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PLATINUM-195 NUCLEAR MAGNETIC RESONANCE

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CONTENTS

ABBREVIATIONS

Me	= methyl	COD	= 1,5-cyclooctadiene
Et	= ethyl	DMSO	= dimethylsulfoxide
Pr^n	= *n*-propyl	py	= pyridine
Pr^i	= *iso*-propyl	cp	= cyclopentadienyl
Bu^n	= *n*-butyl	dppm	= diphenylphosphinomethane
Bz	= benzyl	dppe	= diphenylphosphinoethane
Ph	= phenyl	dppp	= diphenylphosphinopropane
Tol	= *p*-tolyl	dppb	= diphenylphosphinobutane

A. INTRODUCTION

The chemistry of platinum continues to occupy the research efforts of many laboratories and consequently it is not surprising that ^{195}Pt, the platinum isotope with nuclear spin $I = 1/2$, is finally garnering the interest

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of the inorganic nuclear magnetic resonance (NMR) community.

^{195}Pt NMR is just about as old as the NMR method itself [1], but quite rightly fell by the wayside for lack of suitable instrumentation and/or interest. In the middle 1960s, almost simultaneously in Zurich [2] and Oxford [3], these two necessary conditions were fulfilled and the chemical community had a quick glimpse of the sensitivity of the platinum chemical shift to structural change. Unfortunately, the spark did not catch since the sample concentrations required to obtain reasonable signal-to-noise (≈ 1 molar) produced more levity than research funds. Just about this time the NMR spectroscopic community was awakening to the advantages of Fourier transform NMR spectroscopy, with the emphasis, naturally enough, on ^{1}H and ^{13}C NMR. In the early 1970s we noticed that what was possible for ^{13}C (natural abundance = 1.1%, relative sensitivity = 1.59×10^{-2}) should certainly be feasible for ^{195}Pt (natural abundance = 33.7%, relative sensitivity = 9.94×10^{-3}). Indeed, at about 19.34 MHz (21000 Gauss) we readily observed the ^{195}Pt resonance of Na_2PtCl_6 using an HX-90 operating in FT mode. (The Bruker organization is to be commended both for its willingness to provide the hardware, and for its help in finding the first of many elusive signals.)

Since these first pulsed NMR efforts in 1972, the number of instruments capable of measuring ^{195}Pt NMR spectra has increased by about two orders of magnitude and this type of measurement is now almost routine. Since the reports on this nucleus will certainly become more abundant, it seems worthwhile to sketch in some detail what the chemist can expect to achieve, and what problems will arise, from direct measurements of this metal.

B. METHODOLOGY

(i) Measuring techniques

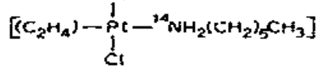
^{195}Pt NMR spectra are recorded directly, using either continous wave or pulsed methods, or indirectly using double resonance methods. The latter requires the presence of a suitable ^{1}H (or ^{31}P ...) signal which has a coupling to ^{195}Pt. Monitoring this more readily observable signal while sweeping the ^{195}Pt spectra allows δ^{195}Pt to be determined on relatively dilute solutions [4]. The disadvantage lies in the necessity of choosing a sample in which at least one resonance is easily seen (e.g., for ^{1}H, PMe_3 complexes are often suitable, but coordinated PPh_3 more problematic). Direct observation, done primarily using pulsed NMR methods, does not have any such chemical limitation, but is not as sensitive in that higher concentrations are required. This type of signal-to-noise limitation is less serious today since spectrometers operating at magnetic fields created by superconducting magnets produce acceptable signal-to-noise on 10^{-3} M solutions after several hours of accumulation. Nevertheless, double resonance methods can be superior in that there may be cases where a ^1H spectrum is obtainable and the metal spectrum proves elusive. It is worthwhile remembering that the instrumental requirements for the direct and indirect methods differ considerably, and that, although both are available, double resonance accessories must be purchased separately.

(ii) Spin–lattice and spin–spin relaxation times

The success of pulsed NMR spectroscopy lies to a large extent in being able to rapidly accumulate spectra. The efficiency of this process depends on the spin–lattice, T_1, and spin–spin, T_2, relaxation times [5]. In the early days of pulsed high resolution ^{13}C NMR it was observed that T_1 values could be either tens of seconds or milliseconds [6]. Not every type of carbon was easily observable [7] and this difficulty led to the development of methods to circumvent this problem [8]. Fortunately, ^{195}Pt T_1 and T_2 measurements to date [9–11] show no such restriction and values ranging from 1.7 s to fractions of a second are not uncommon. The solvent dependence of T_1 is quite large: for $(Bu_4N)_2[PtCl_6]$ in methanol $T_1 = 1.65$ s, whereas this is reduced to 0.89 s in CH_2Cl_2 [10].

Spin rotation is suggested [10] to be the prime mechanism by which ^{195}Pt relaxes; however, there is evidence that the chemical shift anisotropy contribution becomes important at higher magnetic fields. Thus, for the halogen bridged dimer *sym-trans*-$[Pt_2Cl_4(PBu^n_3)_2]$$T_1 \cong 100$ ms at 21.1 kG but only ≈ 10.5 ms at 58.72 kG [11].

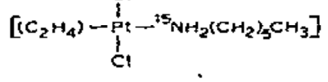
These short T_1 values imply that rapid data acquisition is possible since little or no waiting time between the pulses is necessary. On the other hand, T_2 and therefore ^{195}Pt linewidths, can be troublesome. Although it is possible to find complexes for which the linewidths, $\Delta\nu_{1/2}$, are 5 Hz or less (e.g. see Fig. 1), it is not uncommon to find $\Delta\nu_{1/2}$ values of ≈ 25 Hz, and for complexes containing ligating atoms with large electric quadrupole moments, several hundred hertz is not unusual. The source of the problem is now clear: the relaxation of the quadrupolar nucleus is neither fast enough to decouple it from the ^{195}Pt, nor slow enough to permit observation of the coupling. The case for nitrogen ligands is illustrative. For (I), the line width at half height is ~240 Hz, whereas when the molecule contains ^{15}N enriched nitrogen, $\Delta\nu_{1/2}$



$[(C_2H_4)-PtCl_2-{}^{14}NH_2(CH_2)_5CH_3]$

(I)

$\Delta\nu_{1/2}$ = 240 Hz



$[(C_2H_4)-PtCl_2-{}^{15}NH_2(CH_2)_5CH_3]$

(II)

$\Delta\nu_{1/2}$ = 10 Hz

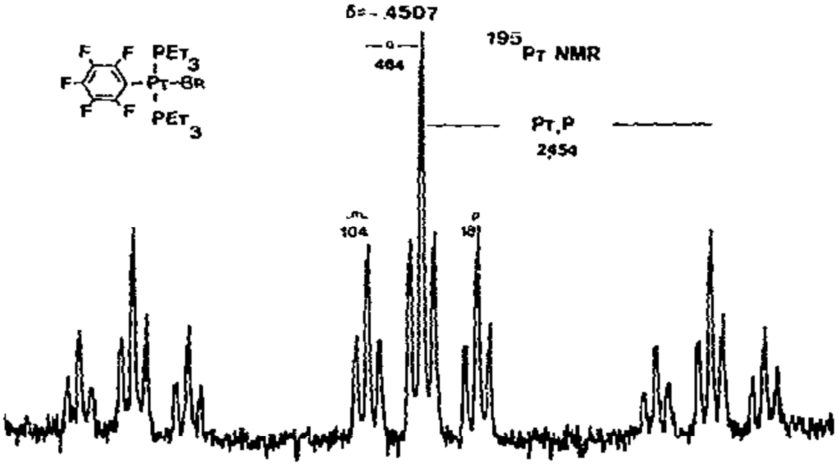


Fig. 1. ^{195}Pt{^{1}H} NMR spectrum of *trans*-[PtBr(C_6F_5)(PEt_3)$_2$]; showing coupling constants to the three types of ^{19}F atoms and the two tertiary phosphines. The correct chemical shift is −4548 ppm.

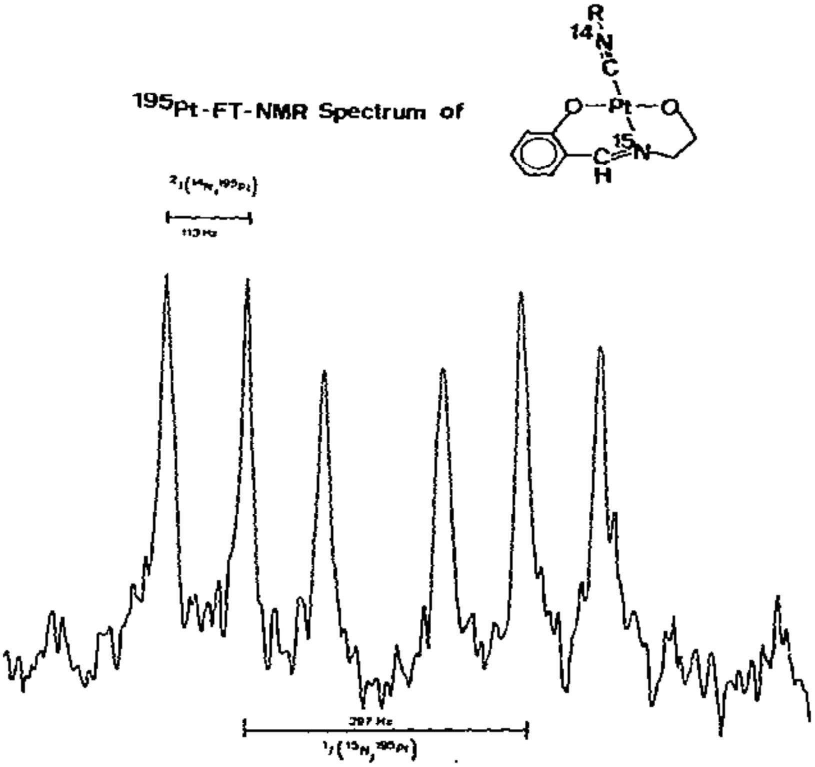


Fig. 2. ^{195}Pt{^{1}H} spectrum of [Pt($OC_6H_4CH{=}^{15}NCH_2CH_2O$)(C≡N(cyclohexyl))] showing both ^{15}N and ^{14}N splittings.

is reduced to only 10 Hz [12]. In general, nitrogen ligands are often troublesome in that once the lone-pair coordinates, the ^{14}N relaxation is slower and often affects the ^{195}Pt spectrum adversely. This point is not trivial for spectroscopists trying to obtain high resolution ^{195}Pt spectra on the cancer drug *cis*-$[PtCl_2(NH_3)_2]$ and its derivatives [13].

In some few cases we have observed the values $^nJ(^{195}Pt, ^{14}N)$ directly, such as for the isonitrile Schiff's base complex $[Pt(OC_6H_4CH={}^{15}NCH_2CH_2O)(C\equiv NC_6H_{11})]$ (Fig. 2, [14]). In addition to the ^{15}N one-bond coupling the isonitrile-^{14}N couples to the metal through carbon. We have also observed $^1J(^{195}Pt, ^{14}N)$ directly for *trans*-$[PtCl_2(C_2H_4)$(2,4,6-trimethyl-pyridine)] [14] and Goodfellow and co-workers [15,16] report extensive $^1J(^{195}Pt, ^{14}N)$ data for thiocyanate and cyanate complexes. Since there is a recent report containing $^2J(^{195}Pt, ^{14}N)$ data on a wider variety of isonitrile complexes [17] it would appear that ^{14}N coupling as well as broadening must be reckoned with in future measurements on this type of molecule. Broad resonances due to the unresolved ^{14}N interaction (e.g., Fig. 3) can be sharpened by either normal or thermal decoupling, the latter taking advantage of the temperature dependence of the ^{14}N relaxation (i.e., the ^{195}Pt lines sharpen at lower temperature).

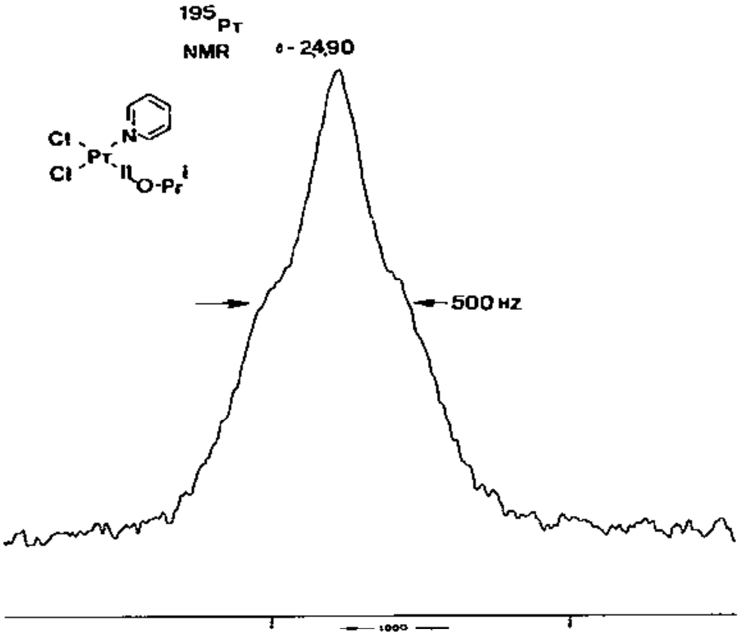


Fig. 3. $^{195}Pt\{^1H\}$ NMR spectrum of *cis*-$[PtCl_2$(pyridine)$(CH_2{=}CHOPr^i)]$. The triplet structure due the ^{14}N splitting is not fully resolved due to ^{14}N relaxation. The correct chemical shift is −2531 ppm. R. Lazzaroni, P. Salvadori and P.S. Pregosin, unpublished results.

