

# Forschung, Wissenschaft

## Nuclear Magnetic Resonance Studies of Coordination Compounds\*, \*\*

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### Summary

The applicability of donor and metal atom nmr to coordination chemistry is briefly reviewed. The following structural studies are discussed: (1) the use of  $^{31}\text{P}$  resonances for the determination of molecular geometry of complexes  $[\text{RuCl}_2(\text{QP})]$ ,  $[\text{Fe}(\text{NCS})_2(\text{QP})]$  and  $[\text{W}(\text{CO})_3(\text{QP})]$  ( $\text{QP} = [\text{o-Ph}_2\text{P}\cdot\text{C}_6\text{H}_4]_3\text{P}$ ); (2) the use of  $^{13}\text{C}$  resonances for the formulation of the carbon moiety  $\text{C}_8\text{H}_{11}\cdot\text{OCH}_3$  coordinated to a palladium atom and (3) the use of  $^{14}\text{N}$  to establish the nature of the donor atom in a number of thiocyanato-complexes. It is further shown that proton-noise decoupled  $^{31}\text{P}$  spectra can be conveniently used to obtain activation parameters for ligand exchange in complexes  $[\text{Ni}\{\text{P}(\text{OR})_3\}_4]$ . A possible interpretation of changes in  $^1|J_{^{105}\text{P}-^{14}\text{N}}|$  parameters, in platinum complexes containing primary amines, in terms of selective hybridization at the platinum atom is presented. Finally, possible future developments in nmr studies of coordination compounds are briefly outlined.

### Introduction

Nuclear magnetic resonance spectroscopy has now established itself as the most valuable physical technique for the study of coordination compounds. This development is largely due to the availability of the so-called "third generation" nmr spectrometers which have the advantages of being truly multi-nuclear as well as simultaneously employing broad-band  $^1\text{H}$ -decoupling and pulse-techniques in conjunction with Fourier-Transform (FT) methods.

The commercial spectrometers most suitable for the studies described in this review are of the types Bruker HX-90, Varian XL-100 and Jeol PS-100. The work actually discussed was carried out using a Bruker HX-90.

The nuclei most studied by this technique are those with spin  $I = 1/2$  because they have the best probability of giving high-resolution spectra. Nuclei with  $I > 1/2$  possess electric quadrupole moments which can cause fast relaxation and thus broad resonances in all but few favourable cases.

The choice of nuclei to be observed is also conditioned by the nuclear sensitivity which effectively controls the potential signal-to-noise ratio for any given number of "active" nuclei. It is here that the advent of pulse-

techniques and FT-methods has made its major contribution by allowing rapid accumulation of spectral data.

Another factor of great practical importance is the natural abundance of the nucleus to be observed. While it is more convenient to obtain spectra of a given nucleus in a compound containing it in its natural abundance, it is often possible to overcome this limitation by the use of enriched materials.

Finally, even for nuclei with  $I = 1/2$  the quality of the spectra can be unfavourably influenced by their relaxation times,  $T_1$  and  $T_2$ , in the compounds under examination.

For details about the principles and practice of nmr spectroscopy the reader is referred to the monograph by Emsley, Feeney and Sutcliffe. [1]

The usefulness of the nmr technique for the coordination chemist can be gauged by perusing Tables 1 and 2. Table 1 summarizes the nuclear properties of a number of common donor atoms and Table 2 gives the corresponding data for some metal atoms with  $I = 1/2$ . As can be seen, donor atoms such as hydrogen, carbon, nitrogen, fluorine, phosphorus, selenium, tin and tellurium all have isotopes with  $I = 1/2$  which, with the exception of  $^{15}\text{N}$ , can be studied at least as easily as the now commonly observed  $^{13}\text{C}$ . In practice, this means that, given a spectrometer of the type mentioned above, one can conveniently measure solutions which are ca.  $10^{-3}\text{M}$  for  $^1\text{H}$ ,  $10^{-2}\text{M}$  for  $^{31}\text{P}$  and  $10^{-1}\text{M}$  for  $^{13}\text{C}$  although in many instances it is generally possible to lower these concentrations by a factor of 10 if necessary. As is apparent from Table 2, of the acceptor atoms, direct observation of the appropriate isotopes of silicon, cadmium, tin, platinum, mercury and thallium will often be possible while chemical shift data for  $^{103}\text{Rh}$ ,  $^{109}\text{Ag}$  and  $^{183}\text{W}$  must be largely obtained by indirect methods, e.g. heteronuclear double-resonance (INDOR).

Finally mention should be made that nmr measurements are generally carried out on diamagnetic compounds as the presence of unpaired electrons usually induces fast relaxation and, therefore, poorly resolved spectra. On the other hand, many paramagnetic compounds afford nmr spectra containing much valuable information. Their mention, however, would go beyond the scope of this review and, therefore, the reader is

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Table 1: NMR Parameters for the more common donor atoms

Isotope	"Nuclear" Relative sensitivity (A)	Natural abundance (%)	"Scaled" Relative sensitivity (B)	Spin <i>I</i> ( $\times h/2\pi$ )	El. quadrupole moment, $Q (\times e \times 10^{-24} \text{ cm}^2)$
$^1\text{H}$	1.000	99.984	1.000	1/2	—
$^{13}\text{C}$	$1.59 \times 10^{-2}$	1.108	$1.76 \times 10^{-4}$	1/2	—
$^{14}\text{N}$	$1.01 \times 10^{-3}$	99.635	$1.01 \times 10^{-3}$	1	$2 \times 10^{-2}$
$^{15}\text{N}$	$1.04 \times 10^{-3}$	0.365	$3.80 \times 10^{-6}$	1/2	—
$^{17}\text{O}$	$2.91 \times 10^{-2}$	$3.7 \times 10^{-2}$	$1.08 \times 10^{-5}$	5/2	$-4 \times 10^{-3}$
$^{19}\text{F}$	0.834	100.00	0.834	1/2	—
$^{31}\text{P}$	$6.64 \times 10^{-2}$	100.00	$6.64 \times 10^{-2}$	1/2	—
$^{33}\text{S}$	$2.26 \times 10^{-3}$	0.74	$1.67 \times 10^{-5}$	3/2	$-6.4 \times 10^{-2}$
$^{35}\text{Cl}$	$4.71 \times 10^{-3}$	75.4	$3.35 \times 10^{-3}$	3/2	$-7.97 \times 10^{-2}$
$^{75}\text{As}$	$2.51 \times 10^{-2}$	100.00	$2.51 \times 10^{-2}$	3/2	0.3
$^{77}\text{Se}$	$6.97 \times 10^{-3}$	7.50	$5.23 \times 10^{-4}$	1/2	—
$^{81}\text{Br}$	$9.84 \times 10^{-2}$	49.43	$4.86 \times 10^{-2}$	3/2	0.28
$^{119}\text{Sn}$	$5.18 \times 10^{-2}$	8.68	$4.50 \times 10^{-3}$	1/2	—
$^{121}\text{Sb}$	0.160	57.25	$9.16 \times 10^{-2}$	5/2	-0.8
$^{125}\text{Te}$	$3.16 \times 10^{-2}$	7.03	$2.22 \times 10^{-3}$	1/2	—
$^{127}\text{I}$	$9.35 \times 10^{-2}$	100.00	$9.35 \times 10^{-2}$	5/2	-0.75

A = For equal number of nuclei at constant field.

