Studies of Platinum(II) Complexes by Heteronuclear Magnetic Double Resonance

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^{1}H–{^{195}Pt} heteronuclear double resonance experiments are shown to be valuable for the identification of species present in mixtures of platinum(II) complexes. The ^{195}Pt chemical shifts can be understood in terms of variations in electronic excitation energies when the *size* of the ligands remains approximately constant, but bulky ligand atoms produce large shifts to high field which then dominate. Coupling constants involving ^{195}Pt are also discussed.

THE magnetic shielding of the nuclei of the transition elements is of interest in connection with the bonding in their complexes, but until recently comparatively little work has been done because relatively few transition elements have abundant isotopes with a suitable nuclear spin, and even those which do (*e.g.*, ^{59}Co, ^{103}Rh, ^{183}W, and ^{195}Pt) present various technical problems.[1] However, the advent of Fourier transform [2] and multiple resonance [3] techniques has alleviated these difficulties considerably, and it is now possible to study many species which are present in low concentration.

Attempts have been made to relate transition-metal chemical shifts to electronic excitation energies, but these have been really successful only in the case of cobalt [4,5] where the overall shielding range is large, although it appears that there may be a correlation for derivatives of tungsten hexafluoride.[6] Work on platinum failed to reveal any definite correlation,[7] and a reason for this is suggested by the present study.

In this work advantage has been taken of the high sensitivity of the proton to n.m.r. detection (a factor of 101 compared with ^{195}Pt), and ^{1}H–{^{195}Pt} heteronuclear double resonance experiments have been used to measure ^{195}Pt chemical shifts in 47 square planar derivatives of platinum(II). The major disadvantage of this approach is that the molecule examined must contain protons which display observable spin coupling to platinum, and so it cannot be used for species such as $PtCl_4^{2-}$; however in many cases this problem does not arise and the technique is then very powerful indeed, being extremely convenient and rapid. Additional advantages are that relative signs of spin coupling constants can be obtained, very dilute solutions can be examined, and the experiments often demonstrate unequivocally how different resonances in the proton and platinum spectra are related, and so permit unambiguous assignments. The last has proved especially valuable in the present work for the study of solutions of mixed platinum-containing species. Previously both the direct and the double resonance techniques have been used to obtain ^{195}Pt n.m.r. parameters in complexes, and coupling constants involving ^{1}H, ^{31}P, and other nuclei have been studied.[7-11]

EXPERIMENTAL

Platinum(II) complexes were prepared by standard methods from K_2PtCl_4. Metathetical reactions were used to make bromo- and iodo-derivatives, and mixed species were prepared in the n.m.r. sample tube from weighed quantities of the parent compounds. Equilibration was esentially complete in 0·25 h for reactions involving halogen transfer, and in 2—3 h for the transfer of sulphur ligands. There was a tendency for *trans*-isomers to predominate when bulky groups such as Br or I were present. Spectra were recorded at 24 ± 1 °C unless otherwise stated by use of a 60 MHz proton spectrometer adapted for heteronuclear double resonance experiments. ^{195}Pt chemical shifts are quoted relative to a solution of *cis*-$(Me_2S)_2PtCl_2$ in deuteriochloroform which is taken [12] as having $\Xi(^{195}Pt) = 21\,420\,980 \pm 10$ Hz, and a positive shift indicates a resonance to low field of the reference compound.

RESULTS

These are listed in the Table and in straightforward cases were obtained by standard methods [3] involving observation of an appropriate satellite line (^{195}Pt has $I = \frac{1}{2}$ and an abundance of 34%) in the proton spectrum with simultaneous irradiation at *ca.* 12·8 MHz to find the platinum resonant frequency. In most cases fine structure arising from $J(^{195}Pt \cdots H) =$ *ca.* 40 Hz was detected (see ref. 8 for an example of a ^{195}Pt INDOR spectrum which illustrates this) and care was then taken to ensure that the position of the centre of the platinum resonance was correctly identified, as an error of $\pm J(^{195}Pt \cdots H)$ corresponds to 3 p.p.m. or more at the polarising field strength used. The double resonance experiments proved to be valuable in the identification of species present in equilibrated mixtures of platinum complexes with labile ligands, and as an example an

