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The Signs of Nuclear Spin-spin Coupling Constants in Some Organoplatinum Compounds

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Summary

The signs and magnitudes of the electron-mediated nuclear spin-spin coupling constants involving ^{1}H, ^{19}F, ^{31}P and ^{195}Pt have been measured in the representative organoplatinum species $[Pt(CF_3C{\equiv}CCF_3)(PPh_3)_2]$, $[Pt(F_2C{=}CF_2)(PPh_3)_2]$ and $[\{Pt(Me)(PMe_2Ph)\mu\text{-}(SMe)\}_2]$ by means of $^{1}H\text{-}\{^{31}P\}$, $^{1}H\text{-}\{^{195}Pt\}$, $^{19}F\text{-}\{^{31}P\}$, $^{19}F\text{-}\{^{195}Pt\}$ and $^{31}P\text{-}\{^{195}Pt, {}^{1}H\}$ double and triple resonance NMR experiments. The results are compared with those for corresponding trifluoromethyl and mononuclear species.

Introduction

A knowledge of the signs (and magnitudes) of the electron-mediated internuclear spin-spin coupling constants in a molecule is necessary for the development of theories which describe their origin, and also ultimately which describe the detailed electronic structure of the molecule. At present these applications are not particularly well developed for the more complex organometallic compounds, but nevertheless a knowledge of the signs of coupling constants can be of great diagnostic utility in the determination of structure. Thus for example, in simple monomeric bis(phosphine) methyl derivatives of platinum(II), the vicinal coupling $^3\underline{J}(^{31}P\text{—}Pt\text{—}C\text{—}^1H)$(cis) is generally positive, whereas the corresponding trans coupling is negative.[1] This also holds for simple organo-platinum(IV) compounds,[2] and appears to be quite general for many organometallic compounds of late transition metal species such as those of gold(III)[3] and of rhodium(III).[4] In the corresponding trifluoromethyl compounds, on the other hand, the couplings $^3\underline{J}(^{31}P\text{—}M\text{—}C\text{—}^{19}F)$(cis) and (trans) are both positive. However, the magnitude of the cis coupling is much the smaller indicating that it has significant negative contributions which may actually predominate in some cases.[3,4] We now report the extension of these relative sign measurements to include representative examples of other interesting organoplatinum structural types; namely, the unsaturated fluorocarbon derivatives $[Pt(F_2C{=}CF_2)(PPh_3)_2]$ and $[Pt(F_3CC{\equiv}CCF_3)(PPh_3)_2]$, together with the binuclear platinum(II) compound syn-$[\{Pt(CH_3)(PMe_2Ph)(\mu\text{-}SMe)\}_2]$.

Experimental

Compounds were made by published methods,[5-7] and examined at 24° as saturated solutions in CH_2Cl_2. The NMR experiments in which ^1H and ^{19}F spectra were observed were carried out in the continuous wave (CW) mode on a JEOL C-60H instrument operating at 60 (^1H) or 56.4 (^{19}F) MHz, which was modified for double resonance experiments by the addition of a second radiofrequency (r.f.) coil in the probe. Experiments involving the observation of ^{31}P were carried out in the pulsed Fourier transform (FT) mode on a JEOL FX 60 instrument in which the proton-irradiation probe circuitry was double tuned to accept an additional radiofrequency. R.f. power at frequencies of _ca_. 24.2 and 12.8 MHz for $\{^{31}P\}$ and $\{^{195}Pt\}$ double irradiation experiments were provided by a Schlumberger FS-30 frequency synthesiser together with a tuned amplifier. C60-H spectra were calibrated using audio-frequency sidebands.

