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TRIFLUOROMETHYLTHIO AND TRIFLUOROVINYL COMPLEXES OF PLATINUM(II): MEASUREMENT OF *cis*- AND *trans*-INFLUENCE BY ^{31}P AND ^{19}F NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

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Summary

^{19}F and ^{31}P NMR data are reported for four series of complexes: (i) *trans*-[PtX(SCF$_3$)(PEt$_3$)$_2$], X = C$_6$H$_5$, CH$_3$, H, CF$_3$, C$_2$F$_3$, CN, NO$_2$, SCF$_3$, N$_3$, I, NCS, Br, Cl, and NO$_3$. (ii) *cis*-[PtX(SCF$_3$)(PEt$_3$)$_2$], X = CH$_3$, NO$_2$, SCF$_3$, N$_3$, NCS, NCO, and Cl. (iii) *trans*-[PtX(C$_2$F$_3$)(PEt$_3$)$_2$], X = CN, NO$_2$, SCF$_3$, N$_3$, I, Br, Cl, and NO$_3$. (iv) *trans*-[Pt(C$_2$F$_3$)(PEt$_3$)$_2$L] [ClO$_4$], L = PEt$_3$, P(OEt)$_3$, P(OMe)$_3$, P(OPh)$_3$, PPh$_3$, CO, and C$_5$H$_5$N. The results are used to establish scales of *cis*- and *trans*-influence for the X and L ligands and comparisons suggest that the *cis*-influence is much more sensitive to π-bonding, and possibly also to steric effects, than is the *trans*-influence. The π-bonding and steric effects are less evident when indirect coupling constants are used to measure the *cis*-influence and under these conditions rough inverse correlations with *trans*-influence may be obtained.

Introduction

The measurement of *trans*-influence by nuclear magnetic resonance spectroscopy has been extensively studied and the phenomena involved are reasonably well understood [1]. Thus, a ligand with high *trans*-influence is believed to weaken the bond *trans* to itself by causing rehybridisation of the metal σ orbitals. This in turn changes NMR coupling constants involving the *trans* bond since these are thought to be dominated by the Fermi contact contribution, which depends partly on the metal valence *s* character and hence on the hybridisation of the metal σ orbitals [1—3]. The original theory for the Fermi contact term applies to one bond ("direct") coupling constants but similar reasoning

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has been used to extend the argument to "indirect" coupling * between atoms separated by two or more bonds [4]. On the basis of these arguments many workers have compiled *trans*-influence series from NMR coupling constant data [1]. In contrast, *cis*-influence studies by NMR have been relatively few and unrewarding and the relationship between *cis*- and *trans*-influence has remained especially problematical [1,5,6]. For example, the theoretical study by Zumdahl and Drago [3] suggested that *cis*- and *trans*-influences should be comparable in magnitude and direction whereas experimental *cis*-influences determined by NMR (or indeed by most other techniques [5]) are generally small and not obviously correlated with *trans*-influence [5—8].

We have recently studied the ^{19}F NMR spectra of an extensive series of *cis*- and *trans*-$[PtX(SCF_3)(PEt_3)_2]$ complexes [9]. The three bond coupling, ^3J(PtF) in these complexes is exceptionally sensitive to *trans*-influence phenomena and in *trans* complexes varies from 42.2 (X = Ph) to 131.4 Hz (X = NO_3). The results also showed an approximate inverse linear correlation between *cis*- and *trans*-influences [9,10]. Other evidence for this trend was sparse but tended to suggest that the effect appears only when indirect couplings are used to measure the *cis*-influence. A further example has been observed subsequently [11]. Thus in the two series of complexes $[PtX(CH_3)(Ph_2PCH_2CH_2PPh_2)]$ and $[PtL(CH_3)(Ph_2PCH_2CH_2PPh_2)]^+$, there are rough inverse correlations between ^1J(PtP) (*trans* to X) and the indirect measure of *cis*-influence, ^2J(PtH) (*cis* to X). However, the direct measure of *cis*-influence, ^1J(PtP) (*cis* to X) does not correlate with ^2J(PtH) [11].

Because of the dearth of correlations between *cis*- and *trans*-influence it was interest to extend our study of SCF_3 complexes to ^{31}P NMR spectra in order to examine the direct Pt—P coupling constants as a measure of *cis*-influence. These results are reported in the present paper and they provide measures of *cis*- and *trans*-influences using both direct and indirect couplings in the same molecules. We also report ^{31}P and ^{19}F spectra of a series of C_2F_3 platinum complexes, *trans*-$[PtX(C_2F_3)(PEt_3)_2]$ and *trans*-$[Pt(C_2F_3)(PEt_3)_2L]^+$, which we synthesized in order to study the transmission of *cis*- and *trans*-influence in a system where the probe ligand has internal π-bonding. The data helps to clarify the role of π-bonding in NMR *cis*- and *trans*-influences and detailed comparisons between the various series suggest that the difficulty of correlating *trans*-influence with *cis*-influence, when direct coupling constants are used for the *cis* series, is due to the sensitivity of these couplings to π-bonding and steric effects.