(iii) Medium effects and referencing

It is important to remember that both solvent and temperature affect ^{195}Pt, with the former often amounting to several hundred parts per million. Even in the octahedral dianion complex $[PtCl_6]^{2-}$ a spread of 400 ppm has been observed on going from H_2O to DMSO with the latter appearing at higher field [10]. Typical examples are shown in Scheme 1 and it has been suggested that a combination of effects including basicity, polarizability, dielectric constant and ion pairing may all be important [10].

In any case, it should be obvious that conclusions as to molecular structure which are based on small differences in δ^{195}Pt are best drawn from measurements made in the same solvent.

The temperature dependence of the platinum shift is also significant with values ranging from ~0.1 to 1.0 ppm K^{-1} [9,18,19,20]. Although this is less of a problem than the solvent dependence, the effect becomes significant when variable temperature measurements are involved. A change in temperature of 100° could result in a 40–50 ppm effect, once again introducing an ambiguity if moderate differences in δ^{195}Pt are important. In connection with small changes, it should not be forgotten that "probe" or "ambient" temperature varies from instrument to instrument and depends markedly on whether broad-band ^{1}H coupling is employed.

As shown in Scheme 1, the $PtCl_6^{2-}$ ion is suggested as reference. We proposed this ion some six years ago since: (a) it is readily available; (b) its resonance appears at one end (low field) of the platinum shift range; and (c) the author and others [21] find it to be stable in solution over relatively long periods of time. (This reference has been criticized and others prefer a frequency scale related to the ^{1}H of TMS. This is certainly an acceptable alternative; however, as the latest generation of instrumentation makes direct measurement more attractive, more practitioners will seek a suitable reference compound and it seems wise to prevent further confusion by settling the issue now.) To be sure, there are several drawbacks: (a) to achieve

Scheme 1 [a]

H_2O	Na_2PtCl_6	0	Na_2PtCl_4	−1614
CH_3OH	$(Bu_4N)_2[PtCl_6]$	−222	$(Bu_4N)_2PtCl_4$	−1477
CH_2Cl_2	$(Bu_4N)_2[PtCl_6]$	−260	$(Bu_4N)_2PtCl_4$	−1416
CH_3CN	$(Bu_4N)_2[PtCl_6]$	−327	$(Bu_4N)_2PtCl_4$	−1388
$(CH_3)_2CO$	$(Bu_4N)_2[PtCl_6]$	−370	$(Bu_4N)_2PtCl_4$	−1384
DMSO	$(Bu_4N)_2[PtCl_6]$	−400	$(Bu_4N)_2PtCl_4$	−1372

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[a] Data from ref. 10.

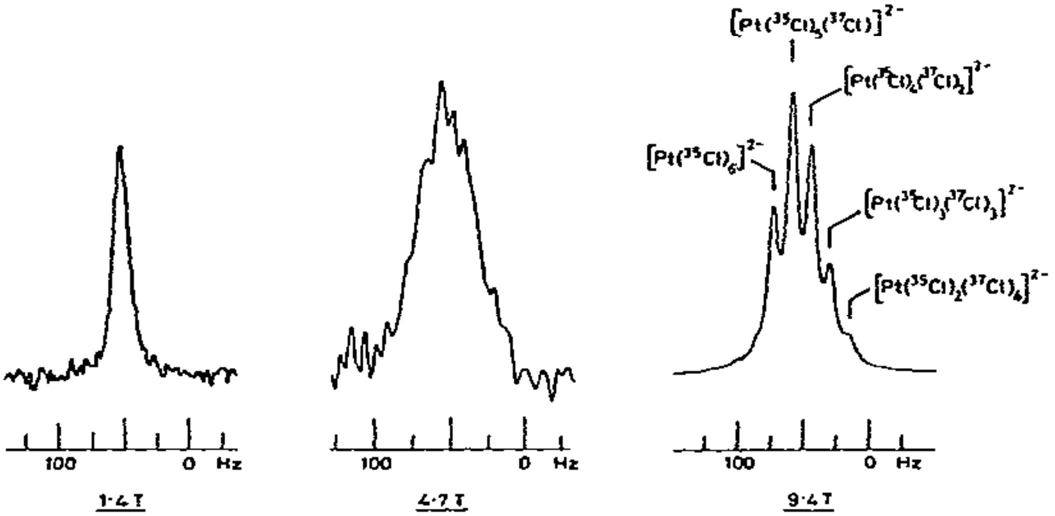


Fig. 4. ^{195}Pt NMR spectra of a 2 M solution of Na_2PtCl_6 in D_2O (10-mm tube, 21°C) at magnetic fields of: (i) 1.4 tesla; (ii) 4.7 tesla; and (iii) 9.4 tesla, from ref. 22.

consistency with the ^{1}H, ^{13}C and ^{31}P literature requires that almost all platinum shifts will be negative; (b) the signal is not very sharp, and indeed, as shown by Ismail et al. [22] is the composite of the various $Pt^{35}Cl^{37}Cl$ isotopomers (see Fig. 4); and (c) this complex is reported to have a large temperature dependence [23]. Nevertheless, this anion, usually available as either a Na^+ or K^+ salt, has a broad appeal to a large segment of those measuring ^{195}Pt spectra.

C. CHEMICAL SHIFTS

(i) Theory

General chemical shift theory [24] allows us to write the following expressions

$$\nu = \gamma H_0(1-\sigma_t)/2\pi, \quad \nu = \text{resonance frequency}$$
$$\sigma_t = \sigma_p + \sigma_d + \sigma_x$$

where σ_t represents the total screening constant and σ_p, σ_d and σ_x are the paramagnetic, diamagnetic and extraneous (e.g. ring current, and other anisotropic contributions) expressions, respectively. For metals, changes in σ_p are recognized to be the determining factors and Dean and Green [25] have obtained a modification of the Ramsey [24] equation which is thought to be correct for ^{195}Pt.

$$\sigma_{\mathrm{p}} \sim \langle r^{-3} \rangle\, C^2_{\mathrm{a_{1g}}} \left[2C^2_{\mathrm{a_{2g}}}\, \Delta E_{\mathrm{A}}^{-1} + C^2_{\mathrm{e_g}}\, \Delta E_{\mathrm{E}}^{-1} \right]$$

where

$$\Delta E_{\mathrm{A}} = E(^1A_{2g}) - E(^1A_{1g})$$

$$\Delta E_{\mathrm{E}} = E(^1E_{g}) - E(^1A_{1g})$$

and $C_{\mathrm{a_{1g}}}$, $C_{\mathrm{a_{2g}}}$ and $C_{\mathrm{e_g}}$ are the coefficients of the platinum *d* orbitals in the molecular orbitals. The r^{-3} represents the mean inverse cube distance of a *d* electron from the nucleus. In essence, if an exact knowledge of the energies of the various H.O.M.O.s and L.U.M.O.s, together with the necessary coefficients were available, existing UV-visible spectroscopic data should provide an excellent starting point for predicting and calculating δ^{195}Pt. For ^{59}Co, a similar approach has been employed and was found to be qualitatively, if not quantitatively, successful [26]. Unfortunately, the ordering of the *d* orbital energy levels based on UV-visible spectroscopy is not obvious and first attempts [3] to empirically correlate δ^{195}Pt data with reciprocal transition energies based on electronic spectra were only modestly rewarded. Nevertheless, several groups have shown that this is the correct approach. Goggin et al. [27] using the anionic complexes $[\mathrm{PtX_3L}]^-$, X = Cl, Br, I, L = X$^-$, NMe$_3$, PMe$_3$, AsMe$_3$, SbMe$_3$, SMe$_2$, SeMe$_2$, TeMe$_2$, C$_2$H$_4$, PF$_3$ and SOMe$_2$, have found a rough linear relationship between ^{195}Pt and $\frac{1}{3}$ $(2\Delta E_{\mathrm{A}}^{-1} + \Delta E_{\mathrm{E}}^{-1})$ *for a given X*. Using the total data base, (all X and all L ligands) the correlation is less satisfactory; however, there is no reason to assume that the *C* terms are all constant and these authors have accounted for the discrepancy using this argument. Indeed, they derived empirical constants, based arbitrarily on Cl$^-$ = 1.0, which may provide an indication of the relative covalency of the Pt–L bond: NMe$_3$, 1.25; PMe$_3$ and SMe$_2$, 0.74; AsMe$_3$ and SeMe$_2$, 0.62; SbMe$_3$ and TeMe$_2$; Br$^-$, 0.83; I$^-$, 0.50.

In a more recent study Koie et al. [28] have combined platinum NMR and extended Hückel molecular orbital calculations in their investigation of the platinum(0) complexes $[\mathrm{Pt(R{-}C{\equiv}C{-}R')(PPh_3)_2}]$. They find that δ^{195}Pt depends on the nature of R and R′ (varying over ~ 168 ppm) and that this effect is directly related to the energy difference between the H.O.M.O., which is primarily either Pt($d_{x^2-y^2}$) or Pt(d_{xz}), and the L.U.M.O., which is a mixture of the acetylene π^* orbital and the Pt(d_{yz}) orbital.

Assuming that the H.O.M.O.–L.U.M.O. separations can be estimated as a metal-to-ligand charge transfer in the UV these authors find correlations between the electronic spectra and (a) changes in δ^{195}Pt as a function of R and R′ and (b) the solvent dependence of δ^{195}Pt. There is, then, reason to believe that the theory for ^{195}Pt chemical shifts is slowly approaching a point where predictions will shortly be possible.

(ii) Empiricisms

Despite the encouraging signs on the theoretical front, the practising platinum chemist requires a more immediate method of relating his chemical shift information to molecular structure. This is generally done empirically and is only as good as the data base is representative. Fortunately, the past ten years have seen a healthy accumulation of measurements so that, qualitatively, the following generalizations are possible (but are to be taken with a definite caveat!):

(a) In a series of closely related chloride complexes the metal resonance moves to high field in the order $P > As > S > N > Cl^- > O$. Thus the anions $[PtCl_3(H_2O)]^-$, $[PtCl_3(NMe_3)]^-$ and $[PtCl_3(PMe_3)]^-$ appear at -1180 [9], -1715 [27] and -3500 [27] ppm, respectively.

(b) As one moves down a group, there is often (but not always) an upfield shift: in δ^{195}Pt; for *trans*-$[PtClX(SMe_2)_2]$, X = Cl, Br, I the chemical shifts are -3424, -3666 and -5131 [27], respectively. A Group VI case is represented by the ions $[PtCl_3L]^-$, L = SMe_2, $SeMe_2$, $TeMe_2$ for which we have ^{195}Pt values of -2757, -2769 and -3059 ppm [27], whereas for the Group IV phosphine complexes *trans*-$[PtIX(PEt_3)_2]$, X = CH_3, SiH_3, GeH_3, we have -4825, -5270 and -5317 ppm, respectively [29]. Note that Group V represents an obvious exception: $[PtCl_3L]^-$, L = NMe_3, PMe_3, $AsMe_3$, $SbMe_3$ appear at -1715, -3500, -3173 and -3143 ppm, respectively [27].

(c) The resonances for Pt(II) complexes often appear at higher field than those for Pt(IV) compounds. The simplest example refers to $[PtCl_6]^{2-} = 0$; whereas $[PtCl_4]^{2-} = 1620$ [3,9]. Others also fit: $[PtBr_6]^{2-} = -1860$ and $[PtBr_4]^{2-} = -2690$ [2]; $[Pt(CN)_6]^{2-} = -3866$ and $[Pt(CN)_4]^{2-} = -4746$ [30]; however, $[PtI_2(CN)_4]^{2-}$ at -4790 [30] places this generalization in question. Further, resonances for Pt(0) complexes are found in the same area as are those for Pt(II) complexes (see Table 8).

(d) There is a dependence of δ^{195}Pt on complex geometry. For $[PtX_2L_2]$ types, where X is a relatively hard ligand such as Cl^-, and L = PR_3 or AsR_3, the *cis* complex is upfield of the *trans* analog by 400–500 ppm [3,27]. Where X and L are not so markedly different, the effect disappears, e.g. *cis*-$[PtBr_2(SMe_2)_2]$ at $\delta = -3879$ is very similar to *trans*-$[PtBr_2(SMe_2)_2]$ with $\delta = -3899$ [27].

Aside from (a)–(d) there are several additional points of interest, the most general of which concerns possible effects on δ^{195}Pt when the ligand atom substituents are changed. By and large substitution of CH_3 for H, i.e. Et for Me, or simply lengthening an alkyl chain, produces relatively small (< 100

Scheme 2

trans-$[PtCl_2(NHMe_2)(C_2H_4)] = -3074$,	*trans*-$[PtCl_2(NHMePr^i)(C_2H_4) = -3030$
trans-$[PtCl_2(AsEt_3)_2] = -3710$,	*trans*-$[PtCl_2(AsPr^i_3)_2] = -3596$
$[PtCl_2(CO)(Et)]^- = -3876$ [33],	$[PtCl_2(CO)(Pr^i)]^- = -3806$ [33]
$[Pt(p\text{-}CH_3C_6H_4)_2(COD)] = -3618$ [34],	$[Pt(o\text{-}CH_3C_6H_4)_2(COD)] = -3536$ [34]
trans-$[PtCl_2(\text{pyridine})(C_2H_4)] = -2979$,	*trans*-$[PtCl_2(2,6\text{-}(CH_3)_2\text{pyridine})(C_2H_4)] = -2877$

ppm) variations in $\delta^{195}Pt$, with the complexes *trans*-$[PtCl_2$(nitrogen ligand)$(C_2H_4)]$ [31] and $[PtCl_2L_2]$, L = tertiary phosphine [27], tertiary arsine [32] dialkyl sulfide and selenide [20] supporting this argument. Interestingly, if the ligand becomes sterically larger, there is a marked downfield shift of the platinum signal, as shown in Scheme 2. There is no clear suggestion connecting chemical shift theory to this observation, but there is a potential for application as we shall shortly see.

