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Solid state ^{31}P NMR spectroscopic studies of tertiary phosphines and their complexes

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CONTENTS

A. INTRODUCTION

The coordination chemistry of tertiary phosphine ligands is a mature subject [1] that has played an important role in the development of homogeneous transition metal catalysts [2] for a number of significant organic transformations [3]. During the evolution of this branch of coordination chemistry, ^{31}P NMR spectroscopy [4] became available as a routine tool for use in characterization and in investigations of reactivity. The ^{31}P nucleus proved to be an excellent candidate for NMR studies with a high sensitivity resulting from its 100% natural abundance and its high magnetogyric ratio (10 829 radians s^{-1} G^{-1}). Over the years, ^{31}P NMR spectroscopy has been a major factor in the development of our understanding of the solution chemistry of tertiary phosphines and their complexes. Solid state structures of tertiary phosphine complexes, on the other hand, have typically been determined by X-ray

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crystallography or, if this technique is not available or is inappropriate, by indirect analytical methods. An ongoing problem in the field is the question of the relationship between structure, most commonly determined for the solid state, and reactivity, typically investigated for solutions. High resolution, solid state NMR techniques can be used to address the problem of relating solid state and solution structures and so may provide a bridge between solution NMR methods and X-ray crystallography. The utility of solid state NMR methods in providing a bridge between solution NMR techniques and solid state structural results is shown in many of the examples described in ref. 5. The importance of having a technique that bridges solution NMR data with solid state structural results can be illustrated by considering the ^{31}P NMR spectrum of phosphorus pentachloride. In carbon disulfide solution, the ^{31}P NMR spectrum of PCl_5 displays one signal at +80 ppm with respect to 85% phosphoric acid [6(a)] whereas, in the solid state, the ^{31}P NMR spectrum of the compound consists of two signals of equal intensity at −96 ppm and +281 ppm with respect to the same reference [6(b)]. By comparison with solution chemical shifts for compounds of known structure, the two signals in the ^{31}P solid state NMR spectrum of PCl_5 were assigned to the species PCl_4^+ (−96 ppm) and PCl_6^- (+281 ppm). (Note that the sign convention for ^{31}P chemical shifts employed in the 1960s was the reverse of the one employed today, i.e. negative shifts represented deshielding.) This experiment is probably the first to indicate clearly to chemists that chemical information similar to that from solution NMR studies could be obtained directly from high resolution, solid state NMR experiments.

In this review article we discuss the application of high resolution, solid state NMR methods to the study of the coordination chemistry of tertiary phosphines with transition metals. We have not discussed the underlying principles of the various solid state NMR experiments in depth since complete discussion is available elsewhere [5, 7–19]. Similarly, we have not attempted to cover exhaustively every reference that mentions a solid state ^{31}P NMR spectrum of a transition metal phosphine complex but rather selectively to describe work that illustrates the real utility of solid state NMR techniques. Where possible we have included references to X-ray crystallographic data for the compounds discussed and have attempted to determine whether or not the reported NMR data were in agreement with the single crystal X-ray diffraction results. For example, a complex containing two phosphine ligands that are entirely equivalent in solution might crystallize in a form where the asymmetric unit contains one entire molecule, i.e. two crystallographically inequivalent phosphorus nuclei. Thus, although the solution ^{31}P NMR spectrum might show one signal, the solid state ^{31}P NMR spectrum might show two. Clearly, the two phosphorus nuclei in the asymmetric unit might give rise to isochronous signals and then only one resonance would be observed. Alternatively, it must be borne in mind that the X-ray crystallographic study involves examination of a single crystal whereas a solid state NMR measurement on a powder requires a bulk sample. Thus, the presence of impurities, other isomers, different polymorphs, various types of solvates, etc., may affect the appearance of the solid state NMR spectrum. Despite these potential complications, there is always the possibility that the solid state NMR experiment might actually shed light on the contents of the asymmetric unit in cases where this is in some doubt and so may prove to be valuable in solving crystallographic space group ambiguities in the future [20].

This review starts with a very brief overview of the basic solid state NMR experiments and the information that can be obtained from them. Studies of tertiary phosphines are described next, followed by discussion of complexes containing the metals of Groups 8–12. No major studies of early transition metal–phosphine complexes have appeared of which we are aware (although a CP/MAS ^{31}P NMR study of $W(PMe_3)_3H_6$ has been performed; see ref. 21). No doubt this situation will soon change.

B. SOLID STATE NMR METHODS

The magic angle spinning, MAS, and cross-polarization magic angle spinning, CP/MAS, NMR experiments are the two solid state NMR experiments that are most commonly used by chemists to obtain information on solid materials. Numerous texts and review articles describing these two experiments have been published [5,7–19] and so the intent of this section is not to provide an in-depth description of these experiments but rather to describe briefly the fundamental features of these two techniques.

(i) The MAS experiment

The total interaction between a spin-1/2 nucleus and a magnetic field is given by

$$\mathscr{H} = \underset{(10^6-10^9)}{\mathscr{H}_Z} + \underset{(0-10^5)}{\mathscr{H}_D} + \underset{(0-10^5)}{\mathscr{H}_{CS}} + \underset{(0-10^4)}{\mathscr{H}_{SC}} \tag{1}$$

with the approximate magnitudes (in Hz) of the different interactions (Z = Zeeman, D = dipolar, CS = chemical shift, SC = scalar) indicated below the appropriate terms.

Equation (1) may be rewritten as

$$\mathscr{H} = \mathscr{H}_Z + (\gamma^2\hbar^2/r^3)\vec{I}_1\cdot\hat{\boldsymbol{D}}\cdot\vec{I}_2 + \gamma\hbar\vec{I}\cdot\hat{\boldsymbol{\sigma}}\cdot\vec{H}_0 + \hbar\vec{I}\cdot\boldsymbol{J}\cdot\vec{S} \tag{2}$$

where γ is the magnetogyric ratio, $\hbar$ is Planck's constant divided by 2π, r is the internuclear distance, $\vec{I}_1$, $\vec{I}_2$, $\vec{I}$, and $\vec{S}$ are the spin angular momenta of the nuclei, and $\vec{H}_0$ is the magnetic field vector. The interactions between the vectors $\vec{I}$, $\vec{H}_0$, etc. are orientation-dependent owing to the fixed orientations of the molecule and the spins in the solid state. They are represented by 3×3 matrices or tensors, $\hat{\boldsymbol{D}}$, $\hat{\boldsymbol{\sigma}}$, $\boldsymbol{J}$. By choice of a suitable coordinate system, each of these tensors may be reduced to a diagonal form, that is having non-zero elements only on the diagonal a_{xx}, a_{yy}, a_{zz} (eqn. (3)). They are called the "principal elements" of the tensor.

$$\begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{bmatrix} \xrightarrow{\text{"diagonalization"}} \begin{bmatrix} a_{xx} & 0 & 0 \\ 0 & a_{yy} & 0 \\ 0 & 0 & a_{zz} \end{bmatrix} \tag{3}$$

The fundamental difference between solution and solid state NMR spectra is that, in the former case, the fast rotational and translational motion of the molecules averages the dipolar, chemical shift, and scalar interactions to their isotropic values. In each case, the average value (a_{iso}) is equal to one third of the sum of the principal elements (or "trace") of the diagonalized matrix

$$a_{\text{iso}} = \frac{1}{3}\,(a_{xx} + a_{yy} + a_{zz}) \tag{4}$$

In solution, rapid reorientation of the molecules reduces the dipolar interactions between like and unlike spins to zero, i.e. $a_{\text{iso}} = 0$. The tensor describing the dipolar interaction is said to be "traceless". In the solid state, however, the dipolar interactions are not zero and, in the case of abundant nuclei having high magnetogyric ratios such as ^{1}H, they dominate over the chemical shift and scalar interactions. As a result of the predominance of the dipolar interactions, broad and featureless absorptions are generally observed in the solid state NMR spectra of abundant nuclei.

The dipolar Hamiltonian for the interaction of two nuclear spins in the solid state may be written as

$$\mathscr{H}_{\text{D}} = -g_{\text{N}}^2\beta_{\text{N}}^2 \sum_{i<j} (1/r_{\text{ij}}^5)[(r_i \cdot r_j - 3\hat{r}_{iz}\hat{r}_{jz}) \times (I_i \cdot I_j - 3\hat{I}_{iz}\hat{I}_{jz})] \tag{5}$$

In this expression, the first term in the square brackets describes the spatial relationship of the spins with respect to each other and the field, and the second the spin magnetization vectors which describe the orientation of the spins themselves. One way of reducing the dipolar interaction to zero is by making the spatial term in eqn. (5) equal to zero. This is accomplished by rapid rotation of the sample about an axis inclined at an angle θ with respect to the magnetic field direction. The θ angle that is chosen is the one that makes eqn. (6) equal to zero, i.e. the one for which ($3\cos^2\theta_{ij} - 1$) equals zero.

$$\mathscr{H}_{\text{D}} = -\frac{1}{2}\,(3\cos^2\theta_{ij} - 1) \sum_{i<j} g_{\text{N}}^2\beta_{\text{N}}^2 \left(\frac{1}{r_{\text{ij}}^3}\right)(1 - 3\cos^2\gamma_{ij}) \tag{6}$$

The value of θ_{ij} for which ($3\cos^2\theta_{ij} - 1$) equals zero, the "magic angle" as it is called, is 54°44′ (see Fig. 1).

In the case of $\hat{\sigma}$ and $\hat{J}$, magic angle spinning reduces these two interactions to

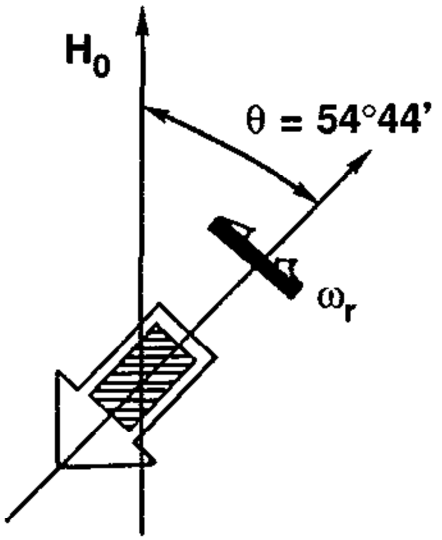

Fig. 1. Orientation of the field and spinning axis vectors in a magic angle spinning (MAS) NMR experiment. (Adapted from ref. 5.)

their non-zero averages, which are the isotropic chemical shifts and spin–spin coupling constants observed in high-resolution solution NMR spectra. The problem is, however, that, by doing so, one loses the information about the three-dimensional nature of these interactions which is present in the spectrum of a static sample. This is illustrated in Fig. 2 in the case of tri-*m*-tolylphosphine sulfide. Figure 2(a) shows the $^{31}P\{^1H\}$ NMR spectrum of a static sample of tri-*m*-tolylphosphine sulfide. It consists of a broad envelope from which the principal elements of the chemical shift tensor, the isotropic shift, and the chemical shift anisotropy may be obtained. Note that two different scales are commonly used by solid state NMR spectroscopists: the δ scale and the σ scale. The two scales are related by the equation

$$\delta = -\sigma \tag{7}$$

The convention chosen for the reporting of shielding tensor components is that of Haeberlen [10]

$$|\delta_{zz} - \delta_{\text{iso}}| \geqslant |\delta_{xx} - \delta_{\text{iso}}| \geqslant |\delta_{yy} - \delta_{\text{iso}}| \tag{8}$$

$$|\sigma_{zz} - \sigma_{\text{iso}}| \geqslant |\sigma_{xx} - \sigma_{\text{iso}}| \geqslant |\sigma_{yy} - \sigma_{\text{iso}}| \tag{9}$$

The isotropic shifts are given in the equations

$$\delta_{\text{iso}} = \frac{1}{3}(\delta_{xx} + \delta_{yy} + \delta_{zz}) \tag{10}$$

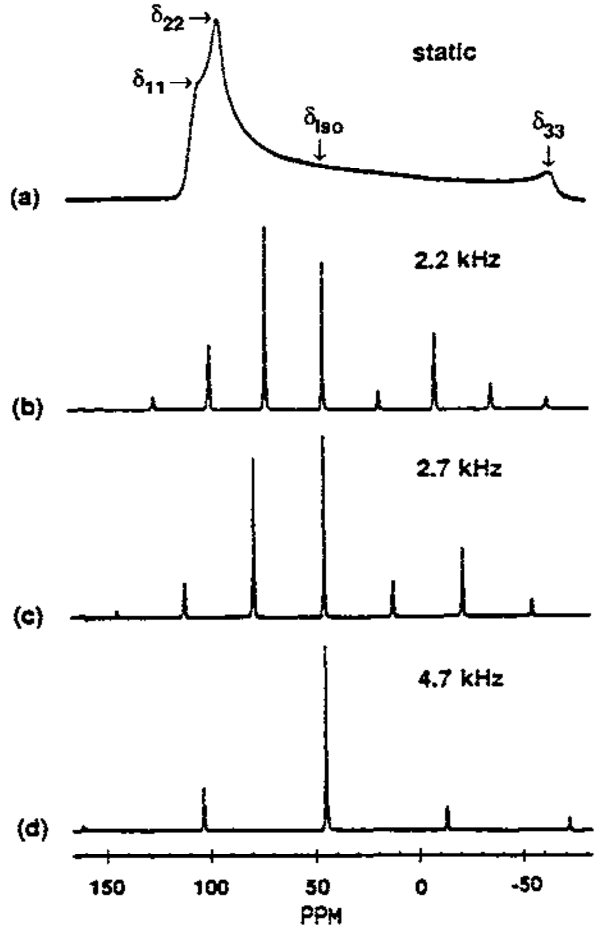

Fig. 2. Cross-polarization $^{31}P\{^{1}H\}$ NMR spectra of tri-*m*-tolylphosphine sulfide.

$$\sigma_{\text{iso}} = \frac{1}{3}\,(\sigma_{xx} + \sigma_{yy} + \sigma_{zz}) \tag{11}$$

It is noteworthy, however, that most solid state NMR spectroscopists do not use the symbols δ_{xx}, δ_{yy}, δ_{zz} and σ_{xx}, σ_{yy}, σ_{zz} for the principal elements of the chemical shift tensor but use instead δ_{11}, δ_{22}, δ_{33} and σ_{11}, σ_{22}, σ_{33}. For tri-*m*-tolylphosphine sulfide it was found that $\delta_{11} = 103.8$, $\delta_{22} = 95.0$, and $\delta_{33} = -64.1$ ppm, in good agreement with the values previously obtained by Robert and Wiesenfeld [22] by computer fitting of the experimental spectrum to a standard powder spectrum, i.e. $\delta_{11} = 98$, $\delta_{22} = 89$, and $\delta_{33} = -79$ ppm. The value of δ_{iso} obtained by calculating one third of the trace of the chemical shift tensor, eqn. (10), is the same as that determined from a series of MAS experiments (see Fig. 2(b), (c), (d)), i.e. $\delta_{\text{iso}} = 44.9$ ppm. The observation of a single resonance in the MAS ^{31}P NMR spectrum of tri-*m*-tolylphosphine sulfide is moreover consistent with its X-ray crystal structure [23], i.e. the compound crystallizes in the orthorhombic space group Pbca with $Z = 8$. From Fig. 2(b), (c), and (d) it is also seen that spinning the sample at a rate approximately equal to the frequency spread of the anisotropy yields the isotropic signal as the predominant signal in the MAS spectrum, whereas spinning at slower rates yields a spectrum where the isotropic resonance is flanked by a series of "spinning sidebands", separated by the spinning frequency, whose intensities reflect approximately the profile of the shift anisotropy pattern. A survey of the literature [5,7–19] indicates that there are several ways of defining the chemical shift anisotropy. Equations (12) and (13) represent the expressions that are most commonly used to calculate the chemical shift anisotropy.