Results

1. *Preparation of complexes*

Preparation and characterization of the *cis*- and *trans*-$[PtX(SCF_3)(PEt_3)_2]$ complexes has been described previous [9].

The complexes *trans*-$[PtX(C_2F_3)(PEt_3)_2]$ (X = CN, NO_2, SCF_3, N_3, I, Br and NO_3) and *trans*-$[Pt(C_2F_3)(PEt_3)_2L][ClO_4]$ (L = PEt_3, $P(OEt)_3$, $P(OMe)_3$, $P(OPh)_3$, PPh_3, CO and C_5H_5N) were prepared by ligand substitution reactions

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* Throughout this paper the term "indirect" coupling signifies coupling between atoms separated by more than one chemical bond. "Direct" coupling is between atoms directly bound to each other.

TABLE 1

NMR DATA FOR *cis*- AND *trans*-$[PtX(SCF_3)(PEt_3)_2]$ COMPLEXES [a]

	trans-Isomer			*cis*-Isomer [b]				
	^3J(PtF)	δ(P)	^1J(PtP)	^3J(PtF)	P *trans* to X		P *trans* to SCF_3	
					δ(P)	^1J(PtP)	δ(P)	^1J(PtP)
C_6H_5	42.2	129.9	2717					
CH_3	46.4	127.0	2740	93.0	130.6	1714	128.8	3557
H	52.0	120.1	2667					
CF_3	55.2	124.7	2651					
C_2F_3	61.2	127.9	2454					
CN	82.0	126.8	2230					
NO_2	88.6	129.5	2537	70.0	147.3	2781	130.5	3174
SCF_3	95.8	130.2	2354	68.7	129.5	3005	129.5	3005
N_3	110.5			64.0	136.2	3223	123.8	3099
I	118.8	134.0	2310					
NCS	122.6	125.8	2296	61.8	140.8	3360	126.9	2866
NCO	123.0			61.8	140.2	3391	127.7	2940
Br	128.0	130.4	2346					
Cl	129.0	127.9	2376	61.2	133.0	3535	126.7	2952
NO_3	131.4	124.5	2483					

[a] J and δ denote respectively NMR coupling constants (Hz) and chemical shifts (ppm upfield from $P(OCH_3)_3$ as external reference). The ^3J(PtF) values are from ref. 1 except for *cis*-$[Pt(CH_3)(SCF_3)(PEt_3)_2]$ which is present work. ^{31}P spectra were recorded in dichloromethane. [b] ^2J(PP) was in the range 17—22 Hz for all the *cis* complexes.

from the known [13] derivative with X = Cl. Chloride was removed by precipitation as NaCl (in acetone) or as AgCl and the appropriate ligands introduced (see Experimental). Preliminary characterisation was by micro-analysis, infrared spectroscopy and ^1H NMR and complete characterisation was from the detailed ^{19}F and ^{31}P NMR studies described below. Infrared spectra showed the expected ligand and anion absorptions including $\nu(C{=}C)$ in the range 1728—1741 cm^{-1}. Other prominent frequencies are given in the experimental. ^1H NMR spectra showed patterns for *trans*-triethylphosphine groups with "virtual coupling" of the phosphorus atoms [14].

2. *Analysis of NMR spectra*

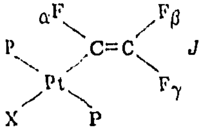
These data are collected in Tables 1, 2 and 3. In all three tables the complexes are listed in order of decreasing *trans*-influence of the X or L ligands as established by ^3J(PtF) in the SCF_3 complexes or by $^2J(PtF_\alpha)$ in the C_2F_3 complexes.

(a) Phosphorus-31. ^{31}P spectra of the complexes, *trans*-$[PtX(SCF_3)(PEt_3)_2]$, *trans*-$[PtX(C_2F_3)(PEt_3)_2]$, and *trans*-$[Pt(C_2F_3)(PEt_3)_2L]^+$ where L = CO or pyridine, were all simple 1/4/1 triplets resulting from coupling to ^{195}Pt (33.8% abundant, I 1/2). The line width did not permit the resolution of the small phosphorus—fluorine couplings. The cations, *trans*-$[Pt(C_2F_3)(PEt_3)_2L]^+$, where L = PR_3 or $P(OR)_3$, showed similar triplets for the PEt_3 groups, doubleted by phosphorus—phosphorus coupling. The L resonances were more complex due to the larger phosphorus—fluorine couplings when L is *trans* to the C_2F_3 group.

