Trifluoromethylthio-complexes of Platinum(II): Measurement of *trans*-Influence by Fluorine-19 Nuclear Magnetic Resonance Spectroscopy

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The synthesis and characterization of the following new complexes is reported: *trans*-$[PtX(SCF_3)(PEt_3)_2]$ (X = Ph, Me, H, CF_3, C_2F_3, CN, NO_2, SCF_3, N_3, I, NCS, NCO, Br, Cl, or NO_3), *cis*-$[PtX(SCF_3)(PEt_3)_2]$ (X = NO_2, SCF_3, N_3, NCS, NCO, Cl, or NO_3), *cis*-$[Pt(SCF_3)_2L_2]$ [L = PBu^n_3, $P(OPh)_3$, PPh_3, $P(OMe)_3$, $PClPh_2$, or C_5H_5N], *trans*-$[Pt(SCF_3)_2L_2]$ (L = PBu^n_3, PPh_3, or C_5H_5N), *trans*-$[Pt(SCF_3)(CH_3)(PPh_3)_2]$, and *trans*-$[PtI(CF_3)(PEt_3)_2]$. Values of ^3J(Pt–F) in *trans*-$[PtX(SCF_3)(PEt_3)_2]$ and *cis*-$[Pt(SCF_3)_2L_2]$ complexes are used to establish a scale of *trans*-influence for the X and L ligands and the results are discussed in terms of existing theories of the Fermi contact interaction. It is concluded that an equation similar to those used previously for directly bound and two-bond couplings is still approximately valid for the longer-range ^3J(Pt–F) couplings. The question of non-zero intercepts in plots comparing *trans*-influence scales derived from couplings to different indicator ligands is discussed. A perturbation approach to the problem shows that non-zero intercepts arise when the indicator ligands have different sensitivities to the perturbation. One possible cause of differing sensitivities is the polarizability of the indicator ligand.

THE measurement of *trans*-influence phenomena by means of n.m.r. spectroscopy is now a well-established technique and the subject has been reviewed recently.[1] The great majority of the studies to date have been concerned with complexes containing a *trans* L–Pt–A or X–Pt–A system where L or X is the ligand whose *trans*-influence is under study and A is an indicator ligand containing a magnetically active nucleus.† The coupling constant between ^{195}Pt (33·8% abundant, $I = \frac{1}{2}$) and the magnetically active nucleus in the indicator ligand is taken as a measure of the *trans*-influence of L or X. Most workers have used indicator ligands where the coupling to ^{195}Pt is over one or two bonds [*e.g.* ^1J(Pt–P), ^1J(Pt–H), ^2J(Pt–CF_3), and ^2J(Pt–CH_3), *etc.*] and data concerning the transmission of these effects over more than two bonds is much more limited in scope.[1] Conse-

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† This symbolism, chosen to conform with ref. 1, is used throughout the present paper. L Represents a neutral ligand and X an anionic ligand.

[1] T. G. Appleton, H. C. Clark, and L. E. Manzer, *Coordination Chem. Rev.*, 1973, **10**, 335, and references therein.

quently, when our recent studies [2,3] of platinum complexes of the trifluoromethylthio-ligand (SCF_3) showed that ^3J(Pt–F) in these complexes is a sensitive indicator of *trans*-influence phenomena, it was of interest to prepare a wide range of these complexes. The results of this study are reported in the present paper. They represent one of the largest *trans*-influence series described to date and also show an unusual, inverse, linear correlation between the *cis*- and *trans*-influences of the anionic ligands included in the study. This last correlation has been presented in a preliminary communication [4] [*] and is consequently not discussed further in the present paper.

RESULTS

The new complexes synthesized are listed in Table 1, which also gives details describing the characterization of the products. The synthetic methods were similar to those used in our previous work on SCF_3 complexes,[2,3] and most generally involved a metathetical reaction between $AgSCF_3$ and a platinum chloro-complex. All the *cis*-$[Pt(SCF_3)_2L_2]$ and *cis*-$[PtX(SCF_3)(PEt_3)_2]$ complexes were obtained by this method as were the *trans*-$[PtX(SCF_3)(PEt_3)_2]$ complexes for X = Cl, Ph, Me, C_2F_3, CN, or CF_3, except that for X = CF_3 the starting material was a platinum iodo-complex. Isomerization of the *cis*-$[Pt(SCF_3)_2L_2]$ complexes using *ca.* 10 mol % of L as catalyst gave the corresponding *trans*-isomers and similar reactions gave the *trans*-$[PtX(SCF_3)(PEt_3)_2]$ complexes for X = N_3, NCS, or NCO. The remaining *trans*-$[PtX(SCF_3)(PEt_3)_2]$ complexes (X = Br, I, NO_2, or NO_3) were obtained from metathetical reactions of *trans*-$[PtCl(SCF_3)(PEt_3)_2]$ with KBr, KI, $AgNO_2$, or $AgNO_3$.

The analytical results shown in Table 1 are in general very satisfactory and comments on those cases where there is significant error are included in the Experimental section. I.r. spectra of the complexes show the appropriate ligand absorptions including very strong, poorly resolved, C–F stretching modes in the 1050—1150 cm^{-1} region. The positions of other prominent absorptions are given as appropriate in Table 1 and the most likely assignments are given using the nomenclature of Nakamoto.[5] The assignments have not been rigorously established and should be approached with caution, particularly in difficult cases such as ν(Pt–N) or ν(Pt–O). Metal–sulphur stretching absorptions were not identified and are expected [6] to lie close to or below 250 cm^{-1}, the limit of our instrumentation. The triethylphosphine absorptions in the 700—800 cm^{-1} and 400—450 cm^{-1} regions serve as a check on the stereochemistry of the complexes. We have recently described the changes found in the former region [7] and, although the latter region is not associated with ν(Pt–P) as was previously thought,[8] the available evidence [9] still suggests that two absorption bands in this region are characteristic of two triethylphosphines in a *cis*-configuration, whereas a single band suggests a *trans*-configuration. The NCS complexes are assigned as N-bonded mainly on the basis of the ν(C–S) frequencies. It has been established [10] that this absorption lies in the range 780—860 cm^{-1} in N-bonded complexes and in the range 690—720 cm^{-1} in S-bonded complexes. *cis*- And *trans*-$[Pt(SCF_3)(NCS)(PEt_3)_2]$ have medium intensity bands at 840 and 857 cm^{-1} respectively, very similar to the values of 830/848 cm^{-1} and 855 cm^{-1} reported previously [11] for *cis*- and *trans*-$[Pt(NCS)_2(PEt_3)_2]$. This type of assignment has been questioned [12] on the grounds that the first overtone of the NCS deformation mode in an S-bonded thiocyanate ($2\nu_2 \sim$ 800—880 cm^{-1}) may be erroneously assigned as ν(C–S) of an N-bonded complex. However, our complexes show no bands in the 400—440 cm^{-1} region assignable to the deformation mode and of intensity comparable to ν(C–S). It therefore seems unlikely that the overtone has sufficient intensity to cause confusion. Accepting that the NCS complexes are N-bonded, the similarity of ^{19}F n.m.r. parameters then suggests that the NCO complexes are also N-bonded. This conclusion is in accord with the absence of any previous examples of O-bonded cyanate complexes of platinum(II).