Returning to ligand electronic effects, there does not seem to be a pronounced aromatic resonance effect on $\delta^{195}Pt$. For the complexes $[Pt(XC_6H_4)_2(COD)]$ [34], *cis*-$[PtCl(SnCl_3)(P(XC_6H_4)_3)_2]$; *trans*-$[PtH(XC_6H_4CO_2)(PEt_3)_2]$ [25] and *cis*-$[PtCl_2(P(pXC_6H_4)_3)]$ [36], the change in metal chemical shift as a function of the *para* substituent is < 100 ppm (< 20 ppm for the benzoate and phenyl complexes).

Empiricisms such as (a)–(d) remind us that the ligand dependence of $\delta^{195}Pt$, as per theory, is quite substantial. All in all the chemical shift range is approximately 13000 ppm and changes within the metal coordination sphere are almost invariably associated with changes of 100 ppm or more. It is difficult to formulate reliable additivity roles when ligands are exchanged, although the very fine work of Goggin et al. [27] reveals that this is not hopeless for the halogens; nevertheless, there is reason to believe that $\delta^{195}Pt$ values in very different complexes can be related to one another. In Fig. 5 data are correlated for a few complexes of the type $[PtCl_3L]^-$ [27] and *trans*-$[PtCl_2(^{15}NH_2C_6H_{13})L]$ [37]. It is premature to suggest that the five points compose a good straight line; however, there is certainly reason to believe that, both empirically and theoretically, we are approaching a time when we shall feel confident about how the ligand affects the metal chemical shift.

Apart from the studies mentioned above there exists a large body of work containing ^{195}Pt data in which this nucleus is studied but not always prominently featured. It is convenient to divide these into sections concerning complexes of nitrogen, phosphorus (the tertiary phosphine ligand appears frequently in all three categories) and carbon ligands and to briefly summarize these.

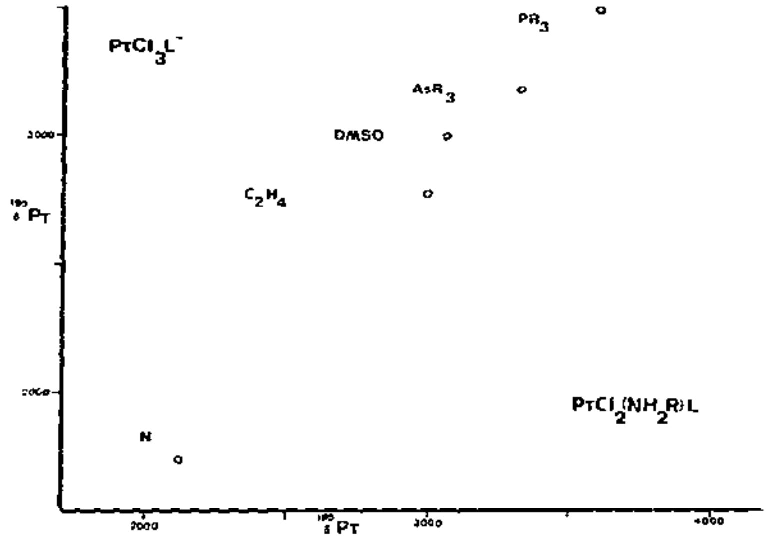


Fig. 5. Plot of δ^{195}Pt in the anions $[PtCl_3L]^-$ [27] vs. δ^{195}Pt for the complexes *trans*-$[PtCl_2(^{15}NH_2(CH_2)_5CH_3)L]$. L for the anions: PMe$_3$, AsMe$_3$, DMSO, C$_2H_4$ and NMe$_3$; for the hexylamine complexes PBu$^n_3$, AsBu$^n_3$, DMSO, C$_2$H$_4$ and $^{15}NH_2(CH_2)_5CH_3$. The δ values are all negative (to lower frequency) with respect to Na$_2$PtCl$_6$.

In the nitrogen ligand area there are metal NMR data for the solvolysis products of *cis*-$[PtCl_2(^{15}NH_3)_2]$ in dimethyl sulfoxide [38]; studies for *trans*-$[PtCl_2(^{15}NH_2(CH_2)_5CH_3)L]$, L = Group V ligands [37], and the tridentate Schiffs base $[Pt(OC_6H_4CH{=}^{15}NCH_2O)L]$, where L is again primarily a Group V ligand [39] and a few examples of metal complexes of the diimine, Bu^{t}N=CH–CH=NBu^t [40]. In all of the above, emphasis is placed on the magnitude and utility of $^1J(^{195}Pt, ^{15}N)$. For the $^{15}NH_2(CH_2)_5CH_3$ complexes there is a correlation of the coordination chemical shift $\Delta\delta^{15}N$ with δ^{15}Pt [37]. Several groups have reported data for thiocyanate complexes with the eventual aim of distinguishing nitrogen from sulfur coordination. Anderson et al. [15,16] using INDOR methods have prepared and looked at an extensive collection of SCN$^-$ complexes with NMe$_3$, PMe$_3$, AsMe$_3$, SbMe$_3$, SeMe$_3$, SeMe$_2$ and TeMe$_2$ and also comment on a few NCO$^-$ derivatives [16], whereas Pregosin et al. [41] have used pulsed NMR methods to discuss the $[Pt(C^{15}NS)_4]^{2-}$ ion. Both groups observe useful metal–nitrogen coupling constant phenomena and reach similar conclusions. McFarlane [20] has discussed δ^{195}Pt for more than 30 different complexes of sulfur ligands.

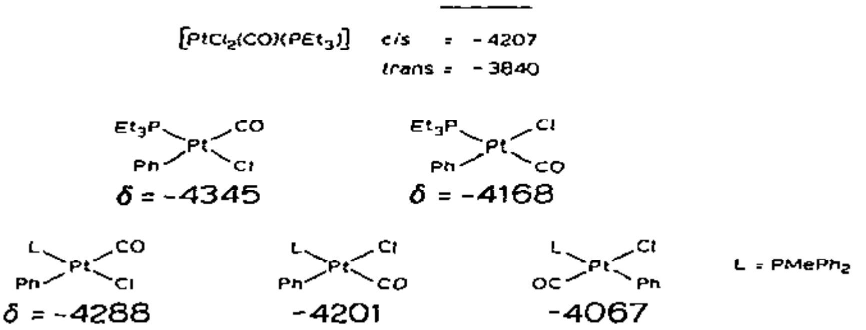
There is no dearth of information for tertiary phosphine complexes, although the favorite phosphine seems to be PEt$_3$. Anderson et al. [29] have reported on 44 phosphine complexes of Pt(II) and Pt(IV) with emphasis on silicon and hydride ligands, whereas Blacklaws et al. [42] have made a similar study using sulfur and selenium derivatives. There are also some few data related to phosphine complexes with silylamines and silylphosphines [43], and recently, platinum–tin complexes have also come under investigation due to their catalytic potential [35,44]. In addition to the earlier work on methyl substituted ligands [27] the Bristol group have done work on halogenated phosphine complexes [45], with special emphasis on fluorophosphine derivatives [46,47,48].

Kennedy et al. [34] have studied the metal NMR characteristics of 78 complexes, most of which have platinum–carbon bonds and either tertiary phosphine or arsine ligands. Their chemical shift information spans the three commonly observed oxidation states of platinum and relates mostly to methyl ligand complexes. Crocker et al. [49] supplement this nicely with Pt(II) and Pt(IV) data on C_6F_5 complexes. Interestingly, δ^{195}Pt for *trans*-$[PtBr(C_6F_5)(PEt_3)_2]$ at -4548 is considerably different than the value of -4323 observed for *trans*-$[PtBr(C_6H_5)(PEt_3)_2]$ [50]. Briggs et al. [51] give results for some cyclic and open alkenyl derivatives containing the "$Pt{-}C{=}CH_2$" moiety whereas Vrieze and co-workers [52] comment on the "ring effect" on δ^{195}Pt in the complexes $[Pt(CH_3)_2(Ph_2P(CH_2)_nPPh_2)]$. It is well known [53] that the ^{31}P chemical shift for $n = 2$ is at much lower field than for either $n = 1$, or $n = 3$; however, in the case of the metal chemical shift, it is the diphenylphosphinomethane compound ($n = 1$) for which a large deviation, 700 ppm, was observed. Hall et al. [54] have measured spectra for $[PtX_2(CH_2CH_2CH_2)(C_5H_5N)_2]$, X = Cl, Br, but, unfortunately, these are not readily compared to the phosphine complexes. Okeya and co-workers [55] have measured some acetylacetone complexes of the type $[Pt(O{-}C(CF_3){=}CHC({=}O)CH_2)L_2]$ which coordinate via carbon and oxygen. For L = PPh_3, $P(p\text{-}ClC_6H_4)_3$, $AsPh_3$ there is only a small change in δ^{195}Pt (-4227, -4230 and -4214).

A few data are available concerning carbonyl complexes of platinum. Browning et al. [33] have measured spectra for the $[NPr^n_4][PtCl_2R(CO)]$ anions, R = Me, Et, Pr^n, Pr^i, Bu^n, Ph and find, little change in δ^{195}Pt as a function of R, with the exception of a possible steric effect. The neutral compounds $[PtX_2(CO)(PMe_3)]$ [56] X = Cl, Br, I show the usual halogen substitution pattern with resonances at $\delta = -4164$, -4404 and -4928. The related phenyl complexes *cis* and *trans*-[PtClPh(CO)(phosphine)] [57] show a dependence of δ on geometry (see Scheme 3).

The cyclic acyl complexes $[Pt(OC_6H_4CO)L_2]$, L = PBu^n_3, $P(p\text{-}CH_3C_6H_4)_3$, $Ph_2PCH_2CH_2PPh_2$, $P(OEt)_3$ all lie between $\delta = -4304$ and -4390 [58]. Brown and co-workers [30], in their work on Pt(II) and Pt(IV) cyano complexes, mention $^{12}C/^{13}C$ and $^1H/^2H$ isotope effects. Data for the former pair are given whereas those involving the complexes *trans*-$[Pt(^1H/^2H)X(PEt_3)_2]$, X = Cl, CN are promised. They suggest that the

Scheme 3 [a]



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[a] Data from ref. 57.

magnitude of the effect depends on the nature of the *trans* ligand.

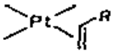
There are a few reports containing platinum chemical shift information for simple olefin complexes [14,59] and one on allene complexes [60], but certainly one of the most promising areas for this NMR probe involves the detection of different diastereomers resulting from olefin coordination and with this theme we move to applications.

(iii) Applications

When should ^{195}Pt NMR be considered as viable alternative to the ^{1}H ^{13}C or ^{31}P probe? Certainly in cases where these or other nuclei are either not available, not readily measured (e.g. ^{15}N in natural abundance or ^{13}C where long T_1s cause problems), or afford very complex spectra. In addition one should add: whenever another NMR form is not sufficiently sensitive to the chemical phenomena of interest. In this last respect the metal is quite useful. Considered the measurement of the diastereomers derived from complexes such as (I) and (II).

$R_3R_4R_5\overset{*}{C}-NR_1R_2-PtXYZ$

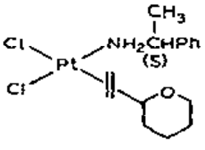
(I)



(II)

Compound (I) contains a chiral carbon center and after the prochiral nitrogen coordinates to the metal, diastereomers are produced. For the ethylene complex *trans*-[PtCl$_2$(amine)(C$_2$H$_4$)], amine = (*S*)-N-methyl-α-methylbenzylamine, the two diastereomers show Pt resonances separated by 51 ppm [31]. The separation is sufficient to allow an easy integration.

In (II) the olefin is prochiral and coordination induces an asymmetric carbon center. For (III), a molecule in this category, the cyclic ether carbon is also a potential source of optical isomers, thereby increasing the number



(III)

of possible optical isomers. Figure 6 shows that three of the four possible diastereomers are clearly visible [61] and the fourth can be observed during an equilibration process. The total difference in δ^{195}Pt is 50 ppm thereby providing a useful alternative to ^{1}H and ^{13}C NMR spectroscopy. Shinoda and co-workers [62] have observed a similar effect on δ^{195}Pt in the complexes *trans*-(*N*,olefin)[PtCl(*N*-methyl-(s)-prolinato)(olefin)] (although the differences in δ^{195}Pt were <20 ppm) as has Müller using various optically active amines and prochiral olefins [63]. The source of the difference in δ^{195}Pt is not clear; however, it has been suggested that steric effects may play a role [31]. For this type of problem metal NMR would seem to have a growing potential.

