The Signs of Nuclear Spin Coupling Constants in Some Trifluoromethyl Derivatives of Platinum and of Gold

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The signs and magnitudes of $^3J(^{31}P\cdots{}^1H)$, $^3J(^{31}P\cdots{}^{19}F)$, and other coupling constants have been determined by multiple-resonance methods in methyl and trifluoromethyl derivatives of platinum(II), platinum(IV), gold(I), and gold(III). Whilst $^3J(^{31}P\cdots{}^1H)$ is more negative when the coupling path is *trans* than when it is *cis*, the converse is true of $^3J(^{31}P\cdots{}^{19}F)$. The couplings fall into ranges which are sufficiently distinct to permit their diagnostic use, and their origin is discussed in terms of the bonding in the complexes.

THE magnitudes and signs of coupling constants between the nuclei of atoms separated by several chemical bonds are often sensitive to the nature of the other atoms in the coupling path. When one of the intervening atoms is a transition metal very marked variations may be observed which may depend upon the geometry of the metal (*e.g.* a *cis*- or *trans*-arrangement) and upon its oxidation state. For example, in square planar phosphine complexes of platinum(II) and palladium(II) the geminal coupling $^2J(^{31}P\text{–}M\text{–}^{31}P)$ is close to zero in the *cis*-isomers and plus several hundred Hz in the *trans*;[1] in some five-co-ordinate hydride phosphine complexes of iridium $^2J(^{31}P\text{–}Ir\text{–}^1H)$ can be large and of either sign depending upon the P–Ir–H interbond angle;[2] and in phosphine complexes of platinum-(II) and -(IV) with methyl groups attached to platinum the *cis*- and *trans*-vicinal couplings $^3J(^{31}P\text{–}Pt\text{–}C\text{–}^1H)$ are of opposite signs.[3]

This kind of information is important for two main reasons: firstly, in many cases it is possible to use the size or the sign of a suitable coupling constant to identify isomers or to assign resonances in an n.m.r. spectrum; and secondly, a knowledge of the signs of the coupling constants makes it possible to assess theories of chemical bonding which claim to predict these parameters, and hence to improve our understanding of the environment of the metal atom in such species. For the first of these uses it is necessary to have available a body of data on molecules of known stereochemistry, and with this in mind we have used multiple resonance techniques to

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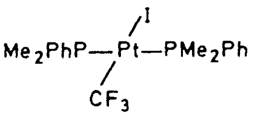
[1] A. Bright, B. E. Mann, C. Masters, B. L. Shaw, R. M. Slade, and R. E. Stainbank, *J. Chem. Soc. (A)*, 1971, 1826.

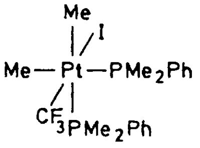
[2] G. Yagupsky and G. Wilkinson, *J. Chem. Soc. (A)*, 1969, 725.

[3] R. Bramley, J. R. Hall, G. A. Swile, and A. B. Tomkins, *Austral. J. Chem.*, 1974, **27**, 2491.

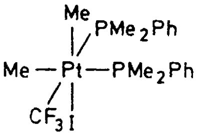
determine the signs and magnitudes of coupling constants in some trifluoromethyl derivatives (I)—(VII) of platinum(II), platinum(IV), gold(I), and gold(III).



(I)



(II)



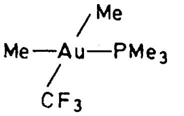
(III)

$CF_3-Au-PMePh_2$

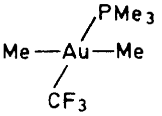
(IV)

$CF_3-Au-PMe_3$

(V)



(VI)



(VII)

In the course of this and other work we have also examined some 20 phosphine complexes of platinum-(II) and -(IV) with methyl groups attached directly to platinum and have confirmed the generality of the claims [3] that in such species $^3J(^{31}P-Pt-C-^1H)$ is positive when the coupling path is *cis* and negative when it is *trans*.

