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THE ELECTRONIC STRUCTURE OF TRANSITION-METAL HYDRIDES BY NUCLEAR MAGNETIC RESONANCE

A thesis submitted for the degree of Doctor of Philosophy at the University of Oxford

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Abstract

The platinum hydride complexes <u>trans</u>-$Pt(PEt_3)_2HL$ have been prepared, where L is a carboxylato ligand. The carboxylato ligands were either substituted benzoato ligands i.e. o-NO_2, m-NO_2, p-NO_2, o-Cl, m-Cl, p-Cl, o-Br, m-Br, p-Br, m-F, m-I, p-I, m-CH_3, p-CH_3, p-CH_3O, m-$(CH_3)_2N$, p-$(CH_3)_2N$, p-CN, 3,5-$(NO_2)_2$, 2,5-$(NO_2)_2$ and 2,4,6-$(NO_2)_3$ or the substituted acetato ligands; CF_3COO, $CHCl_2COO$, CH_2ClCOO, $CH_2(OC_6H_5)COO$. The compounds were fully characterized by analysis, infrared and ^1H nuclear magnetic resonance spectra, and, in the majority of cases, by molecular weight determinations.

The ^1H nuclear magnetic resonance spectra of the complexes were studied in detail and, in particular, magnitudes of the chemical shift, τ_{Pt-H}, and the platinum-hydrogen coupling constant, J_{Pt-H}, of the hydrido ligand were determined. The dependence of these quantities on concentration and solvent was examined. The platinum-hydrogen stretching frequency, ν_{Pt-H}, was also determined.

The parameters τ_{Pt-H}, J_{Pt-H}, ν_{Pt-H} and the pK_a of the parent carboxylic acid HL were examined to see if there was any correlation between them. When one of the parameters being examined was pK_a, three separate

linear correlations were found, one for the ortho-substituted benzoato derivatives, one for the meta- and para- substituted benzoato derivatives and one for the substituted acetato derivatives. A plot between τ Pt-H and $\mathcal{J}$ Pt-H shows two linear correlations namely for the substituted benzoato derivatives and for the substituted acetato derivatives. When the stretching frequency is being plotted either against τ Pt-H or $\mathcal{J}$ Pt-H only one linear correlation is distinguishable.

An attempt was made to interpret the observed variation in chemical shift in terms of the theory of Buckingham and Stephens for shielding in transition metal hydrides. It is concluded that the main cause of variation in shielding constant in the above complexes is change in the metal -hydrogen distance. An attempt to provide further evidence by a ^{2}H nuclear magnetic resonance study of <u>trans</u>-$Pt(PEt_3)_2DCl$ was inconclusive.

The variation in the platinum-hydrogen coupling constant is discussed in terms of the molecular orbital formulation of the Fermi contact term given by Pople and Santry. No conclusion may be drawn as to the relative importance of electronic factors which could cause variation in $\mathcal{J}$ Pt-H in the above complexes, though it seems likely that variation in s-character of the

metal-hydrogen bond is probably significant. However consideration of J_{Pt-H} in a closely related series of platinum hydride complexes where L = NO_3, I, Br, Cl, SCN, NO_2, OCN, CN shows that they fall in the order of the position of L in the spectrochemical series. Although no rigorous theoretical significance may be attached to this fact it seems likely that factors other than the s-character of the metal-hydrogen bond are important in determining the variation of J_{Pt-H} in this series of complexes.

The cobalt complexes $Co(NH_3)_5L^{2+}$ where L = C_6H_5COO, CF_3COO, 3,5-$(NO_2)_2C_6H_3COO$, p-$CH_3OC_6H_4COO$, p-$NO_2C_6H_4COO$ were prepared and their electronic spectra studied in order to ascertain their relation to the correlation found between J_{Pt-H} and the spectrochemical series for the acido ligands listed above. It was found that though they agreed roughly with the correlation between J_{Pt-H} and $1/\Delta E$ where ΔE is the first ligand field band for the cobalt complexes, all the carboxylato complexes had the same ΔE, within experimental error, thus the variation in J_{Pt-H} from one carboxylato complex to another was in no way related to a change in ΔE.

An attempt was made to estimate the shielding constant in platinum hydrides using the variation-

perturbation technique formulated by Karplus and Kolker. Disagreement was found with the expression for shielding given by Karplus and Kolker. Use of the modified expression predicted a value of zero for the "paramagnetic" shielding of the hydrido ligand by the platinum d-electrons.

INDEX

		Page
Chapter I.	Introduction	1
A.	Choice of hydrides.	2
B.	Carboxylato ligands.	8
C.	Metal-hydrogen bond lengths.	9
D.	Nuclear magnetic resonance studies on transition-metal hydrides.	14
E.	Infrared studies.	17
F.	Related nuclear magnetic resonance studies.	21
Chapter II.	trans-Hydridocarboxylatobis-(triethylphosphine)platinum(II) complexes and their proton magnetic resonance spectra.	22
A.	Characterization of the complexes.	22
B.	Properties of the complexes.	26
C.	Proton magnetic resonance spectra.	27
D.	^2H nuclear magnetic resonance spectrum of trans-$Pt(PEt_3)_2DCl$.	45
Chapter III.	Infrared studies.	46
A.	Assignment of mull spectra.	46
B.	Solution spectra of the complexes(I).	53

		Page
Chapter IV.	Discussion of results.	64
	A. Empirical deductions.	64
	B. Ionization constants of carboxylic acids.	79
	C. Discussion of chemical shift data.	81
	D. Discussion of coupling constant data.	89
	E. Platinum-phosphorus coupling constants.	100
	F. Shielding in m- and p-fluoro-phenylplatinum(II) complexes.	103
	G. General conclusions.	105
Chapter V.	Experimental.	106
	A. General.	106
	B. Preparations.	107
	C. Instrumental Methods.	121
Chapter VI.	Variation-perturbation method for calculation of the shielding tensor.	124
	A. Introduction.	124
	B. The Hamiltonian and consideration of the effect of gauge transformation.	125

		Page
C.	Choice of wave functions.	128
D.	Expression for the shielding constant.	130
E.	Transformation of origin.	132
F.	Diamagnetic contribution to the shielding.	134
G.	Paramagnetic contribution to the shielding.	135
H.	Choice of Ψ_o, fi and gi.	136
I.	Reduction of the formulae by symmetry.	137
J.	Calculation of σ_{xx}^{P}.	138
K.	Discussion.	142
Appendix I.	Attempted preparation of rhodium compounds.	144
Appendix II.	Reported mass spectrum.	145
Appendix III.	Infrared spectra.	150
Appendix IV.	Derivation of the general formula for the variation-perturbation method.	157

CHAPTER I

INTRODUCTION

This thesis describes a H^1 nuclear magnetic resonance study of a series of square planar platinum(II) hydride complexes. The relationships of the chemical shift of the hydrido ligand and the platinum-hydrogen coupling constant to other physical and chemical properties are discussed and a theoretical interpretatio n of the trends found in the physical data is attempted.

In the introduction reasons are given for the choice of compounds studied and some particular aspects of the chemistry of transition metal hydrido complexes relevant to this thesis are discussed. The general chemistry of transition metal hydrido complexes has been recently extensively reviewed (1, 2).

Table I

Some isotopes of transition metals and their nuclear properties (3)

Isotope	Natural Abundance	Magnetic moment, μ, in multiples of the nuclear magneton ($eh/4\pi Mc$)	Spin Quantum number
^{103}Rh	100%	-0.0879	$\frac{1}{2}$
^{183}W	14.28%	0.115	$\frac{1}{2}$
^{195}Pt	33.7%	0.6004	$\frac{1}{2}$

A. Choice of hydrides

The choice of the compounds which were studied in this work was determined by various factors.

a) In order to obtain the maximum information from a nuclear magnetic resonance study, a transition metal with a naturally occuring isotope of spin ½ was required. Thus a metal-hydrogen coupling constant could be determined. Isotopes of rhodium, tungsten and platinum have this property (see Table I for their nuclear properties).

b) As the size of a nuclear magnetic resonance signal is proportional to the concentration of the species a high natural abundance of the isotope concerned greatly aids the sensitivity of the nuclear magnetic resonance experiment. This is particularly important if the solubility of the compounds to be studied is low.

c) The coupling constant, between two nuclei, is proportional to the product of their magnetogyric ratios (4). A large magnetogyric ratio for a nucleus produces a correspondingly large coupling constant. This is advantageous as small percentage changes in the coupling constant are easily detectable by the nuclear magnetic resonance experiment.

d) An octahedral or square planar series of hydrides was considered preferable, the members of the series

differing from one another by the other ligands attached to the metal. These two configurations lend themselves to approximate theoretical treatments because of their relatively high symmetry.

e) A series of compounds possessing an assignable d-d spectra was considered to be an advantage because of the information the spectra may give about excited states.

f) Finally the choice was limited by the possibility of preparation of the complexes.

Examination of the literature (see Table II) shows that there are relatively few known series of metal-hydrido compounds that fit the above criteria. For example for tungsten the only known classes are the relatively unstable carbonyl hydrides or the bis-π-cyclopentadienyl, and π-cyclopentadienyl carbonyl hydrides for which no suitable ligand substitution series (other than ring substitution) can be envisaged.

Suitable series of rhodium compounds would be trans- $RhLH(DMG)_2$ (where DMG = dimethylgl yoximato) and L is a series of nitrogen or phosphorous ligands, cis- and trans-$RhLH(en)_2^{2+}$ (when en = ethylenediamine and L is as above) and cis- and trans-$RhHL(PP)_2$ (where PP = $(PPh_2)_2C_2H_4$). Unsuccessful attempts to

Table II. Some hydrides of rhodium, tungsten and platinum.

Compound.	Colour.	M.pt.°C	τ_{M-H}	$J_{M-H(c.p.s)}$	$\nu_{M-H(cm^{-1})}$	$\delta_{M-H(cm^{-1})}$	Reference
$RhHCl_2(AsPh_2Me)_3$	yellow	172-175			2077		5
$RhHBr_2(AsPh_2Me)_3$	orange-yellow	175-178			2073		5
$RhHI_2(AsPh_2Me)_3$	orange-brown	164			2058		5
$RhH\{C_2H_4(PPh_2)_2\}_2$	orange	280 dec.			1902	625	6
$Rh_2H_h\{o\text{-}C_6H_4(PEt_2)_2\}_2$	colourless	360-362					7
$RhH(CO)_4$	yellow	-10					8
$RhH(CO)(PPh_3)_3$	yellow		19.9		2004	784	9
$[RhH(CN)_5]^-$	yellow sol^h		20.9	13.1			10
cis-$[RhH Cl$ trien$]^+$			28.0	27	2081		11
cis-$[RhH_2$ trien$]^+$			32.5	30	1969		11
trans-$[RhH_2$ en$_2]^+$			31.6	27 ± 1			11
$[RhH(NH_3)_5]^{2+}$					2080		11
trans-$[RhCl_2(DMG)_2]^- + BH_4^-$			26.4				11
trans-$[RhCl_2$ py$_4]^+ + BH_4$			28.5				11
trans-$[RhHI$ en$_2]^+$			30.2		2140		11
$(\pi\text{-}C_5H_5)_2WH_2$	yellow	163-165	22.28		1896		12
$[(\pi\text{-}C_5H_5)_2WH_3]^+$	colourless		16.44(A_2) 16.08(B^2)		1943		12
$HW(CO)_5$							13

$[HW_2(CO)_{10}]^-$							13
$H_3W_2(CO)_6(OH)_3$							14
$H_4W_3(CO)_9(OH)_2H_2O$ and salts							14
$H_4W_3(CO)_9(OH)(OCH_3)(CH_3OH)$ and salts							14,1
$H_4W_4(CO)_{12}(H_2O)_4$							14
$[H\ W(CO)_3H_2O]_2C_6H_6$							16
$W\ H(C_6H_5Li)_2$	black						17,18
$(\pi\text{-}C_5H_5)W(CO)_3\ H$	yellow	68.5-69.5	17.33		1845		19
$[\{(\pi\text{-}C_5H_5)W(CO)_3\}_2H]^+$			34.77	38.6			19
$[(\pi\text{-}C_5H_5)_2MoW(CO)_6H]^+$			32.88	38			19
$[(\pi\text{-}C_5H_5)\ W(CO)_3H_2]^+$			11.93 11.90				19
<u>trans</u>-Pt H Cl$(PMe_3)_2$	colourless	132-137dec			2182		20,21
<u>trans</u>-Pt H$(NO_3)(PEt_3)_2$	colourless	47-49	33. 6	1322	2242		21,23
<u>trans</u>-Pt H(CNO)$(PEt_3)_2$	colourless	65-66	27.7,27.0	1080	2229	840	21,23
<u>trans</u>-Pt H Cl$(PEt_3)_2$	colourless	81-82	26.8	1275	2183		20,21,23
<u>trans</u>-Pt H Br$(PEt_3)_2$	colourless	94-97	25.6	1346	2178		20,21,23
<u>trans</u>-Pt H I (PEt_3)	colourless	73-75	22.7	1369	2156		20,21,23
<u>trans</u>-Pt H$(NO_2)(PEt_3)_2$	colourless	60-80	29. 4	1003	2150		21,23
<u>trans</u>-Pt H(SCN)$(Pet)_2$	colourless	61-64	22.95	1233	2112	844	20,21,23
	colourless		27. 6	1086			

trans- Pt H(CN)$(PEt_3)_2$	Colourless	106-107	17.6	778	2041	826	21,23
trans - Pt H Cl$(PPr^n_3)_2$	"	47-49			2183		20,21
trans - Pt H Cl$(PPh\ Et_2)_2$	"				2199		22
trans - Pt H I$(PPhEt_2)_2$	"				2179		22
trans - Pt H Cl$(PPh_2Et)_2$	"	131-132.5			2206		21
trans - Pt H I$(PPh_2Et)_2$	"	115-116			2189		21
trans - Pt H Cl $(PPh_3)_2$	"	215-220dec.			2220		21
trans - Pt H I$(PPh_3)_2$	"	195-212dec			2186		21
trans - Pt H Cl$(AsEt_3)_2$	"	91-93	29.3	1117	2174		20, 21,
trans - Pt HBr $(AsEt_3)_2$	"	107-110	27.75	1185	2167		21,23
trans - Pt H I$(AsEt_3)_2$	"	109-112dec	24.6	1220	2139		21,23
trans - Pt H(SCN)$(AsEt_3)_2$	"	56-57	29.9		2108		21,23
$PtH_2Cl_2\ (PEt_3)_2$	"	dec	24.75		2254		21,22
$[Pt\ H(NH_3)(PEt_3)_2]$ Cl							20,21
$[Pt\ H(NH_3)(AsEt_3)_2]$Cl							21
$Pt\ H_2(PPh_3)_2$	"	117dec			1670	815	24,25
$[Pt\ H\ (PPh_3)_3]^+Cl^-$		110-111			2102	817	27
$[Pt\ H(PPh_3)_3]^+\ NO_3^-$		125-126			2107	813	27
$H\ Pt(CN)_4$	"		18	450			26
$Pt\ (PEt_3)_2\ HGePh_3$	white	150dec.			2051		28
$Pt\ (PEt_3)_2\ HGePh_3$					1957		28
cis -Pt H Cl$(PPh_3)_2$	colourless	215-220			2260		29

prepare series of related chlorides and examine the nuclear magnetic resonance spectra of their reduced species are described in Appendix I.

A series of platinum hydrides which meet our requirements has been prepared by Chatt and Shaw (21) and their nuclear magnetic resonance spectra studied (23). It was decided that this series could be usefully extended by preparing the compounds trans-$Pt(PEt_3)_2$ HL where L is a series of benzoato and acetato ligands. The effect of varying these groups on the physical and chemical properties of compounds, although not completely understood, has been extensively studied, thus empirical correlations between the change of L and the proton magnetic resonance spectra would be expected to be found . Such correlations might provide insight into the nature of the bonding in these complexes and also might provide a testing ground for current theories of chemical shifts and coupling constants applied to these types of compounds.

B. Carboxylato ligands

The carboxylate group can bind to metals in a variety of ways. It may act as a monodentate group bonding through one oxygen of the carboxylate group as in the complex Li(acetate).$2H_2O$ (30). It is also known to act as a chelating ligand as in the compound Zn(acetate)$_2$.$2H_2O$ (31). Carboxylates are also found as bridging bidentate ligands as in the chromium complex, Cr_2(acetate)$_4$.$2H_2O$ (32). Complexes of a largely ionic nature may also exist; sodium formate is believed to be of this type (33).

The type of coordination present in a carboxylato complex may be deduced from its infrared spectra (34). This fact will be used to ascertain that the platinum complexes prepared contain the carboxylato ligands as monodentate groups (see Chapter III).

C. Metal-hydrogen bond lengths

1. Diffraction methods

Diffraction methods have been applied successfully in two cases to the determination of metal hydrogen distances.

The compound potassium rhenium hydride, K_2ReH_9, has been studied by x-ray (35) and neutron (36) diffraction. The average bond length in the ReH_9^{2-} anion is 1.68 $\pm$ 0.01 Å.

In most cases it has been found impossible to detect a hydrogen atom attached to a transition metal by x-ray diffraction alone. However with the compound $RhH(CO)(PPh_3)_3$ it has been observed at a distance 1.60 $\pm$ 0.12 Å from the metal atom (37). The compound has a trigonal bipyramidal structure with the three phosphine groups in axial positions. The rhodium atom lies 0.36 Å below the plane of the three phosphorus atoms towards the carbonyl. Thus the phosphine groups may be imagined as bending away from the carbonyl group towards the less bulky hydrido ligand.

The hydrido ligands were claimed to have been located in the compound bis-π-cyclopentadienyl-molybdenumdihydride (38), a short Mo-H distance of 1.2 $\pm$ 0.3 Å being given. However recalculation of

the data suggests that the hydrogens are undetectable in this compound (39).

Other x-ray studies on hydrides, although not locating the hydrogen precisely give strong indications of its stereochemical position in the molecule.

The compound trans-$Pt(PEt_3)_2HBr$ has been shown to have an approximately square planar configuration (40) the phosphine ligands being bent towards the supposed location of the hydrogen (P-$\hat{Pt}$-Br = 94.1°, 93.7°). The platinum bromine distance is 2.56 Å which is long compared with the distance expected from the sum of covalent rudii (2.43 Å). This has been attributed to the high "trans-effect" of the hydrido ligand.

The compound $OsHBr(CO)(PPh_3)_3$ shows a similar lengthening of the bond trans to the hydrido ligand. X-ray diffraction studies show the configuration to be octahedral (41) with the hydrogen presumed to be in a plane with the three phosphorus atoms. The Os-P distance of the phosphine ligand trans to the hydrogen is 2.56 Å whereas the other two Os-P distances are 2.34 Å. The two phosphine ligands cis to the hydrido ligand appear to be bent towards it.

However the lengthening of the bond trans to the hydrogen is not always found. In the octahedral

compound $HMn(CO)_5$ (42) the Mn-C distances are all within the range 1.821-1.852 Å, the bond <u>trans</u> to the hydrogen being the shortest, however the experimental significance of this latter fact is doubtful. Again the manganese is slightly below the plane of the four equatorial carbonyls towards the fifth carbonyl.

In the compound $RH(CO)(PPh_3)_3$ discussed above, the rhodium carbon distance is 1.829 ± 0.028 Å which is about that expected from covalent radii considerations. Distances of 1.85Å and 1.77Å have been found in $Rh(CO)_2Cl_2$ (37).

<u>2. Solid state nuclear magnetic resonance</u>

Several attempts have been made to obtain metal-hydrogen distances from broad line proton magnetic resonance studies. These are based on Van Vleck's formula for the second moment (43).

A study of $H_2Fe(CO)_4$ assumed the line broadening to be due solely to the intramolecular dipolar interaction between the two hydrogens (44). An H-H distance of 1.88 ± 0.05 Å was deduced which established that both protons were attached to the iron rather than to the carbonyl groups. However a deduction of a metal hydrogen distance of 1.1 Å was uncertain owing to lack of knowledge of the H-$\hat{Fe}$-H angle and the possible effect

of intermolecular interaction on the line width.

Farrar et al. have studied manganese carbonyl hydride, $Mn(CO)_5H$, at low temperatures (45). All the structural parameters are known for this compound except for the position of the hydrogen (42). They assume the broadening due to intermolecular Mn-H interactions to be negligible and consider the effect of intramolecular Mn-H interaction and intermolecular H-H interaction. The x-ray study suggests that the hydrogens in two adjacent molecules are in contact in the crystal (42). A value of 1.28 ± 0.01 Å is found for the Mn-H distance.

Cobalt carbonyl hydride, $Co(CO)_4H$, has also been studied (46) although there is no alternative structural information on it. Thus all intermolecular broadening effects are neglected but additional information is available as the proton resonance shows fine structure. A value of 1.42 ± 0.05 Å is obtained for Co-H from the second moment whereas the value from the line shape is 1.2 ± 0.1 Å.

Sheldrick has criticized these deductions on the grounds that the quadrupolar effects of the manganese and cobalt nuclei are important (47). Taking these into account he obtains values of Mn-H = 1.44 ± 0.03 Å and Co-H 1.59 ± 0.04 Å. These values are more in

keeping with those found from diffraction studies and those expected for a normal metal-hydrogen covalent bond. However errors may still arise owing to neglect of zero-point vibration and torsion, deviation of the M-H vector from the quatization direction and neglect of chemical shift anisotropy.

The known metal hydrogen distances are summarized in Table III. They are indicative of a normal covalent bond between the metal and hydrogen.

Table III

Transition-metal hydrogen bond lengths

Metal	Compound	Length	Method	Ref.
Re	K_2ReH_9	1.68 ± 0.01 Å	Neutron diffraction	36
Rh	$RhH(CO)(PPh_3)_3$	1.60 ± 0.12 Å	x-ray diffraction	37
Mn	$HMn(CO)_5$	1.44 ± 0.03 Å	NMR.	45, 47
Co	$HCo(CO)_4$	1.59 ± 0.04 Å	NMR.	46, 47

D. Nuclear Magnetic Resonance Studies on Transition Metal Hydrides

Hydrido ligands attached to transition metals exhibit a characteristic high field shift in their high resolution H^1 nuclear magnetic resonance spectra (1,2). Resonances are found in the range 12-45 τ. This fact has been used as a diagnostic test for transition metal hydrides(11).

Two theories have been put forward to account for this phenomenon. Both are based on perturbation techniques. The first by Stevens, Kern and Lipscomb (48), attempts to minimize the contribution of the excited states of the molecule to the shielding by choice of a suitable gauge. The theory was applied to cobalt carbonylhydride, $Co(CO)_4H$; various wave functions were used for the diatomic portion Co-H, which gave values for the chemical shift ranging from 4.3-17.6 τ, the experimental value being 20.7 $\pm$ 2.0 τ. Lohr and Lipscomb (49) have also applied this method to other transition metal compounds using L.C.A.O - M.O. one electron wave functions. The main contribution is said to come from the hydrogen 1s electrons. The ligand must be negatively charged to give satisfactory shifts.

Buckingham and Stephens consider the d-electrons of the metal separately (50,51). They show terms in

the perturbation theory involving interaction of excited states which are neglected by Lipscomb et al. are significant for those compounds with partially filled d-orbitals. Contributions to the shift of the order of 30 p.p.m. are estimated for octahedral d^6 complexes (50) and 20 p.p.m. for square planar d^8 complexes (51). The former value is estimated for an M-H distance of 2 a.u.; a more realistic estimate would be around 3 a.u. (see above) and this would considerably reduce the "paramagnetic" contribution to the chemical shift.

These paramagnetic contributions would be expected to be a minimum for the closed shell compounds treated by Lipscomb et al. It is also worth noting that these compounds on the whole have smaller chemical shifts than other transition metal hydrides.

A detailed discussion of the observed trends among chemical shifts of hydrides and the application of these theories to them is given in reference (52).

Although various metal hydrogen coupling constants have been measured (see Table II) only one systematic study has been carried out (23). This was on the platinum hydrides trans-$Pt(MEt_3)_2HX$ where M = P or As and X is a series of anionic ligands. They will be referred to in future as the complexes(II). These

results will be discussed in Chapter IV.

The sign of the ^{195}Pt-H coupling constant in trans- $Pt(PEt_3)_2HCl$ has been determined by double irradiation (53). J Pt-H is found to be positive and J P-H negative.

E. Infrared Studies

Transition metal hydride complexes have characteristic metal-hydrogen stretching frequencies, ν M-H, in the region 1700-2280 (1,2). Because of the small mass of the proton the frequency is normally considered not to be coupled to any other in the molecule.

In a series of hydrides which only differ by the metal the stretching frequency increases on going down the group. This is normally taken as indicative of an increase in metal hydride bond strength, (2).

1. Effect of ligands

The metal hydrogen stretch is very sensitive to the other ligands attached to the metal. In the series of compounds trans-$Pt(MR_3)_2HX$ ν M-H decreases in the following order, (22).

$MR_3 = PPhEt_2 > PMe_3 \sim PEt_3 \sim PPr^n_3 > AsEt_3$

$X = NO_3 > Cl > Br > I > NO_2 > SCN > CN$

See Table IV for values.

This is the same order as for increasing trans-effect in square planar platinum compounds.

For the ruthenium and osmium compounds of the type trans-$RuHX(PP)_2$ when PP is a bidentate phosphorous ligand the order of decrease is (54, 55)

$PP = o\text{-}C_6H_4(PEt_2)_2 \sim CH_2(PPh_2)_2 > C_2H_4(PEt_2)_2 > C_2H_4(PMe_2)_2 > o\text{-}C_6H_4(AsMe_2)_2$

Table IV

Platinum hydride stretching frequencies in a series of complex hydrides of platinum II, $Pt(MR_3)_2HX$ (22)

X	NO_3	Cl	Br	I	$-NO_2$	-NCS	CN
MR_3							
PMe_3		2182*					
PEt_3	2242	2183	2178	2156	2150	2112	2041
P^nPr_3		2183					
$PPhEt_2$		2199		2179			
$AsEt_3$		2174	2167	2139		2108	

Values are for hexane solutions except when marked* when they are in chloroform solutions.

$X = I > Br > Cl > SCN > NO_2 > CN > H.$

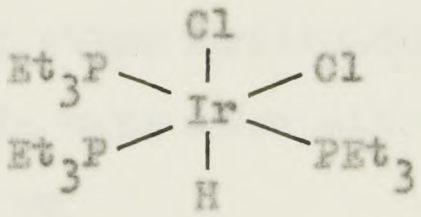
This has a gross similarity to the platinum series order but the order of the halogens and that of the thiocyanate and nitro group are reversed. There is no corresponding data on the trans-effect in these ruthenium and osmium complexes but in the compounds $[Co(NH_3)_5X]^{2+}$ the trans effect is found to increase in the order

$$I < Br < Cl$$

which is the reverse of the order found for the platinum series.

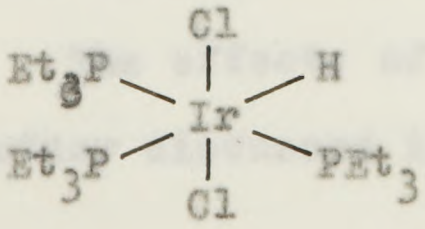
2. Solution Effects

Metal hydrogen stretches can also be very solvent sensitive depending on the configuration of the complex studied (56). For example with the iridium complex.

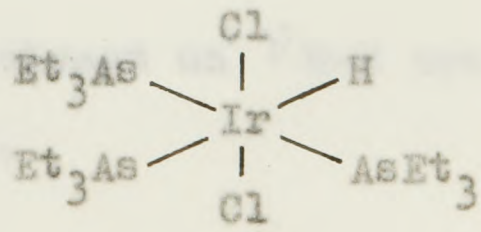


shifts in the range 40 cm^{-1} are found for the metal-hydrogen stretching frequency.

The lowest values are found in n-hexane and the highest in chloroform. When the hydrido ligand is trans to a phosphine or arsine group as in



or



ν M-H is virtually solvent insensitive but when trans to a chloride as in trans-$Pt(PEt_3)_2HCl$ shifts of up to 30-40 cm^{-1} occur, see Table V.

Table V

Dependence of ν Pt-H on solvent (56), for the complex trans- $Pt(PEt_3)_2HCl$

Solvent	ν Pt-H
$n\text{-}C_6H_{14}$	2183
CS_2	2191
Et_2O	2196
C_6H_6	2198
CCl_4	2192
Dioxan	2186
$MtCO_2Et$	2197
$MtNO_2$	2204
$PhNO_2$	2203
$CHCl_3$	2213

These solvent shifts have been attributed to preferential solvation of the halide trans to the hydrogen. The removal of charge from the chloride would further increase its ionization and result in an increase of metal hydrogen bond strength.

The effects of ligand and solvent on ν M-H are further discussed in Chapter III.

F. Related nuclear magnetic studies

Pidcock, Richards and Venanzi (57, 58) have studied the phosphorus P^{31} nuclear magnetic resonance of various platinum(II) and platinum(IV) phosphine complexes. They interpret the platinum-phosphorus coupling constants in terms of the Fermi contact interaction, make deductions as to the degree of s-character of the platinum-phosphorus bond and the nature of the trans-effect in platinum complexes. This work will be discussed more fully in Chapter IV.

Parshall has studied the F^{19} nuclear magnetic resonance spectra of m- and p-fluorophenyl platinum(II) complexes (59). He claims that the fluorine shielding parameters provide a criterion of the electronic characteristics of other metal-ligand bonds in the compounds. Again this work will be discussed more fully in Chapter IV.

CHAPTER II

trans-Hydridocarboxylatobis(triethylphosphine)platinum(II) complexes and their proton magnetic resonance spectra

In this chapter the preparation and characterization of the complexes prepared are discussed. Their ^1H nuclear magnetic resonance spectra are reported, and solvent effects and experimental errors are discussed. Discussion of the results is given in Chapter IV.

A. Characterization of the complexes

Complexes of the type trans-$Pt(PEt_3)_2HL$ (I), where L is a carboxylato ligand, have been prepared. A list of these compounds is given in Table VI. These previously unreported compounds were characterized by analysis (page 106), in the majority of cases by molecular weight determination (page 123) and by their infrared (Chapter III) and nuclear magnetic resonance spectra (Chapter II, section C).

In the case of complex I, L = o-ClC_6H_4COO, rather low analyses were obtained. This was possibly due to decomposition of the compound during the period (about two weeks) before the analyses were carried out. However a mass spectrum (see Appendix II) of a freshly prepared sample indicated that the complex I, L = o-ClC_6H_4COO, was present and all other data are consistent with this formulation.

Table VI

The series of complexes(I), trans-$Pt(PEt_3)_2HL$.

Compound $Pt(PEt_3)_2HL$ L =	Melting point °C	Colour of crystals
CF_3COO	-5	white
CCl_3COO	22	white
CCl_2HCOO	14	white
$CClH_2COO$	-5	white
$CH_2OPhCOO$	-5	white
C_6H_5COO	-	white
m-FC_6H_4COO	65	white
m-ClC_6H_4COO	88	white
p-ClC_6H_4COO	48	white
o-ClC_6H_4COO	50	white
m-BrC_6H_4COO	87	white
p-BrC_6H_4COO	63	white
o-BrC_6H_4COO	64	white
m-IC_6H_4COO	81	white
p -IC_6H_4COO	75	white
m-$NO_2C_6H_4COO$	72-74d.	white
p -$NO_2C_6H_4COO$	83-84d.	white
o-$NO_2C_6H_4COO$	73	pale yellow
m-$CH_3C_6H_4COO$	79	white
p-$CH_3C_6H_4COO$	45	white

Compound $Pt(PEt_3)_2HL$ L =	Melting point °C	Colour of crystals
p-$CH_3OC_6H_4COO$	81-82	white
p-CNC_6H_4COO	87	yellow
m-$NMe_2C_6H_4COO$	70	white
p-$NMe_2C_6H_4COO$	91	white
3,5-$(NO_2)_2C_6H_3COO$	85	pale yellow
2,5-$(NO_2)_2C_6H_3COO$	71	yellow
2,4,6-$(NO_2)_3C_6H_2COO$	82d.	yellow

d. - decomposed

The benzoato derivative L = C_6H_5COO was only characterized by its nuclear magnetic resonance spectra as it decomposed rather quickly.

The complexes were all prepared by treatment of the silver salt of the carboxylic acid with <u>trans</u>-$Pt(PEt_3)_2HCl$, for example.

<u>trans</u>-$Pt(PEt_3)_2HCl + CF_3COOAg = $ <u>trans</u>-$Pt(PEt_3)_2HCF_3COO + AgCl$

B. Properties of the complexes

The complexes(I) were all crystalline solids at room temperature with the exception of the substituted acetato derivatives, L = CF_3COO, CCl_3COO, $CHCl_2COO$, CH_2ClCOO, $CH_2OPhCOO$, which were colourless liquids. Melting points and colours are given in Table VI.

The pure complexes tended to decompose slowly at room temperature giving sticky yellow oils. The rate of decomposition appeared to vary from compound to compound; most samples needed recrystallization after several days. The compounds however could be preserved for several weeks at -5°C.

The compounds were very soluble in acetone, chloroform and methanol, and fairly soluble in benzene and ether. Their solubility in petrol varied as indicated in Chapter V (page 116).

They tended to decompose in solution and were most unstable in chloroform solution. The trichloracetato derivative was readily attacked by acetone.

C. Proton magnetic resonance spectra

1. Benzoato derivatives of complex I.

The spectrum of trans-hydrido o-chlorobenzoato-bis(triethylphosphine)platinum(II) is given in Figure I. This illustrates the five regions of absorption, A-E, characteristic of these benzoato derivatives. Band A is due to the aromatic ^{1}H nuclei of the benzoato ligand, band B is caused by the ^{1}H nuclei of the triethylphosphine ligand and the triplets C, D and E by the platinum-hydrido ^{1}H nuclei. Bands arising from substituents on the aromatic ring were observed where they were expected.