A nice example of complicated chemistry made easier concerns the

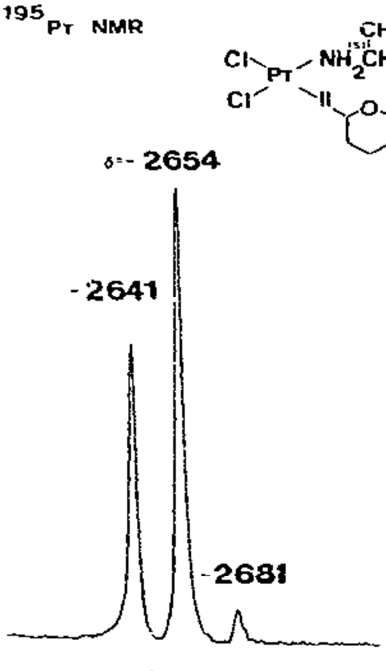
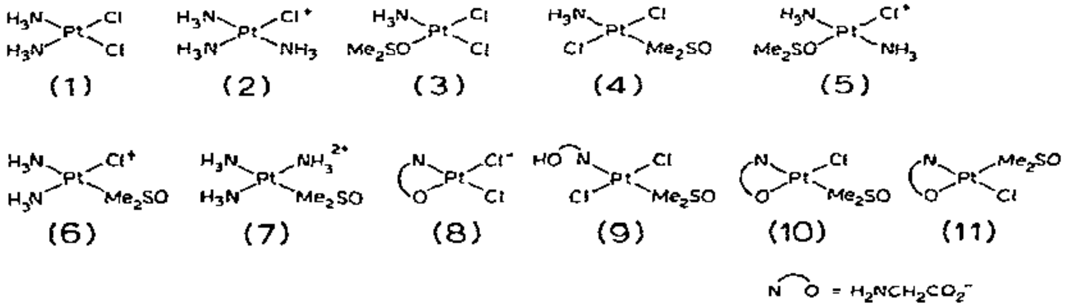


Fig. 6. ^{195}Pt NMR spectrum of *cis*-[$PtCl_2(NH_2CH(CH_3)Ph)(CH_2{=}CH{-}CHOCH_2CH_2CH_2CH_2)$]. The correct chemical shifts are: -2701, -2724 and -2751 ppm. R. Lazzaroni, P. Salvadori and P.S. Pregosin, unpublished work

solvolysis of *cis*-$[PtCl_2(NH_3)_2]$ in DMSO. The reaction can readily be studied as the metal chemical shift (and for $^{15}NH_3$, $^{1}J(^{195}Pt, ^{15}N)$) is sensitive to the types of ligand within the coordination sphere. Despite the presence of six different complexes, a full assignment could be made [38] (see Scheme 4). Moreover, using these data the authors could then identify the more thermodynamically stable isomer of [Pt(glycinate)(DMSO)Cl] as having sulfur *trans* to oxygen. Note that oxygen coordination is associated with a low field shift of $\delta^{195}Pt$, and that the total range of chemical shifts in (**1**)–(**11**) exceeds 1500 ppm.

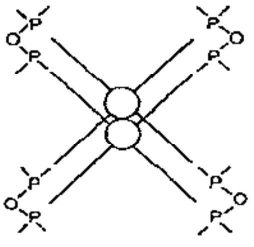
In view of its practical relevance, it is worth noting that the solvolysis of *cis*-$[Pt(NO_3)_2(^{15}NH_3)_2]$ has also been studied using ^{195}Pt NMR [64]. The *cis* diaquodiammineplatinum(II) ion, $\delta = -1600$ (D_2O) and its dimeric ($\delta = -1160$ (D_2O)) and trimeric ($\delta = -1519$ (D_2O)) forms have all been identified and the unusual low-field position of the dimer noted. Although the 0.05 M solutions under investigation do not yet approximate physiologically relevant models, the measurements represent a positive step forward.

Scheme 4



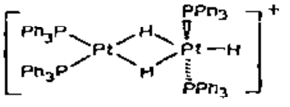
Complex	δ/ppm	$^{1}|J(^{195}Pt-^{15}N)|$/Hz, *trans* to		
		Cl^-	NH_3	Me_2SO
(1)	−2097	312.2	–	–
(2)	−2354	317	278	–
(3)	−3046	336	–	–
(4)	−3067	–	–	232
(5)	−3126	–	287	–
(6)	−3147	340.0	–	233.8
(7)	−3224	–	288	232
(8)	−1602	317	–	–
(9)	−3110	–	–	244
(10)	−2747	–	–	226
(11)	−2902	330	–	–

In some cases the observed multiplicity in the platinum spectrum is informative. The intensely luminescent product from K_2PtCl_4–H_3PO_4 reactions has been shown in the solid state [65] to be the dimer, (IV), bridged by four P–O–P linkages (each P atom has two terminal oxygens).



(IV)

The ^{195}Pt spectrum reveals a quintet of quintets stemming from the four one bond and four long-range platinum–phosphorus coupling constants thereby confirming the dimeric nature in solution. Similarly, the dimeric nature of the hydride complex (V) is established in part by the two different



(V)

resonances observed for the four- and five-coordinate metals, at δ −5104 and −4756 ppm, respectively, together with the observation of the metal–metal coupling constant (325 Hz) [66]. Stepping up from two to nine metals, Brown et al. [67] have shown that for the stacked cluster $[Pt_9(CO)_{18}]^{2-}$ there are distinct resonances for the inner and outer triangles and that: (a) there is intramolecular rotation of the triangles about the principal threefold axis; (b) interexchange of Pt_3 triangles; and (c) lack of edge terminal carbonyl exchange. For the NBu_4^+ salt in acetone the signals from the outer ($\delta = -4463$) and inner ($\delta = -5045$) triangles are well separated. There are other interesting examples exploiting the sensitivity of the metal chemical shift, e.g. the lower field position of N bound NCS^- relative to S-bound [15,16,41], but it is now abundantly clear that the platinum chemist will be able to profit from a knowledge of δ^{195}Pt.

In the tables which appear in this paper the reader will find a selection of chemical shift data which include results on a wide variety of square planar Pt(II) complexes, with special emphasis on the effect of ligand and complex geometry on δ^{195}Pt (see Tables 1–3), a sprinkling of material for Pt(IV) complexes, and some values for homo- and heteronuclear clusters. Tables 5 and 6 place the emphasis on complexes containing Group IV ligands whereas Table 7 contains shift data for olefin complexes. The remaining collections include complexes of nitrogen ligands and a wide variety of Pt(0) and dimeric derivatives.

D. COUPLING CONSTANTS

When complicated organic ligands are involved, it is not uncommon to find spin–spin coupling constants involving platinum and three or four other spin $= \frac{1}{2}$ nuclei. For example, in *trans*-$[PtCl_2(^{15}NH_2(CH_2)_5CH_3)(PBu^n_3)]$ the metal couples to ^1H, ^{13}C, ^{15}N and ^{31}P. For the first two of these there are coupling pathways over two and three bonds, whereas for the heavier spins the one-bond interactions $^1J(^{195}Pt, ^{31}P)$ and $^1J(^{195}Pt, ^{15}N)$ are under consideration. For brevity our discussion here will be limited (a) to $^1J(^{195}Pt, L)$ and (b) primarily to the spins L which have *not* been thoroughly discussed previously. The decision for this limitation stems from the fact that the theory (if it is at all pertinent for a heavy atom such as platinum) is best developed for one-bond coupling constants and that since the last relevant review articles [68,69,70,71,72] there have been no major breakthroughs for ^1H, ^{13}C and ^{31}P.

(i) Theory

Following the early literature, it is usually assumed that the Fermi contact expression suffices to describe the one-bond coupling $^1J(^{195}Pt, L)$. Within this framework, Pople and Santry [73] have described one-bond coupling constants as shown below

$$J(A, B) = (\text{constant})\ \gamma_A\gamma_B|\Psi(0)|^2_A|\Psi(0)|^2_B\pi_{AB}$$

where the γ's are the gyromagnetic ratios, the $|\Psi(0)|^2$ terms the valence s electron densities at the nuclei A and B and π_{AB} is a mutual polarizability expressed as:

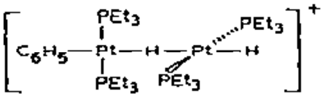
$$\pi_{AB} \approx 4\sum_{i}^{\text{occ}}\sum_{j}^{\text{unocc}}(\epsilon_i - \epsilon_j)^{-1}c_{i_A}c_{i_B}c_{j_A}c_{j_B}$$

The indices i and j refer to occupied and unoccupied LCAO MOs. The c's are the coefficients of the s atomic orbitals used in the linear combinations to form the pertinent molecular orbitals.

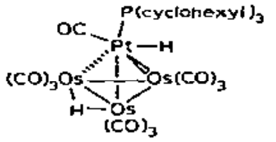
Nuclei with relatively small γ and $|\Psi(0)|^2$ values are expected and found to have smaller magnitudes of $^1J(^{195}Pt, L)$ than the heavier nuclei with larger γ's, e.g. $^1J(^{195}Pt, ^{31}P)$ is often an order of magnitude larger than $^1J(^{195}Pt, ^{15}N)$. In discussions on structure and bonding, it is the π_{AB} term which is most relevant [72]. The most obvious point from theory is that the coupling constants provide direct information only on *s* orbital contributions. If we assume that we understand how to interpret such coupling constant data we can attempt to extrapolate to other types of metal–ligand overlap, e.g. $d\pi$–$d\pi$ back bonding; however, this is not without a certain risk and, at best, is indirect. Further, the importance of electrostatic interactions is also lost as we have no reliable method to relate these to *s* character arguments. Shustorovich [74] has shown that there is some correlation of ^{1}J(M, L) with bond-overlap population and gives some theoretical support to the well-established *trans* influence concept; however, there is not a great deal of theory exploring individual ^{1}J(^{195}Pt, L) values and trends.

(ii) Empiricisms

The single most useful concept relating ^{1}J(^{195}Pt, L) to ground state chemical phenomena is the idea of the *trans* influence series. As far back as 1965, Powell and Shaw [75] could show that ^{1}J(^{195}Pt, ^{1}H) varied from 788 to 1369 Hz in the complexes *trans*-[PtHX(PEt$_3$)$_2$], X = various anionic ligands. The better X donors reduce the coupling, e.g. for X = CN, ^{1}J(^{195}Pt, H) = 778 Hz, whereas poorer donors show the reverse trend. The most extensive collection of data stems from Miyamoto [76] who reports data for 123 hydride complexes of the general formula *trans*-[PtHX(P(CH$_2$Ph)$_3$)$_2$] and *trans*-[PtHL(P(CH$_2$Ph)$_3$)$_2$]BPh$_4$. Despite the addition of many dozens of new derivatives the basic ideas governing changes in ^{1}J(^{195}Pt, H) have not changed in more than fifteen years. There are two new points worthy of note: (a) whereas ^{1}J(^{195}Pt, ^{1}H) often fluctuates between 700 and 1400 Hz, the presumed three-coordinate cation [PtH(PBu$^{t}_{3}$)$_2$]$^+$ shows values between 1500 (acetone) and 2575 (methylene chloride) Hz [77]; (b) bridging hydride ligands often show considerably smaller values. For the binuclear [Pt$_2$H$_2$(μ-H)$_2$(dppm)$_2$]Cl, ^{1}J(^{195}Pt, ^{1}H) = 540 Hz for the bridging hydride [78] whereas for [Pt$_2$H(C$_6$H$_5$)(μ-H)(PEt$_3$)$_4$]$^+$ (VI), ^{1}J(^{195}Pt, ^{1}H) is ~500 Hz to both platinum atoms [79]. For the tetrahedral [Os$_3$Pt(μ-H)$_2$(CO)$_{10}$(P(cyclohexyl)$_3$)] cluster (VII), ^{1}J(^{195}Pt, ^{1}H) = 583 Hz [80].

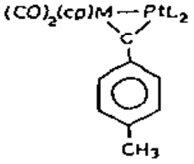


(VI)



(VII)

The literature with regard to ^{1}J(^{195}Pt, ^{13}C) has been reviewed several times [69–72,81]. The studies by Clark and co-workers [82,83], together with reports on monomeric carbonyl complexes [33,84] emphasize *trans* influence effects while pointing out the dependence of ^{1}J(^{195}Pt, ^{13}C) on carbon hybridization. This coupling constant can range from <400 to >2000 Hz for σ-bound carbon ligands in platinum(II) complexes. In the stacked triangular clusters mentioned earlier $^{1}J(^{195}Pt, ^{13}C)$ is of the order of 2160–2223 Hz for the terminal and 769–834 Hz for the bridging carbonyl [67]. For an introduction to the literature on platinum olefin complexes see [85–88].



(VIII)

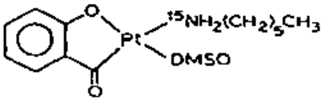
(a) M = Mn, L = PMe_3
(b) M = Re, L = PMe_3
(c) M = Re, L = PMe_2Ph

The carbyne complexes (VIII) show $^{1}J(^{195}Pt, ^{13}C)$ values of 730, 745 and 757 Hz, respectively, to the bridging carbon and these together with their low field ^{13}C shifts ($\delta = 338.1$, 385.2 and 382.6 ppm) represent an interesting spectroscopic feature of this new type of chemistry [89]. There are also extensive spectroscopic results for similar carbene complexes [90].

The platinum–phosphorus one-bond interaction is probably the most widely studied coupling. In [72] there are more than 150 representative examples and it seems likely that another several hundred have appeared since then. In Pt(0) chemistry, values ranging from 2800 to >9000 are known [91], whereas in Pt(II) chemistry $^{1}J(^{195}Pt, ^{31}P)$ values range routinely from 1400 to >5000 Hz [52,58,72,92,93]. There is a tendency to assign the *trans* geometry to a square-planar complex when $^{1}J(^{195}Pt, ^{31}P)$ lies between 2400 and 3000 Hz. Although this is often so, examples are known where the complex has the *trans* geometry and the one-bond coupling constant is both >3000 Hz ([72] and references therein) and <2000 Hz [35] so that care must be taken when assigning structure using this criterion. The complex *trans*-$[Pt(SnCl_3)_2(PPr^n_3)_2]$ is a nice example of this latter point as the value for $^{1}J(^{195}Pt, ^{31}P)$ is only 1850 Hz [94].

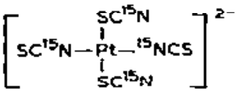
The *trans* influence ideas cover the qualitative aspects of changes in $^{1}J(^{195}Pt, ^{31}P)$ although chelate ring size [52,93,95] and *cis* effects [96] are often quite sizeable. The complexes *trans*-$[PtCl_2L(PBu^n_3)]$, L = PBu^n_3, $P(p\text{-}CH_3C_6H_4)_3$, $AsEt_3$, $As(p\text{-}CH_3C_6H_4)_3$, DMSO, $^{15}NH_2(CH_2)_5CH_3$ show a typical *trans* influence effect with $^{1}J(^{195}Pt, ^{31}P)$ beginning at 2377 Hz for PBu^n_3 and increasing to 3375 Hz [37]. Since such a trend is connected to the coefficients, c_A, c_B, in the polarizability , it is reasonable to expect some relationship between $^{1}J(^{195}Pt, ^{31}P)$ and other physical parameters and indeed there is: the most noteworthy being that relating bond distances to coupling constants [97].