B = For equal number of atoms in which the magnetic nucleus in question is present in natural abundance.

Table 2: NMR Parameters for some metal atoms with nuclear spin  $I = 1/2$  and comparison data

Isotope	"Nuclear" Relative sensitivity (A)	Natural Abundance (%)	"Scaled" Relative sensitivity (B)
$^1\text{H}$	1.000	99.984	1.000
$^{13}\text{C}$	$1.59 \times 10^{-2}$	1.108	$1.76 \times 10^{-4}$
$^{15}\text{N}$	$1.04 \times 10^{-3}$	0.365	$3.80 \times 10^{-6}$
$^{29}\text{Si}$	$7.85 \times 10^{-2}$	4.7	$3.69 \times 10^{-3}$
$^{103}\text{Rh}$	$3.12 \times 10^{-5}$	100.000	$3.12 \times 10^{-5}$
$^{109}\text{Ag}$	$1.01 \times 10^{-4}$	48.65	$4.91 \times 10^{-5}$
$^{113}\text{Cd}$	$1.09 \times 10^{-2}$	12.34	$1.35 \times 10^{-3}$
$^{117}\text{Sn}$	$4.53 \times 10^{-3}$	7.67	$4.50 \times 10^{-2}$
$^{183}\text{W}$	$6.98 \times 10^{-5}$	14.28	$9.97 \times 10^{-6}$
$^{195}\text{Pt}$	$9.94 \times 10^{-3}$	33.67	$3.35 \times 10^{-3}$
$^{199}\text{Hg}$	$5.72 \times 10^{-3}$	16.86	$9.64 \times 10^{-4}$
$^{205}\text{Tl}$	0.192	70.48	0.135

A = For equal number of nuclei at constant field.

B = For equal number of atoms in which the magnetic nucleus in question is present in natural abundance.

referred to a specialized text for a discussion of this type of application. [2]

The bulk of the nmr studies of coordination compounds are based on the observation of proton resonances. This type of application will not be discussed here. In fact, the main purpose of these pages is to stress the advantages consequent upon the direct observation of nmr spectra of donor and/or acceptor atom.

The major advantage of the direct observation of one of the atoms forming the coordinate bond is that one can relate changes in nmr parameters more directly to changes in the nature of such bonds. Furthermore, there are also practical advantages in the observation of "heavy nuclei": (1) they generally give a wider range of chemical shifts, (2) they are more sensitive to small changes in the geometric and/or electronic structures

and (3) they normally give rise to simpler, more directly interpretable spectra. This last circumstance comes about because (a) the observation of "heavy nuclei" is usually carried out under conditions of proton broad-band decoupling, a technique which removes all coupling between the hydrogen atoms present in the molecule and the nucleus under observation, (b) there are usually relatively few "active" nuclei and (c) the differences in their chemical shifts relative to their coupling constants, e.g., phosphorus-phosphorus coupling, is usually such that one observes "first-order" spectra.

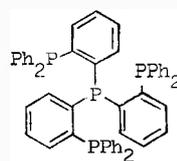
As for proton nmr studies, the desired information is obtained in the form of chemical shifts, nuclear spin-spin coupling constants and, last but not least, by comparing the values obtained with empirical data on related compounds.

The types of applications to be discussed here are meant to show how one obtains information about molecular geometry, solution dynamics and electronic effects. The examples chosen to illustrate each type of application will be taken from the work done in our laboratory. This, however, should not be taken to imply that these are, in any way, more significant than the very extensive studies done by other groups.

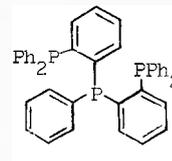
### Structural Applications

#### Determination of coordination numbers and geometries

The examples chosen make use of  $^{31}\text{P}$ -resonances and relate to the complexes of the quadridentate ligand QP.

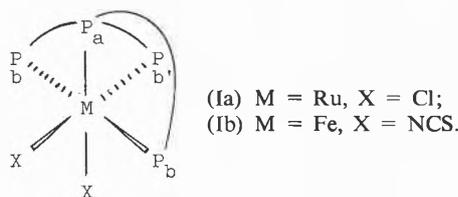


QP



TP

This ligand gives a wide range of coordination compounds [3] and  $^{31}\text{P}$ -nmr has been extensively used for structural assignments. [4] The complex  $[\text{RuCl}_2(\text{QP})]$  has been assigned structure (Ia) on the basis of its  $^{31}\text{P}$ -nmr spectrum [5] which is shown in Fig. 1a.



This spectrum, which is of  $\text{AMX}_2$ -type, clearly shows the three types of inequivalent donor atoms. The assignment of the resonances due to  $\text{P}_a$  and  $\text{P}_b$  was made empirically [4] and the parameters given in Table 3 were obtained after allowing for the coupling between phosphorus atoms.

Table 3:  $^{31}\text{P}$ -NMR Parameters for complexes  $[\text{RuCl}_2(\text{QP})]$  and  $[\text{Fe}(\text{NCS})_2(\text{QP})]$

	$[\text{RuCl}_2(\text{QP})]$	$[\text{Fe}(\text{NCS})_2(\text{QP})]^a$
$\delta_{a,b}$	137.9	173.3
$\delta_{b,b}$	60.9	62.8
$\delta_{b',b}$	83.2	77.6
$J_{\text{P}_a\text{P}_b}^c$	16.2	35.2
$J_{\text{P}_a\text{P}_b'}^c$	19.9	35.2
$J_{\text{P}_b\text{P}_b'}^c$	22.4	40

<sup>a</sup> Calculated values that reproduce the spectrum given in Fig. 1c.

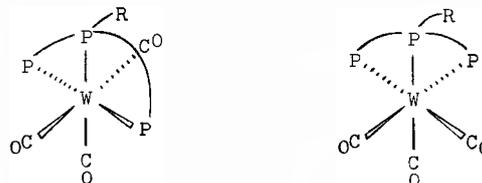
<sup>b</sup> In ppm relative to external  $\text{H}_3\text{PO}_4$ , and estimated to be correct to  $\pm 0.5$  ppm.

<sup>c</sup> In Hz,  $\pm 1$ .