2. Acetato derivatives

The spectrum of trans-hydridotrifluoracetato-bis(triethylphosphine)platinum(II) is given in Figure II. Only the absorption regions B-E are present in this spectrum. Other substituted acetato derivatives show absorptions characteristic of the substituted acetato ligand.

3. Solvents

All the complexes(I) were measured using acetone solutions which permitted observation of regions A, C, D and E. Eight of the compounds were also measured using benzene solutions and chloroform solutions which allowed regions B, C, D and E to be studied. The

Figure I. ^1H nuclear magnetic resonance spectra of <u>trans</u> -$Pt(PEt_3)_2$ Ho -Cl C_6H_4COO

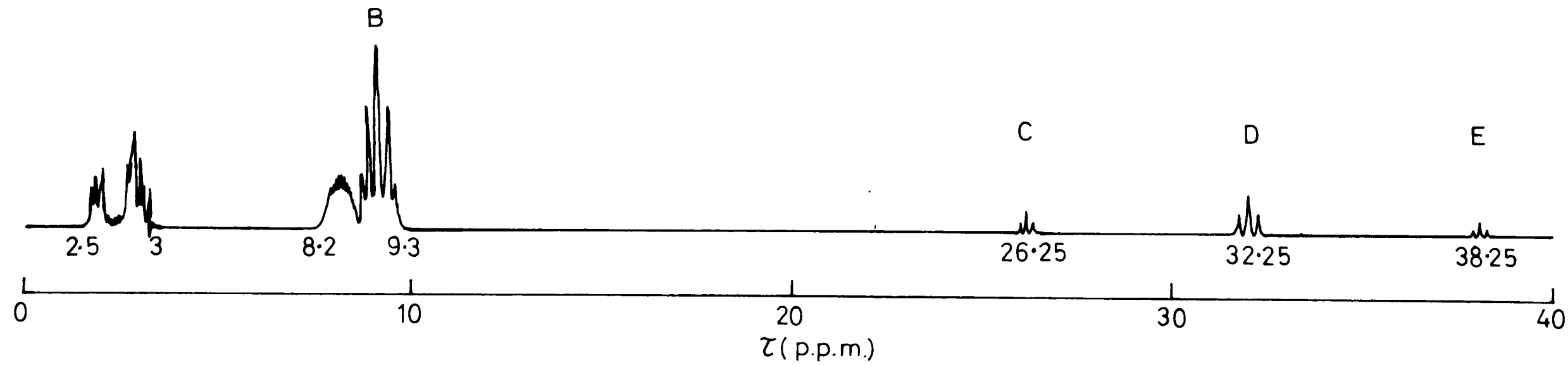
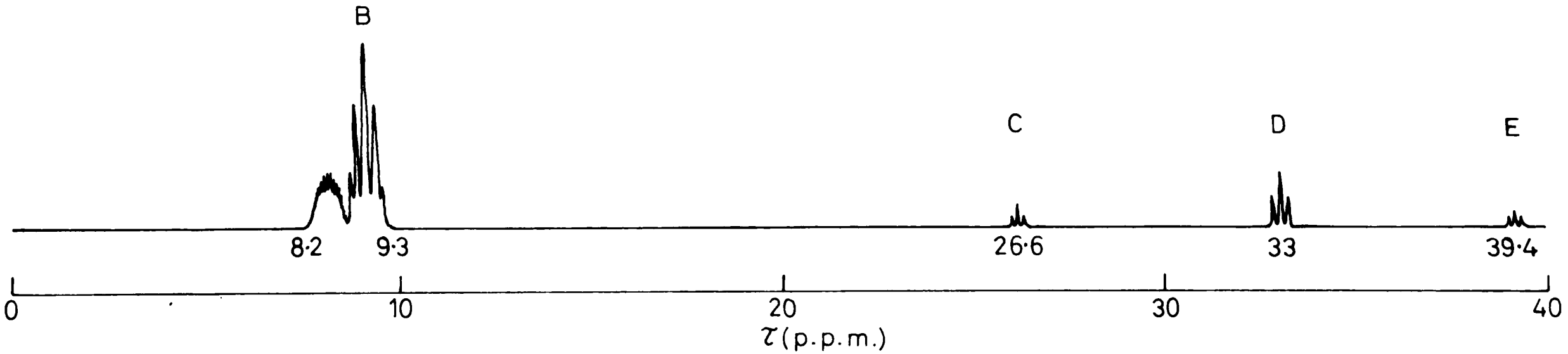


Figure II. ^1H nuclear magnetic resonance spectra of <u>trans</u> - $Pt(PEt_3)_2 H CF_3COO$



five benzoato compounds which were sufficiently soluble in cyclohexane were also studied using this solvent which permitted observation of regions A, C, D and E.

4. Analysis of the spectra

a) Hydrido resonance

The hydrido resonance showed, a large chemical shift and occured in the region 31-34 τ. The ^{1}H nuclei attached to platinum isotopes of zero spin gave the resonance at D which has a symmetrical triplet structure with peak intensities in the ratio 1:2:1 caused by the two equivalent ^{31}P nuclei of spin $\frac{1}{2}$ (100% abundance). This confirms the proposed "trans" structure of the complexes. The resonances at C and E are due to the hydrido signal being split by the ^{195}Pt isotope of spin $\frac{1}{2}$ (33.7% abundance). They also exhibit the triplet structure due to the two phosphorus nuclei. The intensity ratio C:D:E is about 1:4:1 as is expected from the relative abundance of the platinum isotopes. A splitting diagram is given in Figure III.

The chemical shift of the hydrido ligand was given by the position of central peak of D. The coupling constant J_{Pt-H} was taken as the separation of the central peaks of C and E. Twice the deviation of the centre of D from the mean of these two positions was taken as an

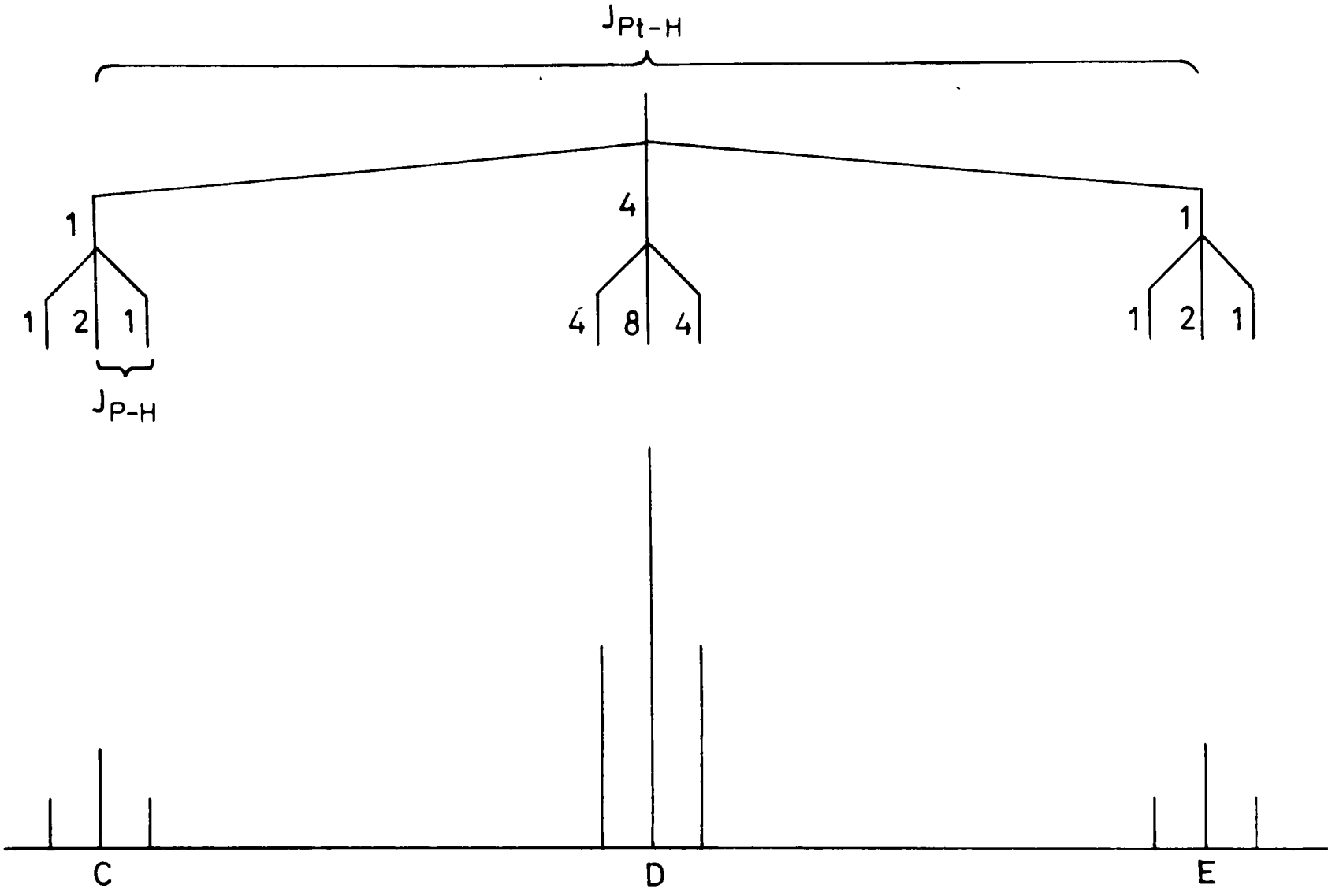


Figure III. Splitting diagram for ^1H resonance

estimate of the error in the determination of J_{Pt-H}. The error in the vast majority of cases was less than 1 cps (i.e. less than 0.1%).

The coupling constant J_{P-H} was taken as an average of the separations of the two outer peaks of D and the central peak. Again an error could be estimated. The error was never greater than 0.55 cps. and was on average less than that for J_{Pt-H} owing to the greater intensity of the D peaks.

The chemical shifts and coupling constants of the hydrido ligand in the various compounds dissolved in acetone are given in Table VII.

Effect of concentration

The compound trans-hydrido o-chlorobenzoatobis(triethylphosphine)platinum(II) was studied at five concentrations and J_{Pt-H}, J_{P-H} and τ_{Pt-H} were found to be constant within experimental error (Table VIII). The peak positions C and D were measured in this instance by the locking on NMR control technique.

Effect of solvent

Five of the compounds(I) were measured in chloroform, acetone, benzene or cyclohexane. Three more were measured in chloroform, acetone and benzene. The values found for J_{Pt-H}, J_{P-H} and τ_{Pt-H} are given in Table IX.

Table VII

Nuclear magnetic resonance data on the hydrido ligand

Compound *trans*-$Pt(PEt_3)_2HL$ where L =	J_{Pt-H} in cps.	τ_{Pt-H} in ppm.	J_{P-H} in cps.
$PhOCH_2COO$	1202.9 ± 0.5	32.342	15.55 ± 0.15
CH_2ClCOO	1216.7 ± 0.5	32.483	15.8 ± 0.2
$CHCl_2COO$	1255.8 ± 0.0	32.765	15.3 ± 0.1
CF_3COO	1295.5 ± 0.7	33.013	15.35 ± 0.05
$p\text{-}NMe_2C_6H_4COO$	1160.9 ± 0.5	31.745	15.75 ± 0.15
$m\text{-}NMe_2C_6H_4COO$	1172.3 ± 1.1	31.857	15.71 ± 0.0
$p\text{-}OMeC_6H_4COO$	1172.0 ± 0.2	31.869	15.7 ± 0.1
$p\text{-}CH_3C_6H_4COO$	1176.2 ± 0.6	31.897	15.55 ± 0.35
$m\text{-}CH_3C_6H_4COO$	1176.5 ± 0.3	31.899	15.4 ± 0.4
C_6H_5COO	1179.1 ± 0.5	31.918	15.65 ± 0.05
$p\text{-}ClC_6H_4COO$	1189.1 ± 0.5	32.036	15.6 ± 0.3
$p\text{-}BrC_6H_4COO$	1191.3 ± 0.2	32.043	15.8 ± 0.15
$p\text{-}IC_6H_4COO$	1193.2 ± 0.4	32.061	15.45 ± 0.15
$m\text{-}FC_6H_4COO$	1193.1 ± 0.1	32.077	15.55 ± 0.05
$m\text{-}IC_6H_4COO$	1197.1 ± 0.3	32.123	15.7 ± 0.0
$m\text{-}ClC_6H_4COO$	1195.5 ± 0.5	32.095	15.5 ± 0.3
$m\text{-}BrC_6H_4COO$	1196.2 ± 0.6	32.105	15.95 ± 0.05
$p\text{-}CNC_6H_4COO$	1203.9 ± 0.7	32.170	15.65 ± 0.05
$m\text{-}NO_2C_6H_4COO$	1210.6 ± 0.2	32.226	15.75 ± 0.1
$p\text{-}NO_2C_6H_4COO$	1209.6 ± 0.4	32.200	15.8 ± 0.0

Compound <u>trans</u>-$Pt(PEt_3)_2HL$ where L =	J_{Pt-H} in cps.	τ_{Pt-H} in ppm.	J_{P-H} in cps.
o-ClC_6H_4COO	1204.0 ± 0.0	32.226	15.65 ± 0.05
o-BrC_6H_4COO	1205.2 ± 0.4	32.257	15.9 ± 0.2
3,5-$(NO_2)_2C_6H_3COO$	1236.8 ± 0.4	32.446	15.6 ± 0.1
o-$NO_2C_6H_4COO$	1226.2 ± 0.8	32.515	15.55 ± 0.5
2,5-$(NO_2)_2C_6H_3COO$	1255.5 ± 0.1	32.715	15.35 ± 0.15
2,4,6-$(NO_2)_3C_6H_2COO$	1298.3 ± 0.3	33.671	15.7 ± 0.0

Table VIII

Variation of hydrido resonance with concentration (given by 0.5 g. in y ml.)

y ml.	0.5	0.6	0.7	0.8	0.9
J_{Pt-H}	1202.4	1203.4	1202.6	1202.8	1203.0
τ_{Pt-H}	32.236	32.227	32.229	32.228	32.230
J_{P-H}	15.75	15.55	15.45	15.75	15.5

The largest apparent errors in the determination of the peak positions were for the chloroform solutions. Also the lines appeared to broaden in these solutions. Transition metal hydrides are notoriously unstable in chlorinated hydrocarbons but platinum hydrides less so than many.

As can be seen from Table IX both the chemical shift of the hydrido ligand and the platinum hydrogen coupling constant are sensitive to the nature of the solvent. The relative sizes are found to be

J_{Pt-H} $CHCl_3 > (CH_3)_2CO > C_6H_6 > C_6H_{12}$

τ_{Pt-H} $CHCl_3 > (CH_3)_2CO > C_6H_{12} > C_6H_6$

It is difficult to detect a trend in the phosphorus hydrogen coupling constant as the differences due to the solvent effect were of the order of the experimental error, but in general it appears that J_{P-H} in chloroform solution is less than in the other solvents.

Table IX

Nuclear magnetic resonance data on the hydrido ligand in various solvents

Compound $Pt(PEt_3)_2HL$ where L=	J_{Pt-H} cps.	Chloroform τ_{Pt-H} p.p.m.	J_{P-H} cps.
$p\text{-}MeOC_6H_4COO$	1192.6 ± 1.12	32.023	15.05 ± 0.5
$p\text{-}CH_3C_6H_4COO$	1195.7 ± 0.5	32.045	15.3 ± 0.3
$m\text{-}CH_3C_6H_4COO$	1198.7 ± 1.1	32.070	15.0 ± 0.2
$p\text{-}BrC_6H_4COO$	1208.3 ± 0.7	32.174	15.4 ± 0.4
$m\text{-}FC_6H_4COO$	1207.3 ± 0.3	32.175	15.0 ± 0.2
$o\text{-}ClC_6H_4COO$	1225.6 ± 0.8	32.411	15.3 ± 0.2
$o\text{-}BrC_6H_4COO$	1224.2 ± 1.4	32.415	15.45 ± 0.55
$o\text{-}NO_2C_6H_4COO$	1245.2 ± 0.2	32.723	15.4 ± 0.1
		Acetone	
$p\text{-}MeOC_6H_4COO$	1172.0 ± 0.2	31.869	15.7 ± 0.1
$p\text{-}CH_3C_6H_4COO$	1176.2 ± 0.6	31.897	15.55 ± 0.35
$m\text{-}CH_3C_6H_4COO$	1176.5 ± 0.3	31.899	15.4 ± 0.4
$p\text{-}BrC_6H_4COO$	1191.3 ± 0.2	32.043	15.80 ± 0.15
$m\text{-}FC_6H_4COO$	1193.1 ± 0.1	32.077	15.55 ± 0.05
$o\text{-}ClC_6H_4COO$	1204.0 ± 0.0	32.226	15.65 ± 0.05
$o\text{-}BrC_6H_4COO$	1205.2 ± 0.4	32.257	15.9 ± 0.2
$o\text{-}NO_2C_6H_4COO$	1226.2 ± 0.8	32.515	15.55 ± 0.5

Compound $Pt(PEt_3)_2HL$ where $^3L^2$=	J_{Pt-H} cps.	Benzene τ_{Pt-H} ppm.	J_{P-H} cps.
p-$MeOC_6H_4COO$	1168.6 ± 0.4	31.528	15.75 ± 0.05
p-$CH_3C_6H_4COO$	1170.0 ± 0.4	31.544	15.75 ± 0.15
m-$CH_3C_6H_4COO$	1169.6 ± 1.2	31.494	15.9 ± 0.1
p-BrC_6H_4COO	1181.7 ± 1.1	31.740	15.95 ± 0.55
m-FC_6H_4COO	1183.4 ± 0.4	31.776	15.55 ± 0.35
o-ClC_6H_4COO	1198.5 ± 0.1	31.876	15.65 ± 0.25
o-BrC_6H_4COO	1196.7 ± 0.5	31.873	15.65 ± 0.05
o-$NO_2C_6H_4COO$	1220.7 ± 0.9	32.224	15.5 ± 0.3
		Cyclohexane	
p-$MeOC_6H_4COO$	–	–	–
p-$CH_3C_6H_4COO$	1158.7 ± 0.1	31.706	15.75 ± 0.15
m-$CH_3C_6H_4COO$	1155.0 ± 0.4	31.675	15.6 ± 0.2
p-BrC_6H_4COO	1174.8 ± 0.8	31.89	15.85 ± 0.55
m-FC_6H_4COO	1174.5 ± 0.3	31.899	15.7 ± 0.5
o-ClC_6H_4COO	1186.7 ±0.1	32.061	15.85 ± 0.25
o-BrC_6H_4COO	–	–	–
o-$NO_2C_6H_4COO$	–	–	–

In general the relative orders of the chemical shifts and coupling constants of the hydrido ligand for the series of compound were the same within experimental error irrespective of solvent. Exceptions were found to this rule: for example the ortho-chloro and ortho-bromo benzoato derivatives were in a reverse order in acetone to their order in benzene and chloroform. However in all three solvents their coupling constants differ by less than 2 cps. and their chemical shifts by less than 0.03 p.p.m.

In conclusion it can be considered legitimate to draw deductions from the relative sizes of the coupling constant and chemical shift of the hydrido ligand in the series of complexes under identical solvent conditions.

b) Triethylphosphine resonance

This is clearly separated into two regions one due to the methyl resonance and the other to the methylene resonance.

The methyl resonance has the appearance of a quintuplet of intensities 1:4:6:4:1. The methyl resonance is split into a triplet by the methylene protons which is further split by the two phosphorus nuclei. These two trans-^{31}P nuclei are so strongly coupled that they behave as a system of 75% spin 1 and 25% spin 0 (60). Thus the methyl protons are

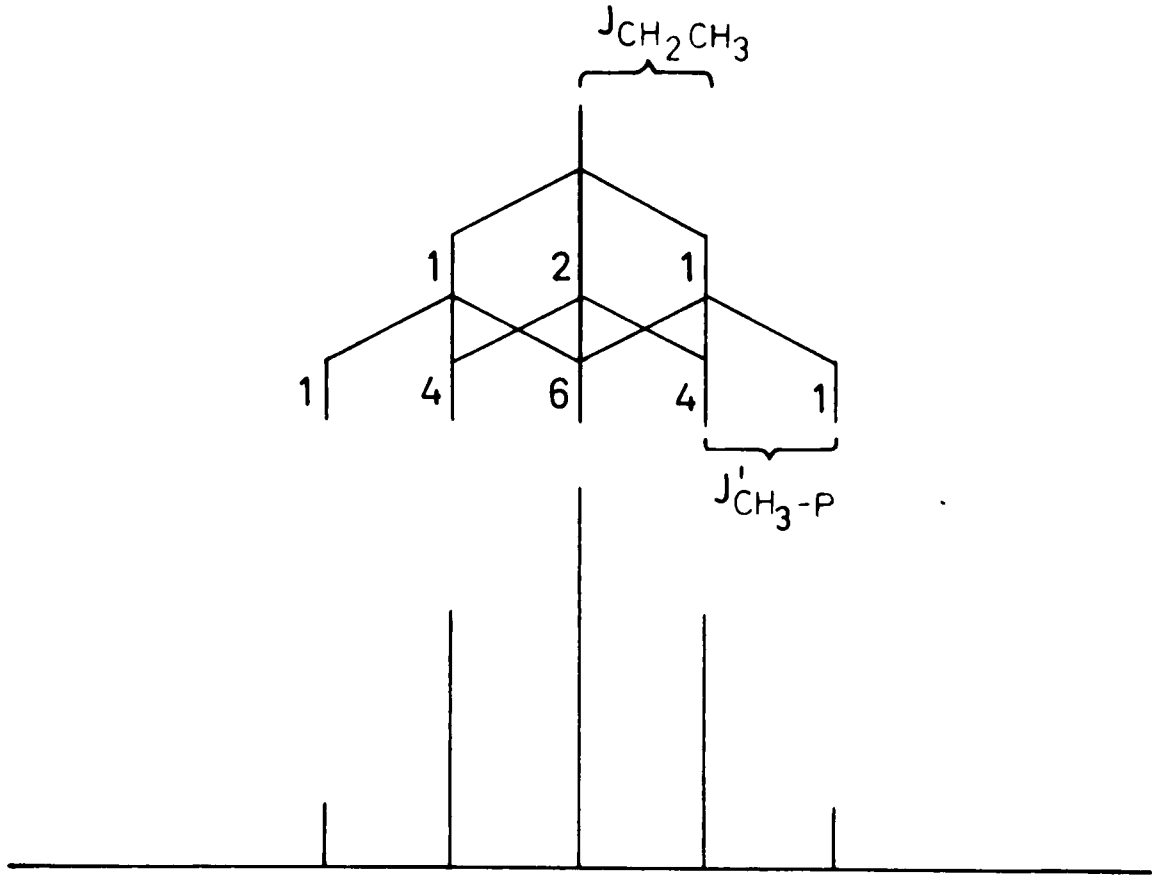


Figure IV. Splitting diagram for methyl resonances

effectively coupled to both phosphorus nuclei, and the three peaks of the triplet are further split into triplets of intensity ratios 1:2:1. The coupling constant given by these triplets is an average of those between the methyl protons and the two ^{31}P nuclei. As a quintuplet is normally observed it is apparent that some of the peaks of these three triplets coincide as shown in Figure IV. This interpretation rationalizes the observed intensity ratios. If $J\,CH_2\text{-}CH_3 = J'\,CH_3P$ ($J'\,CH_3\text{-}P$ being the average of the coupling with the two ^{31}P nuclei), the peaks would be exactly superimposed. The chemical shift of the methyl peak, $J\,CH_2\text{-}CH_3$, and $J'\,CH_3\text{-}P$ are recorded in Table X. We have taken the two coupling constants to be equal but there is likely to be an error of 0.5 c.p.s. in their determination, hence they may differ up to this amount.

The methylene resonance is more complex than the methyl resonance because in addition to coupling with the methyl protons and virtual coupling with both phosphorus nuclei it appears also to interact with the platinum nucleus. Thus the peak is largely unresolved. The positions of the methylene resonances are reported in Table X.

In addition those compounds with methyl substituents

Table X

Nuclear magnetic resonance data on the triethylphosphine groups.

Compound $Pt(PEt_3)_2HL$ where L^2 =	Chloroform τ CH_3 p.p.m.	Chloroform $J_{CH_2-CH_3}$ = $J_{^2CH_3-^3P}$ c.p.s.	Benzene τ CH_3 p.p.m.	Benzene $J_{CH_2-CH_3}$ = $J_{^2CH_3-^3P}$ c.p.s.
p-$MeOC_6H_4COO$	8.875	7.7	8.979	7.4
p-$CH_3C_6H_4COO$	8.897	7.8	8.982	7.7
m-$CH_3C_6H_4COO$	8.878	7.5	8.978	7.7
p-BrC_6H_4COO	8.870	7.8	9.009	7.5
m-FC_6H_4COO	8.862	7.5	9.018	7.5
o-ClC_6H_4COO	8.844	7.9	8.979	7.7
o-BrC_6H_4COO	8.858	7.5	8.967	7.5
o-$NO_2C_6H_4COO$	8.869	7.5	8.977	7.5

Compound $Pt(PEt_3)_2HL$ where L^2 =	τ CH_2	Other shifts observed	τ CH_2	Other shifts observed
p-$MeOC_6H_4COO$	8.202	6.207	8.372	6.626
p-$CH_3C_6H_4COO$	8.225	7.658	8.377	7.830
m-$CH_3C_6H_4COO$	8.212	7.640	8.384	7.761
p-BrC_6H_4COO	8.201		8.404	
m-FC_6H_4COO	8.194		8.320	
o-ClC_6H_4COO	8.148		8.360	
o-BrC_6H_4COO	8.114		8.337	
o-$NO_2C_6H_4COO$	8.182		8.351	

on the benzene ring have had the position of these single resonances recorded in Table X as they were only observed in benzene or chloroform solutions.

c) Aromatic protons

These tend to show rather complex resonances. The para-substituted benzoic acids have four main peaks in their spectrum the positions of which are given in Table XI. However the para-iodo and para-nitro derivatives show only one strong peak. The position of these is also given in Table XI.

The range in which resonance occurs for the aromatic protons for the rest of the compounds are given in Table XII.

Table XI

Nuclear magnetic resonance data on aromatic protons

- para-substituted derivatives

Compound $Pt(PEt_3)_2HL$ where L =	Peak positions of four main peaks (τ)				Average sepn.	
$p\text{-}NMe_2C_6H_4COO$	2.115	2.192	3.354	3.435	0.0780	Acetone
$p\text{-}OMeC_6H_4COO$	2.024	2.104	3.135	3.224	0.0845	
$p\text{-}MeC_6H_4COO$	2.061	2.157	2.858	2.952	0.0950	
$p\text{-}CNC_6H_4COO$	1.825	1.910	2.245	2.328	0.0840	
$p\text{-}ClC_6H_4COO$	1.984	2.060	2.650	2.728	0.0770	
$p\text{-}BrC_6H_4COO$	2.038	2.111	2.495	2.567	0.0725	
$p\text{-}IC_6H_4COO$	Complex peak at 2.259					
$p\text{-}NO_2C_6H_4COO$	peak at 1.906					
$p\text{-}CH_3C_6H_4COO$	2.117	2.179	2.929	3.002	0.0675	Cyclohexane
$p\text{-}BrC_6H_4COO$	2.063	2.153	2.606	2.686	0.075	

Table XII

Nuclear magnetic resonance data on aromatic protons - other derivatives.

Compound $Pt(PEt_3)_2HL$ where L ≅	Range of peaks τ (ppm.) Acetone	Range of peaks τ (ppm.) Cyclohexane
m-$NMe_2C_6H_4COO$	2.5 - 3.35	
m-$CH_3C_6H_4COO$	2.1 - 2.9	2.1 - 3.1
m-FC_6H_4COO	2.1 - 2.95	2.1 - 3.25
m-ClC_6H_4COO	1.9 - 2.7	
m-BrC_6H_4COO	1.8 - 2.85	
m-IC_6H_4COO	1.60 - 2.95	
m-$NO_2C_6H_4COO$	1.15 - 2.45	
o-ClC_6H_4COO	2.35 - 2.7	2.25 - 3.05
o-BrC_6H_4COO	2.3 - 3.0	
o-$NO_2C_6H_4COO$	2.0 - 2.6	
C_6H_5COO	1.95 - 2.85	
2,5-$(NO_2)_2C_6H_3COO$	1.25 - 2.2	
3,5-$(NO_2)_2C_6H_3COO$	0.85 - 1.15	
2,4,6-$(NO_2)_3C_6H_2COO$	Single peak at 1.169	

D. ^2H nuclear magnetic resonance spectra of trans-$Pt(PEt_3)_2DCl$

The ^2H nuclear magnetic resonance spectrum of a saturated solution of trans-$Pt(PEt_3)_2DCl$ in tetrahydrofuran was determined using deuteroacetone as an internal standard. The chemical shift and the platinum-deuterium coupling constant of the deuterido ligand were determined. Experimental details are given in Chapter V. The experiment was repeated using a less concentrated solution at a higher operating frequency to check the value obtained for the chemical shift.

The ^1H nuclear magnetic resonance spectrum of trans-$Pt(PEt_3)_2HCl$ was run under identical solvent conditions for the purposes of comparison.

J_{Pt-D} was found to be 194 $\pm$ 2 c.p.s. which corresponds to a J_{Pt-H} of 1264 $\pm$ 13 c.p.s. From the ^1H nuclear magnetic resonance experiment a value of 1272 c.p.s. for J_{Pt-H} was obtained.

The chemical shift with respect to deuteroacetone was found to be 19.1 $\pm$ 0.3 p.p.m. at an operating frequency of 7.5 Mc/s and 19.2 $\pm$ 1 p.p.m. at an operating frequency of 9.25 Mc/s. The corresponding value from the ^1H magnetic resonance experiment was 19.37 p.p.m.

CHAPTER III

Infrared Studies

The nujol mull spectra of the complexes(I) in the range 4000-625 cm^{-1} are given in Appendix III. (See Chapter V for experimental detail). The spectra of trans-$Pt(PEt_3)_2HCl$ is also given for the purposes of comparison.

Most of the complexes have also been studied in the mull form in the region 625-200 cm^{-1}. These spectra are also recorded in Appendix III.

A. Assignment of mull spectra

Assignable characteristic frequencies are listed in Table XIII. Reasons for the assignments are given below.

1. Platinum hydrogen stretch

Platinum hydrogen stretches have been found in the regio n 1950-2270 cm^{-1}, (see Table II, Chapter II). In the case of trans-$Pt(PEt_3)_2HCN$ for example, this assignment has been confirmed by study of the deuterium analogue (21). All the complexes(I) showed a single medium to strong band in the region 2210-2270 cm^{-1}. This band was therefore assigned as ν Pt-H.

2. Platinum-hydrogen deformation frequency

This is less easy to identify than ν Pt-H as it generally occurs in the region 810-850 cm^{-1} (see Table II,

Table XIII

Characteristic frequencies assigned from the mull spectra.

L =	ν_{Pt-H}	δ_{Pt-H}	$\nu_{as}COO$	$\nu_{s}COO$	ν_{Pt-P}	ν_{Pt-O}
p-$NO_2C_6H_4COO$	2233	820	1633	1325	-	287
p-CNC_6H_4COO	2230	835	1631	1348	-	-
p-IC_6H_4COO	2214	832	1631	1352	-	-
p-BrC_6H_4COO	2238	834	1605	1340	403	271
p-ClC_6H_4COO	2260	830	1605	1335	-	285
p-$CH_3C_6H_4COO$	2215	844	1618	1335	407	283
p-$CH_3OC_6H_4COO$	2235	849	1620	1339	403	286
p-$(CH_3)_2NC_6H_4COO$	2220	834	1603	1350	-	-
m-$NO_2C_6H_4COO$	2244	825	1614	1330	-	282
m-IC_6H_4COO	2240	845	1620	1335	-	290
m-BrC_6H_4COO	2250	834	1622	1335	402	275
m-ClC_6H_4COO	2255	835	1630	1335	408	275
m-FC_6H_4COO	2226	832	1631	1340	404	284
m-$CH_3C_6H_4COO$	2244	842	1621	1335	403	-
m-$(CH_3)_2NC_6H_4COO$	2231	842	1621	1340	-	-
3,5-$(NO_2)_2C_6H_3COO$	2230	843	1643	1345	-	282
o-$NO_2C_6H_4COO$	2250	827	1630	1343	406	290
o-BrC_6H_4COO	2220	834	1631	1348	-	288
o-ClC_6H_4COO	2244	831	1615	1349	-	283
2,5-$(NO_2)_2C_6H_3COO$	2265	832	1643	1345	-	286
2,4,6-$(NO_2)_3C_6H_2COO$	2260	825	1658	1340	-	282
CF_3COO	2255	815	1675	-	-	280

L =	ν_{Pt-H}	δ_{Pt-H}	$\nu_{as}COO$	$\nu_{s}COO$	ν_{Pt-P}	ν_{Pt-O}
$CHCl_2COO$	2248	819	1661	1336	-	-
CH_2ClCOO	2235	819	1601	-	-	-
$CH_2OPhCOO$	2240	823	1621	1310	-	-

Chapter I) where it may well be masked by other frequencies. Again, in the compound trans-$Pt(PEt_3)_2HCN$ the position of δ Pt-H has been ascertained at 826 cm^{-1} by a study of the deuterium analogue. The peaks in the region 815-840 of the complexes(I) are thus assigned to δ M-H. (Some of the complexes show another peak in this region, with others the peak has a shoulder. However by comparison with other similar spectra it was possible to make an assignment.) The platinum hydrogen deformation frequency is apparently less sensitive to variation of the ligand L than the platinum hydrogen stretching frequency.