In contrast to the three previous cases, $^{1}J(^{195}Pt, ^{15}N)$ is a relative newcomer. Before 1973 there was essentially nothing known although today we recognize that this coupling constant can be < 100 Hz as in (IX) [12] or > 600 Hz as in (X) [41].



$^1J(^{195}Pt,^{15}N) = 88$ Hz

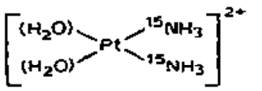
(IX)



$= 617$ Hz

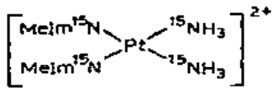
(X)

As with other platinum–ligand coupling constants there is a dependence on oxidation state of the metal as well as *trans* influence. The former point is illustrated by the complexes *cis*-$[PtCl_2(^{15}NH_2(CH_2)_{11}CH_3)_2]$, $^1J(^{195}Pt, ^{15}N) = 351$ Hz and *cis*-$[PtCl_4(^{15}NH_2(CH_2)_{11}CH_3)_2]$, $^1J(^{195}Pt, ^{15}N) = 249$ Hz [98], whereas the three series of compounds shown in Scheme 5 demonstrate the latter. Quite clearly the ligand *trans* to the ^{15}N atom can be responsible for changes of the order of 200 Hz in the metal–nitrogen coupling. The available data base is still rather skimpy. Although there is much for thiocyanate compounds (see Table 10) only a smattering of values can be found for other complexes. These include azobenzenes [100], $Bu^{t15}N{=}CH{-}CH{=}^{15}NBu^t$ complexes [40] a four-membered cyclic platinum complex [101,102], the sulfinyl complex $[Pt(Ph^{15}NSO)(PPh_3)_2]$ [103], two pyridine–olefin complexes [14] and a few $^{15}NH_3$ derivatives [38,64,104]. Despite this paucity, it is quite likely that a working knowledge of this coupling constant will prove as valuable for the nitrogen chemist as the analogous phosphorus coupling has been to the phosphine chemist. Consider (XI) and (XII) [104]:



$^1J(^{195}Pt,^{15}N) = 421$ Hz

(XI)



$MeIm^{15}N$ = 1-methylimidazole

$^1J(^{195}Pt,^{15}N) = 319$ Hz

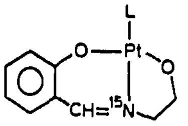
(XII)

the $\sim 25\%$ change in the one-bond coupling will prove useful knowledge for related aqueous chemistry.

There are a number of additional one-bond couplings involving platinum which promise to be of value, e.g. $^1J(^{195}Pt, ^{11}B)$ [105], $^1J(^{195}Pt, ^{77}Se)$ [16,42,106,107] and $^1J(^{195}Pt, ^{125}Te)$ [108], but perhaps the most puzzling is the coupling constant involving a second platinum, $^1J(^{195}Pt, ^{195}Pt)$ and, due to its relevance, $^2J(^{195}Pt, ^{195}Pt)$. Obviously, this parameter stems from polymetallic platinum complexes and consequently might be a source of information with regard to metal–metal bonds. Proceeding in the usual fashion one collects data for a representative sample of complexes in which a Pt–Pt bond is thought to exist and compares the results with derivatives

Scheme 5

$^1J(^{195}Pt, ^{15}N)$ values and the *trans* influence

$[PtCl_2L(^{15}NH_2(CH_2)_5CH_3)]$ [37]		$[PtCl_2L(^{15}NHMe_2)]$ [99]		 [39]	
L	*J*	L	*J*	L	*J*
PBu^n_3	138.3	$^{15}\overset{+}{N}HMe_2CH_2CH_2^-$	107	PBu^n_3	249.1
$PMePh_2$	155.9	PPh_3	171	$P(OEt_3)$	303.0
$P(p\text{-}CH_3C_6H_4)_3$	158.8	DMSO	226–244 [d]	$P(p\text{-}CH_3C_6H_4)_3$	323.6
$AsBu^n_3$	183.8	Aliphatic amine	278–290 [e]	$AsBu^n_3$	366.2
$AsMePh_2$	208.8	C_2H_4	299	CN(Cyclohexyl)	397.1
$As(p\text{-}CH_3C_6H_4)_3$	207.4	Cl^-	312–350 [e]	$As(p\text{-}CH_3C_6H_4)_3$	416.2
$^{14}NH_2(CH_2)_5CH_3$	286.8	Br^-	334–340 [e]	DMSO	431
C_2H_4	283.9			Piperidine	464.7
Cl	336 [b]			$^{15}NH_2(CH_2)_5CH_3$	478.0
Cl	295.6 [c]			Pyridine	494.2

[a] Values are in Hertz.

[b] *cis*-$[PtCl_2(^{15}NH_2(CH_2)_5CH_3)_2]$.

[c] *cis*-$[PtCl_2(^{15}NH_2)(CH_2)_5CH_3)(C_2H_4)]$.

[d] From ref. 38.

[e] Data from ref. 98.

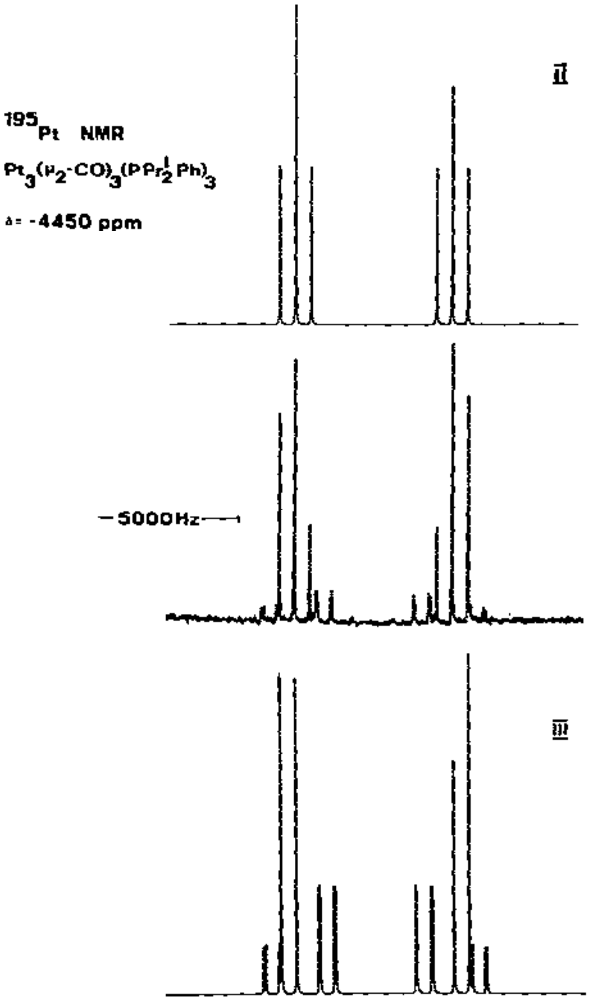


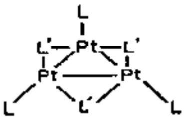
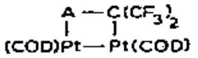
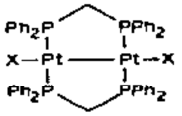
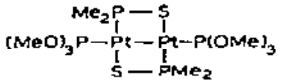
Fig. 7. ^{195}Pt{^{1}H} spectrum of [$Pt_3(\mu_2\text{-}CO)_3(PPr^i_2Ph)_3$] (center) with simulations for the isotopomer with one ^{195}Pt (above) and two ^{195}Pt atoms (below) (from [110]).

where there is believed to be a weak bonding interaction. Indeed the first results were deceptively encouraging. For triangular clusters of the type [$Pt_3(\mu\text{-}CO)_3$(tertiary phosphine)$_3$] the ^{195}Pt spectrum appears as in Fig. 7, and can be analyzed using either the ^{31}P [109] or ^{195}Pt [110] spectra (the most readily observed relevant isotopomer is [$^{195}Pt_2Pt(\mu\text{-}CO)_3(PR_3)_3$]). The $^1J(^{195}Pt, ^{195}Pt)$ results, together with those for more than forty complexes, are given in Table 8 and partially summarized in Scheme 5.

As may be seen for the triangles, as well as several other classes where metal–metal bonds have been inferred, $^1J(^{195}Pt, ^{195}Pt)$ exceeds 1 KHz, and

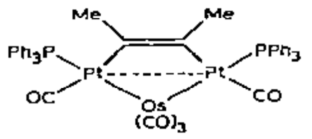
Scheme 6

^{195}Pt–^{195}Pt coupling constants

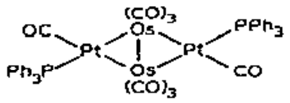
1.		L = tertiary phosphine L′=CO	1571–1770 Hz [109,110]
		L = L′=CNBu^t	188 Hz [109a]
2.		A = O = NH	5355 Hz 6235 Hz [109]
3.		X = Cl Br I	8197 Hz 8828 Hz [109] 9007 Hz
4.			177–880 Hz (see Table 8)
5.			410 Hz [109]
6.	$OsPt_2(CO)_5(PPh_3)_2(\mu_3\text{-}MeC_2Me)$		57 Hz [113]
7.	$Os_2Pt_2(\mu\text{-}H)_2(CO)_8P_2$	P = PPh_3 $P(cyclohexyl)_3$	1744 Hz 1542 Hz

can be considerably > 5 KHz. At first glance this suggests that relatively large values are associated with a direct metal–metal bond. Regrettably, there are a few disturbing anomalies which became obvious during a discussion [109] of $^1J(^{195}Pt, ^{195}Pt)$ and metal–metal separations *d*(Pt, Pt), as determined by X-ray analysis. The compounds (1) (see Scheme 6) show *d*(Pt, Pt) values of < 2.7 Å which would normally be associated with significant metal–metal interactions (see [110] and references therein), nevertheless, the metal–metal coupling in the isonitrile cluster at 188 Hz is relatively small. The same can be said of (5) in that the 2.628 Å distance does not fit well with the moderate 410 Hz coupling constant. Since it is well known that, for (4), $^2J(^{195}Pt, ^{195}Pt)$ can exceed 800 Hz (bridging ligands are RS^- [111] or H^- [112]), the significance of $^1J(^{195}Pt, ^{195}Pt)$ seems open to question.

Further in (XII), where *d*(Pt, Pt) at 3.033(2) Å is long [113], $J(^{195}Pt, ^{195}Pt)$ is 57 Hz. This seems acceptable; however, in (XIV), which has a butterfly structure in the solid state [114], *d*(Pt, Pt) at 3.206(1) Å is longer but now



(XII)



(XIV)

$^1J(^{195}Pt, ^{195}Pt)$ is 1744 Hz *. Although the issue is confusing some few additional data may help us to localize the problem. We know from studies on simple dimeric species such as *sym-trans*-$[Pt_2Cl_2(\mu\text{-}X,Y)(\text{tertiary phosphine})_2]$ [109,111,115] that $J(^{195}Pt, ^{195}Pt)$ through the bridging ligands X and Y can lie between 125 and 880 Hz. Here X and Y are either halogen or sulfur ligands. Complexes containing bridging hydride ligands cover roughly the same range [66,79,112]. Since substituting SPh for Cl in the bridging positions lifts the coupling from 190 Hz in $[Pt_2Cl_2(\mu\text{-}Cl)_2(PBu^n_3)_2]$ to 880 Hz in $[Pt_2Cl_2(\mu\text{-}SPh)_2(PBu^n_3)_2]$, the nature of the bridging atom is important. This raises the question of as yet unknown coupling constants such as $^2J(^{195}Pt\text{-}C(O)^{195}Pt)$ in the clusters and the possibility that ^2J may have an opposite sign to that for ^1J. (There is no reason to believe this must be so. Boag et al. [116] find a positive sign for ^1J in $[Pt_2(CNMe)_6]^{2+}$ and $[Pt_2((CF_3)_2CO)(COD)_2]$ as well as for ^2J in $[PtCl_3(\mu\text{-}SeMe_2)PtCl_2(SeMe_2)]^-$. The comment in [110] on the negative sign for ^2J in [111] is incorrect.) Additionally, we know nothing with regards to three-bond metal–metal coupling constants such as are possible for (2) and (5), but do recognise that the remaining ligands can affect $J(^{195}Pt, ^{195}Pt)$. In (3), changing from Cl to I increases the coupling by 820 Hz. In (2), substitution of NH for O produces an 880 Hz difference and for (V) replacing the *trans* PPh_3 ligands by $P(\text{cyclohexyl})_3$ increases $^2J(^{195}Pt, ^{195}Pt)$ from 325 to 701 Hz. Clearly there are significant gaps to be filled.

Perhaps we should not expect a correlation of *d*(Pt, Pt) with $^1J(^{195}Pt, ^{195}Pt)$. We know that the coupling mechanism will depend on the *s* coefficients in the polarizability term whereas the metal–metal bond length has no such restriction. Perfectly stable bonds could conceivably be made involving MOs containing substantial amounts of *p* and *d* character between the metals. In any case the last word has not yet been spoken and this area will certainly receive increasing attention if we are to understand these and the recently observed platinum–rhodium [116] and platinum–tungsten [117] one-bond spin–spin couplings.

