Reactions of Methyl Fluorosulphate and Triethyloxonium Tetrafluoroborate with Transition-metal Complexes†

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Reactions of $SFO_2(OMe)$ and $[Et_3O][BF_4]$ with a variety of transition-metal complexes have been examined and classified as ligand abstraction, oxidative additions, oxidation, ligand alkylation, or reactions in which an anionic fragment is abstracted from a ligand. Factors influencing the mode of reaction and the mechanisms of some of the reactions are discussed.

WHILST a variety of transition-metal complexes undergo useful reactions with carbanions, there has been little exploration of their reactions with strongly electrophilic alkylating agents such as methyl fluorosulphate and the trialkyloxonium tetrafluoroborates. We have studied the reactions of methyl fluorosulphate and triethyloxonium tetrafluoroborate with a variety of transition-metal complexes and have found that the several modes of reaction may be classified as follows: (*a*) ligand-abstraction reactions in which an anionic or neutral ligand is alkylated and removed from the co-ordination sphere of the metal; (*b*) oxidative-addition reactions in which at least the alkyl group of the reagent becomes bound to the metal; (*c*) oxidation reactions in which the oxidation state of the metal atom increases, but the alkyl group does not become a ligand; (*d*) reactions in which a ligand is alkylated but not abstracted from the complex; and (*e*) reactions in which a ligand is modified by abstraction of an anionic fragment. Our work, which has previously been reported in brief,[1] ‡ has provided examples of reactions in categories (*a*)—(*d*); examples of reactions in category (*e*) are those in which trialkyloxonium salts abstract hydride from cycloheptatriene complexes to form cycloheptatrienyl complexes.[2] In order to give a comprehensive outline of the scope of reactions of these alkylating agents in co-ordination chemistry, we have made reference to related results from the literature in the sections (*a*)—(*d*) below.

RESULTS AND DISCUSSION

Before presenting our results under headings appropriate to the reaction mode, it is useful to outline two aspects of the methods used for characterisation of the reactions and products. First, reactions of methyl fluorosulphate with diamagnetic complexes were readily monitored by ^1H n.m.r. spectroscopy, and it was very convenient to carry out exploratory experiments with the reagents dissolved in deuteriochloroform contained in n.m.r. tubes. The progress of the reactions could then be determined from the change in the intensity of the $SFO_2(OMe)$ resonance at τ 5.88 and the spectra also gave clear indications of the formation of such products as ethane, methyl halides, or methyl complexes. Where the complex contained such ligands as dimethylphenylphosphine the spectra also gave useful stereochemical information. Furthermore, in many instances two layers eventually formed in the n.m.r. sample. This indicated the formation of ionic products and facilitated subsequent isolation procedures.

The second aspect concerns the characterisation of the products of the reactions of the alkylating agents. These invariably contained fluorosulphate or tetrafluoroborate which *a priori* may be ionic or bound to the metal. Although conductivity measurements in a solvent such as nitromethane can often provide a method for distinguishing between such possibilities, it is likely to be ineffective in the present instance due to the high probability of rapid displacement of the ligand $[SFO_3]^-$ or $[BF_4]^-$ by solvent. Fortunately, however, the distinction between ionic and ligand $[SFO_3]^-$ or $[BF_4]^-$ can be made straightforwardly from i.r. spectra, and we have placed great weight on this method for our structural assignments. The ion $[BF_4]^-$ is of T_d symmetry and has two i.r.-active modes, $\nu_{asym}(BF_4)$ at *ca.* 1 050 cm^{-1} and $\delta_{asym}(BF_4)$ at *ca.* 525 cm^{-1}.[3] For pseudotetrahedral ions of C_{3v} symmetry such as unidentate $[BF_4]^-$ or ionic $[SFO_3]^-$ all six fundamental modes are i.r. active. Since none of the spectra of complexes containing tetrafluoroborate gave any indication of departure of $[BF_4]^-$ from T_d symmetry, ionic structures are assigned to these complexes, and we give details only of the bands expected from C_{3v} fluorosulphate. For sodium fluorosulphate the six bands have been assigned as follows: ν_{asym} (SO_3) (E) 1 287; ν_{sym} (SO_3) (A_1) 1 082; $\nu(SF)$ (A_1) 768; δ_{asym} (SO_3) (E) 592;

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† No reprints available.

‡ In ref. 1, the Sn–C cleavage was due to acid formed by hydrolysis of $SFO_2(OMe)$.

[1] C. Eaborn, J. L. Murphy, and A. Pidcock, *J. Organometallic Chem.*, 1973, **55**, C68.

[2] J. A. Connor and E. Rasburn, *J. Organometallic Chem.*, 1970, **24**, 441.

[3] N. Nakamoto, ' Infrared Spectra of Inorganic and Co-ordination Compounds,' Interscience, New York, 1970, p. 112.

δ_{sym} (SO_3) (A_1) 566; and ρ_r (SO_3) (E) 409 cm^{-1}.[4] Co-ordination of $[SFO_3]^-$ through an oxygen atom lowers the local symmetry to C_s and lifts the degeneracy of the E modes. The very strong absorption of ionic $[SFO_3]^-$ at *ca.* 1 287 cm^{-1} is then absent, being replaced by two bands, one at higher and the other at lower frequency.[5] Since these, and usually most of the other features of the $[SFO_3]^-$ spectrum, were clearly distinguishable in the spectra of our complexes in Nujol, the assignment of solid-state structures on this basis is likely to be very reliable. It was also possible to apply this method to the determination of structures in solution. Deuteriochloroform is sufficiently transparent in the region 1 400—1 200 cm^{-1} to permit observation of bands from $[SFO_3]^-$. The compound $[Pr_3MeP][SFO_3]$ and complexes having ionic $[SFO_3]^-$ in the solid state gave $CDCl_3$ solutions which had $\nu_{asym}(SO_3)$ as strong bands at *ca.* 1 285 cm^{-1}. This shows that any ion-pair formation in solution does not cause perceptible splitting of this E mode, so this band can be taken to be characteristic of ionic $[SFO_3]^-$ for the solid state and for solutions. In some instances, detailed below, complexes having bands characteristic of co-ordinated SFO_3 in the solid state had similar bands for $CDCl_3$ solutions in the 1 200—1 400 cm^{-1} region, indicating that at least for some situations this solvent does not solvolyse the metal–fluorosulphate linkage.