3. Carboxylate stretching frequencies

The carboxylate group when bonded to a metal exhibit two strong characteristic stretching frequencies, the symmetric $\nu_s COO$ and antisymmetric $\nu_{as} COO$ stretches (34). It has been established that for a series of salts where the carboxylate group is σ-bonded to the metal through one oxygen only that in general $\nu_{as} COO$ will increase and $\nu_s COO$ will decrease as the M-O bond becomes stronger. Thus the separation between the two frequencies should increase with increasing strength of the metal ligand bond. For a chelate complex a separation of the two frequencies of the order of that in the free carboxylate ion would be expressed e.g. for

the acetate ion the separation is 164 cm^{-1}. For a series of palladium complexes <u>trans-</u> $Pd(OCOR)_2L_2$ (61) the antisymmetric stretch was found in the region 1600-1690 cm^{-1} and the symmetric stretch in the region 1310-1400 cm^{-1}, the separation of the two peaks varying between 210 and 310 $cm.^{-1}$

All the complexes(I) have a strong band in the region 1600-1680 cm^{-1}. Some of the bands have shoulders which may be due to C=C skeletal in plane vibrations which occur in this region. However the intensity of the COO asymmetric stretch makes its assignment unambiguous. The benzoato complexes have a very strong band in the regio n 1320-1350 cm^{-1}, which is absent in the spectra of <u>trans-</u> $Pt(PEt_3)_2HCl$. This was assigned to $\nu_s COO$. The separation of the two COO stretches varied from 253 cm^{-1} to 318 cm^{-1}. This was a strong indication that carboxylate group was bonded through only one oxygen and the platinum(II) complexes were square planar, as is usual.

With the substituted acetato complexes, the symmetric COO stretch was most difficult to assign.

<u>4. Platinum-phosphorous stretch.</u>

In compounds of the type <u>trans-</u> $PtXY(PEt_3)_2$, ν_{Pt-P} has been found in the range 418-406 cm^{-1} (62, 63). For

example in trans- $Pt(PEt_3)_2HCl$ the band at 406.4 cm^{-1} is assigned to this stretch. The spectra of the complexes(I)show a profusion of bands and thus make assignment very chancy. However in some cases it has been possible to distinguish a band in this region which is missing in the free ligand spectra and consequently assigned to a ν Pt-P.

5. Platinum oxygen stretch

Very few definite assignments of metal-oxygen stretching frequencies have been made (64). However they have generally been assigned in the range 300-570 cm^{-1}. The platinum-oxygen stretch in the complexes(I) would be expected to be at the lower end of this range owing to the probable weak nature of the bond when trans- to hydrogen: (Pt-Cl stretches come in the range 343-269 cm^{-1} with trans- $Pt(PEt_3)_2HCl$ having ν Pt-Cl = 269.3 cm^{-1} (65)). For similar reasons the band would be expected to be broad.

In the far infrared spectra of the complexes(I) a weak broad band (width $\sim$ 20 cm^{-1}) is found in the region of 280 cm^{-1}. This region is generally clear in the ligand spectra. Therefore this band is very tentatively assigned to the platinum oxygen stretch as it can be detected in practically all the complexes.

6. Discussion of trends in mull spectra

As the error in peak position in the mull spectra

is likely to be as much as $\pm$ 10 cm^{-1}, it was concluded that it is impossible to draw any firm deductions from the variation in stretching frequency from complex to complex. Thus, as the variation of the platinum hydrogen stretching frequency with L is of particular interest it was decided to study the solution spectra of these complexes on a machine where the scale could be expanded to give maximum accuracy in determining the peak position. It was hoped that environmental effects would be more constant in solution than in a mull.

B. Solution spectra of the complexes(I)

The solution spectra of the complexes(I) were measured in acetone. Some of the complexes were also measured in chloroform, benzene or cyclohexane. Only the region 2300-2150 cm^{-1} was studied in order to determine the position of the platinum-hydrogen stretch. The results are given in Table XIV together with the pK_as of the acids LH (66). Experimental details are given in Chapter V.

1. Effect of concentration on ν_{Pt-H}

The spectrum of trans- $Pt(PEt_3)_2H$-o-$NO_2C_6H_4COO$ in chloroform was measured at four different concentrations. The results are given in Table XV. The peak position was constant within experimental error.

Table XV

Effect of concentration on ν_{Pt-H}

Concentration g. in 2 ml.	ν_{Pt-H}
0.0162	2244
0.0419	2243
0.0615	2246
0.0925	2244

Table XIV

Solution infrared spectra of the complexes(I).

Compound L =	pK_a of HL (66)	ν_{Pt-H} acetone	ν_{Pt-H} chloro-form	ν_{Pt-H} benzene	ν_{Pt-H} cyclo-hexane
$p\text{-}NO_2C_6H_4COO$	3.425	2235			
$p\text{-}IC_6H_4COO$	3.93	2231			
$p\text{-}BrC_6H_4COO$	3.971	2233	2233	2225	2220
$p\text{-}ClC_6H_4COO$	3.977	2231			
$p\text{-}CH_3C_6H_4COO$	4.373	2226	2229		2216
$p\text{-}CH_3OC_6H_4COO$	4.471	2226	2228	2220	
$p\text{-}(CH_3)_2NC_6H_4COO$	4.853	2222			
$m\text{-}NO_2C_6H_4COO$	3.493	2235			
$m\text{-}IC_6H_4COO$	3.851	2232			
$m\text{-}ClC_6H_4COO$	3.830	2232			
$m\text{-}FC_6H_4COO$	3.865	2232	2236	2228	2223
$m\text{-}CH_3C_6H_4COO$	4.272	2225	2232	2222	2218
$m\text{-}(CH_3)_2NC_6H_4COO$	4.744	2224			
$o\text{-}NO_2C_6H_4COO$	2.173	2241	2249	2238	
$o\text{-}BrC_6H_4COO$	2.824	2234	2241	2231	
$o\text{-}ClC_6H_4COO$	2.934	2234	2237	2230	2225
$3,5\text{-}(NO_2)_2C_6H_3COO$	2.824	2243			
$2,5\text{-}(NO_2)_2C_6H_3COO$	1.622	2247			
$2,4,6\text{-}(NO_2)_3C_6H_2CCO$	0.654	2263			
CF_3COO	0.23	2258			
$CHCl_2COO$	1.25	2248			
CH_2ClCOO	2.865	2237			
$CH_2OPhCOO$	3.171	2234			

2. Change of spectra with time

It was found that if the ν Pt-H peak was measured over a period of about two hours, the peak shifted about 20 cm^{-1} to lower frequencies. This occurred for a wide variety of the complexes(I) in all four solvents. That just two peak positions were involved was demonstrated by the isobestic curves obtained. The spectra of the compound <u>trans-</u> $Pt(PEt_3)_2H$ $p\text{-}CH_3C_6H_9COO$ run at intervals over a period of two hours is given in Figure V.

In order to ascertain the cause of this shift a solution of the o-chlorobenzoato derivative was made up and the following experiments performed.

a) A portion of the solution was taken and an infrared spectrum was run until the peak reached its final value.

b) Then a second portion of the solution was taken and the spectrum run. The peak was found to be in the initial position.

c) "Analar" sodium chloride was added to the remaining solution. The infrared spectrum of a third portion was run after one hour. The peak was again found to be at the initial position.

d) The solution (c) was left overnight and the spectrum of a fourth portion again showed the peak at the initial position.

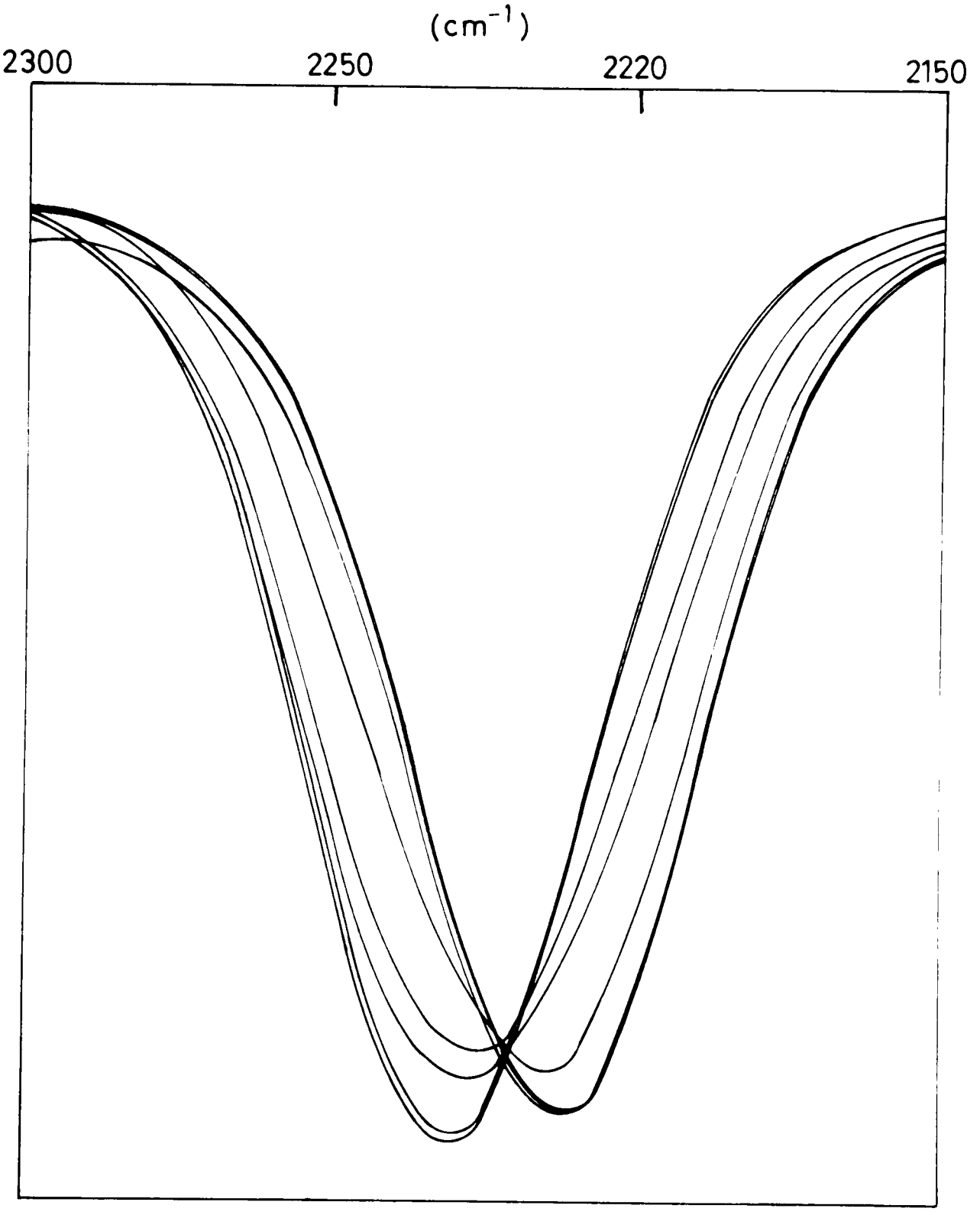


Figure V. Solution infrared spectra of trans-$Pt(PEt_3)_2Hp\text{-}CH_3C_6H_4COO$ over a period of two hours

e) Mercury was added to solution (c) as it is present in the seal of the solution cell. This too failed to shift the peak.

f) The solution containing sodium chloride and mercury was left to stand in the infrared beam for two hours. A portion of this solution was then run, the Pt-H stretch appeared to have decreased in intensity but not to have shifted.

g) Consecutively with experiment (a), the molecular weight was studied as a function of time. No significant change in molecular weight was observed.

It was concluded that the change took place uniquely within the infrared solution cell. If the solution was left in the cell for some time a film was observed to have formed on the surface of the sodium chloride plates. It was therefore assumed that no isomerization of the complex was taking place in solution but that the complex deposited from the solution onto the plates forming a new phase with a correspondingly lower ν Pt-H.

It was concluded that if the solution spectra was measured within five minutes of the solution being introduced into the cell and a symmetric peak was obtained, the position of the peak could be taken as characteristic of ν Pt-H in that solution to an accuracy of $\pm$ 2 cm^{-1}.

Thus the doubts initially raised as to the nature of the species in solution and the implications of this on the significance of the nuclear magnetic resonance spectral measurements were finally assuaged.

3. Nature of the evidence obtainable from infrared studies

All the assignments made above are based on the assumption of characteristic group frequencies. The large mass difference between platinum and hydrogen makes the independence of ν Pt-H a good approximation.

For comparing platinum hydrogen bond strengths force constant data should be used. However it is not possible to relate a given stretching frequency to the force constant governing the stretching of the associated bond without making a full vibrational assignment for the molecule. This task is hardly feasible for the complexes(I) being studied. Nevertheless in a series of closely related complexes such as the series (I) conclusions drawn as to bond strength on arguing from frequency alone are likely to be substantially correct. The platinum hydrogen stretching frequency is very disparate in magnitude from the platinum-phosphorus and platinum oxygen stretches and is thus unlikely to couple with them to any large extent.

4. Discussion of solvent effects

The platinum hydrogen stretching frequency is sensitive to the nature of the solvent. The frequency decrease in the order

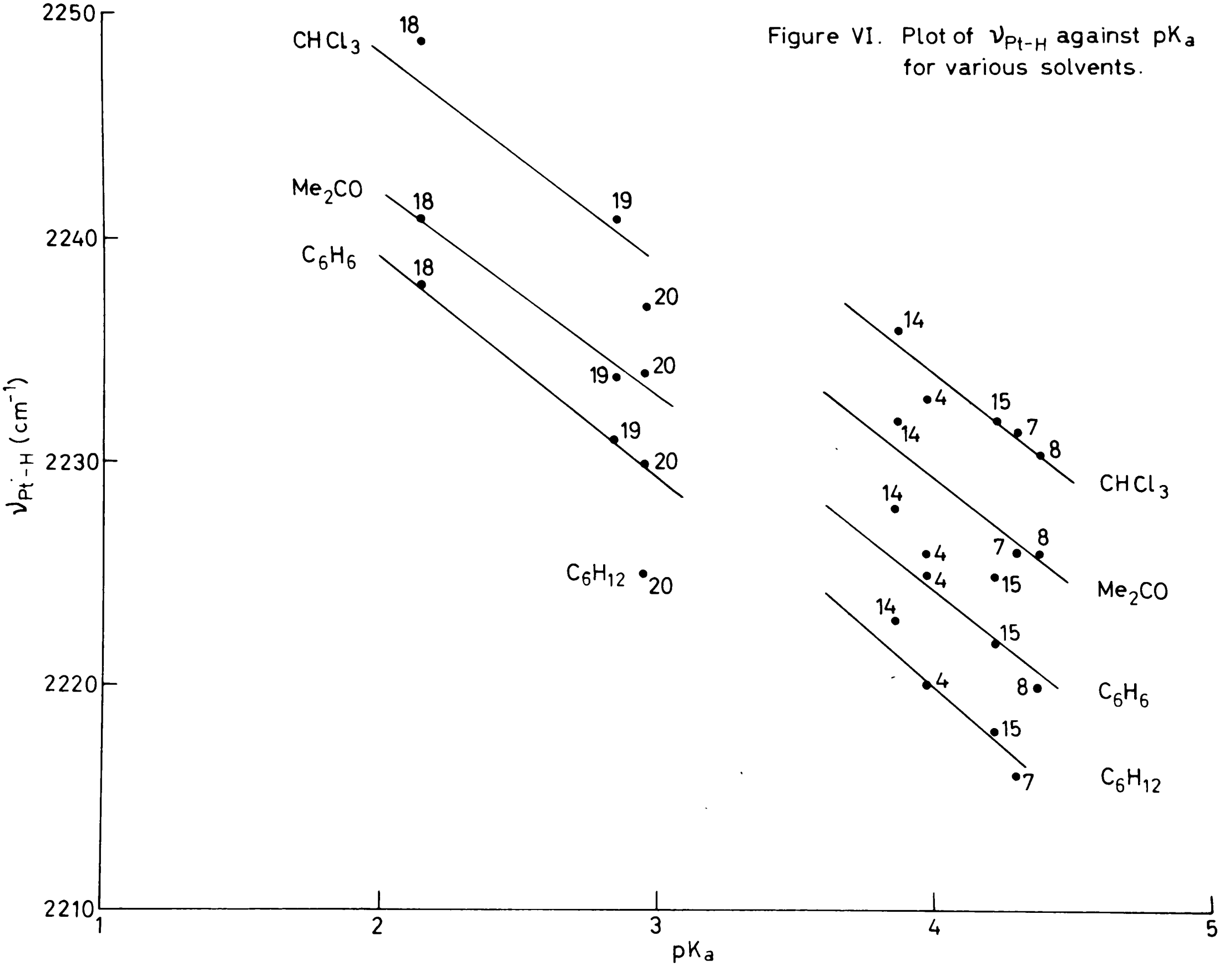
$$\nu\ CHCl_3 > \nu\ (CH_3)_2CO > \nu\ C_6H_6 > \nu\ C_6H_{12}$$

This is in general agreement with the order found by Adams (45) (see Chapter I), but the differences found appear to be slightly smaller. The difference in frequency between chloroform and cyclohexane solutions is found to be 12-14 cm^{-1}. The relative order of the stretching frequencies of the complexes(I) is unaffected by the change of solvent within experimental error (see Figure VI).

The results obtained in this thesis do not co ntradict the solvent shift mechanism of Adams described in the introduction. However it would be expected that the ligating oxygen of a benzoic acid group would be considerably less solvated than a chloride ion partly because of steric inhibition and partly because the negative charge would be expected to be spread around the ligand.

Another mechanism which must be considered is solvation of the platinum atom directly, however although this probably doe s occur it is unlikely that it is the

Figure VI. Plot of ν_{Pt-H} against pK_a for various solvents.



primary cause of solvent shifts as shifts of equal magnitude are found in the hexa-coordinate iridium complexes. Also this idea fails to explain why the metal hydrogen stretch is solvent sensitive when trans- to an anionic ligand but solvent insensitive when trans to a phosphine.

Direct interaction of the solvent with the metal hydrogen system is another possibility. If the apparently legitimate assumption is made that chloroform solvates more strongly than cyclohexane it is difficult to envisage how solvation of the hydrido ligand could strengthen the metal hydrogen bond. The different effects when the hydrido ligand is trans to chloride and phosphorus could be attributed to polarity differences of the metal hydrogen bond in these two cases. There is substantial evidence that the hydrido ligand can have either $\delta+$ or $\delta-$ character depending on its environment (1,2).

In conclusion the nature of the solvent shift in these compounds remains uncertain. However the theory which is in most accord with the evidence is that the chief cause of the effect is solvation of the trans- ligand.

5. Discussion of change of ligand

The change of ligand L in the complexes(I) affects the position of the platinum hydrogen stretch (see Table XIV). The range covered is from 2263 cm^{-1} when L = 2,4,6-$(NO_2)_3C_6H_2COO$ to 2222 cm^{-1} when L = p-$Me_2NC_6H_4COO$. The stretching frequency appears to increase with increasing electronegativity of the ligand.

If the stretching frequency is plotted against the pKa of the parent acid HL the graphs shown in Figures IX and VI are obtained. Figure IX shows the values of the stretching frequencies for acetone solutions for all the complexes studied. Figure VI gives the values for compounds in the various solvents to illustrate that the trends found are general.

There is a linear correlation between the pKa s of the m- and p- benzoic acids and the ν Pt-H of their derivatives. Another correlation is observed when L is ortho-substituted and a third for the substituted acetato derivatives.

The pKa of an acid is rather a crude measure of the electron withdrawing power of its anion (this is discussed in Chapter IV) however the fact that m- and p-substituted benzoic acids have a similar correlation

implies that only the σ-electron withdrawing power of the trans-ligand is important in determining the metal hydrogen bond strength. A similar conclusion has been reached by Adams et al. (65) by studying platinum halogen stretching frequencies in square planar platinum complexes.

Chatt, Duncanson and Shaw also found that the platinum hydrogen stretch increased with increasing electronegativity of the ligand (see Chapter I). Complexes with the thiocyanate and nitro ligands are assumed to have platinum-nitrogen bonds in the crystalline state. Evidence for this has been obtained from the mull spectra (21). This is also the order for decreasing trans-effect of theligand L as has been pointed out by several authors (19, 1, 2, 67).

The relation of ν Pt-H to the nuclear magnetic resonance spectra of the hydrido ligand is discussed in Chapter IV.

CHAPTER IV

Discussion of Results

In this chapter correlations will be drawn between τ_{Pt-H}, J_{Pt-H} and ν_{Pt-H} for the complexes(I) and the pK_as of the acids LH. An attempt will be made to rationalize the observed relationships between these quantities in the light of current theory for chemical shifts and coupling constants.

A. Empirical deductions

The proceedure followed to examine the relationships between τ_{Pt-H}, J_{Pt-H}, ν_{Pt-H} and pK_a, was to plot two of the parameters against each other. Examination of the six resulting graphs led to the expectation that in some cases separate linear correlations exist for the m- and p- substituted benzoato complexes, the o- substituted benzoato complexes and the substituted acetato complexes. Least squares regression was carried out for each combination of two parameters on all the data and on each of the three classes separately in an attempt to establish the validity of the various linear correlations.

The observed data are given in Table XVI and are plotted in Figures VII-XII: the results of the least squares regression analyses are given in Table XVII.

When one of the parameters being plotted is the pK_a of the acid HL, substantially better linear

Table XVI

Data on the complexes(I)

		pK_a(66)	τ_{Pt-H}	J_{Pt-H}	ν_{Pt-H}
1	p-NO_2	3.425	32.200	1209.6	2235
2	p-CN	3.551	32.170	1203.9	
3	p-I	3.93	32.061	1193.2	2231
4	p-Br	3.971	32.043	1191.3	2233
5	p-Cl	3.977	32.036	1189.1	2231
6	H	4.212	31.918	1179.1	
7	p-CH_3	4.373	31.897	1176.2	2226
8	p-OMe	4.471	31.869	1172.0	2226
9	p-NMe_2	(4.853)*	31.745	1160.9	2222
10	m-NO_2	3.493	32.226	1210.6	2235
11	m-I	3.851	32.123	1197.1	2232
12	m-Br	3.812	32.105	1196.2	
13	m-Cl	3.830	32.095	1195.5	2232
14	m-F	3.865	32.077	1193.1	2232
15	m-CH_3	4.272	31.899	1176.5	2225
16	m-NMe_2	(4.744)*	31.857	1172.3	2224
17	3,5-$(NO_2)_2$	2.824	32.446	1236.8	2243
18	o-NO_2	2.173	32.515	1226.2	2241
19	o-Br	2.824	32.257	1205.2	2234
20	o-Cl	2.934	32.226	1204.0	2234
21	2,5-$(NO_2)_2$	1.622	32.715	1255.5	2247

		pK_a(66)	τ_{Pt-H}	J_{Pt-H}	ν_{Pt-H}
22	2,4,6-$(NO_2)_3$	0.654	33.671	1298.3	2263
23	CF_3	0.23	33.013	1285.5	2258
24	$CHCl_2$	1.25	32.765	1255.8	2245
25	CH_2Cl	2.865	32.483	1216.7	2237
26	CH_2OPh	3.171	32.342	1202.9	2234

*pK_a values are for the corresponding p-$NH_2C_6H_4COOH$ and m-$NH_2C_6H_4COOH$.