While, as mentioned earlier, "first order" spectra are the rule, "second order" spectra are frequent exceptions as can be seen from the  $^{31}\text{P}$ -nmr spectrum of  $[\text{Fe}(\text{NCS})_2(\text{QP})]$ , [5] (Ib), which is shown in Fig. 1b. The difference in spectrum between this compound and that of the ruthenium complex largely arises because the ratio  $(\nu_{\text{P}_b} - \nu_{\text{P}_b'})/J(\text{P}_b\text{P}_b')$  is larger for the former compound.

The nmr parameters, however, are obtainable from the spectra using iterative methods based on computer-simulation of the observed spectra. The computed spectrum of the iron complex is shown in Fig. 1c and the parameters used to obtain it are given in Table 3. The third and last example to be discussed in this section relates to the assignment of coordination number and structure to the complex  $[\text{W}(\text{CO})_3(\text{QP})]$ . [6] This complex could be either seven-coordinate or, more likely, six-coordinate, with one of the phosphorus atoms of QP not coordinated to the tungsten atom. The  $^{31}\text{P}$ -nmr spectrum of this compound is shown in Fig. 2. Despite its complex appearance, this spectrum is easily analysed. If one considers only the positions of the four sets of intense resonances one can identify each set as arising from one phosphorus atom in a

given and known environment: (1) resonances at ca.  $-15$  ppm are typical of the phosphorus atoms in the free ligand QP; (2) those at ca. 45 ppm fall in the region of coordinated terminal phosphorus atoms in  $[\text{W}(\text{CO})_3(\text{TP})]$  and (3) those at ca. 70 ppm are diagnostic of a coordinated central phosphorus atom of QP as they have  $\delta$ -values close to those of the central phosphorus atom in  $[\text{W}(\text{CO})_3(\text{TP})]$  (see Table 4).



(IIa)  $\text{R} = \text{Ph} = \text{mer-}[\text{W}(\text{CO})_3(\text{TP})]$

(IIb)  $\text{R} = \text{Ph} = \text{vic-}[\text{W}(\text{CO})_3(\text{TP})]$

(IIIa)  $\text{R} = \text{o-Ph}_2\text{P}\cdot\text{C}_6\text{H}_4 = \text{mer-}[\text{W}(\text{CO})_3(\text{QP})]$

(IIIb)  $\text{R} = \text{o-Ph}_2\text{P}\cdot\text{C}_6\text{H}_4 = \text{vic-}[\text{W}(\text{CO})_3(\text{QP})]$

Table 4:  $^{31}\text{P}$ -NMR Parameters for the ligand QP and for complexes  $[\text{W}(\text{CO})_3(\text{TP})]$  and  $[\text{W}(\text{CO})_3(\text{QP})]$

	$\text{P}_c, (\text{P}_c)_3$	$\text{P}_a, \text{P}_b$	$\text{P}_a, \text{P}_b, \text{P}_c$
$\delta_a^*$	—	+ 68.0	+ 76.0
$\delta_b$	—	+ 43.6	+ 43.2
$\delta_{b'}$	—	—	+ 50.2
$\delta_c$	- 13.1	—	- 14.4
$\delta_{c'}$	- 19.5	—	—
$J_{\text{W}-\text{P}_a}^{**}$	—	223	228
$J_{\text{W}-\text{P}_b}$	—	224	224
$J_{\text{W}-\text{P}_b'}$	—	—	217

\* In ppm, relative to external  $\text{H}_3\text{PO}_4$ .

\*\* In Hz,  $\pm 1$ .

Thus, one can conclude that one of the terminal phosphorus atoms is not coordinated to the tungsten atom and that the two coordinated terminal phosphorus atoms are not equivalent.

The other spectral features can be accounted for as follows: (1) the multiplicity in each set arises from P-P coupling and (2) the low-intensity satellites are due to the coupling of tungsten-183 ( $I = 1/2$ , natl. abund. 14%) to phosphorus-31. This latter information is particularly valuable as it has been established [7] that the values of  $^1|J_{183\text{W}-31\text{P}}|$  fall in the range 220–230 Hz for compounds  $\text{cis-}[\text{W}(\text{CO})_4(\text{R}_3\text{P})_2]$  and in the range 265–275 for the corresponding trans-isomers. Thus, inspection of the data shown in Table 4 allows the assignment of structure (IIIb) to  $[\text{W}(\text{CO})_3(\text{QP})]$ .

The inequivalence of the two coordinated terminal phosphorus atoms is likely to arise from steric interactions: Examination of molecular models indicates that, having coordinated  $\text{P}_a$  and two  $\text{P}_b$  atoms, it is sterically impossible to arrange the "trailing"  $\text{o-C}_6\text{H}_4\text{PPh}_2$  group symmetrically around the coordination polyhedron leading to the inequivalence of the

