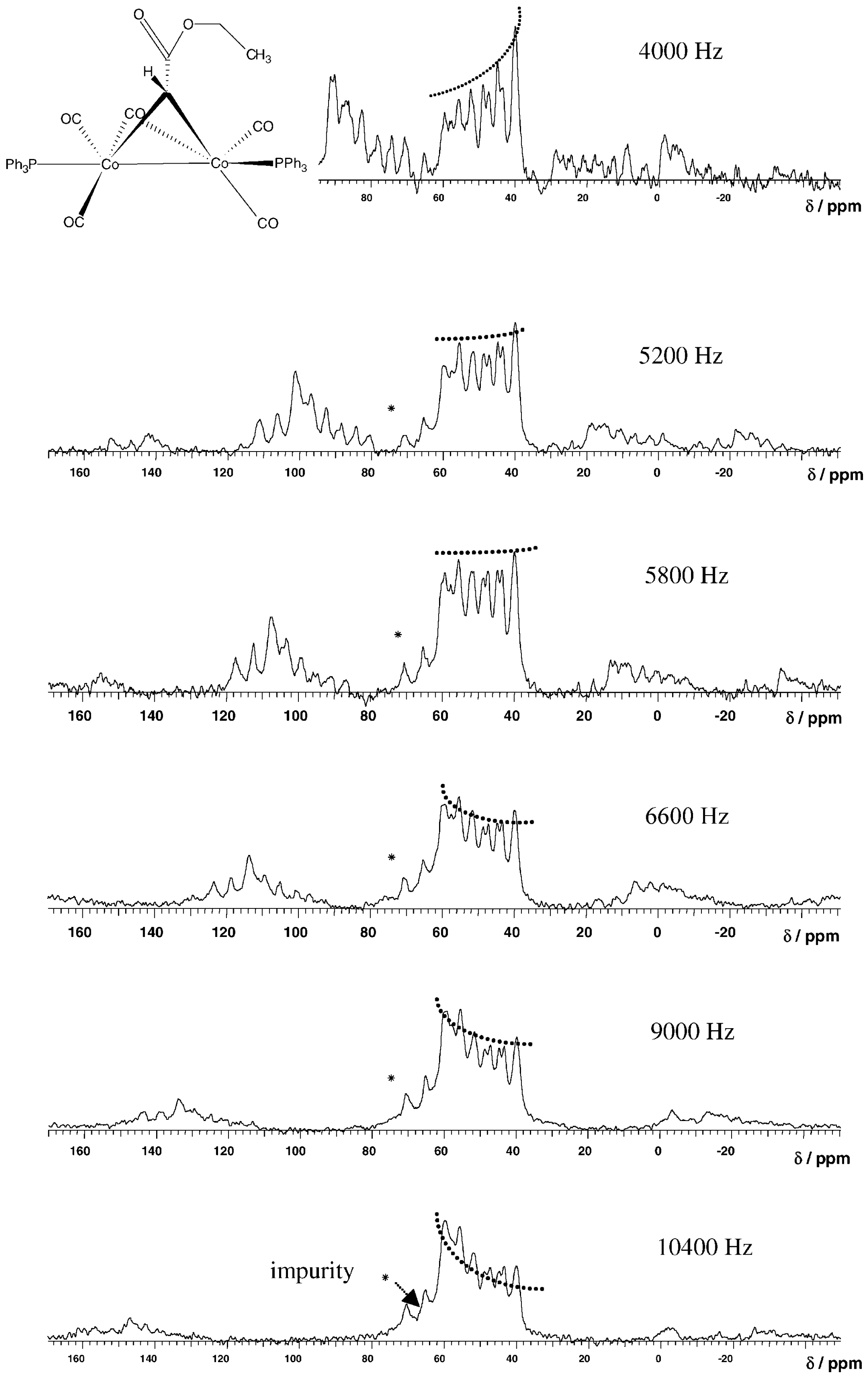


Fig. 5. ^{31}P MAS spectra of **9** recorded at various spinning speeds; 121.42 MHz (7.04 T) [30]