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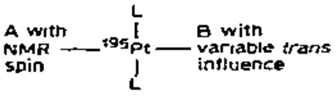
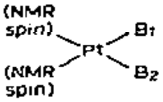
* This value is so similar to those for (1) in Scheme 6 that it is worthwhile asking whether or not the complex might not have some direct Pt–Pt bond in solution.

(iii) Applications

From the many dozens of elegant applications it is difficult to select those few which one might call representative. Having said this, the freedom of mixing the "somewhat different" with the ever present *trans* influence is allowed. The previous discussion has outlined what one normally finds for $^1J(^{195}Pt, ^1H)$ or $^1J(^{195}Pt, ^{31}P)$ in the models (XV) and (XVI). Given that novel

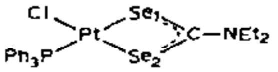


(XV)



(XVI)

spin–spin couplings to platinum are appearing with increasing frequency it is interesting to inquire into the generality of the *trans* influence.



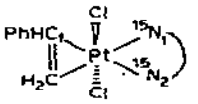
$^1J(^{195}Pt, ^{77}Se_1) = 115.2$ Hz
$^1J(^{195}Pt, ^{77}Se_2) = 291.4$ Hz

(XVII)

cis-$PtCl_2(Te(CH_2CH_2Ph)_2)_2$
$^1J(^{195}Pt, ^{125}Te) = 900$ Hz

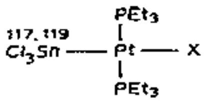
trans-$PtCl_2(Te(CH_2CH_2Ph)_2)_2$
$^1J(^{195}Pt, ^{125}Te) = 544$ Hz

(XVIII)



(XIX)

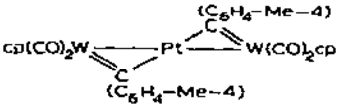
$^{15}N\frown{}^{15}N = Bu^t\ {}^{15}N{=}CH{-}CH{=}{}^{15}NBu^t$
$^1J(^{195}Pt, ^{15}N_1) = 135$ Hz
$^1J(^{195}Pt, ^{15}N_2) = 178$ Hz



(XX)

X	$^1J(^{195}Pt, ^{119}Sn)$
(a) H	9067
(b) $SnCl_3$	23,517
(c) Cl	28,954

In the complexes (XV)–(XX) values for $^1J(^{195}Pt, ^{15}N)$, $^1J(^{195}Pt, ^{77}Se)$, $^1J(^{195}Pt, ^{125}Te)$ and $^1J(^{195}Pt, ^{119}Sn)$ are found which may all be seen to respond to the differences in bonding within the metal coordination sphere. In (XVII) [106], the PPh_3 weakens the Pt–Se bond more than Cl^- and this is reflected in the 2–3 difference in $^1J(^{195}Pt, ^{77}Se)$. In the tellurium complexes (XVIII) [108], the now classical difference between *cis* and *trans* complexes of dichlorides is clearly observable; whereas in our tin complexes, (XX), the hydride assumes its now accepted position as a ligand with a very high *trans* influence. Even in (XIX) [40], where marked differences are not expected, the nitrogen spins feel the very different coordination possibilities for the two carbons (even more than $^1J(^{195}\mathrm{Pt}, {}^{13}\mathrm{C})$ which lie within 5% of each other). Clearly, platinum–ligand one-bond couplings can be very sensitive to the nature of the *trans* ligand and will remain a valuable method for structure assignment. As for metal–metal coupling? We have yet to hear much from $^{199}\mathrm{Hg}$, $^{207}\mathrm{Pb}$ and others, but Ashworth et al. [117] find $^1J(^{195}\mathrm{Pt}, {}^{183}\mathrm{W}) = 177$ Hz in (XXI), which, together with a great deal of other data, including $^1J(^{195}\mathrm{Pt}, {}^{13}\mathrm{C}) = 830$ Hz, $^1J(^{183}\mathrm{W}, {}^{13}\mathrm{C}) = 157$ Hz for the bridging carbyne, help to support the solution structure. There may be further trying moments before we obtain a thorough grasp of the significance of this and the other metal–metal coupling constants: nevertheless the potential for application is assuredly there.



(XXI)

Tables 1–11 are meant to serve as an introduction. They do not constitute a complete listing of all known $\delta^{195}\mathrm{Pt}$ values but rather represent a selection of several hundred complexes from which the reader can obtain an impression as to the effect of various ligands on the platinum chemical shift. Where the original data were expressed relative to the magnetic field which brings the protons of TMS into resonance at exactly 100 MHz, the conversion $\delta\mathrm{PtCl}_6^{2-} = \delta(\mathrm{given}) - 4533$ ppm has been used. Where the data have been referenced to *trans*-[PtHCl(PEt$_3$)$_2$], the conversion is $\delta\mathrm{PtCl}_6^{2-} = \delta(\mathrm{given}) - 4862$ ppm. The reader is strongly recommended to consult the original literature since solvent and temperature effects are *not* taken into account here.

TABLE 1

^{195}Pt chemical shifts for the anions $[PtX_3L]^-$ [a]

X	L								
	NMe_3	PMe_3	$AsMe_3$	$SbMe_3$	SMe_2	$SeMe_2$	$TeMe_2$	$SOMe_2$	C_2H_4
Cl	−1715	−3500	−3173	−3143	−2757	−2769	−3059	−2998	−2785
Br	−2251	−4119	−3869	−3928	−3415	−3476	−3826	−3641	−3473
I		−5506	−5446	−5642	−4973	−5129	−5528		

[a] Data from ref. 27. This is not a complete listing. Values for the mixed complexes $[PtX, Y, Z, L]^-$, X = Cl, Br, I are also available. The counter ion was either $[Pr^n_4N]^+$, $[Ph_4P]^+$ or $[Bu^n_4N]^+$.

TABLE 2

The effect of ligand and geometric isomerization on δ^{195}Pt [a]

	L								
	PMe_3	$AsMe_3$	$SbMe_3$	SMe_2	SMePh	$SeMe_2$	$TeMe_2$	$P(OCH_3)_3$	$SOMe_2$
cis-[$PtCl_2L_2$]	−4408	−4291	−4612	−3551	−3488	−3735	−4369	−4371	−3477
cis-[$PtBr_2L_2$]	−4636	−4625	−5019	−3879	−3858			−4599	−3778
cis-[PtI_2L_2]	−4588		−5816		−4686			−5102	
cis-[$PtClBrL_2$]	−4517	−4448	−4797	−3707	−3664			−4476	−3619
cis-[$PtClIBr_2$]			−5138	−4025	−4021			−4669	
cis-[$PtBrIL_2$]			−5385	−4224	−4224			−4820	
								NMe_3	
trans-[$PtCl_2L_2$]	−3950	−3780		−3424	−3385	−3504		−1886	
trans-[$PtBr_2L_2$]	−4473	−4378		−3899	−3879	−4041		−1988	
trans-[PtI_2L_2]	−5539	−5518		−5789	−4805	−4819	−5664		
trans-[$PtClBrL_2$]		−4075		−3660	−3629	−3769		−1935	
trans-[$PtClIL_2$]	−4741	−4655	−4749	−4141	−4118	−4304			
trans-[$PtBrIL_2$]		−4963	−5131	−4375	−4365	−4573			

[a] Data from ref. 27.

TABLE 3

The effect of different phosphorus ligand on δ^{195}Pt [a]

L	$[PtCl_3L]^-$	*cis*-$[PtCl_2L_2]$	*trans*-$[PtCl_2L_2]$
PMe_3	−3500	−4408	−3950
PEt_3	−3540	−4490, −4475 [b]	−3938, −3916 [b]
PPr^n_3	−3520	−4442	
PBu^n_3	−3524	−4448	−3929
PMe_2Ph	−3511	−4403	
PEt_2Ph		−4426	−3964
$PMePh_2$	−3515	−4439	
PPh_3	−3513		
$P(p\text{-}ClC_6H_4)_3$		−4428 [b]	
$P(p\text{-}CH_3OC_6H_4)_3$		−4407 [b]	
$P(OMe)_3$	−3496 [c]		
$P(OEt)_3$		−4363 [b]	
$P(OPh)_3$		−4298 [b]	
PF_3	−3626		
$PF_2(OMe)$	−3584 [c]		
$PF(OMe)_2$	−3534 [c]		
$PCl(OMe)_2$	−3425 [c]		
$PCl_2(OMe)$	−3354 [c]		

[a] Data from ref. 27 unless otherwise noted. [b] Data from ref. 35. [c] Data from ref. 45.

TABLE 4

^{195}Pt chemical shifts of arsine complexes [a]

Compound	δ^{195}Pt	$\Delta\nu_{1/2}$
cis-$[PtCl_2(AsEt_3)_2]$	−4363	~400
cis-$[PtCl_2(AsPr^n_3)_2]$	−4321	~170
cis-$[PtCl_2(AsMe_2Ph)_2]$	−4287	~180
cis-$[PtCl_2(AsMePh_2)_2]$	−4323	~190
cis-$[PtCl_2(AsPh_3)_2]$	−4351	~115
cis-$[PtCl_2(AsTol_3)_2]$	−4352	~80
cis-$[PtCl_2(AsBzPh_2)_2]$	−4325	~160
trans-$[PtCl_2(AsEt_3)_2]$	−3710	~105
trans-$[PtCl_2(AsPr^n_3)_2]$	−3703	~75
trans-$[PtCl_2(AsBu^n_3)_2]$	−3709	~55
trans-$[PtCl_2(AsPr^i_3)_2]$	−3596	~130
trans-$[PtCl_2(AsMe_2Ph)_2]$	−3771	~100
trans-$[PtCl_2(AsMePh_2)_2]$	−3792	~100
trans-$[PtCl_2(AsPh_3)_2]$	−3803	~65
trans-$[PtCl_2(AsTol_3)_2]$	−3801	~40
sym-trans-$[Pt_2Cl_4(AsEt_3)_2]$	−3023	~225
sym-trans-$[Pt_2Cl_4(AsPr^n_3)_2]$	−3008	~200
sym-trans-$[Pt_2Cl_4(AsBu^n_3)_2]$	−3014	~135
sym-trans-$[Pt_2Cl_4(AsPr^i_3)_2]$	−2983	
trans-$[PtCl_4(AsPr^n_3)_2]$	−1023	~115
cis-$[PtCl_2(PBu^n_3)(PTol_3)]$	−4412	<3

[a] Data from the Ph.D. Thesis of G. Balimann, ETH Zürich, 1977.

TABLE 5

^{195}Pt chemical shifts of complexes with carbon ligands

Compound	δ^{195}Pt	Ref.
cis-$[\mathrm{PtMe_2(PMe_2Ph)_2}]$	−4594	34
cis-$[\mathrm{PtMe_2(PMePh_2)_2}]$	−4649	34
cis-$[\mathrm{Pt(AsEt_3)_2Ph_2}]$	−4584	34
trans-$[\mathrm{Pt(AsEt_3)_2Ph_2}]$	−4475	34
trans-$[\mathrm{Pt(Me)I(PMe_2Ph)_2}]$	−4963	34
trans-$[\mathrm{Pt(Br)Me(PMe_2Ph)_2}]$	−4671	34
trans-$[\mathrm{Pt(Me)Cl(PMe_2Ph)_2}]$	−4484	34
trans-$[\mathrm{Pt(Me)I(PMePh_2)_2}]$	−4965	34
trans-$[\mathrm{PtMe(PMe_2Ph)_2(SePh)}]$	−4833	34
cis-$[\mathrm{Pt(Me)Cl(PMe_2Ph)_2}]$	−4522	34
trans-$[\mathrm{Pt(CF_3)I(PMe_2Ph)_2}]$	−4629	34
trans-$[\mathrm{Pt(Me)I(PEt_3)_2}]$	−4857	34
trans-$[\mathrm{Pt(Me)Cl(PEt_3)_2}]$	−4509	34
trans-$[\mathrm{Pt(AsMe_3)_2IMe}]$	−4859	34
trans-$[\mathrm{Pt(AsMe_3)_2(Br)Me}]$	−4616	34
trans-$[\mathrm{Pt(AsMe_3)_2(Me)Cl}]$	−4474	34
trans-$[\mathrm{Pt(AsMe_3)_2(Br)Ph}]$	−4405	34
trans-$[\mathrm{Pt(AsMe_2Ph)_2(Me)I}]$	−4929	34
trans-$[\mathrm{Pt(AsMe_2Ph)_2(Br)Me}]$	−4681	34
trans-$[\mathrm{Pt(AsMe_2Ph)_2(Me)Cl}]$	−4532	34
$[\{\mathrm{PtMe_3}(\mu_3\text{-I})\}_4]$	−2769	34
fac-$[\mathrm{PtMe_3I(tmen)}]$	−2413	34
fac-$[\mathrm{PtMe_3I(py)_2}]$	−2515	34
fac-$[\mathrm{Pt(AsMe_2Ph)_2(Br)Me_3}]$	−3815	34
fac-$[\mathrm{PtMe_3I(PMe_2Ph)_2}]$	−4289	34
fac-$[\mathrm{PtBrMe_3(PMe_2Ph)_2}]$	−3989	34
fac-$[\mathrm{PtMe_3Cl(PMe_2Ph)_2}]$	−3831	34
fac-$[\mathrm{PtMe_3I(PMePh_2)_2}]$	−4239	34.
fac-$[\mathrm{PtMe_3I(PMe_3)_2}]$	−4353	34
fac-$[\mathrm{PtMe_3I(dppe)}]$	−4517	34
$[\mathrm{PtBr_2Me_2(py)_2}]$	−2251	34
$[\mathrm{PtMe_2I_2(py)_2}]$	−3347	34
$[\mathrm{PtMe_2I_2(PMe_2Ph)_2}]$	−4387	34
$[\mathrm{PtMe_2I_2(PEt_3)_2}]$	−4288	34
$[\mathrm{PtBr_2Me_2(PMe_2Ph_2)}]$	−3816	34
$[\mathrm{PtMe_2Cl_2(PMe_2Ph)_2}]$	−3515	34
$[\mathrm{PtMe_2Cl_2(PMe_2Ph)_2}]$	−3109	34
$[\mathrm{PtBr_3Me(PMe_2Ph)_2}]$	−3732	34
$[\mathrm{PtMe_2(CF_3)I(PMe_2Ph)_2}]$	−3997	34
$[\mathrm{PtMe_2(CF_3)I(PMe_2Ph)_2}]$	−3919	34
$[\mathrm{PtBrMe_2(C_3H_5)(PMe_2Ph)_2}]$	−3929	34
$[\mathrm{PtMe_2(C_3H_5)Cl(PMe_2Ph)_2}]$	−3793	34
$[\mathrm{PtBrMe_2(CH_2Ph)(PMe_2Ph)_2}]$	−3894	34