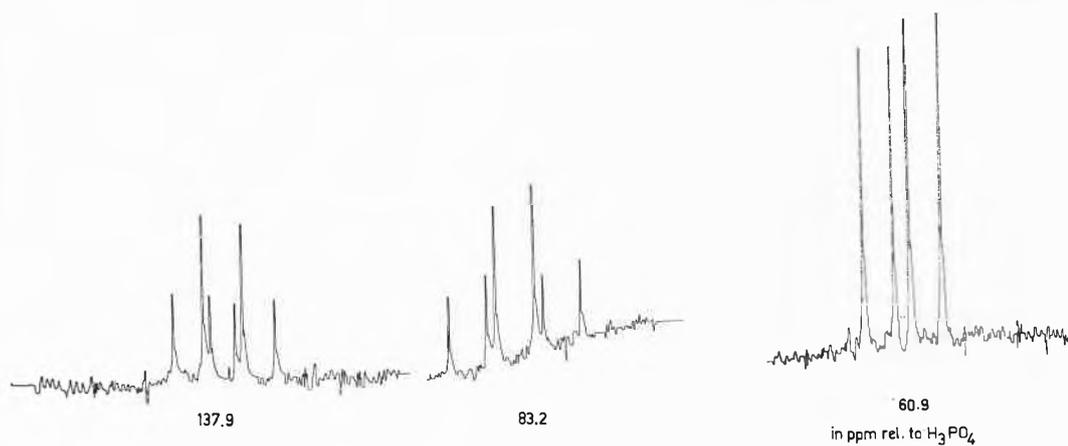


Fig. 1a:  $^{31}\text{P}$ -NMR Spectra of  $[\text{RuCl}_2(\text{QP})]$

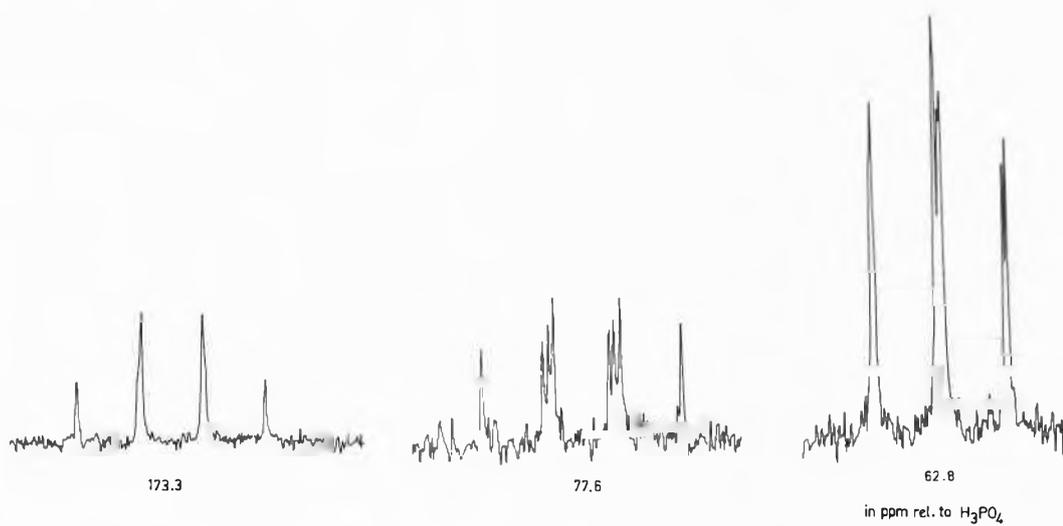


Fig. 1b:  $^{31}\text{P}$ -NMR Spectra of  $[\text{Fe}(\text{NCS})_2(\text{QP})]$  (observed)

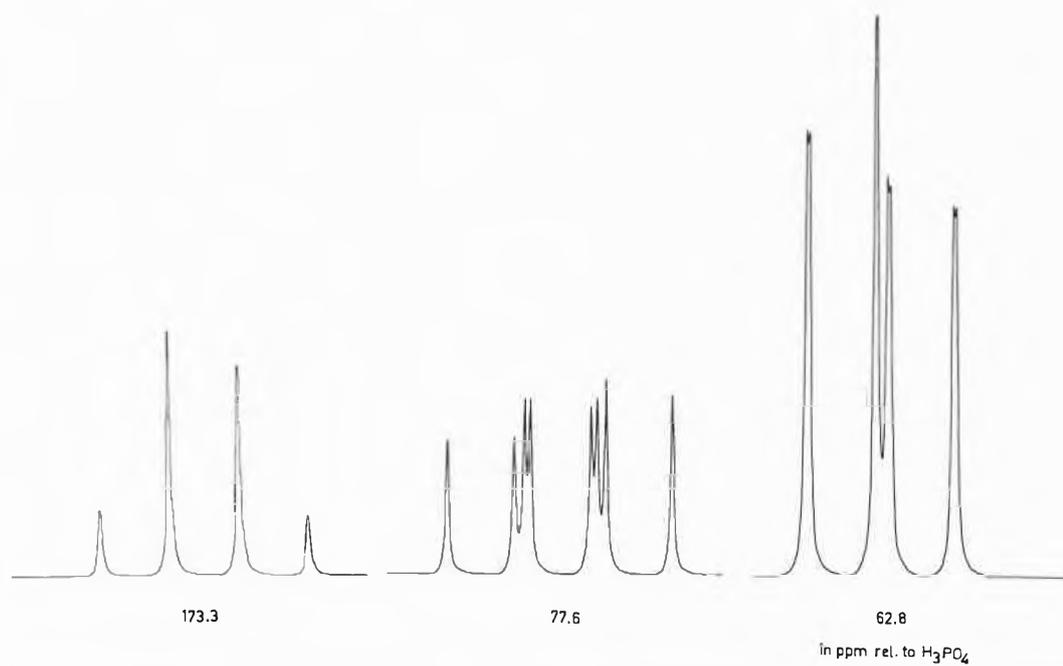


Fig. 1c:  $^{31}\text{P}$ -NMR Spectra of  $[\text{Fe}(\text{NCS})_2(\text{QP})]$  (computed)

two coordinated  $P_b$  atoms. This hypothesis still awaits confirmation by an X-ray structure determination. The final point to be made about this compound is that such a structural assignment would not have been possible using proton nmr!

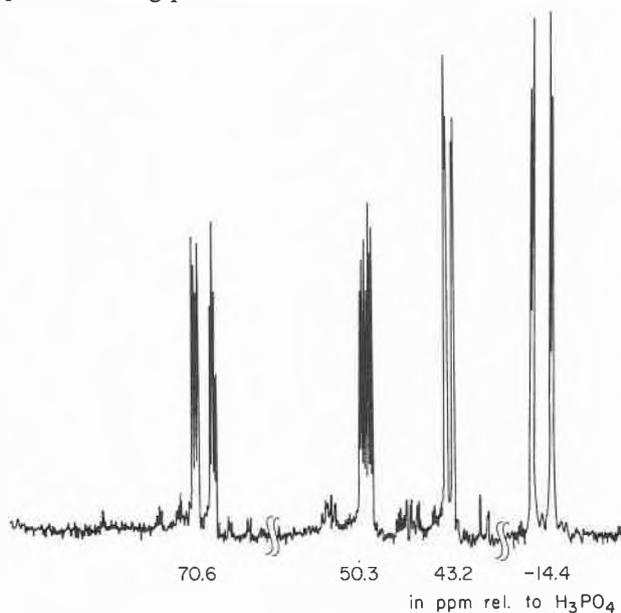
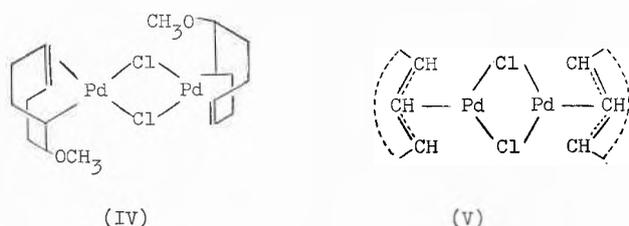


Fig. 2:  $^{31}P$ -NMR Spectrum of  $[W(CO)_3(OP)]$

#### Determination of ligand structure

There are now innumerable reactions occurring at coordinated ligands. While it is often possible to postulate structures for the products from their proton nmr spectra, it is generally more reliable and, at times, essential to base structural assignments on carbon-13 spectra. An example of this type of application is provided by the assignment of structure to the product of the reaction: [8]  $2[PdCl_2(1,5-C_8H_{12})] + 2CH_3OH + Na_2CO_3 \rightarrow [Pd_2Cl_2(C_8H_{11}OCH_3)_2] + 2NaCl + H_2O + CO_2$ .

The product was originally assigned structure (IV) but



later developments [9] raised the possibility that this product might be a  $\pi$ -allylic complex containing a structural unit of type (V).