$$\Delta\delta = \delta_{33} - \frac{1}{2}(\delta_{11} + \delta_{22}) \tag{12}$$

$$\Delta\sigma = \sigma_{33} - \frac{1}{2}(\sigma_{11} + \sigma_{22}) \tag{13}$$

However, several authors such as Fyfe, Wasylishen, and Robert use eqns. (14) and (15) instead.

$$\Delta\delta = |\delta_{33} - \delta_{11}| \tag{14}$$

$$\Delta\sigma = |\sigma_{33} - \sigma_{11}| \tag{15}$$

On the other hand, Harris generally uses the equation

$$\Delta\sigma = \sigma_{33} - \sigma_{\text{iso}} \tag{16}$$

As one can see, equations (12) and (14) and (13) and (15) give the same values for the chemical shift anisotropy when $\delta_{11} = \delta_{22}$ and $\sigma_{11} = \sigma_{22}$. Another parameter that is commonly calculated from the values of $\delta_{11}(\sigma_{11})$, $\delta_{22}(\sigma_{22})$, and $\delta_{33}(\sigma_{33})$ is the asymmetry parameter η. It is defined by the equation

$$\eta = \frac{\delta_{22} - \delta_{11}}{\delta_{33} - \delta_{\text{iso}}} = \frac{\sigma_{22} - \sigma_{11}}{\sigma_{33} - \sigma_{\text{iso}}} \tag{17}$$

Values of η are between 0 and 1. In the case where $\delta_{11}(\sigma_{11})$ equals $\delta_{22}(\sigma_{22})$, η is equal to zero and the chemical shift tensor is said to be "axially symmetric". In other words, $\delta_{11}(\sigma_{11})$ and $\delta_{22}(\sigma_{22})$ are degenerate in a plane perpendicular to $\delta_{33}(\sigma_{33})$, the unique axis. In the case of tri-*m*-tolylphosphine sulfide, the chemical shift anisotropy $\Delta\delta$ defined as in eqn. (12) is equal to -163.5 ppm, whereas the asymmetry parameter η is equal to 0.081, meaning that the chemical shift tensor is almost axially symmetric. This situation is quite common for symmetrically substituted tertiary phosphines and their derivatives owing to the fact that these molecules either have three-fold symmetry in the solid state or their geometry only deviates slightly from C_3 symmetry. For these compounds, it has been established that the most shielded tensor component $\delta_{33}(\sigma_{33})$ lies along the phosphorus lone pair or the P=X bond, whereas the $\delta_{11}(\sigma_{11})$ and $\delta_{22}(\sigma_{22})$ components lie in a plane perpendicular to it. The exact orientations of $\delta_{11}(\sigma_{11})$, $\delta_{22}(\sigma_{22})$ and $\delta_{33}(\sigma_{33})$ with respect to the molecular framework would have to be determined via single-crystal NMR studies. Knowledge of the magnitudes and orientations of the principal elements of the chemical shift tensor with respect to the molecular framework is most useful since it provides information concerning the nature of the bonding of the nucleus under study.

The case of tri-*m*-tolylphosphine sulfide is a simple one since its MAS ^{31}P NMR spectrum consists of a single resonance (see Fig. 2(b), (c), (d)). Consequently, the static spectrum shown in Fig. 2(a) arises from a single type of ^{31}P nucleus. However, it happens quite often that the MAS NMR spectrum of a substance contains more than one resonance so that the static spectrum is, in fact, the result of the superposition of several individual powder spectra. Consequently, the principal elements of the chemical shift tensor $\delta_{11}(\sigma_{11})$, $\delta_{22}(\sigma_{22})$ and $\delta_{33}(\sigma_{33})$ can no longer be obtained from the static spectrum as in the case of tri-*m*-tolylphosphine sulfide. Fortunately, methods have been published in the literature that allow the retrieval of the principal elements of the chemical shift tensor from MAS NMR spectra [24–26].

(ii) The CP/MAS experiment

The cross-polarization magic angle spinning, CP/MAS, experiment combines the advantages brought about by the cross-polarization (CP) technique with those of the magic angle spinning (MAS) technique to obtain high-resolution NMR spectra of solids. Since the features of the MAS experiment have been presented in the previous section, only the CP experiment will be described here.

One of the major problems when recording NMR spectra of solids is that the longitudinal relaxation times (T_1) may be extremely long, whereas the transverse relaxation times (T_2) are usually short. For instance, ^{29}Si T_1 values for layered aluminosilicates [27] have been found to vary between 4 and ca. 5000 s, and ^{31}P T_1 values of 30 s for tetramethyldiphosphine disulfide [28] and greater than 900 s for ethane-1,2-diphosphonic acid [29] have been reported by Harris et al. The cross-polarization experiment provides a way of circumventing the problems caused by the long T_1 values of the dilute spins. A description of the technique was first reported in 1962 by Hartmann and Hahn [30]. In 1972 and 1973, Pines et al. described the combination of this technique with a spin decoupling experiment yielding the cross-polarization experiment as we know it today [31,32]. The object of this technique is to transfer polarization from the more abundant I species (^1H), which in thermodynamic language has a high heat capacity, to the S system (^{29}Si, ^{13}C, ^{31}P, etc.), which has a small heat capacity (Fig. 3).

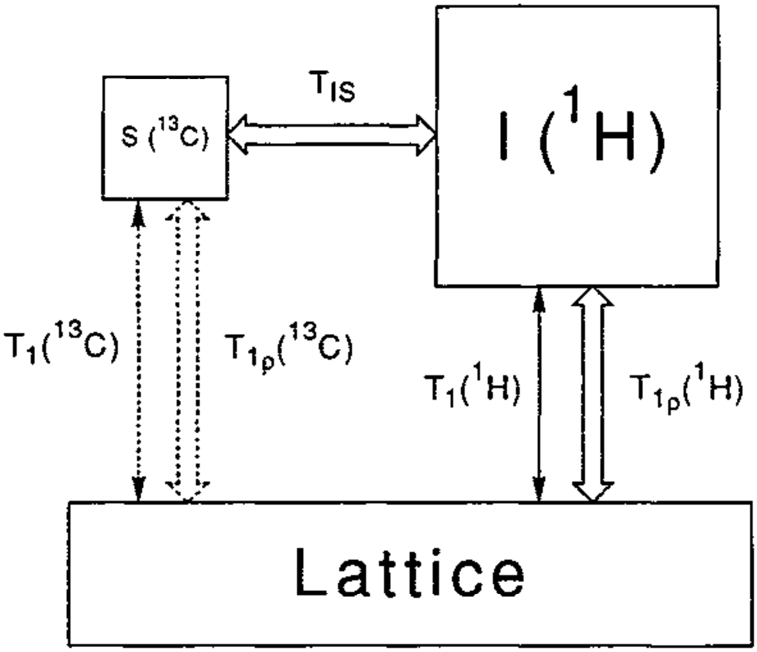

Fig. 3. Thermodynamic representation of I and S spin reservoirs. Note: the $T_{1\rho}(^{13}C)$ and T_{IS} connections are made during CP time, while $T_{1\rho}(^{1}H)$ processes are operative during the entire proton spin lock. Broken lines signify weak coupling (long relaxation times).

Polarization transfer, i.e. the establishment of a thermal link between the two reservoirs, can be accomplished in more than one way, but the most common technique consists of allowing both the I and S spins to precess in their respective rotating frames at some common frequency. This common frequency is that for which the "Hartmann–Hahn" condition, eqn. (18), is satisfied. Under this condition, the Zeeman levels in the rotating frame are matched and effective coupling between the I and S spins occurs via the dipolar interaction.

$$\gamma_H H_{1H} = \gamma_C H_{1C} \tag{18}$$

The sequence of events for establishing contact between the I and S spin systems and observing the S spins is summarized below and in Fig. 4 for $I = {}^1H$ and $S = {}^{13}C$.

Step 1

After establishing ^1H-spin polarization in the static field H_0, the proton magnetization is rotated by 90° to the y' axis in the rotating frame by a strong on-resonance radio frequency pulse applied along the x' axis, and then "spin-locked" along y' by an on-resonance "spin-locking" pulse applied along y'.

Step 2

The ^1H spins are kept locked along y' for a time t. During this time period, a strong on-resonance pulse is applied to the ^{13}C spins which also orient in the y'

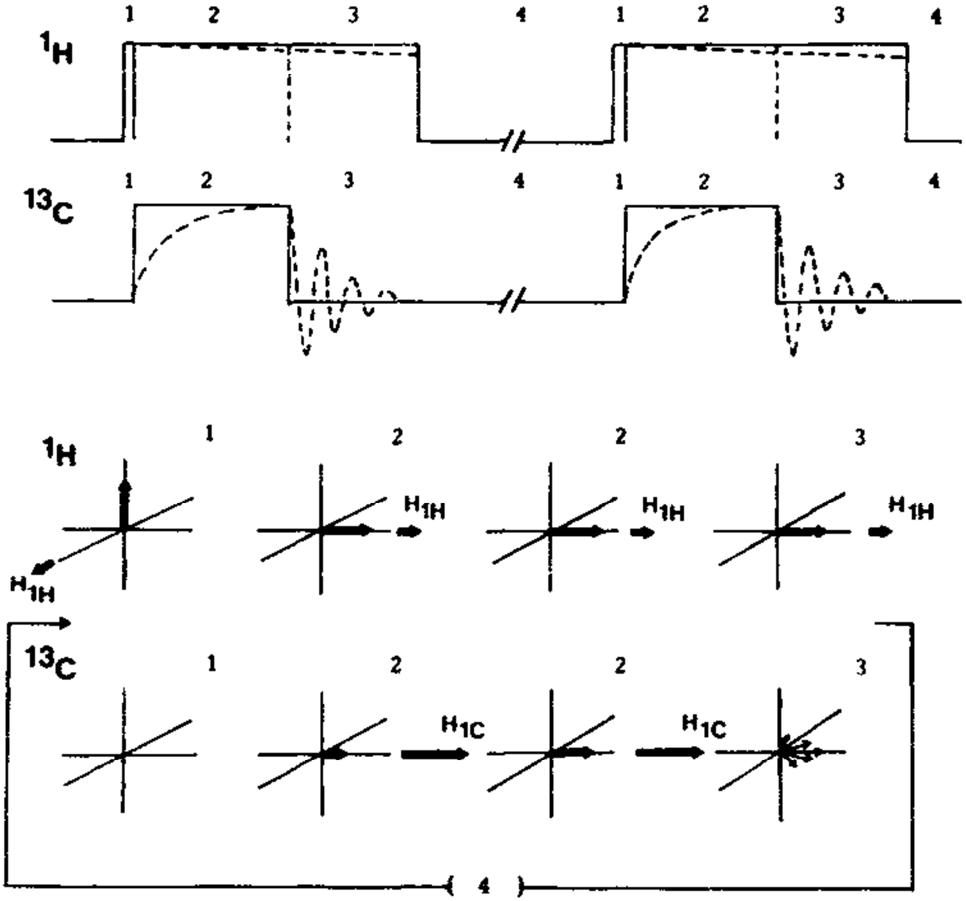

Fig. 4. Pulse sequence and behavior of the ^{1}H and ^{13}C spin magnetizations during the cross-polarization experiment. (Reproduced with permission from ref. 5.)

direction in the ^{13}C rotating frame. In this time period, both sets of spins are "locked" and, by correct choice of the magnitudes of the spin-locking fields H_{1H} and H_{1C}, the net carbon magnetization may be enhanced by the proton reservoir. The spin-locking fields H_{1H} and H_{1C} are chosen so that the "Hartmann–Hahn" condition is satisfied. Since $\gamma_H/\gamma_C = 4/1$, the ^{13}C locking field H_{1C} must be four times H_{1H}.

Step 3

After the carbon magnetization has built up during the matching or "contact" time t, the carbon field is switched off and the carbon FID recorded. The proton field is kept on during this period for heteronuclear decoupling of the proton–carbon dipolar interactions. If the ^{1}H-spin magnetization decays slowly in the rotating frame, i.e. if $T_{1\rho}(^1\text{H})$ is long, it is possible to make several contacts and acquire several FIDs during a single "spin-locking" of the proton system. however. this procedure is generally not used in practice because it requires the H_{1H} field to be on for excessive lengths of time.

Step 4

The proton and carbon spin systems are allowed to return to their equilibrium values in H_0 during a certain time called the "pulse delay" or "recycle delay time" before steps 1, 2, and 3 are repeated.

Thus, an important advantage of the CP technique is that it allows use of recycle delay times of the order of $T_1(^1H)$ instead of $T_1(S)$. In practice, $T_1(S)$ is generally much longer than $T_1(^1H)$ so, in a given time period, many more FIDs can be accumulated using the CP technique than with conventional $\pi/2$ S-spin pulses. The second advantage of the CP technique is that it increases the magnetization of the S-nucleus up to a theoretical maximum factor γ_H/γ_S of 5 for ^{29}Si, 4 for ^{13}C, and 2.5 for ^{31}P.