EXPERIMENTAL

The compounds (I)—(VII) were prepared by literature methods,[4-7] correct elemental analyses and n.m.r. spectra being taken as criteria of purity and isomeric identity. The n.m.r. measurements were done on *ca*. 10% solutions in CH_2Cl_2 at 23 °C at observing frequencies of 60 (^1H) and 56.4 (^{19}F) MHz using a modified JEOL C-60-H spectrometer. R.f. power (at frequencies of 12.8, 24.28, and 56.4 MHz for ^{195}Pt, ^{31}P, and ^{19}F respectively) was provided by a Schlumberger frequency synthesizer model FS-30 and tuned amplifier together with frequency doubling facilities for ^{19}F. The frequency synthesizer was also used to control the 60 MHz spectrometer transmitter for $^1H-\{X\}$ experiments, and the method [8] of generating the observing frequency of 56.4 MHz for the $^{19}F-\{X\}$ experiments was such as to reduce relative frequency drift to a negligible level ($< 1\,Hz\,h^{-1}$). In the $^1H-\{^{31}P,^{19}F\}$ triple-resonance experiments the frequency synthesizer provided power at 56.4 MHz, and a quartz-crystal oscillator generated the ^{31}P irradiating frequency.[9]

RESULTS

The results are given in Tables 1 and 2 and were generally obtained by standard $^1H-\{X\}$ and $^{19}F-\{X\}$ (X = ^{19}F, ^{31}P, or ^{195}Pt) experiments. Whenever possible the magnitudes of the coupling constants were measured directly from calibrated ^1H or ^{19}F spectra, and the signs of the coupling constants are based on the assumption that $^2J(^{31}P\cdots{}^1H)$ is negative in the complexed phosphine, and also for the platinum compounds that $^1J(^{195}Pt-^{31}P)$ is positive.[10] In view of the complexity of some of the spin systems the following points of interpretation are of interest.

(a) trans-$[Pt(CF_3)I(PMe_2Ph)_2]$ (I).—The CF_3 group is symmetrically related to the two phosphorus atoms and therefore the interpretation of the $^{19}F-\{X\}$ double-resonance experiments was straightforward. However, the methyl groups form with the two mutually *trans*-phosphorus nuclei an $[A_6X]_2$ spin system which gave a characteristic deceptively simple ^1H triplet (flanked by ^{195}Pt satellites) from which only the value of $N[= {}^2J(^{31}P\cdots{}^1H) + {}^4J(^{31}P\cdots{}^1H)]$ could be obtained directly. This was found to be negative by comparison with the sign of $^1J(^{195}Pt-^{31}P)$ and since the four bond coupling should be much smaller than the two it can be taken that $^2J(^{31}P\cdots{}^1H)$ is negative also, as expected. The magnitude and sign of $^2J(^{31}P\cdots{}^{31}P)$ were obtained by using $^1H-\{^{31}P\}$ experiments to detect weaker ' outer ' lines in the phosphorus spectrum as described elsewhere.[11] The heights of the *P*–methyl proton resonances were increased by *ca*. 15% by irradiation of the CF_3 resonances, and the differential effects obtained at lower amplitudes of B_2 were used to confirm certain of the relative signs given in Table 1. In addition a value for Ξ (^{19}F) was obtained in this way, thus obviating the need for an internal fluorine reference.

(b) $[Pt(CF_3)IMe_2(PMe_2Ph)_2]$ (II).—The $[A_3X]_2$ sub-system formed by the *Pt*–methyl protons and the mutually *cis*-phosphorus nuclei in this isomer is characterized by a small value of $^2J(^{31}P\cdots{}^{31}P)$ and thus the *Pt*–methyl resonance was a doublet (splitting = N) with additional intensity distributed about the baseline (see Figure 1). It was not possible to get an accurate value for $^2J(^{31}P\cdots{}^{31}P)$ in this molecule, but otherwise the experiments were straightforward. For example, the existence of the small *cis*-coupling $^4J(^{19}F\cdots{}^1H)$ permitted selective sharpening of the *Pt*–methyl resonance (Figure 1) upon irradiation of the ^{19}F

