Forschung, Wissenschaft

The Multinuclear NMR Approach. Contributions to the Chemistry of Platinum *

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Abstract

Applications of heavy atom nuclear magnetic resonance to problems in the chemistry of platinum are presented.
The direct observation of the metal resonance is shown to be both technically feasible and scientifically valuable, often providing a unique picture of the solution chemistry. The question of linkage isomerism in platinum thiocyanate chemistry, a seemingly simple problem, is revealed to be rather complex, whereas investigating the interaction of tin(II) dichloride with platinum (II), a somewhat complicated area, can be made much simpler. The surprisingly large one-bond coupling constant ($>$ 30,000 Hz) between tin and platinum is just one of a number spectroscopic curiosities associated with heavy metal NMR.

1. Introduction

The last ten years have seen nuclear magnetic resonance (NMR) attain a prominent position in the spectroscopic armament of the practicing chemist. The literature for nuclei such as ^{13}C, ^{15}N and ^{31}P has become so abundant, that these measurements are now considered as routine. Although all branches of chemistry have profited from this method, transition metal chemists have only recently begun to harvest benefits. This delay arose from the successes achieved by other forms of spectroscopy in handling the problems of metal electronic structure, combined with the limited capabilities of the earliest spectrometers. In a way this was an unfortunate situation as the NMR spectroscopy of metals and ligands stems from the first days of magnetic resonance and is rich in variety and challenge. More than 30 years ago *Proctor* and *Yu* [1] were able to observe signals for ^{55}Mn in $LiMnO_4$, ^{59}Co in $K_3Co(CN)_6$ and the two nitrogen resonances of NH_4NO_3 [2][1]. We know today that the chemical shifts of the heavier nuclei are extremely sensitive to small structural changes and often provide the most direct method of obtaining vital structural information. Why, then, are studies of metals not a prominent feature of NMR? The answer lies in the poor receptivity of these nuclei. Not every nucleus is readily measured, especially in dilute solution, and inorganic molecules can be quite sparingly soluble. To some extent this problem has been alleviated by the commercial accessibility of NMR instrumentation based on superconducting magnets. These systems afford much improved signal-to-noise ratios and are multinuclear in that they can be based on a computer controlled frequency synthesizer. In some spectrometers nucleus change requires only a few teletype instructions. This has lead to a renewed interest in heavy metal NMR and, although I will draw examples primarily from the chemistry of platinum, it is worthwhile reviewing the key points involved in measuring metals and other heavy atoms.

2. Sensitivity and Relaxation

A glance through the Periodic Table shows us that, ^{7}Li, ^{23}Na, ^{43}Ca, ^{51}V, ^{183}W, ^{57}Fe, ^{103}Rh, ^{195}Pt, ^{109}Ag, ^{199}Hg, ^{205}Tl, ^{119}Sn, ^{77}Se – just to mention a few – are all possible candidates for NMR, and *have been measured* [3].

The factors which are important are: a) the size of the nuclear magnetic moment b) natural abundance and c) the nuclear relaxation properties in the form of their spin-lattice, T_1, and spin-spin, T_2, relaxation times. A nucleus such as ^{31}P with a relatively large magnetic moment (relative sensitivity $= 6.6 \times 10^{-2}$ vs ^{1}H) and favorable natural abundance (100%) is "easy" and has attracted the attention of biochemists working with dilute solutions of phosphates [4], whereas ^{57}Fe, with a much smaller magnetic moment (relative sensitivity $= 3.4 \times 10^{-5}$) and 2.2% abundance is still something of a problem[2]. For ^{59}Co neither sensitivity (0.28) nor abundance (100%) pose a problem; however, this nucleus possesses an electric quadrupole moment ($I = 7/2$) and consequently relaxes so quickly that line

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* Lecture given at the fall meeting of the Swiss Chemical Society, October 17, 1980 in Bern, in response to the Werner-Preis received previously by the author (see CHIMIA *34* [1980] 254).

[1] In 1950 the observation of *two* ^{14}N resonances for NH_4NO_3 was "surprising", as chemical shift phenomena were in their infancy.