Results

The ^{19}F NMR spectrum of $[Pt(F_2C{=}CF_2)(PPh_3)_2]$(I) was that of the X portion of an $[AX_2]_2$ spin system,[8,9] (where X = ^{19}F, A = ^{31}P), coupling to the protons of the phenyl groups being small enough to be neglected in the present context. These lines were flanked by similar satellites due to molecules containing ^{195}Pt (natural abundance 34%) which is at a position of magnetic symmetry in this molecule. $^{19}F-\{^{31}P\}$ and $^{19}F-\{^{195}Pt\}$ experiments on these were straightforward[3] and gave respectively the signs of $^2\underline{J}(^{195}Pt-^{19}F)$ (negative) and $\underline{N}[=^3\underline{J}(^{31}P-^{19}F)$(_cis_) + $^3\underline{J}(^{31}P-^{19}F)$(_trans_)] (positive) relative to $^1\underline{J}(^{195}Pt-^{31}P)$ taken[10] as positive. Analysis of the single resonance spectrum had previously shown[9] that $^3\underline{J}(^{31}P-^{19}F)$(_cis_) and (_trans_) were of the same sign and that their magnitudes were 38.0 and 24.5 Hz; both are therefore positive. The results are summarised in Table 1. The ^{19}F spectrum of $[Pt(F_3CC{\equiv}CCF_3)(PPh_3)_2]$(II) was that of the X part of an $[AX_3]_2$ spin-system, of which the $\underline{N}$ lines[11] were readily visible, but for which the remaining lines were not well resolved, this pattern was also flanked by satellites due to ^{195}Pt, and the $^{19}F-\{^{31}P\}$ and $^{19}F-\{^{195}Pt\}$ experiments were again straightforward (Figure 1). The results for this compound are also given in Table 1.

In the ^1H spectrum of [_cis_-$\{Pt(CH_3)(PMe_2Ph)(\mu\text{-}SMe)\}_2$](III) the _S_-methyl(_trans_ to phosphorus), _P_-methyl, and _Pt_-methyl resonances all exhibited coupling to both ^{195}Pt and ^{31}P,[7] and $^1H-\{^{31}P\}$ and $^1H-\{^{195}Pt\}$ experiments gave the sign of the couplings involving ^{195}Pt and ^{31}P respectively relative to $^1\underline{J}(^{195}Pt-^{31}P)$ again being taken[10] as positive. The _S_-methyl(_cis_ to phosphorus) protons exhibited negligible coupling

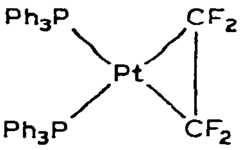
TABLE 1. ^{195}Pt and ^{31}P NMR data for $[Pt(F_2C{=}CF_2)(PPh_3)_2]$ (compound I) and $[Pt(F_3CC{\equiv}CCF_3)(PPh_3)_2]$ (compound II)

	(I)	(II)
$\Xi(^{195}Pt)$/Hz	21 394 430 ± 300	21 397 550 ± 15
$\delta(^{195}Pt)$/ppm[a]	−1240	−1094
$\Xi(^{31}P)$/Hz	40 481 743 ± 8	40 481 255 ± 15
(^{31}P)/ppm[b]	+25.7	+19.7
$^{1}J(^{195}Pt-^{31}P)$/Hz[c]	+2545 ± 30	+3590 ± 10
N/Hz	+61.6 ± 0.7[d]	+10.6 ± 0.2[e]
$^{n}J(^{195}Pt-^{19}F)$/Hz	+279.4 ± 0.7[f]	+66.5 ± 0.2[g]

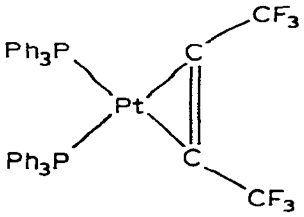
Notes. [a] To high frequency of *cis*$[Pt(Cl)_2(SMe_2)_2]$ in $CDCl_3$ [Ξ = 21 420 980 Hz (ref. 10)]. [b] To high frequency of 85% H_3PO_4 [Ξ = 40 480 790 Hz]. [c] Sign assumed to be positive (ref. 10). [d] $N = {}^{2}J(^{31}P-^{19}F) + {}^{2}J'(^{31}P-^{19}F)$; ref. 9 calculates $|^{2}J|$ and $|^{2}J'|$ as 38.0 and 24.5 Hz. [e] $N = {}^{3}J(^{31}P-^{19}F) + {}^{3}J'(^{31}P-^{19}F)$. [f] $n = 2$. [g] $n = 3$.

$^{4}J(^{31}P-^{1}H)$ which precluded the sign determination for $^{3}J(^{195}Pt-S-C-^{1}H)$ in this case, but it is likely that this latter is of the same sign (i.e. positive) as that for the corresponding coupling to the *S*-methyl protons *trans* to phosphorus.