Carbon-13 nmr is ideally suited for a structural assignment of this type. Literature data [10] indicate that carbon atoms of olefins coordinated to palladium resonate above 100 ppm while carbon atoms  $\sigma$ -bonded to metals resonate at much higher fields. On the other hand  $\pi$ -allyl complexes show a pattern of carbon

resonances [10] consisting of one signal in the 'olefinic' region due to the central carbon atom of one or two signals at higher fields. The spectrum of the product shown above is reproduced in Fig. 3. As can be seen, one observes two resonances in the 'olefinic' region indicating that this spectrum is consistent with structure (IV). The remaining resonances can be assigned as follows:  $H-C-O$ ,  $\delta = 81.5$  ppm,  $OCH_3$ ,  $\delta = 56.7$  ppm,  $-Pd-C-$ ,  $\delta = 52.4$  ppm,  $CH_2$ ,  $\delta = 26.7 - 34.7$  ppm confirming the structural assignment.

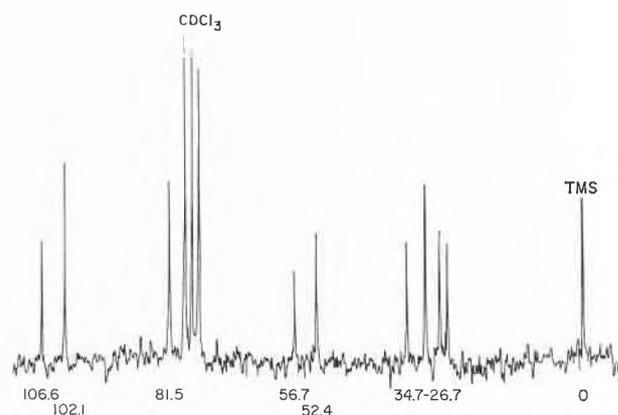


Fig. 3:  $^{13}C$ -NMR Spectrum of  $[Pd_2Cl_2(C_8H_{11}OCH_3)_2]$

#### Study of quadrupolar nuclei

Mention was made earlier of strong preference for the observation of nuclei with  $I = 1/2$ . In a number of favourable instances, however, structural information can be obtained even by observing quadrupolar nuclei. [11] An example of this is provided by nitrogen-14 which has  $I = 1$  and a relatively small nuclear quadrupole. The observed line-widths vary considerably and the narrowest lines are obtained in compounds which contain this nucleus in a symmetrical environment. However, one can get usable data even for compounds in which the nitrogen atom is in an envi-

Table 5:  $^{14}N$ -Chemical shifts,  $\delta$  (ppm), of thiocyanate complexes

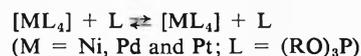
KSCN (pH = 4.5)	$\delta(NO_3^-)$ + 166	$\delta(KSCN)$ 0	Solvent
<i>S-Bonded Complexes</i>			
$Na_2[Pd(SCN)_4]$	+ 148	- 18	$H_2O$
$K_2[Pt(SCN)_4]$	+ 166	0	$H_2O$
$K_3[Rh(SCN)_6]$	+ 158	- 8	$H_2O$
$Na_3[Ir(SCN)_6]$	+ 163	- 3	$H_2O$
$Na_2[Hg(SCN)_4]$	+ 157	- 9	$H_2O$
$C_2H_5SCN$	+ 98.5	- 67.5	$CHCl_3$
<i>N-Bonded Complexes</i>			
cis- $[Pt(NCS)_2(Bu_3P)_2]$	+ 302	+ 136	$CHCl_3$
trans- $[PtH(NCS)(Et_3P)_2]$	+ 239	+ 73	$CHCl_3$
cis- $[Pt(NCS)_2(Bu_3As)_2]$	+ 303	+ 137	$CHCl_3$
trans- $[Ni(NCS)_2(Et_3P)_2]$	+ 293	+ 127	$CHCl_3$
$Na_2[Cd(NCS)_4]$	+ 220	+ 54	$CH_3OH$
$Na_2[Zn(NCS)_4]$	+ 255.5	+ 60	$C_2H_5OH$
$K_2[Ru(NO)(NCS)_6]$	+ 245	+ 79	$H_2O$
$C_2H_5NCS$	+ 268	+ 102	liquid

ronment of low symmetry, e.g., the complexes of the thiocyanate ion. [12] As can be seen from Table 5, nitrogen-14 resonances can be used to distinguish the two types of linkage isomers M-NCS and M-SCN. It should be pointed out here that the data given in Table 5 were obtained many years ago and that if this type of study were to be done using modern spectrometers one could significantly lower the concentrations required, thus widening the applicability of the method.

### Kinetic applications of nmr to coordination chemistry

Such applications are possible because the nmr method is sensitive to dynamic processes and, therefore, shows variations in position and width of resonances on rates of chemical reactions. Although most of these studies have been carried out using proton magnetic resonance, there are many advantages of observing donor atom nmr parameters. One of the major gains of this is due to the fact that, as mentioned earlier, differences in chemical shifts between free and coordinated ligands are larger than in the case of protons. Thus, reactions which are too fast for the nmr method when followed observing proton resonances become accessible by this method if the donor atom is observed. Furthermore, donor atom observation becomes essential when the proton spectra and/or their changes are too complex for a detailed interpretation.

An example of this type of application is provided by the determination of the activation parameters for the ligand-exchange reaction:



The activation parameters for the reactions, where M = Pd and Pt and L = (C<sub>2</sub>H<sub>5</sub>O)<sub>3</sub>P, were obtained by Meier et al [13] following changes in the line-shape proton spectra. While the extension of this type of study to a wide range of other ligands complexes, e.g. triarylphosphines or triarylphosphites, would have been either difficult or impossible, the temperature-dependence of the broad-band decoupled phosphorus-31 spectra of the exchanging ligands proved to be of "textbook" simplicity. [14] Some of the data obtained by this method are shown in Table 6.

Table 6: Activation Parameters for exchange between L and [NiL<sub>4</sub>]

L	$\Delta H^\ddagger$ (kcal/mol <sup>-1</sup> )	$\Delta S^\ddagger$ (e. u.)	Ref.
CO	22.3 ± 0.2	8.4 ± 1	[15]
(EtO) <sub>3</sub> P	26.2 ± 1.0	2 ± 3	[13]
( <i>n</i> -PrO) <sub>3</sub> P	21.6 ± 1.0	15 ± 3	[14]
( <i>i</i> -PrO) <sub>3</sub> P	20.7 ± 1.0	17 ± 3	[14]

### NMR parameters and the nature of the coordinate bond

Many attempts have been made, and are still being made, to obtain information about bonding from nmr parameters. The results obtained to date range from partial successes to complete failures. The main reasons for this state of affairs are attributable to the complex nature of the equations expressing the nmr parameters and to the practical impossibility of obtaining reasonable estimates of most of the terms occurring in these equations.