[2] The prospect for the future seems brighter, see *von Philipsborn* and *Schwenk* 1981.

widths are often in excess of 1 KHz. Nevertheless, one can obtain valuable structural information from the investigation of quadrupolar nuclei and the spectroscopy of ^{59}Co [5], ^{51}V [6] and ^{95}Mo [7], amongst others, seems to be experiencing a rejuvenation.

^{195}Pt, $I = 1/2$, is certainly to be considered favorably. At 9.9×10^{-3}, the sensitivity is similar to that of ^{13}C and in combination with its 33.7% natural abundance, the outlook is bright; however, although T_1 is favorable [8, 9], T_2 can be troublesome.

Complexes with coordinated ligand atoms possessing relatively large electric quadrupole moments, e.g. ^{14}N and ^{75}As, frequently afford very broad ^{195}Pt resonances. For example: the width at half height, $\nu_{1/2}$, for *trans*-$[PtCl_2(C_2H_4)(n\text{-hexylamine})]$ is 240 Hz; whereas $\nu_{1/2}$ for *trans*-$[PtCl_2(C_2H_4)(n\text{-hexylamine-}^{15}N)]$, enriched to $>95\%$ in ^{15}N, is only 10 Hz. Occasionly, the ^{195}Pt spectrum will show fine structure due to the coupling of the quadrupolar nucleus, as in Fig. 1; however, this is the exception and not the rule.

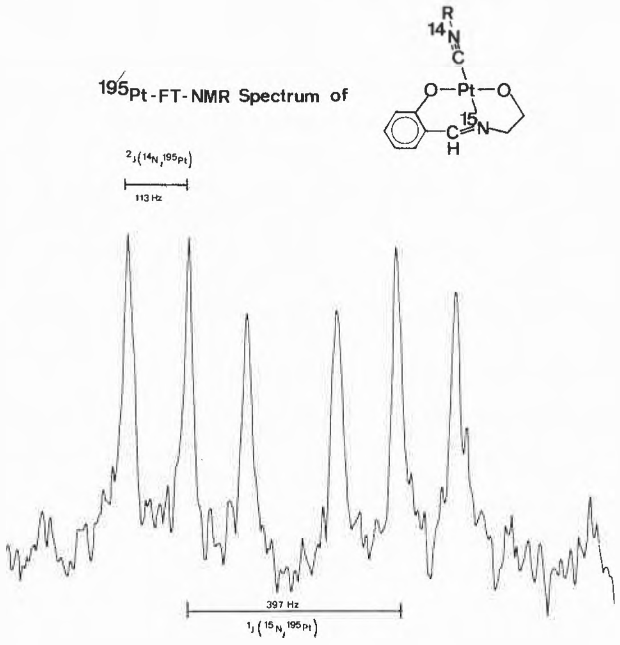


Fig. 1: ^{195}Pt NMR spectrum showing coupling of the platinum to both ^{15}N ($^1J(^{195}Pt, ^{15}N) = 397$ Hz) and ^{14}N($^2J(^{195}Pt, ^{14}N) = 113$ Hz). The spectrum is ^1H decoupled.

A T_2 problem of this kind can often be overcome by a judicious choice of solvent and sample temperature [10] so that, generally speaking, the direct observation of ^{195}Pt resonances presents no insurmountable problems. The scheme shows a listing of those nuclei which may be thought of as readily measurable and a few which are likely to prove more difficult.

3. Applications in Platinum Chemistry

The primary advantages offered by heavy atom NMR are a) chemical shift sensitivity and b) relative spectral simplicity, with the former most pronounced for metals.

Scheme 1: Statistics for Selected * $I = 1/2$ Nuclei

Nucleus	Natural Abundance %	Relative Sensitivity (to ^1H)
A. Readily Observable		
^{13}C	1.1	1.59×10^{-2}
^{29}Si	4.7	7.84×10^{-3}
^{77}Se	7.5	6.93×10^{-3}
^{109}Ag	48.7	1.01×10^{-4}
^{113}Cd	12.3	1.09×10^{-2}
^{119}Sn	8.7	5.18×10^{-2}
^{125}Te	7.0	3.16×10^{-2}
^{129}Xe	26.2	2.12×10^{-2}
^{195}Pt	33.7	9.94×10^{-3}
^{199}Hg	16.9	5.67×10^{-3}
^{207}Pb	21.1	9.13×10^{-3}
B. More Difficult		
^{15}N	0.4	1.04×10^{-3}
^{57}Fe	2.2	3.38×10^{-5}
^{103}Rh	100.0	3.12×10^{-5}
^{183}W	14.3	6.98×10^{-5}