C. TERTIARY PHOSPHINES

The majority of solid state ^{31}P NMR studies of tertiary phosphines have been done on powdered samples using CP/MAS techniques. Fyfe and co-workers [33] have reported ^{31}P CP/MAS NMR data for several monodentate triaryl- and trialkylphosphines including PPh_3, $P(p\text{-}CH_3C_6H_4)_3$, $P(p\text{-}FC_6H_4)_3$, $P(p\text{-}MeOC_6H_4)_3$, and $P(c\text{-}C_6H_{11})_3$. The ^{31}P solid state NMR spectrum of each one of these phosphines was found to display only one signal for which the linewidth ranged from 75 to 83 Hz and the isotropic chemical shift was comparable with that found in solution. Observation of a single resonance in the ^{31}P CP/MAS NMR spectra of triphenylphosphine, tri-*p*-tolylphosphine, and tris(4-methoxyphenyl)phosphine is consistent with the reported X-ray crystal structures of these compounds [34–36], but such a comparison cannot be made in the other two cases since no X-ray data have yet been published. In the case of triphenylphosphine, moreover, the ^{31}P NMR powder spectrum was found to be consistent with an axially symmetric chemical shift tensor (although the symmetry at the phosphorus in solid triphenylphosphine is not C_3) [34] and the chemical shift anisotropy, $\Delta\sigma = 50$ ppm, was substantially larger than the value of 23 ppm obtained from measurements done in liquid crystal solvents [37]. The ^{31}P CP/MAS NMR data obtained for these phosphines, except for that of tris(4-fluorophenyl)phosphine, have been confirmed by Komoroski et al. [38] and by Penner and Wasylishen [39]. In this latter report, it was also pointed out that the ^{31}P NMR powder spectrum of tri-*p*-tolylphosphine was consistent with an axially symmetric chemical shift tensor, as expected from the reported X-ray crystallographic data (the molecule has C_3 symmetry with C—P—C bond angles of 101.7°) [35] whereas that of tricyclohexylphosphine, surprisingly, showed large asymmetry of the chemical shift tensor ($\eta = 0.46$), indicating substantial deviation from C_3 symmetry of the molecule. Other monodentate tertiary phosphines have been analyzed via ^{31}P CP/MAS NMR spectroscopy [39]. The number of signals observed in the ^{31}P solid state NMR spectra of tri-*m*-tolylphosphine, tris(2-cyanoethyl)phosphine, and 1,2,5-triphenylphosphole was found to be consistent with the reported X-ray crystal structures. Contrary to expectations, the first two compounds showed significant deviation from C_3 symmetry as indicated by the large asymmetry parameters, namely 0.39 and 0.58. These findings were explained in the light of the reported X-ray crystallographic data: in the case of tri-*m*-tolylphosphine [23], the loss of C_3 symmetry is due to the fact that two of the methyl groups are on the same side of the molecule as the phosphorus lone pair whereas the third one is on the opposite side. As far as tris(2-cyanoethyl)phosphine is concerned, a mirror plane passing through the molecule and containing the PCH_2CH_2CN moiety is present [40]. The two crystallographically equivalent C–P–C angles are 106.9° and the third one, bisected by the mirror plane, is 97.1°, thus resulting in a geometry that is significantly distorted from three-fold symmetry. Regarding 1,2,5-triphenylphosphole, it is no surprise to find an asymmetry parameter for the chemical shift tensor of 0.54 since the molecule is unsymmetrically substituted. However, the main reason for recording the ^{31}P CP/MAS NMR spectrum of this molecule was to determine if the phosphorus lone pair was delocalized within the phosphole ring in the same way as the nitrogen lone pair is delocalized within a pyrrole ring. Based on the chemical shift tensor components and the anisotropy that were typical of a phosphine, it was concluded that no significant delocalization of the phosphorus lone pair was present in 1,2,5-triphenylphosphole, in agreement with the results from the X-ray crystal structure determination of this compound [41]. Penner and Wasylishen also obtained the ^{31}P solid state NMR spectra of tri-*o*-tolylphosphine, trimesitylphosphine, and diphenyl-*o*-tolylphosphine. The ^{31}P CP/MAS NMR spectrum of tri-*o*-tolylphosphine contains two signals of equal intensity, in agreement with the reported X-ray data [42], i.e. $P\bar{1}$ with $Z=4$. It was noted that the higher frequency ^{31}P resonance had associated with it a shielding tensor of significantly higher asymmetry. Inspection of the results from the X-ray crystal structure determination of this compound indicated that the major difference between the structures of the two independent molecules in the asymmetric unit was in the torsion angles made by the phenyl rings with the pseudo-C_3 axes. One molecule has angles of 46.8, 40.7, and 45.6° whereas the other has angles of 36.7, 49.0 and 43.1°. Since the latter molecule deviates most from C_3 symmetry, it was tentatively assigned to the high-frequency resonance. The ^{31}P CP/MAS NMR spectrum of commercially available trimesitylphosphine displayed three resonances, two sharp signals and a broad absorption probably consisting of two closely spaced resonances. These results did not agree with the reported X-ray crystal structure [43], which indicates that two crystallographically unique molecules are present per asymmetric unit ($P\bar{1}$, $Z=4$). Recrystallization of the sample from chloroform/ethanol, following the procedure used to prepare a single crystal for X-ray studies, followed by ^{31}P CP/MAS NMR analysis of the recrystallized material yielded a spectrum in which the intensity of the broad signal was greatly diminished. This experiment clearly demonstrates that great care must be exercised when analyzing solid state

NMR data, and that complicating factors such as polymorphism may sometimes have to be taken into consideration. The ^{31}P CP/MAS NMR spectra of both tri-*o*-tolylphosphine and trimesitylphosphine showed another interesting feature in that the signals were very shielded, i.e. below -30 ppm with respect to 85% H_3PO_4, as compared with similar phosphines such as tri-*p*-tolylphosphine (-10.4 ppm) and tri-*m*-tolylphosphine (-7.0 ppm). These results were ascribed to the large low-frequency shift of the δ_{11} and δ_{22} components of the chemical shift tensors resulting from the presence of methyl groups in the exo positions (i.e. on the same side of the molecule as the phosphorus lone pair). The same phenomenon was suggested to be responsible for the large low-frequency shift of δ_{22} in diphenyl-*o*-tolylphosphine for which the isotropic shift was found to be -17.4 ppm. The ^{31}P solid state NMR spectra of several bidentate phosphines have also been reported. Fyfe and co-workers [33] have obtained ^{31}P CP/MAS NMR data for $Ph_2PCH_2PPh_2$ (dppm), $Ph_2PCH_2CH_2PPh_2$ (dppe), and $Ph_2PCH_2CH_2AsPh_2$ (appe). In the case of dppm, a single resonance at -23.3 ppm with respect to 85% H_3PO_4 was observed. This result does not agree with the reported X-ray crystal structure of this compound. Schmidbaur et al. [44] have reported that dppm crystallizes in the orthorhombic space group Pbca with $Z = 8$. One entire molecule is thus present in the asymmetric unit and, consequently, two signals should be observed in the ^{31}P CP/MAS NMR spectrum of this compound. If observable ^{31}P–^{31}P spin–spin coupling is present then the spectrum will be correspondingly more complex. One possible explanation for this discrepancy is that the modification analyzed by Fyfe and co-workers was different from that studied by Schmidbaur and co-workers. In order to agree with the solid state NMR results, the polymorph analyzed by Fyfe and his colleagues would have to contain one phosphorus per asymmetric unit, i.e. the two Ph_2P moieties present in the molecule would have to be symmetry-related by a two-fold axis or a mirror plane. Another possibility, of course, is that the separation between the two signals is beyond the resolution of the NMR experiment, which would explain the rather large linewidth of the resonance, namely 127 Hz. A single absorption was also observed in the ^{31}P CP/MAS NMR spectrum of dppe. The X-ray structures of two polymorphs of dppe have been reported [45]. Both modifications crystallize in the monoclinic space group $P2_1/n$ with $Z = 2$ and the conformations of the molecules in the two polymorphs are said to be practically identical. The polymorphs differ only in the packing of these molecules and each polymorph has one half-molecule per asymmetric unit. Thus, the solid state ^{31}P NMR spectrum of either polymorph or, indeed, a mixture of polymorphs is anticipated to exhibit only a single resonance and one signal is in fact observed. The linewidth at half-height of this signal, namely 146 Hz, is, however, significantly larger than that typically found for monodentate tertiary phosphines (vide supra). The broadening of the resonance may be the result of one or a combination of several of the following situations: it may be a relaxation phenomenon, residual ^1H–^{31}P and/or ^{31}P–^{31}P dipolar interactions may have been present, or, indeed, it may arise from the presence of more than one resonance owing to the presence of more than one polymorph in the sample. The ^{31}P CP/MAS NMR spectrum of appe also displayed one signal, however, in this case, the linewidth of the signal at half-height, 98 Hz, was significantly narrower than those found for dppm and dppe. Since no X-ray crystal structure has yet been published for appe, no comments can be made concerning the number of signals observed in the ^{31}P solid state NMR spectrum of this compound. Maciel et al. [46] have reported ^{31}P solid state NMR data for dppe and for several chiral bidentate phosphines. The ^{31}P CP/MAS NMR spectrum of dppe obtained by these workers was identical to that reported by Fyfe and his colleagues. The ^{31}P CP/MAS NMR spectrum of DiPAMP, (*R*,*R*)-1,2-bis(*o*-methoxyphenylphenylphosphino)ethane, exhibits a single resonance at -25.6 ppm with respect to 85% H_3PO_4. These results suggest that, in the solid state, as observed in solution, the two phosphorus nuclei present in the molecule are magnetically equivalent, meaning that the two-fold axis of symmetry passing through the molecule is retained on going from the solution to the solid state (this explanation, of course, does not take into consideration the possibility of having isochronous signals in the solid state spectrum). The solid state ^{31}P NMR spectra of BPPM, (2S,4S)-*N*-*tert*-butoxycarbonyl-4-diphenylphosphine-2-diphenylphosphinomethylpyrrolidine and prophos, (*R*)-1,2-bis(diphenylphosphino)-propane, each display two signals consistent with the presence of one molecule per asymmetric unit. This is in agreement with the absence of symmetry elements in both compounds (except for their identities). In the case of prophos, moreover, the ^{31}P–^{31}P spin–spin coupling observed in the solution spectrum, $^3J(^{31}P, ^{31}P) = 20.4$ Hz, was not observed in the solid state spectrum due to increased linewidth of the signals. The ^{31}P solution NMR spectrum of chiraphos, (*S*,*S*)-2,3-bis(diphenylphosphino)butane, exhibits only one signal due to the presence of a two-fold axis of symmetry passing through the molecule. The ^{31}P CP/MAS NMR spectrum of this compound, however, displays two resonances of equal intensity, indicating the absence of a two-fold axis of symmetry in the solid state or the presence of two half-molecules in the asymmetric unit. Lastly, ^{31}P CP/MAS NMR data have also been reported for several monodentate and bidentate tertiary phosphines anchored to organic polymers and inorganic supports [33, 38, 46–50].

D. TRANSITION METAL COMPLEXES

Numerous ^{31}P solid state NMR studies of metal complexes have been reported. Metal–phosphine complexes have been the most studied but a few reports on complexes with other types of phosphorus-containing ligands have also appeared.

(i) Complexes of the Group 8 metals

Randall and Carty have focused their attention on Group 8 metal complexes. More specifically, they have measured the ^{31}P spin–lattice relaxation times of several iron and ruthenium dinuclear complexes containing phosphido groups and have determined that the chemical shift anisotropy mechanism made a substantial contribution to the phosphorus relaxation in these and related complexes [51]. These conclusions were substantiated by the fact that the rate of relaxation increased linearly with the square of the magnetic field strength [52]. Also, in the same study, the relaxation properties for coordinated triphenylphosphine in both *trans*-$[Ru_2(CO)_5(PPh_3)(\mu\text{-}\eta^2\text{-}C\equiv C^tBu)(\mu\text{-}PPh_2)]$ and Vaska's complex, *trans*-$[Ir(CO)Cl(PPh_3)_2]$, were examined. It was concluded that coordination of the tertiary phosphine to a transition metal led to an increase in both the phosphorus chemical shift anisotropy and the correlation time τ_c, and that these two increases were responsible for the short T_1 values observed for the coordinated phosphine compared with that of the free ligand. In a related study, Carty et al. measured ^{31}P CP/MAS NMR spectra for a series of dinuclear phosphido-bridged complexes of Group 8 metals (Fe, Ru, Os) [53]. These complexes showed chemical shift anisotropies ranging from 113 to 382 ppm and asymmetry parameters between 0.23 and 0.99. A plot of the ^{31}P isotropic shift versus the metal–phosphorus–metal bond angle in these complexes yielded a moderately good correlation, but much better correlations were observed between the individual tensor components σ_{11}, σ_{22}, σ_{33}, or composite measures of these, e.g. $\Delta\sigma = \sigma_{33} - (1/2)(\sigma_{11} + \sigma_{22})$ and $\mu = \sigma_{33} - \sigma_{11}$, and the bond angles. It was also observed that the tensor component σ_{33} in these complexes showed the largest dependence on the bond angle, whereas the σ_{11} and σ_{22} components were only very little affected. Lastly, the observed correlations led these workers to suggest that all the compounds studied had common shift tensor orientations with respect to the molecular frame.

(ii) Complexes of the Group 9 metals

^{31}P solid state NMR studies of Group 9 transition metal complexes appear to have been exclusively directed towards the investigation of rhodium(I) complexes. Veeman and co-workers [54] have obtained the ^{31}P CP/MAS NMR spectrum of Wilkinson's catalyst, $RhCl(PPh_3)_3$. The ^{31}P solid state NMR spectrum of this complex consists of two multiplets. The low-field multiplet is a doublet, $\delta = 50.2$ ppm with respect to 85% H_3PO_4, resulting from coupling between the phosphorus atom trans to chlorine and rhodium ($I = 1/2$, natural abundance = 100%) with a coupling constant $^1J(^{103}Rh, ^{31}P)$ of 185 Hz. The spinning sidebands of this doublet are more intense than those of the high-field multiplet, indicating a larger chemical shift anisotropy. The high-field multiplet was analyzed as the AB part of an ABX spin system (A and B are the magnetically non-equivalent, mutually trans phosphorus nuclei and X is Rh), with $\delta_A = 24.6$ ppm, $\delta_B = 32.0$ ppm, $^1J(^{103}Rh, ^{31}P_A) \approx {}^1J(^{103}Rh, ^{31}P_B) = 139$ Hz, and $^2J(^{31}P_A, ^{31}P_B) = 365$ Hz. Coupling between the cis phosphorus atoms is too small to be observed. The ^{31}P solid state NMR results agree with the X-ray data reported for the red form of $RhCl(PPh_3)_3$, i.e. $Pna2_1$ with $Z = 4$ [55]. It is noteworthy, however, that observation of coupling between the two phosphorus nuclei trans to each other rules out the possibility of the correct space group being the centrosymmetric one, i.e. Pnam (note that in this complex there is a marked distortion towards tetrahedral geometry). Furthermore, Wilkinson's catalyst has been the subject of a single-crystal solid state NMR investigation by Naito et al. [56]. In this study, it was found that the ^{31}P chemical shift tensors are not axially symmetric and that the most shielded principal values for the three phosphorus nuclei are almost parallel to the corresponding P–Rh bonds. Maciel et al. have obtained the ^{31}P CP/MAS NMR spectra of a series of rhodium(I) complexes containing achiral and chiral bidentate phosphines [46]. The ^{31}P CP/MAS NMR spectrum of $[Rh(COD)(dppe)]ClO_4$ (COD = 1,5-cyclooctadiene; dppe = 1,2-bis(diphenylphosphino)ethane) displayed a single doublet at 56.8 ppm with $^1J(^{103}Rh, ^{31}P) = 126$ Hz, in good agreement with the values found in solution. Observation of a single doublet suggests that, in the solid state, the two phosphorus nuclei present in the molecule are symmetry-related by a two-fold axis or a mirror plane, however, the possibility of having isochronous signals cannot be excluded, particularly since the observed ^{103}Rh–^{31}P couplings are relatively small and the linewidths of the signals are quite large. The ^{31}P CP/MAS NMR spectrum of $[Rh(COD)(DiPAMP)]ClO_4$ (DiPAMP = (*R*,*R*)-1,2-bis(*o*-methoxyphenylphenylphosphino)ethane) showed an apparent triplet centered at 48.8 ppm. It was proposed that this group of signals was, in fact, two overlapping doublets, corresponding to non-equivalent phosphorus atoms, each of them with ^{103}Rh–^{31}P spin–spin coupling. According to this interpretation, the two contributing chemical shifts are about 51.6 and 45.8 ppm, with associated $^1J(^{103}Rh, ^{31}P)$ values of 136 and 145 Hz, respectively. Although no X-ray crystal structure has yet been reported for this complex which would allow the correctness of this analysis to be confirmed, that of the tetrafluoroborate analog has been published. The tetrafluoroborate complex was found to crystallize in the orthorhombic space group $P2_12_12_1$ with $Z = 4$ [57]. Consequently, one entire molecule is present in the asymmetric unit (i.e. two phosphorus atoms). The two crystallographically inequivalent phosphorus nuclei should therefore give rise to two sets of doublets, however, overlap of the signals may occur and result into an apparent triplet. Similar observations were made in the ^{31}P CP/MAS NMR spectra of $[Rh(NBD)(chiraphos)]ClO_4$ and $[Rh(COD)(chiraphos)]ClO_4$ (NBD = norbornadiene; chiraphos = (*S*,*S*)-2,3-bis(diphenylphosphino)butane), i.e. they both showed overlapping signals. In both cases it was proposed that the overlapping signals consisted of two doublets with very similar chemical shifts. In the case of $[Rh(NBD)(chiraphos)]ClO_4$, the chemical shifts of the two doublets were determined to be 62.2 and 61.4 ppm with approximate $^1J(^{103}Rh, ^{31}P)$ coupling constants of 107 and 133 Hz. For $[Rh(COD)(chiraphos)]ClO_4$, the overlapping doublets had chemical shifts of 57.6 and 54.6 ppm with $^1J(^{103}Rh, ^{31}P)$ coupling constants of 117 and 125 Hz, respectively. The overlapping doublets were suggested to arise from the presence of two crystallographically inequivalent phosphorus atoms in the asymmetric unit. The X-ray crystal structure of [Rh(NBD)(chiraphos)]ClO$_4$ has not yet been reported, thus precluding confirmation of the interpretation of the solid state NMR results. That of [Rh(COD)(chiraphos)]ClO$_4$ has, however, been reported, i.e. the complex crystallizes in the monoclinic space group P2$_1$ with $Z=2$ [58], and this agrees with the conclusions drawn from the solid state NMR experiment. The ^{31}P CP/MAS NMR spectra of [Rh(NBD)(prophos)]ClO$_4$ and [Rh(COD)(BPPM)]ClO$_4$ (prophos = (*R*)-1,2-bis(diphenylphosphino)propane; BPPM = (2*S*,4*S*)-*N*-*tert*-butoxycarbonyl-4-diphenylphosphine-2-diphenylphosphinomethylpyrrolidine) each showed two separate sets of signals corresponding to the two types of phosphorus atom present in the molecule, these results being not too surprising since the phosphine ligands do not possess any symmetry element (except their identities). In the ^{31}P CP/MAS NMR spectrum of [Rh(NBD)(prophos)]ClO$_4$, two distinct doublets were observed arising from ^{103}Rh–^{31}P spin–spin coupling but no ^{31}P–^{31}P coupling was seen due to the fact that it is on the same order as the linewidth of the solid state NMR signals ($^2J(^{31}\mathrm{P}, ^{31}\mathrm{P}) =$ 33.4 Hz in solution). As far as [Rh(COD)(BPPM)]ClO$_4$ is concerned, information concerning the ^{103}Rh–^{31}P coupling constants and the number of crystallographically inequivalent phosphorus nuclei could not be obtained given that the signals were extremely broad (full width at half-height $\geqslant 20$ ppm). The extreme broadness of the signals observed in this spectrum was ascribed to the quadrupolar ^{14}N nucleus and the presence of multiple underlying signals. Lastly, ^{31}P solid state NMR spectroscopy has also been used to characterize immobilized rhodium(I) catalysts such as the heterogenized analog of [Rh(COD)(BPPM)]$^+$ and samples of montmorillonite loaded with [Rh(PPh$_3$)$_3$]$^+$ [46,59].