TABLE 2

NMR DATA FOR *trans*-[PtX(C_2F_3)(PEt_3)$_2$] COMPLEXES[a]

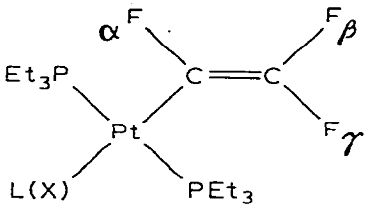
X	δ(P)	^1J(PtP)	$\delta(F_\alpha)$	$\delta(F_\beta)$	$\delta(F_\gamma)$	$^2J(PtF_\alpha)$	$^3J(PtF_\beta)$	$^3J(PtF_\gamma)$	$^3J(PF_\alpha)$	$^4J(PF_\beta)$	$^4J(PF_\gamma)$	$^3J_{\alpha\beta}$	$^3J_{\alpha\gamma}$	$^2J_{\beta\gamma}$
CN	127,0	2314	160,1	95,5	128,6	350	46	43	4,9	5,6	3,9	30	103	101
NO_2	126,2	2590	158,0	95,3	128,4	422	38	52	6,4	6,0	4,2	31	105	101
SCF_3	127,9	2454	153,0	99,0	129,0	441	44	51	3,1	5,6	3,6	32	104	105
N_3	122,6	2539	152,7	102,0	131,7	468	46	59	2,3	5,4	3,6	30	104	105
I	129,9	2441	145,5	102,3	128,9	510	57	59	4,8	6,0	4,2	33	103	102
Br	126,2	2478	146,7	104,8	129,3	519	57	60	<1	6,1	3,5	32	105	103
Cl	124,0	2510	147,9	100,8	130,5	512	56	61	1,5	6,0	3,5	31	105	105
NO_3	120,7	2603	151,5	102,9	131,7	538	52	60	2,3	5,9	4,2	32	105	102

[a] The fluorine atoms are labelled as follows:  *J* and δ denote respectively NMR coupling constants (Hz) and chemical shifts (ppm upfield from $CFCl_3$ or $P(OCH_3)_3$ as external references). ^{31}P spectra were recorded in dichloromethane and ^{19}F spectra in chloroform except for X = N_3 when the solvent was methanol.

The complexes, *cis*-[PtX(SCF$_3$)(PEt$_3$)$_2$] showed two resonances, each with ^{195}Pt sidebands, each split by phosphorus—phosphorus coupling, and with the phosphorus *trans* to SCF$_3$ showing coupling to fluorine (J(PF) (*trans*) ~10 Hz [9]). All of the ^{31}P spectra were satisfactorily accounted for by first-order analysis.

(b) Fluorine-19. ^{19}F spectra of the SCF$_3$ complexes have been reported previously [9] except for *cis*-[PtCH$_3$(SCF$_3$)(PEt$_3$)$_2$]. This complex showed a doublet (^4J(PF) (*trans*) 11 Hz) at 22.0 ppm (upfield from CFCl$_3$) and with ^{195}Pt sidebands (^3J(PtF) 93 Hz).

^{19}F spectra of the C$_2$F$_3$ complexes were very complicated owing to the large number of parameters involved but were all amenable to straightforward first-order analysis. The data are presented in Tables 2 and 3 using the labelling scheme shown.



The α- and γ-resonances both consisted basically of a doublet of doublets due to fluorine—fluorine coupling, each line being split into a triplet by the two phosphorus atoms. The β-resonance was similar except that the fortuitous near equality of $J_{\alpha\beta}$ and $J_{\beta\gamma}$ in most cases resulted in a triplet appearance rather than a doublet of doublets. All three resonances exhibited sidebands due to coupling to ^{195}Pt and in those cases where L = Pr$_3$ or P(OR)$_3$ there was additional splitting due to the phosphorus *trans* to the C$_2$F$_3$ group. These results are entirely consistent with previous analyses of ^{19}F spectra of platinum perfluorovinyl complexes [15,16] but of the particular complexes studied here only chloride [13] and bromide [15] have been prepared previously.

Discussion

1. *Trans-influence*

The *trans*-influence series derived from ^3J(PtF) in the *trans*-SCF$_3$ complexes has been extensively discussed in our previous paper [9]. It is, however, worth noting that the values of ^1J(PtP) (*trans* to X) in *cis*-[PtX(SCF$_3$)(PEt$_3$)$_2$] complexes give the same order of *trans*-influence (CH$_3$ > NO$_2$ > SCF$_3$ > N$_3$ > NCS ~ NCO > Cl) as was derived previously using ^3J(PtF) in the corresponding *trans*-isomers and the two sets of data show a good linear correlation (R = 0.990) *.

In the C$_2$F$_3$ complexes the majority of the phosphorus—fluorine couplings are small and little significance can be attached to their variations. For the phosphorus *trans* to C$_2$F$_3$ in *trans*-[Pt(C$_2$F$_3$)(PEt$_3$)$_2$L]$^+$ complexes, ^3J(PF$_\alpha$) and ^4J(PF$_\beta$) are somewhat larger but their values appear to depend mainly on the

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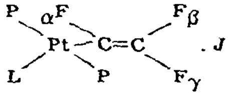
* R is the least squares correlation coefficient. ^3J(PtF) = (0.046 ± 0.003) ^1J(PtP) — (35 ± 4). The error limits are standard deviations (σ).