The stereochemistry of the SCF_3 complexes listed in Table 1 is unambiguously established by the ^{19}F n.m.r. resonances of the SCF_3 ligand. In the *trans*-$[PtX(SCF_3)(PEt_3)_2]$ and *trans*-$[Pt(SCF_3)_2L_2]$ complexes these resonances consist of a 1 : 4 : 1 triplet due to coupling with ^{195}Pt (33·8% abundant, $I = \frac{1}{2}$) and each line of the triplet is further split (except for L = py) into a 1 : 2 : 1 triplet by coupling to two equivalent ^{31}P nuclei. The latter triplet coupling ($^4J_{PF}$) is sometimes not resolved and in those cases the line width indicates that it is *ca.* 1 Hz. In *cis*-$[PtX(SCF_3)(PEt_3)_2]$ complexes the ^{19}F resonances of the SCF_3 group show the same 1 : 4 : 1 pattern due to ^{195}Pt, but coupling to the single *trans* ^{31}P nucleus gives further splitting of each line into a doublet. The expected small coupling to the *cis*-phosphorus is not resolved in these spectra and the line width indicates that it is $<0{\cdot}5$ Hz in all cases.

The ^{19}F resonances of the complexes *cis*-$[Pt(SCF_3)_2L_2]$, [L = PEt_3, PBu^n_3, PPh_3, $PClPh_2$, $P(OMe)_3$, or $P(OPh)_3$], may be approximated as the X,X′ region of an $X_3AA'X'_3$ spectrum (X = X′ = ^{19}F, A = A′ = ^{31}P) and the parameters in Table 1 for these complexes are derived by computer simulation using this type of analysis. However, this type of analysis involves the neglect of remote protons in the phosphine ligand and it has been demonstrated by ourselves [13] and others [14] that this is not always justified. In our cases the spectra are not well resolved and it is difficult to identify the various pairs of lines needed for the $X_3AA'X'_3$ analysis.[15] Consequently the band-fitting procedure by computer involves a further possibility of error. The sum $J_{AX} + J_{AX'}$[^4J(PF*trans*) + ^4J(PF*cis*) in Table 1] is not subject to error as it is the separation of the two strongest

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[*] Ref. 4 contains an important printing error. Pages 374 and 375 should be transposed.

[2] K. R. Dixon, K. C. Moss, and M. A. R. Smith, *J.C.S. Dalton*, 1973, 1528.

[3] K. R. Dixon, K. C. Moss, and M. A. R. Smith, *J.C.S. Dalton*, 1974, 971.

[4] K. R. Dixon, K. C. Moss, and M. A. R. Smith, *Inorg. Nuclear Chem. Letters*, 1974, **10**, 373.

[5] K. Nakamoto, 'Infrared Spectra of Inorganic and Co-ordination Compounds,' 2nd edn., John Wiley and Sons, New York, 1970.

[6] D. Forster and D. M. L. Goodgame, *Inorg. Chem.*, 1965, **4**, 715.

[7] G. W. Bushnell, K. R. Dixon, R. G. Hunter, and J. J. McFarland, *Canad. J. Chem.*, 1972, **50**, 3694.

[8] K. Shobatake and N. Nakamoto, *J. Amer. Chem. Soc.*, 1970, **92**, 3332.

[9] P. L. Goggin and R. J. Goodfellow, *J. Chem. Soc.* (*A*), 1966, 1462.

[10] C. Pecile and A. Turco, *Nature*, 1961, **191**, 66.

[11] C. Pecile, *Inorg. Chem.*, 1966, **5**, 210.

[12] A. Sabatini and I. Bertini, *Inorg. Chem.*, 1965, **4**, 1665.

[13] T. W. Dingle and K. R. Dixon, *Inorg. Chem.*, 1974, **13**, 846.

[14] R. J. Goodfellow, M. J. Hardy, and B. F. Taylor, *J.C.S. Dalton*, 1973, 2450.

[15] R. K. Harris, *Canad. J. Chem.*, 1964, **42**, 2275.

spectral lines. Moreover, $J_{\mathrm{AX'}}$ may be estimated at 1·5 Hz from the observed values of ^4J(PF *cis*) in *trans*-$[\mathrm{Pt(SCF_3)_2L_2}]$ complexes and is unlikely to be in error by >0·5 Hz, thus giving a corresponding error in J_{AX}. $J_{\mathrm{AA'}}[^2J(\mathrm{PP})$ in Table 1] must be approached with more caution. The band-fitting procedure is relatively insensitive to this parameter (~30% change is usually significant) and it is difficult to estimate the errors introduced by neglect of the remote protons due to limitations on the number of nucleii which can be handled by our computer programme. Consequently the ^2J(PP) values serve mainly as order of magnitude estimates which describe the spectra in the $\mathrm{X_3AA'X'_3}$ approximation.

All other n.m.r. data in Table 1 (*e.g.* ^{1}H and ^{19}F parameters for CF$_3$, CH$_3$, C$_2$F$_3$ complexes, *etc.*) are derived from