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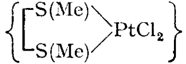
approximately equimolar mixture of $(PhMeS)_2PtCl_2$ and $(PhMeS)_2PtBr_2$ may be considered. (Note that as interconversion of *cis*- and *trans*-isomers occurs quite readily in solution with these species, there is no need to start with isomerically pure samples.) The methyl proton resonances together with attendant ^{195}Pt satellites are shown in the Figure (a) and arise from the species (9), (10), and (13)—(16) given in the Table. Irradiation at ^{195}Pt frequencies corresponding to $\delta(^{195}Pt) = -319$ p.p.m. immediately identifies the lines p and p′ as arising from compound (14) [see Figure (b)], and the lines marked q and q′, and r and r′ were similarly associated with (9) and (10) respectively. Of the two mixed species (15) and (16) the *trans*-isomer should give a single methyl resonance with two satellite lines whereas the *cis*-isomer should have two main methyl resonances and four ^{195}Pt satellites. Each isomer should be associated with a single ^{195}Pt frequency. $\delta(^{195}Pt)$ values of -69 and -114 p.p.m. must be assigned to these species, and as shown in the Figure (c) irradiation at a frequency corresponding to $\delta = -114$ p.p.m. removes the three lines marked s, which must therefore arise from the *cis*-isomer (15). The fourth satellite should lie under the stronger line marked t′ and it can be seen by comparison of (a) and (b) that the ringing following this line is altered by irradiation at this frequency. Although this effect is very small it was completely reproducible and serves to confirm the

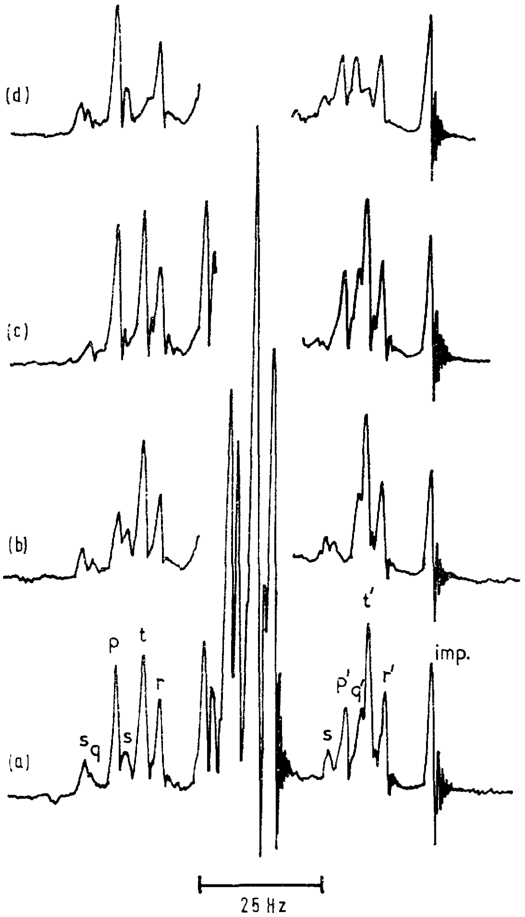
^{195}Pt N.m.r. parameters of platinum(II) complexes