TABLE 3

NMR DATA FOR *trans*-[Pt(C_2F_3)(PEt_3)$_2$L][ClO_4] COMPLEXES [a]

L	*cis* to C_2F_3		*trans* to C_2F_3						
	δ(P)	^1J(PtP)	δ(P)	^1J(PtP)	^2J(PP)	δ(F_α)	δ(F_β)	δ(F_γ)	^2J(PtF_α)
PEt_3	131.2	2319	137.8	2117	22	151.6	92.1	123.5	282
$P(OEt)_3$	125.4	2216	35.5	3706	29	158.8	93.2	124.8	306
$P(OMe)_3$	124.3	2197	29.8	3755	29	159.0	90.9	124.7	309
$P(OPh)_3$	126.6	2163	42.0	3872	29	158.6	91.5	123.0	316
PPh_3	134.5	2261	127.8	2231	21	152.7	92.9	123.1	320
CO	121.6	2021				164.4	96.7	122.7	378
C_5H_5N	125.4	2422				157.2	95.9	127.2	452

[a] The fluorine atoms are labelled as follows:



. *J* and δ denote respectively NMR coupling constants (Hz) and chemical shifts (ppm upfield from $CFCl_3$ or $P(OCH_3)_3$ as external references). ^{31}P spectra were recorded in dichloromethane and ^{19}F spectra in chloroform.

substituents at phosphorus (i.e. phosphites > phosphines). The intra-ligand fluorine—fluorine couplings show little variation except for $^2J_{\beta\gamma}$. This parameter appears to reflect the charge density on the platinum since it is generally larger in cationic than in neutral complexes. Also the ability of the ligand to reduce this charge density by π-bonding is evident in that L = CO gives the smallest value of $^2J_{\beta\gamma}$ among the cationic complexes and L = pyridine, the largest.

Of all the data collected in Tables 2 and 3 only ^2J(PtF_α) appears to be simply correlated with the *trans*-influence of the X and L ligands. Use of this parameter to establish a *trans*-influence series yields: $PEt_3 > P(OEt)_3 > P(OMe)_3 > P(OPh)_3 > PPh_3 > CN > CO > NO_2 > SCF_3 > C_5H_5N > N_3 > I > Cl > Br > NO_3$. This sequence has only five ligands in common (CN, CO, NO_2, I and Cl) with the series previously established by Appleton and co-workers [17] using a different vinyl ligand as the probe, i.e. ^3J(PtF) in *trans*-[Pt{C(CF_3)=C(OCH_3)H}-(PMe_2Ph)$_2$ (X or L)] (0 or 1+). The five ligands occur in the same order in both series. Except for minor variations among the phosphorus ligands and the transposition of Cl and Br, the ^2J(PtF_α) sequence is identical to that obtained from ^3J(PtF) in SCF_3 complexes [9]. It is identical to that obtained from ^2J(PtH) in methylplatinum complexes [4,18] and is also very similar to results on ^2J(PtF) in trifluoromethyl complexes [4]. In all three cases linear correlations are obtained (*R* = 0.961, 0.995 and 0.978, respectively *).

Thus, transmission of the *trans*-influence to substitutents on the α-carbon of the vinyl ligand is similar to its transmission in saturated ligands. The plots of ^2J(PtCH_3) or ^2J(PtCF_3) against ^2J(PtF_α) (Tables 2 and 3) have significant intercepts on the ^2J(PtCH_3) and ^2J(PtCF_3) axes, an indication (see ref. 9 for a detailed discussion) that the C_2F_3 ligand is more sensitive to the *trans*-influence

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* $^2J(PtF_\alpha) = (3.1 \pm 0.4)\ ^3J(PtF) + (126 \pm 19)$
$^2J(PtF_\alpha) = (8.0 \pm 0.3)\ ^2J(PtH) - (143 \pm 10)$
$^2J(PtF_\alpha) = (0.92 \pm 0.07)\ ^2J(PtF) - (190 \pm 17)$

		P *cis* to C_2F_3			P *trans* to C_2F_3					
$^3J(PtF_\beta)$	$^3J(PtF_\gamma)$	$^3J(PF_\alpha)$	$^4J(PF_\beta)$	$^4J(PF_\gamma)$	$^3J(PF_\alpha)$	$^4J(PF_\beta)$	$^4J(PF_\gamma)$	$^3J_{\alpha\beta}$	$^3J_{\alpha\gamma}$	$^2J_{\beta\gamma}$
22	45	6.2	6.2	3.2	33	13	3.2	33	103	95
33	37	5.2	6.0	4.2	50	22	4.2	33	102	96
35	37	5.2	5.8	4.2	51	22	4.2	33	103	96
38	35	5.7	6.7	4.2	54	22	5.0	34	104	94
29	39	6.2	6.9	4.2	35	14	4.2	35	104	96
65	31	4.1	6.6	3.5				33	105	89
41	51	4.0	6.0	4.0				33	107	102

than are the CH_3 and CF_3 groups. In our previous work we attributed the exceptional sensitivity of the SCF_3 ligand to its polarizability and this could also be an explanation here since the unsaturated ligand should be more easily polarized than the saturated groups. Other workers [19] have noted that $^1J(PtSe)$ and $^1J(PtTe)$ in the ions, $[PtX_3L]^-$ (L = dimethylselenide or dimethyltelluride) are unusually sensitive to the nature of the halide (X) and have attributed this effect to the similarity of *trans*-influence between the probe ligands $Y(CH_3)_2$ (Y = Se or Te) and the halides. However, in our work [9] we pointed out that $^1J(PtH)$ in *trans*-$[PtHX(PEt_3)_2]$ complexes is also a sensitive probe for *trans*-influence. Since hydride and SCF_3 are very different in their *trans*-influence this led us to suggest that the common factor was polarizability and it seems possible that this may also be a contributing factor in the $Y(CH_3)_2$ case.