TABLE 1

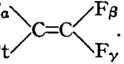
Characterization data

Complex [a]	M.p. (t/°C)	Analytical data (%) [b] C	H	N	^{19}F N.m.r. of SCF$_3$ group [c] δ	^3J (FPt)	^4J (FP*trans*)	^4J (FP*cis*)	Other i.r. and n.m.r. data [c]
trans-$[\mathrm{Pt(SCF_3)(C_6H_5)(PEt_3)_2}]$	122—124	37·9 (37·4)	5·9 (5·8)		19·3	42·2		1·5	$\delta(\mathrm{C_6}H_5) \sim -7$
trans-$[\mathrm{Pt(SCF_3)(CH_3)(PEt_3)_2}]$	Oil	*d*			20·1	46·4		1·0	$\delta(\mathrm{PtC}H_3) = 0{\cdot}47$, $^2J(\mathrm{HPt}) = 73{\cdot}2$, $^3J(\mathrm{HP}\ cis) = 6{\cdot}0$
trans-$[\mathrm{Pt(SCF_3)(H)(PEt_3)_2}]$	*e*				19·7	52·0		0·8	$\delta(\mathrm{Pt}H) = 12{\cdot}8$, $^1J(\mathrm{HPt}) = 1152$, $^2J(\mathrm{HP}\ cis) = 13{\cdot}2$, $^4J(\mathrm{HF}) = 6{\cdot}2$
trans-$[\mathrm{Pt(SCF_3)(CF_3)(PEt_3)_2}]$	51—53	28·5 (27·9)	5·0 (5·0)		20·9	55·2		*f*	$\delta(\mathrm{PtC}F_3) = 11{\cdot}7$, $^2J(\mathrm{FPt}) = 704$, $^3J(\mathrm{FP}) = 14{\cdot}2$, $\nu(\mathrm{CF}) = 1080$vs,b, 980vs,b
trans-$[\mathrm{Pt(SCF_3)(C_2F_3)(PEt_3)_2}]$	90—92	29·9 (29·4)	4·8 (4·9)		20·4	61·2		*f*	$\nu(\mathrm{C{=}C}) = 1720$s, $\nu(\mathrm{CF}) = 1080$vs,b, 980s, $\nu(\mathrm{PtC}) = 540$w or 505w [g]
trans-$[\mathrm{Pt(SCF_3)(CN)(PEt_3)_2}]$	Oil	*d*			21·8	82·0		1·2	$\nu(\mathrm{CN}) = 2170$m
trans-$[\mathrm{Pt(SCF_3)(NO_2)(PEt_3)_2}]$	82—84	27·5 (27·0)	5·5 (5·2)	2·3 (2·4)	23·0	88·6		1·5	$\nu_s(\mathrm{NO_2}) = 1330$s, $\delta'(\mathrm{ONO}) = 820$w, $\rho_w(\mathrm{NO_2}) = 575$w, $\rho_r(\mathrm{NO_2}) = 330$w
trans-$[\mathrm{Pt(SCF_3)_2(PEt_3)_2}]$	90—92	26·8 (26·5)	4·8 (4·8)		22·7	95·8		1·4	
trans-$[\mathrm{Pt(SCF_3)(N_3)(PEt_3)_2}]$	70—72	27·5 (27·2)	5·4 (5·3)	6·5 (7·3)	24·4	110·5		*f*	$\nu_a(\mathrm{NNN}) = 2040$vs, $\nu_s(\mathrm{NNN}) = 1338$w or 1288w
trans-$[\mathrm{Pt(SCF_3)(I)(PEt_3)_2}]$	70—73	23·6 (23·7)	4·7 (4·6)		25·2	118·8		*f*	
trans-$[\mathrm{Pt(SCF_3)(NCS)(PEt_3)_2}]$	113—117	28·8 (28·5)	5·2 (5·1)	2·7 (2·4)	25·0	122·6		*f*	$\nu(\mathrm{CN}) = 2110$vs, $\nu(\mathrm{CS}) = 857$m
trans-$[\mathrm{Pt(SCF_3)(NCO)(PEt_3)_2}]$	Not isolated				25·2	123·0		*f*	
trans-$[\mathrm{Pt(SCF_3)(Br)(PEt_3)_2}]$	64—66	25·9 (25·5)	4·8 (4·9)		25·4	128·0		*f*	
trans-$[\mathrm{Pt(SCF_3)(Cl)(PEt_3)_2}]$	55—57	27·8 (27·5)	5·2 (5·3)		25·4	129·0		*f*	$\nu(\mathrm{PtCl}) = 310$m
trans-$[\mathrm{Pt(SCF_3)(NO_3)(PEt_3)_2}]$	58—62	27·0 (26·3)	5·3 (5·1)	1·8 (2·4)	25·3	131·4		1·3	$\nu_d(\mathrm{NO}) = 1500$s and 1275vs, $\nu_s(\mathrm{NO}) = 975$s, $\nu(\mathrm{PtO}) = 300$w,b
cis-$[\mathrm{Pt(SCF_3)(NO_2)(PEt_3)_2}]$	130—133	27·3 (27·0)	5·4 (5·2)	2·6 (2·4)	23·5	70·0	8·5	*f*	
cis-$[\mathrm{Pt(SCF_3)_2(PEt_3)_2}]$	118—122	26·4 (26·5)	4·6 (4·8)		21·7	68·7	8·5	1·5	$^2J(\mathrm{PP}) = 3$
cis-$[\mathrm{Pt(SCF_3)(N_3)(PEt_3)_2}]$	85—90	27·0 (27·2)	5·3 (5·3)	7·8 (7·3)	23·4	64·0	9·5	*f*	$\nu_a(\mathrm{NNN}) = 2040$vs, $\nu_s(\mathrm{NNN}) = 1336$w or 1287w
cis-$[\mathrm{Pt(SCF_3)(NCS)(PEt_3)_2}]$	101—102	28·9 (28·5)	5·2 (5·1)	2·6 (2·4)	23·3	61·8	9·8	*f*	$\nu(\mathrm{CN}) = 2100$vs, $\nu(\mathrm{CS}) = 840$m
cis-$[\mathrm{Pt(SCF_3)(NCO)(PEt_3)_2}]$	133—140	30·5 (29·4)	5·7 (5·3)		22·9	61·8	10·2	*f*	$\nu_a(\mathrm{NCO}) = 2215$vs, $\nu_s(\mathrm{NCO}) = 1347$m, $\delta(\mathrm{NCO}) = 602$m, $\nu(\mathrm{PtN}) = 325$m
cis-$[\mathrm{Pt(SCF_3)(Cl)(PEt_3)_2}]$	*e*				22·0 [h]	61·2	9·5	*f*	
cis-$[\mathrm{Pt(SCF_3)(NO_3)(PEt_3)_2}]$	117—122	26·3 (26·3)	5·1 (5·1)	2·5 (2·4)	23·2	58·5	9·1	*f*	$\nu_d(\mathrm{NO}) = 1490$s and 1280vs, $\nu_s(\mathrm{NO}) = 990$s, $\nu(\mathrm{PtO}) = 290$w,b
cis-$[\mathrm{Pt(SCF_3)_2(PBu^n{}_3)_2}]$	Not isolated				22·3	65·6	8·0	1·5	$^2J(\mathrm{PP}) = 12$
cis-$[\mathrm{Pt(SCF_3)_2\{P(OPh)_3\}_2}]$	158—160	44·9 (44·8)	3·0 (3·0)		22·1	69·9	14·0	1·5	$^2J(\mathrm{PP}) = 24$
cis-$[\mathrm{Pt(SCF_3)_2(PPh_3)_2}]$	*e*				22·8	70·0	9·5	1·5	$^2J(\mathrm{PP}) = 14$
cis-$[\mathrm{Pt(SCF_3)_2\{P(OMe)_3\}_2}]$	79—80	14·7 (14·9)	2·8 (2·8)		23·1	71·4	15·0	1·5	$\delta(\mathrm{C}H_3) = -3{\cdot}82$, $^3J(\mathrm{HP}) = 12{\cdot}0$, $^2J(\mathrm{PP}) = 10$

TABLE 1 (*Continued*)

Complex [a]	M.p. (t/°C)	Analytical data (%) [b] C	H	N	δ	^{18}F N.m.r. of SCF$_3$ group [c] ^3J (FPt)	^4J (FP*trans*)	^4J (FP*cis*)	Other i.r. and n.m.r. data [c]
cis-$[Pt(SCF_3)_2(PClPh_2)_2]$	90—95 dec.	38·1 (37·2)	2·5 (2·4)		22·7	71·2	11·5	1·5	^2J(PP) = 30
cis-$[Pt(SCF_3)_2(C_5H_5N)_2]$	dec.	26·7 (25·9)	1·9 (1·8)	5·0 (5·0)	26·3	102·6			
trans-$[Pt(SCF_3)_2(PBu^n_3)_2]$	42—43	39·0 (38·9)	6·9 (6·8)		22·6	96·0		1·7	
trans-$[Pt(SCF_3)_2(PPh_3)_2]$	*e*				25·6	83		1·8	
trans-$[Pt(SCF_3)_2(C_5H_5N)_2]$	Not isolated				25·7	90·2			
trans-$[Pt(SCF_3)(CH_3)(PPh_3)_2]$	197—199	55·1 (54·6)	4·0 (4·0)		21·2	43·0		1·6	$\delta(CH_3)$ = 0·0, ^2J(HPt) = 68·5, ^3J(HP *cis*) = 6·5
trans-$[PtI(CF_3)(PEt_3)_2]$	115—118	24·4 (24·9)	4·8 (4·8)						$\delta(CF_3)$ = 8·86, ^2J(FPt) = 789, ^3J(FP) = 16·5, ν(CF) = 1080vs,b, 975vs,b

