Synthesis and Fluorine-19 Nuclear Magnetic Resonance Spectra of Trifluoromethylthio-complexes of Platinum, Palladium, Nickel, and Iridium

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Oxidative addition reactions of $(SCF_3)_2$ to low oxidation state metal complexes and metathetical reactions of $AgSCF_3$ with metal halide complexes lead to the synthesis of the new complexes *cis*- and *trans*-$[Pt(SCF_3)_2(PPh_3)_2]$, *cis*- and *trans*-$[PtCl(SCF_3)(PPh_3)_2]$, *trans*-$[PtH(SCF_3)(PPh_3)_2]$, *trans*-$[PtH(SCF_3)(PEt_3)_2]$, *cis*-$[PtCl(SCF_3)(PEt_3)_2]$, *cis*- and *trans*-$[Pd(SCF_3)_2(PPh_3)_2]$, *trans*-$[PdCl(SCF_3)(PPh_3)_2]$, *trans*-$[PdCl(SCF_3)(PEt_3)_2]$, *trans*-$[Ni(SCF_3)_2(PPh_3)_2]$ and *trans*-$[Ir(SCF_3)(CO)(PPh_3)_2]$. ^{19}F N.m.r. spectra of these complexes are described and used to assign the stereochemistry. The *trans*-influence of the SCF_3 ligand is discussed and the platinum–fluorine coupling constants in a series of SCF_3 complexes are used to establish a *trans*-influence series: $H > PEt_3 \sim PPh_3 > SCF_3 > Cl$.

THERE has been much recent interest in the question of π-bonding between transition metals and ligand atoms having available *d*-orbitals. In particular, the n.m.r. spectra of tertiary phosphine complexes have been extensively studied in order to assess the relative importance of σ- and π-bonding contributions to the high *trans*-influences of these ligands.[1] It has also been pointed out that platinum metal complexes of sulphur containing ligands may have a high degree of involvement of the sulphur *d*-orbitals in the metal–ligand bond.[2] Consequently we considered it of interest to investigate the platinum metal complexes of the trifluoromethylthio-ligand in the hope that the ^{19}F n.m.r. spectra could be used to detect changes in metal to ligand bonds.

Previous studies of trifluoromethylthio-complexes have used three main preparative routes. Grobe and Kober [3] studied thermal reactions of CF_3SX ($X = SCF_3$, SCH_3, SC_6H_5, or Cl) with $Mn_2(CO)_{10}$, Davidson and Sharp [4] utilised photochemical reactions of $(SCF_3)_2$ with a variety of low oxidation state cyclopentadienyl and carbonyl complexes and King and Welcman [5] used metathetical reactions of $AgSCF_3$ with metal carbonyl halides. Prior to our study the only examples [6] of platinum and palladium compounds containing the SCF_3 ligand were diene complexes (*e.g.* $[Pt(SCF_3)_2(C_7H_8)]$) and the complex, $[Pd_2(SCF_3)_4(PPh_3)_2]$.

RESULTS AND DISCUSSION

Platinum Complexes.—Oxidative addition reactions of bis(trifluoromethyl)disulphide to platinum(0), palladium(0), and nickel(0) complexes seemed to offer the simplest route to $[M(SCF_3)_2(PPh_3)_2]$ derivatives. Accordingly the reaction of $[Pt(PPh_3)_4]$ with $(SCF_3)_2$ under Hg irradiation was studied. The greenish yellow product analyses as $[Pt(SCF_3)_2(PPh_3)_2]$ and has a molecular weight in dibromomethane of 911 (calculated, 922). However, ^{19}F n.m.r. spectra show the presence of approximately equal quantities of two compounds which can be assigned as *cis*- and *trans*-isomers.

