

# 8 Answers to Exercises

## 8.1 Chapter 1 exercises

### Workflow

- Identify the NMR active nuclei.
- Divide these into groups based on chemical equivalence.
- Everything that follows will be based on these groups of spins.
- Predict the number of chemical shifts expected in each spectrum.
- Identify the neighbouring groups and predict the splitting each group will cause based on the spins contained in the group.
- Construct a stick diagram to show the result.

**Q. 1.1** In this exercise we will predict the appearance of some NMR spectra knowing only the spins present. **A**, **B** and **C** have spin  $\frac{1}{2}$ . **X** has spin 1 and **Y** spin  $\frac{3}{2}$ . Assume that all groups of spins couple to all other groups of spins present.

- Draw stick diagrams to represent the coupling patterns at **A** in the following spin systems:

### Answers

**AC<sub>2</sub>** One neighbouring group (**C**) containing two spin  $\frac{1}{2}$  so causes 1:2:1 triplet splitting of **A**

**AB<sub>3</sub>** One neighbouring group (**B**) containing three spin  $\frac{1}{2}$  so causes 1:3:3:1 quartet splitting of **A**

**AB<sub>2</sub>X** Two neighbouring groups: **B** contains two spin  $\frac{1}{2}$  so causes 1:2:1 triplet splitting of **A**; **X** contains one spin 1 so causes a further 1:1:1 triplet splitting of **A**.

**AB<sub>2</sub>XY** Three neighbouring groups: **B** contains two spin  $\frac{1}{2}$  so causes 1:2:1 triplet splitting of **A**; **X** contains one spin 1 so causes a further 1:1:1 triplet splitting of **A**; **Y** contains one spin  $\frac{3}{2}$  so causes a further 1:1:1:1 quartet triplet splitting of **A**.

b. What will the coupling pattern at **X** be in **AB<sub>2</sub>X**? At **Y** in **AB<sub>2</sub>XY**?

### Answers

**X** in **AB<sub>2</sub>X** Two neighbouring groups: **A** contains one spin  $\frac{1}{2}$  so causes 1:1 doublet splitting of **X**; **B** contains two spin  $\frac{1}{2}$  so causes a further 1:2:1 triplet splitting of **X**

**Y** in **AB<sub>2</sub>XY** Three neighbouring groups: **A** contains one spin  $\frac{1}{2}$  so causes 1:1 doublet splitting of **Y**; **B** contains two spin  $\frac{1}{2}$  so causes a further 1:2:1 triplet splitting of **Y**; **X** contains one spin 1 so causes a further 1:1:1 triplet splitting of **Y**.

**Q. 1.2** For each of the compounds below:

- a. Identify ALL NMR active nuclei.
- b. If a nucleus is not 100 % abundant, indicate the natural abundance and show the satellites, except for  $^{13}\text{C}$ , in your answers.
- c. Where quadrupolar nuclei occur, indicate their presence.
- d. Group the nuclei you have identified according to the NMR equivalence and hence decide on the number of chemical shifts that will be found in each nucleus's NMR spectrum.
- e. Draw stick diagrams for the elements specified to indicate where coupling will occur and the splittings that result.

**NB** In practice the resonances of, and couplings to, quadrupolar nuclei are often not seen. You should ignore quadrupolar nuclei in the rest of this exercise unless you are explicitly asked to comment on them.

**NB** The NMR spectra of phenyl rings in phosphine ligands are usually complex. You may ignore the phenyl rings in the rest of this exercise. NMR active nuclei are indicated in bold

### Answers

$^{35/37}\text{Cl}$  are quadrupolar so ignored

Groups are indicated by superscripted labels,

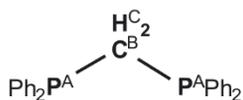
4 *Answers*

Each group gives rise to a chemical shift

Coupling occurs between groups not within groups

The intensity of a line in a satellite doublet is  $\frac{1}{2}$  x natural abundance x the number of equivalent sites in the group causing the satellite (in these examples this is 1) - the intensity is divided between the two lines of the doublet satellite.

Fig. 8.1 Answers to question 1.2

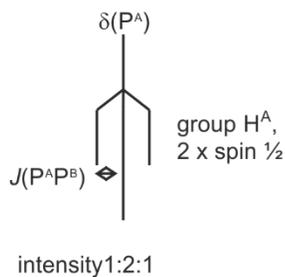


bis-diphenylphosphinomethane

$^{31}\text{P}$  1 chemical shift

$^1\text{H}$  1 chemical shift

$^{13}\text{C}$  1 chemical shift, 1%



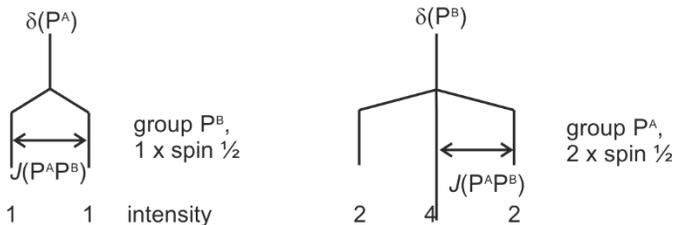
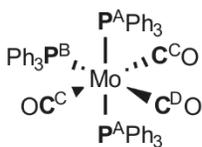
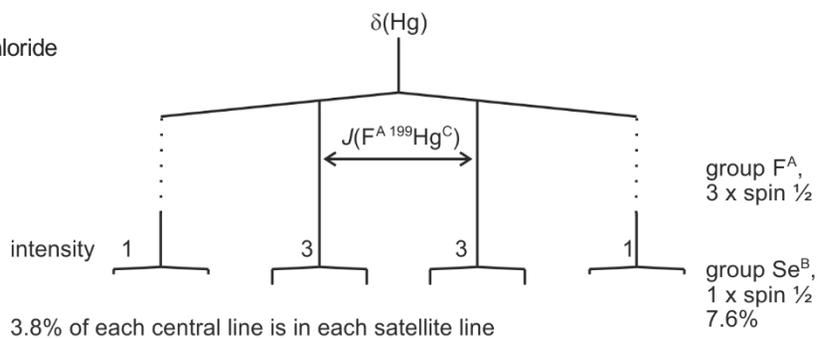
trifluoromethylselenomercuric chloride

$^{19}\text{F}$  1 chemical shift

$^{199}\text{Hg}$  1 chemical shift 16.84%

$^{77}\text{Se}$  1 chemical shift, 7.6%

$^{13}\text{C}$  1 chemical shift, 1.1%

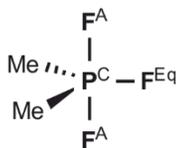


*mer-tris-triphenylphosphinemolybdenumtricarboxyl*

$^{31}\text{P}$  2 chemical shifts

$^{13}\text{C}$  2 chemical shifts, 1%

6 Answers

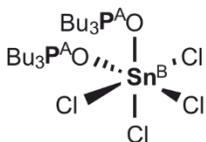
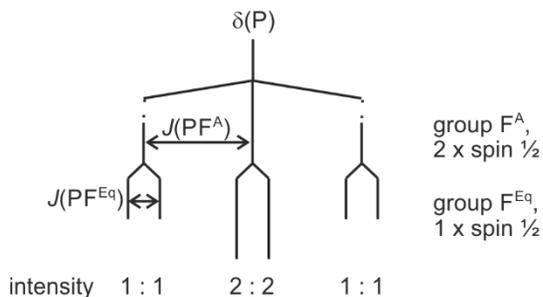


dimethylphosphorotrifluoride

Exclude the methyl groups

$^{19}\text{F}$  2 chemical shifts

$^{31}\text{P}$  1 chemical shift



*cis-bis*-tributylphosphineoxidetinchloride

Exclude the butyl groups

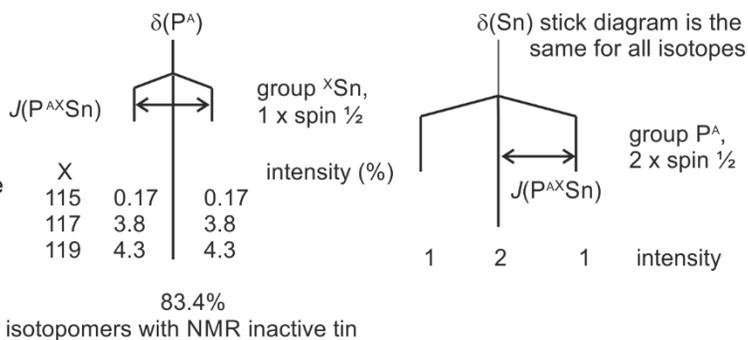
$^{115}\text{Sn}$  1 chemical shift, 0.34%

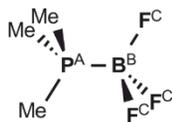
$^{117}\text{Sn}$  1 chemical shift, 7.68%

$^{119}\text{Sn}$  1 chemical shift, 8.59%

$^{31}\text{P}$  1 chemical shift

Quadrupolar  $^{17}\text{O}$  and  $^{35/37}\text{Cl}$





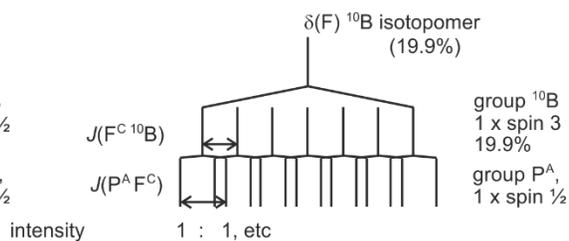
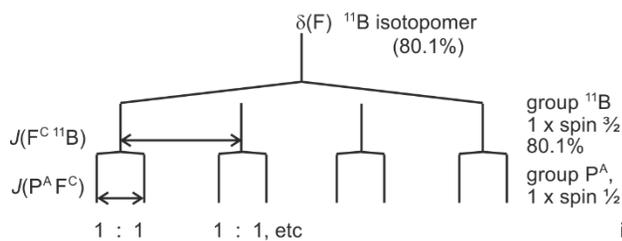
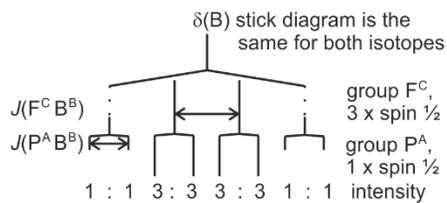
$\text{Me}_3\text{P.BF}_3$

$^{10}\text{B}$  1 chemical shift, 19.9%

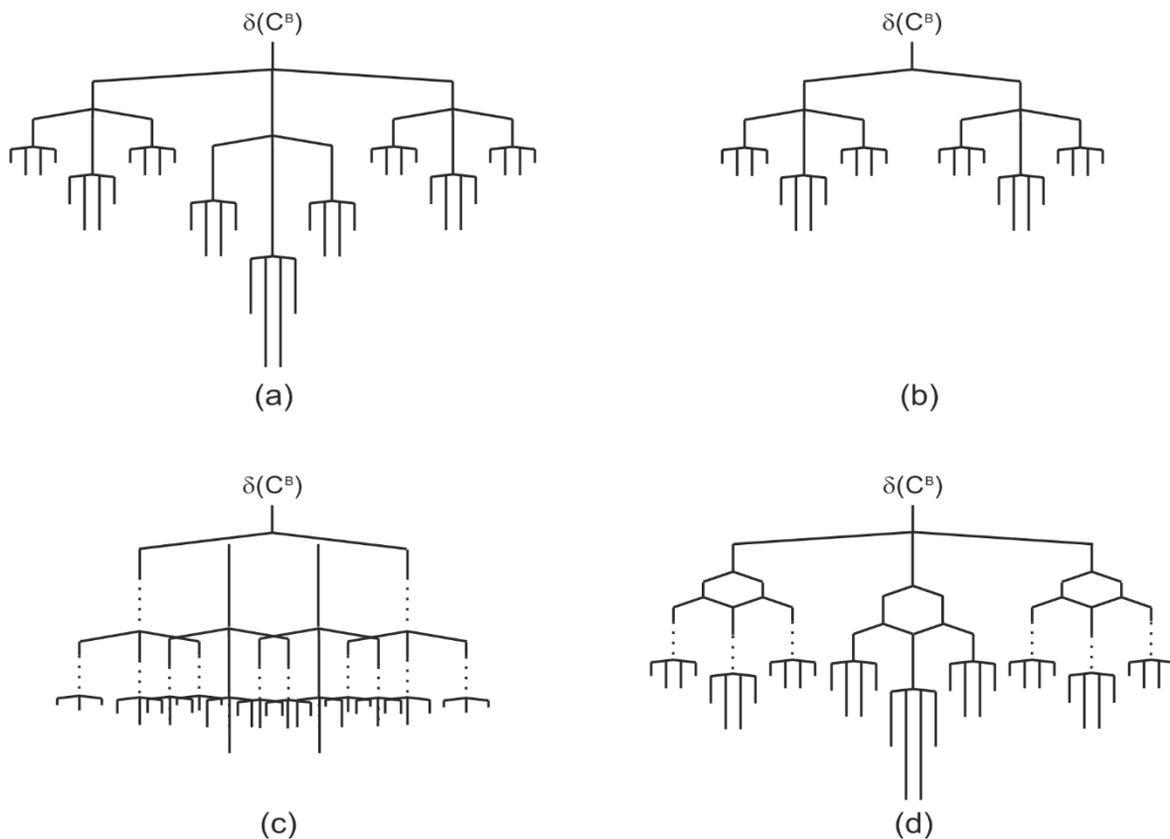
$^{11}\text{B}$  1 chemical shift, 80.1%