Having demonstrated that $^2J(PtF_\alpha)$ yields a normal *trans*-influence series, it is interesting to compare this sequence with the ones derived from F_β and F_γ. Thus, $^3J(PtF_\beta)$ yields $PEt_3 > PPh_3 > P(OEt)_3 > P(OMe)_3 > NO_2 > C_5H_5N > SCF_3 > CN > N_3 > Cl > Br > I > CO$ and $^3J(PtF_\gamma)$ yields $CO > P(OPh)_3 > P(OEt)_3 > P(OMe)_3 > PPh_3 > CN > PEt_3 > C_5H_5N > SCF_3 > NO_2 > N_3 > I > Br > NO_3 > Cl$. The striking variation in the position of CO in the three series immediately suggests that the normal *trans*-influence sequence ($^2J(PtF_\alpha)$) is moderately influenced by π-bonding contribution to the Pt—L (or X) bond, that $^3J(PtF_\gamma)$ is very strongly affected by π-bonding contributions and that $^3J(PtF_\beta)$ is almost completely insensitive. Closer inspection of the three series shows that other ligands show similar shifts in position. For example, CN moves similarly to CO but in a less pronounced manner, and the phosphites, which are generally considered better π-acceptor ligands than phosphines, lead to smaller values of $^3J(PtF_\gamma)$ than do phosphines but larger values of $^3J(PtF_\beta)$.

(2) *Cis-influence*

Sequences of *cis*-influence may be established using $^1J(PtP)$ in either the *trans*- SCF_3 or *trans*- C_2F_3 complexes. Thus, from SCF_3 complexes: CN >

NCS > I > Br > SCF_3 > Cl > C_2F_3 > NO_3 > NO_2 > CF_3 > H > C_6H_5 > CH_3; and from C_2F_3 complexes: CO > $P(OPh)_3$ > $P(OMe)_3$ > $P(OEt)_3$ > PPh_3 > CN > PEt_3 > pyridine > I > SCF_3 > Br > Cl > N_3 > NO_2 > NO_3. Most previous series are less extensive than these but as a comparison we note that ^1J(PtP) in *trans*-$[PtX_2(PBu_3)_2]$ gives the *cis*-influence sequence CN > NCS > I > Br > Cl > NO_3 > NO_2 [12] which is the same as our two except for the transposition of NO_2 and NO_3 in the C_2F_3 series, and which gives good linear correlations with our results (R = 0.990 for SCF_3 complexes, 0.952 for C_2F_3 complexes) *.

The only previous extensive data set to place neutral and anionic ligands in a consistent sequence appears to be the very recent work of Appleton and Bennett [11] on ^1J(PtP) (*cis* to X or L) in the complexes, $[PtX(CH_3)(Ph_2PCH_2CH_2PPh_2)]$ and $[(PtL(CH_3)(Ph_2PCH_2CH_2PPh_2)]^+$. Their ligand set was rather different from ours but for those ligands which were also included in our study they obtained CO > CN > pyridine > $P(OPh)_3$ > I > Cl > NO_2 > CH_3 > PPh_3 > NO_3. Apart from the positions of $P(OPh)_3$ and PPh_3 their series is very similar to our own and it is noticeable that these ligands are easily the largest in the set. The $Ph_2PCH_2CH_2PPh_2$ ligand is also very bulky and it therefore seems likely that these anomalies are due to steric affects.

(3) *The relationship between cis- and trans-influence*

The previous sections have established that our data are generally consistent with the existing literature and we now wish to examine their implications for the mechanism of the *cis*-influence and for its relationship to *trans*-influence. Our previous study [9,10] suggested that the two are inversely correlated when an indirect coupling is used to measure *cis*-influence but that the correlation is obscured by other factors when direct couplings are used to measure the *cis*-influence. In the present results the very low *cis*-influence of the methyl group (^3J(PtF) 93 Hz in *cis*-$[Pt(CH_3)(SCF_3)(PEt_3)_2]$ when compared with its very high *trans*-influence (^3J(PtF) 46.4 Hz in *trans*-$[Pt(CH_3)(SCF_3)(PEt_3)_2]$) represents a significant extension of this correlation since the previous study was limited to the relatively low *trans*-influence ligands, NO_2, SCF_3, N_3, NCS, NCO, Cl and NO_3.