Figure VII. Plot of τ_{Pt-H} against pK_a

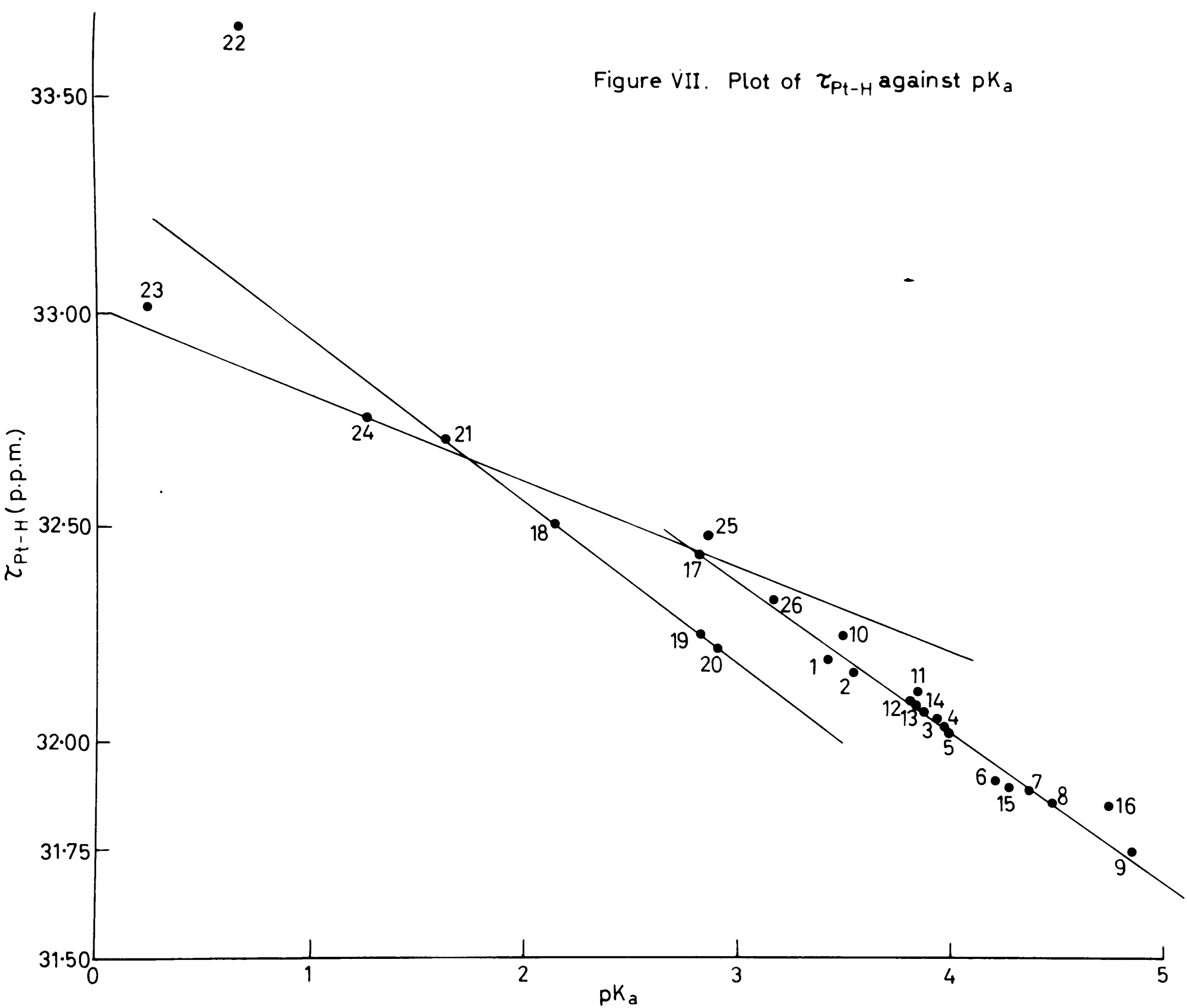


Figure VIII. Plot of J_{Pt-H} against pK_a

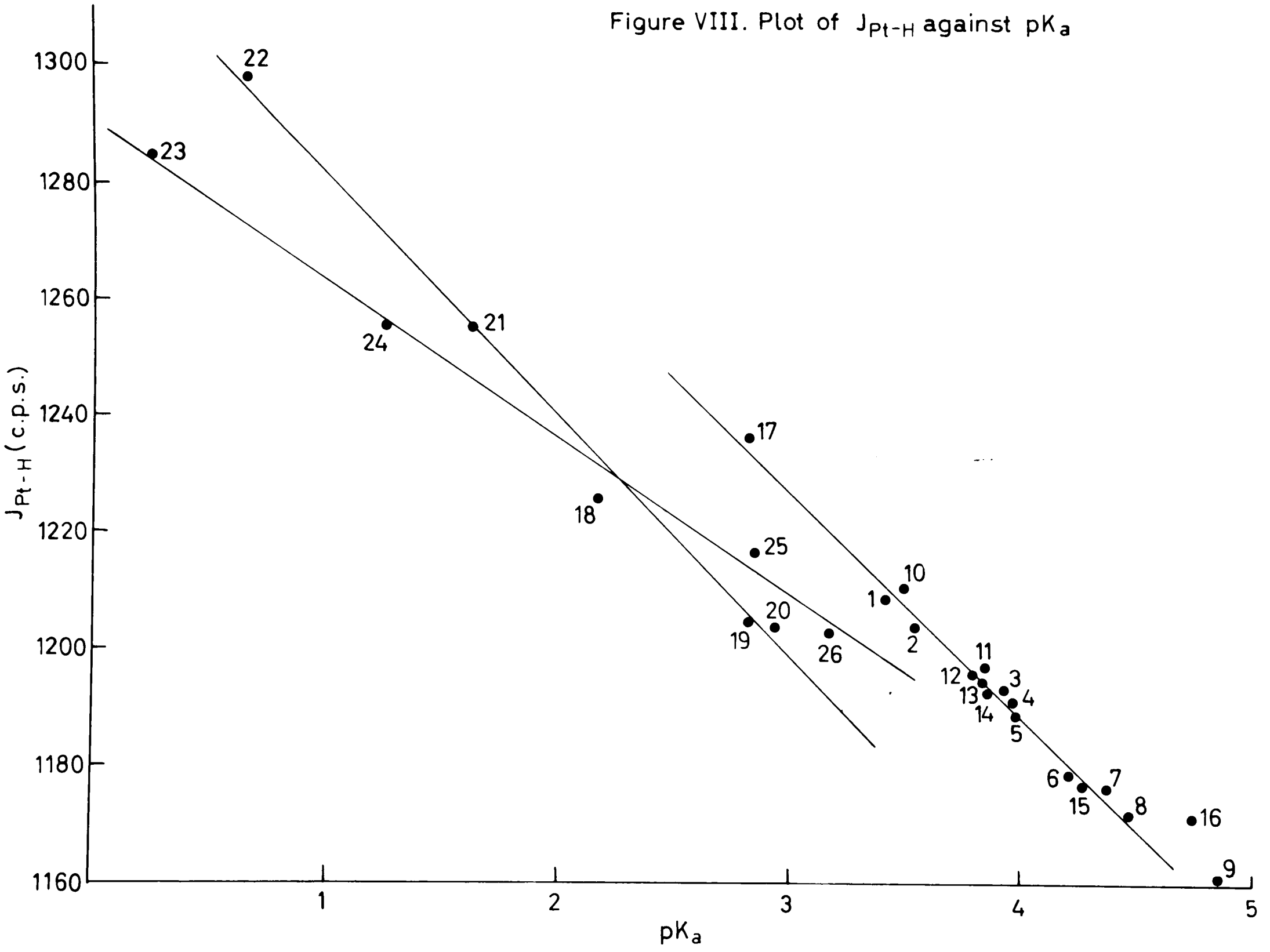


Figure IX. Plot of ν_{Pt-H} against pK_a

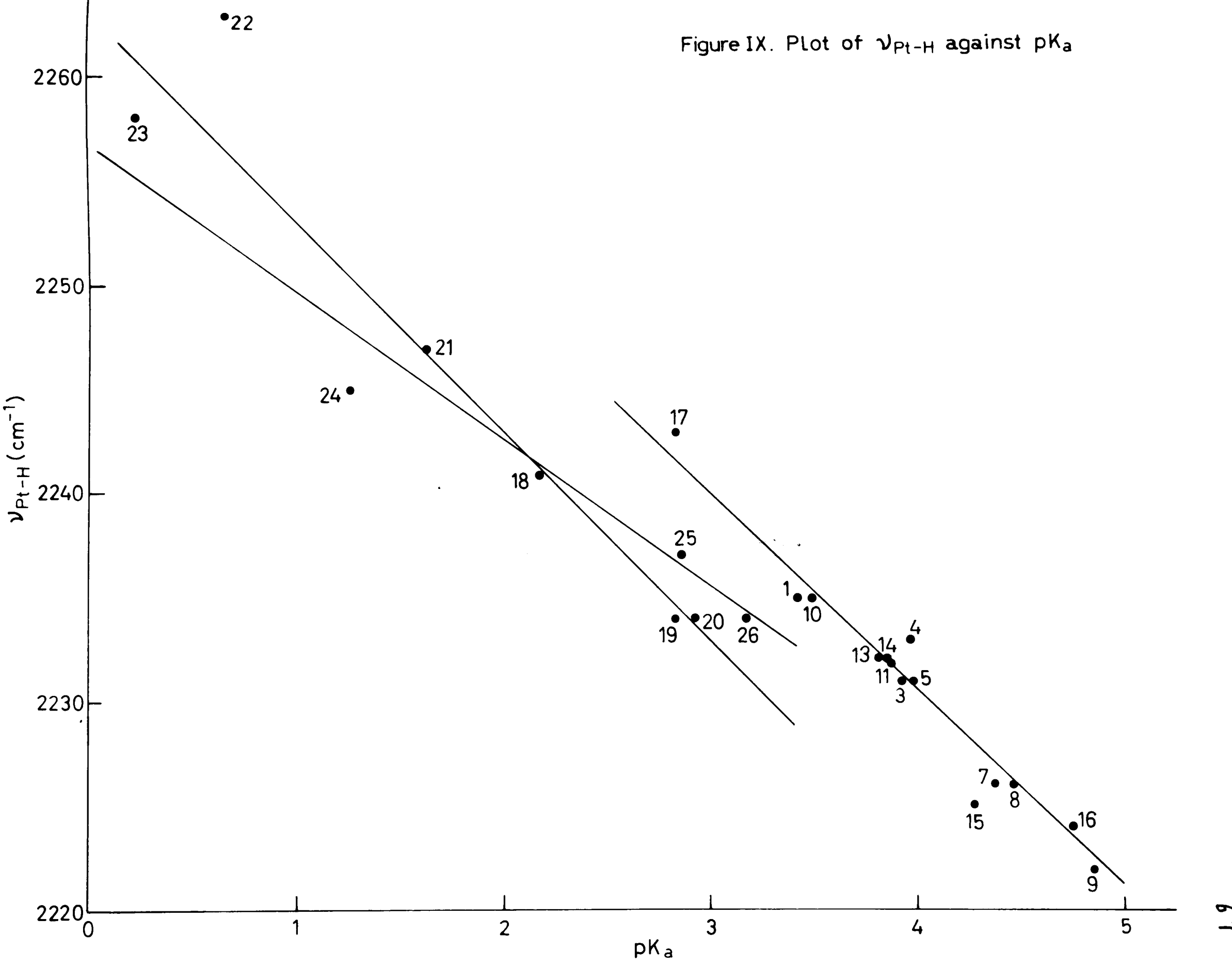


Figure X. Plot of J_{Pt-H} against τ_{Pt-H}

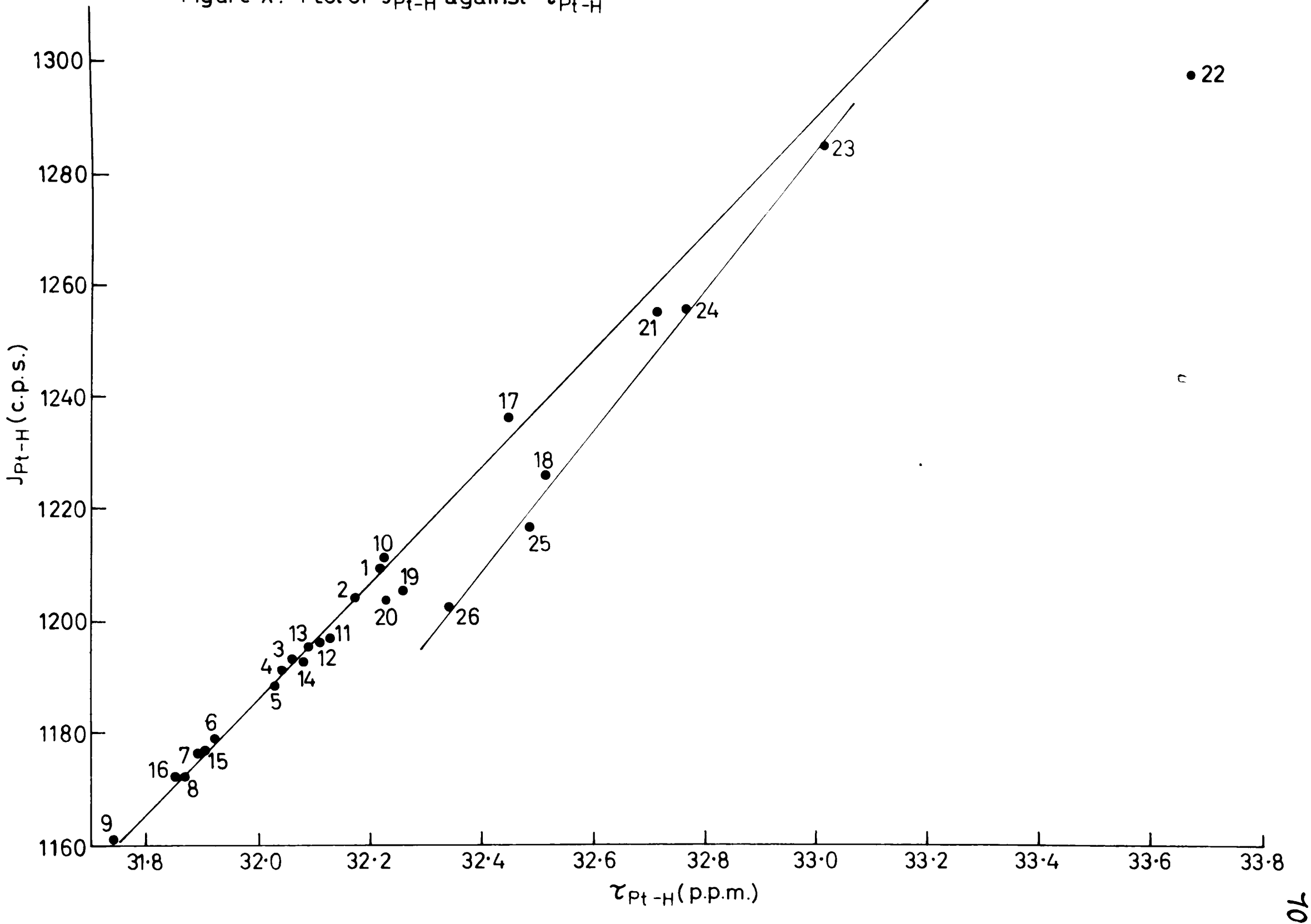


Figure XI. Plot of ν_{Pt-H} against τ_{Pt-H}

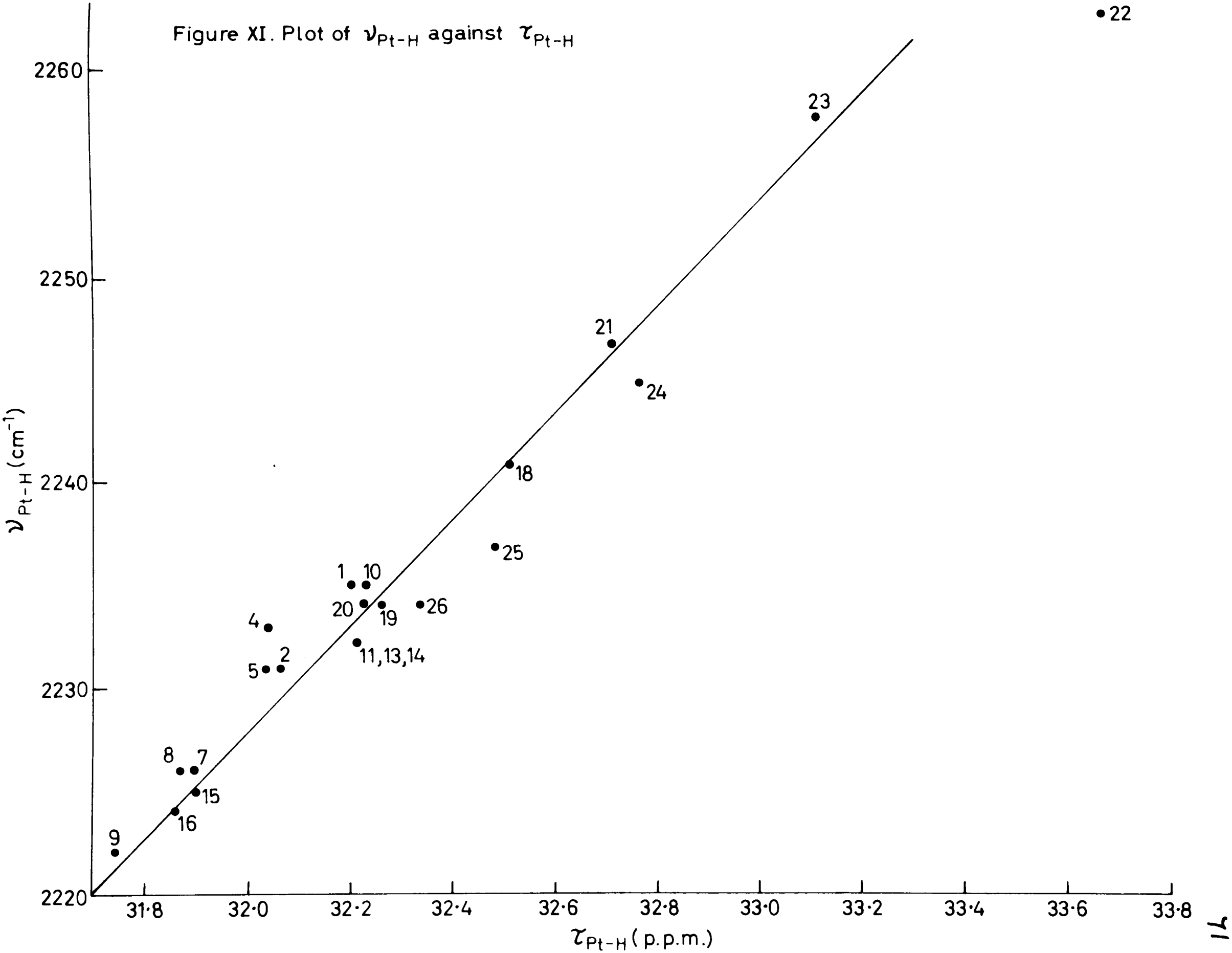


Figure XII. Plot of J_{Pt-H} against ν_{Pt-H}

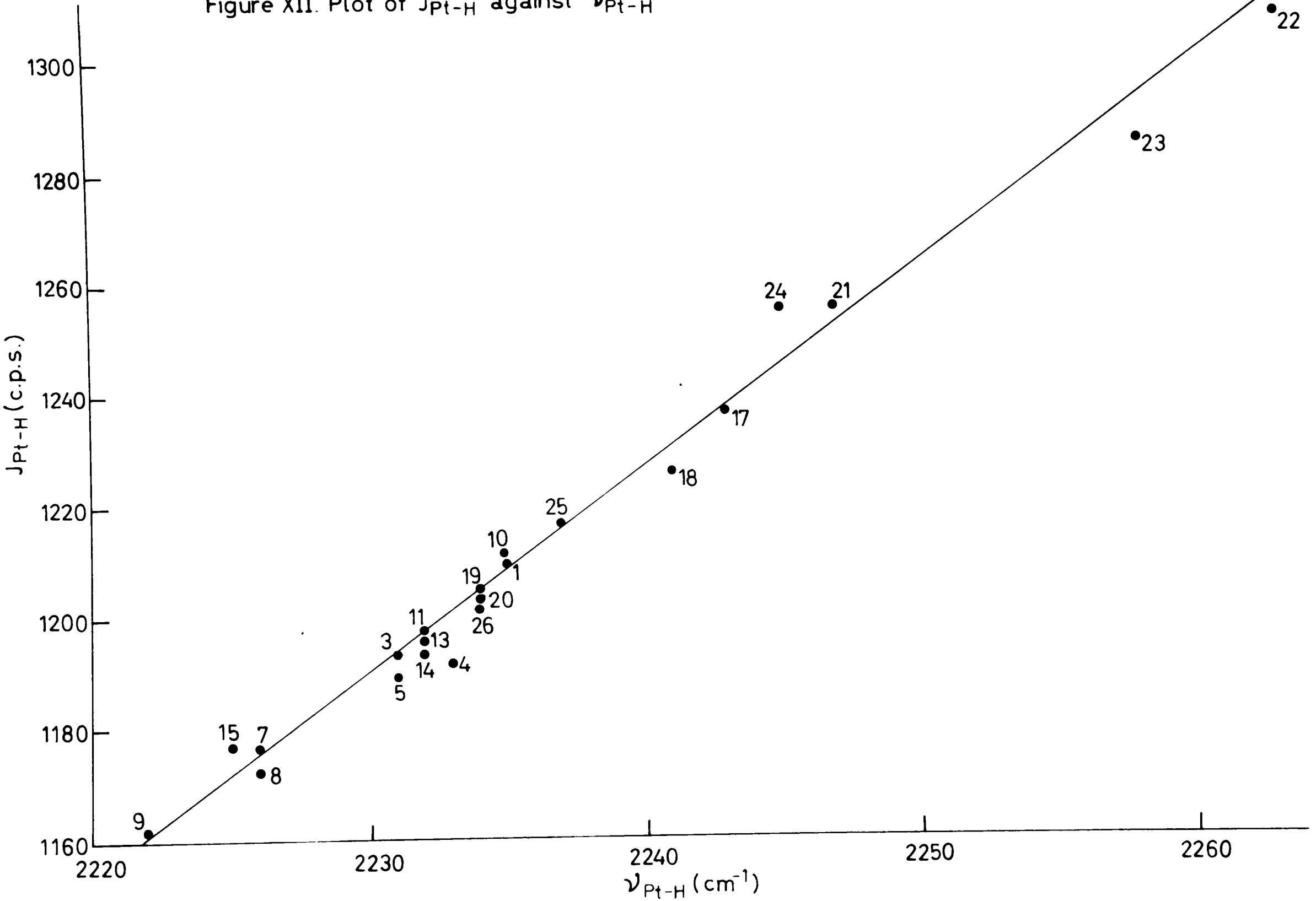


Table XVII

Results of least squares regressions

y	x	Compds.	a	b	Corr.M.C.C.*
pK	ζ	1-26	91.6	-2.73	0.887
		1-17	97.2	-2.90	0.971
		18-22	52.3	-1.54	0.916
		23-26	152	-4.61	0.981
pK	ζ^2	1-26	45.1	-0.0346	0.943
		1-17	36.4	-0.0272	0.970
		18-22	31.2	-0.0235	0.988
		23-26	47.5	-0.0368	0.994
pK	ν	1-26	271	-0.1210	0.913
		1-17	217	-0.0954	0.954
		18-22	178	-0.0773	0.972
		23-26	282	-0.125	0.936
ζ^2	ζ^2	1-26	17.8	0.0120	0.948
		1-17	20.9	0.00933	0.994
		18-22	14.7	0.0145	0.937
		23-26	22.8	0.00794	0.997
ζ^2	ν^2	1-26	-61.7	0.00421	0.948
		1-17	-40.1	0.00324	0.967
		18-22	-76.6	0.00487	0.979
		23-26	-28.8	0.00274	0.949

y	x	Compds.	a	b	Corr. M.C.C.*
$\bar{J}$	ν	1-26	-6590	3.49	0.983
		1-17	-6560	3.47	0.962
		18-22	-6130	3.29	0.986
		23-26	-6480	3.44	0.946

*The multiple correlation coefficient is corrected for the number of points being considered. An M.C.C. of 1 implies a perfect correlation.

correlations are obtained if the o-substituted derivatives are plotted separately from the m- and p- substituted derivatives. This suggests that the o-substituted acids pK_a values may not be a reliable indication of their relative effects on the electronic structure of the complex. This will be discussed below (see Section B). The substituted acetato derivatives also gave a separate correlation when a plot involved pK_a.

When τ_{Pt-H} was plotted against J_{Pt-H} two correlations were found, one for the substituted benzoato complexes and one for the substituted acetato complexes. There was no obvious distinction between the ortho- and the meta- and para- complexes.

When both τ_{Pt-H} and J_{Pt-H} were plotted against ν_{Pt-H} only one correlation could be distinguished. However as the error in measuring ν_{Pt-H} was substantially greater than the error in measuring either τ_{Pt-H} or J_{Pt-H} the existence of separate correlations cannot be ruled out. Extrapolation of the other data would lead out to believe that separate correlations should exist for the substituted benzoato compounds and the substituted acetato compounds.

The data from an examination of the complexes in different solvents are also plotted to demonstrate that the trends found in acetone are general (see Figures XIII-XV).

Figure XIII. Plot of τ_{Pt-H} against pK_a for various solvents

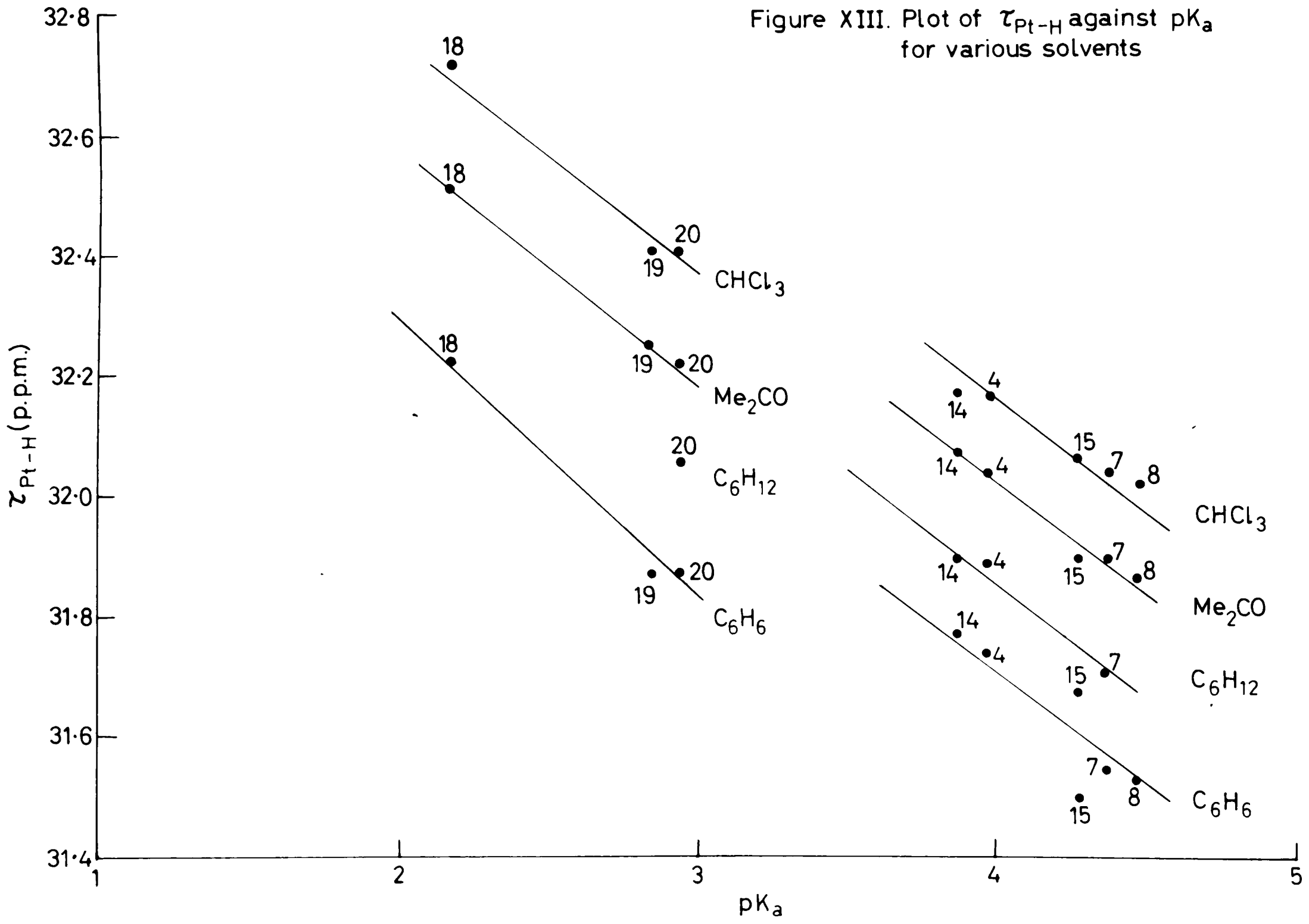


Figure XIV. Plot of J_{Pt-H} against pK_a for various solvents

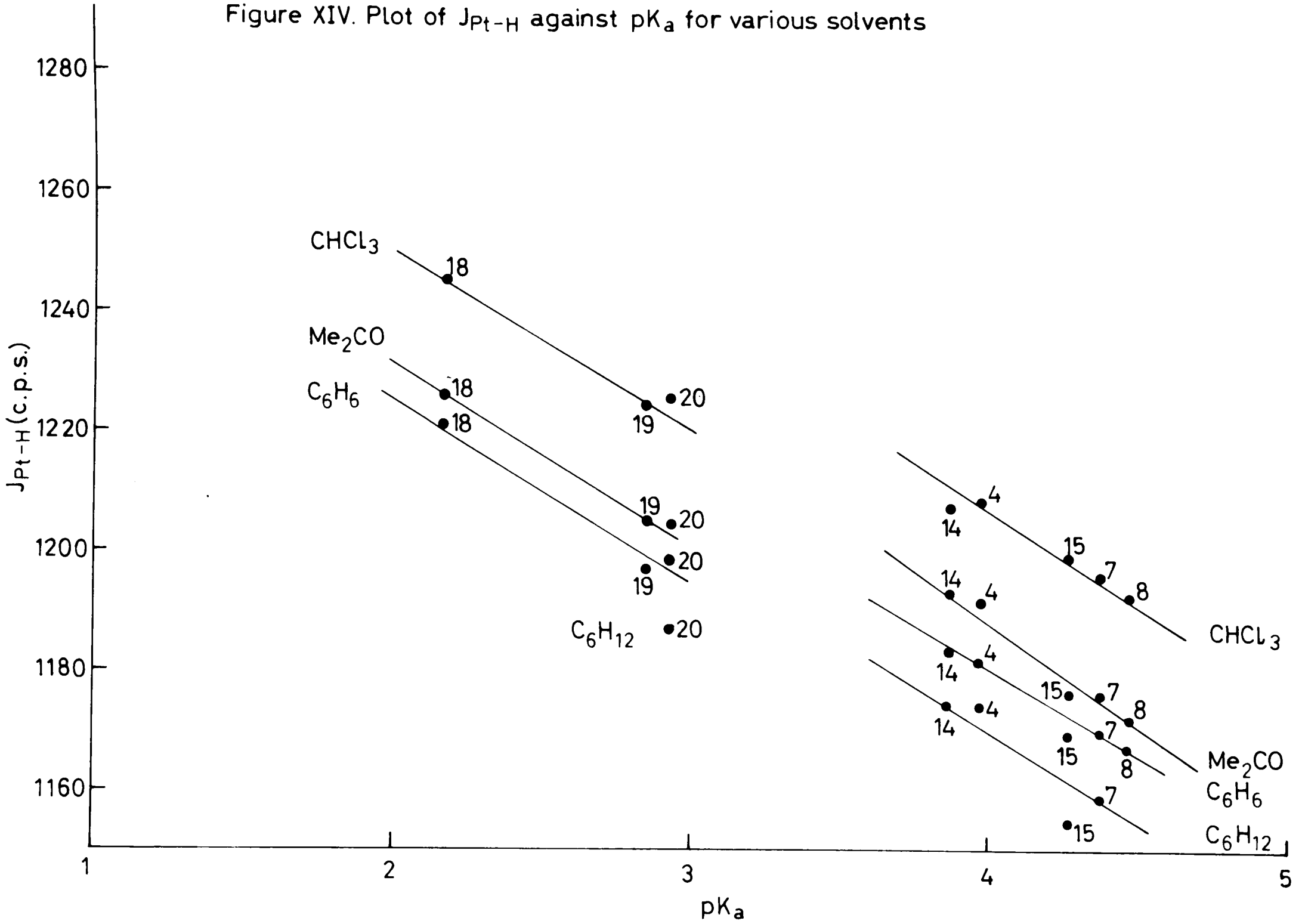
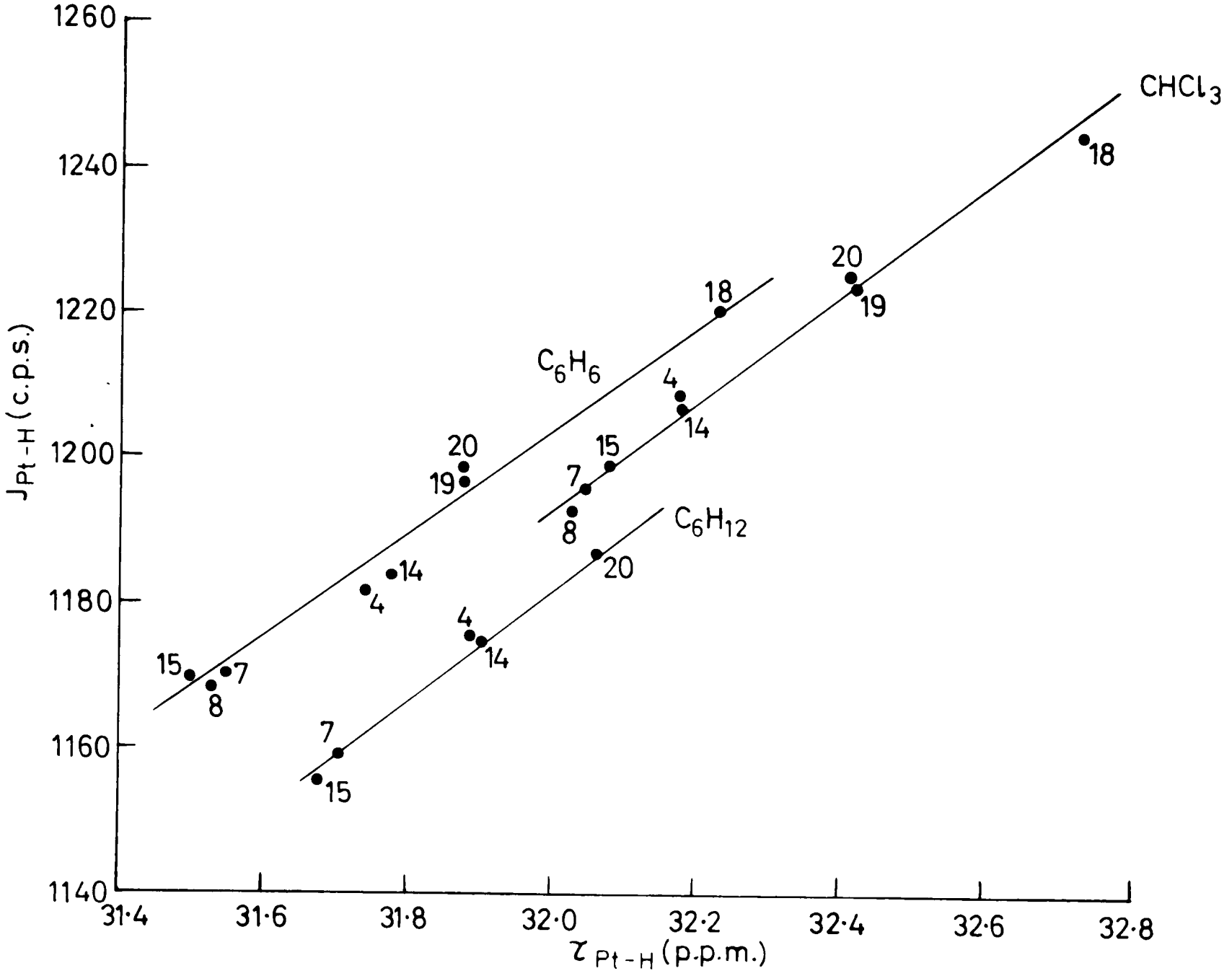


Figure XV. Plot of J_{Pt-H} against τ_{Pt-H} for various solvents



B. Ionization constants of carboxylic acids

The ionization constants of the substituted benzoic acids were used by Hammett to define the polar effect of substituents through the quantity σ (68) where

$$\sigma = \log ({}^{\circ}K_1^{H}/K_1^{H})$$

where K_1^{H} is the equilibrium constant for ionization of the acid and the superscript $^{\circ}$ denotes the value for benzoic acid itself.

For ortho- substituted benzoic acids steric interaction may occur between the ortho- substituent and the carboxylic acid group. If this is the case then the pK_a may well give a false impression of the electron withdrawing power of the o- substituted benzoato ligand. This is believed to be the reason why different correlations are found for the o- and the m- and p- complexes when pK_a is one of the parameters being considered. That the same correlation applies for all three benzoato derivatives when parameters concerned solely with the complexes are considered suggests that ortho- substituents have no specific effects on the complex itself. It may be noted in support of this that Knight and Rossotti (69) have found for a series of copper benzoato complexes that two different linear correlations hold between the pK_a of the substituted

benzoic acid and the log of the stability constant of the related complex, one correlation being for o-benzoates and the other for m- and p-benzoates.

C. Discussion of chemical shift data

The discussion of the chemical shift data will be based on the theory of Buckingham and Stephens for chemical shifts in square planar complexes (51). They attribute the main contribution to the high field shift of platinum hydrides to the paramagnetic shielding, σ^P, of the hydrogen nucleus by the platinum 5d electrons. An explanation of the variation of the shielding in the complexes(I) and (II) will be sought in terms of variation in this paramagnetic term. In the series of compounds(II) variation of σ on changing L from NO_3 to CN is as much as 16 p.p.m.; local shielding effects seem insufficient to account for variations of this order of magnitude.

Buckingham and Stephens note the strong dependence of σ^P on the metal hydrogen distance R predicted by their treatment. They attribute the variation of σ^P in the complexes(II) to changes in R (52).

In view of the correlation which has been found in this work between ν_{Pt-H} and τ_{Pt-H} it seems likely that variation in shielding constant of the complexes(I) can be interpreted solely in terms of a change in platinum hydrogen distance.

The other parameters upon which the paramagnetic contribution to the shielding constant depends are k,

the radial exponent of the d-orbitals, (which is taken to be the same for all the d-orbitals) and ΔE, a measure of $E(^1A_2) - E(^1A_1)$ and $E(^1E) - E(^1A_1)$, these two energy terms being assumed equal.

The ligand field bands of the complexes(I) cannot be observed as the charge transfer bands occur at too low an energy. However extrapolating from the data obtained for cobalt pentammine complexes (see Table XIX), ΔE is unlikely to change significantly on variation of the carboxylato ligand.

It is also considered unlikely that variations in k will be sufficient to account for the observed variation in view of the insensitivity of σ^P to changes in k in the region k = 3-4.

If R is taken as 3 a.u. as seems reasonable (see Chapter I) and k is assumed to have a value in the range 3-4 $(a.u.)^{-1}$, then the parameter $\rho = 2kR$ in the formulae of Buckingham and Stephens is so large (~ 20) that terms of the type $\rho^n e^{-\rho}$ may be neglected. It is then found that σ^P reduces to

$$\sigma^P = \frac{e^2h^2}{m^2c^2R^3\Delta E} \left\{ 3 + \frac{2565}{7\rho^2} \right\}$$

If k and ΔE are taken to be constant in a series of complexes and $\rho \sim 20$ the variation of σ^P with R will

be dominated by the $^1/R^3$ term. That this is the case is demonstrated by a plot of predicted values of σ^P against $^1/R^3$ (see Table XVIII and Figure XVI). Thus in the closely related complexes(I) the chemical shift might be expected to vary as the inverse of the cube of the platinum-hydrogen distance.