[a] All complexes were white or yellow in colour. [b] Required values in parentheses. [c] J And δ denote respectively n.m.r. coupling constants (Hz) and chemical shifts in CH_2Cl_2 solution [p.p.m. from $CFCl_3$ or $Si(CH_3)_4$ as external references, positive values denote upfield shifts]. ν, δ', And ρ denote infrared absorptions (cm^{-1}) using the nomenclature of ref. 5. Approximate relative intensities and widths are denoted by vs (very strong), m (medium), w (weak), b (broad), *etc*. Further comments on the i.r. assignments are given in the results section. [d] Gave correct molecular ion in mass spectrum. [e] Data from ref. 2. [f] Not resolved. [g]



. $\delta(F_\alpha)$ = 153, $\delta(F_\beta)$ = 99, $\delta(F_\gamma)$ = 129, $^3J(PF_\alpha)$ = 3·1, $^4J(PF_\beta)$ = 5·6, $^4J(PF_\gamma)$ = 3·6, $^2J(PtF_\alpha)$ = 441, $^3J(PtF_\beta)$ = 44, $^3J(PtF_\gamma)$ = 51, $^3J(F_\alpha F_\beta)$ = 32, $^3J(F_\alpha F_\gamma)$ = 104, $^2J(F_\beta F_\gamma)$ = 105. [h] Misprinted in ref. 2.

simple first-order analysis of the relevant spectra. ^{1}H N.m.r. data for the triethylphosphine ligands are not included in Table 1, but they served as a final check on the stereochemistry of the complexes. This method, based on the occurrence of ' virtual coupling ' in the *trans*-complexes, has been used by many authors [16] and further details are not needed here.

DISCUSSION

It is now widely accepted [1,17] that the coupling constants involved in the measurement of *trans*-influence phenomena can be assumed to be dominated by the Fermi contact interaction.[18] This assumption might be thought highly suspect in view of recent calculations [19] showing that dipolar and especially orbital contributions to C–C, C–F, and F–F coupling constants are of similar magnitude to the contact interaction. This work would suggest that orbital contributions should not be neglected when using coupling constants such as Pt–F or Pt–P as indicators of *trans*-influence. However, data such as the good linear correlations (see below) between ^2J(Pt–H) and ^2J(Pt–F) or ^1J(Pt–P) give strong support to the assumption of dominance of the Fermi contact interaction since orbital contributions are expected to be negligible for couplings involving hydrogen.[20] The observed correlations are linear and pass through the origin, thus demonstrating either that orbital contributions are negligible for all three types of coupling, or that they vary proportionally with the contact interaction as the *trans*-ligand is changed. In either case rationalizations of *trans*-influence effects may be based on variation of the contact interaction. In the case of the ^3J(Pt–F) values reported here there are more possibilities since the correlations are linear, but do not pass through the origin. Thus constant orbital contributions or ones which vary linearly with the contact interaction are also possible, although they seem unlikely in view of the further discussion below.

The theory of the Fermi contact interaction has been developed in detail only for coupling between directly bound nucleii. It has been suggested [1] that the theory may be extended to indirect couplings (*i.e.* those extending over more than one bond) by the introduction of the term F(A–B $\cdots$ M) which is an unknown constant representing all the electronic and stereochemical factors which affect the transmission of the coupling from Pt to Z in the system Pt–A–B $\cdots$ M–X. The Fermi contact contribution to the Pt–Z coupling is then given by:

$$|^nJ(\text{Pt–Z})| \propto \frac{\gamma_{Pt}\gamma_Z\alpha^2_{Pt}\alpha^2_Z F(\text{A–B} \cdots \text{M–Z})|\psi_{Pt(6s)}(O)|^2|\psi_{Z(ns)}(O)|^2}{^3\Delta E} \quad (1)$$

where γ_{Pt} is the gyromagnetic ratio of Pt, α^2_{Pt} is the *s*-character of the bonding hybrid orbital used by Pt in the Pt–A bond, $|\psi_{Pt(6s)}(O)|$ is the magnitude of the atomic wave function for the valence-shell platinum *s*-orbital evaluated at the Pt nucleus, and $^3\Delta E$ is the mean singlet–triplet excitation energy. It has been established by study of a very wide range of couplings to ^{195}Pt that the principal variable in equation (1) for directly bound nuclei is α^2_{Pt} and ligands are considered to have a high *trans*-influence if they have a high demand for the platinum 6*s*-orbital.[1] Thus, in considering indirect coupling constants as measures of *trans*-influence, the interest is in establishing the validity of the various

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[16] K. R. Dixon, K. C. Moss, and M. A. R. Smith, *Canad. J. Chem.*, 1974, **52**, 692, and references therein.

[17] J. F. Nixon and A. Pidcock, *Ann. Rev. N.M.R. Spectroscopy*, 1969, **2**, 380.

[18] W. McFarlane, *Quart. Rev.*, 1969, 187.

[19] A. C. Blizzard and D. P. Santry, *J. Chem. Phys.*, 1971, **55**, 950.

[20] J. A. Pople and D. P. Santry, *Mol. Phys.*, 1964, **8**, 1.

assumptions in the foregoing theory. Is the Fermi contact interaction still dominant? Can variations in this interaction still be ascribed mainly to α^2_{Pt} and is the use of the constant term F(A–B · · · M–Z) valid?

The ^3J(Pt–F) values given in Table 1 for *trans*-$[\mathrm{Pt(SCF_3)(X)(PEt_3)_2}]$ complexes yield the following *trans*-influence series for anionic ligands: $\mathrm{C_6H_5 > CH_3 > H > CF_3 > C_2F_3 > CN > NO_2 > SCF_3 > N_3 > I > NCS \sim NCO > Br > Cl > NO_3}$. This is more extensive than any previous series, particularly in that it places the alkyl, aryl, and hydride ligands on the same scale as the other anionic ligands. Other series involving platinum(II) have used different types of complexes for the two groups of anionic ligands and the series based on ^2J(Hg–H) in MeHgX complexes does not include hydride and many of the other ligands included here.[1] ^3J(Pt–F) Values from *cis*-$[\mathrm{Pt(SCF_3)_2L_2}]$ complexes are not strictly comparable with the above series since the *cis*-influences involved are different, but if we accept them as an approximate indication of the positions of neutral ligands we can insert: $\mathrm{C_2F_3 > PBu^n_3 > PEt_3 > P(OPh)_3 > PPh_3 > P(OMe)_3 > PClPh_2 > CN > NO_2 > SCF_3 > py > N_3}$. The series thus obtained is closely similar to those derived previously using couplings over one or two bonds, with perhaps the most directly comparable example coming from ^2J(Pt–H) values in the complexes *trans*-$[\mathrm{Pt(CH_3)(X)(PEt_3)_2}]$ [21] and *cis*-$[\mathrm{Pt(CH_3)_2(PR_3)_2}]$.[21,22] This series correlates linearly * with ours and, although more limited in scope, is similar except for minor changes in the positions of CN and I. ^2J(Pt–H) Values also correlate linearly with ^1J(Pt–H) in *trans*-$[\mathrm{PtH(X)(PEt_3)_2}]$ complexes [21,23] and it therefore seems clear that equation (1) is valid, at least in a general way, for the couplings over three bonds as well as for those over one or two bonds. This conclusion is similar to that reached by Clark and his coworkers [24] using a more limited set of 13 complexes of the $\mathrm{-C(CF_3){=}CH(OCH_3)}$ indicator ligand and is also supported by several other studies [25] on small sets of ligands.