The ^{19}F n.m.r. spectrum of *trans*-$[Pt(SCF_3)_2(PPh_3)_2]$ exhibits a simple first order pattern of a triplet of triplets in the relative ratios 1 : 4 : 1, derived from coupling with two equivalent phosphorus atoms and with 33·8% of the platinum atoms (^{195}Pt, $I = 1/2$). The spectral parameters are given in the Table. However, in *cis*-$[Pt(SCF_3)_2(PPh_3)_2]$ the phosphorus atoms are magnetically non-equivalent and the resulting ^{19}F spectrum is not first order. It is an $X_3AA'X'_3$ system consisting of a central multiplet with ^{195}Pt sidebands. The multiplet has a main doublet with fine structure between the two peaks and with additional weak lines either side of the doublet. Analysis by standard methods [7] for an $X_3AA'X'_3$ system, assuming $J(XX') = 0$, gives the parameters shown in the Table. An interesting and important feature of the system is the ability to determine $^2J(PP)$ from the ^{19}F spectrum. Determination of phosphorus–phosphorus coupling constants by analysis of $X_nAA'X'_n$ spectra has previously been restricted, with the exception of a few $[Pt(CH_3)_2(PR_3)_2]$ complexes, to cases where X ($= {}^1H$ or ^{19}F) and A ($= {}^{31}P$) are in the same ligand.[8] The range of phosphorus ligands which can be studied is thus automatically restricted whereas our system is applicable to a wide range of ligands. Further work is in progress to measure a range of $^2J(PP)$ values by this method.

Confirmation that the two spectra are due to *cis*- and *trans*-isomers is obtained by adding *ca.* 10 mol % of triphenylphosphine to the mixture of dichloromethane solution. Over a few hours at 25° the ^{19}F resonances due to the *cis*-isomer decrease in intensity and those due to the *trans*-isomer increase until finally the pure *trans*-isomer can be isolated from the solution.

Pure *cis*-$[Pt(SCF_3)_2(PPh_3)_2]$ is obtained by reaction of *cis*-$[PtCl_2(PPh_3)_2]$ with $AgSCF_3$. *cis*-$[PtCl(SCF_3)(PPh_3)_2]$ is also obtained from this reaction but although the yields of the *mono*- or *bis*-trifluoromethylthio-complexes can be maximised by suitable choice of the Pt : Ag reactant ratio, neither complex can be obtained

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uncontaminated by the other and separation by chromatography is always necessary. The stereochemistry of *cis*-[PtCl(SCF$_3$)(PPh$_3$)$_2$] is confirmed by the ^{19}F n.m.r. spectrum which shows a doublet of doublets (with ^{195}Pt sidebands) due to coupling to two chemically non-equivalent phosphorus atoms. Addition of *ca.* 10 mol % of triphenylphosphine to a solution of *cis*-[PtCl(SCF$_3$)(PPh$_3$)$_2$] in dichloromethane gives conversion to an approximately 1 : 1 mixture of *cis*- and *trans*-isomers after 24 h at 25°. The *trans*-isomer was not isolated but is clearly characterised by its ^{19}F spectrum which is similar to that of *trans*-[Pt(SCF$_3$)$_2$(PPh$_3$)$_2$].

Complex	Colour	M.p. (°C)	Analytical data [a]				^{19}F N.m.r. data [c]			
			%C	%H	%S	*M* [b]	^3J(FPt)	^4J(FP$_{cis}$)	^4J(FP$_{trans}$)	δ
cis-[Pt(SCF$_3$)$_2$(PPh$_3$)$_2$] [d]	Yellow-green	215—217	49·3 (49·5)	3·1 (3·3)		*e*	70	1·8	9·2	22·8
trans-[Pt(SCF$_3$)$_2$(PPh$_3$)$_2$]	Colourless	179—180 [f]	49·9 (49·5)	3·4 (3·3)			83	1·8		25·6
cis-[PtCl(SCF$_3$)(PPh$_3$)$_2$]	Colourless	239—244 dec.	50·9 (51·9)	4·0 (3·5)	4·5 (3·7)	840 (856)	63	1·0	11·5	22·4
trans-[PtCl(SCF$_3$)(PPh$_3$)$_2$]	Yellow-green		Not isolated.				118	1·5		26·4
trans-[PtH(SCF$_3$)(PPh$_3$)$_2$] [g]	Colourless	152—153	54·5 (54·2)	3·9 (3·8)		797 (820)	50	1·0		21·4 [h]
trans-[PtH(SCF$_3$)(PEt$_3$)$_2$] [i]	Yellow	Oil				*j*	52	0·8		19·7 [h]
cis-[PtCl(SCF$_3$)(PEt$_3$)$_2$]	Colourless	85—90	27·6 (27·6)	5·1 (5·3)		*ca.* 567 [j]	61	<1	9·5	20·5
cis-[Pd(SCF$_3$)$_2$(PPh$_3$)$_2$]	Yellow-orange		Not isolated.					3·5	7·5	20·1
trans-[Pd(SCF$_3$)$_2$(PPh$_3$)$_2$]	Yellow-orange	137—143	55·1 (54·8)	4·1 (3·6)	8·6 (7·7)	810 (833)		3·5		22·0
trans-[PdCl(SCF$_3$)(PPh$_3$)$_2$]	Orange	174—176	57·6 (57·9)	3·9 (3·9)	4·7 (4·2)	(dec.)		3·5		22·6
trans-[PdCl(SCF$_3$)(PEt$_3$)$_2$]	Yellow	48—50	33·8 (32·6)	6·6 (6·3)		*ca.* 478 [j]		2·5		21·3
trans-[Ni(SCF$_3$)$_2$(PPh$_3$)$_2$]	Purple	175—185 dec.	58·0 (58·1)	4·0 (3·8)	8·3 (8·2)	740 (786)		<1		43·3
trans-[Ir(SCF$_3$)(CO)(PPh$_3$)$_2$]	Brown	205—215 dec.	51·8 (54·0)	3·9 (3·6)	2·6 (3·8)	836 (846)		1·0		25·4 [k]