No.	Compound	$\delta(^{195}Pt)$ [b] p.p.m.	$J(^{195}Pt–H)$ [c] Hz	Solvent [d]	Notes
(1)	*cis*-$(Me_2S)_2PtCl_2$	0	48·8	A	
(2)	*trans*-$(Me_2S)_2PtCl_2$	+132	40·5	A	
(3)	*trans*-$(Me_2S)_2PtBr_2$	−347	41·8	B	
(4)	*trans*-$(Me_2S)_2PtBrCl$	−106	41·4	B	
(5)	*cis*-$(Me_2S)_2PtBrCl$	−152	?	B	*e*
(6)	*trans*-$(Me_2S)_2PtI_2$	−1254	45·7	A	
(7)	*trans*-$(Me_2S)_2PtClI$	−590	42·0	A	
(8)	*trans*-$(Me_2S)_2PtBrI$	−822	43·4	A	
(9)	*cis*-$(MePhS)_2PtCl_2$	+69	48·8, 49·0	A	2 Me resonances observed below 25 °C
(10)	*trans*-$(MePhS)_2PtCl_2$	+172	44·6	B	
(11)	*cis*-$(Me_2S)(MePhS)PtCl_2$	+29	49·2	A	Coupling to Me_2S
(12)	*trans*-$(Me_2S)(MePhS)PtCl_2$	+156	41·7, 44·1	A	Larger coupling involves Me_2S
(13)	*cis*-$(MePhS)_2PtBr_2$	−309	?	A	*e*
(14)	*trans*-$(MePhS)_2PtBr_2$	−319	44·9	A	
(15)	*cis*-$(MePhS)_2PtBrCl$	−114	47·9, 47·6	A	
(16)	*trans*-$(MePhS)_2PtBrCl$	−69	44·3	A	
(17)	*trans*-$(MePhS)_2PtI_2$	−1262	48·2	B	
(18)	*cis*-$(MePhS)_2PtClI$	−562	48·7	B	
(19)	*trans*-$(MePhS)_2PtClI$	−465	45·8	B	
(20)	*cis*-$(Me_2Se)_2PtCl_2$	−198	41·8	B	$^1J_{PtSe} = 480$ Hz
(21)	*trans*-$(Me_2Se)_2PtCl_2$	+50	36·6	B	$^1J_{PtSe} = 365$ Hz
(22)	*trans*-$(Me_2Se)_2PtBr_2$	−484	37·4	B	
(23)	*cis*-$(Me_2Se)_2PtBrCl$	−182	?	B	*e*
(24)	*trans*-$(Me_2Se)_2PtBrCl$	−216	36·8	B	
(25)	*cis*-$(Et_2S)_2PtCl_2$	−74	?	B	*f*
(26)	*trans*-$(Et_2S)_2PtCl_2$	+127	?	B	*f*
(27)	*cis*-$(Et_2Se)_2PtCl_2$	+40	?	A	*f*
(28)	*trans*-$(Et_2Se)_2PtCl_2$	+64	?	A	*f*
(29)	*cis*-$(Bz_2S)_2PtCl_2$	−9	36, 50	A	See footnote *g*
(30)	*trans*-$(Bz_2S)_2PtCl_2$	+158	34·5	A	
(31)		−248 −233	48·8 48·8	C C	
(32)	?$(Me_2SO)_2PtCl_2$	+544	23·5	D	S-bonded
(33)	*cis*-$(Me_2SO)(Me_2S)PtCl_2$	−8	50·8	B	$^3J_{PtH}(Me_2SO) = 22·1$ Hz
(34)	*trans*-$(Me_2SO)(Me_2S)PtCl_2$	+51	50·8	B	$^3J_{PtH}(Me_2SO) = 21·2$ Hz
(35)	*cis*-$(Me_2S)(Ph_3P)PtCl_2$	−540	46·8	B	$^1J_{PPt} = 3680$ Hz
(36)	*cis*-$(Me_2S)(PCl_3)PtCl_2$	−238	50·4	B	$^1J_{PPt} = 5780$ Hz
(37)	*cis*-$(Et_3P)_2PtCl_2$	−943	27	A	$^1J_{PPt} = 3560$ Hz
(38)	*trans*-$(Et_3P)_2PtCl_2$	−386	19·5	A	$^1J_{PPt} = 2435$ Hz
(39)	*cis*-$(Et_2PhP)_2PtCl_2$	−872	?	A	$^1J_{PPt} = 3530$ Hz [f]
(40)	*trans*-$(Et_2PhP)_2PtCl_2$	−416	?	A	$^1J_{PPt} = 2480$ Hz [f]
(41)	*trans*-$(Bz_2PhP)_2PtCl_2$	−434	?	A	$^1J_{PPt} = 2500$ Hz [f]
(42)	*trans*-$(Et_3P)_2PtHCl$	−1360	1307 ^1J	B	$^1J_{PPt} = 2710$ Hz
(43)	*trans*-$(Ph_3P)_2PtHCl$	−1310	1191 ^1J	B	$^1J_{PPt} = 3030$ Hz
(44)	*cis*-$[(MeO)_3P]_2PtCl_2$	−817	2·1 ^4J	B	$^1J_{PPt} = 5690$ Hz
(45)	*cis*-$[(EtO)_3P]_2PtCl_2$	−805	?	B	$^1J_{PPt} = 5700$ Hz [f]
(46)	*trans*-$[(MeO)_3P{\cdot}(Ph_3P)_2PtCl]^+$	−1116	2·2 ^4J	B	$^1J_{PPt} = 4960, 2890$ Hz
(47)	$[\{(MeO)_3P\}_4Pt]^{2+}$	−1520	2·3 ^4J	B	$^1J_{PPt} = 3450$ Hz