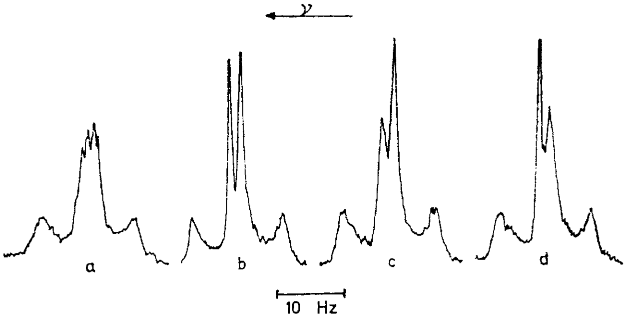


FIGURE 1 *Pt*–Methyl proton resonance of (II) under various conditions of ^{19}F irradiation. (a) Normal spectrum showing small splitting due to $^4J(^{19}F\cdots{}^1H)$ = *ca*. 0.7 Hz. (b) With ^{19}F decoupled. (c) With ^{19}F selectively decoupled by irradiation of the low frequency part of the ^{19}F resonance. (d) With ^{19}F selectively decoupled by irradiation of the high frequency part of the ^{19}F resonance

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[8] W. McFarlane, *Mol. Phys.*, 1970, **18**, 817.

[9] H. C. E. McFarlane, W. McFarlane, and D. S. Rycroft, *J.C.S. Faraday II*, 1972, 1300.

[10] I. J. Colquhoun, J. D. Kennedy, W. McFarlane, and R. J. Puddephatt, *J.C.S. Chem. Comm.*, 1975, 638.

[11] W. McFarlane and D. S. Rycroft, *J.C.S. Faraday II*, 1974, 377.

resonance, and thus the sign of $^{3}J(^{31}P \cdots {}^{19}F)$ was compared with $N[= {}^{3}J(^{31}P \cdots {}^{1}H)$ *cis* $+ {}^{3}J(^{31}P \cdots {}^{1}H)$*trans*] which itself was shown to be positive by $^{1}H-\{^{195}Pt\}$ experiments. It should be noted that the methyl groups on phosphorus are inequivalent in pairs in this isomer owing to effective dissymmetry at platinum.

(c) $[Pt(CF_3)IMe_2(PMe_2Ph)_2]$ (III).—In this isomer the two *Pt*-methyl and the four *P*-methyl groups are all inequivalent, and the resulting complexity of the ^{1}H spectrum precluded detailed analysis. The results listed were, therefore, obtained mainly from the ^{19}F spectrum although the inequivalence of the two phosphorus nuclei made it difficult to get precise values for the two platinum-to-phosphorus coupling constants which appeared to differ by *ca.* 300 Hz. Thus the central part of the ^{19}F spectrum was a typical A_3XX' pattern ($A = {}^{19}F$, $X = {}^{31}P$) showing the two phosphorus nuclei to have identical or almost identical chemical shifts and giving a value of 71.3 Hz for $|[^{3}J(^{31}P \cdots {}^{19}F)$*cis* $+ {}^{3}J(^{31}P \cdots {}^{19}F)$*trans*$]|$, while the large difference in the two values of $^{1}J(^{195}Pt-{}^{31}P)$ resulted in a large effective chemical shift difference for the phosphorus nuclei in molecules containing platinum-195. The platinum-195 satellites of the CF_3 resonance, therefore, had appearances characteristic of the A part of an A_3MX spin system and individual values for and relative signs of the two phosphorus-to-fluorine coupling constants were obtained from these. A $^{19}F-\{^{195}Pt\}$ experiment then gave their absolute signs relative to $^{1}J(^{195}Pt-{}^{31}P)$.