[a] Required values in parentheses. [b] CH$_2$Br$_2$solution at 50°. [c] Coupling constants (Hz); chemical shifts in CH$_2$Cl$_2$ solution (p.p.m. upfield from CFCl$_3$ external reference). [d] ^2J(PP) 6·5 Hz. [e] *A cis–trans*-isomer mixture analysed as follows: C, 49·8 (49·5); H, 3·6(3·3); S, 6·7 (7·0)%; *M* 911 (922). [f] This complex partially melted at 179—180°, resolidified and finally melted at 215—217°, presumably as a result of formation of *cis*-isomer. [g] N.m.r. data for hydridic hydrogen (C$_6$H$_6$ solution): δ = 10·9 p.p.m. upfield from Me$_4$Si external reference, ^1J(HPt) 1000, ^2J(HP) 13·5, ^4J(HF) 6·0 Hz. [h] C$_6$H$_6$ solution. [i] N.m.r. data for hydridic hydrogen (C$_6$H$_6$ solution): δ = 12·8 p.p.m. upfield from Me$_4$Si external reference, ^1J(HPt) 1152, ^2J(HP) 13·2, ^4J(HF) 6·2 Hz. [j] Molecular weight determined by mass spectroscopy, observed isotopic patterns in agreement with those calculated. *trans*-[PtH(SCF$_3$)(PEt$_3$)$_2$] gave [PtH(SCF$_3$)(PEt$_3$)] as the highest mass fragment. [k] CHCl$_3$ solution.

The complexes *trans*-[PtH(SCF$_3$)(PPh$_3$)$_2$], *trans*-[PtH(SCF$_3$)(PEt$_3$)$_2$], and *cis*-[PtCl(SCF$_3$))PEt$_3$)$_2$] are also obtained by reaction of AgSCF$_3$ with the corresponding chloro-complexes and all have the expected first order ^{19}F n.m.r. spectra. The hydrides were used to study the *trans*-influence of the SCF$_3$ ligand (see below) and the last complex serves as a final check on the correctness of our stereochemical assignments. The *cis*-arrangement of triethylphosphine ligands is confirmed by established criteria (using the 700—800 and 400—450 cm^{-1} regions of the i.r. spectrum and the appearance of the methyl resonance as two overlapping triplets in the ^{1}H n.m.r. spectrum) [9] and consequently the similarity of the ^{19}F n.m.r. spectra for *cis*-[PtCl(SCF$_3$)(PEt$_3$)$_2$] and *cis*-[PtCl(SCF$_3$)(PPh$_3$)$_2$] confirms the stereochemistry of the latter complex.