$^{19}\text{F}$  1 chemical shift

$^{31}\text{P}$  1 chemical shift



**Q. 1.3** Each group of neighbouring coupling spins should be represented by its own layer in the stick diagram; the order in which groups are considered is not important and the horizontal separation of lines in a layer does not need to reflect accurately the size of the coupling constant.



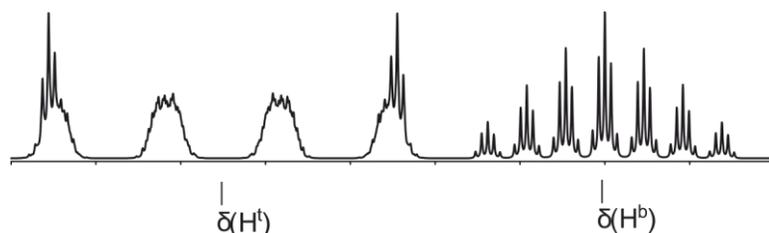
**Fig. 8. 2** Stick diagrams for question 1.3

**Answer**

The three *groups*, CF<sub>3</sub>, CF<sub>2</sub>, and the second CF<sub>2</sub> should be represented as separate layers in the stick diagrams as in figures (a), (b) and (c)

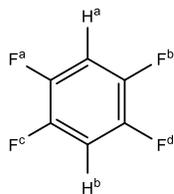
- and (c) correctly show the CF<sub>3</sub> and two CF<sub>2</sub> groups giving a 1:3:3:1 quartet, and two 1:2:1 triplet patterns respectively. The order in which the coupling groups are shown is not important, neither is the magnitude of the “coupling” used, although (a) shows the structure more clearly by choosing separations that avoid overlaps.
- incorrectly shows a doublet of triplets of quartets.
- does not accurately represent the groups of spins present but shows coupling to four neighbouring groups, CF<sub>3</sub>, CF<sub>2</sub>, and two CF groups as a result of misrepresenting one of the CF<sub>2</sub> groups as two CF groups having the same coupling constant. Although the splitting pattern that results is “the same” the important and useful information that the triplet arises from a neighbouring group containing two equivalent spin ½ nuclei is obscured.

Although not shown in figure 8.1, it is good practice to indicate the coupling groups responsible for each layer down the side of the stick diagram – see answer to Q1.2 above.



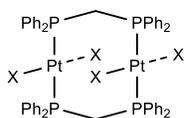
**Fig. 8.3** <sup>1</sup>H NMR spectrum of <sup>11</sup>B<sub>2</sub>H<sub>6</sub>. The complexity is a result not only of coupling to the quadrupolar nucleus <sup>11</sup>B but also to the magnetic inequivalence of the terminal protons and borons resulting in a second order pattern

**Q. 1.4** Identify which of the following molecules will show second order NMR spectra.



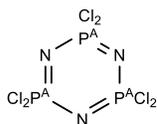
1,2,4,5-tetrafluorobenzene

Fluorines are chemically equivalent but magnetically inequivalent, e.g.  $F^a$  sees the chemically equivalent protons  $H^a$  and  $H^b$  differently. Second order



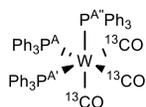
X = acetylide

As above, the phosphoruses are chemically equivalent but magnetically inequivalent, they couple differently to the directly bonded and remote  $^{195}\text{Pt}$  centres. Second order



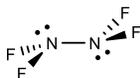
hexachlorotriphosphazene

Coupling to quadrupolar chlorine and  $^{14}\text{N}$  can be ignored. Phosphoruses are chemically and magnetically equivalent. First order



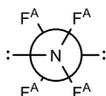
*fac*-tris-triphenylphosphine-molybdenum tris( $^{13}\text{C}$ -carbonyl)

Phosphoruses are chemically equivalent.  $^{13}\text{CO}$  ligands are chemically equivalent. Each phosphorus "sees" one  $^{13}\text{CO}$  trans but the other two cis. Phosphoruses are chemically equivalent but magnetically inequivalent,  $^{13}\text{CO}$  are chemically equivalent but magnetically inequivalent. Second order



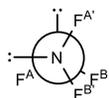
Trans isomer

All the fluorines are chemically equivalent and (if we neglect the quadrupolar  $^{14}\text{N}$ ) do not couple to any other group so are magnetically equivalent. Compare with the proton NMR spectrum of ethene. First order

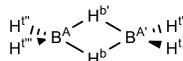


Gauche isomer

$F^A$  and  $F^{A'}$  are chemically equivalent but couple differently to  $F^B$  and  $F^{B'}$ .  $F^A$  has a geminal coupling to  $F^B$   $2J(\text{FAFB})$  but a vicinal coupling to  $F^{B'}$ ,  $3J(\text{FAFB}')$ .  $F^A$  and  $F^{A'}$  are magnetically inequivalent. Second order



tetrafluorohydrazine

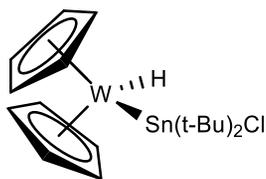


diborane

Borons are chemically equivalent,  $H^a$  are chemically equivalent,  $H^b$  are chemically equivalent. Consider  $H^a$ . This has a one bond coupling to  $B^{A'}$  but a three bond coupling to  $B^A$ ;  $H^a$  to  $H^{a'}$  are magnetically inequivalent as are  $B^A$  and  $B^{A'}$ . Second order

&lt;Unnumbered Chemdraw 8.1&gt;

**Q. 1.5** Write down a stick diagram that represents the couplings present in the  $^1\text{H}$  NMR spectrum of  $[\text{Cp}_2\text{W}(\text{H})(\text{SnCl}(\text{t-Bu})_2)]$ , hydride region only. Exclude coupling to the Cp rings.

**Answer**

The hydride ligand will couple to tin and tungsten, figure 8.4.

&lt;Unnumbered Chemdraw 8.2&gt;

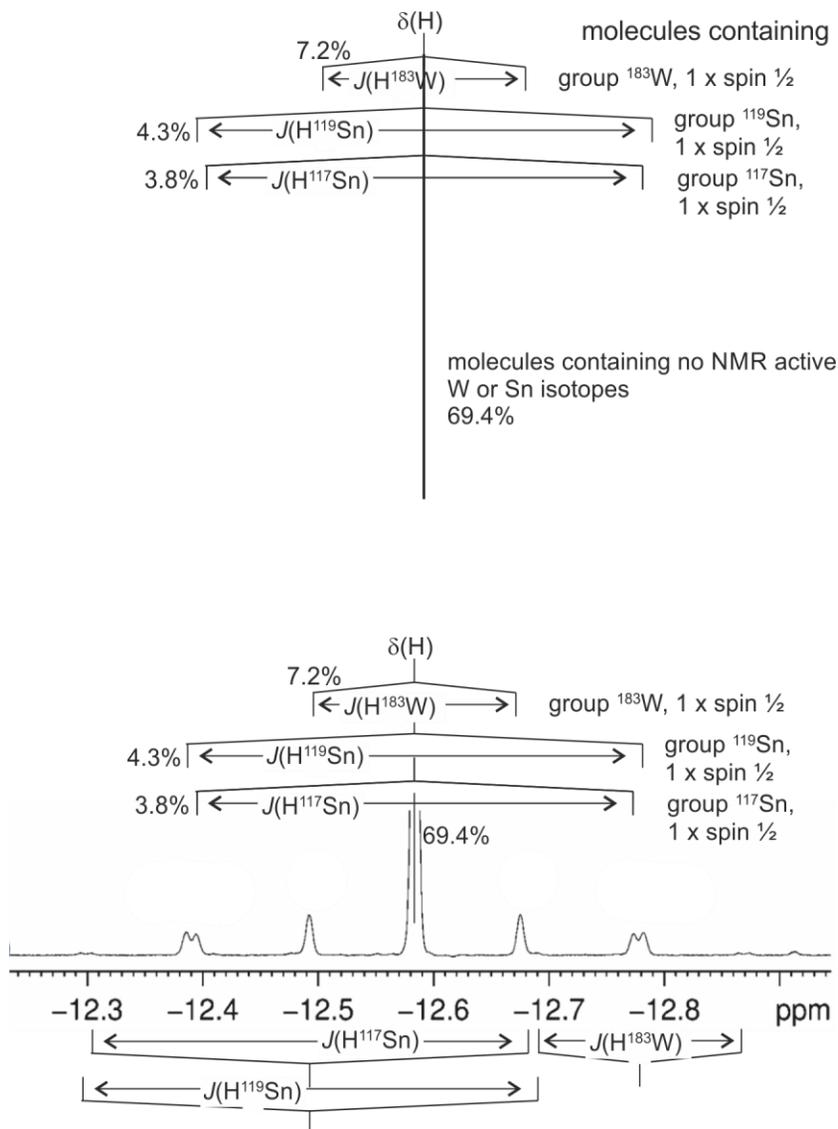
$^{183}\text{W}$  is spin  $\frac{1}{2}$ , 14.4% abundant so will give satellite peaks, a doublet of total intensity 14.4%, i.e. each peak in the doublet will have intensity 7.2%.

Tin has two isotopes of sufficient abundance to give clearly visible satellites  $^{117}\text{Sn}$  (7.6%) and  $^{119}\text{Sn}$  (8.6%), there will be two sets of tin satellites. Both  $^{117}\text{Sn}$  and  $^{119}\text{Sn}$  are spin  $\frac{1}{2}$  so both sets of satellites will be doublets.

The lines in the  $^{117}\text{Sn}$  satellites will have intensity  $7.6/2 = 3.8\%$  and in the  $^{119}\text{Sn}$  satellites 4.3%. The unsplit central line will have intensity  $100 - 14.4 - 7.6 - 8.6 = 69.4\%$ .

Isotopologues containing NMR active tin and tungsten will give satellites on the satellites of very low intensity, e.g.  $(14.4 \times 8.6)/2 = 0.6\%$ . These can just be seen in the

experimental spectrum and are indicated by a stick diagram below the experimental spectrum.



**Fig. 8. 4** Assignment of the  $^1\text{H}$  NMR spectrum of  $[\text{Cp}_2\text{W}(\text{H})(\text{SnCl}(\text{t-Bu})_2)]$ . Experimental spectrum reproduced from Mobley, T. A., *et al.*, *Magn. Reson. Chem.*, 2010, **48**, 787–792. doi:10.1002/mrc.2663, Copyright © John Wiley & Sons.