TABLE 1

N.m.r. parameters of trifluoromethyl platinum compounds

Parameter \ Compound	(I)	(II)	(III)
$J(^{195}Pt-{}^{31}P)$/Hz	$+2\,670 \pm 15$	$+1\,086 \pm 20$	*ca.* 1 400 [a]
$^{2}J(^{195}Pt \cdots {}^{19}F)$/Hz	$+754.0 \pm 1.5$	$+525 \pm 1.5$	$+425.8 \pm 1.5$
$^{2}J(^{195}Pt \cdots {}^{1}H)$/Hz		-57.5 ± 0.5	*b*
$[^{2}J(^{31}P \cdots {}^{1}H) + {}^{4}J(^{31}P \cdots {}^{1}H)]$/Hz	-7.3 ± 0.1	-9.3 ± 0.1	*b*
$^{2}J(^{31}P \cdots {}^{31}P)$/Hz	$+435 \pm 20$	Small	*b*
$^{3}J(^{195}Pt \cdots {}^{1}H)$/Hz	$+29.9 \pm 0.2$	$+10.5 \pm 0.5$	*b*
$[^{3}J(^{31}P \cdots {}^{1}H)_{cis} + {}^{3}J(^{31}P \cdots {}^{1}H)_{trans}]$/Hz		$+1.8 \pm 0.2$	*b*
$^{3}J(^{31}P \cdots {}^{19}F)$/Hz	$+20.9 \pm 0.3$	$+13.6 \pm 0.3$	$+10.9 \pm 0.6$ [*cis*] $+60.4 \pm 0.8$ [*trans*]
$\lvert{}^{4}J(^{19}F \cdots {}^{1}H)\rvert$/Hz	<0.2	0.7 ± 0.1	*b*
$\delta(^{1}H)$/p.p.m.[c] [P–Me]	$+1.92 \pm 0.01$	$+1.59, +1.70, \pm 0.01$	*b*
$\delta(^{1}H)$/p.p.m.[c] [Pt–Me]		$+1.03 \pm 0.01$	*b*
$\Xi(^{195}Pt)$/Hz	$21\,397\,880 \pm 80$	$21\,413\,100 \pm 300$	$21\,411\,420 \pm 150$
$\Xi(^{31}P)$/Hz	$40\,480\,376 \pm 15$	$40\,478\,983 \pm 15$	$40\,478\,930 \pm 20$
$\Xi(^{19}F)$/Hz	$94\,092\,887 \pm 3$	$94\,092\,189 \pm 3$	*b*

[a] Two different values of $^{1}J(^{195}Pt-{}^{31}P)$ are present, differing by *ca.* 300 Hz or more. [b] ^{1}H Spectrum too complex for detailed analysis. [c] To low-field of Me_4Si.

TABLE 2

N.m.r. parameters of trifluoromethyl gold compounds

Parameter \ Compound	(IV)	(V)	(VI)	(VII)
$^{2}J(^{31}P \cdots {}^{1}H)$/Hz	-9.3 ± 0.2	-10.0 ± 0.2	-10.6 ± 0.1	-11.3 ± 0.1
$^{3}J(^{31}P \cdots {}^{19}F)$/Hz [*cis*]			$+7.1 \pm 0.1$	
$^{3}J(^{31}P \cdots {}^{19}F)$/Hz [*trans*]	$+46.0 \pm 0.5$	$+48.3 \pm 0.5$		$+65.9 \pm 0.2$
$^{3}J(^{31}P \cdots {}^{1}H)$/Hz			$+8.5 \pm 0.1$ [*cis*] -8.9 ± 0.1 [*trans*]	$+5.6 \pm 0.1$
$\lvert{}^{4}J(^{19}F \cdots {}^{1}H)\rvert$/Hz			0.4 ± 0.2	0.53 ± 0.05
$\lvert{}^{5}J(^{19}F \cdots {}^{1}H)\rvert$/Hz	<0.2	<0.2	0.15 ± 0.05	0.37 ± 0.5
$\delta(^{1}H)$/p.p.m.[a] [P–Me]	$+1.95 \pm 0.01$	$+1.40 \pm 0.01$	$+1.42 \pm 0.01$	$+1.48 \pm 0.01$
$\delta(^{1}H)$/p.p.m.[a] [Au–Me]			$+0.32 \pm 0.01$ [*cis* to P] $+0.81 \pm 0.01$ [*trans* to P]	$+0.14 \pm 0.01$
$\Xi(^{31}P)$/Hz	$40\,481\,670 \pm 15$	$40\,480\,690 \pm 30$	$40\,480\,563 \pm 15$	$40\,480\,180 \pm 15$
$\Xi(^{19}F)$/Hz	$94\,090\,843 \pm 3$	$94\,091\,317 \pm 3$	$94\,091\,048 \pm 1$	$94\,090\,852 \pm 2$

[a] To low-field of Me_4Si.