Palladium Complexes.—When photochemical reactions of (SCF$_3$)$_2$ with [Pd(PPh$_3$)$_4$] were attempted we experienced some difficulty, since samples of [Pd(PPh$_3$)$_4$] prepared by sodium borohydride reduction of *trans*-[PdCl$_2$(PPh$_3$)$_2$] [10] react with (SCF$_3$)$_2$ to give products containing *trans*-[PdCl(SCF$_3$)(PPh$_3$)$_2$]. Presumably the [Pd(PPh$_3$)$_4$] still contains some reduction intermediates, perhaps a chlorohydride, since (SCF$_3$)$_2$ does not react directly with *trans*-[PdCl$_2$(PPh$_3$)$_2$]. Preparations of [Pd(PPh$_3$)$_4$] by the hydrazine reduction method recently described by Coulson [11] give much higher yields than the previous method and reaction of the product with (SCF$_3$)$_2$ gives only *cis*- and *trans*-[Pd(SCF$_3$)$_2$(PPh$_3$)$_2$]. Only about 10% of *cis*-isomer is formed, whereas platinum gives about 50% *cis*, but this is consistent with known isomer ratios in other complexes.[12] Solutions of the isomer mixture spontaneously isomerise (over *ca.* 1 h) to the pure *trans*-isomer and this, together with the small proportion of *cis*-isomer, prevents us from obtaining a ^{19}F n.m.r. spectrum of the *cis*-isomer of sufficient quality to determine ^2J(PP).

trans-[PdCl(SCF$_3$)(PPh$_3$)$_2$] and *trans*-[PdCl(SCF$_3$)(PEt$_3$)$_2$] result from reactions of the corresponding dichloro-complexes with AgSCF$_3$. Unlike the platinum

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complexes, no problems are encountered with contamination of the products by bis(trifluoromethylthio) complexes, presumably because in the *trans* palladium species the second chlorine is not labilised by a *trans* phosphorus atom as it is in the *cis* platinum compounds.

The ^{19}F n.m.r. spectra of all the palladium complexes are similar to those of the platinum analogues except, of course, for the absence of ^{195}Pt sidebands. The i.r. and ^{1}H n.m.r. criteria mentioned above [9] confirm the stereochemistry of *trans*-$[\mathrm{PdCl(SCF_3)(PEt_3)_2}]$.

Nickel, Rhodium, and Iridium Complexes.—The preparation of $[\mathrm{Ni(PPh_3)_3}]$ by Tolman's method [13] is much improved by the use of sodium borohydride instead of zinc as the reducing agent, since the reaction time is reduced from 24 h to 5 min. The product reacts with $\mathrm{(SCF_3)_2}$, even without irradiation, to give a small yield of *trans*-$[\mathrm{Ni(SCF_3)_2(PPh_3)_2}]$. The *trans* square planar stereochemistry is confirmed by the diamagnetism of the complex (which excludes tetrahedral co-ordination) and by the appearance of the ^{19}F n.m.r. spectrum as a single triplet due to coupling with two equivalent phosphorus atoms.

Photochemical reactions of *trans*-$[\mathrm{IrCl(CO)(PPh_3)_2}]$ or $[\mathrm{RhCl(PPh_3)_3}]$ with $\mathrm{(SCF_3)_2}$ and metathetical reaction of the rhodium complex with $\mathrm{AgSCF_3}$ do not yield isolable $\mathrm{SCF_3}$ complexes but reaction of the iridium complex with $\mathrm{AgSCF_3}$ gives *trans*-$[\mathrm{Ir(SCF_3)(CO)(PPh_3)_2}]$. ^{19}F n.m.r. spectra of this complex show a single triplet due to coupling with phosphorus.

The Trifluoromethylthio-ligand.—Four types of data from our study can yield information on the nature of the $\mathrm{SCF_3}$ ligand.