## 8.2 Chapter 2 exercises

**Q. 2.1** The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of the dimeric phosphinidene  $\{\text{M}(\mu\text{-PAr})\}_2$  **1**, **2**, **3** and the  $^{207}\text{Pb}\{^1\text{H}\}$  spectrum of **2** are shown in figure 2.9. Account for the all couplings observed. Suggest a reason for the inability to observe the  $^{73}\text{Ge}$  NMR spectrum.

### Answers

**$\{\text{Ge}(\mu\text{-PAr})\}_2$**  One symmetrical pattern is seen in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum, i.e. one phosphorus chemical shift so one type of P is present. The resonance is a singlet with satellites due to coupling to  $^{73}\text{Ge}$ , abundance 7.76%,  $I = 9/2$ . The satellites are a 1:1:1: etc decet indicating each P couples to only one  $^{73}\text{Ge}$ . The intensity of each line in the decet is  $7.76/10 = 0.776\%$  of the total intensity, or ca. 0.84% of the central line. Coupling to only one  $^{73}\text{Ge}$  is expected, the chances of both germanium atoms in the molecule being  $^{73}\text{Ge}$  is  $0.0776 \times 0.0776$  or 1 in six thousand. These resonances will be too weak to be seen in the spectrum.

The  $^{73}\text{Ge}$  spectrum cannot be observed due to the large quadrupole moment of  $^{73}\text{Ge}$  and low natural abundance.  $^{73}\text{Ge}$  NMR resonances are expected to be very low intensity compounded by being very broad due to efficient relaxation causing large Heisenberg broadening at the low symmetry Ge site.

**{Sn( $\mu$ -PAr)}<sub>2</sub>** One symmetrical pattern is seen in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum, i.e. one phosphorus chemical shift so one type of P is present. The resonance is a singlet with satellites due to coupling to  $^{117}\text{Sn}$  and  $^{119}\text{Sn}$ , abundance 7.68% and 8.59%,  $I = \frac{1}{2}$ . Satellites due to  $^{115}\text{Sn}$  are too weak to be observed. The satellites are a 1:1 doublets indicating each P couples to only one  $^{11x}\text{Sn}$ . The intensity of each line in the doublets is ca.  $8/2 = 4\%$  of the total intensity, or ca. 5% of the central line. Coupling to only one  $^{11x}\text{Sn}$  is expected, the chances of both tin atoms in the molecule being  $^{11x}\text{Sn}$  is ca.  $0.0768 \times 0.0859$  or around 1 in six thousand. These resonances will be too weak to be seen in the spectrum.

One symmetrical pattern is seen in the  $^{119}\text{Sn}\{^1\text{H}\}$  NMR spectrum, i.e. one tin chemical shift so one type of Sn is present. The resonance is a triplet indicating the tin couples to two equivalent phosphorus centres. Satellites due to coupling to  $^{117}\text{Sn}$  are not seen due to the low abundance of the isotopologue containing  $^{119}\text{Sn}$  at one site and  $^{117}\text{Sn}$  at the other. If both tin nuclei are  $^{119}\text{Sn}$  then the tins are equivalent so do not couple.

**{Pb( $\mu$ -PAr)}<sub>2</sub>** One symmetrical pattern is seen in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum, i.e. one phosphorus chemical shift so one type of P is present. The resonance is a singlet with two sets of satellites due to coupling to  $^{207}\text{Pb}$ , abundance 22.1%,  $I = 1/2$ . The more intense satellites are a 1:1 doublet indicating each P couples to only one  $^{207}\text{Pb}$ . The intensity of each line in the doublet is ca.  $22/2 = 11\%$  of the total intensity, or ca. 14% of the central line. The weaker satellites are due to the isotopologue in which both leads are  $^{207}\text{Pb}$ ,

abundance ca.  $0.22 \times 0.22$  or around 5 in a hundred. The satellites due to this isotopologue will be a triplet (2 equivalent  $I = \frac{1}{2}$  neighbours). The outer lines of the triplet can just be seen, the central line is underneath the main peak in the spectrum.

One symmetrical pattern is seen in the  $^{207}\text{Pb}\{^1\text{H}\}$  NMR spectrum, i.e. one lead chemical shift so one type of lead is present. The resonance is a triplet indicating the lead couples to two equivalent phosphorus centres. If both leads are  $^{207}\text{Pb}$  the two leads are equivalent so do not couple. No satellite peaks are present.

**Q. 2.2** Reaction of  $[\text{PtH}(\text{dtbpx})(\text{MeOH})][\text{OTf}]_2$  **A** with  $^{13}\text{CO}$  affords **B**. The NMR data for **A** and **B** are given in Table 2.1. The  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra are shown in Figs. 8.6 and 8.7.

**Table 8.1 Selected NMR data for the complexes**

	$\delta/\text{ppm}^{\text{a}}$	$J(\text{P}^1\text{-})$	$J(\text{P}^2\text{-})$	$J(\text{Pt-}^{\text{b}})$
Compound				
<b>A</b>				
P <sup>1</sup>	46.2 d	-	6	4312
P <sup>2</sup>	34.6 d	6	-	2095
H	-7.3 dd	18	176	805
Compound				
<b>B</b>				
P <sup>1</sup>	42.2 dd	-	19	2958
P <sup>2</sup>	33.2 dd	19	-	2011
H <sup>c</sup>	-4.2 ddd	15	145	740
CO	179.3 dd	113	8	1299

<sup>a</sup> All spectra recorded with  $^1\text{H}$  decoupling, where given couplings to  $^1\text{H}$  were determined from the  $^1\text{H}$  NMR spectrum. <sup>b</sup>  $^{195}\text{Pt}$  satellites are seen on all resonances. <sup>c</sup>  $J(\text{HC})$  not determined. d = doublet.

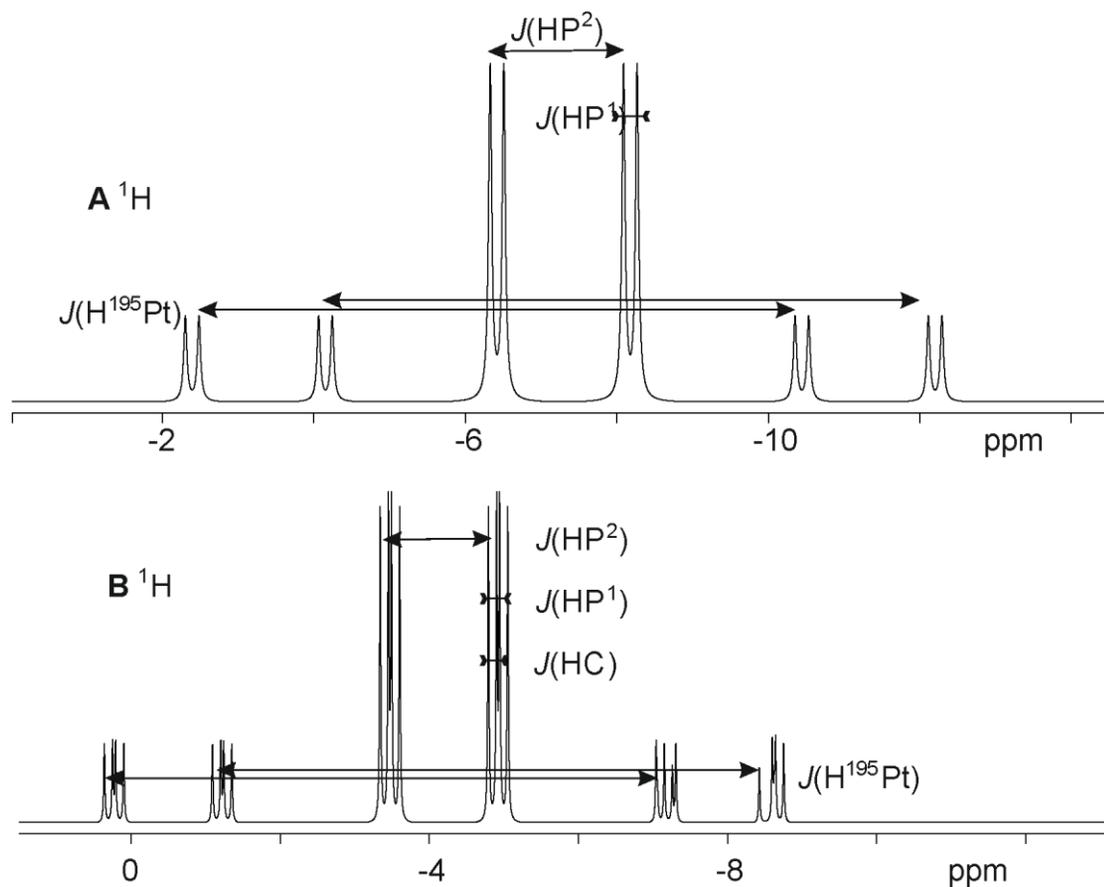
- a. Use the fact that first order coupled multiplets are symmetrical to assign the  $^{195}\text{Pt}$  satellites to their corresponding central peaks in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra in figure 2.10
- b. Use the magnitudes of the various coupling constants to determine the stereochemistry around the Pt centre.
- c. Suggest a reason for the roofing observed in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **B**.

### Answers, figures 8.5 and 8.6

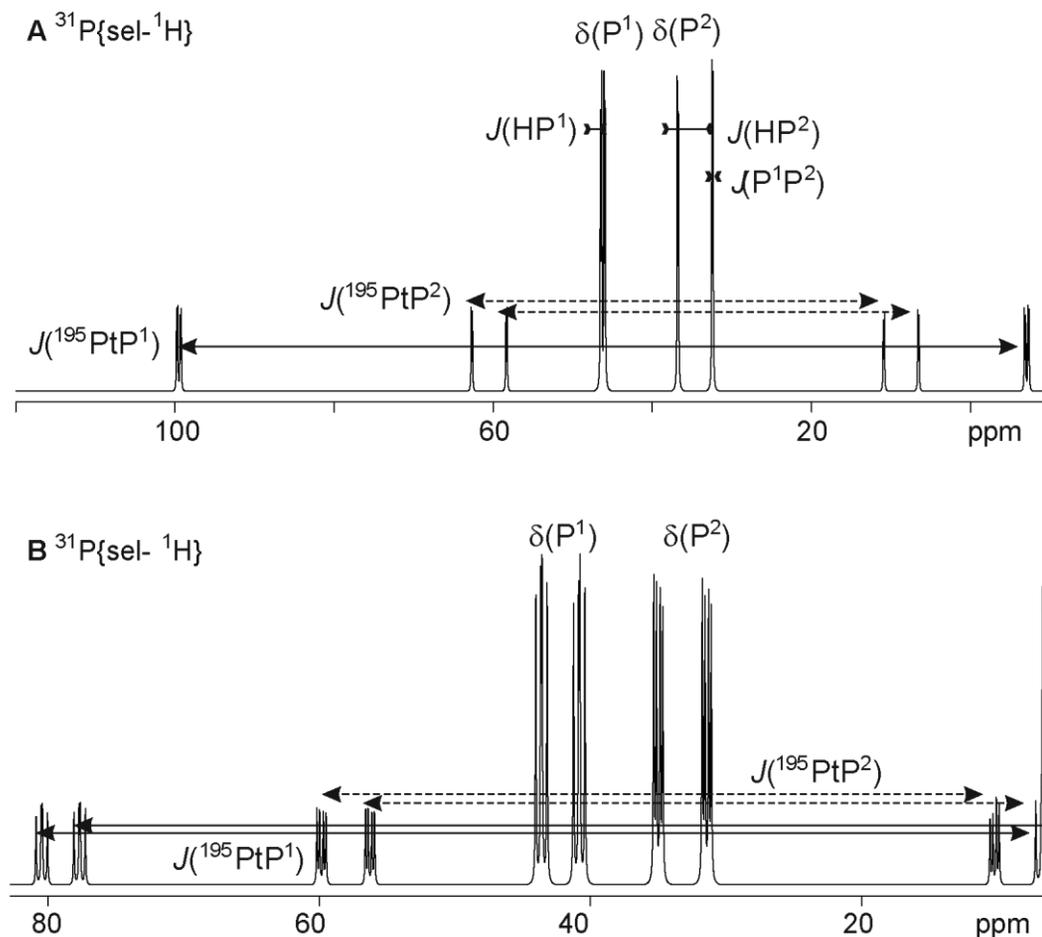
*Trans* couplings are larger than *cis* couplings. The H is *cis* to  $\text{P}^1$  and *trans* to  $\text{P}^2$  in both A and B. The CO is *trans* to  $\text{P}^1$  and *cis* to  $\text{P}^2$  in B.