[a] Compound (31) was kindly donated by Dr. D. V. Bowen; (39) and (40) by Dr. S. O. Grim; and (41) by Dr. J. A. Nash. [b] To low field of reference. Error ±1 p.p.m. [c] ±0·2 Hz. Refers to ^3J unless otherwise stated. [d] Solvents: A, $CDCl_3$; B, CH_2Cl_2; C, $[^2H_6]Me_2SO$; D, D_2O. [e] $^3J(^{195}Pt \cdots H)$ not determined because the position of only one satellite line in the proton spectrum was available. [f] $^3J(^{195}Pt \cdots H)$ was measured owing to complexity of proton spectrum. [g] Two different values of $^3J(^{195}Pt \cdots H)$ observed owing to magnetic inequivalence of the methylene protons. This is described in detail in P. Haake and P. C. Turley, *J. Amer. Chem. Soc.*, 1967, **89**, 4611.

above assignment. The identification of the *trans* isomer (16) is illustrated in (d) and the species present in other mixtures were identified similarly.

The products of displacement reactions can also be conveniently identified by ^{1}H–{^{195}Pt} experiments, especially when phosphorus-containing ligands are present, for the size of $^{1}J(^{195}\mathrm{Pt}–^{31}\mathrm{P})$ can then give useful information. Addition of triphenylphosphine to *cis*-$(\mathrm{Me_2S})_2\mathrm{PtCl_2}$ (1) gave an additional line without ^{195}Pt satellites in the methyl region of the proton spectrum which could be attributed to displaced dimethyl sulphide. The satellites of the line arising from co-ordinated dimethyl sulphide were now found to be associated with *two* ^{195}Pt frequencies (either of which would perturb only *half* the intensity of the satellite) and which were separated by 3680 Hz which is a reasonable magnitude for $^{1}J(^{195}\mathrm{Pt}–^{31}\mathrm{P})$ and thus provides confirmation that the major species present is (35). A similar result was obtained with phosphorus trichloride except that $^{1}J(^{195}\mathrm{Pt}–^{31}\mathrm{P})$ was now much larger owing to the electron-withdrawing influence of the chlorine atoms. With phosphorus tribromide $(\mathrm{Me_2S})_2\mathrm{PtBr_2}$ (3) was formed. The methoxy-resonance of equimolar mixtures of $(\mathrm{Ph_3P})_2\mathrm{PtCl_2}$ and trimethyl phosphite in methylene dichloride is a doublet [$^{3}J(^{31}\mathrm{P}\cdots\mathrm{H}) = 10$ Hz] with ^{195}Pt satellites [$^{4}J(^{195}\mathrm{Pt}\cdots\mathrm{H}) = 2{\cdot}2$ Hz] which were clearly revealed by a ^{31}P decoupling experiment, thus showing that essentially all of the trimethyl phosphite had become co-ordinated to platinum. Further selective ^{1}H–{^{31}P} experiments using these satellites gave the magnitude of $^{1}J(^{195}\mathrm{Pt}–^{31}\mathrm{P})$ as 4960 Hz and also showed that spin coupling between the phosphorus nucleus of the trimethyl phosphite moiety and other phosphorus nuclei in the complex species was less than 5 Hz. ^{1}H–{^{195}Pt} experiments showed that the platinum spectrum consisted of six lines forming a doublet [$J(\mathrm{Pt–P}) = 4960$ Hz] of triplets [$J(\mathrm{Pt–P}) = 2890$ Hz]. These results are consistent with the formulation of the species as (46) in which a chlorine atom has been replaced by trimethyl phosphite and the two triphenylphosphine groups remain mutually *trans*. It is to be expected that $^{2}J(^{31}\mathrm{P}\cdots{}^{31}\mathrm{P})_{cis}$ would be small in this type of complex.[12]