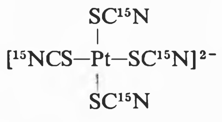
* A number of easily measured candidates have been omitted, e.g. ^{19}F, ^{31}P, ^{205}Tl

For ^{195}Pt we know that substitution of one halogen for another changes $\delta^{195}Pt$ by hundreds and sometimes thousands of ppm, and it seems to be generally the case that the heavier "softer" ligands shift the platinum signal to higher field, relative to the "harder" ligands which appear higher in the Periodic Table. Although there is no completely satisfactory theoretical support for this observation, it is a useful empiricism and is nicely illustrated by considering the question of linkage isomerism in some thiocyanate complexes of platinum (II).

a) Linkage Isomerism

The CNS^- ligand can coordinate to a transition metal *via* either nitrogen or sulfur, i.e., M—N=C=S or M—S—C≡N. If we look at the platinum chemical shift data for the model complexes *trans*-$[PtCl_2(NMe_3)_2]$. $\delta = -1886$ and *trans*-$[PtCl_2(SMe_2)_2]$, $\delta = -3424$, [13] we observe a difference, $\Delta\delta$, of 1538 ppm, with the sulfur complex at higher field (lower frequency).

These few data suggest that it should be possible to identify different linkage isomers through their ^{195}Pt resonance positions. Consider the case of the $Pt(CNS)_4^{2-}$ ion[3], where it is known [14] that, in the solid state, all four ligands are sulfur bound and that the molecule has structure I.



$$\begin{array}{c} \mathrm{SC^{15}N} \\ | \\ [\mathrm{^{15}NCS{-}Pt{-}SC^{15}N}]^{2-} \\ | \\ \mathrm{SC^{15}N} \end{array}$$

(I)

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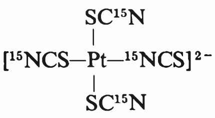
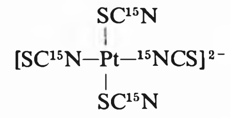
[3] Writing the thiocyanate ion as CNS^- is intended to imply uncertainty as to the mode of coordinate; whereas NCS or SCN should be interpreted as nitrogen or sulfur coordination, respectively.



$$\left[{}^{15}NCS-\overset{SC^{15}N}{\underset{SC^{15}N}{Pt}}-{}^{15}NCS\right]^{2-}$$

(II)



$$\left[SC^{15}N-\overset{SC^{15}N}{\underset{SC^{15}N}{Pt}}-{}^{15}NCS\right]^{2-}$$

(III)

Indeed, the ${}^{195}Pt$ NMR spectrum of I enriched with >95 atom % ${}^{15}N$ shows a pentet at $\delta = -3961$[4], due to four equivalent three-bond platinum-nitrogen coupling constants, in keeping with this expectation. If the solution is permitted to age[5] however, new signals appear, at $\delta = -3431$ and -2805 (see Fig. 2) which are suggestive of structures such as II and III. The ${}^{15}N$ multiplicity is helpful in that ${}^{1}J({}^{195}Pt, {}^{15}N)$, at 491–617 Hz, $\gg {}^{3}J({}^{195}Pt, {}^{15}N)$ at <20 Hz, thereby allowing the immediate recognition of directly bound nitrogen [15].