Roofing indicates the onset of second order effects and is seen when two coupled nuclei have very similar chemical shifts, the difference in shifts being comparable to the coupling constant.

Coupling to  $^1\text{H}$  is not seen in the  $^{13}\text{C}\{^1\text{H}\}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra due to proton decoupling.



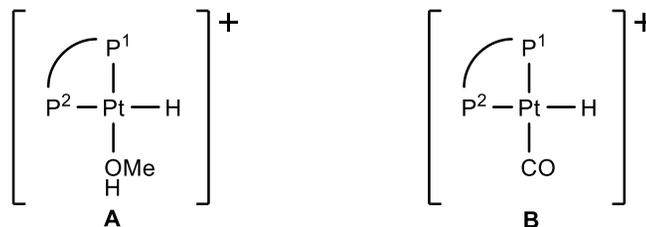
**Fig. 8.5**  $^1\text{H}$  NMR spectra of compounds **A**, and **B** showing the assignment of the  $^{195}\text{Pt}$  satellites. Solid and dotted lines are used to indicate two branches of the same set of satellites.



**Fig. 8.6**  $^{31}\text{P}\{\text{sel-}^1\text{H}\}$  NMR spectra of compounds **A**, and **B** showing the assignment of the  $^{195}\text{Pt}$  satellites. Solid and dotted lines are used to indicate two branches of the same set of satellites. Selective proton decoupling has been used to remove couplings to phenyl protons. The aromatic region of the  $^1\text{H}$  NMR spectra are not shown. A slight second order distortion can be seen in the upfield satellites of the  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of **B**. The latter also contains accidental overlapping of lines the upfield satellites of the two different phosphoruses in **B**.

**Q. 2.3** Advanced question.

Interpret fully the spectra in Figs. Answers Q2.1&2 and Table 2.1 and hence confirm the identities of **A** and **B**.



< Unnumbered Chemdraw 8.3 >

**Answer****Compound A**

**$^1\text{H}$  NMR spectrum.** One resonance is seen in the metal hydride region, i.e. one hydride chemical shift, so one type of hydride ligand is present. The splitting pattern is a doublet of doublets with doublet satellites due to coupling to  $^{195}\text{Pt}$ , so the hydride has two neighbouring groups in addition to platinum. The doublet splittings assigned to  $J(\text{PH})$  in the table tells us there is one  $\text{P}^1$  and one  $\text{P}^2$  in the compound while the doublet splitting of the satellites tells us there is one Pt. The coupling of 176 Hz assigned to  $J(\text{P}^2\text{H})$  is much larger than that assigned to  $J(\text{P}^1\text{H})$  (18 Hz) so  $\text{P}^2$  is *trans* to the hydride and  $\text{P}^1$  is *cis*,

$$J_{\text{trans}} \gg J_{\text{cis}}$$

**$^{31}\text{P}\{^1\text{H}\}$  NMR spectrum.** Two resonances are seen, i.e. two phosphorus chemical shifts, so two types of phosphorus are present. The resonances are doublets with satellites due to coupling to  $^{195}\text{Pt}$ , so each has one neighbouring group in addition to platinum. A coupling of 6 Hz appears in both doublets so is  $J(\text{P}^1\text{P}^2)$ . The doublet splitting tells us there is one  $\text{P}^1$  and one  $\text{P}^2$  in the compound. We are told the  $^{195}\text{Pt}$  satellites are doublets, so one Pt is present confirming our deductions from the  $^1\text{H}$  NMR spectrum.  $^1J(\text{P}^1\text{Pt}) \gg ^1J(\text{P}^2\text{Pt})$  indicating a low *trans* influence ligand (MeOH) is *trans* to  $\text{P}^1$  and a high *trans* influence ligand (hydride) is *trans* to  $\text{P}^2$  consistent with our assignment from the proton NMR spectrum.

Chemical common sense tells us that there can only be one hydride present in the complex; Pt(II),  $d^8$  ion so we expect a square planar complex. The ligands *trans* to each phosphorus must be different since the Ps are different, so cannot both be H. We are given the molecular formula of **A** which confirms our assignment of the spectra. Analysis of the coupling constants allows unequivocal assignment of the stereochemistry.

### Compound B

**$^{13}\text{C}\{^1\text{H}\}$  NMR spectrum.** One resonance is seen in the metal carbonyl region, i.e. one carbon chemical shifts, so one type of carbonyl ligand is present. The splitting pattern is a doublet of doublets with doublet satellites due to coupling to  $^{195}\text{Pt}$ , so the CO has two neighbouring groups, each containing one spin  $\frac{1}{2}$  nucleus in addition to the group containing one platinum. Matching the coupling constants tells us these are  $\text{P}^1$  and  $\text{P}^2$ . The doublet splittings tells us there is one  $\text{P}^1$ , one  $\text{P}^2$  and one Pt in the compound. The

coupling of 113 Hz is assigned to  $J(\text{P}^1\text{C})$  and of 8 Hz to  $J(\text{P}^2\text{C})$  so  $\text{P}^1$  is *trans* to the CO and  $\text{P}^2$  is *cis* –  $J_{\text{trans}} \gg J_{\text{cis}}$ .

**$^{31}\text{P}\{^1\text{H}\}$  NMR spectrum.** Proceeding as above can assign the coupling of 19 Hz that appears in both multiplets to  $J(\text{P}^1\text{P}^2)$  and deduce that there is one  $\text{P}^1$  and one  $\text{P}^2$  in the complex. We note that an extra doublet coupling is seen on all resonances indicating that one  $^{13}\text{CO}$  ligand is present in the complex in addition to the two inequivalent phosphorus ligands.

Both  $^1J(\text{PtP})$  are small indicating both Ps are *trans* to high *trans* influence ligands.  $^1J(\text{PtP}^2)$  in **A** and **B** are comparable suggesting  $\text{P}^2$  is *trans* to the hydride in both complexes.

**$^1\text{H}$  NMR spectrum.** Proceeding as above we can deduce that there is one type of hydride present coupling to two phosphorus groups each containing one phosphorus and to one platinum. We can guess the third doublet splitting arises from coupling to  $^{13}\text{CO}$  and we are told  $J(\text{CH})$  was not determined. The large  $J(\text{PH})$  coupling can be assigned to  $\text{P}^2$ , the phosphorus *trans* to H while the smaller  $J(\text{PH})$  coupling can be assigned to the *cis*  $\text{P}^1$ . This assignment is consistent with our assignment of the  $J(\text{PPt})$  couplings above.

**Q. 2.4** Advanced question.

The three spectra shown in figure 8.8 each show a symmetrical six line pattern in the upfield region yet each arises from a different spin system.

The first spin system comprises: group A containing two equivalent spins and two groups, B and C, containing one spin  $\frac{1}{2}$  nuclei. B and C have similar chemical shifts and do not couple to each other but do couple to group A with, accidentally, the same coupling constant  $J(AB) = J(AC)$ . B and C are of the same element but A is a hetero nucleus.

The second spin system comprises: group A containing one spin  $\frac{1}{2}$  nucleus and two groups, B and C, also containing one spin  $\frac{1}{2}$  nuclei. B and C have similar chemical shifts and couple to each other and to group A, all the coupling constants are, accidentally, the same. A is a hetero nucleus.

Finally, the third spin system comprises: groups A and B each containing one spin  $\frac{1}{2}$  nucleus and group C containing two spin  $\frac{1}{2}$  nuclei. B and C have dissimilar chemical shifts and couple to each other. B also couples to group A but C does not. All the coupling constants are different. B and C are of the same element but A is a hetero nucleus.

Using the workflow in Chapter 2 and paying particular attention to the caveats and information in the side bar box, explain which spectrum corresponds to which spin system and how these can be differentiated.

**Answers**

Spectrum (a) contains two symmetrical patterns indicating two chemical shifts are present, so two groups of spins are expected. However, the upfield resonance is a doublet of triplets indicating coupling to two groups of spins implying three groups of spins must be present in the molecule. The third group does not appear in the spectrum, so must be a heteronuclear group of spins.

The doublet coupling in the downfield multiplet matches the triplet coupling in the upfield multiplet, so the downfield group must contain two spin  $\frac{1}{2}$  nuclei and the upfield group one spin  $\frac{1}{2}$  nucleus.

The large doublet coupling must then be the heteronuclear coupling, so the heteronuclear group must contain one spin  $\frac{1}{2}$ . Spectrum (c) corresponds to the last spin system.

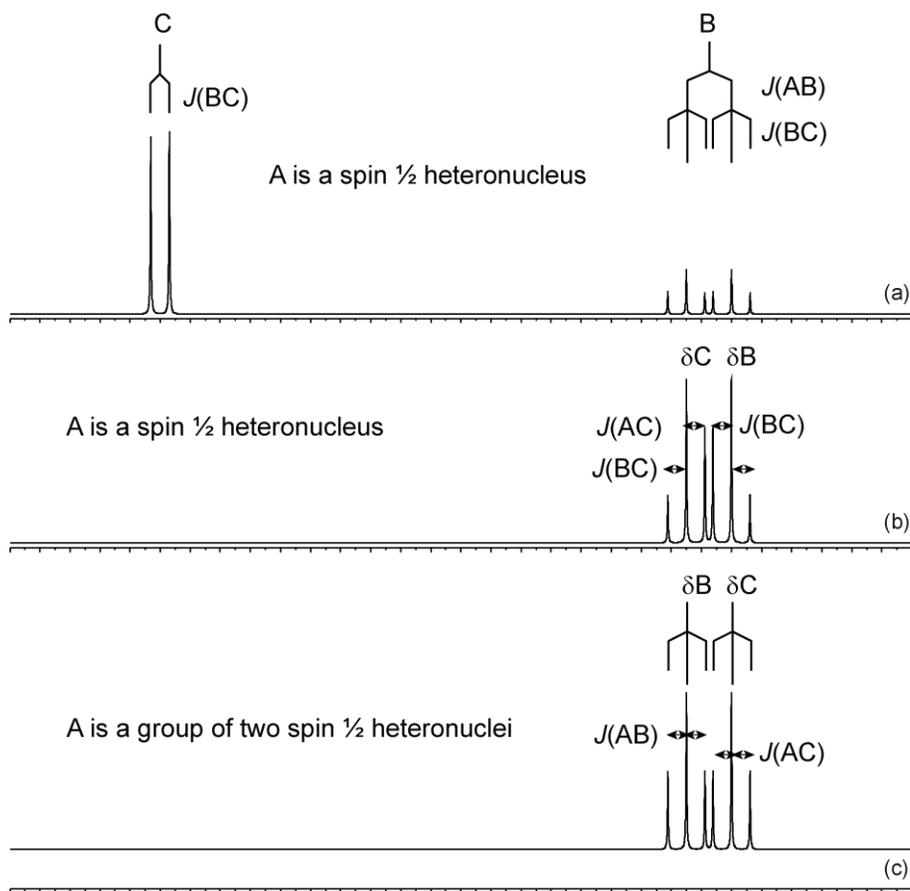
Spectrum (b) contains a single pattern showing distinct roofing. Roofing is commonly seen when two groups of spins having similar chemical shifts couple to each other. This corresponds to groups B and C of the second spin system in the question. Coupling to the heteronuclear spin A splits the AB quartet. The accidental coincidence of all the coupling constants gives the appearance of a roofed doublet of triplets.