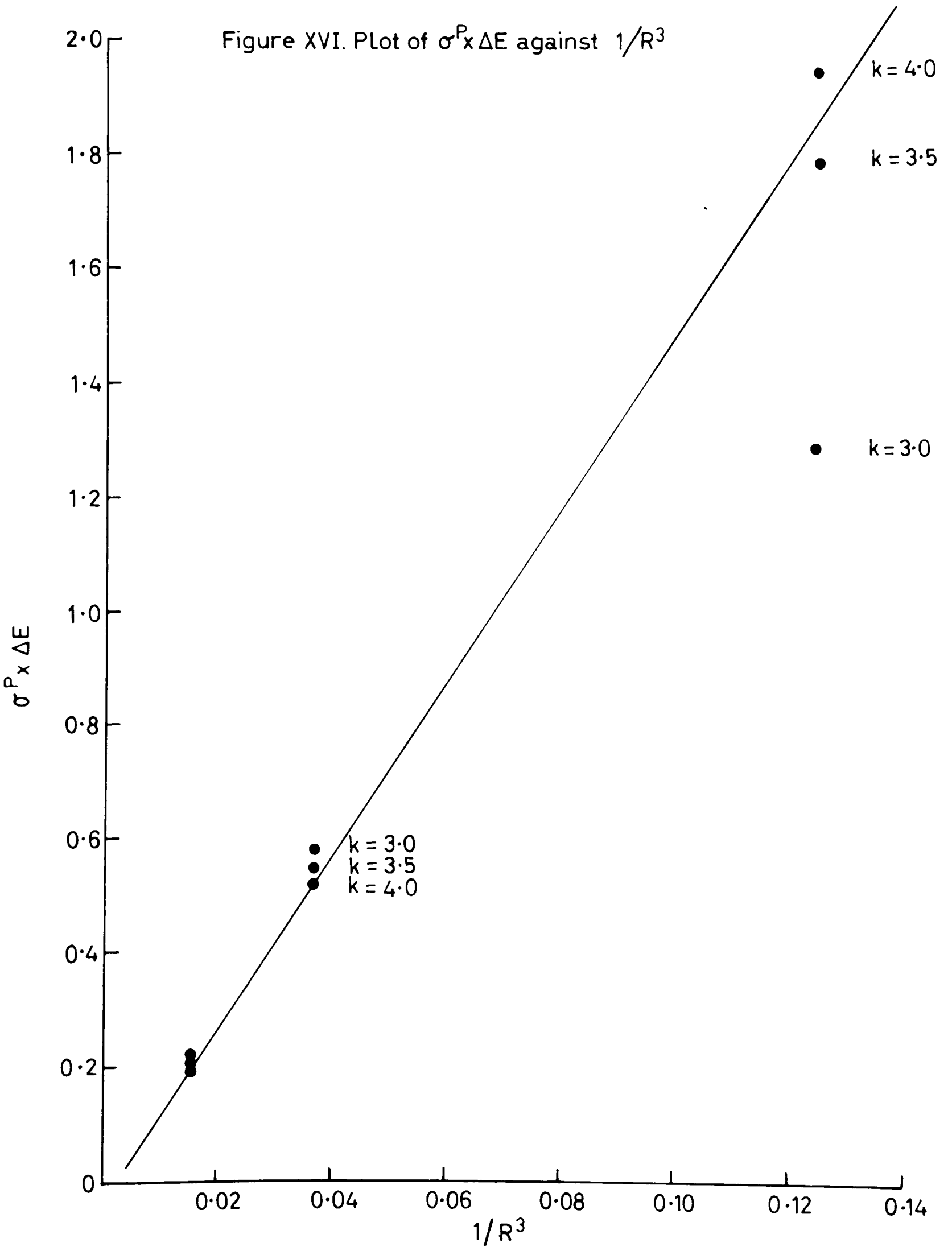
Table XVIII

Predicted values for σ^P for various k and R

	R	$\sigma^P \times \Delta E$	$^1/R^3$
k = 3	2	1.290	0.125
	3	0.576	0.0370
	4	0.221	0.0156
k = 3.5	2	1.793	0.125
	3	0.550	0.0370
	4	0.211	0.0156
k = 4	2	1.949	0.125
	3	0.524	0.0370
	4	0.204	0.0156

Stephens has argued from the Douglas-Clark rule that the relationship between the stretching frequency of a metal hydride and the bond length should be νR^3 = constant (52). Applying this to the complexes(I), a variation in R of 0.02 Å in the complete range is predicted. If this is the case a linear relationship should hold between

Figure XVI. Plot of $\sigma^{P} \times \Delta E$ against $1/R^3$

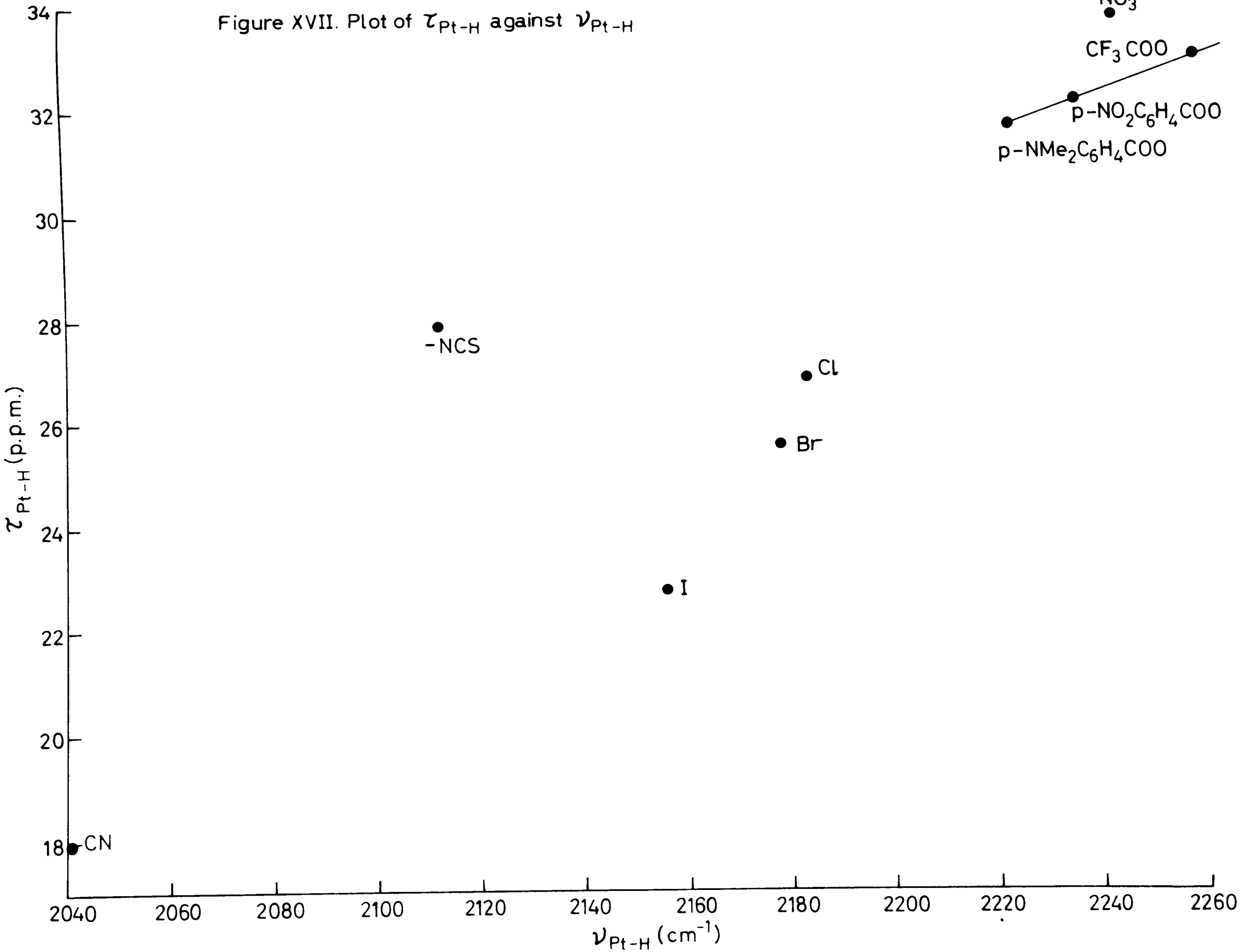


chemical shift and stretching frequency within the limitations discussed above. That this is observed for the complexes(I), where these approximations are most likely to hold, is considered as strong evidence for the argument of Buckingham and Stephens that the main cause of variation of chemical shift in the platinum hydrides is variation in the metal hydrogen distance.

In Figure XVII the shielding constants in the complexes(II) are plotted against stretching frequency. It may be seen that the linear correlation found for the complexes(I) does not extend to these related compounds. When L is a halide instead of a carboxylato ligand both k and ΔE would be expected to be smaller as this is the trend shown by the nephelauxectic and spectrochemical series respectively. Thus the halide complexes could reasonably be expected to have chemical shifts larger than those predicted by extrapolation of the correlation already found. However in fact the values found are smaller than those predicted.

As already noted the order of increase of chemical shift for these complexes(I) is in the same direction as the anticipated decrease in metal hydrogen distance. It must be remembered that the assumptions made in deriving the linear relationship between stretching

Figure XVII. Plot of τ_{Pt-H} against ν_{Pt-H}



frequency and chemical shift for the carboxylato complexes were firstly that the metal hydrogen stretch was independent of the other vibrations of the molecule and secondly that a particular relationship, νR^3 = constant, held between the stretching frequency and the bond length. It is quite feasible that these assumptions are valid for the series of complexes(I) but when radical changes are being made in the complex such as the substitution of one halogen for another they may well break down.

In conclusion the dominant cause of the variation in chemical shift in the complexes(I) and (II) may well be the change in metal hydrogen distance.

Isotopic effects

In order to confirm their predicted dependence of σ^P on R, Buckingham and Stephens, suggested that the chemical shifts in a related hydride and deuteride should be measured. Substitution of a deuteron for a proton should change the effective internuclear distance without changing the local shielding. Assuming a distance R = 3 a.u. they predict a shift to higher fields of 0.08 p.p.m.; for a distance R = 2 a.u. a shift of 0.51 p.p.m. would be expected.

The compounds trans-$PtHCl(PEt_3)_2$ and trans-$PtDCl(PEt_3)_2$ are found to have shifts of the ^1H and ^2H

resonance relative to acetone and deuteroacetone of 19.37 p.p.m. and 19.1 ± 0.3 p.p.m. respectively. Thus a shift of the order of +0.5 p.p.m. on changing ^{1}H to ^{2}H is ruled out. The experiment was not sufficiently accurate to detect whether or not a shift of the order of 0.1 p.p.m. to higher fields had occurred, therefore the results of this study are inconclusive.

A study of the deuteride on a machine capable of higher resolution and at higher operating field should be able to establish whether effects of this order of magnitude occur. It is to be remembered that a change might also occur in the shielding of the acetone H nuclei. A suitable standard for experiments of this nature would be HD.

D. Discussion of coupling constant data

Basing their work on Ramsey's perturbation treatment of indirect coupling between nuclear spins (70) Pople and Santry have derived an L.CAO-MO treatment of coupling between directly bonded atoms (71). The discussion of the coupling constants in the complexes(I) will be based on this approach.

For systems where hydrogen is directly bonded to another atom the contact term is likely to be dominant (71) so only this contribution to the coupling constant will be considered. Pople and Santry give this in terms of the reduced coupling constant, K_{AB}, where

$$K_{AB} = (2\pi/h\ \gamma_A\ \gamma_B)\ \tilde{J}_{AB}$$

This reduced coupling constant is independent of the nuclear moments of A and B and only depends on the electronic environment. For the Fermi contact contribution

$$K_{AB} = -(256\pi^2/9)\ \beta^2\ \langle S_A \mid \delta(\tilde{r}_A) \mid S_A \rangle \langle S_B \mid \delta(\tilde{r}_B) \mid S_B \rangle\ x$$

$$\sum_{i}^{occ} \sum_{j}^{unocc} (^3\Delta E_{i\rightarrow j})^{-1}\ C_{is_A}\ C_{js_A}\ C_{js_B}\ C_{is_B}$$

where S_A and S_B are S-orbitals on atoms A and B respectively, C_{is_A} is the coefficient of orbital S_A in the molecular orbital i and $^3\Delta E_{i\rightarrow j}$ is the singlet-triplet excitation energy on exciting an electron from the occupied

molecular orbital i to the unoccupied orbital j.

If a mean excitation energy approximation is made, replacing all $^3\Delta E_{i \to j}$ by an average value $^3\Delta E$, K_{AB} reduces to

$$K_{AB} = (64\pi^2/9)\,\beta^2\,(^3\Delta E)^{-1} \langle S_A \mid \delta(\tilde{r}_A) \mid S_A \rangle \langle S_B \mid \delta(r_B) \mid S_B \rangle \times P_{S_A S_B}{}^2$$

$P_{S_A S_B}{}^2$ is the S-orbital contribution to the bond and is defined generally as

$$P_{\mu\nu} = 2 \sum_{i=1}^{N} C_{i\mu}\, C_{i\nu}$$

For the complexes(I) the only molecular orbitals which contribute to the contact term are those with both the platinum 6^s orbital and the hydrogen 1^s orbital. The assumption is made that only the molecular orbitals arising from atomic valence orbitals will be significant. Symmetry considerations show that these are the a_1 bonding and antibonding molecular orbitals and also the platinum 6s-orbital will mix with the $5d_z2$ and $5d_{x^2-y^2}$ orbitals. Thus a total of two occupied bonding orbitals one occupied non-bonding (d_z2) orbital and two antibonding unoccupied molecular orbitals must be considered (72).

It is obviously an impossible task to attempt a numerical estimate of K_{AB} under these conditions.

The fact that the m- and p- benzoato derivatives

have the same correlation between their pK_as and coupling constants implies that only changes in the σ- system of the molecule are important in determining the relative sizes of the coupling constants. This may be taken as support for the attempt to interpret changes in the coupling constant purely in terms of changes in the contact contribution.

Consideration of effect of changing the ligand L. Effect on s-electron density at the nucleus.

As the ligand L becomes more electronegative the effective nuclear charge of both the platinum and the hydrogen atoms should increase. This should correspondingly increase their s-electron density at the nucleus. The s-electron density at the platinum nucleus should be affected by both σ- and π- withdrawal and the hydrogen nuclear s-electron density only by σ- withdrawal.

It is impossible to estimate the size of this effect. However it is to be remembered that when the ligand trans to the hydrogen is cyanide, which is a strong π-acceptor in this type of complex (see Section F) (59), the platinum-hydrogen coupling constant is the smallest for this series. This suggests that change in effective nuclear charge is not the dominant effect in determining the relative sizes of the coupling constants, however it

is not ruled out as a contributing factor.

Effect on s-character of the bond

The hydrogen s-orbital as well as bonding with the platinum 6s, $5d_{z^2}$ and $5d_{x^2-y^2}$ orbitals, all of which orbitals have A_1 symmetry, may also bond with the $6p_x$ platinum orbital, (x - is taken as the metal-hydrogen direction). Basically, the competition between these two sets of orbitals for the hydrogen 1s orbital will determine the so-called s-character of the bond. The σ - valence orbital of the ligand trans- to the hydrido ligand has similar interactions with the platinum orbitals, thus the trans-ligand would be expected to some extent to determine the s-character of the platinum-hydrogen bond.

On increasing the electronegativity of the trans-ligand in complexes(I) the platinum-hydrogen bond would be expected to strengthen and shorten as is indicated by the infra-red and chemical shift evidence (see Chapter III and Section C). By analogy with carbon hydrogen bonds (73) this shortening of the platinum-hydrogen bond might be expected to be associated with an increase of the s-character of the bond and a decrease in its p-character. Thus the platinum-hydrogen coupling constant would be expected to increase with increasing

electronegativity of the trans-ligand. This effect is in the same direction as that predicted by consideration of variation in s-electron density at the nucleus, indeed, in the direction found experimentally.

A percentage variation in $P_{S_A S_B}^2$ of $\sim$10% is needed to explain the variation in J_{Pt-H} on passing from L = 2,4,6-$(NO_2)_3C_6H_2COO$ to L = p-$NMe_2C_6H_4COO$ solely in terms of s-character of the bond. This does not appear to be unreasonable.

However extension of this line of argument to the complexes(II) fails, as can be seen from the plots of J_{Pt-H} against τ_{Pt-H} and ν_{Pt-H} for these compounds given in Figures XVIII and XIX respectively. The chemical shift and the stretching frequency are taken as possible indicators of platinum hydrogen bond length and hence s-character.

Thus it may be concluded that while variations in the s-character of the metal hydrogen bond are a possible explanation for variations in J_{Pt-H} for the carboxylato derivatives it seems unlikely that it is the explanation for the corresponding acido-compounds.

Effect of $(^3\Delta E)$

How the six excitations which comprise the mean excitation energy term vary with change of L is difficult

Figure XVIII. Plot of J_{Pt-H} against τ_{Pt-H}

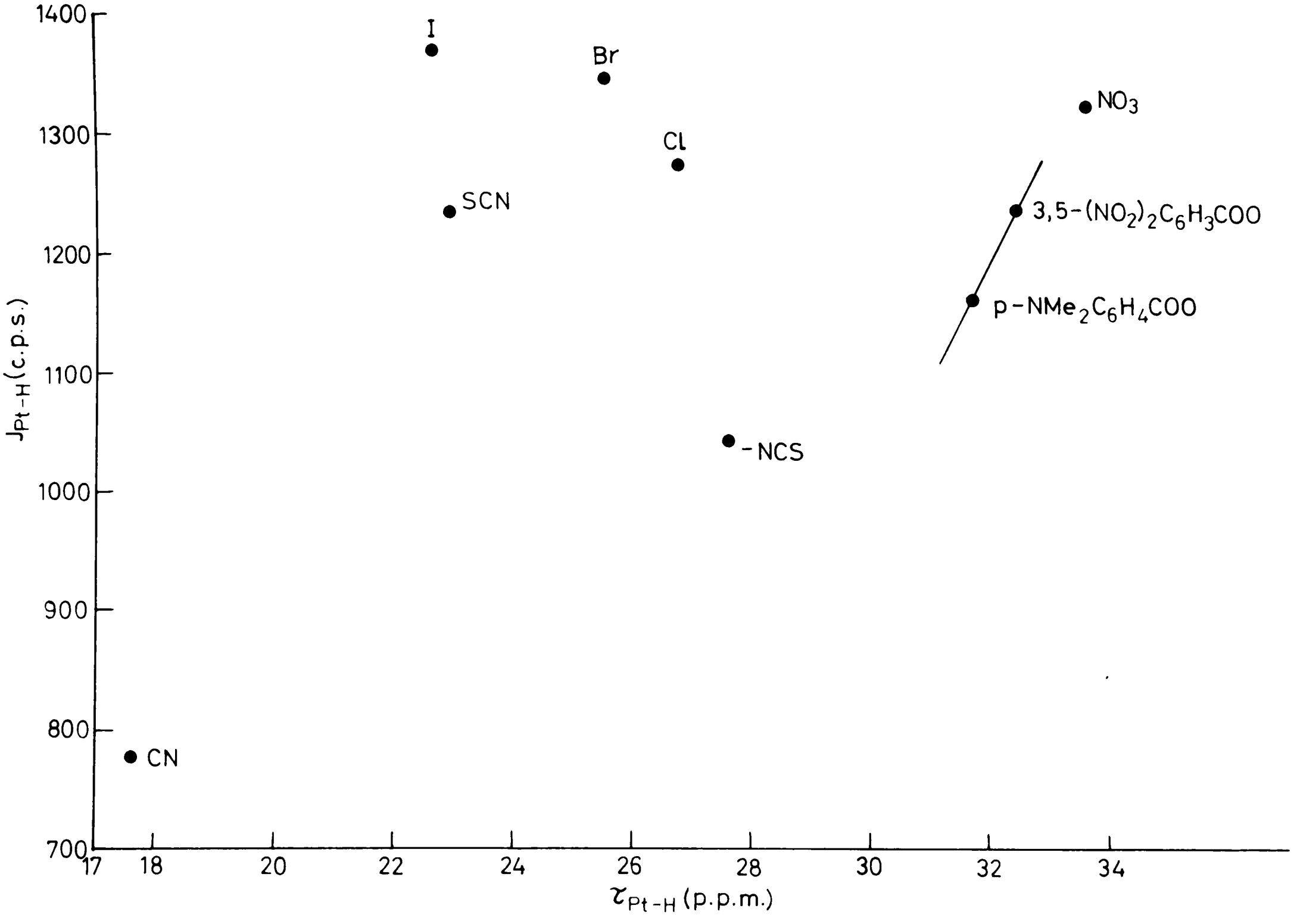
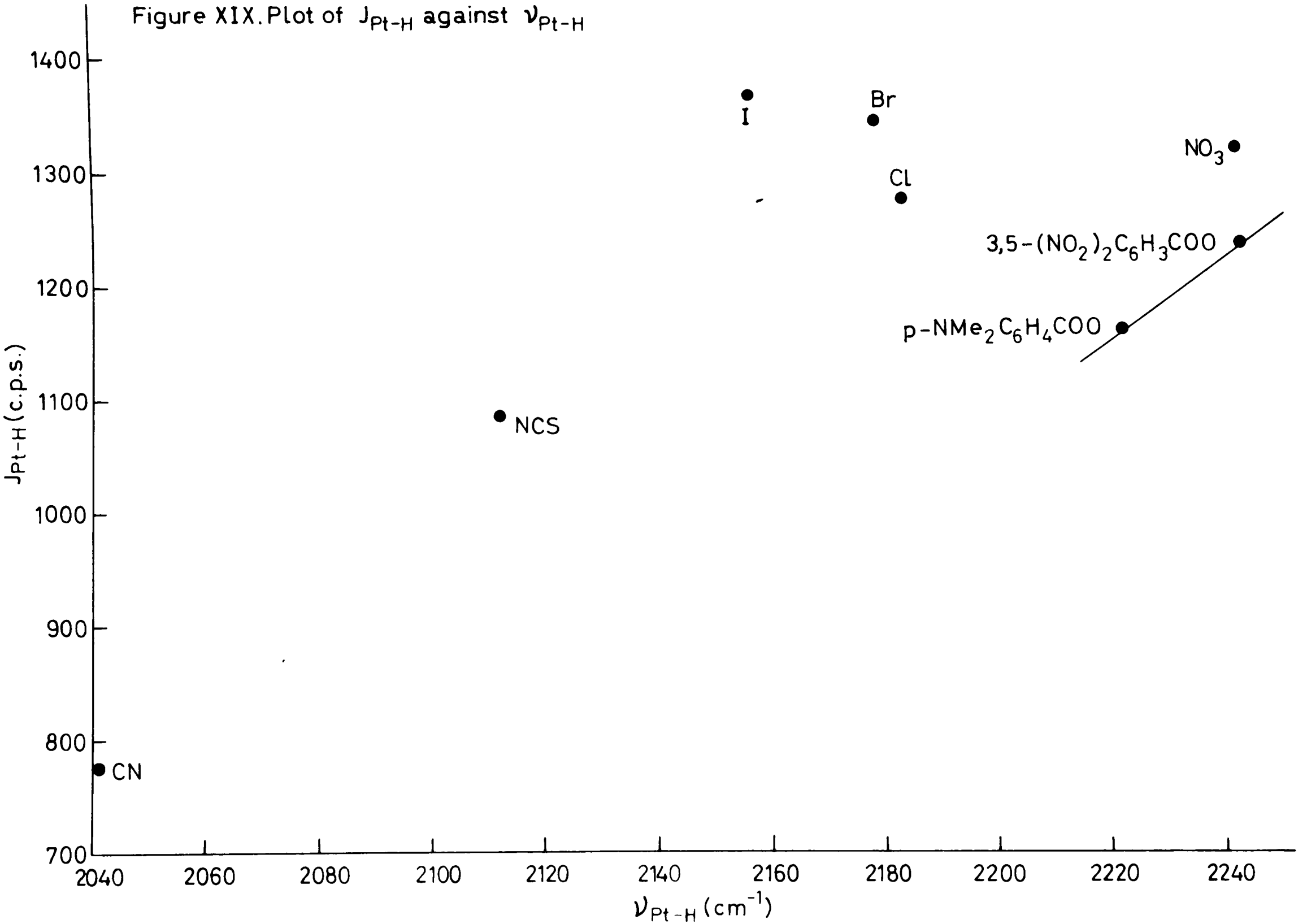


Figure XIX. Plot of J_{Pt-H} against ν_{Pt-H}



to predict. Even if this were known the effect of the changes on the actual quantity $^3\Delta E$ is unascertainable without knowledge of the coefficients C_{ks_x} for the related molecular orbitals.

However the coupling constants of the series of hydrides(II) decrease in the order of the trans-ligand in the spectrochemical series. To illustrate this fact further J_{Pt-H} is plotted against the inverse of the first ligand field band, $^1/_{\Delta E}$, in the series of complexes $[Co(NH_3)_5X]^{2+}$, (see Figure XX). The quantities plotted are given in Table XIX.

The theoretical significance of this correlation is obscure. It must be remembered that the Fermi contact term is concerned solely with excitations between σ-orbitals only two of which, namely

$$\Psi(d_{x^2-y^2}) \rightarrow \Psi^1(d_{x^2-y^2})$$
$$\Psi(d_{z^2}) \rightarrow \Psi^1(d_{z^2})$$

can be considered to have ligand field characteristics. The transitions observed for the cobalt cations $[Co(NH_3)_5X]^{2+}$, are ligand field excitations from filled π- to empty σ- orbitals.

Perhaps the conclusion can be drawn that it would be rash to neglect the effect of the variation of the relevant excitation energies on the size of metal hydrogen

Table XIX

Pt-H for trans-$Pt(PEt_3)_2$ HX and ΔE for $[Co(NH_3)_5X]^{2+}$ (73a)

X	Pt-H(c.p.s.)	ΔE (kK)	$(\Delta E)^{-1} \times 10^2$
I	1369	17.2	5.81
Br	1346	18.2	5.50
Cl	1275	18.7	5.35
CF_3COO	1286	19.9	5.03
$3,5-(NO_2)_2C_6H_3COO$	1237	19.8	5.05
$p-NO_2C_6H_4COO$	1210	19.8	5.05
C_6H_5COO	1179	19.8	5.05
$p-MeOC_6H_4COO$	1172	19.9	5.03
-NCS	1086	20.1	4.98
-ONO	1003	21.9	4.57
CN	778	22.1*	4.53

*Value estimated from those found for $[Co(CN)_6]^{3-}$ and $[Co(NH_3)_6]^{3+}$

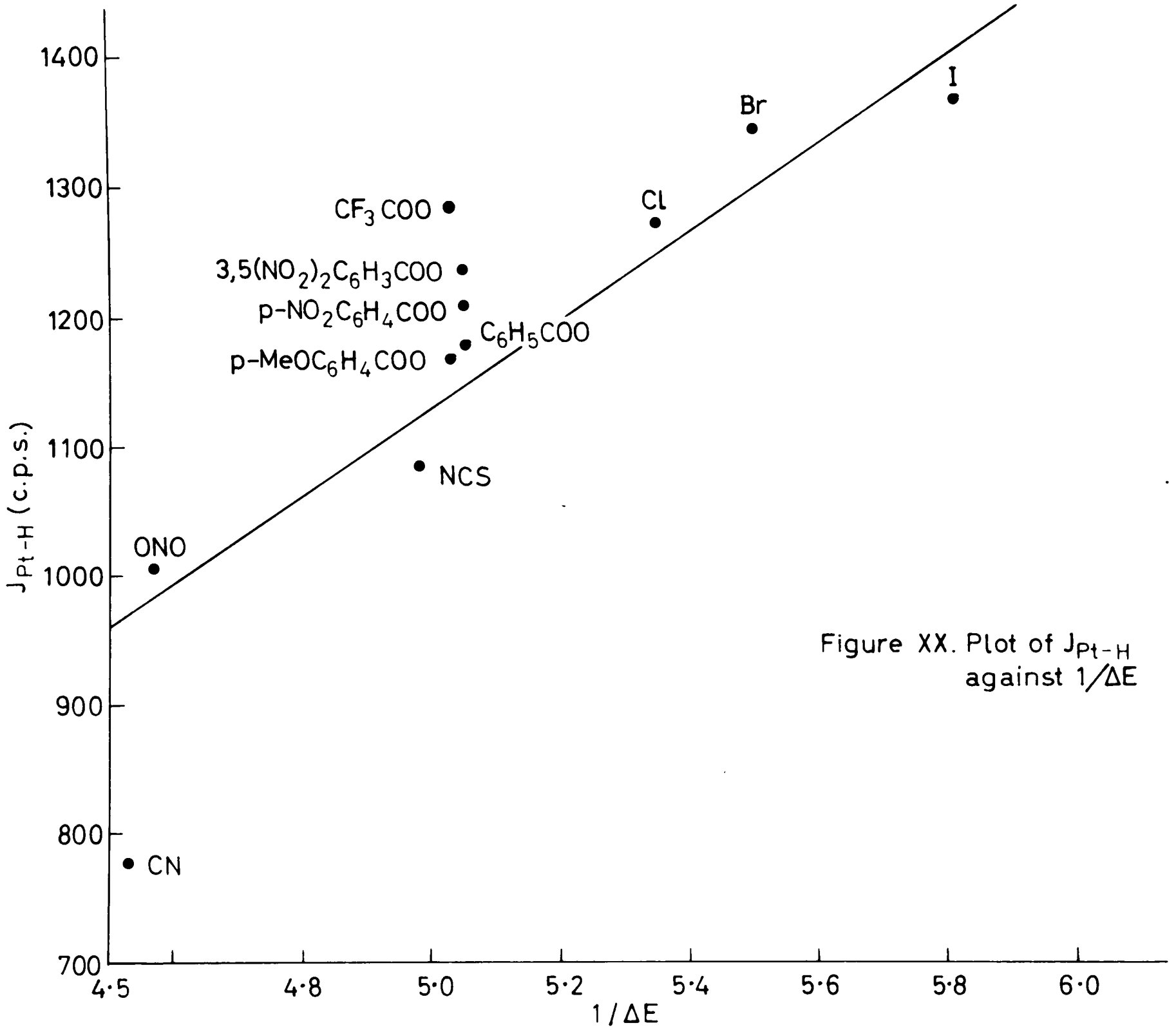


Figure XX. Plot of J_{Pt-H} against $1/\Delta E$

coupling constants.

It is interesting to note that this ligand field band remains almost unchanged in the series of carboxylato cobalt compounds.

E. Platinum-phosphorus coupling constants

Pidcock, Richards and Venanzi have measured J_{Pt-P} for twenty-five platinum complexes (57) and have attempted to rationalize the data found in terms of Pople and Santry's expression for the contact contribution. They deal with the relevant terms in the following way.

When the complexes differ just by a halide ligand the relative sizes of J_{Pt-P} is found to be

$$J_{Pt-P}(Cl) > J_{Pt-P}(Br) > J_{Pt-P}(I).$$

They associate the mean excitation energy term with the lowest energy ligand field transitions and thus the trend in coupling constants predicted from variation in E is opposite to that found. They conclude that variations in $^3\Delta E^{-1}$ are dominated by changes in the other parameters. Even if this conclusion were valid for such related series of complexes as they attempt to establish it for, it seems that to extend it to cases of comparison of J_{Pt-P} between the classes of cis- and trans- four coordinate and six coordinate platinum complexes is inadmissible.

Neglect of variation of the s-electron density at the platinum nucleus is justified by the following argument:- "As in the square-planar platinum(II) complexes the platinum 6s-orbital is shared by four

bonds while in the octahedral platinum(IV) complexes it is shared by six, the s-characters of the platinum hybrids in the cis- and trans- $PtCl_4(Bu_3P)_2$ will be about two-thirds of those in the corresponding cis- and trans- $PtCl_2(Bu_3P)_2$. The ratio of the coupling constant are found to be $J_{Pt(IV)}/J_{Pt(II)} = 0.59$ and 0.61 for cis- and trans- isomers respectively." However it is then pointed out that the compound $PtClCH_3(PEt_3)_2$ must share a mutual $\langle 6s \mid (\tilde{r}_{Pt}) \mid 6s \rangle$ term. This compound shows the presence of two chemically distinct phosphorus resonances with coupling constants with the platinum of 4179 and 1719 c/sec. These variations are attributed to variations in s-character of the bond. If variations of this magnitude can occur in the s-character of the platinum phosphorus bond it is surely largely fortuitous that the ratios found for $J_{Pt(IV)}/J_{Pt(II)}$ are of the order of 0.667.

We therefore conclude that Pidcock, Richards and Venanzi are unjustified in interpreting their results solely in terms of s-component of the platinum-phosphorus bond.

It is of interest in relation to the solvent effects found for the nuclear magnetic resonance spectra of the complexes(I) that the platinum phosphorous coupling

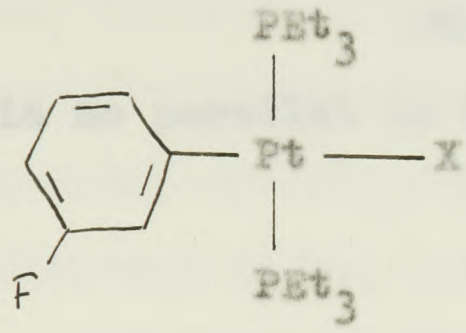
constants are also solvent dependent. However $^{1}J_{Pt-P}$ increases on passing from chloroform to cyclohexane.

$$^{1}J(CHCl_3) < {}^{1}J(C_6H_6) < {}^{1}J(CCl_4) < {}^{1}J(C_6H_{12}) < {}^{1}J(Et_2O)$$

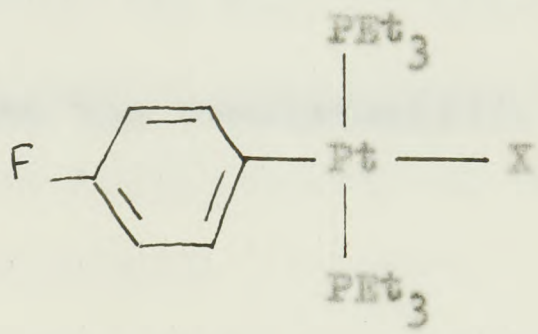
This trend is in the reverse direction to that found for the hydrides.

F. Shielding in m- and p-fluorophenylplatinum(II) complexes

Parshall has determined the F^{19} nuclear magnetic resonance of a series of m- and p-fluorophenylplatinum(II) complexes, (III, IV)



III



IV

The F^{19} shielding parameter is a very sensitive criterion of the electronic nature of the substituent on the aromatic ring. The shielding of the m-fluoro atom is taken as a criterion of the σ -donor power of X, and an order of donor strength is obtained for acetone solutions

$$\begin{matrix} & \text{OCN} & & & & \text{SCN} & \\ \text{or NCO} & > & \text{CN} > \text{Cl} > \text{Br} > & & \text{or NCS} & > & \text{I} \end{matrix}$$

and for cyclohexane solutions

$$\begin{matrix} & & & \text{OCN} & & & \text{SCN} \\ \text{CN} > \text{Cl} > & & & & > \text{Br} > \text{I} > & & \\ & & \text{or NCO} & & & \text{or NCS} & \end{matrix}$$

These parallel neither the sequence for chemical shifts nor the sequence for coupling constant found for the complexes(II).

A π-acceptor capacity of the ligand X is equated with the difference in shielding of the para- and meta-complexes (σ IV- σ III). The order of increasing π-acceptor capacity is found to be

$$Cl \sim I < Br < \underset{\text{or NCO}}{OCN} < \underset{\text{or NCS}}{SCN} < CN$$

Again no parallel is found with the complexes(II).

G. General conclusions

The variations of chemical shift and coupling constant for the hydrido ligands in the complexes(I) can be rationalized in terms of variation of metal-hydrogen distance and variation in s-character of the metal-hydrogen bond, respectively. However in the case of the coupling constant it has proved impossible to exclude the possible relevance of variation of s-electron density at the nuclei and in the relevant excitation energies.

Attempts to extrapolate the correlations found for the complexes(I) to the closely related complexes(II) are moderately successful for the chemical shift data but fail palpably for explanation of the coupling constant in terms of s-character of the bond alone.

This failure of the extrapolation of the results found for the complexes(I) to the complexes(II) is an indication that deductions drawn as to the electronic significance of nuclear magnetic resonance data for the one set of complexes(I) cannot be applied justifiably to data for the other set of complexes(II), in spite of their apparent chemical similarity. The nuclear magnetic resonance experiment is sensitive to several different features of the electronic wave function and the isolation of any one of these does not appear to be feasible.

CHAPTER V

EXPERIMENTAL

A. General

a) Analyses for carbon, hydrogen, nitrogen, oxygen and halogens were carried out by Dr. Bernhardt of the Max-Planck Institute, Mullheim, Germany. Samples were submitted sealed under vacuum and wrapped in black paper to exclude light. Analytical results are given in Tables XX and XXI.

b) Acid washed alumina was prepared by boiling alumina (1000 g.) with dilute hydrochloric acid (4000 ml.), washing until chloride free and finally drying at 180°C for four hour s.

The ether used for the preparation of triethyl-phosphine was dried over sodium wire for one week.

The solvents used for nuclear magnetic resonance and infrared spectroscopy were:-

i) chloroform, "special for spectroscopy"

ii) cyclohexane, "special for spectroscopy".

iii) benzene "for molecular weight determinations".

iv) AnalaR acetone which was dried over 4A molecular sieves.

B. Preparations

Triethylphosphine

Triethylphosphine was prepared following the proceedure of Goodfellow (74). Owing to the obscurity of the reference full experimental details are given below.

The apparatus shown in Figure XXI was used for the preparation of triethylphosphine. A dry ice condensor in addition to a Liebig condensor, was found to be necessary for refluxing the ether.

Ethylmagnesiumbromide was prepared under nitrogen. Dry ethyl bromide (190.5 ml., 2.7 moles) in dry ether (500 ml.) was slowly added from the tap funnel to magnesium turnings (60 g., 2.5 moles) in dry ether (750 ml.) When the addition was complete, the solution was refluxed for thirty minutes. During this process additional ether was added, if necessary.