(1) *Platinum–hydrogen coupling constants and stretching frequencies*. For complex cations of the type, *trans*-$[\mathrm{PtHL(PEt_3)_2}]^+$, where L = neutral ligand, a linear correlation has been established between ^{1}J(PtH) and ν(PtH) as the *trans* ligand L is varied. Small values of J(PtH) and ν(PtH) are considered to reflect a high *trans*-influence for the ligand L and in particular a high affinity for the platinum 6*s* orbital.[14] For the neutral complexes *trans*-$[\mathrm{PtHX(PEt_3)_2}]$, where X = anionic ligand, the correlation of ^{1}J(PtH) with ν(PtH) is rather poor but a general trend certainly exists.[15-22] The data for neutral and cationic species do not appear to have been correlated by previous authors but we find that when both sets are plotted on one graph the spread of data is sufficient to make it unnecessary to postulate two separate lines (*i.e.* one for neutral and one for anionic ligands). Using the previously reported coupling constants, together with our value of 1152 Hz for ^{1}J(PtH) in *trans*-$[\mathrm{PtH(SCF_3)(PEt_3)_2}]$, the following scale of *trans*-influence can be established. $\mathrm{CH_2Si(CH_3)_3}$ [15] $>$ CN [16] $>$ $\mathrm{PEt_3}$ [14] $>$ $\mathrm{P(OMe)_3}$ [14] $>$ $\mathrm{P(OPh)_3}$ [14] $>$ $\mathrm{PPh_3}$ [14] $\sim$ CNAr [14] $\sim$ CNR [14] $>$ $\mathrm{C_2H_4}$ [17] $>$ CO [14] $>$ $\mathrm{NO_2}$ [16] $\sim$ NCO [16] $\sim$ NCS [16] $\sim$ Py [14] $>$ $\mathrm{N_3}$ [18] $\sim$ $\mathrm{SCF_3}$ $>$ SCN [16] $>$ Cl [16] $\sim$ $\mathrm{CF_3CO_2}$ [19] $>$ $\mathrm{NO_3}$ [16] $>$ Br [16] $>$ I.[16] Owing to the poor correlation mentioned above a slightly different scale arises if ν(PtH) values are used {ν(PtH) for *trans*-$[\mathrm{PtH(SCF_3)(PEt_3)_2}]$ = 2132 cm^{-1} (benzene)} but the main features are the same. The stretching frequencies are probably a less reliable probe than the coupling constants because of their greater sensitivity to solvent effects.

The above results indicate that the $\mathrm{SCF_3}$ ligand has a relatively weak *trans*-influence, similar to that of SCN and those of nitrogen donor ligands. There are fewer data for comparison with *trans*-$[\mathrm{PtH(SCF_3)(PPh_3)_2}]$ {^{1}J(PtH) = 1000 Hz, ν(PtH) = 2201 cm^{-1} (Nujol)} but those available suggest similar conclusions {*e.g. trans*-$[\mathrm{PtHCl(PPh_3)_2}]$ has ^{1}J(PtH) = 1210 Hz and ν(PtH) = 2236 cm^{-1} whereas $[\mathrm{PtH(PPh_3)_3}]^+$ has ^{1}J(PtH) = 774 Hz and ν(PtH) = 2145 cm^{-1}}.[23,24]

(2) *Carbonyl stretching frequencies*. ν(CO) in *trans*-$[\mathrm{Ir(SCF_3)(CO)(PPh_3)_2}]$ in chloroform solution occurs at 2007 cm^{-1}. Comparison of this result with those reported by Vaska and Peone [25] for other *trans*-$[\mathrm{IrX(CO)(PPh_3)_2}]$ complexes suggests that $\mathrm{SCF_3}$ is a highly effective competitor for metal to ligand π donation since *trans*-$[\mathrm{Ir(SCF_3)(CO)(PPh_3)_2}]$ has the highest ν(CO) of the series. However, examination of ν(CO) frequencies in other $\mathrm{SCF_3}$ complexes does not support this conclusion. For example, the frequencies of $[\mathrm{Mo(SCF_3)(CO)_3(\pi\text{-}C_5H_5)}]$ (2048, 1981, and 1966 cm^{-1}) [4] and $[\mathrm{MoCl(CO)_3(\pi\text{-}C_5H_5)}]$ (2055, 1980, and 1960 cm^{-1}) [26] are very similar, as are those for $[\mathrm{Re(SCF_3)(CO)_5}]$ (2145, 2042, and 1998 cm^{-1}) [5] and $[\mathrm{ReCl(CO)_5}]$ (2156, 2045, and 1982 cm^{-1}).[27] This suggests that other effects such as steric or solvent interactions may be important in the iridium series and we do not consider that the evidence requires the $\mathrm{SCF_3}$ ligand to have a high affinity for π back donation.