TABLE 5 (continued)

Compound	δ^{195}Pt	Ref.
$[PtMe_2(COMe)Cl(PMe_2Ph)_2]$	−4554	34
$[PtBrMe_2(COMe)(PMe_2Ph)_2]$	−4676	34
$[Pt\{(CH_2)_3\}Cl_2(4Me\text{-}py)_2]$	−1389	34
$[PtBr_2\{(CH_2)_3\}(4Me\text{-}py)_2]$	−1865	34
$[Pt\{(CH_2)_3\}Cl_2(py)_2]$	−1359	34
$[PtBr_2(CH_2)_3(py)_2]$	−1874	34
cis-$[Pt\{(CH_2)_4\}(PMe_2Ph)_2]$	−4677	34
cis-$[Pt(OC(CH_3)=CHCOCH_2)(PPh_3)_2]$	−4227	55
cis-$[Pt(OC(CH_3)=CHCOCH_2)(P(p\text{-}ClC_6H_4)_3)_2]$	−4230	55
cis-$[Pt(OC(CH_3)=CHCOCH_2)(AsPh_3)_2]$	−4214	55
cis-$[PtCl_2(C(=CH_2)CH_2NEt'_3)(PPr^n_3)]$	−3891	51
$[PtCl(C(=CH_2)CH_2NHBu^t)(PPr^n_3)]$	−3704	51
$[Pt_2Cl_2(C(=CH_2)CH_2NHMe)_2(PPr^n_3)_2]$	−4113	51
cis-cis-trans-$[PtBr_2(C_6F_5)_2(PEt_3)_2]$	−3151	49
mer-trans-$[PtCl_3(C_6F_5)(PEt_3)_2]$	−2369	49
mer-trans-$[PtBr_3(C_6F_5)(PEt_3)_2]$	−3298	49
trans-$[PtCl(C_6F_5)(PEt_3)_2]$	−4441	49
trans-$[PtBr(C_6F_5)(PEt_3)_2]$	−4548	49
trans-$[PtI(C_6F_5)(PEt_3)_2]$	−4843	49
$(NBu_4)_2[Pt(CN)_4]$	−4707	30
$K_2[Pt(CN)_4]$	−4746	30
$(NBu_4)_2[PtCl_2(CN)_4]$	−2481	30
$K_2[PtCl_2(CN)_4]$	−2624	30
$(NBu_4)_2[PtBr_2(CN)_4]$	−3349	30
$K_2[PtBr_2(CN)_4]$	−3598	30
$(NBu_4)_2[PtBrCl(CN)_4]$	−2944	30
$(NBu_4)_2[PtI_2(CN)_4]$	−4714	30
$K_2[PtI_2(CN)_4]$	−4790	30
$K_2[PtCl(CN)_5]$	−3294	30
$(NBu_4)_2[PtI(CN)_5]$	−4033	30
$Na_2[PtI(CN)_5]$	−4214	30
$(NBu_4)_2[Pt(CN)_6]$	−3321	30
$K_2[Pt(CN)_6]$	−3866	30
$[PtCl_2(CO)(PMe_3)]$	−4164	56
$[PtBr_2(CO)(PMe_3)]$	−4404	56
$[PtI_2(CO)(PMe_3)]$	−4928	56
$[PtClBr(CO)(PMe_3)]$ Cl *trans* to CO	−4295	56
Br *trans* to CO	−4255	
$[PtClI(CO)(PMe_3)]$	−4513	56
$[PtBrI(CO)(PMe_3)]$	−4655	56
$[PtCl(CO)(PMe_3)_2]BF_4$	−4471	56
$[PtBr(CO)(PMe_3)_2]BF_4$	−4594	56

TABLE 5 (continued)

Compound		δ^{195}Pt	Ref.
$(NPr^n_4)[PtCl_2R(CO)]$			
R			
Me		−3869	33
Et		−3876	33
Pr^n		−3881	33
Pr^i		−3806	33
Bu^n		−3880	33
Ph		−3655	33
$[PtCl_2(CO)(PEt_3)]$	*cis*	−4207	57
	trans	−3840	
$[PtClPh(CO)(PEt_3)]$	P *cis* to CO	−4345	57
	P *trans* to CO	−4168	
$[PtClPh(CO)(PMePh_2)]$	P *trans* to Cl	−4288	57
	P *trans* to CO	−4201	
	P *trans* to Ph	−4067	
$[Pt(OC_6H_4CO)L_2]$			
L			
PBu^n_3		−4304	58
$P(p\text{-}CH_3C_6H_4)_3$		−4316	58
$P(OEt)_3$		−4380	58
$P(OPr^i)_3$		−4390	58

TABLE 6

^{195}Pt chemical shifts of complexes with Si, Ge and Sn ligands

Compound	δ^{195}Pt	Ref.
trans-[PtCl(SiH$_3$)(PEt$_3$)$_2$]	−5067	29
trans-[PtCl(SiH$_2$F)(PEt$_3$)$_2$]	−4935	29
trans-[PtCl(SiH$_2$Cl)(PEt$_3$)$_2$]	−4992	29
trans-[PtCl(SiHCl$_2$)(PEt$_3$)$_2$]	−4853	29
trans-[PtCl(SiH$_2$CCH)(PEt$_3$)$_2$]	−5049	29
trans-[PtCl(SiH$_2$CCCF$_3$)(PEt$_3$)$_2$]	−5035	29
trans-[PtBr(SiH$_2$Br)(PEt$_3$)$_2$]	−5061	29
trans-[PtBr(SiHBr$_2$)(PEt$_3$)$_2$]	−4902	29
trans-[PtI(SiH$_3$)(PEt$_3$)$_2$]	−5270	29
trans-[PtI(SiH$_2$Cl)(PEt$_3$)$_2$]	−5198	29
trans-[PtI(SiH$_2$I)(PEt$_3$)$_2$]	−5164	29
trans-[PtI(SiH$_2$)(PEt$_3$)$_2$]$_2$S	−5181	29
trans-[PtI(SiH$_2$)(PEt$_3$)$_2$]$_2$Se	−5168	29
trans-[PtI(SiH$_2$SeSiH$_3$)(PEt$_3$)$_2$]	−5178	29
trans-[PtI(SiHICCH)(PEt$_3$)$_2$]	−5110	29
trans-[PtCl(GeH$_2$Cl)(PEt$_3$)$_2$]	−4904	29
trans-[PtI(GeH$_3$)(PEt$_3$)$_2$]	−5317	29
trans-[PtI(SiH$_2$NHSiH$_3$)(PEt$_3$)$_2$]	−5262	43
trans-[PtI(SiH$_2$)]$_2$NH	−5250	43
trans-[PtI(SiH$_2$NSiH$_3$)$_2$(PEt$_3$)$_2$]	−5240	43
trans-[PtI(SiH$_2$P(SiH$_3$)$_2$)(PEt$_3$)$_2$]	−5177	43
trans-[PtCl(SnCl$_3$)(PEt$_3$)$_2$]	−4780	44
trans-[Pt(SnCl$_3$)$_3$(PEt$_3$)$_2$]$^-$	−5152	44
trans-[Pt(SnCl$_3$)$_3$(P(OEt)$_3$)$_2$]$^-$	−5234	44
trans-[Pt(C$_6$H$_5$)(SnCl$_3$)(PEt$_3$)$_2$]	−4799	44
trans-[PtH(SnCl$_3$)(PEt$_3$)$_2$]	−5302	12
trans-[PtH(SnCl$_3$)(PPh$_2$CH$_2$Ph)$_2$]	−5322	12
trans-[PtH(SnCl$_3$)(PPh$_3$)$_2$]	−5195	12
trans-[$\overline{\mathrm{Pt(C}}$(CO$_2$Et)=CHCO$_2$Et)(SnCl$_3$)(PPh$_3$)$_2$]	−4771	12
trans-[PtCl(SnCl$_3$)(P(*p*-ClC$_6$H$_4$)$_3$)$_2$]	−4812	35
cis-[PtCl(SnCl$_3$)(P(*p*-CH$_3$OC$_6$H$_4$)$_3$)$_2$]	−4742	35
cis-[PtCl(SnCl$_3$)(P(*p*-CH$_3$C$_6$H$_4$)$_3$)$_2$]	−4718	94
trans-[PtCl(SnCl$_3$)(AsEt$_3$)$_2$]	−4857	94
cis-[PtCl(SnCl$_3$(As(*p*-CH$_3$C$_6$H$_4$)$_3$)$_2$]	−4785	94
trans-[PtCl(SnCl$_3$)(As(*p*-CH$_3$C$_6$H$_4$)$_3$)$_2$]	−4835	94
[Pt$_2$Cl$_2$(SnCl$_3$)$_2$(PEt$_3$)$_2$]	−4266	44

TABLE 7

Olefin complexes of Pt(II)

Compound	δ^{195}Pt	Ref.
$K[PtCl_3(C_2H_4)]$	−2743, −2785	27, 59
$(Pr_4N)[PtCl_3($*n*-octene$)]$	−2718	27
trans-$[PtCl_2($amine$)(C_2H_4)]$		
amine		
$MeNH_2$	−3040	31
$EtNH_2$	−3020	31
Pr^iNH_2	−3008	31
$PhCH_2NH_2$	−3030	31
$PhCH(CH_3)NH_2$	−3016	31
$PhCH(Bu^t)NH_2$	−2990	31
Me_2NH	−3074	31
EtMeNH	−3049	31
Pr^iMeNH	−3030	31
$PhCH_2MeNH$	−3047	31
(S)-$PhCH(CH_3)MeNH$		
S.S.	−3045	31
S.R.	−2996	31
Piperidine	−3087	31
2,6-Me_2-Piperidine	−2953	31
trans-$[PtCl_2($substituted pyridine$)(C_2H_4)]$		
2,4,6-$(CH_3)_3$	−2871 [a] (−2849) [b]	14
2,6-$(CH_3)_2$	−2877	14
2,4-$(CH_3)_2$	−2930 [a] (−2909) [b]	14
2-CH_3	−2937	14
4-$N(CH_3)_2$	−2980	14
4-CH_3	−2979	14
4-H	−2979	14
4-Cl	−2986	14
4-$COCH_3$	−2984	14
4-CN	−2992	14
trans-$[PtCl_2($piperidine$)($*cis*-2-butene$)]$	−2943	59
trans-$[PtCl_2($piperidine$)($*trans*-2-butene$)]$	−2941	59
trans-$[PtClBr_2(C_2H_4)]$	−3360	27
cis-$[PtCl_2Br(C_2H_4)]$	−3062	27
cis-$[PtClBr_2(C_2H_4)]$	−3155	27
$[NPr_4^n][PtBr_3(C_2H_4)]$	−3473	27
trans-(N,olefin)-[PtCl(N-Me-S-proline)(olefin)]		
olefin		
propene R	−2532	62
S	−2532	
trans-2-butene R	−2523	62
S	−2523	
Bu^t-ethylene R	−2495	62
S	−2490	

TABLE 7 (continued)

Compound		δ^{195}Pt	Ref.
p-chlorostyrene	R	−2391	62
	S	−2402	
styrene	R	−2391	62
	S	−2395	
p-methoxystyrene	R	−2365	62
	S	−2371	
$[PtCl_2(1,5\text{-}COD)]$		−3361	34
$[PtMe_2(1,5\text{-}COD)]$		−3594	34
$[PtPh_2(1,5\text{-}COD)]$		−3624	34
$[Pt(p\text{-}ClC_6H_4)_2(1,5\text{-}COD)]$		−3626	34
$[Pt(p\text{-}PhC_6H_4)_2(1,5\text{-}COD)]$		−3624	34
$[Pt(p\text{-}CH_3C_6H_4)_2(1,5\text{-}COD)]$		−3618	34
$[Pt(p\text{-}FC_6H_4)_2(1,5\text{-}COD)]$		−3614	34
$[Pt(o\text{-}CH_3C_6H_4)_2(1,5\text{-}COD)]$		−3536	34
cis-$[PtCl_3(H_2C{=}C{=}CH_2)]$		−2496	60
cis-$[PtCl_2(H_2C{=}C{=}CH_2)(PPr^n_3)]$		−3633	60
cis-$[PtCl_2(H_2C{=}C{=}CH_2)(PMe_2Et)]$		−3639	60

[a] $CDCl_3$.

[b] Acetone.