The reaction mixture was then cooled to -60°C in an acetone/carbon dioxide bath and a cold solution of phosphorus trichloride (58.5 ml., 0.7 moles) in dry ether (500 ml.) was added dropwise from the tap funnel with vigorous stirring. The mixture was then allowed to warm up to 0°C. and stood in ice. For hydrolysis a cold solution of ammonium chloride (500 g.) in water

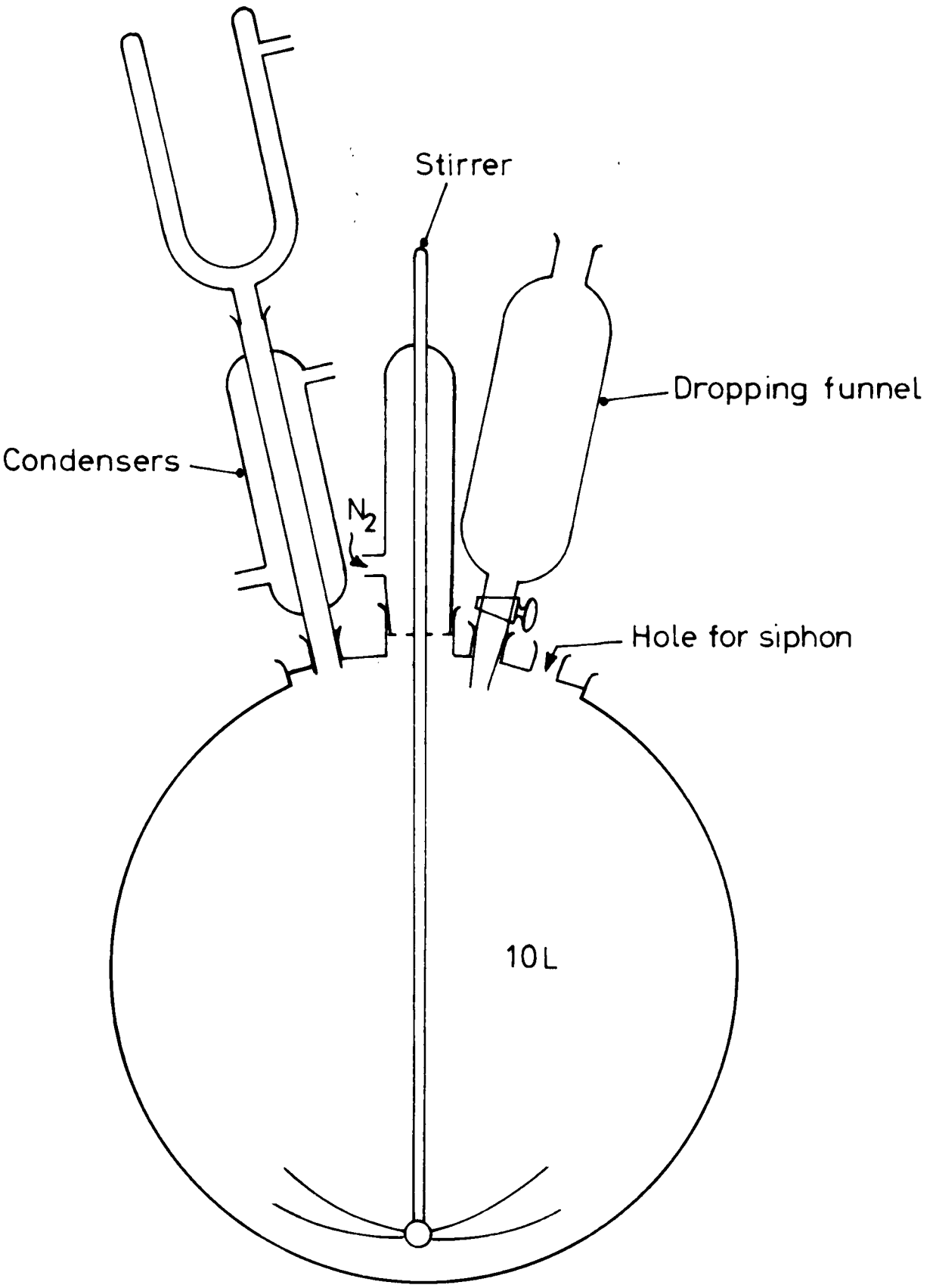


Figure XXI. Apparatus for the preparation of PEt_3

(2000 ml.) was added, slowly at first but rapidly to finish. The solution was then stirred for one hour. The siphon tube was put into the reaction flask and connected to a flask containing sodium sulphate (200 g.) The whole was flushed with nitrogen and the siphon started by blocking all exits to the reaction flask and increasing the nitrogen pressure. The ether layer was siphoned off and the aqueous layer extracted with two 500 ml. volumes of ether. The ether solution was left to dry under nitrogen for thirty six hours.

The solution was then siphoned into a dropping funnel which was connected to a distillation apparatus and the ether was distilled off under nitrogen, see Figure XXII.

The remaining solution was transferred to a smaller distillation apparatus and triethylphosphine was distilled over between 128°-131° at atmospheric pressure, see Figure XXIII.

The triethyl phosphine was transferred to phials and sealed off. Yield (37.4 g., 0.317 moles) 45%.

cis-Dichlorobis(triethylphosphine)platinum(II)

The complex cis-dichlorobis(triethylphosphine)-platinum(II) was prepared from sodium chloroplatinite tetrahydrate and triethylphosphine by the method of Chatt and Venanzi (75). The yield from 35.7 g. of

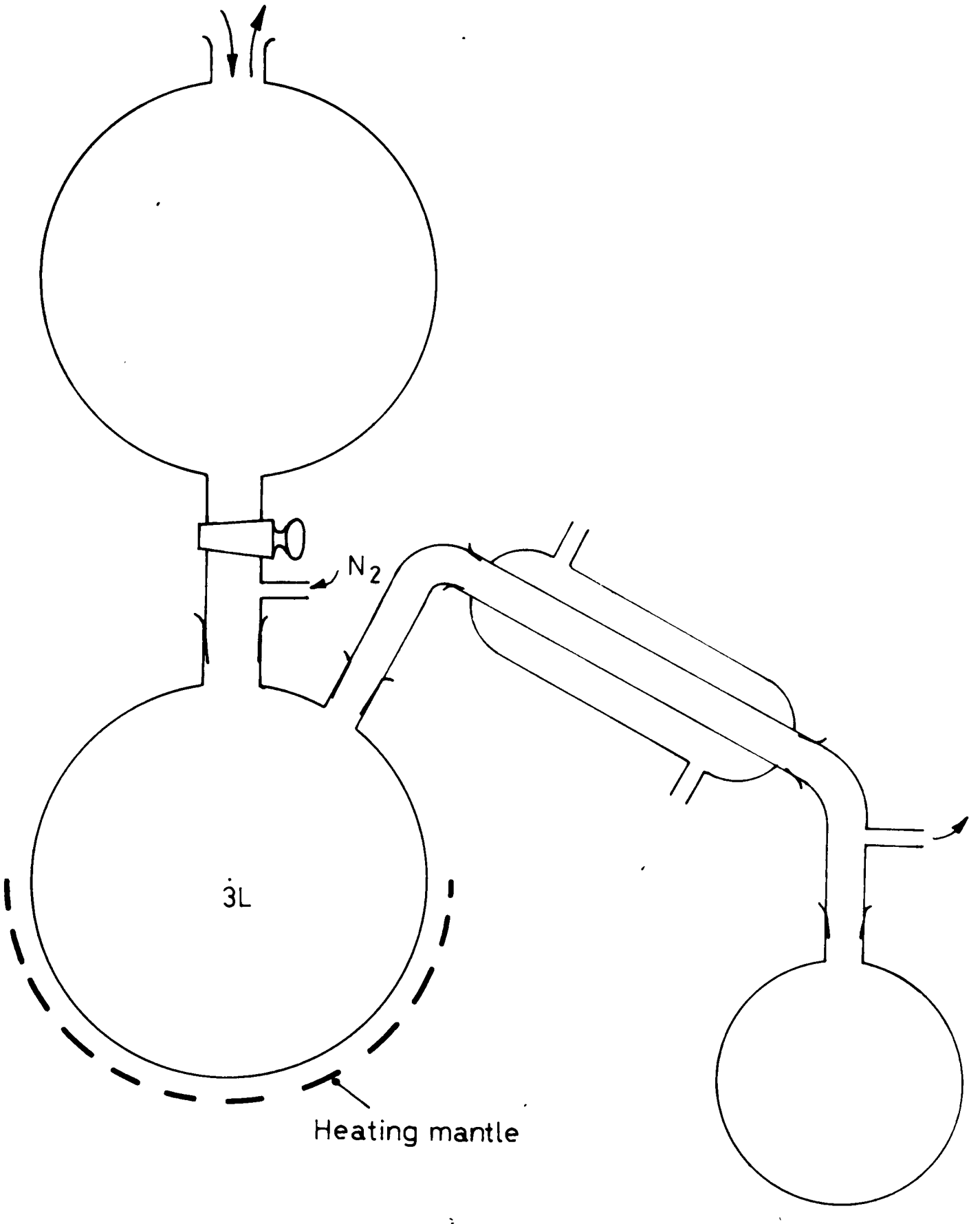


Figure XXII . Distillation of Ether

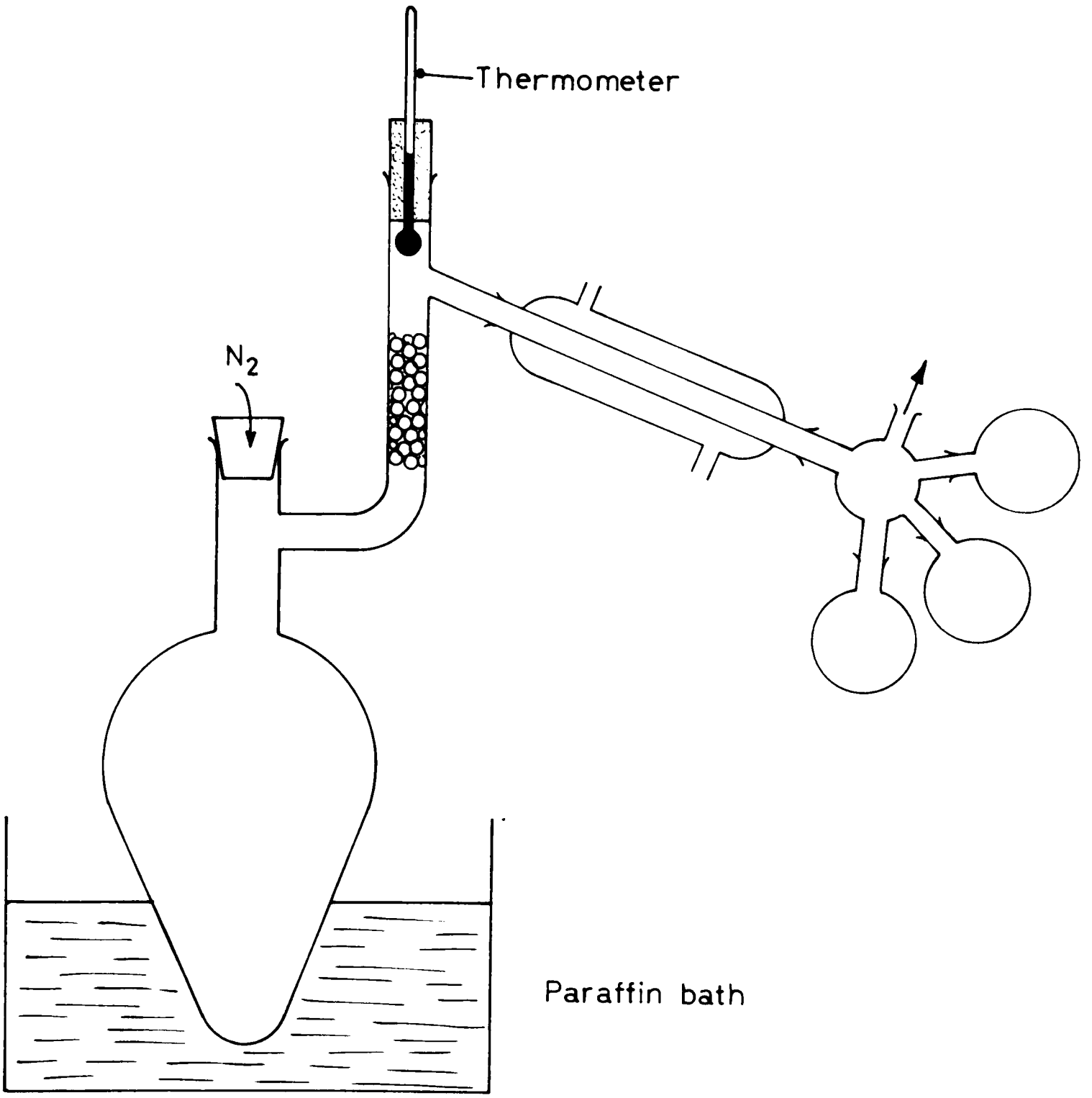


Figure XXIII. Distillation of PEt_3

sodium chloroplatinite tetrahydrate was 60% (24.3 g.) of the desired compound.

trans-Hydridochlorobis(triethylphosphine)platinum(II)

The complex trans-hydridochlorobis(triethylphosphine)-platinum(II) was prepared by reduction of cis-dichlorobis(triethylphosphine)platinum(II) with hydrazine in the manner described by Chatt and Shaw (21). The yield from 9.8 g. of cis-dichlorobis(triethylphosphine)platinum(II) was 91% (8.3 g.) of the desired compound.

Preparation of silver salts of organic carboxylic acids

Most of the silver salts of thesubstituted benzoic acids were prepared in the following manner. The acid (3 g.) was dissolved in water (20 ml.) to which was added 0.880 ammonia. The solution was heated to drive off excess ammonia, and then cooled. A strong solution of silver nitrate in water was added cautiously to the solution of ammonium salt, while stirring the solution, until precipitation appeared complete. The solution was then filtered; the precipitate was washed thoroughly with water, then with acetone and was dried under vacuum for twelve hours.

The silver salt of 2,4,6-trinitrobenzoic acid was prepared in a similar fashion but was not dried due to possible explosion hazard. Instead the precipitate

was washed with methanol and allowed to remain damp.

Silver trifluoracetate was prepared by treating silver carbonate with trifluoracetic acid and evaporating the resulting mixture to dryness.

Silver trichloracetate was prepared by reaction of excess silver carbonate with an aqueous solution of trichloracetic acid, followed by extraction of the resulting solution with ether. The silver salt was obtained by reducing the ethereal extract under vacuum and by allowing to crystallize.

The remaining substituted acetates were prepared by the general method given above.

Preparation of the trans-hydridoacidobis(triethylphosphine)-platinum(II) complexes

Essentially the same proceedure was used for the preparation of all these compounds. Two typical methods are given below. Method II was used only in those cases where the silver salt of the organic acid is soluble in ether, for example for the trifluoracetato and trichloracetato derivatives.

Method I. trans-Hydridop-bromobenzatobis(triethyl-phosphine)platinum(II)

A solution of trans-hydridochlorobis(triethylphosphine)-platinum(II) (1g., 0.00214 moles) in methanol (15 ml.) was

placed in a centrifuge tube (50 ml.) and cooled in liquid nitrogen to about -30°C. A suspension of silver p-bromobenzoate (0.69 g., 0.00224 moles) in methanol (10 ml.), cooled in a similar fashion, was added to the hydride solution. The mixture was shaken vigorously for two to three minutes and then was rapidly centrifuged to remove the silver chloride precipitate. The supernatant liquid was decanted and evaporated to dryness under vacuum. The resulting dirty brown solid was extracted with 40°-60° petrol and centrifuged. The clear solution was separated from insoluble residues and cooled until white crystals separated. These were isolated by centrifuging and finally recrystallized from 40°-60° petrol. Yield (1.2 g., 0.0019 moles) 89%.

Method II. trans-Hydridotrifluoracetatobis(triethylphosphine)platinum(II)

trans-Hydridochlorobis(triethylphosphine)platinum(II) (1 g., 0.00214 moles) in diethylether (15 ml.) was placed in a centrifuge tube (50 ml.) and cooled in liquid nitrogen to about -30°C. A solution of silver trifluoracetate (0.4959, 0.00224 moles) in ether (10 ml.) was cooled in a similar fashion, added to the hydride solution and the mixture vigorously shaken. The mixture

was then centrifuged and the product extracted and purified as given in Method I.

General Notes

The purification proceedure was modified from preparation to preparation according to the nature and relative solubility of the impurities. When the products were insoluble in petrol, petrol/ether mixtures were used for recrystallization. Under these circumstances yellow oils frequently accompanied the desired product but could usually be removed by repeated cooling and centrifuging. Occasionally chromatography on alumina was used, the column being made up in petrol and eluted with petrol/ether mixtures. Colloidal metal was sometimes present as impurity and this was removed by filtering through an alumina column made up in petrol.

Yields varied between 50% and 90% of the theoretical yield and were occasionally lower, for example trans-hydridobenzoatobis(triethylphosphine)platinum(II) co uld only be prepared in very low yields.

As the silver 2,4,6-trinitrobenzoate has been left wet with methanol, the amount required for the reaction had to be estimated by titration. A suspension of a known weight of the wet silver salts was titrated

Table XX

Analytical and molecular weight data on complexes (I)

$Pt(PEt_3)_2HL$ where L=	Carbon Calc.	Carbon Found	Hydrogen Calc.	Hydrogen Found	Nitrogen Calc.	Nitrogen Found	Halogen Calc.	Halogen Found	Molecular weight Calc.	Molecular weight Found
*CF_3COO (a)	30.80	30.70	5.72	5.72					545.5	562
*$CH\ Cl_2COO$	29.98	30.16	5.75	5.72			12.65	10.35	560.4	
*$CH_2Cl\ COO$	31.95	31.74	6.32	6.21			6.74	6.70	525.9	
*$CH_2OPh\ COO$	41.14	40.41	6.56	6.55					583.5	
*m-F C_6H_4COO	39.90	40.16	6.17	6.30					571.5	565
m-Cl C_6H_4COO	38.78	38.91	5.99	6.03			6.03	5.97	588.0	590
*p-Cl C_6H_4COO	38.78	39.03	5.99	6.18			6.03	5.84	588.0	589
*O-Cl C_6H_4COO	38.78	37.94	5.99	5.92			6.03	4.89	588.0	587
m-BrC_6H_4COO	36.06	36.21	5.57	5.78			12.63	12.49	632.4	654
*p-Br C_6H_4COO	36.06	36.24	5.57	5.48			12.63	12.37	632.4	641
O-Br C_6H_4COO	36.06	36.28	5.57	5.72			12.63	12.49	632.4	631
m-I C_6H_4COO	33.56	33.44	5.19	5.31			18.68	18.55	679.4	677
p-I C_6H_4COO	33.56	33.79	5.19	5.49			18.68	18.56	679.4	697

m-$NO_2C_6H_4COO$	38.10	37.88	5.89	6.16	2.34	2.54	598.5	602
p-$NO_2C_6H_4COO$	38.10	37.86	5.89	5.78	2.34	2.51	598.5	579
o-$NO_2C_6H_4COO$	38.10	38.19	5.89	6.00	2.34	2.53	598.5	616
*m-MeC_6H_4COO	42.30	42.60	6.74	6.84			567.5	583
*p-MeC_6H_4COO	42.30	42.22	6.74	6.56			567.5	553
p-$MeOC_6H_4COO$	41.14	41.51	6.56	6.73			583.5	581
p-CNC_6H_4COO	41.49	41.72	6.09	6.22	2.42	2.52	578.5	
m-$Me_2NC_6H_4COO$	42.25	42.03	6.92	6.93	2.34	2.45	596.6	614
p-$Me_2NC_6H_4COO$	42.25	42.08	6.92	6.88	2.34	2.42	596.6	602
3,5-$(NO_2)_2C_6H_3COO$	35.44	35.55	5.32	5.48	4.35	4.23	643.5	650
2,5-$(NO_2)_2C_6H_3COO$	35.44	35.61	5.32	5.52	4.35	4.23	643.5	688
2,4,6-$(NO_2)_3C_6H_2COO$	33.12	33.36	4.83	4.99	6.10	6.31	688.5	688

(a) Oxygen analysis: calc.5.86, found 6.10

* denotes ready solubility in petrol.

against N/5 hydrochloric acid using fluorescein indicator. The weight of wet salt required for the reaction could then be estimated.

Preparation of trans-chlorodeuteridobistriethylphosphine-platinum(II)

The hydride trans-$Pt(PEt_3)_2HCl$ (1 g.) in tetrahydrofuran (2 ml.) was treated with a little hydrogen chloride gas which precipitated out the dehydride $Pt(PEt_3)_2H_2Cl_2$. The mixture was treated with deuterium oxide (2 ml.) and warmed to 80°C for thirty minutes. The solvent was removed under vacuum, a further 1 ml. of tetrahydrofuran and 1 ml. deuterium oxide were added to the residue and the mixture was warmed to 80°C for four hours.

Removal of the solvent and recrystallization of the residue from light petroleum gave a 8:2 mixture of trans-$Pt(PEt_3)_2DCl$ and trans-$Pt(PEt_3)_2HCl$ which was used for the deuterium magnetic resonance experiment. The percentage purity of the deuteride was estimated both from ^1H nuclear magnetic resonance and from the infrared spectrum.

Preparation of carboxylatopentamininecobalt(III) salts

The method used is essentially that described by Gould and Taube (76). The principle of the method is

the displacement of the aquoligand from the complex $[Co(NH_3)_5H_2O]^{3+}$ by the carboxylato anion. The chief problem of the method is that in order to prevent decomposition of the pentammino complex, the pH of the solution should be between 4 and 6. However many of the carboxylic acids are only moderately or slightly soluble in dilute acid solution and hence sufficient concentration of anion may be difficult to obtain at these pH values. At elevated temperatures the solubility of the carboxylic acid increases. Therefore a typical preparation is to treat a hot saturated solution of the pure $[Co(NH_3)_5H_2O](ClO_4)_3$ in water with a hot saturated solution of a 1:1 mixture of the sodium salt of the carboxylic acid and the acid itself, and warm the mixture for one hour. The carboxylato complexes crystallized on cooling and were purified by recrystallizing from hot 1M $HClO_4$. They were dried by washing with ethanol, ether and finally in vacuum. Yield of the pure complexes was 15-25%. They were characterized by analysis, the results of which are given in Table XXI.

Table XXI

Analytical data on the complexes $[Co(NH_3)_5L](ClO_4)_2$

L =	Carbon		Hydrogen	
	Calculated	Found	Calculated	Found
C_6H_5COO	18.11	18.04	4.31	4.44
CF_3COO	5.26	5.44	3.29	3.44
$3,5\text{-}(NO_2)_2C_6H_3COO$	15.17	15.33	3.25	3.42
$p\text{-}CH_3OC_6H_4COO$	19.44	19.25	4.45	4.58
$p\text{-}NO_2C_6H_4COO$	16.51	16.45	3.73	3.86

C. Instrumental Methods

Proton Magnetic Resonance

Proton magnetic resonance spectra were measured using a Japan Electron Optics Laboratory 100 megacycle instrument (JNM 4H-100). Pyrex spinning tubes of outside diameter 5 mm. were used.

Samples were prepared by dissolving about 0.3 gm. of the purified compound in 0.6 mls. of solvent, filtering the solution through a small glass sinter with the aid of nitrogen pressure and collecting the solution in the nuclear magnetic resonance tube. Three drops of tetramethylsilane were then added as a standard and a polythene cap was placed on the tube.

The positions of the peaks in the hydrido multiplet were measured by means of superimposition of bands. A sideband of the tetramethyl silane signal was arranged to coincide with the peak to be measured. Its position was varied by 0.2 c.p.s. intervals and the weight of the superimposed signal observed. Exact coincidence was taken to occur when the signal had maximum weight. Several runs were carried out increasing and decreasing the frequency of the tetramethysilane sideband.

An independent check on the accuracy of this method was possible as for both $\mathcal{J}_{P-H}$ and $\mathcal{J}_{Pt-H}$ the positions

of three peaks could be used to give information on one coupling constant. The errors indicated were usually less than 1 c.p.s. and they are given in Table X.

The proton spectrum below 10 τ was recorded and calibrated using a control locking system. The tetramethyl silane signal was again used as the reference.

The deuterium resonance measurements were made using a Varian Wide-Line nuclear magnetic resonance spectrometer (V4200B). The coupling constant and chemical shift were plotted by sweeping the radio-frequency near to 7.5 Mc./sec. and 9.25 Mc./sec. The frequencies at which the peaks appeared were determined successfvely twelve times and the sets of readings plotted against the time of observation. It was thus possible to correct for magnetic field drift. The measurements were carried out by Dr. Gary Haller.

Infrared spectroscopy

The region 4000-625 cm^{-1} was studied using an Infracord 337. The samples were measured in the form of Nujol mulls between sodium chloride plates. The spectra were calibrated using a polystyrene film.

The region 625-70 cm^{-1} was investigated on a Beckmann IR 11 machine. Samples were again measured as Nujol mulls but in this case polythene plates were used. The instrument was self calibrating.

Solution spectra were measured on a Perkin Elmer 221 spectrometer. Solutions of concentration about 10 mg in 0.1 ml were used and inserted in a solution cell, thickness 1 mm with sodium chloride windows. The spectra were calibrated by measuring the carbon dioxide of the atmosphere by a single beam.

Molecular weights

Molecular weights were measured on a Mechrolab osmometer by Mr. C.A. McAuliffe. Benzene solutions of concentration 0.02-0.04 M were used.

Mass spectrum

The mass spectrum was determined on an MS.9 by Dr. Aplin of the Dyson Perrins Laboratory.

Ultraviolet spectroscopy

Ultraviolet and visible spectra were run on a Unicam SP 700. Aqueous solutions in silica cells were employed.

CHAPTER VI

Variation-perturbation method for calculation of the shielding tensor

A. Introduction

An attempt has been made to calculate the contribution to the shielding constant of a hydrogen nucleus directly attached to platinum, due to the 5-d electrons. Buckingham and Stevens (50,51) have attributed the greater part of the high field shift of transition metal hydrides to this cause. Buckingham and Stephens' calculation gave reasonable values for the chemical shift, the magnitude being dependent on ΔE the energy separation of the ground and excited states, R_H the metal-hydrogen internuclear distance, and k a factor of the d-orbital exponent. The methods of Stephens (77) and Karplus and Kolker (78, 79) for the calculation of shielding constants for first and second row diatomics are based on variation-perturbation theory where instead of expansion of the perturbed wave function in terms of the excited states of the molecule, a polynomial is introduced to represent the perturbed wave function and the coefficients of the polynomial and hence the shielding constant found by minimization of the energy. The calculation below employs this method for calculation of the shielding constant.

B. The Hamiltonian and consideration of the effect of gauge transformation

The Hamiltonian $\mathcal{H}$ for the electrons of the system is

$$\mathcal{H} = \frac{1}{2m} \sum_k (p_k + \frac{e}{c} \tilde{A}_k)^2 + V_{H.F.} \qquad (1)$$

where $\tilde{A}_k$ is the vector potential and $V_{H.F.}$ the Hartree-Fock effective potential. If a change of gauge is made in order to simplify $\mathcal{H}$, the Schrödinger equation must be invariant to this transformation. That is if the original Schrödinger equation is represented by

$$\mathcal{H} \Psi = E \Psi \qquad (2)$$

the eigen functions Ψ' of the new Hamiltonian $\mathcal{H}'$ must be such that

$$\mathcal{H}' \Psi' = E \Psi' \qquad (3)$$

For a gauge transformation

$$A \rightarrow A' = A + \nabla \lambda \, c/e \qquad (4)$$

where λ is any scalar, it may be shown that

$$\Psi \rightarrow \Psi' = \Psi \, e^{\lambda / i\hbar} \qquad (5)$$

If Ψ has the form

$$\Psi = \Psi_o \exp (\Lambda / i\hbar) \qquad (6)$$

where Ψ_o and Λ are real, if the gauge is changed from A to A'

$$\Psi_o \, e^{\Lambda/i\hbar} = \Psi \rightarrow \Psi' = \Psi_o \, e^{(\Lambda + \lambda)/i\hbar} \qquad (7)$$

thus $\Psi_o \rightarrow \Psi_o$ and $\Lambda \rightarrow \Lambda + \lambda$. When both Λ and λ

are small

$$\psi \approx \psi_0(1 + \frac{\Lambda}{i\hbar}) \rightarrow \psi_0(1 + \frac{\Lambda}{i\hbar} + \frac{\lambda}{i\hbar}) \qquad (8)$$

Consequently if any change of gauge is made in the Hamiltonian $\mathcal{H}$, a corresponding change must be made in Λ to $\Lambda + \lambda$, where λ may be obtained from

$$\nabla \lambda = \frac{e}{c}(\tilde{A}' - \tilde{A}) \qquad (9)$$

The vector potential is taken initially as

$$\tilde{A}_k = \frac{1}{2}\tilde{H} \times \tilde{r}_{Hk} + \frac{\tilde{\mu}_H \times \tilde{r}_{Hk}}{r_{Hk}^3} \qquad (10)$$

The Hamiltonian may then be expanded, dropping the subscripts k for simplicity and retaining terms up to those bilinear in H and μ, as

$$\mathcal{H} = \frac{1}{2m} p^2 + V_{H.F.} + \frac{e}{2mc} \tilde{H} \times \tilde{r}_H \cdot \tilde{p} + \frac{e}{mc} r_H^{-3} \tilde{\mu}_H \times \tilde{r}_H \cdot \tilde{p} +$$

$$\frac{e^2}{2mc^2} r_H^{-3}(\tilde{H} \times \tilde{r}_H).(\tilde{\mu}_H \times \tilde{r}_H)$$

$$= \mathcal{H}_0 + \frac{e}{2mc} \tilde{H}.\tilde{L}_H + \frac{e}{mc} r_H^{-3} \tilde{\mu} .\tilde{L}_H + \frac{e^2}{2mc^2} r_H^{-3} H^\alpha \mu^\beta$$

$$(\delta^{\alpha\beta} r_H^2 - r_H^\alpha r_H^\beta) \qquad (11)$$

where $\tilde{L}_H = \tilde{r}_H \times \tilde{p}$

The energy of a molecule in the presence of a magnetic field H, to terms bilinear in μ and H, can be written as

$$E = E_0 - \mu_\alpha H_\alpha + \mu_\alpha H_\beta \sigma_{\alpha\beta} \qquad (12)$$

is a tensor describing the shielding of the magnetic nucleus by the electrons. The shielding in solution is

given by an average of $\sigma_{\alpha\beta}$ over all directions i.e.

$$\sigma = \frac{1}{3}(\sigma_{11} + \sigma_{22} + \sigma_{33})$$

C. Choice of wave functions

Following Karplus and Kolker (78), the ground state wave function, $\bar{\Psi}^{\circ}$, was taken to have the form of a single determinant

$$\bar{\Psi}^{\circ}(1,2 \text{ ---} 2n) = (2n!)^{-\frac{1}{2}} \left| \phi_1^{\circ}(1)\, \phi_2^{\circ}(2) \text{ ---} \phi_{2n}^{\circ}(2n) \right| \quad (13)$$

where $\phi^{\circ}_{(2i-1)}$ and ϕ°_{2i} are identical except $\phi^{\circ}_{(2i-1)}$ has α spin and ϕ_{2i} has β spin. As this is not a true solution of the unperturbed Hamiltonian, $\mathcal{H}^{\circ}$, a model system with a Hamiltonian $\mathcal{H}_a^{\circ}$ is in fact being considered, where

$$\mathcal{H}_a^{\circ}\ \bar{\Psi}^{\circ} = E_a^{\circ}\ \bar{\Psi}^{\circ}$$

The errors involved in this have been discussed by Karplus and Kolker (78).

The perturbed wave function is taken as

$$\bar{\Psi}^{1} = \sum_i \bar{\Psi}_i^{1} \quad (14)$$

$$\bar{\Psi}_i^{1} = (2n!)^{-\frac{1}{2}} \left| \phi_1^{\circ}(1) \text{ --- } \phi^{\circ}_{(i-1)}(i-1)\, \phi_i^{1}(i)\, \phi^{\circ}_{(i+1)}(i+1) \text{ ---- } \phi^{\circ}_{2n}(2n) \right| \quad (15)$$

$$\phi_i^{1} = \phi_i^{\circ}(i)\left[1 + (e/2mc)\,\tilde{H}.\tilde{r}i + (e/mc)\,\tilde{\mu}_{N.}\tilde{g}i\right] \quad (16)$$

One consequence of taking this product form for ϕ_i^{1} is that two electron integrals do not occur in the energy expression (78). However it is restrictive in the sense that nodes in the unperturbed orbitals are reproduced in

the perturbed orbitals.