(iii) Complexes of the Group 10 metals

Group 10 metal complexes have been the subject of numerous ^{31}P solid state NMR investigations. Benn et al. [60] have been interested in studying the fluxional behavior of nickel(0) complexes in solution and in the solid state. [Ni(C$_{10}$H$_8$)(dippp)] and [Ni(C$_{10}$H$_8$)(dippe)], where C$_{10}$H$_8$ = naphthalene, dippp = 1,3-bis(diisopropylphosphino)propane and dippe = 1,2-bis(diisopropylphosphino)ethane, were the compounds that were selected for these studies. Combination of variable-temperature one- and two-dimensional solution ^{13}C{^{1}H} NMR data with results obtained from solid-state ^{31}P MAS and ^{13}C CP/MAS NMR analyses led these workers to the conclusion that the shape of these complexes was the same in both states, i.e. the arene group was η^2-bonded to the nickel center. Furthermore, it was determined that in both the solution and the solid states the P$_2$Ni moiety moved between the 1,2 and 3,4 positions within one ring of the naphthalene ligand, but that this motion did not interchange the phosphorus atoms. Fyfe and co-workers have reported ^{31}P CP/MAS NMR data for three Ni(II) phosphine complexes, namely *trans*-[NiCl$_2$(Ph$_2$PCH$_2$CH$_2$Si{OEt}$_3$)$_2$], *trans*-[NiCl$_2$(PCy$_3$)$_2$], and *trans*-[NiCl$_2$(PPh$_2$Me)$_2$] [33]. The ^{31}P solid state NMR spectra of these complexes each displayed a single resonance with no observable ^{31}P–^{31}P spin–spin coupling. These results indicate that, in the absence of accidentally isochronous signals, the asymmetric unit of each one of these complexes contains a single phosphorus atom as a result of the molecule occupying a special position. These conclusions could be confirmed in the case of *trans*-[$NiCl_2(PCy_3)_2$], which was found to crystallize in the triclinic space group $P\bar{1}$ with $Z=1$ (the molecule lies on the center of inversion) [61], but not in the other two cases since their X-ray crystal structures have not yet been reported. However, it is noteworthy that single-crystal X-ray diffraction studies of *trans*-[$NiCl_2(PPh_3)_2$] showed that the molecule was also lying on a center of inversion [62]. Also, in the same study, Fyfe and co-workers employed ^{31}P CP/MAS NMR spectroscopy to monitor the immobilization of *trans*-[$NiCl_2(Ph_2PCH_2CH_2Si\{OEt\}_3)_2$] on high-surface-area glass beads and silica gel. Hillhouse and co-workers [63] have described the ^{31}P CP/MAS NMR spectrum of the carbon suboxide complex $Ni(PPh_3)_2(C,C'{:}\eta^2\text{-}C_3O_2)$. Two resonances (24.8 and 43.6 ppm) in a 1 : 1 integrated intensity were observed, consistent with a cis geometry with an unobservably small coupling between the phosphorus nuclei. No X-ray crystallographic study has been reported as yet but the NMR data suggest, in the absence of accidentally isochronous signals, that the asymmetric unit contains a single molecule of the complex.

Several papers have been published concerning the analysis of palladium complexes via ^{31}P solid state NMR spectroscopy. Fyfe and co-workers [33] have reported the only ^{31}P solid state NMR data available thus far on palladium(0)–phosphine complexes: these workers recorded the ^{31}P CP/MAS NMR spectrum of $Pd(PPh_3)_4$. This complex is most interesting to study via ^{31}P solid state NMR methods owing to the fact that the isolated molecule contains four equivalent phosphorus atoms (the geometry of the complex in solution is tetrahedral) and that, depending upon the symmetry of the molecule in the solid state, up to four signals may be observed in its ^{31}P CP/MAS NMR spectrum (this analysis does not, of course, take into account ^{31}P–^{31}P spin–spin coupling and the possibility of having more than one molecule per asymmetric unit). The ^{31}P CP/MAS NMR spectrum of this complex displays one signal at 15.0 ppm with no observable ^{31}P–^{31}P spin–spin coupling. These results therefore indicate that only one phosphorus is present in the asymmetric unit (if one excludes the possibility of having isochronous signals). These conclusions are reasonable in view of the fact that the benzene solvate of $Pd(PPh_3)_4$ was reported to crystallize in the cubic space group Pa3 with $Z=8$, i.e. the complex has three-fold symmetry [64]. The rest of the ^{31}P solid state NMR data reported on palladium complexes have been obtained on palladium(II) compounds. Interestingly, a large number of *trans*-[$PdX_2(PR_3)_2$] complexes ($X=$ halide; $PR_3=$ monodentate tertiary phosphine) showed ^{31}P solid state NMR spectra consisting of a single resonance with no observable ^{31}P–^{31}P spin–spin coupling. This particular pattern has been observed in the ^{31}P NMR spectra of *trans*-[$PdCl_2(Ph_2PCH_2CH_2Si\{OEt\}_3)_2$]

[33,38]*, *trans*-[$PdCl_2(PPh_3)_2$] [38], *trans*-[$PdCl_2\{P(c\text{-}C_6H_{11})_3\}_2$] [38], *trans*-[$PdCl_2\{(c\text{-}C_6H_{11})_2P(CH_2)_3Si(OEt)_3\}_2$] [38], *trans*-[$PdI_2(PPh_2Me)_2$] [65], and *trans*-[$PdI_2(PPhMe_2)_2$] [65]. Observation of a single ^{31}P resonance with no ^{31}P–^{31}P spin–spin coupling suggests that, in the solid state, the two phosphorus atoms present in the molecule are crystallographically equivalent as a result of the molecule occupying a special position. These conclusions could not be confirmed for every single compound listed above but, for *trans*-[$PdCl_2(PPh_3)_2$] [66] and *trans*-[$PdI_2(PPhMe_2)_2$] [67], single-crystal X-ray diffraction studies showed that the molecules were lying on centers of inversion. Interpretation of the ^{31}P solid state NMR results obtained for $PdCl_2(PPh_2Me)_2$ and $PdCl_2(PPhMe_2)_2$ proved to be somewhat more difficult due to the fact that some of the samples that were analyzed were mixtures of the cis and trans isomers. The ^{31}P CP/MAS NMR spectrum of a sample of $PdCl_2(PPh_2Me)_2$ was reported in 1987 by Nelson et al. to consist of a single resonance at 17.2 ppm [68]. Unfortunately, the geometry of the complex was not recognized at the time and was erroneously assigned to the cis isomer. This misassignment was, however, corrected in 1989 [65]. Nelson et al. recorded the ^{31}P CP/MAS NMR spectrum of a mixture of *cis*- and *trans*-[$PdCl_2(PPh_2Me)_2$] and found that the ^{31}P solid state NMR spectrum of the cis isomer in fact consisted of two signals at 26.3 and 28.9 ppm. These results agree with the fact that *cis*-[$PdCl_2(PPh_2Me)_2$] crystallizes in the orthorhombic space group $P2_12_12_1$ with $Z=4$ [69], i.e. the two signals observed in the ^{31}P solid state NMR spectrum correspond to the two phosphorus atoms present in the asymmetric unit. The case of $PdCl_2(PPhMe_2)_2$ is of particular interest. The ^{31}P CP/MAS NMR spectrum of a sample of $PdCl_2(PPhMe_2)_2$ was reported in 1987 to consist of two signals at 14.2 and 25.8 ppm [68]. The two signals were attributed to the presence of both cis and trans isomers. In 1989, the ^{31}P CP/MAS NMR spectrum of a second sample of $PdCl_2(PPhMe_2)_2$ was reported to consist of two signals at 4.8 and 16.1 ppm [65]. In this case, however, the two signals were attributed to the presence of a single isomer, i.e. the cis isomer. This interpretation is most likely incorrect since, based on the X-ray crystal structure reported for *cis*-[$PdCl_2(PPhMe_2)_2$], i.e. $P4_2/n$ with $Z=4$ [70], only one phosphorus atom of the two present in the molecule is crystallographically unique. Consequently, the ^{31}P CP/

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* Note that a discrepancy exists concerning the solid state ^{31}P isotropic shift of *trans*-[$PdCl_2(Ph_2PCH_2CH_2Si(OEt)_3)_2$]. In ref. 33, the solid state ^{31}P isotropic shift of this complex was reported to be 40.2 ppm with respect to 85% H_3PO_4 versus 21.1 ppm with respect to the same reference in ref. 38. Both samples were prepared by reaction of $PdCl_2(NCPh)_2$ with $Ph_2PCH_2CH_2Si(OEt)_3$. The only difference appears to be in the solvents used to perform the synthesis and to isolate the product: in ref. 33, the reaction was performed using benzene as a solvent and the compound was isolated from hexane, whereas in ref. 38, the reaction was performed in CH_2Cl_2 and the product precipitated upon addition of ethanol. As to whether or not this difference is sufficient to explain the observed discrepancy remains to be determined, however, it has been reported in the literature that samples of $PdCl_2(PPhMe_2)_2$ isolated from a CH_2Cl_2/CH_3OH mixture had the cis geometry, whereas isolation from hot benzene by addition of 100–120°C petroleum ether produced the trans isomer as a solid (see ref. 65).

MAS NMR spectrum of the cis isomer of $PdCl_2(PPhMe_2)_2$ should show only one resonance. Moreover, for *cis*-$[PdX_2L_2]$ complexes, the separation between the two resonances typically does not exceed 3 ppm (vide infra). Observation of two signals in fact suggests that the sample may have contained a mixture of the cis and trans isomers and that, based upon the ^{13}C solid state NMR data obtained for this sample (three methyl resonances in a 1:1:2 intensity ratio were observed), the relative amount of each isomer was approximately 50%. No mention of $^{13}C-^{31}P$ coupling in the ^{13}C solid state NMR spectrum of $PdCl_2(PPhMe_2)_2$ was made. This analysis still does not explain why the peak positions reported in 1987 by Nelson et al. are so different from those reported in 1989 unless one considers the possibility that the samples may have been different due, for example, to the presence of different polymorphs or because of the presence of solvates or impurities (e.g. phosphine oxide). It is noteworthy, however, that this lack of reproducibility in the results was also observed in the solution ^{31}P NMR data: the chemical shift value of *cis*-$[PdCl_2(PPhMe_2)_2]$ was reported to be 6.6 ppm in 1987 and 5.0 ppm in 1989. It would be incorrect to believe that *trans*-palladium(II)–phosphine complexes always give rise to ^{31}P solid state NMR spectra consisting of a single resonance with no $^{31}P-^{31}P$ spin–spin coupling. Two complexes, namely *trans*-$[Pd(CN)_2(PPh_2Me)_2]$ and *trans*-$[Pd(CN)_2(PPhMe_2)_2]$, were reported by Nelson and co-workers to give rise to AB-type spectra ($^2J(^{31}P, ^{31}P)_{trans} \approx 420$ Hz) [65]. Observation of $^{31}P-^{31}P$ spin–spin coupling in the ^{31}P CP/MAS NMR spectra of these complexes requires that the two phosphorus atoms present in each molecule be crystallographically inequivalent. However, confirmation of these conclusions is not possible since no X-ray data have yet been published on these compounds. A large number of *cis*-$[PdX_2L_2]$ complexes were found to give rise to ^{31}P CP/MAS NMR spectra consisting of two closely spaced resonances, typically separated by less than 3 ppm, with no observable $^{31}P-^{31}P$ spin–spin coupling. (The absence of observable $^{31}P-^{31}P$ spin–spin coupling in the ^{31}P solid state NMR spectra of *cis*-$[MX_2L_2]$ complexes can be rationalized since $^2J(^{31}P, ^{31}P)_{cis}$ may be small compared with the solid state linewidth. See ref. 4.) This pattern has been encountered in the ^{31}P CP/MAS NMR spectra of *cis*-$[PdCl_2(DMPP)_2]$ where DMPP = 1-phenyl-3,4-dimethylphosphole [68], *cis*-$[PdX_2(PPh_2Me)_2]$ complexes where X = Cl, Br, N_3 [65], and *cis*-$[PdX_2(PPhMe_2)_2]$ complexes where X = Br, N_3 [65]. The only *cis*-palladium(II)–phosphine complex so far analyzed that should not follow this pattern is *cis*-$[PdCl_2(PPhMe_2)_2]$ since, in this compound, only one phosphorus atom is crystallographically unique. However, for reasons previously described, confirmation of this analysis cannot be obtained from the data available in the literature. Observation of two closely spaced resonances with no observable $^{31}P-^{31}P$ spin–spin coupling in the ^{31}P CP/MAS NMR spectra of most *cis*-$[PdX_2L_2]$ complexes suggests that the asymmetric unit contains two independent phosphorus nuclei that may or may not belong to the same molecule. These conclusions could be confirmed only in the case of *cis*-$[PdCl_2(DMPP)_2]$ for which structural investigations via single crystal X-ray diffraction techniques indicated that the complex crystallizes in the non-centrosymmetric space group Cc with $Z=4$ [71]. (Note that a space group ambiguity exists between Cc and C2/c and that, in this case, C2/c would disagree with the solid state ^{31}P NMR results.) ^{31}P solid state NMR studies of palladium(II) complexes with bidentate phosphine ligands have also been reported. Fyfe and co-workers have recorded the ^{31}P CP/MAS NMR spectrum of $Pd(CN)_2(dppe)$ [33]. Komoroski et al. [38] have obtained ^{31}P solid state NMR data for $PdCl_2(dppm)$, $PdCl_2(dppe)$, and $PdCl_2(dppp)$ (dppp = 1,3-bis(diphenylphosphino)propane). The ^{31}P NMR spectra of $Pd(CN)_2(dppe)$, $PdCl_2(dppm)$, and $PdCl_2(dppe)$ were made up of a single resonance, whereas that of $PdCl_2(dppp)$ consisted of two signals. No conclusion can be drawn about the NMR results obtained for $Pd(CN)_2(dppe)$ since the X-ray crystal structure of this compound is not known. However, the X-ray crystal structures of the other three complexes have been reported*. The X-ray data indicate that the ^{31}P CP/MAS NMR spectrum of each of these complexes should consist of two signals. As one can see, these expectations are verified only for $PdCl_2(dppp)$ (in this case a separation of 12.1 ppm is observed between the signals). Inspection of the various bond lengths and angles does not reveal any obvious reason as to why the ^{31}P CP/MAS NMR spectra of $PdCl_2(dppm)$ and $PdCl_2(dppe)$ should be so different from that of $PdCl_2(dppp)$, and as to why the chemical shift difference between the ^{31}P resonances in the NMR spectrum of $PdCl_2(dppp)$ is so large. However, one possible explanation may be that the change in the ring size has a much greater effect on the individual shift tensor components in the case of $PdCl_2(dppp)$ than it does in the other two cases. A single-crystal ^{31}P NMR investigation of these compounds would certainly prove most helpful in understanding these results. Lastly, in addition to the work done on molecular complexes of palladium, several groups have used ^{31}P solid state NMR spectroscopy to characterize palladium(II) complexes immobilized on inorganic supports such as high-surface-area glass beads [33], silica gel [33,38], and phosphinated montmorillonite [50].