Spectrum (c) shows a single, undistorted apparent doublet of triplets. This would imply two heteronuclear neighbouring groups, one containing two spin  $\frac{1}{2}$  nuclei the other one spin  $\frac{1}{2}$ . None of the spin systems correspond to this.

However, we note that the first spin system contains two groups A and B that have similar chemical shifts but do not couple. In the absence of any other groups of spins, this would

give two singlets. If we introduce a third group, A, which is heteronuclear, containing two spin  $\frac{1}{2}$  nuclei, the singlets would each split into triplets. Since  $J(AB) = J(AC)$ , an apparent doublet of triplets results.

We thank a reviewer for suggesting these situations.



**Fig. 8. 7** Simulated NMR spectra for Q2.4.

### 8.3 Chapter 3 exercises

**Q 3.1** Suggest two ways in which NMR measurements might be used to determine order the basicity of a library of phosphine ligands.

- The magnitude of the selenium-phosphorus coupling in organophosphorus selenides,  $R_3PSe$ , increases as the basicity of the phosphine, decreases,  $Me < Ph < OMe$ , Figure 3.15.
- As the phosphine becomes more basic/electron donating from  $P(OPh)_3$  to  $PBu_3$ , the  $^{13}CO$  chemical shift increases; see figure 3.6 which plots the  $^{13}CO$  chemical shift against the Tolman electronic parameter of the phosphorus ligand or CO stretching frequency for two series of complexes  $W(CO)_5L$  and  $CpFe(CO)(PR_3)(SnPh_3)$ .
- $^1J(PtP)$  in  $cis-PtCl_2(PR_3)_2$  reflects the basicity of the phosphorus ligand being 3508 Hz in  $cis-PtCl_2(PBu_3)_2$  and  $cis-PtCl_2\{P(OEt)_3\}_2$  is 5698 Hz. Interestingly, the ratio of the phosphine and phosphite coupling constants is fairly independent of the nature of the acceptor; being 1.62 in these platinum complexes and 1.53 in the borane complexes  $Me_3P-BH_3$ ,  $^1J(^{11}BP)$  64 Hz, and  $(MeO)_3P-BH_3$ , 97 Hz

**Q 3.2** What is meant by “paramagnetic term” in discussing the chemical shift of transition metals?

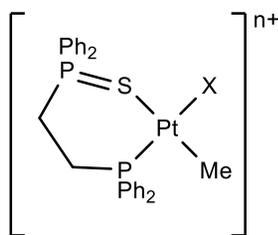
**Answer** The term refers to shielding caused by mixing in of excited states, this can cause either shielding or deshielding.

**Q 3.3** A series of Pt complexes **1** has been prepared where one of X and Y is a methyl group and the other is one of the following ligands: acetone, acyl, SnCl<sub>2</sub> or CO.

$^1J(^{195}\text{Pt}^{31}\text{P})$  in the complexes varies from 3367 to 3995 to 4036 to 5003. By considering the effect of *trans*-influence, decide if X or Y is the methyl group. Pair each ligand with the appropriate  $^1J(^{195}\text{Pt}^{31}\text{P})$ .

**Answer**  $^1J(^{195}\text{Pt}^{31}\text{P})$  is strongly influenced by the *trans* ligand. Since  $^1J(^{195}\text{Pt}^{31}\text{P})$  is observed to vary widely between the complexes, it is reasonable to assume that it is the ligand *trans* to the phosphine that is varying, hence Y is the invariant Me ligand. The order of *trans*-influence in the complexes is CO > acyl > SnCl<sub>2</sub> > acetone which is the order in which  $^1J(^{195}\text{Pt}^{31}\text{P})$  increases.

<Unnumbered Chemdraw 8.4>

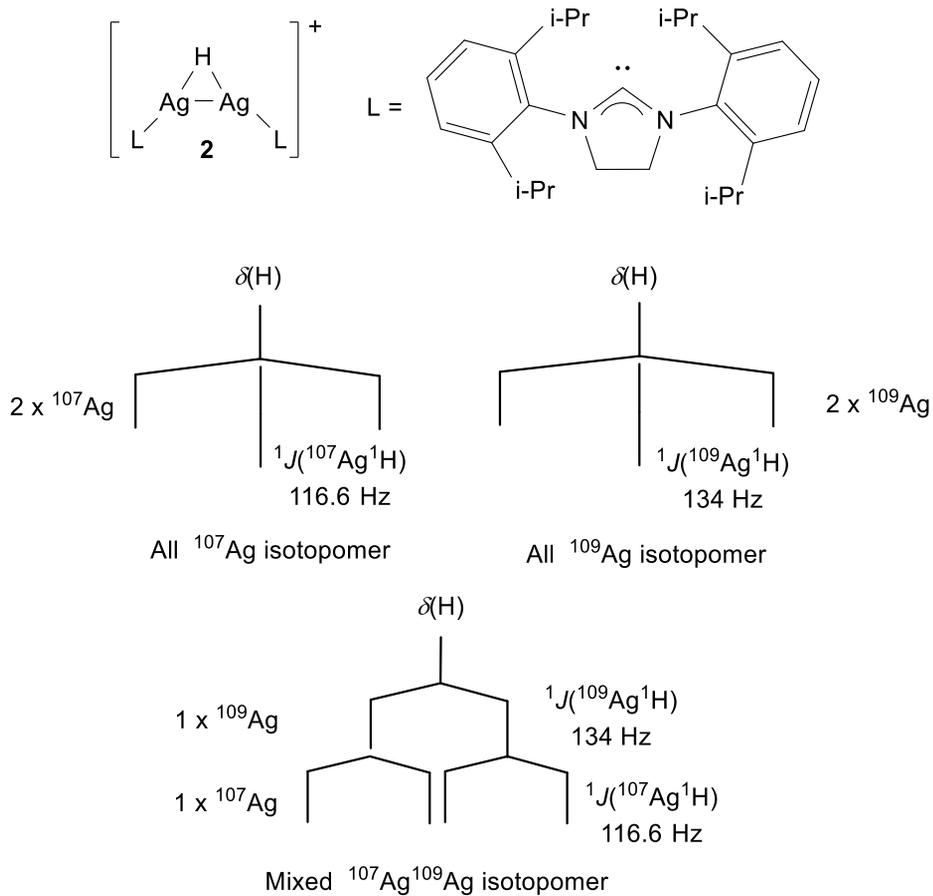


**1** n = 0 or 1

**Q 3.4** Sketch stick diagrams to illustrate the couplings present in the  $^1\text{H}$  NMR spectrum of each isotopologue of **2**.  $^1J(^{109}\text{Ag}^1\text{H})$  in the dinuclear silver compound **2** is 134 Hz. Use the data in Table 1.2 to calculate  $^1J(^{107}\text{Ag}^1\text{H})$ . From data in B. K. Tate *et al.*, *Chem. Sci.* 2013, **4**, 3068.

**Answer** For coupling over bonds in which only the isotopes of the coupling partners have changed, the value of  $J$  scales as the gyromagnetic ratios.  $\gamma(^{107}\text{Ag}) = -1.088918 \times 10^7$   $\text{rad}\cdot\text{s}^{-1}\cdot\text{T}^{-1}$  and  $\gamma(^{109}\text{Ag}) = -1.2519 \times 10^7$   $\text{rad}\cdot\text{s}^{-1}\cdot\text{T}^{-1}$  so  $^1J(^{107}\text{Ag}^1\text{H}) = 116.6$  Hz.

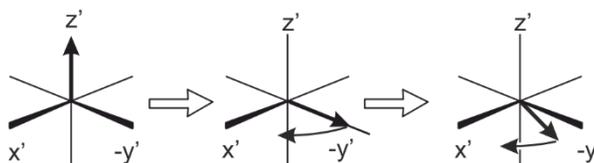
Both isotopes of silver are spin  $\frac{1}{2}$  so in the  $^{107}\text{Ag}^{107}\text{Ag}$  and  $^{109}\text{Ag}^{109}\text{Ag}$  isotopologues the proton will split into a triplet (two equivalent spin  $\frac{1}{2}$  neighbours) with  $^1J(^{107}\text{Ag}^1\text{H})$  116.6 Hz and  $^1J(^{109}\text{Ag}^1\text{H})$  134 Hz respectively. The silvers are chemically equivalent, so we cannot distinguish the  $^{107}\text{Ag}^{109}\text{Ag}$  isotopologue from the  $^{109}\text{Ag}^{107}\text{Ag}$  isotopologue the proton is split into a doublet of doublets  $^1J(^{107}\text{Ag}^1\text{H})$  116.6 Hz and  $^1J(^{109}\text{Ag}^1\text{H})$  134 Hz. It does not matter which coupling is taken first in the stick diagram. The isotopic abundance of  $^{107}\text{Ag} = 51.8\%$  and of  $^{109}\text{Ag} = 48.1\%$ , which for simplicity we can take as 50:50.



**Fig. 8.8** Stick diagrams for Q3.4

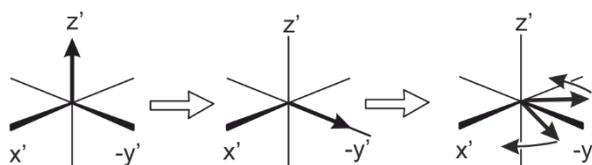
## 8.4 Chapter 4 exercises

**Q 4.1** There is one, isolated group of  $^{19}\text{F}$  spins in  $\text{CF}_3\text{Br}$ . Before the  $90^\circ$  pulse, the magnetization will be aligned along the  $z$ -axis in the rotating frame. The  $-x$  pulse rotates the magnetization through  $90^\circ$  in a clockwise direction (looking back along  $x$  to the origin) along the  $x$ -axis. The magnetization now lies in the  $xy$  plane and is aligned along the  $y$ -axis. After the pulse the magnetization will start to precess in the  $xy$  plane at a rate that depends on the chemical shift offset from the Larmor frequency. Since there is only one chemical shift and no  $J$  coupling a single, precessing magnetization vector is seen, Fig. 8.9.



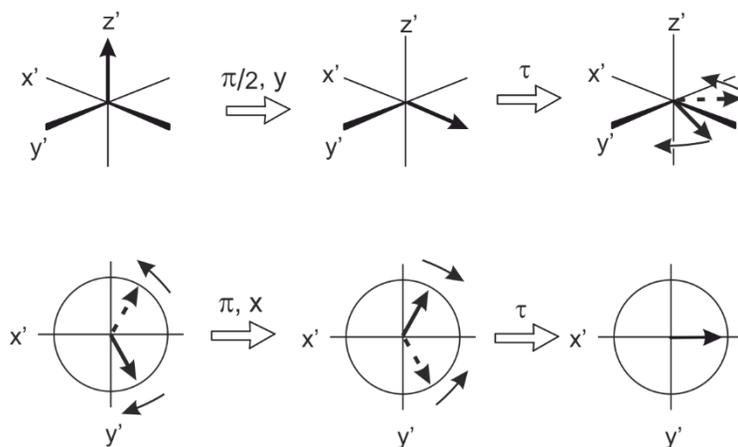
**Fig. 8.9** Effect of a  $\pi/2$   $x$  pulse and subsequent evolution of the magnetization of an isolated group of spins.

**Q 4.2** In  $\text{CHF}_3$  coupling between the H and F, splits the  $^{19}\text{F}$  resonance into a doublet. There will be two magnetization vectors that will precess at different rates,  $\pm J(\text{HF})/2$ , i.e. separated by  $J(\text{HF})$ , Fig. 8.10.



**Fig. 8.10** Effect of a  $\pi/2$ -x pulse and subsequent evolution of the magnetization of a group of spins with one spin  $\frac{1}{2}$  neighbour. The effect of chemical shift (Fig. 4.7) is omitted for clarity.