60 MHz methyl proton resonance of a mixture of $(\mathrm{PhMeS})_2\mathrm{PtCl_2}$ and $(\mathrm{PhMeS})_2\mathrm{PtBr_2}$ in $\mathrm{CDCl_3}$ at 24 °C. (a) Normal single resonance spectrum with ^{195}Pt satellites labelled s—t'; (b) with simultaneous irradiation at a frequency corresponding to $\delta(^{195}\mathrm{Pt}) = -319$ p.p.m.: p and p' which arise from species (14) are affected; (c) with irradiation at $\delta(^{195}\mathrm{Pt}) = -114$ p.p.m.: the three lines marked s and also a weak line hidden by t' which arise from compound (15) are affected; (d) with irradiation at $\delta(^{195}\mathrm{Pt}) = -69$ p.p.m.: t and t' which arise from (16) are affected

Species containing the ligand PhMeS can exhibit isomerism owing to dissymmetry at the sulphur atom, but only in two cases were effects due to this observed in the n.m.r. spectra. (*a*) The methyl resonance of *cis*-$(\mathrm{PhMeS})_2\mathrm{PtCl_2}$ (9) was a singlet (flanked by ^{195}Pt satellites) at room temperature, but at −25 °C split into a symmetrical doublet, whereas the *trans*-isomer (10) gave a singlet down to −60 °C. (*b*) The dimethyl sulphide resonance of *cis*-$(\mathrm{Me_2S})(\mathrm{MePhS})\mathrm{PtCl_2}$ (11) was a singlet at +50 °C in deuteriochloroform, but was broad at room temperature and gave *two* lines of equal intensity at 0 °C. The *trans*-isomer (12) gave a single line from −20 °C to +50 °C. The temperature dependence of these effects, and the fact that they are observed only in the *cis*-isomers, indicates that whilst they depend basically upon the presence of a chiral centre at sulphur the magnitude is largely dominated by differences in rotamer populations. In case (*a*) where there are two distinct molecules involved, attempts were made to detect a ^{195}Pt chemical-shift difference between the diastereomers, but any such difference was found to be less than 1 p.p.m. By contrast a difference of 15 p.p.m. was found for compound (31) in which the relative orientations are fixed. On account of low solubility these two isomers were examined in [$^{2}\mathrm{H_6}$]dimethyl sulphoxide solution but no displacement of the ligand was observed [*cf.* the behaviour[13] of $(\mathrm{Me_2S})_2\mathrm{PtCl_2}$ in the same solvent] and any solvent effect upon the platinum chemical shift should be small compared with the overall range.

The temperature dependence of the ^{195}Pt chemical shift of compounds (9), (10), and (20) was found to be $+0{\cdot}47 \pm 0{\cdot}05$ p.p.m./°C (*i.e.*, a decrease in shielding with increasing temperature) in benzonitrile solution in the range 23—145 °C, and $+0{\cdot}35 \pm 0{\cdot}05$ p.p.m./°C in deuteriochloroform in the range −60 to +60 °C.