(a) *Ligand Abstraction.*—Perhaps the most general and useful of all the reactions of $SFO_2(OMe)$ or $[Et_3O][BF_4]$ is that in which a halide ligand of a complex is abstracted as alkyl halide. These reactions are easily detected and monitored by ^1H n.m.r. spectroscopy with $SFO_2(OMe)$ as reagent, and the spectra are usually sufficiently well resolved for this purpose even when the complexes are paramagnetic. The alkyl halide products and residual alkylating agent are readily removed after the reaction, and isolation of the product complexes is usually straightforward. We found that ionic complexes were particularly easily isolated as the fluoroborate salts. As reagents for halide abstraction, the alkylating agents may be compared with silver salts. The alkylating agents can be used in non-hydroxylic solvents such as chloroform or benzene, and they do not require the sometimes inconvenient filtration step that is usually necessary following the use of silver salts. Both the alkylating agents and silver salts may be used in the presence of neutral donors L to effect replacement of halide ligand by L, but the use of alkylating agents is somewhat limited by their tendency to alkylate rapidly donors such as amines or phosphines with the formation of quaternary salts.

The complexes $[ML_2X_2]$ (M = Pd or Pt; X = Cl, Br, or I; L = amine, phosphine, arsine, or isonitrile) reacted in dichloromethane under mild conditions with the alkylating agents to produce salts of the halogen-bridged cations $[M_2L_4X_2]^{2+}$ [equations (1) and (2)]. Difficulty was encountered with the isolation of some of the fluorosulphate salts, but the tetrafluoroborates were very easily crystallised (Table 1). The halide-abstraction reaction with the alkylating agent $[Me_3O][BF_4]$ has been reported previously for a number of

$$[ML_2X_2] + 2SFO_2(OMe) \longrightarrow [M_2L_4X_2][SFO_3]_2 + 2MeX \quad (1)$$

$$[ML_2X_2] + 2[Et_3O][BF_4] \longrightarrow [M_2L_4X_2][BF_4]_2 + 2EtX + 2Et_2O \quad (2)$$

platinum complexes (L = PEt_3, $PMePh_2$, PPh_3, or p-CNC_6H_4Me, X = Cl; L = CNMe, X = Cl, Br, or I),[6] and boron halides [7,8] or silver(I) tetrafluoroborate [9] have been used in place of the alkylating agents. The alkylating agents appear to react with a wider range of complexes $[ML_2X_2]$ than do the boron halides or $Ag[BF_4]$, and the yields obtained are generally very high (Table 1). Thus, $[Et_3O][BF_4]$ reacts with *cis*- or *trans*-$[PtCl_2(PBu_3)_2]$, but boron trifluoride does not react with the *trans* isomer.[7] The reactions of $SFO_2(OMe)$ with *cis*-$[PdCl_2L_2]$ (L = PMe_2Ph or PPh_3) were shown by ^1H n.m.r. spectroscopy to be complete within 30 min at 25 °C, whereas, in reactions with BF_3, *cis*-$[PdCl_2(PEt_3)_2]$ required 20 h at 75 °C and *cis*-$[PdCl_2(PPh_3)_2]$ required 24 h at 120 °C.[8] Furthermore, $[Et_3O][BF_4]$ abstracts iodide from $[PdI_2(PMe_2Ph)_2]$ (Table 1), but BF_3 reacts with $[PtI_2(PEt_3)_2]$ to give $[Pt_2I_4(PEt_3)_2]$ and $Et_3P{\cdot}BF_3$,[8] while the reaction between $Ag[BF_4]$ and $[PdI_2(PEt_3)_2]$ gives no characterisable products.[9] In experiments monitored by ^1H n.m.r. spectroscopy the rate of halide abstraction by $SFO_2(OMe)$ decreased in the sequence $Cl > Br > I$.

The i.r. spectra of the cations have been studied previously and it has been suggested that the relatively high values of $\nu(M-X)$ (Table 1) for bridging chlorides are due to the positive charges on the complex.[7] The fluorosulphate salts have clearly distinguishable bands at 1 285vs, br, 1 055ms, and 585s (sharp) cm^{-1} in mull spectra, characteristic of ionic $[SFO_3]^-$, and the band due to $\nu_{asym}(SO_3)$ is almost unchanged at 1 288 cm^{-1} in deuteriochloroform solutions of $[Pt_2Cl_2(PPh_3)_4][SFO_3]_2$.

These complexes readily undergo the usual bridge-cleavage reactions with a variety of anionic and neutral donors and are therefore very useful intermediates in platinum(II) chemistry.[10] The complex $[Pt_2Cl_2(PEt_3)_4][BF_4]_2$ reacted at room temperature with MeNC in methanol to give *trans*-$[Pt(CNMe)Cl(PEt_3)_2][BF_4]$, with MeCN to give *cis*-$[Pt(NCMe)Cl(PEt_3)_2][BF_4]$, and with concentrated hydrochloric acid to give *cis*-$[PtCl_2(PEt_3)_2]$,

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[8] H. C. Clark, K. R. Dixon, and W. J. Jacobs, *J. Amer. Chem. Soc.*, 1968, **90**, 2259; H. C. Clark and K. R. Dixon, *ibid.*, 1969, **91**, 596.