It is well-established that the *trans*-influence of a ligand depends primarily on the position of the ligand atom in the Periodic Table, the general order being Group IV > Group V > Group VI > Group VII and Period II > Period I.[1] Our series is in complete accord with these principles and the order is approximately that expected if high electronegativity of the ligand atom leads to a low *trans*-influence. Thus, as the Pt–L or Pt–X bond becomes increasingly polar, involvement of the platinum 6*s*-orbital in the bonding combination decreases and this orbital is more available for the Pt–A bond. The order of electronegativity is not exactly followed, however, and some compromise between this factor and the ability of the elements to form strong covalent bonds seems to operate. The importance of electronegativity is further illustrated by the sequence: $\mathrm{C_6H_5 > CH_3 > H > CF_3 > C_2F_3 > CN}$. A similar series $[\mathrm{C_6H_5 > CH_3 > CF_3 > H > C(CF_3){=}CH(OCH_3)}]$ may be derived [26] using ^3J(Pt–H) in $\mathrm{PMe_2Ph}$ complexes but this parameter is very insensitive to *trans*-influence compared to our ^3J(Pt–F) values. Comparison of our series with the Taft σ_{I} values [27] $\mathrm{CH_3}$ (−0·05) < H (0·0) < $\mathrm{C_2H_3}$ (0·05) < $\mathrm{C_6H_5}$ (0·10) < $\mathrm{CF_3}$ (0·41) < CN (0·58) shows that the *trans*-influence order almost exactly follows electron-withdrawing power. The vinyl groups are lower in the *trans*-influence series, consistent with increase in their effective electronegativity by the F and $\mathrm{CF_3}$ substituents, and the only real anomaly is the position of $\mathrm{C_6H_5}$. This has a much larger *trans*-influence than is expected from its electron-withdrawing power and may be a genuine example of π-bonding contributions since this explanation is commonly used to rationalize stability trends in *ortho*-substituted aryl complexes of square planar metals.[28] Interestingly, this anomaly does not occur in the *trans*-influence series at mercury(II) [*i.e.* $\mathrm{CH_3 > C_2H_3 > C_6H_5 > CN}$, established by ^2J(Hg–H) in $\mathrm{XHgCH_3}$ complexes].[1]

Further support for the idea that effective electronegativity is an important factor in the *trans*-influence comes from the order of phosphorus ligands established above, with $\mathrm{PBu^n_3 > PEt_3 > PPh_3 > PClPh_2}$. However, in this case also the traditionally π-bonding phosphites are higher in the series than might be predicted from electronegativity considerations alone.

We have already seen that equation (1) is valid in a general way, but it is of interest to examine the resulting correlations in more detail. In order to deal only with cases where all complexes in a given series are of the same type, it is necessary to restrict consideration to the anionic ligand set CN, $\mathrm{NO_2}$, $\mathrm{N_3}$, I, NCS, NCO, Br, Cl, and $\mathrm{NO_3}$, and Table 2 gives data for one-, two-, and three-bond coupling constants measured *trans* to these ligands. Table 3 summarises the least-squares correlations between these various data sets and shows that, with the exception of ^1J(Pt–H) against ^3J(Pt–F), the best straight lines divide into two groups: those with $R_c > 0{\cdot}99$ and which pass through or close to the origin (intercept $<4\sigma$) and those with $R_c \sim 0{\cdot}94$ and which do not pass through the origin (intercept $>8\sigma$). This distinction is introduced for convenience and in fact the discussion below indicates that a continuum of intercepts is possible. The first group of lines includes those involving only ^1J(Pt–P), ^2J(Pt–H), or ^2J(Pt–F) and the second group involves

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* $R_c = 0{\cdot}906$; $^2J(\mathrm{Pt{-}H}) = (0{\cdot}30 \pm 0{\cdot}05)\,^3J(\mathrm{Pt{-}F}) + (44 \pm 4)$.

[21] F. H. Allen and A. Pidcock, *J. Chem. Soc.* (*A*), 1968, 2700.

[22] E. O. Greaves, R. Bruce, and P. M. Maitlis, *Chem. Comm.*, 1967, 860.

[23] T. G. Appleton, M. H. Chisholm, H. C. Clark, and L. E. Manzer, *Inorg. Chem.*, 1972, **11**, 1786.

[24] T. G. Appleton, M. H. Chisholm, H. C. Clark, and L. E. Manzer, *Canad. J. Chem.*, 1973, **51**, 2243.

[25] T. F. Schaaf and J. P. Oliver, *Inorg. Chem.*, 1971, **10**, 1521; F. Glockling and K. A. Hooton, *J. Chem. Soc.* (*A*), 1967, 1066; P. L. Goggin, R. J. Goodfellow, S. R. Haddock, and (in part) J. G. Eary, *J.C.S. Dalton*, 1972, 647; see also Table 11 in ref. 1.

[26] See Table 11 in ref. 1.

[27] J. March, 'Advanced Organic Chemistry: Reactions, Mechanisms and Structure,' McGraw-Hill, New York, 1968; C. D. Ritchie and W. F. Sager, *Progr. Phys. Org. Chem.*, 1964, **2**, 323.

[28] G. E. Coates, M. L. H. Green, P. Powell, and K. Wade, 'Principles of Organometallic Chemistry,' Methuen, London, 1971, p. 185.

plots of ${}^1J$(Pt–H) or ${}^3J$(Pt–F) against any of the other three parameters.