The present results also provide several more detailed tests of the correlation of *cis*- and *trans*-influences using both direct and indirect couplings as measures of the *cis*-influence. Thus, using direct couplings we can: (a) plot ^1J(PtP) (*cis* to X) against ^3J(PtF) (*trans* to X) in *trans*-$[PtX(SCF_3)(PEt_3)_2]$; (b) plot ^1J(PtP) (*cis* to X) against ^1J(PtP) (*trans* to X) in *cis*-$[PtX(SCF_3)(PEt_3)_2]$. Neither of these plots yields any overall correlation between *cis*- and *trans*-influence but it is interesting that there is an approximate inverse correlation for the C-bonded ligands in plot "a" and the point for X = H also lies on the same line. Changing to an indirect coupling constant as the measure of *cis*-influence, we can plot ^3J(PtF) (*cis* to X) against ^1J(PtP) (*trans* to X) in *cis*-$[PtX(SCF_3)(PEt_3)_2]$ complexes (see Table 1). This yields an approximate inverse correlation (R = —0.991) ** and the situation is entirely analogous to the plot mentioned in the

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* SCF_3 complexes: $^1J(PtBu_3) = (1.5 \pm 0.1)\ ^1J(PtPEt_3) - (1170 \pm 25)$.
C_2F_3 complexes: $^1J(PtBu_3) = (1.5 \pm 0.2)\ ^1J(PtPEt_3) - (1250 \pm 60)$.

** $^1J(PtP) = -(55 \pm 3)\ ^3J(PtF) + (6750 \pm 90)$.

introduction of ^2J(PtH) (*cis* to X) against ^1J(PtP) (*trans* to X) in [PtX(CH_3)-($Ph_2PCH_2CH_2PPh_2$)] complexes [11].

If we combine the ^{31}P data on the *trans*-SCF_3 and -C_2F_3 complexes, allowing for the fact that ^1J(PtP) values in the C_2F_3 complexes are consistently 80—130 Hz higher than those in corresponding SCF_3 complexes, the two data sets taken together provide a *cis*-influence series for 21 ligands based on direct coupling constants. CO > P(OPh)$_3$ > P(OMe)$_3$ > P(OEt)$_3$ > PPh$_3$ > CN ~ PEt$_3$ > pyridine ~ NCS > I > SCF_3 ~ Br > Cl > N_3 ~ C_2F_3 > NO_2 ~ NO_3 > CF_3 > H > Ph > CH_3. This sequence is clearly not simply related to the *trans*-influence series since ligands of high *trans*-influence occur at both extremes of the *cis*-influence scale. It is especially noteworthy that the high *trans*-influence ligands which also exhibit high *cis*-influence are those for which significant π-bonding might be expected. Thus phosphorus ligands and cyanide are high in both series whereas CH_3 and hydride which cannot π-bond to the metal are very low in the *cis*-influence series but have very high *trans*-influence. The carbonyl ligand, which is well-known for its π-bonding ability has only moderate *trans*-influence but has the highest *cis*-influence of the ligands studied here.

Moreover, Appleton and Bennett [11] in their study of [PtX(CH_3)(Ph_2PCH_2-CH_2PPh_2)] and [PtL(CH_3)($Ph_2PCH_2CH_2PPh_2$)]$^+$ complexes also pointed out that the ligands CO, CN and C≡CPh had significantly higher *cis*-influences than the other ligands studied. Russell and co-workers [20] have noted that Pt—P bond lengths show significant variations as the *cis*-ligands are varied even though the ligand *trans* to phosphorus is unchanged. Thus for the complexes, *cis*-[$PtCl_2(PR_3)$X] the Pt—P bond lengths are 227.9 (X = CO) [21], 224.8 (X = PMe$_3$) [22], 223.4 (X = carbene) [23] and 221.5 (X = Cl^-) [24] pm. Clearly, π-bonding to X weakens the *cis* Pt—P bond and Russell and co-workers [20] attribute this to isotropic competition between π-acceptors which affects *cis* and *trans* ligands equally but only if they are π-acceptor ligands. The changes in Pt—P bonds are thus evidence for π-bonding to phosphorus even though its importance in transition metal complexes has been widely doubted [25]. Our results clearly support these proposals and permit their extension to a much wider range of complexes than those for which bond length data are available.

The preceding two paragraphs have provided further evidence for our suggestion that *cis*- and *trans*-influences are inversely correlated when indirect constants are used to measure the *cis*-influence and have also indicated that direct coupling constants are very markedly reduced by π-bonding to a *cis* ligand. In section 2 above we noted that large steric bulk for a ligand may lead to a reduction in its *cis*-influence as measured by a direct coupling constant. This is in accord with the work of Clark and Ward [6] who observed that ^1J(PtC) in [PtL(CH_3)(diars)]$^+$ complexes decreased as the cone angle of L increased in the ligand sequence; γ-picoline, anisonitrile, ethyl isocyanide, carbon monoxide. Thus we suggest that the lack of correlation (with *trans*-influence) observed when direct couplings are used to measure *cis*-influence arises from a greater sensitivity of the direct coupling to π-bonding and steric effects. Further, although the available evidence is still fragmentary, there does appear to be an indication that *cis*- and *trans*-influences operating by a σ-only mechanism are inversely correlated. Pidcock [25] has argued that only σ-effects are required to explain the majority of NMR *trans*-influence phenomena. Evidently this is because the *trans*-σ-influence is much larger than π-bonding and steric factors, whereas in the *cis*-influence σ, π and steric factors are all of comparable magnitude.