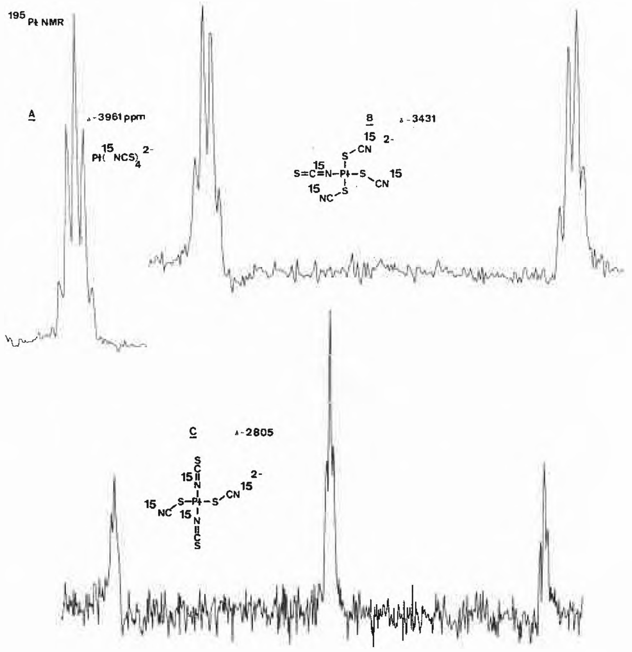


Fig. 2: ${}^{195}Pt$ NMR spectrum of $(Bu_4N)_2[Pt(C^{15}NS)_4]$ in CD_2Cl_2. There are resonances at -3961, I, -3431, II and -2805 ppm, III. The further splitting is due to ${}^{1}J({}^{195}Pt, {}^{15}N)$ and ${}^{3}J({}^{195}Pt, {}^{15}N)$.

Even without these data, the metal chemical shift is revealing. Inversion of a single *S*CN is accompanied by a low field shift in $\delta^{195}Pt$ of >500 ppm, which is just what we expect when nitrogen "substitutes" sulfur. A second inversion produces a similar change, so that the metal chemical shift is, indeed, useful.

The introduction of nitrogen-15 enriched SCN^- serves our purpose in several ways. It helps to answer the specific question concerning the $Pt(CNS)_4^{2-}$ ion, *via* platinum-nitrogen coupling constants and, in combination with further measurements allows us to establish an empirical tool based on *nitrogen-15* chemical shift values. We have been able to confirm [15] that the nitrogen chemical shift is a more general probe for SCN bonding, with N-coordinated CNS differing from the S-coordinated isomer by 80 ppm or more. This is an important feature if the metal chemical shift is not readily available, e.g., $\delta^{15}N$ for $Hg(SCN)_4^{2-}$ is 214.5 ppm; whereas $Zn(NCS)_4^{2-}$ has $\delta^{15}N$ equal to 131.1 ppm. As complexation of nitrogen to transition metals often induces substantial high field shifts of the nitrogen resonance [15], these data allow us to assign sulfur coordination to mercury and nitrogen coordination to Zn in these binary complexes. Clearly, whether it is the metal itself, or the directly coordinated ligand atom, heavy atom NMR has something to offer.

b) Platinum-Tin Chemistry

Metal-metal bonds in transition metal complexes are attracting increasing interest in academic circles. In the case of platinum coordinated to tin there is also an industrial interest as platinum complexes of tertiary phosphines combine with tin(II) dichloride to provide active hydrogenation [16] and hydroformylation [17] catalysts.

Since catalytic reactions often involve labile intermediates which are not easily isolated, heavy metal NMR, and ${}^{119}Sn$, $I = {}^{1}/_{2}$, in particular, should prove helpful in the identification of transient platinum-tin complexes. Combined with the relatively easy ${}^{31}P$ method we are equipped to address ourselves to aspects of the metal catalysed hydrogenation reaction (1), and specifically equations (2)–(4).

$$RCH{=}CH_2 + H_2 \xrightarrow[PtCl_2(PR_3)_2\,+\,SnCl_2]{} \text{alkane} \quad (1)$$

$$PtCl_2(PR_3)_2 + n\,SnCl_2 \longrightarrow \text{“A”} \quad (2)$$

$$\text{intermediate “A”} + H_2 \longrightarrow \text{“B”} \quad (3)$$

$$\text{intermediate “B”} + \text{unsaturated organic molecules} \longrightarrow \text{“C”} \quad (4)$$

We begin this study knowing that the reaction (1) functions best with five or more equivalents of tin [16]. Further, trichlorostannate complexes of transition metals often contain the "$M{-}SnCl_3$" moiety, IV [18–20]; although, both V [21a] and VI [21b] are real possibilities.

$M{-}SnCl_3$	$M^{(+)}SnCl_3^{(-)}$	$M{-}Cl{-}SnCl_2$
IV	V	VI

We can now ask the following questions:

1. What can we discover about A, B and C?
2. Why are 5 equivalents of $SnCl_2$ necessary?
3. Which of the units IV–VI appear in solution?