Clark and his co-workers[24] have discussed three possible reasons for non-zero intercepts in *trans*-influence plots: (*a*) π-bonding; (*b*) orbital ('through space') contributions; and (*c*) non-constancy of the F(A–B ⋯ M–Z) factor. Many considerations arising from our present study argue against these explanations but some of the more important points are: (i) the plot of ${}^1J$(Pt–H) against ${}^2J$(Pt–H) does not involve (*a*) or (*b*) for either parameter and yet does not pass through the origin; (ii) the plot of ${}^2J$(Pt–H) against ${}^2J$(Pt–F) involves parameters which should have very different orbital contributions and yet passes through the origin; (iii) the similarity of plots involving ${}^1J$(Pt–H) to those involving ${}^3J$(Pt–F) argues for similar causes for the non-zero intercepts, whereas none of the factors (*a*), (*b*), or (*c*) can affect ${}^1J$(Pt–H); [The plot of ${}^1J$(Pt–H) against ${}^3J$(Pt–F) apparently passes through the origin, although this result should be approached with caution in view of the poor correlation coefficient.] (iv) the intercepts in the plots of ${}^3J$(Pt–F) against ${}^1J$(Pt–P), ${}^2J$(Pt–H), or ${}^2J$(Pt–F) are all on the axes involving the latter parameters, whereas if the ${}^3J$(Pt–F) were enhanced by π-bonding to sulphur we would expect intercepts on the ${}^3J$(Pt–F) axes.

TABLE 2

Coupling constants (Hz) measured *trans* to various anionic ligands

	CN	NO_2	N_3	I	NCS	NCO	Br	Cl	NO_3
${}^1J$(Pt–H) [a]	778	1003	1155 [b]	1369	1086	1080	1346	1275	1322
${}^1J$(Pt–P) [c]	4086	4775	5266	5587	5402	5344	5679	5640	5810
${}^2J$(Pt–H) [d]	60·2	70·9	78·6	82·4	78·6	79·5	83·0	84·2	86·0
${}^2J$(Pt–F) [e]	565	644	710	754	721	714	763	757	795
${}^3J$(Pt–F) [f]	82·0	88·6	110·5	118·8	122·6	123·0	128·0	129·0	131·4

[a] ${}^1J$(Pt–H) data is for *trans*-[$PtHX(PEt_3)_2$] complexes from J. Powell and B. L. Shaw, *J. Chem. Soc.*, 1965, 3879. [b] Present work. [c] ${}^1J$(Pt–P) data is for *trans*-[$PtX\{(PhO)_2PO\}(PBu_3)_2$] complexes from ref. 35. [d] ${}^2J$(Pt–H) data is for *trans*-[$PtX(CH_3)(PEt_3)_2$] complexes from ref. 21. [e] ${}^2J$(Pt–F) data is for *trans*-[$PtX(CF_3)(PMe_2Ph)$] complexes from ref. 23. [f] ${}^3J$(Pt–F) data is for *trans*-[$PtX(SCF_3)(PEt_3)_2$] complexes from present work.

TABLE 3

Correlation coefficients and least-squares straight lines for the data sets from Table 2

	${}^3J$(Pt–F)	${}^2J$(Pt–F)	${}^2J$(Pt–H)	${}^1J$(Pt–P)
${}^2J$(Pt–F)	0·946 3·7 ± 0·5 288 ± 24			
${}^2J$(Pt–H)	0·943 0·42 ± 0·06 30 ± 3	0·992 0·113 ± 0·005 −3 ± 1		
${}^1J$(Pt–P)	0·953 29 ± 4 1973 ± 177	0·995 7·7 ± 0·3 −220 ± 55	0·996 67 ± 2 24 ± 52	
${}^1J$(Pt–H)	0·829 9 ± 2 129 ± 116	0·945 2·6 ± 0·3 −700 ± 68	0·932 23 ± 3 −599 ± 75	0·935 0·33 ± 0·05 −604 ± 74

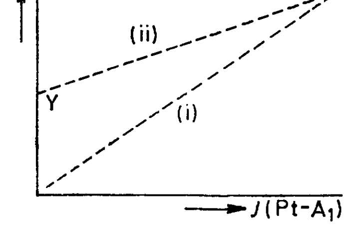
The data refer to the equation, $y = mx + b$, where x is the parameter at the head of each column. Correlation coefficients (R_c), slopes (m), and intercepts (b) are given in that order and the error limits are calculated standard deviations (σ).

We suggest that explanations such as (*a*), (*b*), and (*c*) above are unnecessary, and that the situation can be understood by viewing the *trans*-influence as a perturbation of the Pt–A bond, introduced by the approaching ligand, L. Thus:

$$\mathrm{L}\cdots\cdots\cdots\mathrm{Pt{-}A}$$

For two different indicator ligands A_1 and A_2 the couplings in the unperturbed three-co-ordinate species will give a point at U in the Figure. As the *trans*-influence perturbation is increased a straight line passing through the origin is only obtained if J(Pt–A_1) and J(Pt–A_2) have equal sensitivity (% change) to the perturbation. Clearly, this will only occur in especially favourable circumstances and it is not surprising that many plots do not pass through the origin. At point Y in the Figure we are essentially saying that the *trans*-influence is sufficient to cleave the Pt–A_1 bond but not the Pt–A_2 bond.

Mathematically, this argument may be presented in terms of four parameters: $(\alpha_A{}^L)^2$, Pt(6*s*) character of Pt–A bond *trans* to ligand, L; $(\alpha_A{}^0)^2$, Pt(6*s*) character of unperturbed Pt–A bond; T_L, *trans*-influence of ligand, L; S_A, sensitivity of indicator ligand, A. If we regard the perturbation as a rehybridization in which



Hypothetical coupling plots for the indicator ligands A_1 and A_2: (i) A_1 and A_2 equally sensitive to *trans*-influence perturbations; (ii) A_1 more sensitive than A_2. The significance of points U and Y is discussed in the text

Pt(6s) character is gained by the Pt–L bond and lost by the Pt–A bond, then we can write

$$(\alpha_A{}^L)^2 = (\alpha_A{}^O)^2(1 - T_LS_A)$$

and substitutions into equation (1) give expressions of the type $J(\text{Pt–A}_1) = k_1(1 - T_LS_1)$ and $J(\text{Pt–A}_2) = k_2(1 - T_LS_2)$ where all constant terms are incorporated in k_1 and k_2. The plot of $J(\text{Pt–A}_1)$ against $J(\text{Pt–A}_2)$ is then linear but passes through the origin only when $S_1 = S_2$.* This simple approach is admittedly unlikely to be complete and the other factors [(a), (b), and (c) above] discussed by Clark and his co-workers [24] probably do play a role in some cases. However, most of our assumptions are those common to previous treatments of *trans*-influence and our approach shows that non-zero intercepts do not of themselves necessitate considerations beyond equation (1).

Viewed in the light of this discussion, Table 3 shows that ^1J(Pt–H) and ^3J(Pt–F) are both unusually sensitive to the *trans*-influence. The origin of this enhanced sensitivity remains uncertain. Clark and co-workers [1] have suggested that the differing sensitivities of ν(Pt–C) and ν(Pt–Cl) may be attributed to the very different Pt(6s) requirements of Cl and the C-bonded ligands. This is clearly not the explanation in the present case, however, since H and SCF_3 are very different in *trans*-influence but both show high sensitivity. A possible explanation may lie in the polarisability of the H and SCF_3 ligands. The ligand atoms in the $PtCH_3$, $PtCF_3$, and $PtPO(OPh)_2$ groups have all their valence-shell electrons involved in bonding pairs whereas in the $PtSCF_3$ group there are two lone pairs. The correspondingly smaller effective nuclear charge at sulphur may give a Pt–S bonding orbital which is more readily polarized towards platinum, thus increasing the coefficient of the Pt(6s) orbital in the bonding combination. The SCF_3 ligand would then be especially sensitive to the electronegativity contributions to the *trans*-influence discussed above. The hydride ligand is well-known to be highly polarizable and to show wide variation in the ionic character of its bonds and in consequence may be expected to show enhanced sensitivity to *trans*-influence for similar reasons to those given for SCF_3. The plot of ^1J(Pt–H) against ^3J(Pt–F) does pass through the origin. However, it is unlikely that such different groups as Pt–H and Pt–SCF_3 would respond to perturbation in exactly the same way and it is not surprising that the correlation coefficient is poor. One important factor is the possibility of conformational differences between various complexes of the bent Pt–SCF_3 group. The complexes are sterically crowded [3] and preliminary observations [29] have shown that some of the ^3J(Pt–F) values reported here show variation with temperature of up to 4% in the range 210—300 K. This suggests that different conformers having slightly different energies and coupling constants are present.