A large number of platinum complexes have been analyzed by ^{31}P solid state NMR spectroscopy. Surprisingly, only one platinum(0)–phosphine complex, (mesityl-(diphenylmethylene)phosphine)bis(triphenylphosphine)platinum(0), has so far been the subject of such studies. The X-ray crystal structure of $Pt(PPh_3)_2(P(mesityl){=}CPh_2)$ was solved some time ago by Bickelhaupt and co-workers who showed that the phosphaalkene ligand was η^1-coordinated to platinum via the phosphorus atom [73]. However, the X-ray results were found to disagree with the results obtained from low-temperature solution ^{31}P NMR measurements which indicated η^2-coordination for this complex. η^2-Coordination was suggested by the non-equivalence of the triphenylphosphine resonances, the upfield shift of the ^{31}P resonance corresponding to the phosphaalkene ligand, and the weak coupling (approximately 500 Hz)

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* $PdCl_2(dppm)$: monoclinic space group $P2_1/n$ with $Z=4$; $PdCl_2(dppe)\cdot CH_2Cl_2$: monoclinic space group $P2_1/c$ with $Z=4$; $PdCl_2(dppp)$: triclinic space group $P\bar{1}$ with $Z=2$ (see ref. 72).

between the phosphaalkene phosphorus and platinum [73]. This discrepancy was resolved using ^{31}P solid state NMR spectroscopy. The ^{31}P solid state NMR spectrum of this complex has been obtained by two research teams [74.75] and has been further discussed by Mann in his review on recent developments in NMR spectroscopy of organometallic compounds [76]. The spectrum consists of three sets of multiplets; two sets of signals are centered at 40.5 and 49.8 ppm and these correspond to the triphenylphosphine ligands, and one is centered at 247 ppm, instead of -30.9 ppm in solution, which corresponds to the phosphaalkene moiety. In this case, however, the coupling constant between the phosphaalkene phosphorus and platinum was found to be 4720 Hz, confirming the presence of a η^1-bonded species in the solid state. The majority of the ^{31}P solid state NMR studies on platinum complexes have been performed on platinum(II) compounds. Fyfe and co-workers have reported ^{31}P CP/MAS NMR data for several platinum(II) complexes containing a single phosphine ligand. These workers have obtained the ^{31}P solid state NMR spectra of four carbonyl complexes, *cis*-[$PtCl_2(CO)(PR_3)$] where $PR_3 = P(p\text{-}CH_3C_6H_4)_3$, $P(p\text{-}FC_6H_4)_3$, $P(c\text{-}C_6H_{11})_3$, and P^nBu_3 [33], and two pyridine complexes, namely *cis*- and *trans*-[$PtCl_2(PPh_3)$(pyridine)] [48]. The ^{31}P NMR spectra of each of these complexes displayed a single resonance flanked by satellites due to ^{195}Pt–^{31}P coupling, with values for the isotropic shifts and coupling constants in good agreement with those found in solution. Unfortunately, none of the complexes listed above was characterized via single-crystal X-ray diffraction techniques, but structural investigations of related compounds, i.e. *cis*-[$PtCl_2(CO)(PPh_3)$] (which crystallizes in the triclinic space group $P\bar{1}$ with $Z=2$ [77]), *cis*-[$PtCl_2(CO)(PEt_3)$] (which crystallizes in the orthorhombic space group $Pca2_1$ with $Z=4$ [78]), and *trans*-[$PtCl_2(PEt_3)$(pyrrolidine)] (which crystallizes in the monoclinic space group $P2_1/c$ with $Z=4$ [79]), indicated that, in each case, the asymmetric unit contained a single molecule. Similar to *trans*-[PdX_2L_2] complexes, a large number of *trans*-[PtX_2L_2] compounds show ^{31}P solid state NMR spectra consisting of a single resonance with no observable ^{31}P–^{31}P spin–spin coupling. The only difference is that, in this case, ^{195}Pt–^{31}P coupling, approximately 2500 Hz, is also observed (note that similar observations concerning the ^{31}P solid state NMR spectra of *trans*-[PtX_2L_2] complexes have been made by Clark and Hampden-Smith [80]). This pattern was observed in the ^{31}P solid state NMR spectra of *trans*-[$PtCl_2(P^iPr_3)_2$] [33,81], *trans*-[$PtCl_2(Ph_2PCH_2CH_2Si(OEt)_3)_2$] [33], *trans*-[$PtX_2(PR_3)_2$] complexes where X = I, CN and $PR_3 = PPh_2Me$, $PPhMe_2$ [65], *trans*-[$PtCl_2(PCy_3)_2$] [81], and several other *trans*-[PtX_2L_2] complexes [81]. If the possibility of having isochronous signals is excluded, these results indicate that the phosphorus atoms in each molecule are crystallographically equivalent as a result of the molecules occupying special positions. Structural investigations of *trans*-[$PtCl_2(P^iPr_3)_2$] [82] and *trans*-[$PtCl_2(PCy_3)_2$] [83] via single-crystal X-ray diffraction techniques confirmed these conclusions, i.e. in both cases the molecules lie on centers of inversion. Furthermore, in the case of *trans*-[$PtCl_2(PCy_3)_2$], the X-ray diffraction data rule out the possibility suggested in ref. 81 that the molecule may be conformationally mobile in the solid state. Observation of a single central resonance in the ^{31}P solid state NMR spectra of *trans*-[PtX_2L_2] complexes is most common; however, $^{31}P-^{31}P$ spin–spin coupling has sometimes been observed as in the case of *trans*-[$PtI_2(P^nBu_3)_2$] where $^2J(^{31}P, ^{31}P)_{trans} = 440$ Hz [81]. These results suggest that, in the solid state, the two phosphine ligands are not crystallographically equivalent and that the molecule does not lie on a center of inversion. Unfortunately, the X-ray crystal structure of this complex has not yet been reported. Another situation that may lead to observation of $^{31}P-^{31}P$ spin–spin coupling in the ^{31}P solid state NMR spectra of *trans*-[PtX_2L_2] complexes is the one where the molecule no longer possesses C_{2h} symmetry, i.e. in solution, the molecule no longer has a center of inversion. This situation is encountered when the phosphine ligands or the X groups are different. Clark and Hampden-Smith [80] have obtained the solid state ^{31}P NMR spectra of *trans*-[$PtH(SnPh_3)(PCy_3)_2$] and *trans*-[$PtCl(SiCl_2Ph)(PCy_3)_2$] and found that the central portions in both spectra were AB patterns. These results are in accord with the reported X-ray crystal structures, i.e. $P2_1$ with $Z = 2$ for *trans*-[$PtH(SnPh_3)(PCy_3)_2$] [84] and $P\bar{1}$ with $Z = 2$ for *trans*-[$PtCl(SiCl_2Ph)(PCy_3)_2$] [85]. A few *trans*-[PtX_2L_2] complexes have also been found to show ^{31}P solid state NMR spectra that did not follow either one of the patterns described above. The ^{31}P CP/MAS NMR spectrum of *trans*-[$PtCl_2(PPh_3)_2$] was reported to consist of two signals at 19.0 and 20.9 ppm with no apparent $^{31}P-^{31}P$ coupling [33]. Inspection of the data obtained by Fyfe and co-workers (see Fig. 5) indicates that, if present, such coupling could have been easily missed due to the large linewidths of the signals and the presence of appreciable amounts of the cis isomer. Several causes may be suggested that could account for the presence of two signals, e.g. polymorphism, solvation, crystallographic disorder, however, the fact that the signals have approximately equal intensities could also mean that a crystallographic superstructure is present or that the compound crystallizes with two half-molecules in the asymmetric unit. Nelson and co-workers [81] have reported the observation of multiple signals in the ^{31}P CP/MAS NMR spectra of *trans*-[$PtCl_2(P^nPr_3)_2$], *trans*-[$PtBr_2(P^nBu_3)_2$], *trans*-[$PtCl_2\{P(benzyl)_3\}_2$], and *trans*-[$PtBr_2\{P(benzyl)_3\}_2$]. Specifically, five signals were observed in the resolution-enhanced ^{31}P NMR spectrum of *trans*-[$PtCl_2(P^nPr_3)_2$], three in the ^{31}P NMR spectrum of *trans*-[$PtBr_2(P^nBu_3)_2$], and two in the other two cases. In the cases where two signals were observed, any one of the causes suggested above is possible, especially since the intensities of the signals are not known; however, in the case of *trans*-[$PtCl_2(P^nPr_3)_2$] and *trans*-[$PtBr_2(P^nBu_3)_2$], polymorphism, solvation, and crystallographic disorder are most likely responsible for the observation of several signals given the complexity of the spectra. As already observed in the case of *cis*-[PdX_2L_2] complexes, most *cis*-[PtX_2L_2] compounds also show ^{31}P solid state NMR spectra consisting of two closely spaced resonances with no observable $^{31}P-^{31}P$ spin–spin coupling. Among the *cis*-platinum(II)–phosphine complexes that were reported to follow this pattern are found *cis*-[$PtCl_2(PPh_3)_2$] [33,81,87], *cis*-[$PtCl_2(PEt_3)_2$]

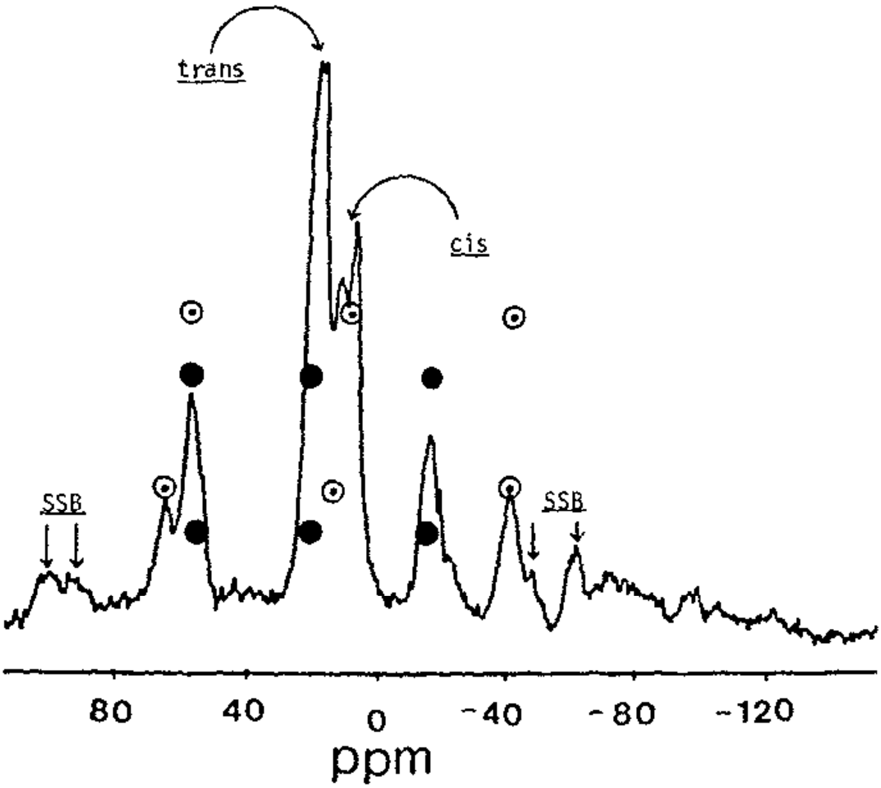

Fig. 5. CP/MAS ^{31}P NMR spectrum of *cis*-[$PtCl_2(PPh_3)_2$] (minor) plus *trans*-[$PtCl_2(PPh_3)_2$] (major) obtained by Fyfe et al. [86].