DISCUSSION

The results for compound (9) and also for (31) indicate that conformational effects upon the platinum shielding are probably small compared with the overall range observed, although it would be necessary to study a

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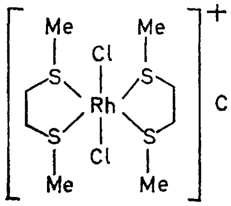
[13] W. McFarlane and F. R. M. White, *Chem. Comm.*, 1969, 439.

greater number of compounds to establish this with certainty. However, in the remainder of this Discussion such effects will be ignored. By contrast, with ^{103}Rh differences in shielding of up to 81 p.p.m. were found[14] in the complex (I) according to the orientations of the methyl groups (and hence of the sulphur electron lone pairs). This apparent greater sensitivity may be associated with a larger sensitivity to changes in ΔE in the case of rhodium since the temperature dependence of the shielding is also larger.



(I)

Explanations of the magnetic shielding of the heavier nuclei have usually assumed dominance by the paramagnetic contribution of Ramsey.[15,16] However, it has been pointed out[17] that the diamagnetic contribution from immediate neighbours as calculated by Flygare and Goodisman's formula[18] may also be important and should also be considered. For the atoms bound to platinum in the species studied here this has the following approximate values: N, 31; O, 36; P, 61; S, 63; Cl, 68; Se, 128; Br, 129; and I, 181 p.p.m. (Note that opposite sign conventions are now advocated for magnetic shielding and for chemical shifts.) Compared with the range of values observed experimentally for the total platinum shielding these represent quite small corrections and cannot account for anomalies observed by other workers.[7,9] Similar difficulties arise when the neighbouring diamagnetic correction is applied to ^{119}Sn chemical shifts.[19]

In general the neighbouring-atom diamagnetic correction gives quite good results when applied to the shielding of the nuclei of elements in the first row of the Periodic Table,[17] but is less successful for the shielding of heavier nuclei. Experimentally the necessary corrections then appear to be much larger so that whilst there is a 'bulky atom effect' which increases the shielding this is probably related to the paramagnetic term, and may depend upon the polarisability of the atom in question.

Studies of ^{59}Co chemical shifts in a range of complexes revealed quite good correlations with the mean electronic excitation energies as measured from absorption spectra,[4,5] and it is significant that with only one exception all of the neighbours of the cobalt atom were of comparable size (*i.e.*, N or O) so that any 'bulky atom' correction could be ignored. In the exceptional case there was a chlorine atom attached to cobalt and the observed chemical shift was then significantly to high field of the predicted value. By contrast, attempts to correlate ^{195}Pt chemical shifts with electronic excitation energies were largely unsuccessful,[7] and this was probably due to the use of complexes with ligand atoms of widely differeing sizes (*e.g.*, N, P, and As) so that the 'bulky atom' effect could not be ignored.

In the present work it appears that in cases where the bulky atom effect should be approximately constant there is a dependence of the platinum shielding upon ΔE as required by Ramsey's equation.[15] Thus the *trans*-isomers of $(R_3P)_2PtCl_2$ have ^{195}Pt chemical shifts some 500 p.p.m. to low field of the corresponding *cis*-isomers and this is consistent with the shorter-wavelength absorption (*i.e.*, ΔE larger) of the latter. In species with smaller differences of ΔE between *cis*- and *trans*-isomers (*e.g.*, complexes of ligands with Group VI donor atoms) the ^{195}Pt chemical-shift differences are also smaller. When two of the ligands have a much greater '*trans*-effect' than the other two the difference in ΔE between *cis*- and *trans*-isomers is usually large and it is then possible to use the ^{195}Pt chemical shift to determine the stereochemistry, the *trans*-isomer giving a resonance at lower field.