TABLE 8

^{195}Pt chemical shifts [a] and $^{n}J(^{195}Pt, ^{195}Pt)$ coupling constants [b] in zerovalent and polymetallic complexes

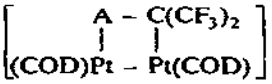
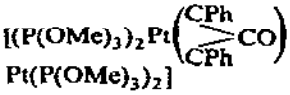
Complex	^{195}Pt	$^{1}J(^{195}Pt, ^{195}Pt)$	Ref.
1. $[Pt_3(CO)_6]^{2-\ b}$	−4581		67
2. $[Pt_6(CO)_{12}]^{2-\ b}$	−4500		67
3. $[Pt_9(CO)_{18}]^{2-\ c}$	−4463 (2)		67
		822	
	−5045 (1)		
4. $[Pt_{12}(CO)_{24}]^{2-\ d}$	−4426		67
		750	
	−5078		
5. $[Pt_{15}(CO)_{30}]^{2-\ e}$	−4411 (2)		67
	−5020 (1)		
	−5091 (2)		
6. $[Pt_3(\mu_2\text{-}CO)_3(PR_3)_3]$			
PR_3			
(a) $P(cyclohexyl)_3$	−4392	1571	110
(b) PPr^i_3	−4530	1607	110
(c) PPr^i_2Ph	−4450	1610	110
(d) $P(CH_2Ph)Ph_2$	−4448	1619	110
(e) PBu^t_2Me		1770	109
7. $[Os_2Pt_2(\mu\text{-}H)_2(CO)_8(PR_3)]$ (butterfly cluster)			
(a) PPh_3		1744	114
(b) $P(cyclohexyl)_3$		1542	114
8. $[OsPt_2(CO)_5(PPh_3)_2(\mu_3\text{-}MeC_2Me)]$		57	113
9. $[FeWPt(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO_6)(PMe_2Ph)(\eta\text{-}C_5H_5)_2]$	−4924		119
10. $[W_2Pt(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_4(\eta\text{-}C_5H_5)_2]$	−2882	$^{1}J(^{195}Pt, ^{183}W) = 177$	117
11. $[Rh_2Pt(\mu\text{-}CO)_2(CO)_2(\mu\text{-}C_5Me_5)_2]$	−4481	$^{1}J(^{195}Pt, ^{103}Rh) = 15$	116
12. $[Rh_2Pt(\mu\text{-}CO)_2(COD)(\mu\text{-}C_5Me_5)_2]$	−3599		116
13. $[Pt_2(\mu\text{-}(SiMe_3C{\equiv}CSiBu^tMe_2))(COD)_2]$	−3914		120
14.  $\left[(COD)Pt(\mu\text{-}A\text{-}C(CF_3)_2)Pt(COD)\right]$			
(a) A=O	−3709	+5355	109
(b) NH	−3916	+6235	109
15. $[L_2Pt(\mu\text{-}PhC{\equiv}CPh)PtL'_2]$			
(a) $L=L'=PMe_3$		470	109
(b) $L=PMe_2$ $L'L'=PhC{\equiv}CPh$	−4693	1006	109
16.  $[(P(OMe)_3)_2Pt(\mu\text{-}(CPh)_2CO)Pt(P(OMe)_3)_2]$		1976	109

TABLE 8 (continued)

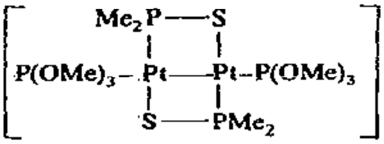
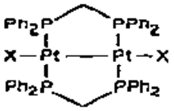
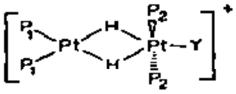
Complex	^{195}Pt	$^{1}J(^{195}Pt, ^{195}Pt)$	Ref.
17. $[Pt_3(\mu\text{-}C{\equiv}NBu^t)_3(C{\equiv}NBu^t)_3]$		188	109a
18. $[\{PtCl(CO)(PPh_3)\}_2]$		760	109
19. $[\{Pt(C{\equiv}NMe)_3\}_2]$	−4568	+507	109
20. 	−5139	410	109
21. 		188	109
22. 			
(a) X = Cl		8197	109
(b) Br		8828	109
(c) I		9007	109
23. $[(CH_3)_2Pt(\mu\text{-}Ph_2PCH_2PPh_2)_2PtCH_3]$		332	121
24. $[\{Pt(\mu\text{-}H)(PBu^t_2Me)(Si(OEt)_3)\}_2]$	−4577	92	118
25. $[Pt(C_6H_5)(PEt_3)_2(\mu\text{-}H)PtH(PEt_3)_2]$		366	79
26. 			
$P_1 = P_2 = PEt_3$, $Y = Ph$			
[a] five-coordinate:	−4369	796	112
four-coordinate:	−5265		
$P_1 = P_2 = PEt_3$, $Y = H$ [b]	−4855 −5204	886	112
$P_1 = P_2 = P(cyclohexyl)_3$, $Y = H$ [c]	−4812 −5328	268	112
$P_1 = P_2 = PPh_3$, $Y = H$ [d]	−4756 −5104	325	66
$P_1 = PPh_3$, $P_2 = P(cyclohexyl)_3$ [e]	−4908 −5255	701	112
$[Pt_2H_3(Bu^t_2P(CH_2)_nPBu^t_2)_2]^+$			
R = 2		815.4	122
R = 3		840.2	122
27. *sym-trans*-$[Pt_2X_4L_2]$			
X L			
Cl PEt_3		193	115b
Cl PPr_2Bu^t		125	115b

TABLE 8 (continued)

Complex		^{195}Pt	$^{1}J(^{195}$Pt, ^{195}Pt)	Ref.
Cl	PBu^n_3		199	115
Cl	PPr^n_3		200	109
Cl	PMe_2Et		117	109
Cl	$PMeEt_2$		190	109
Br	PMe_2Et		219	109
Br	PPr^n_3		239	109
I	PBu^n_3		380	115
I	PMe_2Et		377	109
I	$PMeEt_2$		383	109
I	PPr^n_3		391	109
Cl	PMe_3	−3410		27
Cl	$AsMe_3$	−3034		27
Cl	$AsEt_3$	−3023		f
Cl	$AsPr_3$	−3008		f
Cl	$AsPr^i_3$	−2983		f
Cl	$AsBu^n_3$	−3014		f
Br	PMe_3	−3985		27
Br	$AsMe_3$	−3701		27
Br	$SbMe_3$	−3772		27
I	PMe_3	−5297		27
I	$AsMe_3$	−5212		27
I	$SbMe_3$	−5386		27
I	SMe_2	−4827		27
	two isomers	−4795		
28. $[(PPr^n_3)_2Pt(\mu\text{-}Cl)_2Pt(PPr^n_3)_2]^{2+}$		−4255	137	27
29. $[Cl_3Pt_1(\mu\text{-}SeMe_2)Pt_2Cl_2(SeMe_2)]$				
Pt_1		−2807	516	109
Pt_2		−3749		
30. $[(P)ClPt(\mu\text{-}X,Y)PtCl(P)]$				
(a) X=Cl X=$S(CH_2Ph)_2$ P=PBu^n_3		−3884	390	11
(b) X=Y=$S(CH_2Ph)_2$ P=PBu^n_3		−3843	880	11
(c) X=Y=SPh P=PMe_2Ph		−4018		11
(d) X=Y=SEt P=PMe_2Ph		−3807		11
$[Pt(PMe_2Ph)_4]$		−4728		27
$[Pt(P(OMe)_3)_4]$		−5830		27
$[Pt(FPOC_6H_4O)_4]$		−5629		56
$[Pt(FP(OPh)_2)_4]$		−5590		56
$[Pt(PEt_3)_2(CO(CF_3)_2)]$		−4941		27
$[Pt(C_2F_4)(PEt_3)_2]$		−4784		27
$[Pt(C_2F_4)(PPh_3)_2]$		−4791		34
$[Pt(C_2H_4)(PPh_3)_2]$		−5065		34

TABLE 8 (continued)

Complex		^{195}Pt	$^1J(^{195}Pt, ^{195}Pt)$	Ref.
$[Pt(R_1-C{\equiv}C-R_2)(PPh_3)_2]$				
R_1	R_2			
CF_3	CF_3	−4645		34
Ph	Ph	−4741		28
Ph	Me	−4727		28
Ph	CO_2Me	−4710		28
Ph	H	−4690		28
Et	Et	−4689		28
Me	CO_2Me	−4682		28
Me	Me	−4674		28
H	H	−4658		28
CO_2Et	CO_2Et	−4655		28
CO_2Me	CO_2Me	−5653		28
CF_3	CF_3	−4645		28
Ph	CN	−4640		28
$CF_3CH_2CO_2$	$CF_3CH_2CO_2$	−4626		28
Me	CN	−4598		28
H	CN	−4573		28
CN	CN	−4586		28

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[a] Chemical shifts are in ppm with respect to $NaPtCl_6$(aq). Na_2PtCl_6(aq) is taken as 4533 ppm to low field of the reference frequency 21.4 MHz when the ^1H resonance of internal TMS is at exactly 100 MHz. Coupling constants are in Hz.

[b] 25°C, THF.

[c] 25°C, acetone-d_6, numbers in parentheses are relative integrals, high-field resonance is associated with the inner triangles, low-field resonance with the outer triangles. $J(^{195}Pt_0, ^{195}Pt_i)$ is an estimation of the non time averaged values.

[d] −90°C, THF/Acetone-d_6, see footnote c.

[e] −99°C, THF/Acetone-d_6, resonance at −4411 is due to outer Pt_3 triangle.

[f] Ph.D. Thesis, G. Balimann, ETH Zürich, 1977.

TABLE 9

^{195}Pt chemical shifts for complexes of several nitrogen ligands

Compound	δ^{195}Pt	Ref.
trans-$[PtCl_2(^{15}NH_2(CH_2)_5CH_3)L]$		
L		
PBu^n_3	−3612	37
$PMePh_2$	−3597	37
$P(p\text{-}CH_3C_6H_4)_3$	−3489	37
$AsBu^n_3$	−3328	37
$AsMePh_2$	−3324	37
$As(p\text{-}CH_3C_6H_4)_3$	−3322	37
$^{15}NH_2(CH_2)_5CH_3$	−2130	37
C_2H_4	−3006	37
cis-$[PtCl_2(NH_2(CH_2)_5CH_3)_2]$	−2215	37
cis-$[PtCl_2(NH_2(CH_2)_5CH_3)(C_2H_4)]$	−2805	37
trans-$PtCl_2L(PBu^n_3)]$		
L		
pyridine	−3505	40
2,6-Me$_2$-pyridine	−3451	40
Bu^tNH_2	−3534	40
$PhNH_2$	−3601	40
$[PtCl_2(PhCH{=}CH_2)(Bu^tN{=}CH{-}CH{=}NBu^t)]$	−1996	40
$[PtCl_2(Bu^tN{=}CH{-}CH{=}NBu^t)(PBu^n_3)]$ 4-coordinate	−3415	40
$[PtCl_2(PBu^n_3)]_2(Bu^tN{=}CH{-}CH{=}NBu^t)$	−3412	40
$(Bu^n_4N)_2[Pt(SC^{15}N)_4]$	−3961	41
$(Bu^n_4N)_2[Pt(^{15}NCS)(SC^{15}N)_3]$	−3431	41
trans-$[Pt(^{15}NCS)_2(PBu^n_3)_2]$	−3881	41
trans-$[Pt(^{15}NCS)(SC^{15}N)(PBu^n_3)_2]$	−4244	41
trans-$[Pt(SC^{15}N)(PBu^n_3)_2]$	−4526	41
$[Pt(OC_6H_4CH{=}NCH_2CH_2O)L]$		
L		
PBu^n_3	−2510	39
$P(OEt)_3$	−2647	39
$P(p\text{-}CH_3C_6H_4)_3$	−2511	39
$AsBu^n_3$	−2207	39
$C{\equiv}N$(cyclohexyl)	−2364	39
$As(p\text{-}CH_3C_6H_4)_3$	−2233	39
DMSO	−2463	39
Piperidine	−1630	39
$^{15}NH_2(CH_2)_5CH_3$	−1532	39
Pyridine	−1598	39

TABLE 10

$^1J(^{195}Pt, ^{14}N)$ values for some thiocyanate and cyanate complexes

L	Isomer [a]	$^1J(^{195}Pt, ^{14}N)$
NMR parameters of some anionic complexes $[Pt(CNS)_3L]^-$ [16]		
NMe_3	NSN	460 ± 5
PMe_3	NSS	355 ± 5
	NSN	439 ± 5
	SNS	205 ± 5
PMe_2Et	NSS	340 ± 10
	SNS	215 ± 5
$AsMe_3$	NSS	353 ± 5
	SNS	290 ± 10
$AsMe_2Et$	NSS	360 ± 5
	SNS	270 ± 5
SMe_2	NSS	370 ± 5
	NSN	450 ± 30
	SNS	360 ± 10
SMe_2	NSS	375 ± 5
	NSN	438 ± 5
	SNS	368 ± 10
$TeMe_2$	NSS	367 ± 5
NMR parameters for some neutral cyanate complexes [15]		
trans-$[Pt(NCO)_2(NMe_3)_2]$		420 ± 20
trans-$[PtCl(NCO)(NMe_3)_2]$		470 ± 10
cis-$[Pt(NCO)_2(PMe_2Et)_2]$		200 ± 20
Neutral thiocyanate complexes [15]		
trans-$[Pt(CNS)_2(NMe_3)_2]$	NN	288 ± 1
trans-$[Pt(CNS)_2(AsMe_3)_2]$	NS	288 ± 5
trans-$[Pt(CNS)_2(SMe_2)_2]$	NS	271 ± 1
	NN	308 ± 1
trans-$[Pt(CNS)_2(SeMe_2)_2]$	NS	275 ± 1
	NN	313 ± 1
cis-$[Pt(CNS)_2(PMe_2Et)_2]$	NS	205 ± 5
	NN	220 ± 10
cis-$[Pt(CNS)_2(PMeEt_2)_2]$	NS	245 ± 5
	NN	220 ± 5
trans-$[Pt(CNS)_2(PEt_3)_2]$	NN	424 ± 2

[a] The coordinated atoms of the CNS^- group are given in order around the metal starting with the group next to L.

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