[33,81], *cis*-[$PtX_2(PPh_2Me)_2$] complexes where $X = Cl$, I, N_3 [33,65,68,88], *cis*-[$PtX_2(PPhMe_2)_2$] complexes where $X = Cl$, Br [65], *cis*-[$PtMe_2(PPh_3)_2$] [33], *cis*-[$PtCl_2(PPh_2C_6H_4CH{=}CH_2)_2$] [47,48,89], *cis*-[$PtCl_2\{PPh(CH{=}CH_2)_2\}_2$] [68,81], *cis*-[$PtCl_2(DMPP)_2$] [68], and several other *cis*-[PtX_2L_2] complexes [81]. Observation of two closely spaced resonances with no ^{31}P–^{31}P spin–spin coupling requires that the asymmetric unit of each one of these complexes contain two crystallographically inequivalent phosphorus atoms that may or may not belong to the same molecule. In the case of the acetone solvate of *cis*-[$PtCl_2(PPh_3)_2$] (*cis*-[$PtCl_2(PPh_3)_2$]·acetone crystallizes in the monoclinic space group $P2_1/c$ with $Z = 4$ [90]), *cis*-[$PtCl_2(PEt_3)_2$] (which crystallizes in the monoclinic space group $P2_1/n$ with $Z = 4$ [91]), *cis*-[$PtCl_2(PPh_2Me)_2$]*, *cis*-[$PtCl_2(PPhMe_2)_2$] (which crystallizes in the triclinic space group $P\bar{1}$ with $Z = 2$ [93]), *cis*-[$PtCl_2\{PPh(CH{=}CH_2)_2\}_2$] (which

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* The X-ray crystal structures of two modifications of *cis*-[$PtCl_2(PPh_2Me)_2$] have been reported, an orthorhombic one that crystallizes in the non-centrosymmetric space group $P2_12_12_1$ with $Z = 4$, and a monoclinic one that crystallizes in the centrosymmetric space group $P2_1/c$ with $Z = 4$ [92].

crystallizes in the triclinic space group P$\bar{1}$ with $Z=2$ [94]), and *cis*-[$PtCl_2(DMPP)_2$] (which crystallizes in the monoclinic space group $P2_1/c$ with $Z=4$ [94]), these conclusions were found to agree with the structural data obtained from single crystal X-ray diffraction studies. Nonetheless, some of the ^{31}P solid state NMR results require further discussion. The ^{31}P CP/MAS NMR data for *cis*-[$PtCl_2(PPh_3)_2$] reported by Fyfe and co-workers [33], i.e. $\delta=8.6$ and 12.9 ppm with $^1J(^{195}Pt, ^{31}P)=$ 3623 and 3877 Hz, were confirmed by Allman [87] who found $\delta=7.8$ and 12.6 ppm with $^1J(^{195}Pt, ^{31}P)=3580$ and 3750 Hz. Those reported by Nelson and co-workers [81], however, were significantly different from those described above, i.e. $\delta=-4.1$ and 7.9 ppm with $^1J(^{195}Pt, ^{31}P)=3421$ and 3625 Hz. It was suggested by Nelson and his colleagues [81] that this differrence in the NMR results may be due to "environmental effects" given that the sample analyzed by Fyfe and co-workers was a mixture of the cis and trans isomers, but this suggestion is most likely incorrect (note that the solution $^{31}P\{^1H\}$ NMR data of the sample analyzed in ref. 81, i.e. $\delta=-7.8$ ppm and $^1J(^{195}Pt, ^{31}P)=3551$ Hz, are incorrectly reported and that the correct solution $^{31}P\{^1H\}$ NMR data for *cis*-[$PtCl_2(PPh_3)_2$] are those indicated in ref. 33, i.e. $\delta=$ 14.3 ppm and $^1J(^{195}Pt, ^{31}P)=3673$ Hz). The ^{31}P CP/MAS NMR spectrum of *cis*-[$PtCl_2(PEt_3)_2$] was reported to consist of a single resonance in ref. 33 and two closely spaced resonances in ref. 81, the latter results being in accord with the reported X-ray crystal structure for this complex. This discrepancy in the ^{31}P solid state NMR results is most likely due to the fact that a lower field strength was employed in the first study and perhaps also because a larger line-broadening factor was used to process the data. The case of *cis*-[$PtCl_2(PPh_2Me)_2$] is most puzzling. Fyfe and co-workers [33] reported that the ^{31}P CP/MAS NMR spectrum of *cis*-[$PtCl_2(PPh_2Me)_2$] consisted of two signals at -2.1 and 1.6 ppm with $^1J(^{195}Pt, ^{31}P)$ coupling constants of 3466 and 3759 Hz. The solid state ^{31}P NMR data for *cis*-[$PtCl_2(PPh_2Me)_2$] reported by Nelson et al. in 1987 [68] were $\delta=13.8$ and 16.3 ppm with $^1J(^{195}Pt, ^{31}P)=3662$ and 3648 Hz, whereas those published in 1989 by the same group [65] were $\delta=7.7$ and 10.2 ppm with $^1J(^{195}Pt, ^{31}P)=3682$ and 3828 Hz. It is not clear at the moment as to why such large differences exist in the solid state ^{31}P NMR data of this complex especially since similar solution ^{31}P NMR spectra were obtained for all three samples. It is noteworthy, however, that, since *cis*-[$PtCl_2(PPh_2Me)_2$] crystallizes in two different polymorphic forms, slight differences in the solid state ^{31}P NMR results might be expected, depending upon the modification being analyzed, but the differences observed here are on the same order of magnitude as those observed when the nature of the phosphine ligand is changed. Note that not only symmetrically substituted *cis*-[PtX_2L_2] complexes have been found to give rise to ^{31}P solid state NMR spectra consisting of two signals with equal intensities but also unsymmetrically substituted complexes such as [PtClMe(dppe)] [33] and *cis*-[$PtCl(PPh_3)_2$(pyridine)]ClO_4 [48]. However in this case, the two resonances are further apart, e.g. 37.5 and 45.6 ppm for [PtClMe(dppe)] and 6.4 and 15.6 ppm for *cis*-[$PtCl(PPh_3)_2$(pyridine)]ClO_4. These observations are reasonable in view of the fact that in these complexes the phosphine ligands are both crystallographically and chemically different. A few *cis*-platinum(II)–phosphine complexes have also been encountered for which the solid state ^{31}P NMR spectra did not consist of two resonances with equal intensities. Thus, the ^{31}P solid state NMR spectra of *cis*-$[PtBr_2(PPh_2Me)_2]$ [65], *cis*-$[PtX_2(PPhMe_2)_2]$ complexes where X = I, N_3 [65], *cis*-$[PtCl_2(PMe_3)_2]$ [81], *cis*-$[PtCl_2\{P(benzyl)_3\}_2]$ [81], *cis*-$[PtBr_2\{PPh_2(CH{=}CH_2)\}_2]$ [81], and *cis*-$[PtI_2(DMPP)_2]$ [81] were found to consist of a single central resonance. Two explanations are possible to account for the observation of a single central resonance in the ^{31}P solid state NMR spectra of these complexes: one possibility is that only one phosphorus atom is present in the asymmetric unit. Another possible explanation is that the phosphorus nuclei have accidentally isochronous signals. Among the several complexes listed above, only *cis*-$[PtCl_2(PMe_3)_2]$ has been structurally characterized via single-crystal X-ray diffraction techniques. The crystal structure of this complex was successfully refined in the non-standard and non-centrosymmetric space group $B2_1$ with $Z = 4$ ($R = 0.024$ and $R_w = 0.025$) [95,96]. For *cis*-$[PtCl_2(PMe_3)_2]$, the X-ray data therefore rule out the first possibility mentioned above as being the reason for the isochronism of the signals since two phosphorus atoms are present in the asymmetric unit. Also, the data disagree with the suggestion made in ref. 81 that the presence of low-energy molecular librations renders the two phosphorus nuclei equivalent on the NMR time scale since the thermal parameters of all the non-hydrogen atoms showed no unusual features. Single-crystal ^{31}P NMR studies of this compound would certainly shine some light on the MAS results. Low-energy librations were also suggested to be responsible for the single broad resonance observed in the ^{31}P CP/MAS NMR spectrum of *cis*-$[PtBr_2\{PPh_2(CH{=}CH_2)\}_2]$. As to whether or not this suggestion is correct cannot be determined since the X-ray crystal structure of this complex has not yet been reported, however, the 430 Hz linewidth could also easily be accounted for by simply considering the possibility of having two overlapping resonances. As far as *cis*-$[PtBr_2(PPh_2Me)_2]$, *cis*-$[Pt(N_3)_2(PPhMe_2)_2]$, and *cis*-$[PtCl_2\{P(benzyl)_3\}_2]$ are concerned, the presence of a central ^{31}P resonance most likely results from the two expected signals being isochronous. The ^{13}C CP/MAS NMR spectra of these complexes showed two methyl signals in the case of *cis*-$[PtBr_2(PPh_2Me)_2]$, three methyl signals in the case of *cis*-$[Pt(N_3)_2(PPhMe_2)_2]$, and five methylene signals in the case of *cis*-$[PtCl_2\{P(benzyl)_3\}_2]$. Interpretation of these data is problematic since both inequivalence and ^{13}C–^{31}P coupling will contribute to the number of signals observed. However, in the absence of observable ^{13}C–^{31}P coupling, the ^{13}C solid state NMR results are consistent with the presence of one entire molecule in the asymmetric unit of these compounds. Isochronism of the signals is also probably responsible for the observation of a single central ^{31}P resonance in the case of *cis*-$[PtI_2(DMPP)_2]$, however, in this case, it is not clear as to why the ^{13}C CP/MAS NMR spectrum of this material shows five methyl signals and five signals for C_β. Concerning *cis*-$[PtI_2(PPhMe_2)_2]$, the single central ^{31}P resonance probably originates from only half a molecule being present in the asymmetric unit since the ^{13}C CP/MAS NMR spectrum of a mixture of the cis and trans isomers of this material only showed three signals (a maximum of four resonances should be observed if this analysis is correct). A suitable test compound for which it would be worth obtaining both ^{31}P and ^{13}C solid state NMR spectra is *cis*-$[PtCl_2\{PPh(benzyl)_2\}_2]$ since this complex is known to have crystallographic two-fold symmetry (space group C2/c with $Z=4$) [97]. Several *cis*-platinum(II)–phosphine complexes have also been encountered for which the ^{31}P solid state NMR spectra showed more than two central resonances. Fyfe and co-workers [33,88] reported some time ago that the ^{31}P CP/MAS NMR spectrum of *cis*-$[PtCl_2(Ph_2PCH_2CH_2Si\{OEt\}_3)_2]$ consisted of three central components, each of these exhibiting scalar coupling to ^{195}Pt characteristic of the cis isomer. At first glance the reported spectrum looks as if the sample contained two polymorphs, one responsible for the close lines at 12.9 and 15.3 ppm and one responsible for the broad absorption at 4.8 ppm, in about equal amounts since the intensities of the two sets of signals are approximately the same. However, these workers did a series of ^{31}P CP/MAS NMR experiments where the recycle delay time was varied from 0.5 to 20 s and found that no relative intensity enhancement of any of the central resonances was observed, indicating that the presence of different crystalline polymorphs was unlikely. Provided the results from this experiment are reliable, the only explanation that is left is that two molecules are present in the asymmetric unit of this compound and in one of them the principal elements of the ^{31}P chemical shift tensors are such that their averages are almost the same. Here again, single-crystal ^{31}P NMR investigations would prove most helpful in the elucidation of this problem. More recently, Nelson and co-workers [81] reported the observation of three signals in the ^{31}P solid state NMR spectra of *cis*-$[PtCl_2\{PPh_2(benzyl)\}_2]$ and *cis*-$[PtCl_2\{PPh_2(CH{=}CH_2)\}_2]$, four in that of *cis*-$[PtI_2\{PPh_2(CH{=}CH_2)\}_2]$, six in that of *cis*-$[PtI_2\{PPh(CH{=}CH_2)_2\}_2]$, and at least eight resonances in that of *cis*-$[PtBr_2\{PPh(CH_2CH_2CN)_2\}_2]$. In the cases where three or four resonances were observed, many explanations are possible including the presence of two molecules in the asymmetric unit. However, the complexity of the last two spectra is suggestive of the presence of several polymorphs, solvates, and/or problems due to disordered structures. Lastly, Fyfe and co-workers have demonstrated the usefulness of ^{31}P solid state NMR spectroscopy in the characterization of heterogenized platinum(II)–phosphine complexes resulting from the immobilization of soluble platinum(II) compounds on silica gel and glass beads [33,88], phosphinated polystyrenes [47–49,89], and poly(4-vinylpyridine) [47,48]. Some aspects of this work have also been described in a review article [89].

(iv) Complexes of the Group 11 metals

Group 11 metal complexes were among the first complexes that were investigated via ^{31}P solid state NMR spectroscopy. Veeman and co-workers have reported the ^{31}P CP/MAS NMR spectra of two copper(I)–phosphine complexes, namely $(Ph_3P)_2CuNO_3$ and $(Ph_3P)_3CuCl$ [54]. The ^{31}P CP/MAS NMR spectrum of $(Ph_3P)_2CuNO_3$ consists of an asymmetric quartet with lines at +26.0, +13.1, −7.0, and −31.1 ppm, the outer signals being accompanied by satellite peaks due to coupling to the second isotope of copper, i.e. ^{65}Cu (natural abundance = 30.91%). The four main signals correspond to the two crystallographically equivalent triphenylphosphine ligands*.The splitting of the single expected resonance into four signals arises from combined scalar and dipolar coupling of the ^{31}P nuclear spin ($I = 1/2$) with the ^{63}Cu nuclear spin ($I = 3/2$) as evidenced by the fact that the distances between the lines (expressed in ppm) are different for spectra measured at various fields. The asymmetry of the quartet originates from the fact that the Cu quadrupole interaction is not small compared with the Cu Zeeman interaction, thus resulting in the axis of quantization of Cu being tipped away from the applied magnetic field B_0. Observation of a large Cu quadrupole interaction is, in fact, not too surprising owing to the low symmetry of this complex in the solid state, i.e. C_{2v}. The splitting of the signals observed in the ^{31}P CP/MAS NMR spectrum of $(Ph_3P)_2CuNO_3$ has furthermore been the subject of two theoretical analyses by Menger and Veeman [99], and by Olivieri [100], a value for the scalar coupling constant of 1450 Hz being obtained in the former study. The ^{31}P CP/MAS NMR spectrum of $(Ph_3P)_3CuCl$ displays two sets of quartets in a 1:2 intensity ratio. These results are in agreement with the reported X-ray crystal structure of this compound, i.e. P3 with $Z = 3$ [101], assuming that two out of the three expected quartets are isochronous. In this case, however, the splittings within each quartet were found to be quite similar, between 900 and 940 Hz. These observations indicate a smaller Cu quadrupole interaction compared with $(Ph_3P)_2CuNO_3$, which is reasonable in view of the higher local symmetry (C_{3v}) around Cu in $(Ph_3P)_3CuCl$. Healy and co-workers have extended the work done by Veeman et al. to other copper(I)–phosphine complexes with various phosphine/copper ratios and, for a given phosphine/copper ratio, different geometries. The complexes that were investigated include the tetrameric "cubane" and "step" clusters $[CuXPPh_3]_4$ where X = Cl, Br, I [102,103], the mononuclear 2:1 adducts of triphenylphosphine with copper(I) halides $[Cu(PPh_3)_2X]$ where X = Cl, Br, I, BH_4, NO_3 [104], the mononuclear 2:1 adducts of diphenyl-*o*-tolylphosphine with copper(I) halides $(PPh_2\text{-}o\text{-tol})_2CuX$ where X = Cl, Br, I [105], the mononuclear 3:1 adducts of triphenylphosphine with copper(I) halides $[Cu(PPh_3)_3X]$ where X = Cl, Br, I [106], the 1:1 monomeric adducts (tris(2,4,6-trimethoxyphenyl)phosphine)copper(I)chloride and bromide [107], and the halogenocuprate(I) complexes $[PPh_3Me][(Ph_3P)CuBr_2]$, $[PPh_3Me][(Ph_3P)_2CuI_2]$, $[PPh_3Me][(Ph_3P)CuI_3Cu(PPh_3)]$ [108,109]. The ^{31}P CP/MAS NMR spectra of these complexes were all quite similar, i.e. they consisted of asymmetric quartets resulting from combined scalar and dipolar coupling between

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* The X-ray crystal structure of $(Ph_3P)_2CuNO_3$ was solved in the monoclinic space group I2/a, a non-standard setting of C2/c, with four molecules per unit cell [98].