A typical example of the difficulties inherent in this type of study is provided by the interpretation of changes in  $^1|J_{195\text{Pt}-x\text{L}}|$  coupling constants ( $x\text{L} = ^{31}\text{PR}_3$  or  $^{15}\text{NH}_2\text{R}$ ) in terms of changes in the nature of the Pt-L bonds.

Earlier work [16] on complexes of the types cis-[PtX<sub>2</sub>(R<sub>3</sub>P)<sub>2</sub>] and trans-[PtX<sub>2</sub>(R<sub>3</sub>P)<sub>2</sub>] clearly showed that the  $^1|J_{195\text{Pt}-^{31}\text{P}}|$  values are strongly influenced by the ligand in trans-position to the nucleus being observed. Thus, the J-values for arrangements A and B differ by as much as 50%.



One can write expressions for such one-bond coupling constants but it is only after very drastic simplification that one obtains equations in forms that might be of practical use. The standard type of equation used for this purpose is: [16]

$$J_{(A-B)} \approx \gamma_A \gamma_B \Delta E^{-1} \alpha_A^2 \alpha_B^2 |\psi_{(ns)_A}(0)|^2 |\psi_{(ns)_B}(0)|^2,$$

where  $\gamma_A$  and  $\gamma_B$  are the magnetogyric ratios of the two nuclei,  $\Delta E$  is an average singlet-to-triplet excitation energy, the  $\alpha^2$ -terms represent the s-character of the hybrids used by each atom to bind to the other and the  $|\psi_{(ns)}(0)|^2$  terms express the electron densities of the orbitals indicated, evaluated at the appropriate nucleus.

This expression was arrived at by making the following assumptions:

1. that the dominant contributions to  $J$  comes from the so-called "Fermi Contact Term";
2. that all the singlet-to-triplet excitation energies can be adequately expressed by an average term;
3. that of the many  $|\psi_{(ns)}(0)|^2$  terms only those due to the outermost s-orbitals need be considered.

Even after making such drastic assumptions the simplified equation for  $J_{(A-B)}$  cannot be used except in the most empirical way and, in any case, only after testing its applicability to the problem under study.

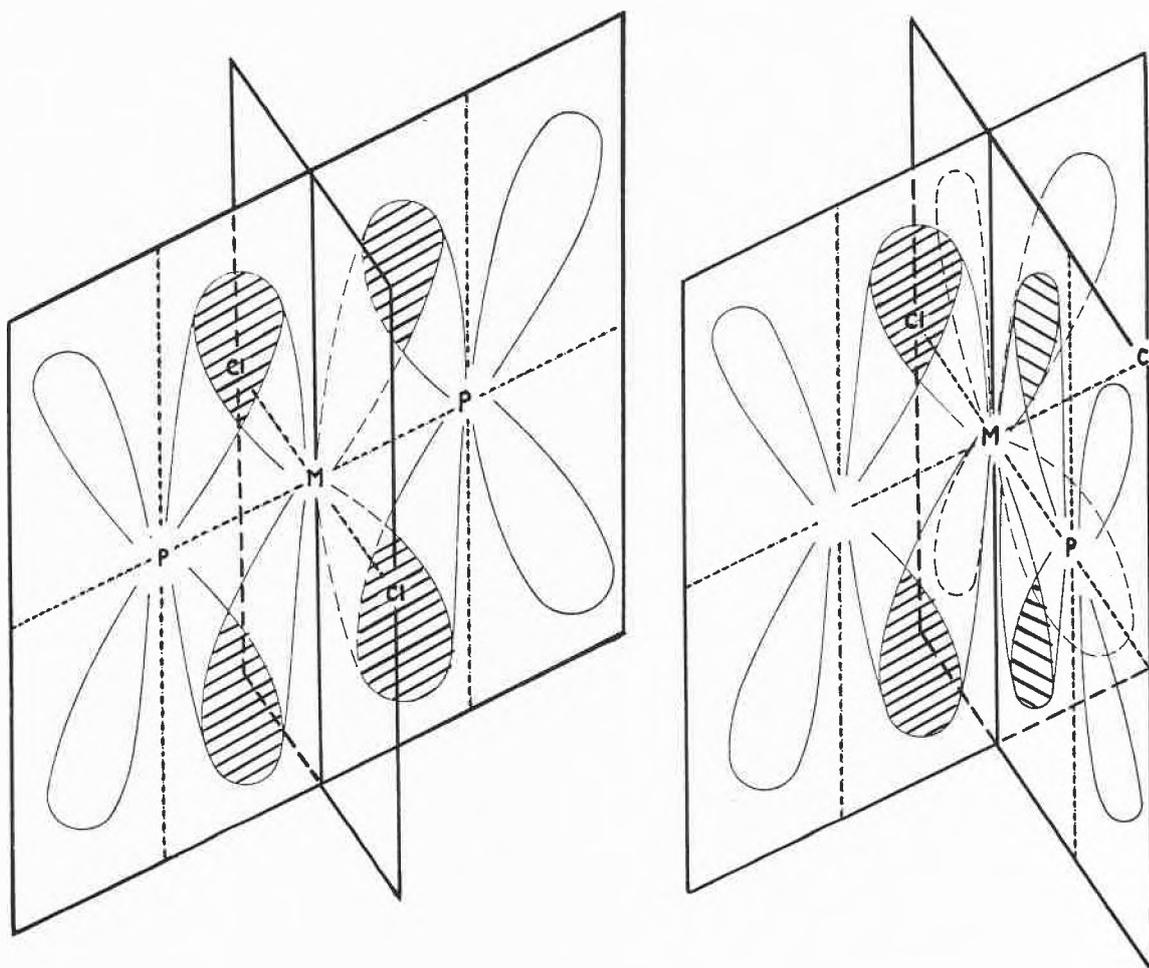


Fig.4:  $\pi$ -Bonding Scheme for complexes *cis*- and *trans*-[PtCl<sub>2</sub>(R<sub>3</sub>P)<sub>2</sub>]

A number of such tests [16] were carried out using a variety of platinum-phosphine complexes, and one reached the conclusion that if one compared different isomeric complexes of the same phosphine and the same anionic ligand, the  $\alpha^2_{Pt}$ -term in the above equation was dominant. Thus, one concluded that the large differences in  $J_{Pt-P}$  arising from changes in the nature of the ligand in *trans*-position to the Pt-P bond, whose  $J$ -value was being considered, could be attributed to changes in the  $s$ -character of the hybrid used by the platinum atom to bind the phosphorus atom; i.e., that there is a greater amount of  $s$ -character in the hybrid used by platinum in the Pt-P-bond in *cis*-[PtCl<sub>2</sub>(R<sub>3</sub>P)<sub>2</sub>] than there is in the corresponding *trans*-isomer.