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TABLE 1

Synthesis [a] and characterisation of complexes $[ML_4X_2][A]_2$

					Analysis (%)						Conditions		
					Found		Calc.		Λ				
L	M	X	A	M.p. (θ_c/°C)	C	H	C	H	S cm^2 mol^{-1}	ν(M–X) cm^{-1}	Reaction	Crystallisation	Yield (%)
PEt_3	Pt	Cl	BF_4	230—235	25.9	5.5	26.1	5.5	175	305, 280	*b*	*c*	72
PMe_2Ph	Pt	Cl	BF_4	240—250	32.0	3.9	31.8	3.7	170	310, 272	*b*	*c*	85
PPh_3	Pt	Cl	BF_4	240—250	50.3	3.9	49.7	3.6	142	312br	*b*	*c*	75
PPh_3	Pt	Cl	BF_4	240—250	50.5	3.9	50.1	3.5	145	310br	*b*	*c*	73
PBu_3	Pt	Cl	SFO_3	110—115 (decomp.)	40.6	7.6	40.9	7.5	166	306br	*b*	*c*	62
$AsEt_3$	Pt	Cl	BF_4	222—224	22.5	4.7	22.8	4.8	124		*b*	*c*	55
PMe_2Ph	Pd	Cl	BF_4	175—180	39.0	4.7	38.1	4.3	145	275	*d*	*c*	93
PPh_3	Pd	Cl	BF_4	245—250 (decomp.)	57.1	4.3	57.4	4.0	130	295br	*d*	*e*	82
py [f]	Pd	Cl	BF_4	210—220 (decomp.)	31.4	2.9	31.1	2.6	110		*b*	*e*	86
PEt_3	Pt	Br	SFO_3	170—180 (decomp.)	23.7	5.2	23.6	4.9	168	<250	*b*	*c*	72
PEt_3	Pt	Br	BF_4	165—175	24.2	5.3	24.1	5.1	173	<250	*b*	*c*	63
PMe_2Ph	Pt	Br	BF_4	165—175	30.3	3.8	30.1	3.5	159	<250	*b*	*c*	81
PMe_2Ph [f]	Pt	I	BF_4	114—117	28.1	3.4	28.0	3.2	132	<250	*d*	*c*	67

[a] Starting materials *cis*-$[ML_2X_2]$ except as stated otherwise. [b] The solution was stirred for 15 h at room temperature. [c] Methanol–diethyl ether–hexane. [d] The solution was heated under reflux for 3h. [e] Dichloromethane–hexane. [f] Starting material, *trans*-$[PtL_2X_2]$.

all in excellent yields. Since the chlorine-bridged cation can be made from *trans*-$[PtCl_2(PEt_3)_2]$ by reaction with $[Et_3O][BF_4]$, reaction of the *trans* complex with the oxonium salt followed by treatment with hydrochloric acid provides a method of conversion into the *cis* isomer. When instead of treating $[Pt_2Cl_2(PEt_3)_4][BF_4]_2$ with MeNC, an excess of MeNC was present during the reaction of *cis*-$[PtCl_2(PEt_3)_2]$ with $[Et_3O][BF_4]$ (in dichloromethane), the chloride abstraction proceeded to completion and *trans*-$[Pt(CNMe)_2(PEt_3)_2][BF_4]_2$ was isolated in good yield. This method can be expected to have quite wide application, since there are many donors which form stable complexes with heavier transition metals, but which react only slowly or not at all with the alkylating agents.

In work to be described fully in subsequent papers it has been shown that chloride abstraction from complexes $[MCl_2(diolefin)]$ (M = Pd or Pt) occurs with $[Et_3O][BF_4]$ to produce salts of the previously unknown and highly reactive cations $[M_2Cl_2(diolefin)_2]^{2+}$,[11] and that complexes $[ML_2X_2]$ (M = Pd or Pt; X = N_3, NCS, NO_2, or NO_3; L = phosphine or arsine) undergo abstraction of X with $[Et_3O][BF_4]$ or $SFO_2(OMe)$ to form binuclear cationic complexes with bridging X (X = N_3 or NCS) or hydroxyl (X = NO_2 or NO_3).[12] Abstraction of azide from palladium complexes by $[Me_3O][BF_4]$ has also been demonstrated by Beck *et al.*[13]

A limitation of this method for the synthesis of cations $[ML_4X_2]^{2+}$ was discovered in the reaction of $SFO_2(OMe)$ with *cis*-$[PtCl_2(SEt_2)_2]$. Here the product isolated was $[Pt_2Cl_4(SEt_2)_2]$ and the cation $[MeEt_2S]^+$ was identified in the reaction mixture from the ^1H n.m.r. spectrum. These products may derive either from alkylation of dissociated SEt_2 as in equations (3) and (4) or from direct alkylation of the available lone pair of the SEt_2 ligand.

^1H N.m.r. spectra demonstrated the formation of MeCl and the retention of *trans* configurations in the

$$2[PtCl_2(SEt_2)_2] \rightleftharpoons [Pt_2Cl_4(SEt_2)_2] + 2SEt_2 \quad (3)$$

$$SEt_2 + SFO_2(OMe) \longrightarrow [MeEt_2S][SFO_3] \quad (4)$$

reactions of $SFO_2(OMe)$ with the platinum(II) complexes *trans*-$[PtClH(PMe_2Ph)_2]$, *trans*-$[PtCl(PMe_2Ph)_2(SiPh_3)]$, *trans*-$[PtMe(Cl)(PMe_2Ph)_2]$, and *trans*-$[PtPh(Cl)(PEt_3)_2]$. The work with the hydride complexes has been described previously.[14] These reactions are presumed to form complexes with solvent or $[SFO_3]^-$ in place of abstracted chloride. An orange solid was isolated from the reaction of $SFO_2(OMe)$ with *trans*-$[PtCl(PMe_2Ph)_2(SiPh_3)]$ in presence of an excess of MeNC. This material was too unstable for analysis and it lost MeNC on attempted recrystallisation, but its formulation as *trans*-$[Pt(CNMe)(PMe_2Ph)_2(SiPh_3)][SFO_3]$ is supported by the i.r. spectrum which demonstrates the presence of co-ordinated MeNC [ν(NC) at 2 280 cm^{-1}] and ionic $[SFO_3]^-$ [$\nu_{asym}(SO_3)$ at 1 285 cm^{-1}].