^{31}P and ^{63}Cu with distances $\Delta\nu$ between the lines, typically between 1000 and 2000 Hz, increasing on going from the low-field end of the spectrum to the high-field end. In some cases, several quartets were observed due to the presence of more than one crystallographically unique phosphorus in the asymmetric unit, but a few examples have also been encountered for which crystallographically inequivalent phosphorus nuclei had isochronous signals. The only complex that showed a ^{31}P CP/MAS NMR spectrum that was significantly different from the others is $[PPh_3Me][(Ph_3P)CuI_3Cu(PPh_3)]$ [109] for which the outermost components of the quartet were almost unresolved. It was suggested that the shorter Cu···Cu distance in this complex may have something to do with the unexpected form of the spectrum, but no evidence of a relationship between these two observations has yet been obtained. These workers have also employed ^{31}P solid state NMR spectroscopy in their investigations of mixed-ligand copper(I) complexes. They reported some time ago the preparation of mixed-ligand copper(I) complexes of triphenylphosphine and acetonitrile, $[(Ph_3P)_x(CH_3CN)_{4-x}Cu]ClO_4$ where $x = 2$, 3, 4, via reaction of $[(CH_3CN)_4Cu]ClO_4$ with appropriate amounts of triphenylphosphine, along with the characterization of these complexes via single-crystal X-ray diffraction techniques and ^{31}P CP/MAS NMR spectroscopy [110,111]. Recently, they focused their attention on mixed-ligand complexes of triphenylphosphine and 2,2′-bipyridine (bpy) with copper(I) halides, $[(PPh_3)(bpy)CuX]$ where $X = Cl$, Br, I [112,113]. The ^{31}P CP/MAS NMR spectra of the bromide and iodide complexes each displayed a single asymmetric quartet consistent with the presence of one molecule per asymmetric unit [112]. The case of $[(PPh_3)(bpy)CuCl]$, however, proved more interesting in that two types of ^{31}P CP/MAS NMR spectra could be obtained depending upon the sample used to perform the analysis. This apparent discrepancy in the results was resolved [113] and was shown to arise from the existence of two polymorphs of $[(PPh_3)(bpy)CuCl]$, a yellow-colored polymorph having one molecule per asymmetric unit, and an orange-colored one possessing two molecules per asymmetric unit. Only one report seems to have been published so far on the analysis of silver(I)–phosphine complexes via ^{31}P solid state NMR spectroscopy. Healy and co-workers [114] have prepared and analyzed adducts of triphenylphosphine with silver(I) nitrate with various phosphine/silver ratios, i.e. $Ag(PPh_3)_xNO_3$ where $x = 1$–4. The ^{31}P CP/MAS NMR spectra of these complexes each displayed doublets arising from ^{107}Ag–^{31}P and ^{109}Ag–^{31}P spin–spin coupling, and the magnitude of the silver–phosphorus coupling, between 190 and 780 Hz, was found to decrease with increasing coordination number, exactly as observed in solution. The ^{31}P CP/MAS NMR spectrum of $Ag(PPh_3)NO_3$ showed a single doublet consistent with the results from its X-ray crystal structure determination, i.e. $P2_1/c$ with $Z = 4$ [115]. The ^{31}P CP/MAS NMR spectra of $Ag(PPh_3)_2NO_3$, $Ag(PPh_3)_3NO_3$, and $Ag(PPh_3)_4NO_3$ were expected to display more than one doublet owing to the presence of more than one crystallographically unique phosphorus in the asymmetric unit. However, only in the case of $Ag(PPh_3)_2NO_3$ could separate signals for the crystallographically inequivalent phosphorus nuclei in the asymmetric unit be observed. Several reports have been published concerning the analysis of gold–phosphine compounds via ^{31}P solid state NMR spectroscopy. Unlike copper(I)–phosphine complexes, gold–phosphine compounds do not show ^{31}P CP/MAS NMR spectra consisting of asymmetric quartets (although the nuclear spin of gold is also 3/2) but, instead, show fairly broad absorptions, e.g. 300 Hz on a spectrometer operating at 200 MHz for ^{1}H [116]. It has been argued [117] that the lack of observable ^{197}Au–^{31}P spin–spin coupling was due to the large quadrupolar relaxation of ^{197}Au owing to the large quadrupole moment of this nucleus ($Q = 0.58 \times 10^{-28}$ m^2) [118], this argument being substantiated by the fact that it has neither been possible to observe a ^{197}Au NMR spectrum nor to observe coupling between ^{197}Au and other nuclei, even in spherically symmetrical ions such as $[AuF_6]^-$ [119]. Note, however, that if it were observable, ^{197}Au–^{31}P scalar coupling would be small given the low magnetogyric ratio of ^{197}Au (0.357×10^7 radians s^{-1} T^{-1}) compared with that of ^{63}Cu (7.0965×10^7 radians s^{-1} T^{-1}) and, consequently, broadened solid state NMR signals would probably be observed as well. Veeman and co-workers [54] and Mingos and co-workers [116] have employed ^{31}P CP/MAS NMR spectroscopy to characterize gold cluster compounds. In both studies, ^{31}P NMR spectra consisting of several signals were obtained, resulting from the presence of more than one crystallographically unique phosphorus in the asymmetric unit of these compounds. These results may appear somewhat surprising since a large number of these molecules are known to be fluxional in solution, and several are not frozen out at temperatures of −90°C and below [116]. The ^{31}P CP/MAS NMR data therefore indicate that gold cluster compounds are stereochemically rigid at room temperature in the solid state. One exception has, however, been reported: the ^{31}P solid state NMR spectrum of $[Au_{11}(PMe_2Ph)_{10}][BPh_4]_3$ was found to consist of a single resonance. Unfortunately, the X-ray crystal structure of this compound could not be determined due to the presence of a crystallographic disorder [116]. Mononuclear gold(I)–phosphine complexes have also been investigated via ^{31}P solid state NMR spectroscopy. Healy and co-workers [104,120] have reported ^{31}P CP/MAS NMR data for several linear, two-coordinate 1 : 1 adducts of triphenylphosphine with gold(I) salts, $(Ph_3P)AuX$ where $X = NO_3$, CH_3COO, Cl, Br, I, SCN, CN, CH_3. The NMR results proved most interesting but, at the same time, most confusing. The ^{31}P CP/MAS NMR spectra of the nitrate and the methyl compounds each displayed a single broad resonance, in accord with their reported X-ray crystal structures [120,121]. The signal observed in the ^{31}P NMR spectrum of the nitrate compound was, however, for some unidentified reason, significantly broader than that of the methyl compound. The ^{31}P CP/MAS NMR spectra of the triphenylphosphinegold(I) halides each displayed two signals of equal intensity separated by 4–8 ppm (on a 300 MHz instrument) depending upon the halide. These results do not agree with the X-ray crystal structures of these complexes, i.e. the three compounds are isomorphous and crystallize in the orthorhombic space group $P2_12_12_1$ with $Z = 4$ [120,122]. A suggestion has been made to explain this discrepancy in the results that the presence of "two virtually enantiomeric molecules" in the asymmetric unit results in "diastereoisomeric phosphorus environments". This argument would therefore imply that the powders analyzed by ^{31}P CP/MAS NMR spectroscopy are not isostructural with the crystals whose X-ray crystal structures have been solved. X-ray powder diffraction analyses of the samples used in the ^{31}P CP/MAS NMR experiments would have proved most helpful in resolving this discrepancy. Another possibility not mentioned by these workers is that the volumes of the actual unit cells are, in fact, twice the size of the reported ones. Given that, in $P2_12_12_1$, doubling of one of the unit cell axes is not possible, doubling of the unit cell contents would therefore require the correct space group to be $P2_12_12$ instead of $P2_12_12_1$. Even more intriguing is the fact that the acetato, thiocyanato, and cyano complexes, which also crystallize in the orthorhombic space group $P2_12_12_1$ with $Z=4$ [120,123,124], do not show ^{31}P solid state NMR spectra consisting of one "doublet". The ^{31}P solid state NMR spectra of these complexes each displayed a single fairly sharp resonance, in accord with the reported X-ray data. Note that a distinct hump was also present in the ^{31}P CP/MAS NMR spectrum of the thiocyanato complex which was attributed to an impurity. However, it was not specified whether or not this impurity was also observed in the solution ^{31}P NMR spectrum of the sample, thus preventing the assignment of the impurity peak observed in the solid state NMR spectrum to a different compound or to another polymorph of the same material. The same group has also recorded the ^{31}P solid state NMR spectra of the 3:1 and 2:1 adducts of triphenylphosphine with gold(I) chloride [104]. The ^{31}P CP/MAS NMR spectrum of $Au(PPh_3)_3Cl$ was found to consist of a single fairly sharp resonance, these results disagreeing with the reported X-ray crystallographic data for this compound, i.e. $P2_1/n$ with $Z=4$ [125], unless one assumes that the three expected resonances are isochronous. The ^{31}P CP/MAS NMR spectrum of $Au(PPh_3)_2Cl$ displayed a single broad absorption probably resulting from the overlap of several signals. These observations agree with the fact that the compound was found to crystallize in the triclinic space group $P1$ with $Z=2$ [104]. Nelson and co-workers [117] have recorded the ^{31}P CP/MAS NMR spectra of $Au(PPh_3)Cl$ and $Au(PPh_3)_3Cl$, and have confirmed the results obtained by Healy et al. These workers attributed the two signals observed in the ^{31}P CP/MAS NMR spectrum of $Au(PPh_3)Cl$ to "conformational effects". Additionally, Nelson and co-workers [117] have obtained the ^{31}P solid state NMR spectra of several adducts of 1-phenyl-3,4-dimethylphosphole (DMPP) and 1-phenyldibenzophosphole (DBP) with gold(I) halides. The ^{31}P CP/MAS NMR spectrum of (DBP)AuCl displayed two signals of equal intensity in agreement with the reported X-ray crystal structure, i.e. $P\bar{1}$ with $Z=4$ [117]. The ^{31}P CP/MAS NMR spectrum of the bromide analog showed a single broad absorption with $\Delta\nu_{1/2}=855$ Hz, whereas that of the iodide complex showed a broad absorption accompanied by a broad hump in the base of it. The X-ray crystal structures of (DBP)AuBr and (DBP)AuI have not yet been reported. Based on the assumption that the bromide and the iodide complexes are isostructural with (DBP)AuCl, it has been suggested that the broad absorption in the ^{31}P CP/MAS NMR spectrum of (DBP)AuBr was due to the overlap of the two expected resonances, and that the broad resonance and the broad hump observed in the ^{31}P CP/MAS NMR spectrum of (DBP)AuI corresponded to the two crystallographically inequivalent phosphorus nuclei present in the asymmetric unit. Moreover, the large linewidth of the hump present in the ^{31}P CP/MAS NMR spectrum of (DBP)AuI was attributed to a relaxation phenomenon. These conclusions may, however, not be correct: first, the possibility exists that (DBP)AuBr and (DBP)AuI may not be isostructural with (DBP)AuCl given that, for example, $Au(PPh_3)_2Br$ and $Au(PPh_3)_2I$ are not isostructural with $Au(PPh_3)_2Cl$ [104]. Secondly, amorphous materials also typically give rise to broad resonances (e.g. polymers). The ^{31}P solid state NMR spectra of (DMPP)AuX complexes, where X = Cl, Br, I, proved most perplexing. The ^{31}P CP/MAS NMR spectrum of (DMPP)AuCl was found to consist of three resonances, with approximately equal intensities and with peak separations of about 4 ppm, whose chemical shifts were field-independent. These results do not agree with the reported X-ray crystal structure, i.e. C2/c with $Z = 8$ [117]. Unfortunately, no explanation concerning the origin of these anomalies was given. The ^{31}P CP/MAS NMR spectrum of (DMPP)AuBr showed a striking resemblance to that of $(Ph_3P)AuCl$, i.e. it consisted of two signals of equal intensity separated by 8.3 ppm (8.1 ppm in the case of $(Ph_3P)AuCl$). The ^{31}P CP/MAS NMR spectrum of the iodide complex was different from that of the other two halides in that it was made up of a single broad resonance. As to why the ^{31}P solid state NMR spectra of (DMPP)AuBr and (DMPP)AuI are so different from that of (DMPP)AuCl, this cannot be determined since the X-ray crystal structures of the former two complexes have not yet been solved. The ^{31}P solid state NMR spectra of $(DBP)_3AuX$ complexes, where X = Cl, Br, I, have also been recorded. The ^{31}P CP/MAS NMR spectrum of the chloride complex was found to consist of two signals in a 2:1 intensity ratio, in accord with the reported X-ray crystal structure, i.e. $P\bar{1}$ with $Z = 2$ [117]. To explain the dichotomy between the ^{31}P CP/MAS NMR spectrum of $(Ph_3P)_3AuCl$, which consists of a single resonance (vide supra), and that of $(DBP)_3AuCl$, made up of two lines in a 2:1 intensity ratio, it was suggested that "in $(Ph_3P)_3AuCl$ the three Ph_3P ligands can attain similar environments by way of low-energy libration* of the phenyl groups whereas, in $(DBP)_3AuCl$, two of the DBP ligands are held in a parallel arrangement, and thus mirror symmetry is perceived in the solid state NMR experiment". It is noteworthy, however, that low-energy libration of the phenyl groups, which, if present, would be reflected in the thermal parameters of the carbon atoms constituting these groups, was not mentioned in the report describing the X-ray crystal structure of $(Ph_3P)_3AuCl$ [125]. The ^{31}P CP/MAS NMR spectrum of $(DBP)_3AuBr$ displayed two signals in a 2:1 intensity ratio whereas that of $(DBP)_3AuI$ displayed three signals of equal intensity, thus showing

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* Libration refers to a form of motion that may be described as a vibration along an arc rather than along a straight line (see ref. 126).

a closer relationship of $(DBP)_3AuBr$ to $(DBP)_3AuCl$ than to $(DBP)_3AuI$. However, no X-ray data have yet been reported for $(DBP)_3AuBr$ and $(DBP)_3AuI$ that would support these conclusions. Lastly, the ^{31}P solid state NMR spectrum of $[(DBP)_4Au]PF_6$ was recorded to assess whether or not, in the solid state, the four phosphole ligands coordinate to the gold(I) center in a similar way. The ^{31}P CP/MAS NMR spectrum of $[(DBP)_4Au]PF_6$ showed a single absorption at 13.1 ppm that is close to the value observed in solution, i.e. 12.8 ppm. These observations led Nelson et al. to the conclusion that, in the solid state, $[(DBP)_4Au]PF_6$ has a similar geometry to that found in solution, i.e. the complex is tetrahedral.