(3) *Metal–chlorine stretching frequencies*. ν(PtCl) frequencies have also been correlated with ^{1}J(PtH) values and with *trans*-influence series.[14] Only a few of our complexes have $\mathrm{SCF_3}$ *trans* to Cl but the results are in line with our conclusions in (1) above. Thus ν(PdCl) *trans* to $\mathrm{SCF_3}$ occurs at 317 and 318 cm^{-1} in Nujol mulls of *trans*-$[\mathrm{PdCl(SCF_3)(PEt_3)_2}]$ and *trans*-$[\mathrm{PdCl(SCF_3)(PPh_3)_2}]$ respectively; ν(PdCl) *trans* to Cl is at 360 cm^{-1} in *trans*-

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$[PdCl_2(PPh_3)_2]$ [28] and ν(MCl) *trans* to PPh_3 is at 290, 300, and 312 cm^{-1} in *cis*-$[PtCl(SCF_3)(PEt_3)_2]$, *cis*-$[PtCl(SCF_3)(PPh_3)_2]$ and $[PdCl(PPh_3)_3][BF_4]$ [29] respectively.

(4) *Platinum–fluorine coupling constants.* A scale of *trans*-influence can also be established using SCF_3 itself as a probe ligand. The variation of ^3J(PtF) values (Table) with the ligand *trans* to the SCF_3 group gives the following order of *trans*-influence: $H > PEt_3 \sim PPh_3 > SCF_3 > Cl$. This is similar to the series derived above from hydride data and also to the series obtained by previous authors using ^2J(PtF) in trifluoromethyl platinum complexes.[30] However, compared with previous probe ligands the SCF_3 probe is very sensitive. ^3J(PtF) changes by almost 100% when the *trans* group changes from PEt_3 to Cl whereas ^1J(PtF) in the trifluoromethyl complexes [30] changes by 40%. We attribute this sensitivity to the fact that SCF_3 is itself a rather weak *trans*-influence ligand and further work is in progress to use SCF_3 to establish *trans*-influences for a wide range of ligands.

EXPERIMENTAL

Data relating to the characterisation of the complexes are given in the Table. Microanalyses were by Schwartzkopf Microanalytical Laboratory, New York, or by Chemalytics Inc., Tempe, Arizona. Molecular weights were determined for the triphenylphosphine complexes by osmometry in dibromomethane solution at 50° using a Hitachi–Perkin-Elmer model 115 vapour phase osmometer and for the triethylphosphine complexes by mass spectrometry using a Hitachi–Perkin-Elmer RMU7E, double focussing spectrometer. N.m.r. spectra were recorded on Perkin-Elmer R 12A or Varian HA 60 spectrometers using tetramethylsilane and fluorotrichloromethane as external references and with signal to noise enhancement using a Northern Scientific NS 560 time averaging computer. The diamagnetism of *trans*-$[Ni(SCF_3)_2(PPh_3)_2]$ was established by the n.m.r. method of Evans [31] using tertiary butyl alcohol as the reference signal in chloroform solution. 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. In general these spectra showed the expected ligand absorptions including very strong, poorly resolved C–F stretching absorptions in the 1050—1150 cm^{-1} region. The positions of other important absorptions are given where appropriate in the Discussion section. Metal–sulphur stretching absorptions were not identified and are expected [32] to occur close to or below 250 cm^{-1}, the limit of our instrumentation.

Reactions were conducted in an atmosphere of nitrogen deoxygenated by passage through acidic chromous chloride solution and dried by 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.

Bis(trifluoromethyl) disulphide was obtained from Peninsula Chemicals, Florida, and was used as received. The complexes $[MCl_2L_2]$, M = Pd [28] or Pt [33,34] and L = PEt_3 or PPh_3; *trans*-$[PtHClL_2]$, L = PEt_3 [20] or PPh_3 [34]; $[M(PPh_3)_4]$, M = Pd [11] or Pt [35]; *trans*-$[IrCl(CO)(PPh_3)_2]$ [36] and $AgSCF_3$ [37] were prepared as previously described. $[Ni(PPh_3)_3]$ was prepared by a modification (see below) of the published procedure.[13]

Preparations using $(SCF_3)_2$.—These were carried out by irradiation of the reactants in either Pyrex or silica vessels using a low pressure mercury lamp. Reactions in Pyrex generally gave better yields but reactions in silica gave no evidence for the formation of elemental sulphur which had been reported previously.[38]