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[4] Chemical shifts are relative to external Na_2PtCl_6 (aq) which is a low field reference.

[5] Coincidently, we chose to remeasure this solution after several months.

4. What role does the tin(II) chloride play in the catalysis?

These objectives seem within reach and we start with equation (2), for PEt_3. Reaction of colorless *cis*-$[PtCl_2(PEt_3)_2]$ with only one mole of $SnCl_2$ in acetone-d_6 affords a yellow solution from which the yellow complex *trans*-$[PtCl(SnCl_3)(PEt_3)_2]$ can be isolated [22].

The $^{31}P\{^1H\}$ spectra of both the dissolved solid and the original solution show a single resonance from equivalent phosphines, flanked by ^{195}Pt and $^{117,119}Sn$ satellites. The $^{195}Pt\{^1H\}$ spectrum reveals triplet multiplicity from the phosphorus atoms and further signals attributable to ^{117}Sn and ^{119}Sn satellites. Relative to the starting dichloride the platinum absorption is shifted by > 800 ppm to higher field suggesting that a new, substantially different, ligand atom is now coordinated. The ^{119}Sn spectrum reflects, the ^{31}P and ^{195}Pt observations in showing triplet splitting accompanied by ^{195}Pt satellites. In the spectra of both metals the extremely large $^1J(^{195}Pt, ^{119}Sn)$ coupling is strongly suggestive of a metal-metal bond (see Table 1). Taken together these NMR data suggest an isomerization reaction which we show as the first step in the second scheme.

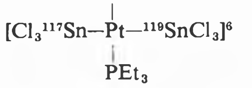
Table 1: ^{195}Pt NMR Data [a] for Some Platinum-Tin Complexes

Complex	$\delta^{195}Pt$	$^1J(^{195}Pt, ^{119}Sn)$
$Pt_2Cl_2(SnCl_3)_2(PEt_3)_2$, X	− 4,266	35,034
trans-$[PtCl(SnCl_3)(PEt_3)_2]$	− 4,780	28,954
trans-$[Pt(SnCl_3)_2(PEt_3)_2]$ [b]	− 5,152	20,410
trans-$[Pt(SnCl_3)_2(P(OEt)_3)_2]$ [b]	− 5,234	19,043
trans-$[PtH(SnCl_3)(PEt_3)_2]$	− 5,302	9,067
trans-$[Pt(C_6H_5)(SnCl_3)(PEt_3)_2]$	− 4,799	6,745

[a] Chemical shifts are relative to external Na_2PtCl_6 (a low field reference), with negative values indicating a shift to higher field. δ values are in ppm. J values in Hz.

[b] see footnote 6.

Addition of a second mole of tin(II) chloride results in an equilibrium between the *mono* and *bis* trichlorostannate complexes. A third equivalent of tin produces *trans*-$[Pt(SnCl_3)_2(PEt_3)_2]$, in > 90% yield (in solution) and this may be isolated and characterized [23][6]. Further addition of tin does not change the ^{31}P spectrum. The structural assignment for the *bis* tin compound *trans*-$[Pt(SnCl_3)_2(PEt_3)_2]$[6] (and *trans*-$[Pt(SnCl_3)_2(P(OEt)_3)_2]$[6], amongst others) is once again based on ^{31}P, ^{195}Pt and ^{119}Sn NMR methods.