(v) Complexes of the Group 12 metals

^{31}P solid state NMR studies of Group 12 metal complexes are quite scarce. Kubo and McDowell have recorded the ^{31}P solid state NMR spectrum of zinc(II) bis(*O*,*O'*-diethyldithiophosphate), $Zn[S_2P(OC_2H_5)_2]_2$, under MAS conditions and studied the influence of the spinning frequency on the spin-diffusion time constant T_{SD} for this complex [127]. Allman and Lenkinski [128] have measured the ^{31}P CP/MAS NMR spectra of several Hg(II)–phosphine complexes HgX_2L_2 where X = Cl, Br, I, CN, SCN, OAc, NO_3, ClO_4, and L = PPh_3, PCy_3. In solution, these complexes give rise to AX-type spectra due to ^{199}Hg–^{31}P coupling (^{201}Hg–^{31}P coupling is not observed due to rapid relaxation of the ^{201}Hg quadrupolar nucleus) and owing to the fact that the two phosphorus nuclei in the molecule are magnetically equivalent. In the solid state, however, several of these complexes were found to give rise to ABX-type spectra due to coupling between the two magnetically inequivalent phosphorus nuclei in each molecule, thus indicating that the phosphorus atoms are no longer symmetry-related ($^2J(P_A,P_B) = 110 - 240$ Hz and $^1J(^{199}Hg,^{31}P) = 2330 - 5560$ Hz). Among the nine complexes that were analyzed, six of them, namely $HgX_2(PPh_3)_2$ where X = Cl, Br, I, CN, OAc, and $Hg(ClO_4)_2(PCy_3)_2$, showed ABX-type spectra. For $HgX_2(PPh_3)_2$ where X = Cl, Br, I, CN, and for $Hg(ClO_4)_2(PCy_3)_2$ the ^{31}P solid state NMR results were in accord with the reported X-ray crystal structures, i.e. the asymmetric unit of each one of these complexes was found to contain one entire molecule [129–132]. It is noteworthy, however, that the presence of one entire molecule per asymmetric unit is not the only situation that could lead to observation of an ABX-type spectrum. In the case where a plane of symmetry containing the P–Hg–P fragment is present, one would also observe an ABX-type spectrum despite the fact that only one half of each molecule is crystallographically unique. This remark is of importance since in cases where a space group ambiguity exists, such as those of $HgBr_2(PPh_3)_2$ and $Hg(CN)_2(PPh_3)_2$ whose X-ray crystal structures were solved in the orthorhombic space groups $Pna2_1$ and $Pn2_1a$ with $Z = 4$ [129,131], ^{31}P solid state NMR spectroscopy would be unable to differentiate between the non-centrosymmetric space groups, i.e. $Pna2_1$ and $Pn2_1a$, and the centrosymmetric ones, namely Pnam and Pnma. As far as $Hg(OAc)_2(PPh_3)_2$ is concerned, an ABX-type spectrum was also observed indicating the presence of two crystallographically inequivalent phosphorus nuclei in the asymmetric unit, but no X-ray crystallographic data have yet been published for this complex that would provide confirmation of these conclusions. The case of $Hg(SCN)_2(PPh_3)_2$ proved to be a little more complex in that ABX- and AX-type spectra were obtained depending upon the method employed to recrystallize the sample used in the solid state NMR experiment. Observation of an ABX-type spectrum agrees with the reported X-ray crystal structure of $Hg(SCN)_2(PPh_3)_2$, i.e. $P2_1/c$ with $Z=4$ [133], whereas observation of an AX-type spectrum suggests the presence of a second polymorph of this material in which the two phosphorus nuclei are crystallographically equivalent (or they may be crystallographically inequivalent and have isochronous signals). The ^{31}P CP/MAS NMR spectra of $Hg(NO_3)_2(PPh_3)_2$ and $Hg(OAc)_2(PCy_3)_2$ showed no observable ^{31}P–^{31}P coupling. In the case of $Hg(NO_3)_2(PPh_3)_2$, these results are consistent with the reported X-ray crystal structure, i.e. $C2/c$ with $Z=4$ [131]. $Hg(OAc)_2(PCy_3)_2$ was reported to crystallize in the monoclinic space group $P2/c$ with $Z=4$ [132]. The absence of ^{31}P–^{31}P coupling in the ^{31}P CP/MAS NMR spectrum of this compound is explained by the fact that the asymmetric unit consists of two independent half-molecules (each molecule present in the unit cell sits on a two-fold axis of symmetry). Additionally, in the same study, Allman and Lenkinski performed some simple valence bond calculations in an attempt to relate calculated s characters of bonding orbitals to the measured ^{199}Hg–^{31}P coupling constants, but found that the correlation predicted by an approximation to the Fermi contact term was not realized. Lastly, in a more recent study, Allman reported the ^{31}P CP/MAS COSY and *J*-resolved spectra of $Hg(ClO_4)_2(PCy_3)_2$ [87].

E. CONCLUDING REMARKS

In this review article we have discussed work that clearly demonstrates the complementary nature of solid state NMR spectroscopy and X-ray crystallography in the study of tertiary phosphines and their transition metal complexes. Significant structural information can be deduced from the results of appropriate solid state NMR studies but great care must be applied in interpretation, particularly in the absence of reliable X-ray data. In many of the transition metal complexes discussed in this review the metal centers themselves possess suitable magnetic properties for direct observation in solid state NMR experiments and so this area could provide additional information to assist in structural elucidation. A separate article describing progress in solid state NMR studies of metal nuclei will appear [134].

NOTE ADDED IN PROOF

Since the submission of this article, a number of papers have appeared or have come to our attention that are of importance to the subject of this review. In this journal an article by Yamasaki was published [135] that provides an introduction to the topic and a list of references. A useful text has also appeared that contains much information on both the theory and practice of solid state NMR spectroscopy [136].

Solid state ^{31}P and ^{29}Si NMR studies of a phosphine-functionalized polysiloxane have been reported [137] and these results are of interest in terms of previous work on phosphine-functionalized silica gels and high-surface-area glasses, described earlier in this review. The functionalized siloxane was prepared by condensation of $Si(OEt)_4$ and the phosphine ether ligand $(MeO)_3Si(CH_2)_6P(Ph)CH_2CH_2OCH_3$ to generate a material with the idealized stoichiometry $[SiO_{3/2}(CH_2)_6P(Ph)CH_2CH_2OCH_3]\cdot 2SiO_2$. This material showed a single resonance at -31.7 ppm with a linewidth at half-height of 120 Hz in the solid state ^{31}P NMR spectrum. Treatment of the functionalized siloxane with a solution of $[RuCl_2(CO)_2]_n$ in 2-methoxyethanol caused the complete disappearance of the signal at -31.7 ppm and the appearance of a new resonance at 6.5 ppm, consistent with the formation of surface-bound *all-trans*-$[RuCl_2(CO)_2(PR_3)_2]$ (where $PR_3 = [SiO_{3/2}(CH_2)_6P(Ph)CH_2CH_2OCH_3]\cdot 2SiO_2$).

Work on tertiary phosphine complexes of metals from Groups 6 and 7 has now begun to appear. Work mentioned earlier in this review on $W(PMe_3)_3H_6$ [21] has now been published [138]. Since 9-coordinate transition metal complexes are always fluxional in solution, solid state NMR spectroscopy provides an opportunity to study structure under conditions where the barriers to geometry interconversions may be higher and hence the processes slower. Variable temperature solid state ^{13}C and ^{31}P NMR studies of the tungsten hydride indicate that the complex has a tricapped-trigonal-prismatic structure with one phosphine capping a prismatic face and the other two phosphines opposite in eclipsed prismatic sites that are inequivalent. At temperatures above 340 K, complete ligand scrambling occurs in a manner that requires only minimal movement of the phosphine ligands within the crystal lattice. The process appears to involve polyhedral edge stretches through a monocapped-square-antiprismatic geometry to an intermediate of tricapped-trigonal-prismatic geometry with the phosphines in capping positions. In solution, the ^{31}P NMR spectrum of $W(PMe_3)_3H_6$ shows a single resonance at -18.55 ppm with coupling to ^{183}W of 73 Hz. In the solid state, at room temperature, two signals at -2.65 (triplet) and -23.15 (doublet) ppm in the intensity ratio of 1:2 are observed. The two components of the doublet, however, were of unequal intensities and linewidths. Processing of the data with resolution enhancement revealed the tungsten satellites, and analysis of the processed spectrum gave rise to spin–spin coupling constants of 92 and 117 Hz for the shielded and deshielded signals, respectively.

Lindner et al. [139] have recently studied the relationship between conformation and chemical shift for several phosphorus-containing metallacycles of the Group 6 and 7 metals. The conformation of the phosphatungstenacyclopentane $W(Ph_2PCH_2CH_2CH_2)(CO)_2(\eta^5\text{-}C_5H_5)$ in the solid state as determined by single-crystal X-ray diffraction techniques was found to be different from that in solution as determined by ^{1}H NMR spectroscopy. Evidence of this conformational difference was also obtained from ^{31}P NMR measurements: it was found that the difference in the ^{31}P chemical shifts measured in solution and in the solid state was approximately 9 ppm in the case of $W(Ph_2PCH_2CH_2CH_2)(CO)_2(\eta^5\text{-}C_5H_5)$ whereas this difference did not exceed 3 ppm for the other compounds analyzed. Lindner et al. have also recently described [140] an investigation of the relationship between ^{31}P chemical shift tensor components and structure for a series of cyclic and acyclic metal phosphine complexes of manganese and tungsten. While it was generally observed that isotropic shifts were the same for solutions and for solid samples, there were clear differences in the tensor components between certain structural types. For example, a large difference in δ_{11} (ca. 70 ppm) was observed between *cis*-$[W(Ph_2PBu)(CO)_2(\eta^5\text{-}C_5H_5Cl]$ and *trans*-$[W(Ph_2PBu)(CO)_2(\eta^5\text{-}C_5H_5)CH_3]$, while the values of δ_{22} and δ_{33} remained essentially the same, this effect being attributed to the large difference in trans influence between chloride and methyl ligands. Interestingly, scalar spin–spin couplings between ^{31}P and ^{55}Mn or ^{95,97}Mo could be observed in certain of the solid state spectra. These couplings are not normally seen in spectra measured for solutions since rapid relaxation processes effectively decouple the nuclei. Where scalar coupling between ^{31}P and ^{55}Mn is well resolved in the solid state spectra, a multiplet of six lines with uneven spacings is observed due to the dipolar interaction of the ^{31}P nucleus with the quadrupole of ^{55}Mn.

The solid state ^{31}P NMR spectra of a series of nickel(II) complexes of bidentate tertiary phosphines have been reported [141]. Specifically, spectra of the complexes Ni(dppe)X_2 (X = Cl, Br, I), $[Ni(dppe)_2](NO_3)_2$, and N(dppey)X_2 (dppey = *cis*-1,2-bis(diphenylphosphino)ethylene; X = Cl, Br) were described. Four resonances were observed in the solid state CP/MAS ^{31}P{^{1}H} NMR spectrum of Ni(dppe)Cl_2, two in the NMR spectra of Ni(dppe)Br_2, Ni(dppe)I_2, and Ni(dppey)Cl_2, and one in those of $[Ni(dppe)_2](NO_3)_2$ and Ni(dppey)Br_2. Observation of four resonances in the solid state CP/MAS ^{31}P{^{1}H} NMR spectrum of Ni(dppe)Cl_2 does not agree with the reported X-ray crystallographic data [142]. The form of Ni(dppe)Cl_2 characterized by single-crystal X-ray diffraction is a methylene chloride solvate. It crystallizes in the monoclinic space group $P2_1/c$ with $Z = 4$, and so two resonances are anticipated in the solid state CP/MAS ^{31}P{^{1}H} NMR spectrum of this form. The presence of four resonances in the actual solid state NMR spetrum may be due to the fact that a different modification with four crystallographically inequivalent phosphorus nuclei in the asymmetric unit was being analyzed. Alternatively, it seems equally likely that the sample employed in the solid state NMR experiment may have been a mixture of several crystalline forms of [Ni(dppe)Cl_2]. Indeed, two forms of [Ni(dppe)Cl_2] have been identified by infrared spectroscopy [141]. Also, the sample used in the solid state NMR experiment could have been a mixture of solvated and unsolvated forms of [Ni(dppe)Cl_2]. These latter two possibilities are not unreasonable since significant differences seem to exist in the intensities of the central resonances in the observed spectrum (even though the cross-polarization experiment is not a reliable technique to estimate the composition of mixtures of compounds and despite the fact that the chemical shift anisotropies of the ^{31}P nuclei are slightly different), and also because the chemical shfit difference between the down-field resonances and the high-field signals are significantly larger than those encountered for the other complexes analyzed in the same study. Observation of two signals in the solid state CP/MAS $^{31}P\{^1H\}$ spectra of Ni(dppe)Br_2, Ni(dppe)I_2, and Ni(dppey)Cl_2 suggests that the two phosphorus nuclei present in these molecules are crystallographically inequivalent. Examination of the reported single-crystal X-ray diffraction data on these compounds indicates that this is indeed true in the case of Ni(dppe)Br_2 [143], but great care must be exercised since this complex crystallizes as a dichloromethane solvate. Both $[Ni(dppe)_2](NO_3)_2$ and Ni(dppey)Br_2 display solid state $^{31}P\{^1H\}$ NMR spectra consisting of single resonances. However, the linewidths of the signals, 1000±100 Hz and 610±70 Hz, suggest that the signals may in fact consist of several resonances. The X-ray crystal structure of $[Ni(dppe)_2[(NO_3)_2$ has been reported [144]. The complex crystallizes in the monoclinic space group $P2_1/n$ with $Z=2$ and each molecule in the unit cell lies on a center of inversion. Consequently, two resonances are anticipated in the solid state ^{31}P NMR spectrum of this complex, in agreement with the conclusions previously drawn.

A number of clusters based on Ru_3 and Ru_4 units containing Cu and/or Ag and/or Au phosphine fragments have been examined by solid state ^{31}P NMR techniques [145]. Interestingly, it was observed that some of the samples showed more signals than anticipated from the known structures if the clsuters were recrystallized from a dichloromethane/light petroleum mixture, but that this problem was not apparent in samples crystallized from a diethyl ether/light petroleum mixture. Presumably, solvation problems are the cause of this effect. As might be expected, copper-containing clusters gave rise to asymmetric "quartets" due to the copper quadrupole and gold-containing clusters gave rise to signals that were broader than typical, presumably due to dipolar coupling between ^{31}P and ^{197}Au. Clusters containing silver gave rise to spectra consisting of doublets due to coupling to $^{107,109}Ag$. No evidence of the dynamic processes that dominate the solution chemistry of these clusters was found in the solid state spectra.

The solid state ^{31}P NMR spectrum of $Hg_2(CF_3CO_2)_4(PPh_3)_2$ has been reported to consist of two central resonances with the expected coupling to ^{199}Hg; this is unusual since most dimeric mercury complexes of this general type crystallize with the dimer lying on a center of inversion [146]. In this case, however, the X-ray crystal structure is reported [146] to show that the material crystallizes in the monoclinic space group $P2_1/c$ with $Z=2$ and it is said that this is in agreement with the observed solid state ^{31}P NMR spectrum. In fact, our inspection of the reported density and unit cell volume suggests that there is an error in the report of the X-ray crystal structure and that actually $Z=4$ in this case. The observed spectrum is exactly as anticipated if the dimer does indeed crystallize in $P2_1/c$ with $Z=4$. Interestingly, no coupling between the crystallographically inequivalent phosphorus nuclei is apparent in the spectrum. A number of mercury(II) complexes of the unusual phosphine 1,3,5-triaza-7-phosphaadamantane (PTA) have been examined in the solid state by ^{31}P NMR methods [147]. The spectra of complexes of the type $Hg(PTA)X_2$ frequently showed the presence of a contaminant, tentatively assigned as $Hg(PTA)_4X_2$, and either one central resonance ($X = Cl$, Br, I) or two central resonances ($X = CN$. SCN). The two signals for the cyanide and thiocyanate complexes were tentatively attributed to the presence of more than one crystalline form in the bulk sample. In the absence of reliable X-ray crystallographic data for these complexes, no meaningful assignments can be made.

Wasylishen and co-workers [148] have reported a study of the anisotropy of the spin–spin coupling constant between ^{31}P and ^{199}Hg in the complex $Hg_2(P\{o\text{-tolyl}\}_3)_2(NO_3)_4$. While much is known about the anisotropy of ^{31}P chemical shifts, the same is not true about coupling constants involving ^{31}P, and this study represents a rare example of much-needed work in this area. The study allows two conclusions to be made: the sign of ${}^1J({}^{199}Hg, {}^{31}P)$ is positive and the value of the anisotropy of the indirect spin–spin coupling tensor, ΔJ, is 5170 Hz, i.e. J(parallel) = 13110 Hz and J(perpendicular) = 7940 Hz (assuming that the tensor is axially symmetric). The estimated errors in these values are ± 250 Hz. This anisotropy is said to imply a substantial role for mechanisms other than Fermi contact in the transfer of spin information between the two nuclei. A related study of coupling constant anisotropies in mercury(II) phosphonates has recently appeared [149] indicating that a useful base of information may be developing in this area.

In addition to the work on molecular complexes described in the preceding paragraphs, two papers concerning solid state ^{31}P NMR spectroscopy of surface-attached species have come to our attention: one dealing with triosmium clusters [150] and one dealing with ruthenium carbonyl complexes [151]. These papers add to the existing literature on this topic which is described in the main body of this article.

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