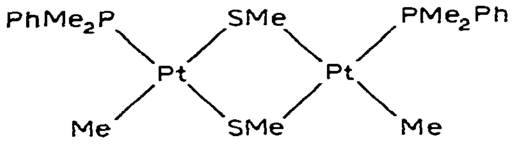
The $^{31}P-\{^{1}H(broadband)\}$ spectrum of (III) consisted of a central singlet from species containing only non-magnetic platinum, flanked by two sets of satellites from species containing one ^{195}Pt nucleus and



(I)



(II)



(III)

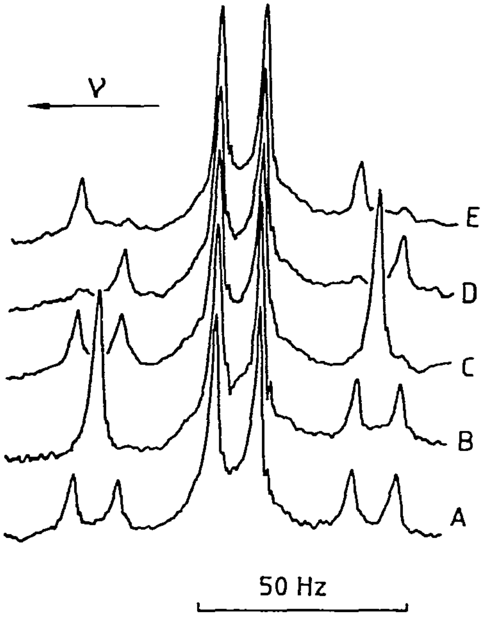


Figure 1 56.4 MHz ^{19}F, ^{19}F-$\{^{31}$P$\}$ and ^{19}F-$\{^{195}$Pt$\}$ NMR spectra of II; normal ^{19}F spectrum (A), and with simultaneous irradiation at (B) [$\nu(^{31}$P) + $\frac{1}{2}$ $^{1}\underline{J}(^{195}$Pt–^{31}P)], (C) [$\nu(^{31}$P) – $\frac{1}{2}$ $^{1}\underline{J}(^{195}$Pt–^{31}P)], (D) [$\nu(^{195}$Pt) + $^{1}\underline{J}(^{195}$Pt–^{31}P)], and (E) [$\nu(^{195}$Pt) – $^{1}\underline{J}(^{195}$Pt–^{31}P)].

associated with the couplings ${}^{1}\underline{J}({}^{195}Pt{-}{}^{31}P)$ and ${}^{3}\underline{J}({}^{195}Pt{-}S{-}Pt{-}{}^{31}P)$. The positions of the former set confirmed the value of the one-bond coupling obtained by the ${}^{1}H{-}\{{}^{195}Pt\}$ and ${}^{1}H{-}\{{}^{31}P\}$ experiments. Both inner and outer satellites actually arise from an AA′X (A = ${}^{31}P$, X = ${}^{195}Pt$) spin system and showed a splitting due to ${}^{4}\underline{J}({}^{31}P{-}{}^{31}P) = \pm 7$ Hz The effective chemical shift difference introduced between A and A′ in the different sub-spectra by ${}^{1}\underline{J}({}^{195}Pt{-}{}^{31}P)$ is so large that the system is effectively first order and the intensity pattern could not be used to give the relative signs of the two ${}^{195}Pt{-}{}^{31}P$ couplings. However, this was deduced from the spectrum of species containing two ${}^{195}Pt$ nuclei (vide infra). The sign of ${}^{4}\underline{J}({}^{31}P{-}{}^{31}P)$ was compared with that of ${}^{3}\underline{J}({}^{195}Pt{-}{}^{31}P)$ by a ${}^{31}P{-}\{{}^{195}Pt, {}^{1}H\}$ triple resonance experiment in which the components of the ${}^{195}Pt$ doublets were irradiated selectively. The observed spin-tickling behaviour of the outer satellites in the ${}^{31}P$ spectrum then showed these two couplings to be of like sign; that is ${}^{4}\underline{J}({}^{31}P{-}{}^{31}P)$ is negative. In addition to the foregoing there were lines which constituted the A part of an $[AX]_2$ spin system[12,13] from the 11% of molecules containing two ${}^{195}Pt$ nuclei. This spectrum is shown schematically in Figure 2, and the ${}^{195}Pt$ spectrum will be identical.[12] Half of the total intensity is in the two major lines of separation $\underline{N}[= {}^{1}\underline{J}({}^{195}Pt{-}{}^{31}P) + {}^{3}\underline{J}({}^{195}Pt{-}{}^{31}P)$ in this case]; since $|\underline{N}| < |{}^{1}\underline{J}({}^{195}Pt{-}{}^{31}P)|$ it follows that the two platinum-phosphorus couplings are of opposite sign, i.e. the long range one is negative. The remaining intensity is in the eight weaker lines numbered 1 to 8 for the ${}^{31}P$ spectrum and 1′ to 8′ for the ${}^{195}Pt$ spectrum, of which the positions depend upon $\underline{K}[= {}^{2}\underline{J}({}^{195}Pt{-}{}^{195}Pt) + {}^{4}\underline{J}({}^{31}P{-}{}^{31}P)]$, $\underline{L}[= {}^{1}\underline{J}({}^{195}Pt{-}{}^{31}P) - {}^{3}\underline{J}({}^{195}Pt{-}{}^{31}P)]$ and $\underline{M}[= {}^{4}\underline{J}({}^{31}P{-}{}^{31}P) - {}^{2}\underline{J}({}^{195}Pt{-}{}^{195}Pt)]$. The spectral analysis and inspection of the energy level diagram show that half (namely 1, 4, 5 and 8) of these weaker ${}^{31}P$ lines depend on $\underline{K}$ and are connected with the ${}^{195}Pt$ $\underline{N}$ lines and vice versa. It was found that when line 8′ in the ${}^{195}Pt$ spectrum was irradiated then line N_1 in the ${}^{31}P$ spectrum was perturbed but line N_2 remained unaffected.