If the expression

$$i\hbar \left[(e/2mc)\, \tilde{H}.\tilde{f}i + (e/mc)\, \hat{\mu}_N.\tilde{g}i\right]$$

is sufficiently small it may be equated to Λ and ϕ_i^1 considered to have the form given in (6).

$$\phi_i^1 = \phi_i^0 \exp\left(\Lambda/ih\right)$$

D. Expression for the shielding constant

Following Karplus and Kolker (79) terms which contain $\mu_\alpha H_\beta$ are extracted from the energy expressions

$$E_a^{\,1} = \langle \bar{\Psi}_a^{\,0} | \mathcal{H}^1 | \bar{\Psi}_a^{\,0} \rangle \tag{17}$$

$$E_a^{\,2} = \sum_{i=1}^{2n} \sum_{i=1}^{2n} \langle \bar{\Psi}_i^{\,1} | \mathcal{H}_a^{\,0} - E_a^{\,0} | \bar{\Psi}_i^{\,1} \rangle + \sum_{i=1}^{2n} \Big\{ \langle \bar{\Psi}_a^{\,0} | \mathcal{H}^1 - \Delta E_a^{\,1} | \bar{\Psi}_i^{\,1} \rangle + \langle \bar{\Psi}_i^{\,1} | \mathcal{H}^1 - \Delta E_a^{\,1} | \bar{\Psi}_a^{\,0} \rangle \Big\} \tag{18}$$

to give an expression for $\sigma_{\alpha\beta}$. This may be divided into a "diamagnetic" part which is not a function of fi and gi

$$\sigma_{\alpha\beta}^{\,D} = \frac{e^2}{2mc^2} \langle \bar{\Psi}_a^{\,0} | \sum_k \frac{(r_k^{\,2}\delta_{\alpha\beta} - r_{k\alpha}\, r_{k\beta})}{r_k^{\,3}} | \bar{\Psi}_a^{\,0} \rangle \tag{19}$$

and a "paramagnetic" part which is

$$\sigma_{\alpha|\alpha}^{\,P} = \frac{e^2}{m^2c^2} \sum_{i=1}^{n} \Big\{ -\frac{\hbar^2}{m} \langle \psi_i^{\,0} | \nabla\, fi^{\alpha|} \nabla\, gi^{\alpha} | \psi_i^{\,0} \rangle + \langle \psi_i^{\,0} | (L_H^{\alpha|}\, gi^{\alpha}) + r_H^{-3} (L_H^{\alpha|}\, fi^{\alpha}) | \psi_i^{\,0} \rangle$$

$$+ \sum_{j\neq i}^{n} \Big[\frac{\hbar^2}{2m} \big(\langle \psi_i^{\,0} | \nabla\, gi_{\cdot}^{\alpha|} \nabla | \psi_j^{\,0} \rangle - \langle \psi_j^{\,0} | \nabla\, gi_{\cdot}^{\alpha|} \nabla | \psi_i^{\,0} \rangle \big)$$

$$\langle \psi_i^{\,0} | fi^{\alpha} | \psi_j^{\,0} \rangle + \frac{\hbar^2}{2m} \big(\langle \psi_i^{\,0} | \nabla\, fi_{\cdot}^{\alpha|} \nabla | \psi_j^{\,0} \rangle -$$

$$\langle \psi_j^{\,0} | \nabla\, fi_{\cdot}^{\alpha|} \nabla | \psi_i^{\,0} \rangle \big) \langle \psi_i^{\,0} | gi^{\alpha} | \psi_j^{\,0} \rangle$$

$$+ 2\langle \psi_j^0 | L_H^{\alpha 1} | \psi_i^0 \rangle \langle \psi_i^0 | g_i^{\alpha} | \psi_j^0 \rangle$$

$$+ 2\langle \psi_j^0 | r^{-3} L_H^{\alpha 1} | \psi_i^0 \rangle \langle \psi_i^0 | f_i^{\alpha} | \psi_j^0 \rangle \qquad (20)$$

where the sum is over occupied spatial orbitals, ψ_i, rather than spin orbitals, ϕ_i, as previously. This expression is derived in Appendix V. It differs from that obtained by Karplus and Kolker (79). This is shown also in Appendix V.

The exchange terms involving ∇g_i and ∇f_i can be conveniently dropped from the expression (20) as they will be zero for d-orbitals ψ_i and ψ_j of the same exponent which we shall consider.

E. Transformation of origin

The origin of the coordinate system is now transferred from the hydrogen to the metal nucleus, see Figure XXIV.

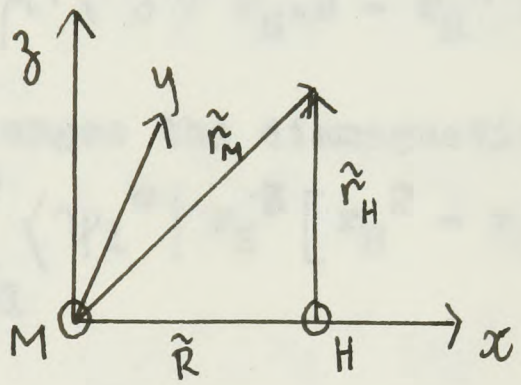


Figure XXIV

$$\tilde{r}_H = \tilde{r}_M - \tilde{R} \tag{21}$$

The new vector potential is taken as

$$\tilde{A}' = \frac{1}{2}\tilde{H} \times \tilde{r}_M + \frac{\tilde{\mu} \times \tilde{r}_H}{r_H^3} \tag{22}$$

This may be written

$$\tilde{A}' = \tilde{A} + \frac{1}{2}\tilde{H} \times \tilde{R} \tag{23}$$

Thus from (9)

$$\lambda = \frac{e}{2c}\tilde{H}.(\tilde{R} \times \tilde{r}_M) + \text{constant} \tag{24}$$

The wave function ψ must be transformed as follows

$$\psi \rightarrow \psi_i^{\circ}\left(1 + \frac{e}{2mc}\tilde{H}.\tilde{fi} + \frac{e}{mc}\tilde{\mu}.\tilde{gi} + \frac{e}{ih2c}\tilde{H}.\tilde{R} \times \tilde{r}_M\right) \tag{25}$$

Thus $\tilde{g}i \rightarrow \tilde{g}i$

$$\tilde{f}i \rightarrow \left(\frac{m}{i\hbar}\right)(\tilde{R} \times \tilde{r}_M) + \tilde{f}i$$

The Hamiltonian becomes

$$\mathcal{H}^1 = \mathcal{H}_0 + \frac{e}{2mc}\,\tilde{H}.\tilde{L}_M + \frac{e}{mc}\,r_H^{-3}\,\tilde{\mu}.\tilde{L}_M + \frac{e^2}{2mc^2}\,H^\alpha \mu^\beta$$

$$(\delta^{\alpha\beta} r_H^2 - r_H^\alpha r_H\beta)\, r_H^{-3} - \frac{e\hbar}{mci}\, r_H^{-3}\,\tilde{\mu}.\tilde{R} \times \nabla$$

$$+ \frac{e^2}{2mc^2}\, H^\alpha \mu^\beta (\delta^{\alpha\beta}\,\tilde{r}_H.\tilde{R} - r_H^\alpha R^\beta) r_H^{-3} \qquad (26)$$

Under these changes the diamagnetic term becomes.

$$\sigma^D_{\alpha|\alpha} = \frac{e^2}{mc^2} \sum_{i=1}^{n} \left\langle \psi_i^0 \,\middle|\, r_H^{-3}\left[r_H^2 - r_H^{\alpha|} r_H^\alpha + \tilde{r}_H.\tilde{R} - r_H^{\alpha|} R^\alpha\right] \middle| \psi_i^0 \right\rangle \qquad (27)$$

and the paramagnetic term becomes

$$\sigma^P_{\alpha|\alpha} = \frac{e^2}{m^2c^2} \sum_{i=1}^{n} \Big\{ -\frac{\hbar^2}{m} \left\langle \psi_i^0 \,\middle|\, \nabla f_i^{\alpha|}.\nabla g_i^\alpha \,\middle|\, \psi_i^0 \right\rangle$$

$$-\frac{\hbar}{i}\left\langle \psi_i^0 \,\middle|\, \nabla\left[(\tilde{R} \times \tilde{r}_M)^{\alpha|}\right].\nabla g_i^\alpha \,\middle|\, \psi_i^0 \right\rangle$$

$$+ \left\langle \psi_i^0 \,\middle|\, (L_M^{\alpha|} g_i^\alpha) + r_H^{-3}\left(\left[L_M^{\alpha|} - \frac{\hbar}{i}(\tilde{R} \times \nabla)^{\alpha|}\right]\right.\right.$$

$$\left.\left.\left[f_i^\alpha + \frac{m}{i\hbar}(\tilde{R} \times \tilde{r}_M)^\alpha\right]\right) \middle| \psi_i^0 \right\rangle$$

$$+ 2 \sum_{j\neq i}^{n} \Big[\left\langle \psi_j^0 \,\middle|\, L_M^{\alpha|} \,\middle|\, \psi_i^0 \right\rangle \left\langle \psi_i^0 \,\middle|\, g_i^\alpha \,\middle|\, \psi_j^0 \right\rangle$$

$$+ \left\langle \psi_j^0 \,\middle|\, r_H^{-3}\left(L_M^{\alpha|} - \frac{\hbar}{i}(\tilde{R} \times \nabla)^{\alpha|}\right) \middle| \psi_i^0 \right\rangle$$

$$\left\langle \psi_i^0 \,\middle|\, f_i^\alpha + \frac{m}{i\hbar}(\tilde{R} \times \tilde{r}_M)^\alpha \,\middle|\, \psi_j^0 \right\rangle \Big\} \qquad (28)$$

F. Diamagnetic contribution to the shielding

From (27)

$$\sigma^D = \frac{1}{3}\sigma_{\alpha\alpha}$$

$$= \frac{e^2}{3mc^2}\sum_{i=1}^{n}\left\langle \psi_i^0 \middle| r_H^{-3}\left[\delta^{\alpha\alpha} r_H^2 - r_H^\alpha r_H^\alpha + \tilde{r}_H\cdot\tilde{R}\,\delta^{\alpha\alpha} - r_H^\alpha R^\alpha\right| \psi_i^0\right\rangle$$

$$= \frac{e^2}{3mc^2}\sum_{i=1}^{n}\left\langle \psi_i^0 \middle| r_H^{-3}\left[3r_H^2 - r_H^2 + 3\tilde{r}_H\cdot\tilde{R} - r_H\cdot R\right]\middle|\psi_i^0\right\rangle$$

$$= \frac{2e^2}{3mc^2}\sum_{i=1}^{n}\left\langle \psi_i^0 \middle| r_H^{-3}\left(r_H^2 + r_H\cdot R\right)\middle|\psi_i^0\right\rangle$$

$$= \frac{2e^2}{3mc^2}\sum_{i=1}^{n}\left\langle \psi_i^0 \middle| r_H^{-3}\left(r_H^2 + \varkappa_H R\right)\middle|\psi_i^0\right\rangle \qquad (29)$$

This is identical with the expression obtained by Buckingham and Stephens (51) using the same coordinate origin.

G. Paramagnetic contribution to the shielding

The expression (28) may be simplified by the following relationships, $\hat{\epsilon}_\alpha$ is a unit vector ($\hat{i}$, $\hat{j}$, $\hat{k}$)

$$\tilde{R} \times \tilde{r}_M = Ry_M \hat{k} - Rz_M \hat{j} \tag{30}$$

$$L_M^{\alpha|} (\tilde{R} \times \tilde{r}_M)^\alpha = \frac{\hbar}{i} (\tilde{r}_M . \tilde{R}) - \frac{\hbar}{i} \tilde{r}_M . \tilde{\epsilon}_\alpha \tilde{R} . \tilde{\epsilon}_\alpha \tag{31}$$

$$\left[\nabla (\tilde{R} \times \tilde{r}_M)^{\alpha|}\right] . \nabla gi^\alpha = (\tilde{R} \times \nabla)^{\alpha|} gi^\alpha \tag{32}$$

$$(\tilde{R} \times \nabla_M)^{\alpha|} (\tilde{R} \times \tilde{r}_M)^\alpha = R^2 - \tilde{R} . \tilde{\epsilon}_\alpha R . \tilde{\epsilon}_\alpha$$

Thus

$$\sigma^P_{\alpha|\alpha} = \frac{e^2}{m^2 c^2} \sum_{i=1}^{n} \Big\{ - \frac{\hbar^2}{m} \langle \psi_i^\circ | \nabla fi^{\alpha|} . \nabla gi^{\alpha|} \psi_i^\circ \rangle$$

$$+ \langle \psi_i^\circ | (L_M^{\alpha|} gi^\alpha + r_H^{-3} (L_M^{\alpha|} fi^\alpha) | \psi_i^\circ \rangle$$

$$- \frac{\hbar}{i} \langle \psi_i^\circ | (\tilde{R} \times \nabla)^{\alpha|} gi^\alpha | \psi_i^\circ \rangle - \langle \psi_i^\circ | r_H^{-3}$$

$$m \left[(\tilde{r}_M . \tilde{R}) - \tilde{r}_M . \hat{\epsilon}_\alpha \hat{R} . \hat{\epsilon}_\alpha \right] | \psi_i^\circ \rangle$$

$$- \frac{\hbar}{i} \langle \psi_i^\circ | \left[r_H^{-3} (\tilde{R} \times \nabla)^{\alpha|} fi^\alpha \right] | \psi_i^\circ \rangle$$

$$+ \langle \psi_i^\circ | r_H^{-3} m \left[R^2 - \tilde{R} . \hat{\epsilon}_\alpha \tilde{R} . \hat{\epsilon}_\alpha \right] | \psi_i^\circ \rangle$$

$$+ 2 \sum_{j \neq i}^{n} \Big[\langle \psi_j^\circ | L_M^{\alpha|} | \psi_i^\circ \rangle \langle \psi_i^\circ | gi^\alpha | \psi_j^\circ \rangle$$

$$+ \langle \psi_j^\circ | r_H^{-3} L_M^{\alpha|} | \psi_i^\circ \rangle \langle \psi_j^\circ | fi^\alpha | \psi_i^\circ \rangle$$

$$+ \frac{m}{im} \langle \psi_j^\circ | r_H^{-3} L_M^{\alpha|} | \psi_i^\circ \rangle \langle \psi_i^\circ | (\tilde{R} \times \tilde{r}_M)^\alpha | \psi_j^\circ \rangle$$

$$- \frac{\hbar}{i} \langle \psi_j^\circ | r_H^{-3} (\tilde{R} \times \nabla)^{\alpha|} | \psi_i^\circ \rangle \langle \psi_i^\circ | fi^\alpha | \psi_j^\circ \rangle$$

$$+ m \langle \psi_j^\circ | r_H^{-3} (\tilde{R} \times \nabla)^{\alpha|} | \psi_i^\circ \rangle \langle \psi_i^\circ | (\tilde{R} \times \tilde{r}_M)^\alpha | \psi_j^\circ \rangle \Big] \Big\} \tag{33}$$

H. Choice of Ψ_o, fi and gi

The following expressions were taken for Ψ_o, fi and gi

$$\Psi_o = |\, d_{z^2}^{+}\ d_{z^2}^{-}\ d_{xy}^{+}\ d_{xy}^{-}\ d_{yz}^{+}\ d_{yz}^{-}\ d_{xz}^{+}\ d_{xz}^{-} \rangle \qquad (34)$$

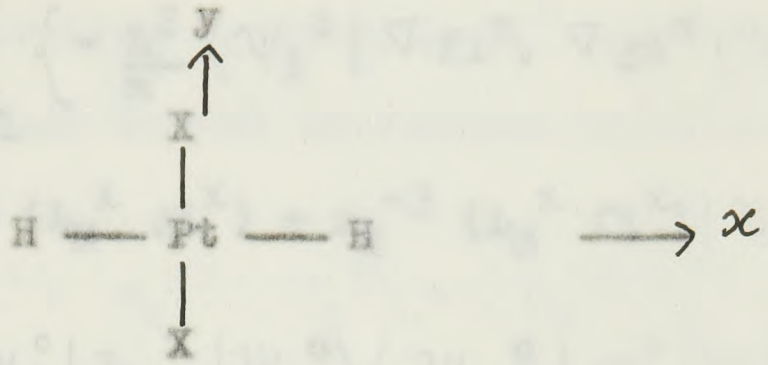
This was chosen as only the shielding effect of the transition metal d-electrons on the proton is being considered, compare Buckingham and Stephens (51). $|\ \rangle$ represents a normalized antisymmetrized function and the d-orbitals are taken to have Slater form with kr exponent (80)

$$fi = (a_1^i x + a_2^i y + a_z^i z + a_4^i xy + a_5^i xz + a_6^i yz + a_7^i x^2 + a_8^i y^2 + a_9^i z^2) \qquad (35)$$

$$gi = (b_1^i x + b_2^i y + b_3^i z + b_4^i xy + b_5^i xz + b_6^i yz + b_7^i x^2 + b_8^i y^2 + b_9^i z^2) \qquad (36)$$

I. Reduction of the formulae by symmetry

A hypothetical molecule of D_{2h} symmetry is considered



Only some terms in the polynomials fi and gi give non-zero integrals when substituted into (23). These are easily selected on the basis of their behaviour under inversion of the coordinates. Also the nature of the L_M^{α} operators causes other integrals to vanish

J. Calculation of σ_{xx}^{P}.

From (33)

$$\sigma_{xx}^{P} = \frac{e^2}{m^2c^2} \sum_{i=1}^{n} \Big\{ -\frac{\hbar^2}{m} \langle \psi_i^{\circ} | \nabla f_i^{x} . \nabla g_i^{x} | \psi_i^{\circ} \rangle$$
$$+ \langle \psi_i^{\circ} | (L_M^{x} g_i^{x}) + r_H^{-3} (L_M^{x} f_i^{x}) | \psi_i^{\circ} \rangle$$
$$+ 2 \sum_{j \neq i}^{n} \langle \psi_j^{\circ} | L_M^{x} | \psi_i^{\circ} \rangle \langle \psi_i^{\circ} | g_i^{x} | \psi_j^{\circ} \rangle$$
$$+ \langle \psi_j^{\circ} | r_H^{-3} L_M^{x} | \psi_i^{\circ} \rangle \langle \psi_i^{\circ} | h^{x} | \psi_j^{\circ} \rangle \qquad (37)$$

For terms of the type $\langle \psi_i^{\circ} | \nabla f_i^{x} . \nabla g_i^{x} | \psi_i^{\circ} \rangle$

$$\nabla f_i^{x} = (a_1 + a_4 y + a_5 z + 2a_7)\,\hat{i} + (a_2 + a_4 x + a_6 z + 2a_8 y)\,\hat{j}$$
$$+ (a_3 + a_5 x + a_6 y + 2a_9 z)\,\hat{k}$$

$$\nabla g_i^{x} = \text{do.} \quad a \rightarrow b$$

Thus

$$\langle \psi_i^{\circ} | \nabla f_i^{x} . \nabla g_i^{x} | \psi_i^{\circ} \rangle = \langle \psi_i^{\circ} | a_1 b_1 + a_2 b_2 + a_3 b_3$$
$$+ x^2 (a_4 b_4 + a_5 b_5 + 4a_7 b_7) + y^2 (a_4 b_4 + a_6 b_6 + 4a_8 b_8)$$
$$+ z^2 (a_5 b_5 + a_6 b_6 + 4a_9 b_9) | \psi_i^{\circ} \rangle \qquad (38)$$

The complex is assumed to have a centre of inversion thus terms odd in x, y and z disappear.

For the terms $\langle \psi_i^{\circ} | (L_M^{x} g_i^{x}) | \psi_i^{\circ} \rangle$, L_M^{x} transforms as yz, therefore g_i^{x} must transform as yz, thus from the polynomials only b_6 yz remains.

For the exchange terms also gi^{α} must transform in the same way as $L_M{}^{\alpha}$, so again only b_6 yz remains.

The corresponding terms with fi^{α} are two-centre integrals thus they cannot be reduced by symmetry arguments in the same way.

$$\langle \psi_i{}^0 | (L_M{}^{\alpha} f_i{}^{\alpha}) \; r_H{}^{-3} | \psi_i{}^0 \rangle = \langle \psi_i{}^0 | L_M{}^{\alpha} (a_2 y + a_3 z + a_4 xy + a_5 xz + a_6 yz + a_8 y^2 + a_9 z^2) \; r_H{}^{-3} | \psi_i{}^0 \rangle$$

$$= \frac{\hbar}{i} \langle \psi_i{}^0 | (- a_2 z + a_3 y - a_4 xz + a_5 xy + a_6 (y^2 - z^2) - 2a_8 yz + 2a_9 yz) \; r_H{}^{-3} | \psi_i{}^0 \rangle \qquad (39)$$

For the exchange terms which are functions of fi, fi^{α} must transform in the same way as ψ_j.

Considering the contribution to σ_{xx}^{P} when $\psi_i = d_{z^2}$

$$\sigma_{xx}{}^{P}(d_{z^2}) = \frac{e^2}{m^2 c^2} \left\{ - \frac{\hbar^2}{m} \langle d_{z^2} | a_1 b_1 + a_2 b_2 + a_3 b_3 \right.$$

$$x^2 (a_4 b_4 + a_5 b_5 + 4a_7 b_7) + y^2 (a_4 b_4 + a_6 b_6 + 4a_8 b_8) + z^2 (a_5 b_5 + a_6 b_6 + 4a_9 b_9) | d_{z^2} \rangle + \langle d_{z^2} | (L_M{}^{\alpha} b_6 yz) | d_{z^2} \rangle$$

$$+ \frac{\hbar}{i} \langle d_{z^2} | r_H{}^{-3} (- a_2 z + a_3 y - a_4 xz + a_5 xy + a_6 (y^2 - z^2) - 2a_8 yz + 2a_9 yz) | d_{z^2} \rangle$$

$$+ 2 \langle d_{yz} | L_M{}^{\alpha} | d_{z^2} \rangle \langle d_{z^2} | b_6 yz | d_{yz} \rangle + 2 \langle d_{yz} | r_H{}^{-3} L_M{}^{\alpha} | d_{z^2} \rangle \langle d_{z^2} | a_6 yz | d_{yz} \rangle + 2 \langle d_{xy} | r_H{}^{-3} L_M{}^{\alpha} | d_{z^2} \rangle \langle d_{z^2} | a_4 xy | d_{xy} \rangle + 2 \langle d_{xz} | r_H{}^{-3} L_M{}^{\alpha} | d_{z^2} \rangle \langle d_{z^2} | a_5 xz | d_{xz} \rangle \Big\} \qquad (40)$$

This expression must now be extremized with respect to variations in the coefficient a_n and b_n. Clearly

$$a_1 = b_1 = a_2 = a_3 = a_4 = a_5 = a_7 = b_7 = a_8 = a_9 = 0$$

The expression (40) may be expressed in the form

$$\sigma_{xx}^{P}(d_z 2) = (a_6 b_6 X + a_6 Y + b_6 Z) \frac{e^2}{m^2 c^2}$$

where $X = -\frac{\hbar^2}{m} \langle d_z 2 \mid y^2 + z^2 \mid d_z 2 \rangle$

$$Y = \frac{\hbar}{i} \langle d_z 2 \mid r_H^{-3} (y^2 - z^2) \mid d_z 2 \rangle$$

$$+ 2 \langle d_{yz} \mid r_H^{-3} L_M^{\alpha} \mid d_z 2 \rangle \langle d_z 2 \mid yz \mid d_{yz} \rangle$$

$$Z = \langle d_z 2 \mid (L_M^{\alpha} yz) \mid d_z 2 \rangle + 2 \langle d_{yz} \mid L_M^{\alpha} \mid d_z 2 \rangle$$

$$\langle d_z 2 \mid yz \mid d_{yz} \rangle$$

On extremization

$$a_6 = -Z/X$$

$$b_6 = -Y/X$$

Hence

$$\sigma_{xx}^{P}(d_z 2) = -\frac{YZ}{X} \qquad (41)$$

The term Z may be written more generally

$$Z = \langle \psi_i^{o} \mid (L_M^{\alpha 1} gi^{\alpha}) \mid \psi_i^{o} \rangle + \sum_{j \neq i}^{2} \langle \psi_j^{o} \mid L_M^{\alpha 1} \mid \psi_i^{o} \rangle$$

$$\langle \psi_i^{o} \mid gi^{\alpha} \mid \psi_j^{o} \rangle$$

Only one orbital from the sum will contribute to Z namely that which transforms in the same way as L_M^{α}. Let this orbital be denoted ψ_k^{o}.

$$Z = \langle \psi_i^0 | (L_M^{\alpha|} \, gi^{\alpha}) | \psi_i^0 \rangle + 2 \langle \psi_k^0 | L_M^{\alpha|} | \psi_i^0 \rangle \langle \psi_i^0 | gi^{\alpha} | \psi_k^0 \rangle$$

$$= -2 \langle \psi_i^0 | gi^{\alpha|} L_M^{\alpha} | \psi_i^0 \rangle + 2 \langle \psi_k^0 | L_M^{\alpha|} | \psi_i^0 \rangle \langle \psi_i^0 | gi^{\alpha} | \psi_k^0 \rangle$$

As the ψ_i^0 are d-orbitals $L_M^{\alpha} \psi_i^0 = c \psi_k^0$ where c is a constant. Therefore

$$Z = -2c \langle \psi_i^0 | gi^{\alpha} | \psi_k^0 \rangle + 2c \langle \psi_i^0 | gi^{\alpha} | \psi_k^0 \rangle$$

$$= 0$$

As Z is zero the expression for $\sigma_{xx}^{P}(d_{z^2})$ becomes zero.

The other contributions to σ_{xx}^{P} vanish in a similar way. Also σ_{zz}^{P} and σ_{yy}^{P}, although they are more complex as there are additional terms resulting from the gauge transformation, are found to be zero.

K. Discussion

The above calculation was attempted in order to see whether the variation-perturbation method was suitable for estimating the shielding in transition metal hydrides. During the course of the work, disagreement was found with the formulae of Karplus and Kolker for magnetic susceptibility (78) and nuclear shielding (79), (see Appendix IV). Owing to the brevity of the derivations in the publications it was difficult to ascertain at which precise point the disagreement arose and so far we have received no further enlightenment from the authors on this matter.

Use of our equation for shielding predicts the paramagnetic shielding of the hydrido ligand by the d-electrons of the platinum to be zero. Therefore the model must be regarded as unsatisfactory. The vanishing of this contribution to the shielding is the result of the cancellation of the diagonal and exchange terms. However if the exchange terms are neglected a negative shielding is predicted.

As the expression of Karplus and Kolker differs from ours in the sign and coefficients of the exchange terms, use of their expression does not predict σ^P to be zero. Moreover their term X which is the

denominator in the minimized expression for σ^P is also of opposite sign thus σ^P is positive as would be expected.

If our expression for the shielding is the correct one it is difficult to see how the model could be improved, as the vanishing of σ^P is not a direct consequence of the type of polynomial used but rather a consequence of the ground state wave function.

The disadvantages of the method are discussed by Karplus and Kolker (78) and they point out that the treatment is most likely to be inaccurate when the ground state wave function has modes as is also pointed out by Mclachlan and Baker (80a).

Also extremization of the expression of σ^P does not give a true minimum (i.e. $\delta^2(\sigma^P)$ is not + ve), thus the variation principle is not being correctly applied.

Either of these two deficiencies may well be the cause of our unsatisfactory result. Also it may well be the case that the error is in our derivation rather than Karplus and Kolker's. In conclusion the problem demands further investigation.

Appendix I

Some studies on rhodium complexes

At the outset of the work described in this thesis it was decided that possible series of complexes which fulfil the criteria laid down in Chapter I would be the rhodium(III) complexes $[Rhen_2HX]^+ A^-$, $[Rhen_2Hpy]^{2+} 2A^-$ or $[Rh(DMG)_2LH]$.

The chloride complexes corresponding to the hydrides were prepared. Their reaction with a variety of reducing agents e.g. BH_4^-, Zn/HAc, H_3PO_2, N_2H_4aq., H_2/Ni was was investigated and the reaction products briefly studied, using ^1H nuclear magnetic resonance and infrared spectroscopy in order to ascertain whether a rhodium hydride species had been prepared. In some cases, for example the reaction of $[Rhen_2Cl_2]^+$ and $[Rhen_2Cl.py]^{2+}$ with zinc and acetic acid, positive evidence for rhodium hydride species was found, as had been previously noted for the former case (11). However, after six months, it was not found possible to prepare and isolate any hexa-coordinate rhodium hydride complexes and further exploration along these lines was abandoned.

Appendix II

Mass spectrum of trans-o-chlorobenzoatohydridobistriethylphosphineplatinum(II)

The mass spectrum of trans- $Pt(PEt_3)_2Ho\text{-}ClC_6H_4COO$ is given in Table XXII. The peaks in the region 586-592 are consistent with the parent ion of the above molecule the pattern being that expected from the natural abundance of chlorine and platinum isotopes (81).

Table XXII

Mass	Peak Intensity	Mass	Peak Intensity	Mass	Peak Intensity	Mass	Peak Intensity
41	12	63	27	85	16	108	4
42	16	64	96	86	5	109	14
43	59	65	22	87	11	110	6
44	52	66	8	88	12	111	210
45	66	67	17	89	53	112	30
46	11	68	10	90	580	113	68
47	36	69	48	91	41	114	10
48	6	70	10	92	9	115	6
49	22	71	16	93	10	116	6
50	85	72	3	94	340	117	110
51	55	73	30	95	37	118	400
52	15	74	40	96	15	119	900
53	12	75	20	97	26	120	56
54	11	76	64	98	9	121	10
55	140	77	78	99	5	122	38
56	19	78	59	1101	5	123	7
57	120	79	12	102	3	124	5
58	50	80	4	103	160	125	6
59	160	81	18	104	15	128	14
60	51	82	15	105	75	129	3
61	400	83	25	106	37	130	4
62	660	84	8	107	11	133	7

Mass	Peak Intensity	Mass	Peak Intensity	Mass	Peak Intensity	Mass	Peak Intensity
134	9	269	8	297	4	320	63
135	15	270	8	298	5	321	11
136	3	271	10	299	5	322	23
137	5	272	5	300	5	324	5
138	2	273	5	301	7	325	7
139	60	274	3	302	5	326	5
140	53	275	3	303	5	327	6
251	9	277	5	304	3	328	7
252	20	278	5	305	3	329	8
253	52	279	22	306	2	330	4
254	48	280	25	307	6	331	6
255	58	281	48	308	6	332	5
256	50	282	38	309	29	333	5
257	55	283	72	310	30	334	3
258	28	284	60	311	69	335	6
259	15	285	66	312	64	336	6
260	5	286	44	313	85	337	20
261	5	287	39	314	80	338	22
262	4	288	22	315	81	339	65
264	52	289	12	316	54	340	70
265	10	290	16	317	27	341	110
267	4	291	12	318	94	342	120
268	3	292	9	319	84	343	130

Mass	Peak Intensity	Mass	Peak Intensity	Mass	Peak Intensity	Mass	Peak Intensity
344	88	368	62	394	18	426	43
345	50	369	130	395	52	427	84
346	340	370	110	396	42	428	79
347	350	371	140	397	93	429	93
348	260	372	110	398	65	430	860
349	30	373	83	399	110	431	1000
350	80	374	710	400	91	432	760
351	10	375	770	401	110	433	125
352	11	376	660	402	780	434	195
353	9	377	65	403	870	435	26
354	6	378	160	404	670	436	6
355	7	379	18	405	80	437	6
356	6	380	8	406	170	438	3
357	5	381	7	407	20	439	3
358	4	382	5	408	5	464	4
359	9	383	3	409	3	465	8
360	6	387	5	410	3	466	130
361	6	388	3	411	2	467	150
363	6	389	5	421	5	468	155
364	5	390	5	422	6	469	60
365	26	391	6	423	24	470	60
366	24	392	5	424	20	471	9
367	69	393	18	425	51	472	10

Mass	Peak Intensity
557	6
558	6
559	7
560	3
561	1
586	26
587	31
588	34
589	15
590	16
591	2
592	2

Appendix III

The Infrared Spectra of the Complexes I

The infrared spectra of the complexes(I) in the region 4000-600 cm^{-1} are given below. The complex is denoted solely by the carboxylato ligand L. The spectra were measured as Nujol mulls on sodium chloride plates.