It has been experimentally established that Pt-P-bonds in *cis*-complexes are stronger than in the corresponding *trans*-isomers and this difference is generally attributed to the difference in  $d_\pi$ - $d_\pi$  character between such bonds, i.e., in a *trans*-complex the main  $\pi$ -interaction arises from overlap between one filled metal  $d$ -orbital and the two empty  $d$ -orbitals, one on each of the phosphorus atoms; on the other hand, in a *cis*-complex two metal  $d$ -orbitals are available for overlap with the two phosphorus  $d$ -orbitals.

One can use this bonding scheme to explain the observed differences in  $J_{(Pt-P)}$  in *cis*- and *trans*-complexes by assuming:

1. that an increase in  $\pi$ -character of the Pt-P bond, by a synergic effect, strengthens the  $\sigma$ -component of that bond and
2. that the differential strengthening of the  $\sigma$ -component occurs mostly through  $s$ -orbital contributions.

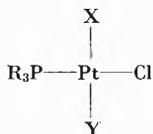
This explanation, however, is not unique and the differences in Pt-P bond strengths in *cis*- and *trans*-platinum complexes can also be rationalized exclusively in terms of  $\sigma$ -effects. This idea is based on a hypothesis put forward by Syrkin [17] which can be roughly stated as follows:

1. the relative order of the platinum  $d$ -energy levels is  $5d < 6s < 6p$ ;
2. the strongest covalent bond in the complex will be formed using more of the low-energy platinum orbitals.

In complexes [PtCl<sub>2</sub>(R<sub>3</sub>P)<sub>2</sub>] we expect the Pt-P bonds to have more covalent character than the Pt-Cl bonds

and, therefore, we suppose that the platinum hybrids used by platinum for bonding to phosphorus have greater d- and s-character than the platinum hybrids used for the Pt-Cl bonds.

For illustrative purpose, let us discuss a limiting, hypothetical case, i.e., that where the platinum atom uses only d- and s-orbitals to bond to the phosphorus atom in a complex of the type



The directional properties of the appropriate ds-hybrids are shown in Fig. 5. Thus, in terms of this model, the Pt-P bond would use one of the ds-hybrids, e.g. (s+d), and the Cl ligand would be restricted to the use of a pure p-orbital. This is clearly a limiting model, but the directional properties are clear: the two most strongly covalent bonds should prefer a mutually cis-orientation. In their original publication Pidcock et al., preferred this latter model for the interpretation of the differences in  $J_{(\text{Pt}-\text{P})}$ -values between cis- and trans-complexes.

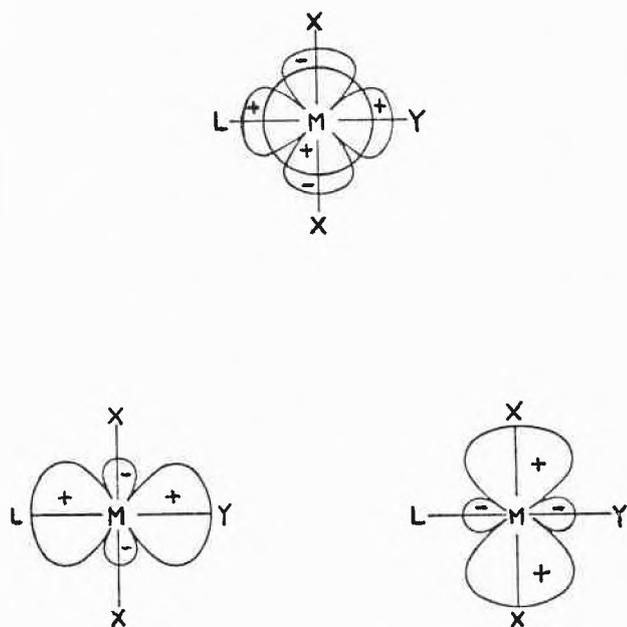


Fig. 5: Directional properties of s-d-hybrids

In an attempt to gain more information about the applicability of the "selective hybridization" idea outlined above Pregosin et al. [18], conducted a similar study on complexes containing ligands which could not form  $\pi$ -bonds, i.e., primary amines.

As mentioned earlier, nitrogen-15 has  $I = 1/2$  but suffers from low "nuclear" relative sensitivity and very low natural abundance (see Table 1). Therefore, for this study the complexes containing 96% nitrogen-15 enriched n-dodecylamine, am, were chosen. The complexes cis- and trans- $[\text{PtX}_2(\text{am})_2]$  as well as  $[\text{PtX}(\text{am})_3]\text{X}$

Table 7:  $^1|J_{195\text{Pt}-15\text{N}}|$  Coupling constants in some platinum complexes of n-dodecylamine (am)

Complex	$J$ (Hz)	$J_{\text{cis}}/J_{\text{trans}}$
cis- $[\text{PtBr}_2(\text{am})_2]$	334	1.20
trans- $[\text{PtBr}_2(\text{am})_2]$	279	
$[\text{PtBr}(\text{am})_3]\text{Br}$	242 <sup>1</sup> 288 <sup>2</sup>	1.19

<sup>1</sup> For the nitrogen atom in trans-position to bromine.

<sup>2</sup> For the nitrogen atoms in trans-positions to each other.

(X = Cl and Br) were prepared and their spectra recorded. Some of the data collected are presented in Table 7. For the interpretation of  $^1|J_{195\text{Pt}-15\text{N}}|$  an expression analogous to that used for the phosphorus study was used. The usual checks about the applicability of this expression were made and, as in the case of the phosphorus work, it could be shown that, within the framework of this approximation, the dominant contribution appeared to come from the  $\alpha^2_{\text{Pt}}$ -term.

As can be seen from the data in Table 7,  $J_{\text{Pt}-\text{N}}(\text{cis}) > J_{\text{Pt}-\text{N}}(\text{trans})$  and it was concluded that, also in the case of the nitrogen complexes, the hybrid used by platinum to bind to that nitrogen with a halogen atom in trans-position has a greater s-character than that of the platinum hybrid used to bind to a nitrogen having another nitrogen atom in trans-position. In other words, as found for the corresponding phosphine complexes, cis-trans-isomerization in complexes  $[\text{PtX}_2(\text{am})_2]$  is accompanied by a significant amount of re-hybridization which, in this case, can only be attributed to  $\sigma$ -effects. The ratio  $J_{\text{cis}}/J_{\text{trans}}$  in the amine complexes is 1.2 (see Table 7) as compared with 1.5 in the phosphine complexes. [16] This, however, cannot be taken as an indication that the extent of the re-hybridization is smaller in the amine complexes because of the nature of the equations used to interpret the results. Thus, while our nitrogen-15 study provides evidence which supports the "selective hybridization" hypothesis, it does not answer the question whether the observed changes in  $J_{\text{Pt}-\text{P}}$  are due, at least in part, to the indirect operation of  $\pi$ -bonding effects.