The lability of the chloride ligand *trans* to phosphorus in *mer*-$[RhCl_3(PMe_2Ph)_3]$ has been established in substitution reactions with anionic reagents [15] and it appears that this ligand is abstracted in reactions with alkylating agents. The product from the reaction with $SFO_2(OMe)$ in dichloromethane gave a satisfactory analysis for $[RhCl_2(PMe_2Ph)_3(SFO_3)]$. The formulation as a molecular complex in the solid state is based on the observation of bands at 1 226 and 1 343 cm^{-1} in the i.r. spectrum (Nujol), which are attributed to co-ordinated $[SFO_3]^-$. These bands were also present (at 1 230 and 1 330

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[12] J. L. Murphy and A. Pidcock, unpublished work.

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[14] C. Eaborn, N. Farrell, and A. Pidcock, *J.C.S. Chem. Comm.*, 1973, 766.

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TABLE 2

^{31}P N.m.r. parameters of rhodium(III) complexes in dichloromethane at −60 °C [a]

Complex	δ [b] p.p.m.	Multiplicity [c]	^1J(Rh–P) Hz	^2J(PRh–P) Hz
mer-$[RhCl_3(PMe_2Ph)_3]$	-4.2_0	d of t	112	24
	$+7.0_4$	d of d	84	
$[RhCl_2(PMe_2Ph)_3(SFO_3)]$	−15.3	d of t	118	27
	+5.3	d of d	83	
$[RhCl_2(PMe_2Ph)_3(SFO_3)]$ + $MeNO_2$	−15.4	d of t	117	27
	+5.4	d of d	84	
	−3.8 [d]	d of t	108	28
	+7.4 [d]	d of d	81	
$[Rh_2Cl_4(PMe_2Ph)_6][BF_4]_2$	−17.7	d of t	119	27
	+5.1	d of d	83	
$[Rh_2Cl_4(PMe_2Ph)_6][BF_4]_2$ + $MeNO_2$	−17.0	d of t	119	27
	+5.1	d of d	83	
	−3.8 [d]	d of t	107	28
	+7.3 [d]	d of d	79	

[a] Obtained from ^{31}P–{^{1}H} spectra (40.5 MHz). [b] Positive shifts are to high field of the external reference $PO(OMe)_3$ in CD_2Cl_2. [c] d of d = Doublet of doublets ($I = 2$), d of t = doublet of triplets ($I = 1$). [d] Assigned to $[RhCl_2(O_2NMe)(PMe_2Ph)_3]^+$.

cm^{-1}) in spectra of deuteriochloroform solutions and there was no indication of the strong absorption of ionic $[SFO_3]^-$ at *ca.* 1 285 cm^{-1} in either phase. In nitromethane the conductivity corresponded to a 1 : 1 electrolyte and the bands in the i.r. spectrum corresponding to co-ordinated $[SFO_3]^-$ were replaced by a strong absorption at 1 285 cm^{-1}.

The ^{31}P–{^{1}H} n.m.r. spectrum of the freshly prepared complex in dichloromethane at −60 °C comprised a doublet of triplets (intensity 1) and a doublet of doublets (intensity 2) at higher field, together with an apparently similar set of lines of much lower intensity which were poorly resolved from the principal resonances (Table 2). The principal set of resonances can be attributed to $[RhCl_2(PMe_2Ph)_3(SFO_3)]$ with a meridional configuration of phosphines. In view of the sensitivity of couplings ^1J(M–P) to the nature of the *trans* ligand,[16] the difference in the coupling constants for the unique phosphine ligands in *mer*-$[RhCl_3(PMe_2Ph)_3]$ and in *mer*-$[RhCl_2(PMe_2Ph)_3(SFO_3)]$ (Table 2) implies that the SFO_3 ligand is *trans* to the unique phosphine. Addition of nitromethane to dichloromethane solutions of $[RhCl_2(PMe_2Ph)_3(SFO_3)]$ gave ^{31}P–{^{1}H} spectra at −60 °C which indicated the presence of unchanged complex together with a new meridional complex with substantially different parameters for the unique phosphine. The SFO_3 ligand is thus shown by i.r. and ^{31}P–{^{1}H} spectra to be readily solvolysed and replaced by nitromethane. We are unable to assign a structure to the complex responsible for the minor set of resonances in the dichloromethane solution of the SFO_3 complex. With aged samples of the complex or less rigorous purification of dichloromethane and protection from atmospheric moisture, we obtained complicated spectra corresponding to the presence of up to four meridional tris(phosphine) complexes. The lability of the fluorosulphate complex was also indicated by the broadening of the ^{31}P–{^{1}H} resonances as the temperature was raised above −60 °C; at room temperature the spectrum comprised a single broad resonance.