(d) cis- *and* trans-$[Au(CF_3)Me_2(PMe_3)]$ (VI) *and* (VII).—These complexes were present in the same solution and in each case the existence of the small but finite couplings $^{4}J(^{19}F \cdots {}^{1}H)$ and $^{5}J(^{19}F \cdots {}^{1}H)$ permitted the various $^{1}H-\{^{19}F\}$ selective decoupling experiments which were needed to give the relative signs of the other coupling constants.

(e) $[Au(CF_3)(PMePh_2)]$ (IV).—Under our conditions of measurement there was no detectable coupling between fluorine and the methyl protons and so $^{1}H-\{^{19}F\}$ [and $^{19}F-\{^{1}H\}$] experiments designed to compare the signs of the couplings between these nuclei and phosphorus were unsuccessful. However, the magnitudes of $^{2}J(^{31}P \cdots {}^{1}H)$ and $^{3}J(^{31}P \cdots {}^{19}F)$ are such that a $^{1}H-\{^{31}P,{}^{19}F\}$ heteronuclear triple resonance experiment gave the required information [12] (see Figure 2). The degeneracy in the proton spectrum [(a)] associated with different spin states of ^{19}F was lifted by irradiation of a group of ^{31}P transitions associated with a particular value of $\Sigma F_z(^{19}F)$ with an r.f. field such that $\gamma(^{31}P)B_2/2\pi < |^{2}J(^{31}P \cdots {}^{1}H|$ [(b)]. Simultaneous irradiation at tickling power levels of transitions in the ^{19}F spectrum then produced observable effects in the ^{1}H spectrum and showed that the high frequency ^{19}F lines were associated with low frequency ^{1}H lines and *vice versa*. Thus

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[12] A. D. Cohen, R. Freeman, K. A. McLauchlan, and D. H. Whiffen, *Mol. Phys.*, 1963, **7**, 45; W. McFarlane, *J. Chem. Soc.* (*A*), 1967, 1148.

$^{2}J(^{31}\mathrm{P}\cdots{}^{1}\mathrm{H})$ and $^{3}J(^{31}\mathrm{P}\cdots{}^{19}\mathrm{F})$ are of opposite sign, *i.e.* the latter is positive.

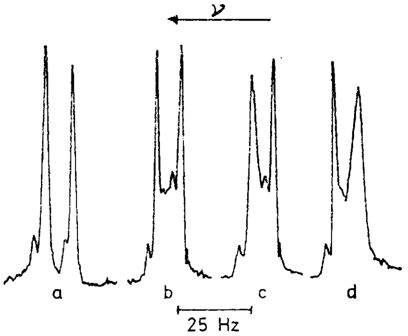

FIGURE 2 Triple resonance experiments on the CH_3 resonance of (IV). (a) Normal spectrum at reduced gain. (b) With selective irradiation of low frequency part of ^{31}P spectrum. (c) As for (b) with simultaneous irradiation (tickling) of the low frequency ^{19}F line. (d) As for (b) with simultaneous irradiation (tickling) of the high frequency ^{19}F line

DISCUSSION

It is apparent from our results for the four types of complex measured, namely platinum(II), platinum(IV), gold(I), and gold(III), that the differences between couplings *via* the *cis*- and *trans*-paths are large enough for both $^{3}J(^{31}\mathrm{P}\cdots{}^{1}\mathrm{H})$ and $^{3}J(^{31}\mathrm{P}\cdots{}^{19}\mathrm{F})$ to be used diagnostically. In particular we confirm the results of Bramley and his co-workers for methylplatinum compounds,[3] and show that these generalizations also extent to gold(III). The vicinal phosphorus-to-fluorine coupling constants also fall into distinct ranges according to whether the coupling path is *cis* or *trans*, and therefore should prove to be equally valuable in this context although in this case the couplings appear to be always positive. [It should be noted, however, that the relatively small value of $^{3}J(^{31}\mathrm{P}\cdots{}^{13}\mathrm{F})$ in (VI) indicates that in some molecules this *cis*-coupling may be negative.]