#### Future Developments

It is clear that the greater availability of nmr spectrometers operating in the Fourier mode will widely extend the range of structural applications of all types. We are also likely to see rapid development in the use

of metal-resonances for "analytical" and dynamic applications. An example of a nucleus which will receive increasing attention is platinum-195. This isotope has very reasonable nmr characteristics (see Table 2) and the very extensive coordination chemistry of the element will benefit greatly from the direct observation of resonances for this nucleus. Our present knowledge of the nmr parameters of platinum compounds shows many interesting and valuable features, e.g., the range of chemical shifts observed to date encompasses ca. 15.000 ppm as can be seen from

Table 8: Some  $^{195}\text{Pt}$  NMR chemical shifts (in ppm)

Compound	$\delta_{\text{Pt}}$	Ref.
$\text{K}_2[\text{PtF}_6]$	-7326	[19]
$\text{Na}_2[\text{PtCl}_6]$	0	[20]
$[\text{PtBr}_2(\text{RNH}_2)_4]\text{Br}_2^1$	793	[5]
$\text{Na}_2[\text{PtCl}_4]^2$	1647	[20, 21]
trans- $[\text{PtBr}_2(\text{RNH}_2)_2]^1$	2485	[5]
cis- $[\text{PtBr}_2(\text{RNH}_2)_2]^1$	2544	[5]
trans- $[\text{PtCl}_2(\text{Pr}_3\text{P})_2]$	3727	[22]
cis- $[\text{PtCl}_2(\text{Pr}_3\text{P})_2]$	4344	[22]
$\text{Na}_2[\text{Pt}(\text{CN})_4]$	4770	[20]
$\text{H}_2[\text{PtI}_6]$	6300	[20]

<sup>1</sup> R = *n*-C<sub>12</sub>H<sub>24</sub>.

<sup>2</sup>  $\delta$  for this compound is concentration-dependent [19] and this value refers to ca. 2 M H<sub>2</sub>O-solutions.

Table 8. Furthermore, it has also become apparent that its nmr parameters are very sensitive to changes of chemical and, in some types of complexes, even physical environment [21] and thus platinum-195 nmr will provide a very sensitive probe for the study of the coordination chemistry of this element. Similar considerations will apply to the direct observation of resonances due to silicon-29, cadmium-113, tin-117, mercury-199 and thallium-205.

We are also likely to see an increasing amount of work based on the observation of quadrupolar nuclei. Mention has already been made of some early work on nitrogen-14. The use of "Fourier-spectrometers" will widely extend the range of applications. The observation of resonances due to oxygen-17 is also likely to become more common. Both of these nuclei have small nuclear quadrupoles and thus, while they give broad resonances, these are still chemically useful. The limits of the solution studies on quadrupolar nuclei can be clearly seen from some recent nmr studies of arsenic-75 compounds. Here, broad but observable resonances are obtained only for very symmetrical species, e.g.  $[\text{AsF}_6]^-$ ,  $[\text{As}(\text{C}_2\text{H}_5)_4]^+$ ,  $[\text{AsO}_4]^{3-}$  etc. [23]

Lastly, further extension of the use of the nmr technique will come from instrumental advance. The availability of spectrometers using increasingly higher fields is unlikely to be of major benefit to the coordination chemist interested in "heavy nuclei". Fields of 90-100

MHz are sufficient to resolve most of the resonances in which he is interested. More useful, however, will be the availability of spectrometers using larger sample tubes, e.g. that recently produced by Bruker-Spectrospin, working at a field of 180 MHz, which takes 30 mm-diameter tubes! This is the "dream" instrument of coordination chemists. For most of us, however, it will remain a dream because in addition to the substantial cost of the spectrometer and its recurrent expenditure for liquid helium, it will need vast-amounts of very high-quality deuterated solvents!

Dreams apart there is still a vast amount of most interesting chemistry that can be done with the present generation of spectrometers.

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## References

- 1 J. W. Emsley, J. Feeney and L. H. Sutcliffe: "High Resolution Nuclear Magnetic Resonance", Pergamon Press, Oxford 1965, Vol. 1.
- 2 "NMR of Paramagnetic Molecules: Principles and Applications", Eds. G. N. La Mar, W. de W. Horrocks, Jr., and R. H. Holm, Academic Press, New York 1973.
- 3 L. M. Venanzi: *Angew. Chem.* 76 (1964) 621; *Angew. Chem. Internat. Edit.* 3 (1964) 453.
- 4 J. W. Dawson and L. M. Venanzi: *J. Amer. Chem. Soc.* 90 (1968) 7229.
- 5 P. S. Pregosin and L. M. Venanzi: unpublished observation.
- 6 R. J. Mynott, P. S. Pregosin and L. M. Venanzi: *J. Coord. Chem.* 3 (1973) 145.
- 7 S. O. Grim and D. A. Wheatland: *Inorg. Chem.* 8 (1969) 1716.
- 8 J. Chatt, L. M. Vallarino and L. M. Venanzi: *J. Chem. Soc.* (1957) 3413.
- 9 P. M. Maitlis: "The Organic Chemistry of Palladium", Academic Press 1971, see Chapter V.
- 10 B. E. Mann: *Adv. Organomet. Chem.* 12 (1974) 135.
- 11 J. W. Emsley, J. Feeney and L. H. Sutcliffe: "High Resolution Nuclear Magnetic Resonance Spectroscopy", Pergamon Press, Oxford 1966, Vol. 2, Chapter 12.
- 12 O. W. Howarth, R. E. Richards and L. M. Venanzi: *J. Chem. Soc.* (1964) 3335.
- 13 M. Maier, F. Basolo and R. G. Pearson: *Inorg. Chem.* 8 (1969) 795.
- 14 J. S. Bradley: D. Phil. Thesis, Oxford 1971.
- 15 J. P. Day, F. Basolo and R. G. Pearson: *J. Amer. Chem. Soc.* 90 (1968) 6927.
- 16 A. Pidcock, R. E. Richards and L. M. Venanzi: *J. Chem. Soc. (A)* (1966) 1707.
- 17 Y. K. Syrkin: *Bull. Acad. Sci. U.S.S.R., Classe sci. chim.* (1948) 69.
- 18 P. S. Pregosin, H. Omura and L. M. Venanzi: *J. Amer. Chem. Soc.* 94 (1972) 2979.
- 19 R. J. Goodfellow et al.: private communication.
- 20 A. v. Zelewski: *Helv. Chim. Acta* 51 (1968) 803.
- 21 W. Freeman, P. S. Pregosin, S. N. Sze and L. M. Venanzi: *J. Mag. Res.*, in press.
- 22 A. Pidcock, R. E. Richards and L. M. Venanzi: *J. Chem. Soc. (A)* (1968) 1970.
- 23 G. Balimann, P. S. Pregosin and L. M. Venanzi: unpublished observations.