Reaction of $[Et_3O][BF_4]$ with *mer*-$[RhCl_3(PMe_2Ph)_3]$ in dichloromethane under reflux gave a red solution from which deep red needles were obtained after addition of hexane. I.r. spectra showed the presence of ionic $[BF_4]^-$ and the analytical results were in good agreement with the formulation as a chlorine-bridged binuclear complex, $[Rh_2Cl_4(PMe_2Ph)_6][BF_4]_2$. At *ca.* −60 °C in dichloromethane this gave a ^{31}P–{^{1}H} spectrum characteristic of a meridional arrangement of phosphines about rhodium. The parameters of this spectrum (Table 2) are rather similar to those for *mer*-$[RhCl_2(PMe_2Ph)_3(SFO_3)]$, but, consistent with the structures assigned, the shifts of unique phosphorus nuclei differ significantly. The ^{31}P–{^{1}H} spectrum of the fluoroborate complex in a mixture of dichloromethane and nitromethane at −60 °C indicated the presence of two complexes with meridional phosphine arrangements. The spectral parameters for one complex correspond very closely with those of the dichloromethane solution and for the other complex with the product of solvolysis of the SFO_3 complex in nitromethane. This assignment is also supported by the similarity of the rate of broadening of lines of corresponding complexes as the temperature is raised. The simplest explanation for these results is given in the Scheme. The bridged complex is written with a *trans* arrangement of the phosphines in the plane of the bridge. This is the usual arrangement for bridged platinum(II) compounds [17] and cleavage of the bridge by nitromethane would then be expected to give two moles of a single complex, as we observed. However, an arrangement with *cis*-phosphines is not excluded by the spectra, and the fact that the n.m.r. lines broaden at higher temperatures implies that there may be sufficient lability at −60 °C for the single nitromethane complex to be the result of thermodynamic control rather than the direct outcome of a reaction of a *trans*-bridged complex.

The complex $[RhCl_2(PMe_2Ph)_3(SFO_3)]$ reacted with PMe_2Ph to form $[RhCl_2(PMe_2Ph)_4][SFO_3]$, which had i.r. bands characteristic of ionic $[SFO_3]^-$ both for the

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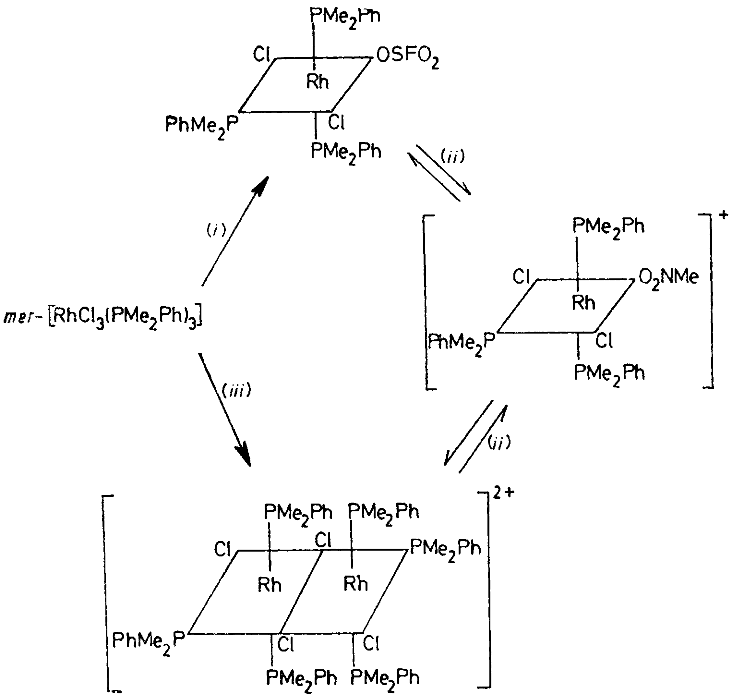
[17] U. Belluco, 'Organometallic and Coordination Chemistry of Platinum,' Academic Press, London, 1974, p. 71.



SCHEME (*i*), $SFO_2(OMe)$; (*ii*), $MeNO_2$; (*iii*), $[Et_3O][BF_4]$.

solid state and for deuteriochloroform solutions. The $^{31}P-\{^1H\}$ n.m.r. spectrum of a dichloromethane solution at *ca.* −60 °C was complicated and lay to high field of the resonances for the other rhodium complexes. Spectra of solutions of $[RhCl_2(PMe_2Ph)_3(SFO_3)]$ or the bridged cation to which small amounts of PMe_2Ph had been added indicated that $[RhCl_2(PMe_2Ph)_4]^{2+}$ was formed in these solutions, but was not involved in the processes responsible for the line broadening observed at temperatures above −60 °C.

Chloride abstraction by $SFO_2(OMe)$ was demonstrated by the appearance of sharp lines at τ 6.95 (MeCl) in the ^1H n.m.r. spectra of deuteriochloroform solutions of $[MoCl(\eta\text{-}C_5H_5)(CO)_3]$, *mer*-$[ReCl_3(PEt_2Ph)_3]$, $[RuCl_2(PPh_3)_3]$, *mer*-$[OsCl_3(PMe_2Ph)_3]$, $[Rh(C_8H_{12})Cl(PPh_3)_2]$, *fac*-$[RhCl_3(PMe_2Ph)_3]$, *mer*-$[IrCl_3(PBu_2Ph)_3]$, and $[AuCl(PPh_3)_3]$. With *mer*-$[OsCl_3(PMe_2Ph)_2]$ a red oil was isolated which had an i.r. spectrum similar to that of *mer*-$[RhCl_2(PMe_2Ph)_3(SFO_3)]$ and on reaction with PMe_2Ph it was converted into a purple oil which contained ionic $[SFO_3]^-$ and which is tentatively formulated as $[OsCl_2(PMe_2Ph)_4][SFO_3]$.