(a) *trans*-$[Pt(SCF_3)_2(PPh_3)_2]$. $Pt(PPh_3)_4$ (2·1 g, 1·7 mmol) and $(SCF_3)_2$ (2 g, 10 mmol) in pentane (100 ml) were irradiated with vigorous stirring at 25° for 30 min. The off-white precipitate was separated by filtration and dissolved in the minimum volume of acetone. Addition of water until a precipitate just began to form followed by cooling to −20° gave a 45 : 55 mixture of *cis*- and *trans*-$[Pt(SCF_3)_2(PPh_3)_2]$ (0·90 g, 0·98 mmol) as yellow-green platelets. A sample of the isomer mixture was dissolved in acetone with PPh_3 (*ca.* 10 mol %) and, after 24 h, diethyl ether was added to precipitate the *complex*. Recrystallisation from acetone–water as above gave almost colourless platelets.

(b) *trans*-$[Pd(SCF_3)_2(PPh_3)_2]$. A similar procedure using $Pd(PPh_3)_4$ (3·0 g, 2·6 mmol) and $(SCF_3)_2$ (2 g, 10 mmol) gave a 10 : 90 mixture of *cis*- and *trans*-$[Pd(SCF_3)_2(PPh_3)_2]$ 1·9 g, 2·3 mmol). Stirring in ethanol to remove ethanol soluble impurities followed by recrystallisation from acetone by addition of an equal volume of heptane, followed by cooling to −20°, gave the *complex* as yellow-orange crystals.

(c) *trans*-$[Ni(SCF_3)_2(PPh_3)_2]$. $NiCl_2$ (0·71 g, 5·5 mmol) and PPh_3 (5·5 g, 21 mmol) were heated under reflux in acetonitrile (75 ml) for 45 min. After cooling to 25° $NaBH_4$ (0·42 g, 11 mmol) was added to the stirred solution. After 10 min the resulting red-brown precipitate of $Ni(PPh_3)_3$ was separated by filtration and transferred under a nitrogen atmosphere to the irradiation apparatus. $(SCF_3)_2$ (2 g, 10 mmol) and heptane (100 ml) were added and the mixture irradiated for 45 min. The resulting purple-brown precipitate was dissolved in a minimum of acetone and brown impurities precipitated by addition of pentane. After filtration the product slowly crystallised from the filtrate. Final purification by chromatography on a Florisil column eluted with benzene gave the *complex* as purple crystals (0·25 g, 0·32 mmol).

Preparations using $AgSCF_3$.—(a) *cis*-$[PtCl(SCF_3)(PPh_3)_2]$. A solution of $AgSCF_3$ (0·23 g, 1·1 mmol) in acetone (10 ml) was added dropwise to a stirred solution of *cis*-$[PtCl_2(PPh_3)_2]$ (0·67 g, 0·85 mmol) in dichloromethane (15 ml) at 25°. After stirring for 30 min filtration gave impure AgCl (0·17 g, *ca.* 1·1 mmol). Evaporation of the filtrate to small bulk

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under reduced pressure followed by addition of diethyl ether gave white crystals (0·55 g). Chromatography of this product on a Florisil column gave *cis*-[Pt(SCF$_3$)$_2$(PPh$_3$)$_2$] (0·15 g, 0·16 mmol) on elution with benzene and the *complex* (0·33 g, 0·39 mmol) on elution with acetone. The complex was recrystallised from dichloromethane by addition of diethyl ether until precipitation just began, followed by standing at 25°. The use of 1·3 mol of AgSCF$_3$ per mol of *cis*-[PtCl$_2$(PPh$_3$)$_2$] in the above reaction was designed to minimise contamination of products by unreacted *cis*-[PtCl$_2$(PPh$_3$)$_2$].

(b) *cis*-[Pt(SCF$_3$)$_2$(PPh$_3$)$_2$]. A procedure similar to (a) above but using AgSCF$_3$ (0·26 g, 1·2 mmol) and *cis*-[PtCl$_2$(PPh$_3$)$_2$] (0·49 g, 0·62 mmol) gave *cis*-[PtCl(SCF$_3$)-(PPh$_3$)$_2$] (0·11 g, 0·13 mmol) and the *complex* (0·29 g, 0·32 mmol). The latter product was recrystallised from acetone by addition of water until precipitation just began, followed by cooling to −20°.