The observed temperature dependence of the ^{195}Pt chemical shift of *ca.* +0·5 p.p.m./°C is also consistent with a dependence of the platinum shielding upon ΔE. Similar but somewhat larger dependences have been found for ^{59}Co (+3 p.p.m./°C in low-spin d^6 complexes) and ^{103}Rh (+0·8 p.p.m./°C in a low-spin d^6 complex) and are believed to arise from an increase in the population of higher vibrational energy levels which effectively reduces ΔE and so increases the paramagnetic term. By contrast, the shielding of the nuclei of non-transition elements[20] (*e.g.*, ^{119}Sn) or of transition elements in complexes with closed *d*-shells[21] (*e.g.*, ^{63}Cu in Cu^{I} complexes) has been found to be essentially independent of temperature provided that conformational or chemical changes do not occur.

On the basis of *dominance* of the platinum shielding by variations in ΔE the chemical shifts of species L_2PtX_2 (X = Cl, Br, or I) should move to lower field in this order. In fact the reverse trend is observed and this is not greatly altered by the neighbouring-atom diamagnetic correction. Thus it appears that the effect upon the paramagnetic term due to a bulky atom is dominant in these cases. The same effect is found for the ^{119}Sn chemical shifts of the tin halides including mixed species, and for these there is an accurate linear additivity relationship.[22] With platinum the additivity is less precise, but the results for mixed species show that

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[14] W. McFarlane, *Chem. Comm.*, 1969, 700.

[15] A. Saika and C. P. Slichter, *J. Chem. Phys.*, 1954, **22**, 26.

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[17] J. Mason, *J. Chem. Soc.* (*A*), 1971, 1038.

[18] W. H. Flygare and J. Goodisman, *J. Chem. Phys.*, 1968, **49**, 3122.

[19] J. Mason, personal communication.

[20] J. D. Kennedy, J. M. Seaby, and W. McFarlane, unpublished observations.

[21] W. McFarlane and D. S. Rycroft, unpublished observations.

[22] J. J. Burke and P. C. Lauterbur, *J. Amer. Chem. Soc.*, 1961, **83**, 326.

it still holds, and increments of *ca.* 240 and 700 p.p.m. to high field accompany replacement of a chlorine atom by bromine or iodine respectively.

The nuclear shielding should also depend upon the electronegativity of the groups attached to platinum as this will affect the electronic imbalence in the bonds to the platinum atom.[16] An increase in the electronegativity should give a shift to low field. The results for several other nuclei suggest that it would be reasonable to expect the electronegativity difference to account for a ^{195}Pt chemical shift of 20—40 p.p.m. to high field when chlorine is replaced by bromine, whereas the observed effects are much larger than this.

The high-field platinum chemical shifts found for the hydrides $(R_3P)_2PtHCl$, the phosphite complexes, and the cationic species containing three or four phosphorus atoms bound to platinum can be attributed to smaller values of ΔE.

The various coupling constants involving platinum are in accord with results obtained previously. Thus when ligands which can exert a strong *trans*-effect are present there are quite large differences between *cis*- and *trans*-isomers, whereas when such groups are absent the differences are smaller. In compound (46) the coupling of 4960 Hz between ^{195}Pt and the phosphorus of the trimethyl phosphite moiety is large because (*a*) the other phosphorus substituents are strongly electron withdrawing and (*b*) this phosphorus atom is *trans* to a chlorine atom. The coupling between ^{195}Pt and the phosphorus of the triphenylphosphine moiety is small because the phenyl groups are less strongly electron withdrawing and each phosphorus atom is *trans* to phosphorus. The effect upon $^1J(^{195}Pt-^{31}P)$ of electronegative groups on phosphorus is well brought out by the different values in compounds (35) and (36). $^1J(^{195}Pt-^{77}Se)$ should behave similarly to $^1J(^{195}Pt-^{31}P)$ and the values in compounds (20) and (21) show that this is so. The smaller percentage difference between them compared with phosphine complexes can be attributed the weaker *trans*-effect of organoselenides.

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