Some experiments with complexes of first-row transition metals were made. From $[NiCl_2(PPh_3)_2]$ and $SFO_2(OMe)$ in dichloromethane we isolated only $NiCl_2$ and $[Ph_3MeP][SFO_3]$, and phosphonium salts were also obtained from $[NiCl_2(PEt_3)_2]$ with $[Et_3O][BF_4]$ and from $[CoCl_2(PPh_3)_2]$ with $SFO_2(OMe)$. In an attempt to favour chloride over phosphine abstraction for Ni^{II}, we studied the reactions of $[NiCl_2(dppe)]$ [dppe = 1,2-bis(diphenylphosphino)ethane] with both alkylating agents. However, although chloride abstraction did occur, chlorine-bridged complexes were not obtained; the products were salts of $[Ni(dppe)_2]^{2+}$. It is, therefore, clear that the reagents are capable of abstracting chloride from phosphine complexes of Ni^{II} (and therefore probably Co^{II} also), but in complexes of unidentate phosphines there is sufficient phosphine dissociation for the alkylating agents to react preferentially with free phosphine rather than co-ordinated chloride. The precipitation of the metal dichlorides then prevents subsequent chloride abstraction.

Although the phosphines in mercury(II) complexes such as $[Hg(PMe_2Ph)_2X_2]$ (X = Cl, Br, or I) are known from ^1H n.m.r. spectra at various temperatures to be undergoing exchange processes involving dissociation of phosphine,[18] with an excess of $SFO_2(OMe)$ or $[Et_3O][BF_4]$ halide abstraction occurred with formation of salts of $[HgL_2]^{2+}$ (L = phosphine). With complexes $[Hg_2L_2X_4]$, salts of $[HgLX]^+$ (X = Cl or Br; L = phosphine) were formed. These complexes will be the subject of a subsequent paper, but it may be noted that phosphine dissociation from Hg^{II} is probably much less extensive than from Co^{II} or Ni^{II}, so halide abstraction is favoured over phosphine alkylation for Hg^{II} in comparison with Co^{II} or Ni^{II}.

(b) *Oxidative Addition.*—Vaska's complex, *trans*-$[Ir(CO)Cl(PPh_3)_2]$, underwent an oxidative-addition reaction with $SFO_2(OMe)$ in benzene to give a white precipitate of $[IrMe(Cl)(PPh_3)_2(SFO_3)]$ on addition of hexane. This reaction has also been reported by Peterson *et al.*[19] and by Stope and Shriver,[20,21] and we

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[18] G. G. Mather and A. Pidcock, unpublished work.

[19] J. L. Peterson, T. E. Nappier, and D. W. Meek, *J. Amer. Chem. Soc.*, 1973, **95**, 8195.

[20] D. Stope and D. F. Shriver, *J. Amer. Chem. Soc.*, 1973, **95**, 8197.

[21] D. Stope and D. F. Shriver, *Inorg. Chem.*, 1974, **13**, 2652.

have shown that the same product can be obtained from the adducts of Vaska's complex with O_2, SO_2, or C_2F_4. The formulation of the product as a molecular complex,[1] which is now accepted by Stope and Shriver,[21] is supported by the observation of bands due to co-ordinated fluorosulphate at 1 350 (shoulder at 1 340) and 1 230 cm^{-1} and the absence of absorption at *ca.* 1 287 cm^{-1} in the i.r. spectrum of a sample in Nujol. Both the solid complex and mull were colourless, but the complex formed yellow solutions in dichloromethane or nitromethane for which i.r. absorption at *ca.* 1 287 cm^{-1} was observed. The conductivity of the nitromethane solution was characteristic of a 1 : 1 electrolyte, so it is evident that the co-ordinated $[SFO_3]^-$ is easily displaced by polar solvents. The complex was insufficiently soluble in deuteriobenzene for an i.r. spectrum to be obtained. The SFO_3 ligand was also displaced by *p*-MeC_6H_4NC (in benzene) or chloride ($[Et_4N]Cl$ in $CHCl_3$) to form [IrMe(CNC_6H_4Me-*p*)(CO)Cl$(PPh_3)_2$][SFO_3] or [IrMe(CO)$Cl_2(PPh_3)_2$]. The triplet character of the Ir–Me resonance of the isocyanide complex shows that the phosphines are *trans* and the ^{1}H n.m.r. parameters of the Ir–Me group and ν(CO) for the dichloride are similar to those reported for [IrMe(CO)$Cl_2(PMePh_2)_2$].[22] In these and similar complexes the ligands of Vaska's complex retain their configuration and methyl and the sixth ligand are *trans*, above and below the original plane.

The ^{1}H n.m.r. spectrum of the Pt–Me groups of *cis*-[$PtMe_2(PMe_2Ph)_2$] [23] in deuteriobenzene changed on addition of SFO_2(OMe) and indicated the formation of [$PtMe_3(PMe_2Ph)_2(SFO_3)$]. Two Pt–CH_3 resonances of relative intensity 1 : 2 were observed, each of triplet character due to coupling with two equivalent phosphorus nuclei. The P–CH_3 spectrum exhibited 'virtual coupling.' The phosphines are, therefore, *trans* and the methyl ligands have meridional configuration with the unique methyl group *trans* to SFO_3 (or possibly a solvent molecule). When the reaction of SFO_2(OMe) with *cis*-[$PtMe_2(PMe_2Ph)_2$] was carried out in deuteriochloroform, ^{1}H n.m.r. spectra indicated the formation of a *trans*-bis(phosphine) complex that contained only one Pt–Me group, and in addition a sharp line appeared at τ 9.06 which indicated the formation of ethane. Treatment of reaction mixtures on a preparative scale with $[Et_4N]Cl$ led to the isolation of *trans*-[PtMe(Cl)$(PMe_2Ph)_2$]. It is probable that the platinum(IV) complex [$PtMe_3(PMe_2Ph)_2(SFO_3)$] is formed in both solvents, but that in deuteriochloroform this complex rapidly undergoes reductive elimination of ethane to form *trans*-[$PtMe(PMe_2Ph)_2(SFO_3)$].