$p\text{-}NO_2C_6H_4COO$ - 3090(w) 3055(w) 3037(w) 2245(s) 1962(w) 1830(w) 1750(w) 1633(s) 1598(s) 1515(s) 1405(sh) 1325(v.s.) 1261(sh) 1250(sh) 1167(w) 1130(w) 1119(m) 1102(sh) 1088(w) 1051(s) 1043(s) 1016(s) 998(m) 883(s) 859(sh) 830(sh) 825(s) 790(m) 763(v.s.) 753(v.s) 735(sh) 725(s) 691(m) 623(m) 570(m)

$p\text{-}CNC_6H_4COO$ - 3040(w) 2230(s) 1965(w) 1834(w) 1631(s) 1557(m) 1415(sh) 1348(s) 1259(m) 1178(sh) 1173(m) 1146(w) 1130(w) 1122(sh) 1095(w) 1051(sh) 1042(sh) 1036(s) 1019(sh) 998(sh) 985(sh) 944(w) 904(w) 879(s) 850(m) 835(sh) 780(vs) 768(vs) 757(vs) 745(sh) 735(s) 693(m) 623(m) 587(sh)

$p\text{-}IC_6H_4COO$ - 3040(w) 2845(sh) 2214(s) 1919(w) 1700(sh) 1630(vs) 1583(sh) 1558(sh) 1420(sh) 1340(vs) 1300(sh) 1278(sh) 1261(m) 1176(s) 1131(m) 1105(w) 1087(w) 1055(sh) 1038(s) 1010(s) 852(s) 832(s) 775(sh) 761(vs) 732(s) 700(sh) 684(sh) 627(m)

$p\text{-}BrC_6H_4COO$ - 2238(s) 1946(w) 1679(sh) 1605(s) 1580(sh) 1570(sh) 1410(sh) 1340(vs) 1300(sh) 1280(s) 1266(sh) 1256(sh) 1162(s) 1130(m) 1106(w) 1090(m) 1064(s) 1050(sh)

1036(s) 1006(s) 978(sh) 961(sh) 861(s) 848(sh) 834(s)
828(sh) 768(vs) 722(sh) 704(sh) 682(m) 675(sh) 667(sh)
648(sh) 640(m) 622(sh) 562(sh)

p-ClC_6H_4COO - 2260(s) 1944(w) 1605(s) 1565(s) 1543(m)
1393(w) 1335(vs) 1298(sh) 1281(s) 1261(s) 1169(s) 1130(m)
1092(s) 1081(s) 1060(sh) 1041(sh) 1035(s) 1016(sh) 1009(s)
1000(sh) 863(s) 850(sh) 848(sh) 830(s) 778(sh) 768(vs)
755(sh) 722(sh) 701(sh) 697(sh) 685(m) 648(sh) 638(m)
626(m) 569(sh)

p-$CH_3C_6H_4COO$ - 3050(w) 2215(s) 1687(sh) 1618(s) 1560(sh)
1499(sh) 1407(sh) 1335(vs) 1291(sh) 1255(s) 1244(sh)
1211(w) 1172(s) 1130(m) 1109(w) 1095(m) 1048(sh) 1034(s)
1020(sh) 997(sh) 855(sh) 844(s) 760(vs) 740(sh) 728(sh)
690(m) 626(m) 598(sh)

p-$CH_3OC_6H_4COO$ - 3060(w) 2858(sh) 2235(s) 1620(s) 1606(sh)
1562(sh) 1492(sh) 1406(sh) 1339(s) 1300(m) 1352(s) 1187(m)
1168(m) 1099(w) 1044(m) 1025(m) 998(sh) 849(s) 838(sh)
773(sh) 762(s) 690(m) 634(m) 620(sh)

p-$(CH_3)_2NC_6H_4COO$ - 2220(s) 1603(s) 1538(sh) 1416(sh) 1382(sh)
1350(sh) 1307(sh) 1260(m) 1232(m) 1192(s) 1166(sh) 1133(w)
1111(sh) 1058(sh) 1042(s) 996(m) 940(m) 834(s) 763(vs)
755(sh) 740(sh) 716(sh) 693(m) 620(sh)

m-$NO_2C_6H_4COO$ - 3095(w) 2244(s) 1614(s) 1560(w) 1504(s)
1400(sh) 1330(vs) 1270(m) 1262(sh) 1250(sh) 1161(m) 1104(w)
1079(m) 1061(s) 1052(s) 1039(s) 1014(w) 1000(w) 949(w)

931(m) 901(w) 840(sh) 825(s) 782(s) 767(vs) 756(sh)
729(vs) 721(sh) 696(m) 675(w) 665(w) 650(w) 622(m)

m-IC_6H_4COO - 3055(w) 2240(s) 1950(w) 1890(w) 1830(w)
1620(s) 1552(s) 1408(sh) 1335(vs) 1283(sh) 1266(s) 1258(sh)
1245(sh) 1163(w) 1127(w) 1078(w) 1054(sh) 1037(s) 999(s)
979(sh) 923(w) 910(w) 845(s) 811(w) 779(vs) 751(vs) 745(sh)
710(s) 673(sh) 642(sh) 627(m)

m-BrC_6H_4COO - 3050(w) 2250(s) 1954(w) 1895(w) 1820(w)
1667(sh) 1622(s) 1598(w) 1580(s) 1405(m) 1335(s) 1292(sh)
1266(s) 1260(sh) 1248(sh) 1155(w) 1130(w) 1074(w) 1061(m)
1049(sh) 1037(s) 1010(w) 995(s) 921(w) 907(m) 849(m) 834(m)
809(w) 765(vs) 750(vs) 734(sh) 720(s) 692(m) 672(m) 646(sh)
625(s)

m-ClC_6H_4COO - 3060(w) 2255(s) 1960(w) 1900(w) 1780(w)
1680(sh) 1630(s) 1567(s) 1410(m) 1335(vs) 1295(sh) 1265(m)
1249(sh) 1157(w) 1136(w) 1115(w) 1067(m) 1049(s) 1040(s)
1013(sh) 995(s) 910(s) 864(s) 854(sh) 835(m) 812(sh)
760(vs) 736(sh) 690(m) 673(m) 654(sh) 624(m)

m-FC_6H_4COO - 3066(w) 2226(s) 1890(w) 1794(w) 1710(sh)
1631(s) 1589(s) 1340(vs) 1310(sh) 1270(s) 1260(sh) 1245(sh)
1220(s) 1153(w) 1085(s) 1061(sh) 1048(s) 1038(s) 1006(sh)
998(s) 918(s) 897(s) 847(sh) 832(m) 807(m) 792(s) 765(vs)
734(sh) 693(m) 673(m) 622(m) 605(w)

m-$CH_3C_6H_4COO$ - 3075(w) 2244(s) 1960(w) 1890(w) 1738(w)
1621(s) 1580(sh) 1412(sh) 1335(vs) 1258(s) 1248(sh) 1160(w)

1109(w) 1086(m) 1060(sh) 1040(s) 1014(w) 997(s) 931(w)
908(w) 858(sh) 842(m) 821(w) 790(sh) 761(vs) 740(sh)
720(sh) 695(s) 687(sh) 675(sh) 628(s)

m-$(CH_3)_2NC_6H_4COO$ - 3079(w) 2731(m) 1621(sh) 1599(s)
1574(sh) 1492(sh) 1403(w) 1340(s) 1261(w) 1233(m) 1121(w)
1044(m) 998(m) 964(w) 890(w) 869(w) 842(w) 767(sh) 754(s)
736(sh) 722(sh) 685(m) 668(w) 629(sh)

o-$NO_2C_6H_4COO$ - 3060(w) 2859(sh) 2250(s) 1630(s) 1571(m)
1529(s) 1413(sh) 1343(s) 1253(m) 1179(w) 1153(w) 1140(w)
1080(m) 1049(s) 1039(sh) 1005(w) 987(w) 861(m) 837(sh)
827(s) 797(m) 779(s) 760(vs) 748(sh) 723(s) 686(s) 628(m)
606(m)

o-BrC_6H_4COO - 3055(w) 2857(sh) 2220(s) 2038(w) 1957(w)
1631(s) 1590(sh) 1560(sh) 1429(sh) 1352(s) 1260(m) 1179(w)
1155(w) 1120(w) 1053(sh) 1040(s) 1027(sh) 1005(sh) 944(w)
834(m) 769(vs) 752(vs) 737(sh) 728(sh) 698(m) 643(m)
626(sh)

o-ClC_6H_4COO - 3060(w) 2875(sh) 2244(s) 1990(w) 1950(w)
1834(w) 1615(s) 1595(sh) 1561(sh) 1431(sh) 1408(sh)
1349(vs) 1263(m) 1160(sh) 1152(m) 1119(w) 1050(s) 1035(s)
1000(w) 831(s) 802(w) 769(sh) 760(vs) 730(sh) 717(sh)
696(m) 685(sh) 649(m) 623(m)

3,5-$(NO_2)_2C_6H_3COO$ - 3105(s) 2858(sh) 2230(s) 1870(w)
1642(s) 1620(sh) 1595(sh) 1550(s) 1535(s) 1410(sh) 1335(vs)
1255(m) 1189(m) 1084(sh) 1074(s) 1051(sh) 1035(s) 1015(w)

997(w) 931(m) 917(s) 848(m) 785(sh) 771(s) 760(sh) 730(vs)
723(vs) 705(sh) 680(sh) 645(sh) 626(m)

$2,5\text{-}(NO_2)_2C_6H_3COO$ - 3117(w) 3103(w) 3070(w) 2855(sh)
1643(s) 1622(sh) 1588(sh) 1553(s) 1540(s) 1412(sh) 1345(vs)
1318(sh) 1256(m) 1242(sh) 1160(w) 1136(w) 1107(m) 1056(sh)
1035(s) 1004(m) 986(w) 976(w) 920(m) 855(sh) 850(sh) 843(s)
793(w) 765(s) 758(sh) 740(sh) 730(s) 713(sh) 692(m) 677(w)
662(m) 631(m)

$2,4,6\text{-}(NO_2)_3C_6H_2COO$ - 3100(m) 2848(sh) 2260(s) 1658(vs)
1603(m) 1549(vs) 1410(sh) 1340(vs) 1262(w) 1180(w) 1072(m)
1051(sh) 1043(sh) 1036(s) 1014(sh) 997(w) 940(w) 907(m)
850(w) 825(m) 817(s) 799(w) 791(w) 769(s) 753(sh) 734(s)
723(sh) 698(m) 624(sh)

CF_3COO - 2910(sh) 2255(m) 1675(s) 1437(m) 1383(m) 1356(sh)
1225(sh) 1181(s) 1173(sh) 1120(s) 1025(s) 815(m) 781(sh)
759(s) 717(s) 690(sh)

$CHCl_2COO$ - 2902(sh) 2248(m) 1680(sh) 1661(s) 1603(sh)
1459(m) 1416(sh) 1379(sh) 1362(sh) 1336(s) 1259(m) 1225(sh)
1200(sh) 1052(sh) 1036(s) 1015(sh) 935(w) 850(sh) 819(m)
764(s) 721(s) 655(w) 621(w)

CH_2ClCOO - 2910(sh) 2235(m) 1601(s) 1434(m) 1410(s) 1395(sh)
1382(sh) 1278(sh) 1259(s) 1248(sh) 1051(s) 1046(sh) 1036(sh)
999(m) 930(m) 926(sh) 819(m) 762(s) 744(sh) 738(sh) 691(sh)
684(m) 667(w) 620(w)

$CH_2OPhCOO$ - 3090(w) 3060(w) 2912(sh) 2240(m) 1650(sh) 1621(s) 1585(sh) 1488(s) 1407(sh) 1310(sh) 1271(s) 1231(s) 1179(m) 1156(w) 1084(m) 1065(sh) 1052(sh) 1036(s) 1004(sh) 938(w) 915(w) 839(m) 823(sh) 784(sh) 765(s) 752(s) 730(sh) 685(m) 621(m)

The spectra in the region 600-200 cm^{-1} are given below. They were measured as Nujol mulls on polythene plates.

$p\text{-}NO_2C_6H_4COO$ - 578(s) 529(m) 500(s) 440(m) 420(sh) 399(m) 386(sh) 356(s) 328(sh) 287(w) 203(m)

$p\text{-}BrC_6H_4COO$ - 576(m) 556(sh) 480(s) 472(sh) 444(w) 403(w) 386(w) 351(m) 271(w) 244(w) 196(w)

$p\text{-}ClC_6H_4COO$ - 576(m) 556(sh) 515(m) 479(w) 443(w) 385(w) 370(w) 350(w) 285(sh) 272(m)

$p\text{-}CH_3C_6H_4COO$ - 553(w) 472(m) 407(m) 351(w) 283(w) 248(w)

$p\text{-}CH_3OC_6H_4COO$ - 604(s) 553(m) 511(m) 446(w) 403(sh) 399(m) 368(sh) 344(m) 286(m)

$m\text{-}NO_2C_6H_4COO$ - 580(m) 556(w) 539(sh) 431(s) 396(m) 390(sh) 378(sh) 354(m) 328(sh) 303(w) 282(sh) 272(w) 240(sh)

$m\text{-}IC_6H_4COO$ - 556(m) 510(w) 478(w) 440(m) 427(w) 390(w) 290(w) 242(w) 188(w)

$m\text{-}BrC_6H_4COO$ - 571(m) 555(sh) 490(m) 441(s) 430(sh) 419(s) 402(s) 395(sh) 349(sh) 343(s) 275(w) 210(w) 159(m)

$m\text{-}ClC_6H_4COO$ - 580(m) 560(sh) 505(sh) 474(w) 444(s) 436(sh) 426(s) 408(s) 391(sh) 354(sh) 347(s) 275(w) 226(w) 190(s)

m-FC_6H_4COO - 567(w) 539(m) 519(w) 442(m) 404(s) 358(m) 348(sh) 284(w) 230(w)

m-$CH_3C_6H_4COO$ - 576(w) 552(w) 521(m) 495(m) 441(sh) 428(m) 403(m) 354(sh) 346(m) 285(w) 229(m)

3,5-$(NO_2)_2C_6H_3COO$ - 555(m) 435(m) 420(sh) 390(w) 354(w) 282(w) 239(w)

2,5-$(NO_2)_2C_6H_3COO$ - 605(sh) 588(m) 570(w) 524(w) 470(w) 440(sh) 422(m) 415(sh) 387(w) 332(w) 286(w) 239(w)

2,4,6-$(NO_2)_3C_6H_2COO$ - 562(sh) 553(m) 517(w) 488(m) 441(w) 432(w) 390(w) 354(w) 310(w) 282(w) 243(w)

CF_3COO- 554(w) 521(w) 495(w) 440(w) 390(w) 351(w) 293(sh) 280(w) 240(w)

Appendix IV

Derivation of the general formula for the variation-perturbation method

Using the notation of Karplus and Kolker (78)

$$\Delta E_a^{2}(\bar{\Psi}_a^{1}) = \langle \bar{\Psi}_a^{1} | H_a^{o} - E_a^{o} | \bar{\Psi}_a^{1} \rangle + \langle \bar{\Psi}_a^{1} | H^{1} - \Delta E_a^{1} | \bar{\Psi}_a^{o} \rangle + \langle \bar{\Psi}_a^{o} | H^{1} - \Delta E_a^{1} | \bar{\Psi}_a^{1} \rangle \quad (1)$$

$$\bar{\Psi}_a^{1} = \sum_i \bar{\Psi}_{ai}^{1} \quad (2)$$

$$\bar{\Psi}_{ai}^{1} = (2n!)^{-\frac{1}{2}} | \phi_1^{o}(1) \cdots \phi_{(i-1)}^{o}(i)\, \phi_i^{1}(i) \cdots \phi_{(i+1)}^{o}(i+1) \cdots \phi_{2n}^{o}(2n) | \quad (3)$$

$$\phi_i^{1}(i) = fi(i)\, \phi_i^{o}(i) \quad (4)$$

$$H^{1}(1,2 \cdots 2n) = \sum_i h^{1}(i) \quad (5)$$

Introducing (2) into (1)

$$\Delta E_a^{2} = \sum_{i=1}^{2n} \sum_{i=1}^{2n} \langle \bar{\Psi}_{ai}^{1} | H_a^{o} - E_a^{o} | \bar{\Psi}_{ai}^{1} \rangle + \sum_{i=1}^{2n} \left\{ \langle \bar{\Psi}_a^{o} | H^{1} - \Delta E_a^{1} | \bar{\Psi}_{ai}^{1} \rangle + \langle \bar{\Psi}_{ai}^{1} | H^{1} - \Delta E_a^{1} | \bar{\Psi}_a^{o} \rangle \right\} \quad (6)$$

Considering the second term of equation (6) and substituting in (3), (4) and (5)

$$\langle \bar{\Psi}_a^{\,o} \mid H^1 - \Delta E_a^{\,1} \mid \bar{\Psi}_{ai}^{\,1} \rangle = (2n!)^{-1}$$

$$\langle \mid \phi_1^{\,o}(1) -- \phi_i^{\,o}(i) -- \phi_{2n}^{\,o}(2n) \mid \mid$$

$$\sum_j (h^1(j) - \Delta\epsilon_j^{\,1}) \mid \mid \phi_i^{\,o}(1) --- fi(i)$$

$$\phi_i^{\,o}(i) --- \phi_{2n}^{\,o}(2n) \mid \rangle$$

$$= \langle \phi_i^{\,o} \mid h^1 - \Delta\epsilon_i^{\,1} \mid fi\,\phi_i^{\,o} \rangle - \sum_{j \neq i}^{2n} \langle \phi_i^{\,o} \mid h^1 \mid \phi_j^{\,o} \rangle$$

$$\langle \phi_j^{\,o} \mid fi\,\phi_i^{\,o} \rangle \qquad (7)$$

Similarly the third term of equation (6) on substitution reduces to

$$\langle \bar{\Psi}_{ai}^{\,1} \mid H^1 - \Delta E_a^{\,1} \mid \bar{\Psi}_a^{\,o} \rangle = \langle fi\,\phi_i^{\,o} \mid h^1 - \Delta\epsilon_i^{\,1} \mid \phi_i^{\,o} \rangle$$

$$- \sum_{j \neq i}^{2n} \langle \phi_j^{\,o} \mid h^1 \mid \phi_i^{\,o} \rangle \langle fi\,\phi_i^{\,o} \mid \phi_j^{\,o} \rangle \qquad (8)$$

Considering the first term of equation (6)

$$H_a^{\,o} \bar{\Psi}_{ai}^{\,1} = \left[-\left(\frac{\hbar^2}{2m}\right) \nabla^2 + V_a^{\,o} \right] \bar{\Psi}_{ai}^{\,1}$$

$$= -(2n!)^{-\frac{1}{2}} \mid \phi_1^{\,o} --- \nabla^2 (fi\,\phi_i^{\,o}) --- \phi_{2n}^{\,o}$$

$$+ V_a^{\,o} \bar{\Psi}_{ai}^{\,1}$$

Considering the identity

$$\nabla^2 (fi\,\phi_i^{\,o}) = fi\,\nabla^2 \phi_i^{\,o} + \phi_i^{\,o} \nabla^2 fi + 2\,\nabla fi . \nabla \phi_i^{\,o}$$

$$= E_a^{\circ} \bar{\Psi}_{ai}^{1} - \frac{h^2}{2m} (2n.)^{-\frac{1}{2}} \Big\{ | \phi_1^{\circ}(1) \text{---} \phi_i^{\circ}(i) \nabla^2 fi(i) \text{---} \phi_{2n}^{\circ}(2n)| + 2| \phi_1^{\circ}(1) \text{---} \nabla fi(i). \nabla \phi_i^{\circ}(i) \text{---} \phi_{2n}^{\circ}(2n)| \Big\} \quad (9)$$

Introducing (9) into the first term of (6)

$$\langle \bar{\Psi}_{ai}^{1} | H_a^{\circ} - E_a^{\circ} | \bar{\Psi}_{ai}^{1} \rangle = -\frac{h^2}{2m} (2n.)^{-1} \Big\{ \langle | \phi_i^{\circ}(1) \text{---} fi\, \phi_i^{\circ}(i) \text{---} \phi_{2n}^{\circ}(2n)| | \phi_1^{\circ}(1) \text{---} \phi_i^{\circ}(i) \nabla^2 fi(i) \text{---} \phi_{2n}^{\circ}(2n)| \rangle + 2 \langle | \phi_1^{\circ}(1) \text{---} fi\, \phi_i^{\circ}(i) \text{---} \phi_{2n}^{\circ}(2n)| | \phi_1^{\circ}(1) \text{---} \nabla fi(i). \nabla \phi_i^{\circ}(i) \text{---} \phi_{2n}^{\circ}(2n)| \rangle$$

$$= -\frac{h^2}{2m} \Big\{ \langle fi\, \phi_i^{\circ} | (\nabla^2 fi) | \phi_i^{\circ} \rangle + 2 \langle fi\, \phi_i^{\circ} | \nabla fi. \nabla | \phi_i^{\circ} \rangle - \sum_{j \neq i}^{2n} \Big[\langle fi\, \phi_i^{\circ} | \phi_j^{\circ} \rangle \langle \phi_j^{\circ} | (\nabla^2 fi) | \phi_i^{\circ} \rangle + 2 \langle fi \phi_i^{\circ} | \phi_j^{\circ} \rangle \times \langle \phi_j^{\circ} | \nabla fi. \nabla | \phi_i^{\circ} \rangle \Big] \Big\} \quad (10)$$

Integration by parts of the $\nabla^2 fi$ terms in (10) gives

$$\langle \bar{\Psi}_{ai}^{1} | H_a^{\circ} - E_a^{\circ} | \bar{\Psi}_{ai}^{1} \rangle = \frac{h^2}{2m} \Big\{ \langle \phi_i^{\circ} | \nabla fi^*. \nabla fi | \phi_i^{\circ} \rangle - \sum_{j \neq i}^{2n} \langle fi\, \phi_i | \phi_j \rangle \Big[\langle \phi_i^{\circ} | \nabla fi. \nabla | \phi_j^{\circ} \rangle - \langle \phi_j^{\circ} | \nabla fi. \nabla | \phi_i^{\circ} \rangle \Big] \Big\} \quad (11)$$

It may be shown that

$$\langle \bar{\Psi}_{aj}^{1} \mid H_a^{0} - E_a^{0} \mid \bar{\Psi}_{ai}^{1} \rangle = 0$$

Substituting from (7) (8) and (11) into (6)

$$\Delta E_a^{2} = \sum_{i=1}^{2n} \Big[\frac{\hbar^2}{2m} \langle \phi_i^{0} \mid \nabla f_i^{*} . \nabla f_i \mid \phi_i^{0} \rangle$$

$$+ \langle \phi_i^{0} \mid h^{1} - \Delta \epsilon_i^{1} \mid f_i \phi_i^{0} \rangle$$

$$+ \langle f_i \phi_i^{0} \mid h^{1} - \Delta \epsilon_i^{1} \mid \phi_i^{0} \rangle$$

$$- \sum_{j \neq i}^{2n} \Big\{ \frac{\hbar^2}{2m} \langle f_i \phi_i \mid \phi_j \rangle \Big[\langle \phi_i^{0} \mid \nabla f_i . \nabla \mid \phi_j^{0} \rangle$$

$$- \langle \phi_j^{0} \mid \nabla f_i . \nabla \mid \phi_i^{0} \rangle \Big]$$

$$+ \langle \phi_i^{0} \mid h^{1} \mid \phi_j^{0} \rangle \langle \phi_j^{0} \mid f_i \phi_i^{0} \rangle$$

$$+ \langle \phi_j^{0} \mid h^{1} \mid \phi_i^{0} \rangle \langle f_i \phi_i^{0} \mid \phi_j^{0} \rangle \Big\} \Big] \qquad (12)$$

This is identical with the expression derived by Karplus and Kolker.

Derivation of expression for susceptibility

$$h^1 = \frac{e}{2mc}\ \tilde{m}.\ \tilde{H} \qquad (14)$$

Let the spin orbitals ϕ_i° be replaced by space orbitals ψ_i°

$$\psi_i' = fi\ \psi_i^{\circ} = \left[\frac{e}{2mc}\ \tilde{H}.\tilde{R}_i\right]\ \psi_i^{\circ} \qquad (15)$$

Substituting in (12) and retaining only the terms in H^2.

$$\Delta E_a^{\,2} = \frac{H^2 e^2}{2m^2c^2} \sum_{i=1}^{n} \Big[\frac{\hbar^2}{2m} \langle \psi_i^{\circ} | (\nabla R_i^{*}.\nabla R_i) | \psi_i^{\circ} \rangle$$

$$+ \langle \psi_i^{\circ} | m | R_i \psi_i^{\circ} \rangle + \langle R_i \psi_i^{\circ} | m | \psi_i^{\circ} \rangle$$

$$- \sum_{j \neq i}^{n} \Big\{ \frac{\hbar^2}{2m} \langle R_i \psi_i^{\circ} | \psi_j^{\circ} \rangle \big[\langle \psi_i^{\circ} | \nabla R_i.\nabla | \psi_j^{\circ} \rangle$$

$$- \langle \psi_j^{\circ} | \nabla R_i.\nabla | \psi_i^{\circ} \rangle \big] + \langle \psi_i^{\circ} | m | \psi_j^{\circ} \rangle$$

$$\langle \psi_j^{\circ} | R_i \psi_i^{\circ} \rangle + \langle \psi_j^{\circ} | m | \psi_i^{\circ} \rangle \langle R_i \psi_i^{\circ} | \psi_j^{\circ} \rangle \qquad (16)$$

The susceptibility tensor χ is defined as

$$\Delta E = -\tfrac{1}{2}\, H.\chi.H$$

Therefore from (16)

$$\chi_{\mu\mu}^{\,P} = -\frac{e^2}{m^2c^2} \sum_{i=1}^{n} \Big\{ \frac{\hbar^2}{2m} \langle \psi_i^{\circ} | (\nabla R_i^{*}.\nabla R_i) | \psi_i^{\circ} \rangle$$

$$+ \langle \psi_i^{\circ} | m_\mu | R_{i\mu} \psi_i^{\circ} \rangle + \langle R_{i\mu} \psi_i^{\circ} | m_\mu | \psi_i^{\circ} \rangle$$

$$- \sum_{j\neq i}^{n} \left\{ \frac{\hbar^2}{2m} \langle R_{i\mu} \psi_i^{\circ} | \psi_j^{\circ} \rangle \left[\langle \psi_i^{\circ} | \nabla R_{i\mu} \nabla | \psi_j^{\circ} \rangle \right.\right.$$
$$- \langle \psi_j^{\circ} | \nabla R_{i\mu} \nabla | \psi_i^{\circ} \rangle]$$
$$+ \langle \psi_i^{\circ} | m_{\mu} | \psi_j^{\circ} \rangle \langle \psi_j^{\circ} | R_{i\mu} | \psi_i^{\circ} \rangle$$
$$\left.\left. + \langle \psi_j^{\circ} | m_{\mu} | \psi_i^{\circ} \rangle \langle R_i \psi_i^{\circ} | \psi_j^{\circ} \rangle \right\}\right\}$$

As m is Hermitian and pure imaginary, if R_i is also pure imaginary this may be reduced to

$$\chi_{\mu\mu}^{P} = - \frac{e^2}{m^2c^2} \sum_{i=1}^{n} \left\{ \frac{\hbar^2}{2m} \langle \psi_i^{\circ} | (\nabla R_{i\mu}^{*} \nabla R_{i\mu}) | \psi_i^{\circ} \rangle \right.$$
$$+ \langle \psi_i^{\circ} | (m_{\mu} R_{i\mu}) | \psi_i^{\circ} \rangle$$
$$- \sum_{j\neq i}^{n} \left\{ \frac{\hbar^2}{2m} \langle R_{i\mu} \psi_i^{\circ} | \psi_j^{\circ} \rangle \right.$$
$$[\langle \psi_i^{\circ} | \nabla R_{i\mu} \nabla | \psi_j^{\circ} \rangle - \langle \psi_j^{\circ} | \nabla R_{i\mu} \nabla | \psi_i^{\circ} \rangle]$$
$$\left.\left. + 2 \langle \psi_i^{\circ} | m_{\mu} | \psi_j^{\circ} \rangle \langle \psi_j^{\circ} | R_{i\mu} | \psi_i^{\circ} \rangle \right\}\right\} \quad (17)$$

For this to be compared with Karplus and Kolker's formula (42) the orbitals must be treated as though they were Hartree-Foch orbitals. Then on integration by parts

$$(\hbar^2/2m) (\langle \psi_i^{\circ} | \nabla R_{i\mu} \cdot \nabla | \psi_j^{\circ} \rangle - \langle \psi_j^{\circ} | \nabla R_i \cdot \nabla | \psi_i^{\circ} \rangle)$$
$$= - (\hbar^2/2m) (\langle \psi_i^{\circ} | R_{i\mu} \nabla^2 | \psi_j^{\circ} \rangle - \langle \psi_j^{\circ} | R_{i\mu} \nabla^2 | \psi_i^{\circ} \rangle)$$
$$= (\epsilon_j^{\circ} - \epsilon_i^{\circ}) \langle \psi_j^{\circ} | R_{i\mu} | \psi_i^{\circ} \rangle$$

Substituting into (17)

$$\chi_{\mu\mu}{}^{P} = -\frac{e^2}{m^2c^2}\sum_{i=1}^{n}\Big\{\frac{\hbar^2}{2m}\langle\psi_i{}^{o}\,|\,(\nabla R_{i\mu}{}^{*}\nabla R_{i\mu})\,|\,\psi_i{}^{o}\rangle$$

$$+\langle\psi_i{}^{o}\,|\,(m_\mu R_{i\mu})\,|\,\psi_i{}^{o}\rangle$$

$$-\sum_{j\neq i}^{n}\Big[(\epsilon_j{}^{o}-\epsilon_i{}^{o})\langle\psi_i{}^{o}\,|\,R_{i\mu}{}^{*}\,|\,\psi_j{}^{o}\rangle\langle\psi_j{}^{o}\,|\,R_{i\mu}\,|\,\psi_i{}^{o}\rangle$$

$$+2\langle\psi_i{}^{o}\,|\,m_\mu\,|\,\psi_j{}^{o}\rangle\langle\psi_j{}^{o}\,|\,R_{i\mu}\,|\,\psi_i{}^{o}\rangle\Big\}\qquad(18)$$

This differs from Karplus and Kolker's expression (42) in the sign of the exchange terms (78).

Derivation of expression for shielding

$$h^1 = (e/2mc)\,\tilde{H}.\tilde{m} + (e/mc)\,r^{-3}\,\tilde{\mu}.\tilde{m} \qquad (19)$$

$$fi = 1 + (e/2mc)\,\tilde{H}.\tilde{fi} + (e/mc)\,\tilde{\mu}.\tilde{gi} \qquad (20)$$

Subetituting (19) and (20) into (12) and extracting terms in $\mu^{\alpha} H^{\alpha}$

$$\begin{aligned}
\sigma_{\alpha|\alpha}{}^{P} = \sum_{i=1}^{2n} \Bigg\{ & \frac{\hbar^2}{2m} \cdot \frac{e^2}{2m^2c^2} \langle \phi_i{}^{o} | \nabla fi^{\alpha|*} . \nabla gi^{\alpha} \\
& + \nabla gi^{\alpha|*} . \nabla fi^{\alpha} | \phi_i{}^{o} \rangle \\
& + \frac{e^2}{2m^2c^2} \langle \phi_i{}^{o} | m^{\alpha|} | gi^{\alpha} \phi_i{}^{o} \rangle \\
& + \frac{e^2}{2m^2c^2} \langle gi^{\alpha|} \phi_i{}^{o} | m^{\alpha} | \phi_i{}^{o} \rangle \\
& + \frac{e^2}{2m^2c^2} \langle \phi_i{}^{o} | r^{-3} m^{\alpha|} fi^{\alpha} | \phi_i{}^{o} \rangle \\
& [illegible] \\
& + \frac{e^2}{2m^2c^2} \langle fi^{\alpha|} \phi_i{}^{o} | r^{-3} m^{\alpha} | \phi_i{}^{o} \rangle \\
- \frac{e^2}{2m^2c^2} \sum_{j \neq i}^{2n} \Big[& \frac{\hbar^2}{2m} \big(\langle \phi_i{}^{o} | \nabla gi^{\alpha|} . \nabla | \phi_j{}^{o} \rangle \\
& - \langle \phi_j{}^{o} | \nabla gi^{\alpha|} . \nabla | \phi_i{}^{o} \rangle \big) \langle fi^{\alpha} \phi_i{}^{o} | \phi_j{}^{o} \rangle \\
& + \frac{h^2}{2m} \big(\langle \phi_i{}^{o} | \nabla fi^{\alpha|} . \nabla | \phi_j{}^{o} \rangle - \langle \phi_j{}^{o} | \nabla fi^{\alpha} . \nabla | \phi_i{}^{o} \big) \\
& \langle gi^{\alpha} \phi_i{}^{o} | \phi_j{}^{o} \rangle + 2 \big(\langle \phi_i{}^{o} | m^{\alpha|} | \phi_j{}^{o} \rangle \langle \phi_j{}^{o} | gi^{\alpha} \phi_i{}^{o} \rangle \\
& + \langle \phi_i{}^{o} | r^{-3} m^{\alpha|} | \phi_j 8 \rangle \times \langle \phi_j{}^{o} | fi^{\alpha} | \phi_i{}^{o} \rangle \big) \Big] \Bigg\} \qquad (21)
\end{aligned}$$

Assuming fi and gi are pure imaginary and summing over spatial rather than spin orbitals

$$\sigma_{\alpha|\alpha}{}^{P} = \frac{e^2}{m^2c^2} \sum_{i=1}^{n} \Big\{ -\frac{\hbar^2}{m} \langle \psi_i{}^{o} | \nabla f_i{}^{\alpha|} \cdot \nabla g_i{}^{\alpha} | \psi_i{}^{o} \rangle$$

$$+ \langle \psi_i{}^{o} | (m^{\alpha|} g_i{}^{\alpha} + r^{-3} m^{\alpha|} f_i{}^{\alpha}) | \psi_i{}^{o} \rangle$$

$$- \sum_{j \neq i}^{n} \Big[\frac{\hbar^2}{2m} \big(\langle \psi_i{}^{o} | \nabla g_i{}^{\alpha|} \cdot \nabla | \psi_j{}^{o} \rangle$$

$$- \langle \psi_j{}^{o} | \nabla g_i{}^{\alpha|} \cdot \nabla | \psi_i{}^{o} \rangle \big) \langle f_i \psi_i{}^{o} | \psi_j{}^{o} \rangle$$

$$+ \frac{\hbar^2}{2m} \big(\langle \psi_i{}^{o} | \nabla f_i{}^{\alpha|} \cdot \nabla | \psi_j{}^{o} \rangle$$

$$- \langle \psi_j{}^{o} | \nabla f_i{}^{\alpha|} \cdot \nabla | \psi_i{}^{o} \rangle \big) \langle g_i{}^{\alpha} \psi_i{}^{o} | \psi_j{}^{o} \rangle \qquad (22)$$

Assuming that the $\psi_i{}^{o}$ are Hartree-Fock orbitals

$$= \frac{e^2}{m^2c^2} \sum_{i=1}^{n} \Big\{ -\frac{\hbar^2}{m} \langle \psi_i{}^{o} | \nabla f_i{}^{\alpha|} \cdot \nabla g_i{}^{\alpha} | \psi_i{}^{o} \rangle$$

$$+ \langle \psi_i{}^{o} | (m^{\alpha|} g_i{}^{\alpha} + r^{-3} m^{\alpha|} f_i{}^{\alpha}) | \psi_i{}^{o} \rangle$$

$$+ 2 \sum_{j \neq i}^{n} \Big[\langle \psi_j{}^{o} | m^{\alpha|} | \psi_i{}^{o} \rangle \langle \psi_j{}^{o} | g_i{}^{\alpha} | \psi_i{}^{o} \rangle$$

$$+ \langle \psi_j{}^{o} | r^{-3} m^{\alpha|} | \psi_i{}^{o} \rangle \times \langle \psi_j{}^{o} | f_i{}^{\alpha} | \psi_i{}^{o} \rangle$$

$$+ (\epsilon_j{}^{o} - \epsilon_i{}^{o}) \langle \psi_i{}^{o} | f_i{}^{\alpha|} | \psi_j{}^{o} \rangle \langle \psi_j{}^{o} | g_i{}^{\alpha} | \psi_i{}^{o} \rangle$$

Again this is found to differ from the expression derived by Karplus and Kolker (79).

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