Further support for our view of the origin of non-zero intercepts comes from the –C(CF_3)=CH(OCH_3) indicator ligand. Plots of ^3J(Pt–H) and ^3J(Pt–F) against ^2J(Pt–H) and ^2J(Pt–F) in corresponding CH_3 and CF_3 complexes all show intercepts on the axis appropriate for enhanced sensitivity of the vinyl ligand,[24] consistent with a greater polarizability of the sp^2 carbon compared with the sp^3 ligands.

Finally, omitting the case just discussed of ^1J(Pt–H) against ^3J(Pt–F), it is noticeable that those plots (Table 3) which do not pass through the origin have considerably poorer correlation coefficients than those which do. This is understandable in terms of the above ideas since we suggest an enhanced sensitivity to only one component of the *trans*-influence (*i.e.* electronegativity) and, as Clark and his co-workers [1] have pointed out, the relative proportions of different components will vary from ligand to ligand.

EXPERIMENTAL

Data relating to the characterization of the complexes are given in Table 1. Microanalyses were by Chemalytic Inc., Tempe, Arizona, or by Mr. D. L. McGillivray of this department. ^{1}H and ^{19}F N.m.r. spectra were recorded at 60·0 and 56·4 MHz respectively on Perkin-Elmer R12A or Varian HA60 spectrometers using tetramethylsilane or fluorotrichloromethane as external references and with signal-to-noise enhancement using a Northern Scientific NS 560 time-averaging computer. Chemical shifts are given in p.p.m. and positive values denote upfield shifts. Simulated n.m.r. spectra were calculated using the UEAITR programme [30] on an IBM 370/145 computer and plotted on a Calcomp 563 Drum Plotter using a programme based on the NMR PLOT programme.[31] Mass spectra were recorded using a Hitachi–Perkin-Elmer RMU7E double-focussing spectrometer. I.r. spectra were recorded (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.

Reactions were conducted at 25 °C (unless otherwise stated below) in an atmosphere of nitrogen deoxygenated by passage through acidic chromous chloride solution and dried by calcium chloride and type 4A molecular sieves. Pentane was dried by distillation from P_2O_5 and stored over sodium. Benzene was dried by sodium and other solvents were dried by type 4A molecular sieves. All yields given below were recorded after recrystallization. In general, much higher yields (80—90%) of crude products could be obtained. $AgSCF_3$ Was prepared as previously described [32] and details of other preparations follow.

(1) [$PtCl_2L_2$] *Complexes*.—(a) For L = PPh_3, PEt_3, $PBu^n{}_3$,

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* The alternative assumption $(\alpha_A{}^L)^2 = T_LS_A(\alpha_A{}^O)^2$, which at first sight permits different values of S_1 and S_2 and still gives lines passing through the origin, is unlikely in terms of hybridization theory. In any case, it cannot describe the present situation since at U (see Figure) $T_LS_1 = T_LS_2 = 1$, which is impossible if $S_1 \neq S_2$.

[29] K. R. Dixon, unpublished observations.

[30] R. B. Johannesen, J. A. Ferretti, and R. K. Harris, *J. Magnetic Resonance*, 1970, **3**, 84.

[31] J. D. Swalen in 'Computer Programmes for Chemistry,' vol. I, D. F. Detar, ed., W. A. Benjamin Inc., New York, 1968.

[32] H. J. Emeléus and D. E. MacDuffie, *J. Chem. Soc.*, 1961, 2597.

PhCN, or py the *cis*-complexes were obtained as previously described,[33] as was the *cis–trans* mixture for L = SEt_2.[34]

(b) L = $P(OPh)_3$. $P(OPh)_3$ (1·07 g, 3·45 mmol) In benzene was added to *cis*-$[PtCl_2(PhCN)_2]$ (0·81 g, 1·72 mmol) in benzene at 60 °C. Evaporation under reduced pressure followed by extraction of the residue with dichloromethane and addition of diethyl ether to the extract gave the known[35] complex, *cis*-$[PtCl_2\{P(OPh)_3\}_2]$ (1·33 g, 1·50 mmol).

(c) L = $P(OMe)_3$. $P(OMe)_3$ (0·56 g, 4·51 mmol) In acetone (3 ml) was added to *cis*- and *trans*-$[PtCl_2(SEt_2)_2]$ (1·00 g, 2·24 mmol) in acetone (10 ml). Evaporation under reduced pressure to *ca.* 2 ml followed by addition of diethyl ether gave the known[36] complex, *cis*-$[PtCl_2\{P(OMe)_3\}_2]$ (0·88 g, 1·71 mmol).

(d) L = $PClPh_2$. $PClPh_2$ (1·40 g, 6·35 mmol) Was added to $PtCl_2$ (0·84 g, 3·16 mmol) in *p*-xylene (30 ml). After the mixture had been stirred for 5 h the solids were filtered off and extracted with dichloromethane. Addition of diethyl ether to the extract gave the known[37] complex, *cis*-$[PtCl_2(PClPh_2)_2]$ (0·88, 1·24 mmol) (Found: C, 40·4; H, 4·9. Calc. for $C_{24}H_{20}Cl_3P_2Pt$: C, 40·8; H, 4·9%).

(2) $[PtClX(PEt_3)_2]$ *Complexes*.—For X = SCN, N_3, NO_2, NCO, or NO_3 the *cis*-complexes were obtained as previously described,[16] as was the *trans*-complex for X = C_2F_3.[38] For X = Me or Ph, *trans*-complexes were prepared by treatment of *cis*-$[PtX_2(PEt_3)_2]$ (X = Ph[39] or Me[40]) with an ethereal solution of HCl.[40,41] For X = CN, a solution of *trans*-$[PtH(CN)(PEt_3)_2]$ in CCl_4 was stored at 25 °C for 2 weeks resulting in essentially quantitative conversion to *trans*-$[PtCl(CN)(PEt_3)_2]$.[42]

(3) trans-$[PtI(CF_3)(PEt_3)_2]$.—*cis*-$[PtMe_2(PEt_3)_2]$[40] (0·305 g, 0·661 mmol) And CF_3I (2 ml) were sealed in a Pyrex tube. After 48 h at 25 °C volatile products were removed *in vacuo* and the residue extracted with dichloromethane. Evaporation of the extract under reduced pressure gave a white powder (0·375 g) which was shown by ^{19}F and ^1H n.m.r. to be a mixture of *trans*-$[PtI(CF_3)(PEt_3)_2]$ (90%) and $[PtI(CF_3)(CH_3)_2(PEt_3)_2]$ (10%). Recrystallization from methanol gave the pure platinum(II) complex.