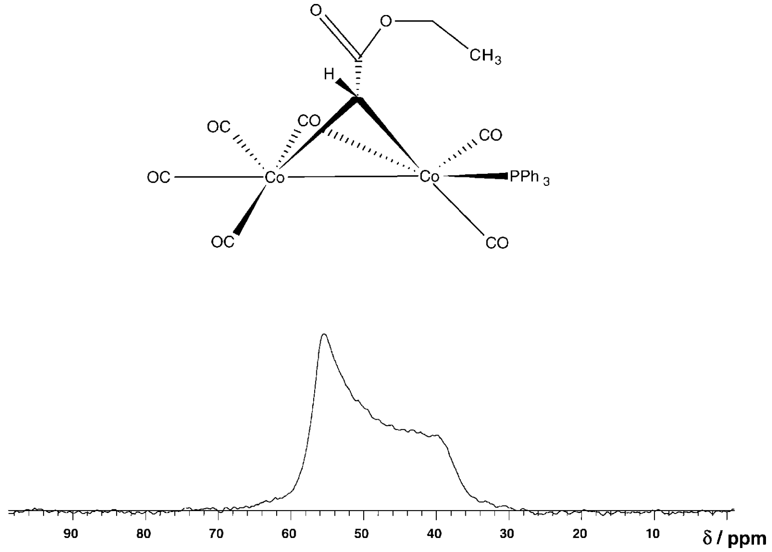


Fig. 6. ^{31}P MAS spectra of (centerbands only). Spinning speed was 9800 Hz, recorded at 121.42 MHz (7.04 T). The Co–Co–P angle was 124.8°

Compound **10**: $Co_2(CO)_6(PPh_3)CHCOOCH_2CH_3$. The X-ray data [30] show a Co–P distance of 2.242 Å, the cobalt atoms are six-coordinated in a strongly distorted octahedral environment. In this case the Co–Co–P angle is only about 124.8 degrees. The isotropic chemical shift is 38.4 ppm in CD_2Cl_2, whereas in the solid phase it is 40.2 ppm. In the ^{31}P MAS spectrum the *J*-coupling is not resolved (see Fig. 6), one phosphorus environment is observed as far as one can judge. The total span of the signal is about 2800 Hz what suggests a $^{1}J(^{59}\text{Co}–^{31}\text{P})$ coupling value of about 400 Hz. This proves that the mediating dipolar field is present, the reason for the loss of coupling information can be the relatively fast cobalt relaxation.

A possible reason for the fast cobalt relaxation can be the strongly distorted octahedral environment of the cobalt atoms (as confirmed by the X-ray data, note the substantial differences in the Co–Co–P angles of **8** and **10**), which likely results in highly asymmetric shielding and EFG tensors.

Experimental

Compounds

$(CH_3)_3C–C(O)Co(CO)_3PPh_3$ (**1**, $C_{26}H_{24}O_4CoP$) [21], $(CH_3)_2CH–C(O)Co(CO)_3PPh_3$ (**2**, $C_{25}H_{22}O_4CoP$) [21], $CH_3–CH(OH)–CH_2–C(O)Co(CO)_3PPh_3$ (**3**, $C_{25}H_{22}O_5CoP$) [21], $CH_3O–CO–CH_2–CH(COOCH_3)–C(O)Co(CO)_3PPh_3$ (**4**, $C_{28}H_{24}O_4CoP$) [21], $CH_2{=}CH–CH_2–Co(CO)_2PPh_3$ (**5**, $C_{23}H_{20}O_2Co_1P_1$) [25], $Ph_2MeP–Co(CO)_3–Co(CO)_3–PMePh_2$ (**6**, $C_{32}H_{26}O_6Co_2P_2$) [26], $Ph_3P–Co(CO)_3–Co(CO)_3–PPh_3$ (**7**, $C_{42}H_{30}O_6Co_2P_2$) [3], $Co_2(CO)_2(PPh_3)_2(1,3\text{-}\eta\text{-}S_2CSMe)(\mu\text{-}1,2\text{-}\eta\text{-}SCSMe)$ (**8**, $C_{50}H_{48}O_4S_5Co_2P_2$) [29], $Co_2(CO)_5(PPh_3)_2CHCOOCH_2CH_3$ (**9**, $C_{45}H_{36}O_7Co_2P_2$) [30], $Co_2(CO)_5(PPh_3)_2CHCOOCH_2CH_3$ (**10**, $C_{28}H_{21}O_8Co_2P$) [30].

Spectroscopy

Most of the spectra were recorded on a Varian UNITY 300 spectrometer using a Doty XC5 room temperature probe under the conditions of high-power proton decoupling and magic-angle spinning.

The ^{31}P 90° pulse duration was about 3.5 μsec, spectral width 50000 Hz, acquisition time 0.05 sec, number of transients 128–512, recycle delay 20–60 sec. Depending on the line widths obtained 10–50 Hz line broadening function was applied. The rotation rates were varied between 3000 and 11000 Hz. Centerbands were located by changing the sample rotation rate. Phosphorus chemical shifts were obtained by the substitution method and are quoted relative to the 85% H_3PO_4. The proper MAS conditions were checked with crystalline PPh_3 ($\delta_P = -6$ ppm) put in an insert of about 35 mm^3. For this sample resolutions better than 30 Hz were obtained using 5 mm Si_3N_4 Doty rotors. The 109.38 MHz ^{31}P MAS spectra were obtained on a JEOL GX 270/89 spectrometer using 6 mm o. d. zirconia rotors. The accuracy of the J values obtained clearly depend on the spectral resolution and are indicated in the text where appropriate, consequently the accuracy of the calculated second-order shift values is not better than ± 15 Hz.

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