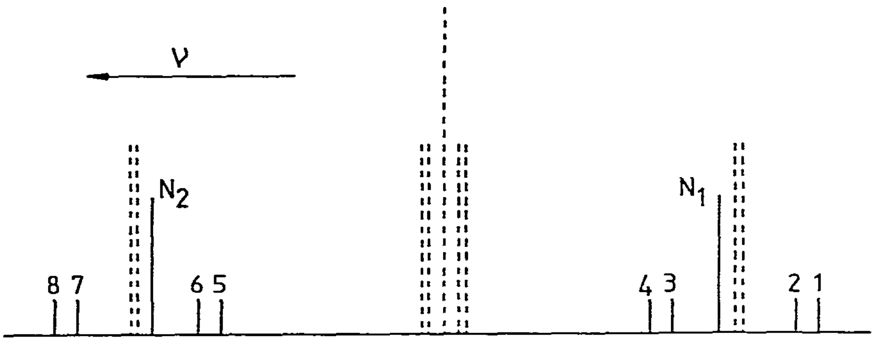


Figure 2 Schematic $^{31}P-\{^{1}H(broad\ band)\}$ NMR spectrum of III showing lines from species containing two ^{195}Pt nuclei. Broken lines indicate the positions of lines from species with one or no magnetic platinum nucleus. The intensities and positions are not to scale

It follows from this that K and N are of opposite sign and hence in this case that $^{2}J(^{195}Pt-^{195}Pt)$ is negative. Similar experiments involving the irradiation of the other ^{195}Pt lines 5′, 4′ and 1′ gave results leading to the same conclusion, and it should be noted that although these experiments probably involved simultaneous perturbation of the ^{195}Pt M lines (7′, 6′, 3′ and 2′) this does not affect the outcome since these lines are completely unconnected with the N lines. In principle this experiment could also be conducted by irradiating a ^{195}Pt N line and observing which of the phosphorus lines 1, 4, 5 and 8 were affected, but the method actually used is better because it involved observing a relatively strong line and thus provided a better signal-to-noise ratio. The results for compound (III) are summarised in Table 2, together with those of the chloro- analogue cis-$[\{Pt(Cl)(PMe_2Ph)\mu-(SMe_2)\}_2]$ (compound IV) for comparison.

TABLE 2. ^{195}Pt, ^{31}P and ^{1}H NMR data for *cis*-[{Pt(CH$_3$)(PMe$_2$Ph) μ-(SCH$_3$)}$_2$] (compound III) and *cis*[{Pt(Cl)(PMe$_2$Ph)μ-(SCH$_3$)}$_2$] (compound IV)