**Q 4.3** The  $90^\circ$  -y-pulse rotates the magnetization to the -x-axis. (NB It's easier to rotate the cartesian axes in the figure, making the y-axis come out of the paper towards us than to draw the magnetization vectors behind the plane of the paper.) After time  $\tau$  the two branches of the doublet, shown as a solid and a dotted arrow, will have split and lie between -x and y and -x and -y. For clarity we now look down along z-axis, the xy plane lies in the paper. The  $180^\circ$  x-pulse flips the magnetization vectors about the x-axis so that the vector that was between -x and y is now between -x and -y and *vice versa*. However, the direction in which the two vectors precess does not change, so after a further time  $\tau$  the vectors come back together along -x, figure 8.11



**Fig. 8. 11** The effect of the pulse sequence is to form a spin echo. The magnetization refocuses along the -x axis. The effect of chemical shift (Fig. 4.7) is omitted for clarity.

**Q 4.4** The “zero-crossing” times,  $t$ , occurs when the magnetization has relaxed back along the z-axis to the origin, i.e. at the “halfway” point. For a first order process, rearranging Eq. 4.3 and solving for  $M_t = 0$  shows this occurs when  $t = T_1 \ln 2$ .

L	PPr <sub>3</sub>	PBu <sub>3</sub>	P(C <sub>6</sub> H <sub>11</sub> ) <sub>3</sub>	P(Me <sub>2</sub> Ph) <sub>3</sub>	P(MePh <sub>2</sub> ) <sub>3</sub>	P( <i>p</i> -tol) <sub>3</sub>
<b>t/s</b>	4.4	3	2.5	9.6	7.5	7.2
<b>T<sub>1</sub>/s</b>	6.4	4.3	3.6	13.9	10.8	10.4

The faster spin-lattice relaxation observed for the trialkyl phosphines is attributed to dipole-dipole relaxation of the <sup>31</sup>P spins by the adjacent proton spins, which are more numerous in the trialkyl phosphines than in the aryl phosphines.

## 8.5 Chapter 5 exercises

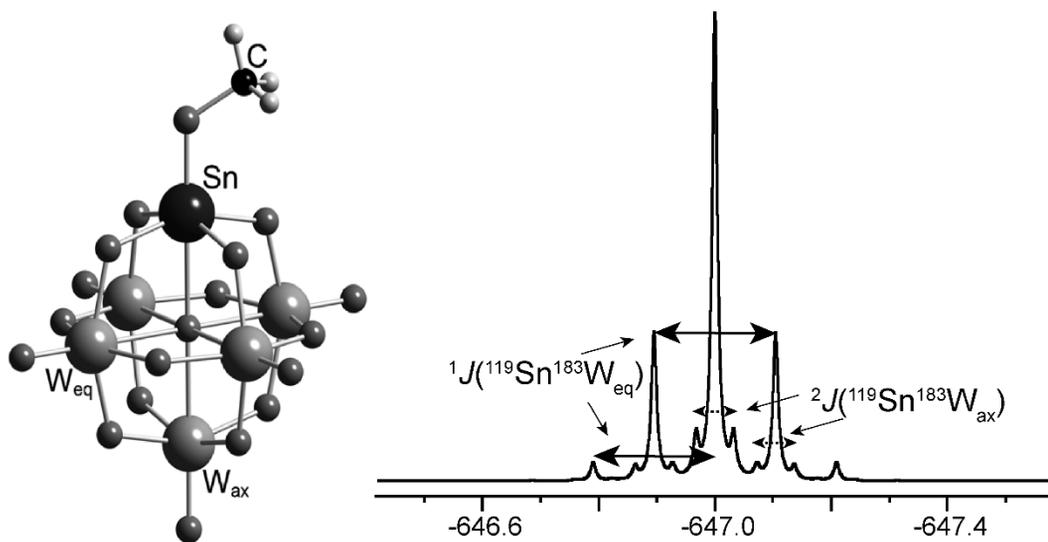
**Q 5.1** Figure 5.20 shows the structure and the  $^{119}\text{Sn}\{^1\text{H}\}$  refocused INEPT NMR spectrum of the polyoxometalate anion  $[(\text{MeO})\text{SnW}_5\text{O}_{18}]^{3-}$  in which there are two tungsten environments,  $W_{\text{eq}}$  and  $W_{\text{ax}}$ . The nuclear spin and abundance of the isotopes of tin and tungsten are given in Table 1.2.

- Explain why the INEPT experiment is preferred rather than a simple proton decoupling experiment for observation of  $^{119}\text{Sn}$ ?
- Assign the couplings seen in the  $^{119}\text{Sn}\{^1\text{H}\}$  spectrum and account for the observation that the main satellite sub-spectrum is a doublet.
- Predict the appearance of the  $^{183}\text{W}\{^1\text{H}\}$  spectrum.

### Answer

- The INEPT experiment affords a signal enhancement of  $\gamma_{\text{H}}/\gamma_{\text{Sn}} \approx 2.7$ . Further signal:noise enhancement is available since the scan repetition rate is determined by the faster, proton relaxation allowing more scans to be acquired in the same experiment time.

- b. The natural abundance of  $^{183}\text{W}$  is 14.31%. The chances of having two equatorial  $^{183}\text{W}_{\text{ax}}$  are thus  $0.14 \times 0.14 \times 6$  (number of different ways of placing two  $^{183}\text{W}_{\text{ax}}$  in equatorial sites and ignoring double counting from 3 or 4  $^{183}\text{W}_{\text{ax}}$  isotopologues) in the molecule are  $\sim 12\%$ . This intensity would be split into a 1:2:1 triplet centred on the “no  $^{183}\text{W}_{\text{ax}}$ ” peak at  $\delta = -647$  ppm. The central peak of the triplet lies beneath the “no  $^{183}\text{W}_{\text{ax}}$ ” peak and the outlying peaks have 3% of the total spectral intensity and are at located at  $^1J(^{119}\text{Sn}^{183}\text{W}_{\text{eq}})$  from the central line and can be seen at ca.  $-646.8$  and  $-647.2$  ppm), figure 8.12.



**Fig. 8.12.** Assignment of  $^{119}\text{Sn}\{^1\text{H}\}$  refocused INEPT NMR spectrum of  $[(\text{MeO})\text{SnW}_5\text{O}_{18}]^{3-}$ .

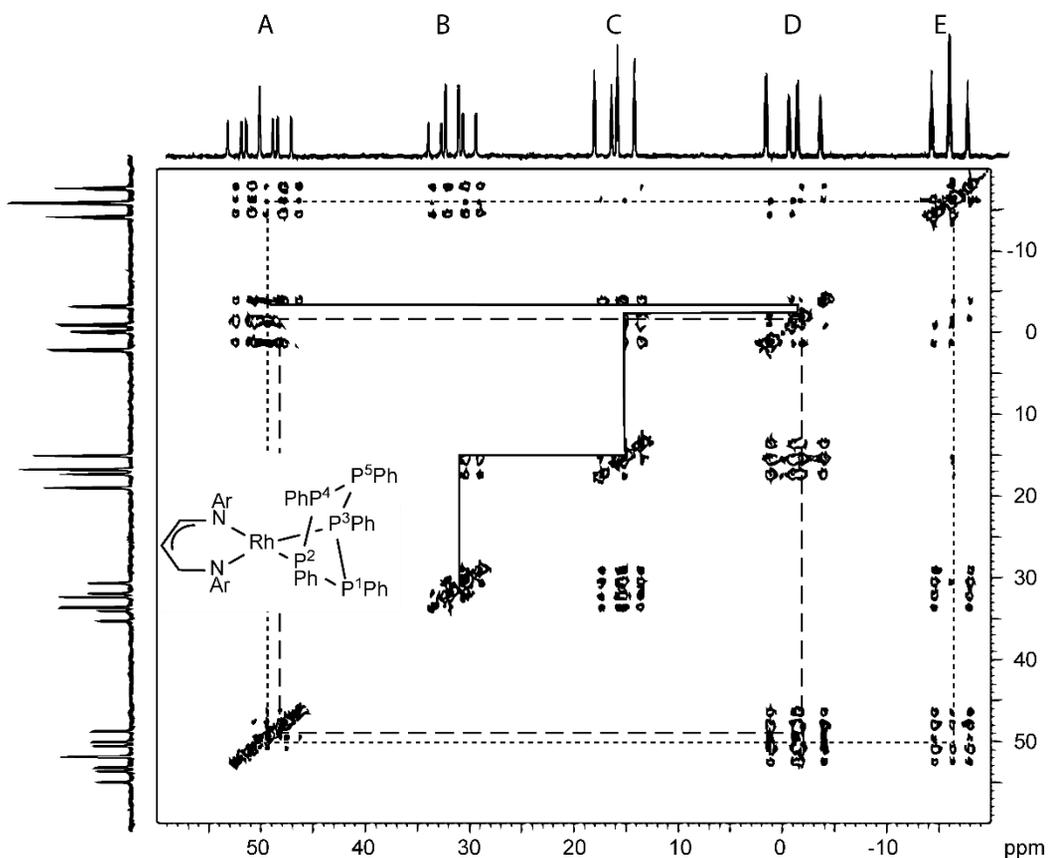
Adapted with permission from B. Kandasamy *et al.*, *Chem. Eur. J.*, 2012, **18**, 59–62.

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- c. The  $^{183}\text{W}\{^1\text{H}\}$  NMR spectrum will show two chemical shifts  $\delta_{\text{ax}}$  and  $\delta_{\text{eq}}$  in the ratio 1:4. Both will show satellites due to coupling to  $^{115}\text{Sn}$ ,  $^{117}\text{Sn}$ , and  $^{119}\text{Sn}$ . Each set of satellites will be a doublet. The satellite sub-spectra will have intensities 0.17%, 3.84% and 4.29% respectively, i.e. half the natural abundance of each isotope of tin since the total intensity in each sub-spectrum is split in two on forming a doublet. The close similarity of  $\gamma(^{119}\text{Sn})$  and  $\gamma(^{117}\text{Sn})$  results in the doublets due to  $^1J(^{119}\text{Sn}^{183}\text{W})$  (38 Hz) and  $^1J(^{117}\text{Sn}^{183}\text{W})$  (36 Hz) being unresolved due to the linewidth ( $> 2$  Hz).

**Q 5.2** Figure 8.13 shows the  $^{31}\text{P}$ ,  $^{31}\text{P}$ -COSY of  $(\text{NacNac})\text{Rh}(\text{P}_5\text{Ph}_5)$ .

- Identify the number of distinct phosphorus sites in the molecule.
- Using the information about coordination shifts given in chapter 2, identify the resonances of P2 and P3.
- Hence assign the remaining correlations in the spectrum and attempt an assignment of the couplings in the 1D  $^{31}\text{P}\{^1\text{H}\}$  spectrum along on the F1 and F2 axes.



**Fig. 8.13.**  $^{31}\text{P}, ^{31}\text{P}$ -COSY for  $(\text{NacNac})\text{Rh}(\text{P}_5\text{Ph}_5)$ . Correlations between A and E (dotted line), A and D (dashed line) and ADCB (solid line) are indicated. Adapted from S. J. Geier and D. W. Stephan, *Chem. Commun.*, 2008, 2779–2781 with permission from The Royal Society of Chemistry.