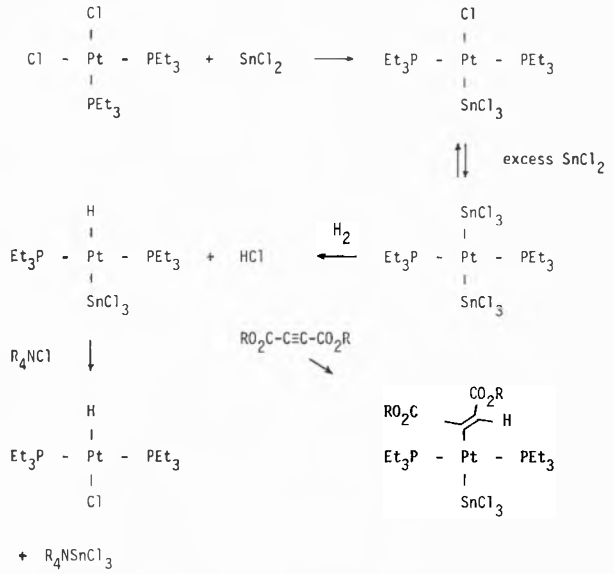


$$[Cl_3{}^{117}Sn{-}\underset{PEt_3}{\overset{PEt_3}{Pt}}{-}{}^{119}SnCl_3]^6$$

VII

Key points here are: a) the recognition of VII *via* the throug-metal tin-117 to tin-119 coupling constant in the ^{119}Sn spectrum see Figure 3 and b) the interpretation of the values $^1J(^{195}Pt, ^{119}Sn)$ and $^2J(^{119}Sn, ^{117}Sn)$, which we discuss in the following section.

Scheme 2:



Interestingly, the solution behavior of the dichlorides depends upon both tertiary phosphine and solvent. For *cis*-$[PtCl_2(P(p\text{-}CH_3C_6H_4)_3)_2]$, in CD_2Cl_2, we observe first *cis*-$[PtCl(SnCl_3)(P(p\text{-}CH_3C_6H_4)_3)_2]$, i.e. insertion of $SnCl_2$ without isomerization, but only *trans*-$[Pt(SnCl_3)_2(P(p\text{-}CH_3C_6H_4)_3)_2]$[6].

Reaction of a methanol solution of *cis*-$[PtCl_2(PEt_3)_2]$ and two equivalents of $SnCl_2$ with H_2 produces (amongst others) *trans*-$[PtH(SnCl_3)(PEt_3)_2]$. We have characterized this as its chloride complex, *trans*-$[PtHCl(PEt_3)_2]$ (see scheme), although there is no difficulty in preparing analytically pure samples of the hydrido-tin derivative [24, 25]. Indeed, the complexes *trans*-$[PtH(SnCl_3)P_2]$, P = PEt_3, PPh_2CH_2Ph, PPh_3 all show large $^2J(^{119}Sn, ^1H)$ values: ≈ 1600–1700 Hz, and this knowledge [25] has proved useful in the identification of hydrido-tin complexes. Once again, the $SnCl_3$ coordinates to platinum via the metal, although the reduced $^1J(^{195}Pt, ^{119}Sn)$ value (see Table) and the − 70 to − 80° temperatures required for sharp ^{31}P and ^{119}Sn resonances suggest that there are significant differences between the Pt-$SnCl_3$ moieties in our complexes. All of our hydrido-tin complexes give satisfactory ^{31}P, ^{195}Pt and ^{119}Sn spectra.

In view of the extensive literature describing the further reactions of platinum-hydrides with olefins and acetylenes [26], the observation that these hydrides can be easily generated from the platinum-tin complexes seems significant. Indeed, this reaction is so facile that it has preparative value, as the hydrido-tin complexes afford good yields of the hydridochloride analogs, after precipitation of R_4NSnCl_3[7].

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[6] There is some question as to whether the *trans*-$[Pt(SnCl_3)_2(PR_3)_2]$ complexes might not be better formulated as 5-coordinate $[Pt(SnCl_2)(SnCl_3)_2(PR_3)_2]$ or $[Pt(SnCl_3)_3(PR_3)_2]$.

[7] This procedure has the advantage of consuming less energy than other methods, e.g., the reaction of *cis*-$[PtCl_2P_2]$ with NH_2NH_2 in refluxing ethanol. A separate report is in preparation.

Although our studies involving the further reactions of the *trans*-[PtH($SnCl_3$)P_2] complexes are still in progress the complexes *trans*-[Pt(carbon ligand) ($SnCl_3$)P_2] are quite stable [27] and the Table shows some new data for these as well.

Based on our relatively few NMR measurements we can now attempt to answer some of our questions. The products of reactions 2-4 are phosphine complexes of platinum which contain the coordinated trichlorostannate ion. In all of our molecules we find that the $SnCl_3^-$ ligand coordinates to platinum *via* tin as evidenced by the metal-metal coupling constants. We cannot exclude dissociation of the $SnCl_3^-$ during the reactions since many of these molecules seem to be involved in exchange and isomerization processes.