	(III)	(IV)
$\Xi(^{195}\mathrm{Pt})$/Hz	21 407 730 ± 70	21 415 565 ± 70
$\delta(^{195}\mathrm{Pt})$/ppm[a]	-619	-253
$\Xi(^{31}\mathrm{P})$/Hz	40 480 257 ± 15	40 480 192 ± 8
$\delta(^{31}\mathrm{P})$/ppm[b]	-13.2 ± 0.4	-14.8 ± 0.2
$^{1}J(^{195}\mathrm{Pt}-^{31}\mathrm{P})$/Hz[c]	+3750 ± 15	+3260 ± 10
$^{3}J(^{195}\mathrm{Pt-S-Pt}-^{31}\mathrm{P})$/Hz	-38 ± 4	[d]
$^{2}J(^{195}\mathrm{Pt-S}-^{195}\mathrm{Pt})$/Hz	-202 ± 3	[d]
$^{4}J(^{31}\mathrm{P-Pt-S-Pt}-^{31}\mathrm{P})$/Hz	-7 ± 1	[d]
$\delta(^{1}\mathrm{H})(\mathrm{CH_3Pt})$/ppm[e]	+0.23	-
$^{2}J(^{195}\mathrm{Pt-C}-^{1}\mathrm{H})$/Hz	-71.2 ± 0.2	-
$^{3}J(^{31}\mathrm{P-Pt-C}-^{1}\mathrm{H})$/Hz	+4.4 ± 0.2	-
$\delta(^{1}\mathrm{H})(\mathrm{CH_3P})$/ppm[e]	+1.60	+1.67 and +1.70
$^{3}J(^{195}\mathrm{Pt-P-C}-^{1}\mathrm{H})$/Hz	+37.1 ± 0.3	+31.3 ± 0.2
$^{2}J(^{31}\mathrm{P-C}-^{1}\mathrm{H})$/Hz	-9.7 ± 0.3	-10.9 ± 0.2
$\delta(^{1}\mathrm{H})(\mathrm{CH_3S})$(*trans* to P)/ppm[e]	+2.07	+2.27
$^{3}J(^{195}\mathrm{Pt-S-C}-^{1}\mathrm{H})$/Hz	+39.0 ± 0.5	+30.0 ± 0.5
$^{4}J(^{31}\mathrm{P-Pt-S-C}-^{1}\mathrm{H})$/Hz	+4.8 ± 0.3	+4.8 ± 0.2
$\delta(^{1}\mathrm{H})(\mathrm{CH_3S})$(*cis* to P)/ppm[e]	+2.04	+2.00
$\lvert{}^{3}J(^{195}\mathrm{Pt-S-C}-^{1}\mathrm{H})\rvert$/Hz[f]	23.4 ± 0.3	60.5 ± 0.5
$^{4}J(^{31}\mathrm{P-Pt-S-C}-^{1}\mathrm{H})$/Hz	*ca.* zero	*ca.* zero

Notes. [a] To high frequency of *cis*-[Pt(Cl)$_2$(SMe$_2$)$_2$] in CDCl$_3$ [Ξ = 21 420 980 Hz (ref. 10)]. [b] To high frequency of 85% H$_3$PO$_4$ [Ξ taken as 40 480 790 Hz]. [c] Sign assumed to be positive (ref. 10) Other signs are given relative to this. [d] Not measured. [e] To high frequency of (CH$_3$)$_4$Si [Ξ = 100 000 000 Hz]. [f] Sign could not be determined since $^{4}J(^{31}\mathrm{P}-^{1}\mathrm{H})$ was effectively zero; probably positive.

Discussion

The electron-mediated nuclear spin-spin coupling constant $^{2}\underline{J}(^{195}Pt-^{19}F)$ in compound (I) is of the same sign (positive) and similar magnitude as in a trifluoromethyl group which is also trans to a phosphine ligand.[3] However this is probably not diagnostic of a platinum(II) platinacyclopropane structure rather than an olefinic π-donor ligand platinum(0) species since the equivalent coupling $^{2}\underline{J}(^{195}Pt-^{1}H)$ in the π-ligand compound trans$[Pt(CH_2{=}CH_2)(Cl)(py)_2]$ is -60.6 Hz[14] which is also very similar to the values of -50 to -80 Hz found[15] for many methyl derivatives of platinum(II). The sign of this coupling in the hydrocarbon analogue $[Pt(CH_2{=}CH_2)(PPh_3)_2]$ (magnitude ca.60 Hz) is also probably negative, although in this case the sign determinations have so far been frustrated by the lability[17] of this compound in solution. The very similar values for the cis and trans couplings $^{3}\underline{J}(^{31}P-Pt-C-^{19}F)$ mean that these two are also of little diagnostic use, since it is probable that a change in substituent will easily produce a reversal of their relative magnitudes. This is in contrast to $^{3}\underline{J}(^{31}P-Pt-C-^{19}F)$(cis) and (trans) in trifluoromethylplatinum compounds which typically[3] differ by a factor of ca. 6, and to $^{3}\underline{J}(^{31}P-Pt-C-^{1}H)$(cis) and (trans) in corresponding methyl derivatives which are of opposite sign[1-3] as noted in the introduction.