In octahedral and square planar transition-metal complexes the geminal coupling $^{2}J(^{31}\mathrm{P}\cdots{}^{31}\mathrm{P})$ is generally substantially more positive when the coupling route is *trans* than when it is *cis*, and indeed the two routes can lead to couplings of opposite sign.[1] This is because excitations involving the metal *p*-orbitals can make dominant (positive) contributions to the *trans*-coupling but not to the *cis*.[13] The sp^3 hybrid orbitals used by phosphorus in these complexes are of similar energy to the orbitals used by carbon or hydrogen in species with direct M–C or M–H bonds, and thus the couplings $^{2}J(^{31}\mathrm{P}\cdots{}^{13}\mathrm{C})$ and $^{2}J(^{31}\mathrm{P}\cdots{}^{1}\mathrm{H})$ should behave in a similar manner to $^{2}J(^{31}\mathrm{P}\cdots{}^{31}\mathrm{P})$. This is indeed found to be the case.[14]

The electronic excitations referred to above will contribute also to *vicinal* couplings involving phosphorus and another nucleus and, therefore, similar marked differences between the *cis*- and *trans*-paths are to be expected for these couplings as well. For $^{3}J(^{31}\mathrm{P}\cdots{}^{1}\mathrm{H})$ when the intervening carbon atom has a hybridization close to sp^3 (as will be the case in the molecules studied here) a sign reversal compared with the corresponding geminal coupling is to be expected and is observed. More specifically, the *trans*-relationship should, in general, lead to the more negative values of $^{3}J(^{31}\mathrm{P}\cdots{}^{1}\mathrm{H})$. We would also predict that $^{3}J(^{31}\mathrm{P}\cdots{}^{13}\mathrm{C})$ will be more negative when the coupling path is *trans* although no experimental evidence is available on this point.

Coupling constants involving fluorine are very much more difficult to understand than those involving hydrogen because the spin-dipolar and orbital terms can make appreciable contributions in addition to the more usual Fermi contact interaction.[15] Nonetheless it is true to say that couplings $^{n}J(^{19}\mathrm{F}\cdots\mathrm{X})$ are often of opposite sign to the corresponding couplings $^{n}J(^{1}\mathrm{H}\cdots\mathrm{X})$ and, further, that trends in coupling constants which involve fluorine are often in the opposite direction to those involving the proton. In the case of one-bond couplings this can be ascribed to π_{FX} and π_{HX}, the mutual polarizabilities of the valence *s* orbitals, having relatively large magnitudes and being negative and positive respectively. More generally, the behaviour stems from the large energy difference which normally exists between the valence *s* and *p* electrons of fluorine which leads to dominance of the Fermi contact coupling contribution by different excitations.

These general features can account for the trends observed in the present work: thus $^{2}J(^{195}\mathrm{Pt}\cdots{}^{19}\mathrm{F})$ is of opposite sign to $^{2}J(^{195}\mathrm{Pt}\cdots{}^{1}\mathrm{H})$, and in the case of $^{3}J(^{31}\mathrm{P}\cdots{}^{19}\mathrm{F})$ it is the *trans*-relationship which leads to the more positive value for the coupling constant although in the molecules studied so far the *cis*- and *trans*-couplings are actually of the same sign.

A further possibility which cannot be ruled out completely is that of ‘ through space ’ coupling[16] between phosphorus and fluorine when the relationship is *cis*. However, our results can be explained without recourse to this hypothesis.

Thus we believe that the differences between couplings $^{3}J(^{31}\mathrm{P}\cdots{}^{1}\mathrm{H})$ and $^{3}J(^{31}\mathrm{P}\cdots{}^{19}\mathrm{F})$ in these complexes arise from large differences in the relative energies of the valence *s* electrons of hydrogen and fluorine, while the differences between the *cis*- and *trans*-coupling paths are due to the availability of electronic excitations involving metal *p* orbitals of appropriate symmetry for the *trans*-relationship only.

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