**Answer**

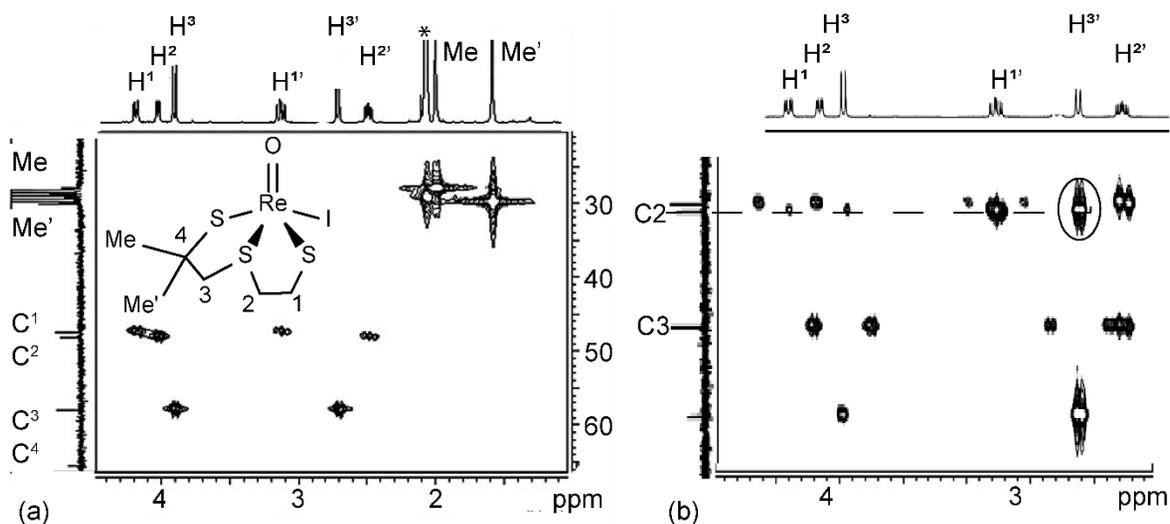
- a. 5  $^{31}\text{P}$  shifts are seen so 5 distinct types of phosphorus are present, figure 8.13.
- b. Coordination to a transition metal is expected to result in a down field shift of the phosphorus resonances suggesting P3 and P2 give the resonances at ca. 50 (A) and 30 (B) ppm. P2 and P3 will also show  $^1J(\text{RhP})$  whereas P1, P4 and P5 will show smaller  $^2J(\text{RhP})$  confirming the assignment. The apparent triplet sub-structure in the multiplets A and B is due to the accidental degeneracy of two coupling constants in each multiplet.
- c. Resonance E couples to both A and B suggesting E is P1. A also couples to D which couples to C which couples to B indicating ABCD are either P2P4P5P3 or P3P5P4P2, the data does not distinguish these possibilities. Weak correlations attributed to long range couplings are also seen between D and E and C and E.

**Q 5.3** Figure 8.14 shows the  $^1\text{H},^{13}\text{C}$ -HMQC NMR spectrum of the 1,1-dimethyl-1,5-dithiol-3-thiapentane oxorhenium complex shown. The  $^{13}\text{C}$  spectrum has been fully assigned.

- a. Account for the occurrence of eight sets of resonances in the  $^1\text{H}$  NMR spectrum.
- b. Given only  $^1J_{\text{CH}}$  correlations are observed, assign the  $^1\text{H}$  spectrum indicating to which carbon in the backbone each proton is bonded.
- c. How might C(1) and C(2) be distinguished?

**Answer**

- a. The proton/methyl group on each carbon is directed either beneath the  $S_3I$  plane i.e. under the Re centre (*exo*, indicated with primes), or towards the O atom (*endo*). The *endo* protons are deshielded by the Re=O bond.
- b. See figure. Only the *exo*- and *endo*-Me groups are shown for clarity
- c. C(1) and C(2) can be distinguished by an HMBC spectrum in which a long range correlation is seen between C(3) and H(2') but not between C(3) and H(1) or H(1').



**Fig. 8.14.** (a)  $^1\text{H}$ ,  $^{13}\text{C}$ -HMBC NMR spectrum of chiral oxorhenium complex, containing 1,1-dimethyl-1,5-dithiol-3-thiapentane ligands in acetone- $d_6$ . A residual acetone peak (\*) can be seen at 2.05 ppm. (b) Fragment of HMBC spectrum, correlation between  $\text{C}(2)$  and  $\text{H}(3')$  indicated. Doublets are due to  $^1J(\text{CH})$  correlations. Adapted from F. De Montigny *et al.*, *Phys. Chem. Chem. Phys.*, 2010, **12**, 8792–8803 with permission from the PCCP Owner Societies.

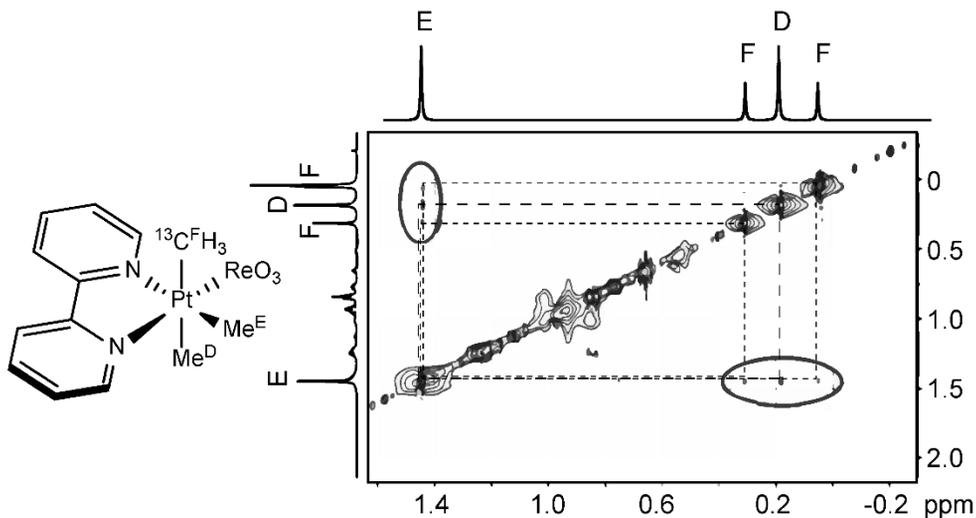
**Q 5.4** Figure 8.15 shows part of the NOESY spectrum of the reaction product from the addition of  $^{13}\text{C}$ -enriched  $\text{MeReO}_3$  to  $[(\text{bpy})\text{PtMe}_2]$  ( $\text{bpy} = 2,2'$ -bipyridine) recorded at  $^1\text{H} = 500$  MHz.

- Identify the resonances of the  $^{13}\text{CH}_3$  group.
- Use the NOESY correlations to assign the correlations observed.
- Hence decide if *cis* or *trans* oxidative addition of  $\text{MeReO}_3$  to  $[(\text{bpy})\text{PtMe}_2]$  has occurred.

### Answer

- The spectral lines, labelled F, at ca 0.05 and 0.31 ppm have half the intensity of the other lines and are separated by ca 130 Hz, both observations are consistent with these lines being the  $^{13}\text{C}$  coupled doublet of the  $^{13}\text{CH}_3$  protons, figure 8.15.
- The resonances F show a NOESY correlation (short dashes) to the resonance E at 1.4 ppm but not to the resonance D at 0.18 ppm placing the  $^{13}\text{CH}_3$  group adjacent to E but remote from D. D shows a NOESY correlation (long dashes) to E indicating D is adjacent to E. Finally, the chemical shift of D is similar to that of the  $^{13}\text{CH}_3$  doublet F suggesting both methyl groups occupy similar environments at Pt. These data are consistent with F and D being remote from each other, i.e. occupying axial sites, while E is *cis* to both, i.e. occupies an equatorial site.

c. The data indicate *cis* oxidative addition has occurred.



**Fig. 8.15.** NOESY spectrum of the reaction product from addition of  $^{13}\text{C}$ -enriched  $\text{MeReO}_3$  to  $[(\text{bpy})\text{PtMe}_2]$  ( $\text{bpy} = 2,2'$ -bipyridine). Adapted with permission from K. H. Pichaandi *et al.*, *Inorg. Chem.* 2017, **56**, 2145–2152. Copyright © 2017, American Chemical Society.

## 8.6 Chapter 6 exercises

**Q 6.1.** Q1. Figure 6.19 shows the variable temperature  $^{31}\text{P}$  NMR spectra of  $[\text{Ni}(\text{L})_2]$ ,  $\text{L} = \text{SeSPPPh}_2$ . Suggest a dynamic process that accounts for the high and low temperature spectra.

**Answer** Two isomers exist of the square planar complex. In one the S donors are mutually *cis* in the other they are mutually *trans*. At high temperature, rapid interchange of the isomers occurs *via* a tetrahedral intermediate, while at low temperature interchange is frozen out. Note the  $^{77}\text{Se}$  satellites visible at low and high temperature.

**Q 6.2.** Figure 6-20 shows the  $^{19}\text{F}$  NMR spectra of  $\text{AgBF}_4$  in acetone recorded at low, intermediate and high temperature. Explain why two chemical shifts, with different coupling patterns and intensities, are expected at low temperature. Suggest an explanation for the collapse of the resonances to a singlet, at a shift closer to low T quartet than to the low septet at high T. Suggest two possible reasons why the coupling in the septet is lost before that in the quartet.

**Answer** Boron has two NMR active isotopes,  $^{10}\text{B}$  (~20%, spin 3) and  $^{11}\text{B}$  (~80%, spin  $\frac{3}{2}$ ). At low temperature separate resonances are seen for  $^{10}\text{BF}_4^-$  and  $^{11}\text{BF}_4^-$  at slightly different chemical shift due to zero point energy effects – an isotopologue shift.  $^{10}\text{B}$  splits the  $^{19}\text{F}$  into seven equally intense lines ( $2I+1$ ) while  $^{11}\text{B}$  splits the fluorine resonance into

four lines. As the temperature is raised, exchange of fluorine between  $[\text{}^{10}\text{BF}_4]^-$  and  $[\text{}^{11}\text{BF}_4]^-$  occurs and an exchange decoupled resonance at the weighted average chemical shift is seen.

The magnitude of a coupling constant scales with the gyromagnetic ratio for isotopologues of same coupling partners;  $\gamma^{11}\text{B} = 8.58406$ ,  $\gamma^{10}\text{B} = 2.67085 \times 10^7 \text{radT}^{-1}\text{s}^{-1}$  so  $J(^{11}\text{B}^{19}\text{F})$  is  $\sim 4$  times  $J(^{10}\text{B}^{19}\text{F})$ .

As the bond between B and F breaks, exchange decoupling occurs. Since  $[\text{}^{10}\text{BF}_4]^-$  is less abundant than  $[\text{}^{11}\text{BF}_4]^-$  its rate of site leaving must be higher. Furthermore,  $J(^{10}\text{B}^{19}\text{F})$  is smaller than  $J(^{11}\text{B}^{19}\text{F})$ , so requires a lower rate of site leaving to be exchange decoupled. These factors work together and coupling to  $^{10}\text{B}$  is lost at a lower rate of exchange (lower T) than coupling to  $^{11}\text{B}$ .

**Q 6.3.** Account fully for the temperature dependence of the  $^{13}\text{C}$  NMR spectra of  $[\text{Rh}(\text{PBU}_3)_2(\text{CO})\text{Cl}]$  in the presence of traces of dissolved CO, figure 6.21.

**Answer** In the absence of CO the  $^{13}\text{C}$  NMR spectrum of  $[\text{Rh}(\text{PBU}_3)_2(^{13}\text{CO})\text{Cl}]$  shows a well resolved doublet of triplets due to coupling to the two equivalent phosphines and  $^{103}\text{Rh}$ . Addition of traces of CO results in loss of the small coupling to phosphorus, simplistically, the rate of bond breaking is greater than the phosphorus-carbon coupling constant so the coupling disappears, the phosphorus is exchange decoupled from the carbon. This is

consistent with the on-set of *intermolecular* exchange of free and co-ordinated CO giving exchange decoupling and loss of  ${}^2J_{PC}$ .

The larger rhodium-carbon coupling, however, is still present, even though it is the rhodium-carbon bond that is breaking, since the rate of bond cleavage does not yet exceed this coupling constant. At high CO concentration, exchange of free and co-ordinated CO becomes fast enough to decouple the rhodium and carbon nuclei and a singlet is seen.

**Q 6.4.1** Figure 6.22-left shows the variable temperature  ${}^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of a mixture of  $[\text{PPh}_3\text{Cl}]\text{Br}$  and  $[\text{PPh}_3\text{Br}]\text{Cl}$ . Account for the observation of separate resonances at  $-60\text{ }^\circ\text{C}$  but a single resonance at  $+20\text{ }^\circ\text{C}$ .