That $^{3}\underline{J}(^{195}Pt-^{19}F)$ in compounds (II) is also positive is of interest, since the insertion of an sp^3 hybridised carbon atom in a σ-coupling path generally results in a sign reversal in the absence of any other coupling mechanism. In the present case however the increase in polarisability of the Pt-bonded carbon atom in the platinacyclopropenyl (compound II) as compared to the platinacyclopropyl (compound I) system will probably account[18] for both this and the dominant positive contributions to $^{4}\underline{J}(^{31}P-^{19}F)$ which would also otherwise be expected to be negative when compared with the positive value of $^{3}\underline{J}(^{31}P-^{19}F)$ in compound (I).

In compound (III) the signs of the coupling constants involving protons are generally as expected for square planar platinum(II) compounds,[1-3,15,16] $^{3}J(^{195}Pt{-}S{-}C{-}^{1}H)$ is positive, indicating that there is no substantial diversion of S-electron character into the non-coordinated sulphur lone pair. The negative value of $^{2}J(^{195}Pt{-}S{-}^{195}Pt)$ contrasts to the positive value determined[19] for the dimethylsulphide bridged complex $[Pt(Cl)_3\mu\text{-}(SMe_2)Pt(Cl)_2(SMe_2)]^-$ but there are such large fluctuations in the magnitudes of $^{2}J(^{195}Pt{-}^{195}Pt)$ among the compounds that have so far been measured that it would be unwise to generalise at this stage.

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References

1. M.A. Bennett, R. Bramley and I.B. Tomkins, J.C.S. Dalton, (1973) 166.
2. R. Bramley, J.R. Hall, G.A. Swile and I.B. Tomkins, Austral. J Chem., 27 (1974) 2491.
3. J.D. Kennedy, W. McFarlane and R.J. Puddephatt, J.C.S. Dalton, (1976) 745.
4. E.M. Hyde, J.D. Kennedy, B.L. Shaw and W. McFarlane, J.C.S. Dalton, (1977) 1577.
5. R.D.W. Kemmitt and R.D. Moore, J. Chem. Soc.(A), (1971) 2472.
6. E.O. Greaves, C.J.L. Lock and P.M. Maitlis, Canad J. Chem., 46 (1968) 3879.
7. M.P. Brown, R.J. Puddephatt and C.E.E. Upton, J.C.S. Dalton, (1978) 2490.
8. R.M. Lynden-Bell, Mol Phys., 6 (1963) 601.
9. M. Green, R.B.L. Osborn, A.J. Rest and F.G.A. Stone, J. Chem. Soc.(A), (1968) 2525.

10. W. McFarlane, J. Chem. Soc.(A), (1967) 1922

11. R.K. Harris, Canad. J. Chem., 42 (1964) 2275.

12. J. Emsley, J. Feeney and L. Sutcliffe, High Resolution NMR Spectroscopy, (Pergamon, 1966) Vol. 1.

13. W. McFarlane, J. Chem. Soc.(A), (1968) 1715.

14. D.R. McMillin and R.S. Drago, Inorg. Chem., 13 (1974) 546.

15. J.D. Kennedy and W. McFarlane, unpublished results on the various methylplatinum compounds listed in ref. 16; these all had $^{2}J(^{195}Pt{-}C{-}^{1}H)$ negative

16. J.D. Kennedy, W. McFarlane, R.J. Puddephatt and P.J. Thompson, J.C.S. Dalton, (1976) 874.

17. C.D. Cook and K.Y. Wan, J. Amer. Chem. Soc , 92 (1970) 2595

18. Based on an extension of the arguments put forward by C. Schumann and H. Dreeskamp, J. Magnetic Res., 3 (1970) 204, to account for variations in couplings $^{2}J(XY)$.

19. N.M. Boag, J. Browning, C. Crocker, P.L. Goggin, R.J. Goodfellow, M. Murray and J.L. Spencer, J. Chem. Research (S), (1978) 228 [and (M), (1978) 2962].