(4) cis-$[Pt(SCF_3)_2L_2]$ *Complexes*.—In a typical reaction $AgSCF_3$ (0·260 g, 1·24 mmol) in acetone (10 ml) was added dropwise with stirring to *cis*-$[PtCl_2(PEt_3)_2]$ (0·285 g, 0·567 mmol) in dichloromethane (15 ml). After the mixture had been stirred for 30 min, AgCl was filtered off and the filtrate evaporated under reduced pressure. Extraction with dichloromethane (leaving unchanged $AgSCF_3$ as residue) and addition of diethyl ether to the extract gave *cis*-$[Pt(SCF_3)_2(PEt_3)_2]$ (0·220 g, 0·347 mmol) as a white precipitate.

Other reactions were similar except that those involving phosphite complexes were conducted in acetone and the dichloromethane extracts were recrystallized from acetone by addition of diethyl ether and refrigeration at −20 °C. The following yields were obtained after recrystallization: L = $PClPh_2$ (50%), $P(OPh)_3$ (60%), $P(OMe)_3$ (20%), C_5H_5N (35%, after stirring for 3 h). *cis*-$[Pt(SCF_3)_2(PBu_3)_2]$ Was identified by its ^{19}F n.m.r. spectrum but it isomerized spontaneously to the *trans*-complex and was isolated only as the latter isomer.

(5) trans-$[Pt(SCF_3)_2L_2]$ *Complexes*.—These were obtained by isomerization of the corresponding *cis*-complexes in dichloromethane solution using *ca.* 10 mol % of L as catalyst. Reaction times up to one week at 25 °C were required. For L = PEt_3 and PBu^n_3, the products were recrystallized from aqueous ethanol (90%) by cooling solutions to −20 °C. For L = C_5H_5N, isomerization was only *ca.* 50% complete and the *trans*-complex was not isolated. For L = $P(OPh)_3$ and $P(OMe)_3$, no isomerization was detected and for L = $PClPh_2$, extensive decomposition occurred on attempted isomerization.

(6) cis-$[PtX(SCF_3)(PEt_3)_2]$ *Complexes*.—These complexes were prepared by reaction of *cis*-$[PtXCl(PEt_3)_2]$ (1 mmol) with $AgSCF_3$ (1 mmol), both in acetone solution, by a procedure similar to (4) above. Products were recrystallized in the indicated yields from aqueous ethanol (90%) by cooling to −20 °C (X = NCS, 40%; NO_2, 70%; NCO, 45%) or from acetone by addition of diethyl ether (X = N_3, 65%). Some decomposition of the complex for X = NCO occurred during recrystallization and the analytical results shown in Table 1 are rather poor. For X = NO_3, crystallization from ethanol by addition of diethyl ether gave only $[Pt_2(SCF_3)_2(PEt_3)_4][ClO_4]_2$ {probably from $[Pt_2Cl_2(PEt_3)_4][ClO_4]_2$ impurity in the *cis*-$[Pt(NO_3)Cl(PEt_3)_2]$ starting material[16]} but refrigeration of the filtrate gave *cis*-$[Pt(NO_3)(SCF_3)(PEt_3)_2]$ (20%).

(7) trans-$[PtX(SCF_3)(PEt_3)_2]$ *Complexes*.—(a) X = Cl, Ph, Me, C_2F_3, *or* CN. These complexes were prepared by reaction of *trans*-$[PtXCl(PEt_3)_2]$ (1 mmol) with $AgSCF_3$ (1 mmol), both in acetone solution, by a procedure similar to (4) above except that for X = Cl reaction was for 1½ h at 50 °C. Products were obtained by evaporation of the dichloromethane extract and recrystallized in the indicated yields as follows; X = Cl [aqueous ethanol (90%) by cooling to −20 °C, 75%], Ph [light petroleum (b.p. 60—90 °C), 70%], C_2F_3 (pentane, 55%), yield essentially quantitative before recrystallization. Complexes for X = Me and CN could not be crystallized but mass spectra and ^1H and ^{19}F n.m.r. clearly established their identity.

(b) X = CF_3. The procedure was similar to (7a) above except that *trans*-$[PtI(CF_3)(PEt_3)_2]$ was the reactant and reaction was for 1½ h. An oily product which crystallized with time was obtained by evaporation of the dichloromethane extract; yield 85%. Attempts to recrystallize this product were unsuccessful.

(c) X = N_3, NCS, *or* NCO. These complexes were obtained by isomerization of the corresponding *cis*-complexes in dichloromethane solution using *ca.* 10 mol % PEt_3 as catalyst. The product for X = N_3 was recrystallized from aqueous ethanol (90%) and for X = NCS from aqueous acetone (90%). *trans*-$[Pt(NCO)(SCF_3)(PEt_3)_2]$ Showed some decomposition during recrystallization and was not obtained pure.

(d) X = Br, I, NO_2, *or* NO_3. *trans*-$[PtCl(SCF_3)(PEt_3)_2]$ (1 mmol) In acetone was stirred with KBr (5 mmol) for 13 h, KI (1 mmol) for ½ h, $AgNO_2$ (1 mmol) for 1 h, or $AgNO_3$

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[33] F. R. Hartley, *Organometallic Chem. Rev. A*, 1970, **6**, 119, and references therein.

[34] G. B. Kauffman and D. O. Cowan, *Inorg. Synth.*, 1960, **6**, 211.

[35] F. H. Allen, A. Pidcock, and C. R. Waterhouse, *J. Chem. Soc.* (*A*), 1970, 2087.

[36] A. E. Arbuzov and V. M. Zoroastra, *Izvest. Akad. Nauk S.S.S.R., Otdel Khim. Nauk*, 1952, 809 (*Chem. Abs.*, 1953, **47**, 9899f).

[37] T. E. Austin, Ph.D. Thesis, University of North Carolina, 1966.

[38] H. C. Clark, K. R. Dixon, and W. J. Jacobs, *J. Amer. Chem. Soc.*, 1968, **90**, 2259.

[39] H. C. Clark and K. R. Dixon, *J. Amer. Chem. Soc.*, 1969, **91**, 596.

[40] J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1959, 705.

[41] J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1959, 4020.

[42] A. Pidcock, personal communication.

(1 mmol) for 1½ h. After filtration from KCl or AgCl the complexes having X = Br, NO_2, or NO_3 were isolated by evaporation of the filtrate under reduced pressure and extraction of the residue with dichloromethane. Evaporation of the extract under reduced pressure gave the complexes which were recrystallized in the indicated yields from methanol (X = NO_3, 40%) or aqueous ethanol (X = Br, 53% or NO_2, 56%) by cooling to −20 °C. For X = I, evaporation of the acetone filtrate gave a residue which was washed with water and recrystallized in 65% yield from aqueous ethanol (90%) by cooling to −20 °C.

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