Experimental

^{19}F NMR spectra of the C_2F_3 complexes were recorded at 56.4 MHz on a Varian HA 60 spectrometer modified for extended offset operation. The lock signal and external reference was provided by a capillary insert containing fluorotrichloromethane and the solvent was chloroform except for spectra of *trans*-$[Pt(N_3)(C_2F_3)(PEt_3)_2]$ which were recorded in methanol. The multiple splitting of each resonance necessitated extensive signal to noise enhancement which was achieved by compiling many spectra in a Northern Scientific NS 560 time-averaging computer. ^1H NMR spectra of the C_2F_3 complexes were recorded at 60 MHz in the same solvents or their deuterated analogues using a Perkin—Elmer R12A spectrometer. ^{31}P NMR spectra of all the complexes were recorded in dichloromethane solution using a JEOL PFT 100 Fourier transform spectrometer operating at 40.49 MHz. External deuterium lock and phosphorus reference signals were provided by a capillary insert containing C_6D_6 and $P(OCH_3)_3$ and all chemical shifts are upfield from this reference. Protons were decoupled by broad band (2.5 kHz) "noise" irradiation and 8192 data points were used in a sweep width of 10 kHz giving resolution of 2.44 Hz. The reported coupling constants and chemical shifts are therefore subject to errors of this magnitude. Infrared spectra were recorded from 4000—250 cm^{-1} with accuracy ± 3 cm^{-1} on a Beckman IR 20 spectrophotometer calibrated against polystyrene film and water vapour. Solid samples were examined as Nujol mulls between caesium iodide plates. Melting points were determined on a Reichert hot-stage apparatus and are uncorrected. Microanalyses were by Dr. D.L. McGillivray of this department.

The SCF_3 complexes were prepared as previously described [9] except that *cis*-$[Pt(CH_3)(SCF_3)(PEt_3)_2]$ was obtained as an oil from reaction of $AgSCF_3$ with *cis*-$[Pt(CH_3)Cl(PEt_3)_2]$ in acetone. The product was characterized by ^{31}P and ^{19}F NMR spectroscopy. The C_2F_3 complexes were prepared as described individually below. Unless otherwise stated, reactions were conducted at 25°C in an atmosphere of dry nitrogen. The products were stable to moist air. Solvents were dried over type 4A molecular sieves with the exception of n-pentane which was distilled from P_2O_5 and stored over sodium.

trans-$[Pt(C_2F_3)X(PEt_3)_2]$ complexes

(a) X = Cl. This compound was prepared by minor modification of the method of Clark and Tsang [13]. *trans*-$[PtHCl(PEt_3)_2]$ (0.500 g, 1.07 mmol) and C_2F_4 (0.500 g, 5.0 mmol) were heated together at 110°C in cyclohexane (50 ml) in a new, evacuated heavy wall Pyrex tube for 30 h. The solvent and all volatile products were removed in vacuo and the solid products were separated by chromatography on a Florisil column using chloroform/pentane (2/1) as eluant. The complex (0.450 g, 0.82 mmol) was the first product off the column. The reaction temperature (110°C instead of 90°C), solvent (cyclohexane instead of benzene) and the use of new Pyrex tubes for each preparation all led to significant improvement in the yield compared with the previous work [13].

(b) X = I. Sodium iodide (0.344 g, 2.3 mmol) was added to a solution of *trans*-[$PtCl(C_2F_3)(PEt_3)_2$] (0.125 g, 0.229 mmol) in acetone (5 ml). The mixture was stirred for 1 h, the precipitated sodium chloride removed by filtration and the filtrate evaporated under reduced pressure. The solid residue was extracted with diethyl ether and the extract washed with water and dried over magnesium sulphate. Evaporation of the ether gave *trans*-[$PtI(C_2F_3)(PEt_3)_2$] (0.125 g, 0.198 mmol) which was recrystallized by addition of water to a methanol solution followed by cooling to —20°C. M.p. 104—106°C. Analysis: Found: C, 25.64; H, 4.54. $C_{14}H_{30}F_3IP_2Pt$ calcd.: C, 26.22; H, 4.72%.

(c) X = Br. *trans*-[$PtBr(C_2F_3)(PEt_3)_2$] was prepared by a method similar to "b" above except that lithium bromide was the reagent and the extraction was with dichloromethane. Yield: 78%. M.p. 83—84°C (lit. [15] 82—83°C). Analysis: Found: C, 27.98; H, 4.99. $C_{14}H_{30}BrFP_2Pt$ calcd.: C, 28.29; H, 5.09%.

(d) X = NO_2. A solution of $AgBF_4$ (0.054 g, 0.275 mmol) in 1/1 water/methanol (2 ml) was added to a stirred solution of *trans*-[$PtCl(C_2F_3)_2(PEt_3)_2$] (0.125 g, 0.228 mmol) in methanol (5 ml). Precipitated silver chloride was removed by filtration and the filtrate evaporated under reduced pressure. The solid residue was extracted with diethyl ether and the extract washed with water and dried over magnesium sulphate. Evaporation of the ether gave *trans*-[$Pt(NO_2)(C_2F_3)(PEt_3)_2$] (0.094 g, 0.171 mmol) which was recrystallized by addition of water to a methanol solution followed by cooling to —20°C. M.p. 122—124°C. Analysis: Found: C, 30.42; H, 5.39; N, 2.50. $C_{14}H_{30}NO_2F_3P_2Pt$ calcd.: C, 30.11; H, 5.42, N, 2.51%.