Reactions of platinum(0) complexes with SFO_2(OMe) were also studied. Addition of SFO_2(OMe) to a dichloromethane solution of [$Pt(PPh_3)_4$] led to the isolation of [Ph_3MeP][SFO_3] together with a yellow oil which could not be crystallised. Formation of the phosphonium salt is not surprising in view of the tendency of [$Pt(PPh_3)_4$] to dissociate in solution.[24] Addition of SFO_2(OMe) to a benzene solution of [$Pt(PPh_3)_3$] resulted in the precipitation of a white solid formulated as [$PtMe(PPh_3)_3$][SFO_3] on the basis of microanalysis results and i.r. absorptions characteristic of ionic $[SFO_3]^-$. The formulation was supported by the ^{1}H n.m.r. spectrum, which was as reported by Peterson *et al.*,[19] and by the ^{31}P–{^{1}H} spectrum which showed the presence of mutually *trans* phosphines [^1J(Pt–P) 2 925 Hz] and a phosphine *trans* to methyl [^1J(Pt–P) 1 919 Hz]. The unique phosphine is evidently labilised by the *trans* effect of the methyl group, since treatment of the complex in chloroform with $[Et_4N]I$ gave *trans*-[PtMe(I)$(PPh_3)_2$].

(c) *Oxidation.*—The alkylating agents are capable of acting as oxidising agents. In the examples we encountered, this mode of action was confined to substrates in which the stable oxidation states differ by one unit. With *trans*-[$MoCl_2(dppe)_2$] in dichloromethane, SFO_2(OMe) and [Et_3O][BF_4] gave *trans*-[$MoCl_2(dppe)_2$]X (X = SFO_3 or BF_4) for which ν(MoCl) was at higher frequency than in the starting material (345 as compared with 319 cm^{-1}). Similar reactions occurred with silver salts AgX (X = ClO_4 or PF_6), and the resulting salts had magnetic moments, μ_{eff} 3.35 (X = ClO_4) and 3.47 B.M. (X = PF_6),* close to the spin-only values for three unpaired electrons (3.87 B.M.), and are normal for molybdenum(III) complexes. The complex [$Re(CO)_3Cl(PPh_3)_2$] was oxidised to the corresponding monopositive cation by [Et_3O][BF_4].

(d) *Ligand Alkylation.*—It is clear from the organic chemistry of SFO_2(OMe) and [Et_3O][BF_4] that ligands having basic groups additional to those co-ordinated to the metal are liable to be alkylated by these reagents. Use has previously been made of this in carbene synthesis [25] where moieties such as Cr–CMe(O^-) have been methylated by use of [Me_3O][BF_4] and more recently by Casey *et al.*[26] and ourselves [1] by use of SFO_2(OMe). In work to be published in detail elsewhere,[12] we have

$$trans\text{-}[Pt(CN)_2(PMe_2Ph)_2] + 2SFO_2(OMe) \longrightarrow trans\text{-}[Pt(CNMe)_2(PMe_2Ph)_2][SFO_3]_2 \quad (5)$$

$$K_3[Cr(CN)_5(NO)] + 5SFO_2(OMe) \longrightarrow [Cr(CNMe)_5(NO)][SFO_3]_2 + 3K[SFO_3] \quad (6)$$

shown that SFO_2(OMe) and [Et_3O][BF_4] alkylate co-ordinated cyanide in, for example, dicyanobis(phosphine) complexes of Pd^{II} and Pt^{II} [equation (5)] and also that SFO_2(OMe) reacts directly with some solid potassium salts of polycyano-complexes usually to give the fully methylated products [*e.g.*, equation (6)]. Whilst our

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* 1 B.M. ≈ 9.27 × 10^{-24} A m^2.

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work was in progress Treichel *et al.*[27] reported methylation of co-ordinated cyanide in palladium(II) and platinum(II) complexes by $[Me_3O][BF_4]$; this reagent requires a somewhat less convenient procedure than $SFO_2(OMe)$.

The reaction of $SFO_2(OMe)$ with *trans*-$[PtCl\{PO(OPh)_2\}(PBu_3)_2]$ is of interest because it may lead to methylation of the $P-O^-$ group or, if chloride abstraction occurs, a dimeric complex with phosphonato-ligands as bridging groups could be formed. The product of the reaction was obtained only as an oily solid and the product from the analogous Et_3P complex was similar. However, ^1H n.m.r. spectra showed that POMe groups were produced [τ 6.1 (doublet), $^3J(POCH)$ 12 Hz; three protons per molecule] and there was no indication of chloride abstraction. The course of the reaction is therefore as in equation (7).

$$trans\text{-}[PtCl\{PO(OPh)_2\}(PBu_3)_2] + SFO_2(OMe) \longrightarrow trans\text{-}[PtCl\{P(OMe)(OPh)_2\}(PBu_3)_2][SFO_3] \quad (7)$$

Mechanisms and General Observations.—The convenience of these reagents in transition-metal chemistry deserves emphasis; in halide-abstraction reactions they are much more trouble-free than silver salts, and when they are used as oxidising agents the excess of reagent is more conveniently removed than is the case for many alternatives. Although their mode of action can vary, the present study should provide reasonably good guidance in a new situation, but in general the mode of action can be determined very rapidly by monitoring a reaction with $SFO_2(OMe)$ (or $[Me_3O][BF_4]$) by ^1H n.m.r. spectroscopy. The i.r. spectra of the $[SFO_3]^-$ and $[BF_4]^-$ species are also useful in this respect.

Several mechanisms for the halide abstraction may be envisaged, and it is quite possible that the mechanism is not the same for all systems. Treichel *et al.*[6] suggested that the halide abstraction from $[PtL_2X_2]$ by $[Me_3O][BF_4]$ may proceed *via* initial exchange of halide and $[BF_4]^-$ followed by decomposition of $[Me_3O]Cl$, or by attachment of Me^+ to the metal followed by elimination of MeCl. The first of these mechanisms appears to be highly improbable. The $[BF_4]^-$ ion is a very weak nucleophile and is not expected to displace chloride from Pt^{II}; nor is the solvent used (dichloromethane) expected to cause appreciable solvolysis of the Pt–Cl bonds. Thus, acetone solutions of *cis*-$[PtCl_2L_2]$ and $Na[ClO_4]$ precipitate NaCl only on addition of nucleophiles (such as amines) capable of displacing chloride,[28] and $[ClO_4]^-$, which is probably a better nucleophile than $[BF_4]^-$, is ineffective when used alone. The very weak nucleophilic character of the oxygen atoms of $SFO_2(OMe)$ must also rule out displacement of chloride by this reagent.