Certainly one of the important functions of the excess tin(II) chloride is to shift the equilibrium in favor of coordinated trichlorostannate compounds. These derivatives, in contrast to the starting dichloro complexes, activate the platinum towards reaction with molecular hydrogen. To be sure this chemistry is far from completely clear; however, as in the linkage isomerization problem, the heavy atom NMR approach allows us to directly address a subtle chemical puzzle and point the way towards further progress.

c) Spectroscopy

The decision to monitor a chemical process *via* some change in the NMR characteristics of nuclei such as ^{15}N, ^{119}Sn or ^{195}Pt often leads to new, sometimes surprising, spectroscopic information.

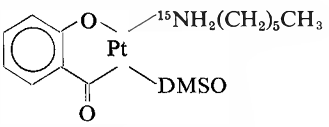
In the area of nitrogen chemistry we have contributed to the identification and understanding of the Pt–N bond through the use of the previously unexplored $^1J(^{195}Pt, ^{15}N)$ parameter [15, 28–30]. These coupling constants vary from 88 to 617 Hz [15, 29, 39] in agreement with expectations based on the acceptance of the Fermi contact term, plus a consideration of the nitrogen gyromagnetic ratio, ν_N, and the s-density expectation values $|\psi_N(O)|^2_{2s}$ (see equation 5).

$$^1J(A,B) \sim \gamma_A \gamma_B \left|\psi_{ns_A}(O)\right|^2 \left|\psi_{ns_B}(O)\right|^2 \pi_{A,B} \qquad (5)$$

$$\pi_{A,B} = \sum_i^{occ} \sum_j^{unocc} (\varepsilon_j - \varepsilon_i)^{-1} C_{iA} C_{iB} C_{jA} C_{jB}$$

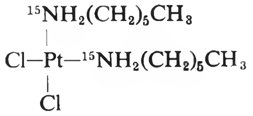
ε_j and ε_i are energies of unoccupied and occupied M.O.'s and the C terms are s-coefficients of the atomic orbitals used in the combinations which make up the M.O.'s.

As is often the case, the relative differences, and not absolute magnitudes, prove to be most interesting. Complexes VIII and IX differ in $^1J(^{195}Pt, ^{15}N)$ by roughly a factor of four, although the four "substituents" on nitrogen are identical, thus raising interesting questions concerned with differences in the nature of the platinum-nitrogen bond.



(VIII)

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

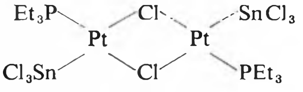


$$\begin{array}{c} ^{15}NH_2(CH_2)_5CH_3 \\ | \\ Cl{-}Pt{-}^{15}NH_2(CH_2)_5CH_3 \\ | \\ Cl \end{array}$$

(IX)

$^1J(^{195}Pt, ^{15}N) = 336$ Hz

Very occasionally, the absolute magnitude of a coupling constant draws some attention and we believe that the values $^1J(^{195}Pt, ^{119}Sn)$ [31] and $^2J(^{119}Sn, ^{117}Sn)$ [32] are two such cases. For a nucleus L, such as ^1H, ^{13}C or ^{31}P, it is not unusual for $^1J(^{195}Pt, L)$ to lie between 1,000 and 5,000 Hz; however, one-bond platinum-tin values can exceed 35,000 Hz, making these the largest known nuclear spin-spin coupling constants. As in the platinum-nitrogen example it is informative to relate such a number to other one-bond $^1J(^{195}Pt, L)$ values, using the Fermi contact expression. Specifically, one can eliminate differences due to γ_{Sn} by reporting the reduced coupling constant $^1K(\propto {}^1J/\gamma_{Sn}\gamma_{Pt})$ instead of ^1J, but this is not critical when the nuclei to be compared have qualitatively similar gyromagnetic ratios, as is the case for ^{119}Sn and ^{31}P. ($\gamma\,^{119}Sn/\gamma\,^{31}P = 0.92$). Consider compound X[8] in which we have both a $^1J(^{195}Pt, ^{119}Sn)$ and $^1J(^{195}Pt, ^{31}P)$ coupling constant.



(X)

$^1J(^{195}Pt, ^{119}Sn) = 35{,}034$ Hz, $^1J(^{195}Pt, ^{31}P) = 3{,}503$ Hz.

The difference between these two is ≈ a factor of 10 and we ask: How shall we account for this?