(e) X = NO_3. The procedure for the preparation of *trans*-[$Pt(NO_3)(C_2F_3)(PEt_3)_2$] was the same as that in "d" above except that the reagent was $AgNO_3$ and the product was recrystallized from light petroleum (60—90°C). Yield, 61%. M.p. 120—122°C. Analysis: Found: C, 29.90; H, 5.32; N, 2.34. $C_{14}H_{30}F_3NO_3P_2Pt$ calcd.: C, 29.27; H, 5.26; N, 2.44%.

(f) X = CN. The procedure for the preparation of *trans*-[$Pt(CN)(C_2F_3)(PEt_3)_2$] was the same as that in "d" above except that the reagents were NaCN and $AgBF_4$. Yield, 68%. M.p. 105—107°C. $\nu(C{\equiv}N)$ 2150 cm^{-1}. Analysis: Found: C, 32.91; H, 5.40; N, 2.34. $C_{15}H_{30}F_3NP_2Pt$ calcd.: C, 33.34; H, 5.60; N, 2.59%.

(g) X = N_3. The procedure for the preparation of *trans*-[$Pt(N_3)(C_2F_3)(PEt_3)_2$] was the same as that in "d" above except that after removal of AgCl the CH_3OH solution was passed through a short column of Florisil to remove ionic species and prevent formation of silver azide. Yield, 58%. M.p. 70—71°C. $\nu(N{\equiv}N)$ 2045 cm^{-1}. Analysis: Found: C, 30.10; H, 5.23; N, 7.50. $C_{14}H_{30}F_3N_3P_2Pt$ calcd.: C, 30.22; H, 5.43; N, 7.55%.

trans-[$Pt(C_2F_3)(PEt_3)_2(L)$][ClO_4] complexes

These were prepared by methods analogous to those used previously for *trans*-[$PtCl(PEt_3)_2(L)$][ClO_4] complexes [8].

(a) trans-[$Pt(C_2F_3)(PEt_3)_2\{P(OEt)_3\}$][$ClO_4$]. Triethyl phosphite (53 µl, 0.309 mmol) and sodium perchlorate monohydrate (0.049 g, 0.349 mmol) in acetone solution were added to *trans*-[$Pt(C_2F_3)Cl(PEt_3)_2$] (0.153 g, 0.270 mmol) in acetone (4 ml). The mixture was stirred for 2 h, the precipitated sodium chloride removed by filtration and the filtrate evaporated under

reduced pressure. The residue was extracted with diethyl ether to remove unreacted starting materials and then with methylene chloride to extract the product which was recrystallized from chloroform by the slow addition of diethyl ether. Yield: 0.195 g, 0.252 mmol. M.p. 136—137°C. Analysis: Found: C, 30.87; H, 5.75. $C_{20}H_{45}ClF_3O_4P_3Pt$ calcd.: C, 30.83; H, 5.83%.

(b) trans-[Pt(C_2F_3)(PEt_3)$_2$(CO)] [ClO_4]. Silver perchlorate (0.042 g, 0.203 mmol) in acetone solution was added to *trans*-[Pt(C_2F_3)Cl(PEt_3)$_2$] (0.151 g, 0.276 mmol) in acetone (5 ml). Carbon monoxide was bubbled through the solution for 30 min and product work-up was as in "a" above. Yield: 74% based on $AgClO_4$. M.p. 134—136°C. Analysis: Found: C, 28.27; H, 4.73. $C_{15}H_{30}ClF_3O_4P_2Pt$ calcd.: C, 28.16; H, 4.73%. $\nu(C{\equiv}O)$ 2115 cm^{-1}.

(c) Other trans-[Pt(C_2F_3)(PEt_3)$_2$(L)] [ClO_4] complexes. These were obtained by procedures analogous to that described in "a" above for L = $P(OEt)_3$. Yields and characterization data were as follows:

L = pyridine. Yield: 50%. M.p. 152—153°C. Analysis: Found: C, 32.90; H, 5.11; N, 2.12. $C_{19}H_{35}ClF_3NO_4P_2Pt$ calcd.: C, 33.03; H, 5.11; N, 2.03%.

L = trimethylphosphite. Yield: 93%. M.p. 140—142°C. Analysis: Found: C, 27.44; H, 5.15. $C_{17}H_{39}ClF_3O_7P_3Pt$ calcd.: C, 27.74; H, 5.34%.

L = triphenylphosphite. Yield: 73%. M.p. 70—72°C. Analysis: Found: C, 41.23; H, 4.77%. $C_{32}H_{45}ClF_3O_4P_3Pt$ calcd.: C, 41.68; H, 4.72%.

L = triphenylphosphine. Yield: 44%. M.p. 163—164°C. Analysis: Found: C, 43.96; H, 5.18%. $C_{33}H_{45}ClF_3O_4P_3Pt$ calcd.: C, 43.71; H, 5.19%.

L = triethylphosphine. Yield: 66%. M.p. 127—129°C (dec.). Found: C, 33.11; H, 6.27%. $C_{20}H_{45}ClF_3O_4P_3Pt$ calcd.: C, 32.89; H, 6.20%.

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