(c) *trans*-[PtH(SCF$_3$)(PPh$_3$)$_2$]. A procedure similar to (a) above but using AgSCF$_3$ (0·088 g, 0·42 mmol) and *trans*-[PtHCl(PPh$_3$)$_2$],CH$_3$OH (0·33 g, 0·42 mmol) gave AgCl and a yellowish filtrate. Evaporation to 10 ml under reduced pressure followed by dropwise addition of methanol gave the *complex* (0·14 g, 0·17 mmol) as colourless crystals. The product was recrystallised from acetone by addition of diethyl ether until a precipitate just began to form, followed by standing at 25°.

(d) *trans*-[PtH(SCF$_3$)(PEt$_3$)$_2$]. A procedure similar to (a) above but using AgSCF$_3$ (0·18 g, 0·88 mmol) and *trans*-[PtHCl(PEt$_3$)$_2$] (0·41 g, 0·88 mmol) gave AgCl and a yellow filtrate. Evaporation of the filtrate under reduced pressure gave the *complex* as a yellow oil. Attempts to crystallise this product resulted in some decomposition to metallic platinum but its ^{1}H and ^{19}F n.m.r. spectra clearly established the above formulation.

(e) *cis*-[PtCl(SCF$_3$)(PEt$_3$)$_2$]. A procedure similar to (a) above but using AgSCF$_3$ (0·19 g, 0·90 mmol) and *cis*-[PtCl$_2$(PEt$_3$)$_2$] (0·45 g, 0·89 mmol) gave AgCl and a pale yellow filtrate. Addition of diethyl ether gave first *cis*-[PtCl$_2$(PEt$_3$)$_2$] (0·12 g, 0·24 mmol) followed by the *complex* (0·22 g, 0·38 mmol). The product was purified by solution in acetone followed by addition of diethyl ether until precipitation just began. The small precipitate of *cis*-[PtCl$_2$(PEt$_3$)$_2$] was removed and the filtrate left for 1 week in light to decompose silver salts. Silver metal was filtered off and the solution left to evaporate and crystallise.

(f) *trans*-[PdCl(SCF$_3$)(PPh$_3$)$_2$]. A procedure similar to (a) above but using AgSCF$_3$ (0·14 g, 0·66 mmol) and *trans*-[PdCl$_2$(PPh$_3$)$_2$] (0·35 g, 0·49 mmol) in acetone suspension gave AgCl and an orange-yellow filtrate. Evaporation to 5 ml under reduced pressure followed by addition of diethyl ether (5 ml) and cooling to 0° gave the *complex* (0·22 g, 0·29 mmol). This product was not recrystallised because of a tendency to decompose in solution to give a red complex (probably [Pd$_2$Cl$_2$(SCF$_3$)$_2$(PPh$_3$)$_2$]). This reaction also prevented us from obtaining a molecular weight measurement.

(g) *trans*-[PdCl(SCF$_3$)(PEt$_3$)$_2$]. A procedure similar to (a) above but using AgSCF$_3$ (0·19 g, 0·89 mmol) and *trans*-[PdCl$_2$(PEt$_3$)$_2$] (0·37 g, 0·89 mmol) gave AgCl and a yellow filtrate. Evaporation to 3 ml under reduced pressure followed by addition of diethyl ether until a precipitate just began to form gave a small quantity of unidentified precipitate. The filtrate was left to evaporate and crystallise to give the *complex* (0·32 g, 0·67 mmol) which was recrystallised from pentane.

(h) *trans*-[Ir(SCF$_3$)(CO)(PPh$_3$)$_2$]. A procedure similar to (a) above but using AgSCF$_3$ (0·16 g, 0·77 mmol) and *trans*-[IrCl(CO)(PPh$_3$)$_2$] (0·60 g, 0·77 mmol) in degassed acetone at 40° for 15 h gave AgCl and a yellow-brown filtrate. Evaporation to small volume under reduced pressure followed by addition of ethanol gave the *complex* (0·30 g, 0·35 mmol) which was reprecipitated from chloroform by addition of ethanol. The solid product absorbs oxygen on exposure to air and a new band appears in the i.r. spectrum at 860 cm^{-1} as expected for an oxygen complex.[39] This probably accounts for the low analytical figures obtained for carbon and sulphur but ^{19}F n.m.r. and molecular weight data on the fresh product leave no doubt as to the structure. I.r. spectra also show the presence of traces of *trans*-[IrCl(CO)-(PPh$_3$)$_2$].

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