**Answer** The  ${}^{31}\text{P}\{^1\text{H}\}$  VT NMR shows interconversion of  $[\text{PPh}_3\text{-Cl}]\text{Br}$  and  $[\text{PPh}_3\text{-Br}]\text{Cl}$  is slow, (low temperature limit) at  $-60\text{ }^\circ\text{C}$ . As T is raised, the rate of interconversion increases until coalescence is reached at  $0\text{ }^\circ\text{C}$ . Above  $10\text{ }^\circ\text{C}$  exchange is fast, a single average resonance is seen which narrows as the exchange rate increases.

**Q 6.4.2** Figure 6.22-centre also shows the EXSY spectrum of a mixture 1-X. Identify which species participate in exchange and assign the exchanging pairs. By considering the chiral information decide if exchange occurs with retention or inversion at phosphorus.

**Answer** The peaks at 68/72 and 72/68 ppm correspond to bromide self-exchange. The four remaining peaks correspond to cross-exchange between bromo and chloro species. S-1-Cl is paired with R-1-Br and S-1-Br with R-1-Cl. No cross-peaks are seen linking S-1-Cl is paired with S-1-Br or R-1-Br with R-1-Cl; nucleophilic exchange in halophosphonium species occurs with inversion of configuration at P.

## 8.7 Chapter 7 exercises

**Q 7.1** Figure 8.16 shows the  $^{103}\text{Rh}\{^1\text{H}\}$  CP/MAS NMR spectrum of the symmetrical dimeric Rh cation  $[(\text{H}_2\text{O})_4\text{Rh}(\mu^2\text{-OH})_2\text{Rh}(\text{H}_2\text{O})_4]$ , recorded at two different MAS rates (1.0 kHz, top; 4.0 kHz).

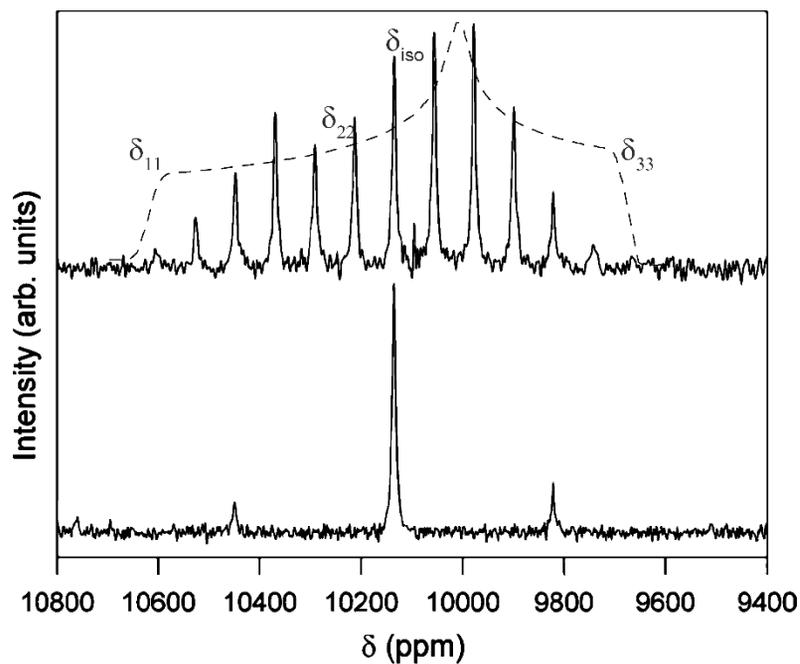
- At what frequency,  $\nu_0$ , were the spectra recorded?
- Can the CSA principal values of  $\delta_{11}$ ,  $\delta_{22}$ ,  $\delta_{33}$ , and  $\delta_{\text{iso}}$  be estimated from the spectra? If so, give approximate values.
- Explain why the intensity of the CP spectrum first increases then dies away.

### Answer

- For this sample 4 kHz is a high enough spinning rate for a resonance at the isotropic chemical shift to be observed. The remaining side bands occur on either side of the isotropic peak offset at a frequency equal to the spinning rate, 4 kHz.

By inspection of the spectrum, figure 8.16, the offset in ppm is  $\sim 310$  ppm, thus the observation frequency is approximately  $4000 = 310 \times \nu_0/10^6$  giving  $\nu_0 = 12.9$  MHz – the actual spectrometer operating frequency was 12.76 MHz.

- b. At high enough spinning rates a resonance at the isotropic chemical shift is observed. Here, 4 kHz is fast enough to estimate of the isotropic chemical shift,  $\delta_{\text{iso}} \approx 10150$  ppm, directly from the spectrum. At lower spinning rates computer fitting of the static lineshape or spinning sidebands is used to obtain the principal components of the chemical shift tensor,  $\delta_{11}$ ,  $\delta_{22}$ ,  $\delta_{33}$ . Here, estimates of  $\delta_{11}$  and  $\delta_{33}$  can be obtained by visual inspection of the spectrum at 1 kHz. Since a reasonable approximation of  $\delta_{\text{iso}}$  can be obtained from the 4 kHz spectrum,  $\delta_{22}$  can be approximated from the definition of  $\delta_{\text{iso}} = \frac{1}{3}(\delta_{11} + \delta_{22} + \delta_{33})$ . Finally, note that various conventions are used to order  $\delta_{11}$ ,  $\delta_{22}$ ,  $\delta_{33}$ . Here  $\delta_{11} \geq \delta_{22} \geq \delta_{33}$  has been used giving  $\delta_{11} \approx 10650$ ,  $\delta_{22} \approx 10100$ ,  $\delta_{33} \approx 9700$  ppm. The values determined by fitting the sidebands at a spinning rate of 1 kHz are:  $\delta_{11} = 10551$ ,  $\delta_{22} = 10048$ ,  $\delta_{33} = 9793$  ppm.
- c. Cross-polarization builds up during the contact time when the irradiation used to transfer polarization between spins is “switched on” increasing the S spin signal, however, relaxation of the S spins also occurs during this time reducing the signal; signal intensity thus initially builds up due to CP and then falls away due to relaxation.



**Fig. 8.16**  $^{103}\text{Rh}\{^1\text{H}\}$  CP/MAS NMR spectrum of and CP build up curve for the symmetrical dimeric Rh cation  $[(\text{H}_2\text{O})_4\text{Rh}(\mu^2\text{-OH})_2\text{Rh}(\text{H}_2\text{O})_4]$ . Adapted with permission from B. L. Phillips *et al.*, *J. Amer. Chem. Soc.*, 2006, **128**, 3912-3913. Copyright © 2017, American Chemical Society.

**Q7.2** Figure 7.24 shows the  $^{13}\text{C}\{^1\text{H}\}$  and  $^{31}\text{P}\{^1\text{H}\}$  spectra of  $[\text{Pd}(\text{dppp})(\text{dte})]\text{BF}_4$  (dppp = diphenylphosphinopropane, dte = *N,N*-diethyldithiocarbamate) in solution and the solid state. Suggest an explanation for the differences between the solution and solid state spectra.

### Answer

- a. In solution molecular motions are fast but in the solid state are restricted. Thus, molecular tumbling in solution averages out dipolar interactions and chemical shift anisotropy resulting in sharp NMR lines. In the solid state spectra, however, the MAS spinning rate is not sufficient to average out these line broadening interactions resulting in broader spectral lines. Furthermore, in solution, vibrational motions of the ligands create a plane of symmetry through the nitrogen, palladium and the central carbon of the diphosphine ligand backbone that equivalences the two sides of the molecule. Thus, in solution a single chemical shift for phosphorus is observed and the  $^{13}\text{C}\{^1\text{H}\}$  spectrum shows a one shift for each of the types of carbon present (thiocarbamate methyl and methylene; *ortho*, *meta*, *para* and *ipso* carbons of the phenyl rings, C(1) and C(3) of the ligand backbone, and finally the central carbon. Anchoring the Pd complex to a silica surface restricts these molecular motions severely, breaking the molecular symmetry; the two sides of the molecule become distinct and two resonances are observed  $^{31}\text{P}\{^1\text{H}\}$  CPMAS spectrum.

Similarly, additional resonances are seen in the solid-state  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra as the previously equivalent aromatic carbons become distinct.

Finally, as expected, the  $^{13}\text{C}$  resonance of the chloroform solvent is absent from the solid-state spectrum.

b. Crystal packing can also result in inequivalencing of sites.

**Q 7.3** In a cross polarization experiment a 9.4 T spectrometer was used;  $^1\text{H}$  was the polarization source and  $^{109}\text{Ag}$  was the polarization receiver.

(a) What is the maximum signal enhancement that can be obtained neglecting relaxation effects?

Signal enhancement =  $\gamma_I/\gamma_S = \gamma_{^1\text{H}}/\gamma_{^{109}\text{Ag}} = |26.75 \times 10^7 / -1.25 \times 10^7| = 21.4$ . (Or 20.4 if the negative  $\gamma$  correction applies as in INEPT)

(b) The proton  $B_1$  field used was 1.4 mT. What  $B_1$  field is required at  $^{109}\text{Ag}$  to fulfil Hartmann-Hahn matching condition at a MAS rate of 16 kHz?

The Hartmann-Hahn matching condition is  $B_1^{\text{H}} \gamma_{^1\text{H}} = B_1^{\text{Ag}} \gamma_{^{109}\text{Ag}} \pm n \times 2\pi \times (\text{MAS rate})$ . The gyromagnetic ratios in Table 1.2 are given in  $10^7 \text{rad} \cdot \text{T}^{-1} \cdot \text{s}^{-1}$  so  $^1\text{H}$  will precess about the proton spin-lock field at  $B_1^{\text{H}} \times 26.75 \times 10^7 / 2\pi = 59.6$  kHz.  $n$  can take any positive or negative integer value, taking  $n = 1$ , the  $^{109}\text{Ag}$  must precess about the  $^{109}\text{Ag}$  spin-lock

field at  $59.6 - 16 = 43.6$  kHz whence  $B_1^{\text{Ag}} g_{109\text{Ag}} = 43.6$  kHz giving  $B_1^{\text{Ag}} = 43600 \times 2\pi / \gamma_{109\text{Ag}}$   
 $= 21.9$  mT.

**Q7.4** The cathode (positive electrode) of a rechargeable battery is the electrode where reduction takes place during the discharge cycle; for lithium-ion cells this is the lithium-based electrode. Li-ion batteries typically comprise a lithium-doped cobalt oxide (LCO) positive electrode, and a hard carbon or graphite negative electrode, a porous separator, and a solution of a lithium salt in an organic liquid, figure 7.25. Overcharging of lithium ion batteries is reported to promote the growth of lithium metal dendrites on the cathode. Metal nuclei in metals are shielded by the metal conduction electrons so characteristically show large down field shifts (the Knight shift) whereas Li ions in solution typically have very small chemical shifts.

- Assign the  $^7\text{Li}$  solid-state NMR spectra shown in figure 7.25, the  $^7\text{Li}$  resonance of LCO is very broad and the electrolyte is 1 M  $\text{LiPF}_6$ .
- Is your assignment consistent with the formation of Li dendrites?

### Answer

- Spectrum (a) contains two resonances which can be assigned to the electrolyte ( $\sim 0$  ppm) and Li metal (a Knight shifted resonance at  $\sim 250$  ppm). During the charge-discharge-recharge cycle (spectra b, c, and d respectively) a broad resonance around 40 ppm disappears then reappears and can be assigned to lithium carbides based on this behaviour and the absence of a Knight shift.

Overcharging results in a broad, Knight shifted resonance around 270 ppm that is assigned to dendritic lithium on the cathode. Finally, a very broad resonance around 0 ppm is attributed to lithium in LCO.

- b. The appearance of a Knight shifted resonance on overcharging is consistent with overcharging causing dendritic lithium being deposited on the cathode.