It is known [33] that electron withdrawing groups on an atom coupled to platinum can change ^1J by ≈ 2 and this will be relevant for $SnCl_3$ vs PR_3. We have no knowledge of the differences between $|\psi(O)|^2_{Sn}$ and $|\psi(O)|^2_P$, although a factor of ≈ 2.5 might be a good approximation [34]. Combining these two $^1J(^{195}Pt, ^{119}Sn)$ might be a factor of 5 larger than $^1J(^{195}Pt, ^{31}P)$, but we are still a factor of ~2 short of the observed ratio of almost exactly 10. Complex X does not stand alone as a similar ratio exists for *trans*-[Pt($SnCl_3$)$_2$(PEt_3)$_2$][6], VII, in which $^1J(^{195}Pt, ^{119}Sn) = 20{,}410$ Hz, $^1J(^{195}Pt, ^{31}P) = 1{,}460$ Hz. Obviously, there are some interesting differences between the π_{AB} terms in these molecules. Continuing in this vein we note that the two-bond tin-tin coupling constants in our *bis* trichlorostannate derivatives also represent something of a new record. For VII, $^2J(^{119}Sn, ^{117}Sn)_{trans} = 18{,}192$ Hz and the palladium analog is larger yet at 20,990 Hz. An analogous $^2J(^{31}P, ^{31}P)_{trans}$ value would be ≈ 500-600 Hz, so once again, we must seek an explanation based

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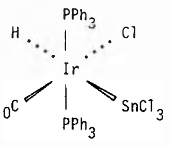
[8] The *sym-trans* is presumed correct, but a *sym-cis* structure cannot be excluded.

in the bonding characteristics of the tin. The two-bond coupling phenomena seems to be somewhat general. We find $^2J(^{119}Sn, ^{21}P)$ to be > 4 KHz [22] and $^2J(^{119}Sn, ^1H)$ to exceed 1.5 KHz [25] with this last observation having relevance in the hydride chemistry of other metals. The orientation of the hydride and tin ligands in the complex XI, can be shown to be *trans*, since $^2J(^{119}Sn, ^1H)$ = 1,567 Hz [35].



(XI)

We do not as yet have a suitable explanation for all of these data, although we do have a working hypothesis [32]. Whether this develops satisfactorily or not, the challenge is certainly there!

Summation

In the preceeding paragraphs I have presented examples of a multinuclear NMR approach to problems in platinum chemistry. Essentially, this boils down to nothing more than finding the most sensitive probe closest to the site of interest. In our work this has meant ^{195}Pt and ^{119}Sn NMR amongst others; however, for an enzyme chemist, involved with Group IIb complexes, ^{113}Cd or ^{199}Hg studies might be relevant, whereas for an organic chemist, ^{13}C and ^{15}N could be the weapons of choice. Admittedly, NMR is not always the ideal method for every problem; nevertheless, there exist NMR measurements for more than forty different nuclear spins and these encompass a considerable area of our science. A glance through the "NMR Periodic Table" might prove rewarding.

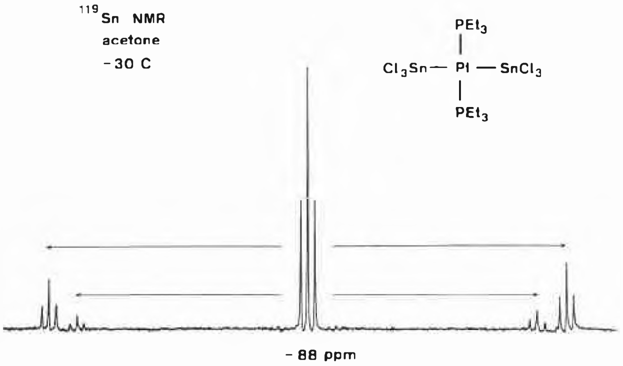


Fig. 3: ^{119}Sn NMR spectrum of *trans*-[Pt(SnCl$_3$)$_2$(PEt$_3$)$_2$][6]. The separation of the more intense satellites corresponds to $^1J(^{195}Pt, ^{119}Sn)$ whereas the separation of the less intense satellites equals $^2J(^{119}Sn, ^{117}Sn)$. The triplet structure on the main signal arises from ^{31}P coupling. The spectrum is ^1H decoupled.

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