That the abstraction of halide may be the consequence of initial oxidative addition by the alkylating agent followed by reductive elimination of alkyl halide is certainly possible for platinum(II) complexes and would be somewhat analogous to the observed oxidation of *cis*-$[PtMe_2(PMe_2Ph)_2]$ to *trans*-$[PtMe_3(PMe_2Ph)_2(SFO_3)]$ and the reductive elimination of ethane from the platinum(IV) complex. However, chloride abstraction was also observed for *mer*-$[RhCl_3(PMe_2Ph)_3]$ and a number of other co-ordinatively saturated complexes of Re^{III}, Ru^{II}, Os^{III}, and Ir^{III} which are incapable of undergoing oxidative addition and which are probably negligibly solvolysed in deuteriochloroform. Since free chloride ion reacts rapidly with the alkylating agents by an S_N2 mechanism, it is probable that in some circumstances co-ordinated chloride may be sufficiently nucleophilic to behave in a similar manner, and this appears to be the most plausible mechanism for co-ordinatively saturated complexes. Since the Pt–Cl bonds in platinum(II) complexes [29] are longer and therefore more ionic than in platinum(IV) complexes,[30] it is probable that the chloride ligands in platinum(II) complexes are more nucleophilic than in some of the co-ordinatively saturated complexes which undergo the abstraction reaction. The ability of chloride ligands to bind a second metal to form chlorine bridges is also greater for lower oxidation states of metal atoms, so there is reason to expect chloride ligands in Pt^{II} to be sufficiently nucleophilic to react directly with the alkylating agents.

We made a brief attempt to investigate the mechanism of abstraction for platinum(II) complexes. A mechanism with oxidative addition as the first step would involve one or both of the vacant sites above and below the square-planar array of ligands and this should be true irrespective of whether the oxidative addition involves a polar or a radical process.[31] Direct interaction of the alkylating agent with the halide ligand would not involve another co-ordination site on the metal. The presence of methyl groups *ortho* to the platinum atom in aryl complexes is known to inhibit ligand-substitution reactions by steric blocking of the co-ordination sites above and below the square plane. This effect was discovered by Basolo *et al.*[32] who found that replacement of Cl^- by pyridine was slower by a factor of *ca.* 40 in *trans*-$[Pt(C_6H_2Me_3\text{-}2,4,6)Cl(PEt_3)_2]$ than in *trans*-$[PtPh(Cl)(PEt_3)_2]$. Recently these systems have been shown to be more complex than originally supposed and the reactivity factor of *ca.* 810 determined with CN^- as nucleophile is more reliable.[33] We compared the rates of formation of MeBr after addition of $SFO_2(OMe)$ to the corresponding bromo-complexes in deuteriochloroform solutions by monitoring the ^1H n.m.r. spectra. Although they lacked high precision, these experiments indicated that the mesityl complex reacted at about the same rate as or slightly faster than the phenyl complex,

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and, since the substitution of bromide for chloride is unlikely to have a qualitative effect on the comparison, we tentatively conclude that halogen abstraction involves direct interaction of the alkylating agent $[SFO_2(OMe)$ or $[R_3O]^+]$ with the halide ligand for platinum(II) complexes as well as co-ordinatively saturated complexes.

EXPERIMENTAL

I.r. spectra were recorded with Perkin-Elmer model 457 (4 000—250 cm^{-1}) or Grubb-Parsons DM4 grating spectrometers (500—200 cm^{-1}) as Nujol mulls unless otherwise stated. N.m.r. spectra were obtained with Varian T60 (^1H, 60 MHz), HA 100 (^1H, 100 MHz), or JEOL [$^{31}P-\{^1H\}$, 40.5 MHz] spectrometers using deuteriochloroform as solvent except as specified. Magnetic susceptibilities at 20 °C were measured for solid-state samples with an automatic Faraday balance. Conductivities of *ca.* 10^{-3} mol dm^{-3} solutions in nitromethane were determined with a Portland conductivity bridge. Melting points (uncorrected) were obtained with a Kofler block, and molecular weights with a Mechrolab vapour-pressure osmometer.

All manipulations were in a dry nitrogen atmosphere and solvents were dry and air free. Established methods were used for the preparation of methyl fluorosulphate [34] and triethyloxonium tetrafluoroborate,[35] and also for the metal complexes used as starting materials. Microanalyses were by the Microanalytical Laboratory of the School of Molecular Sciences or by Bernhardt Laboratories, West Germany.

Preparation of Complexes $[M_2L_4X_2][A]_2$ (M = Pd *or* Pt; A = BF_4 *or* SFO_3).—A typical procedure was as follows. A solution of *cis*-$[PtCl_2(PEt_3)_2]$ (0.35 g, 0.7 mmol) and $[Et_3O][BF_4]$ (0.25 g, 1.3 mmol) in dichloromethane (25 cm^3) was stirred overnight, during which time two layers formed. The solid obtained after evaporation of solvent was dissolved in the minimum volume of methanol. After addition of an equal volume of diethyl ether and filtration, hexane was added until the solution became cloudy. Colourless needles of $[Pt_2Cl_2(PEt_3)_4][BF_4]_2$ separated on standing. Procedures and characterisation data are summarised in Table 1.

Reactions of $[Pt_2Cl_2(PEt_3)_4][BF_4]_2$.—(a) *With* MeNC. Addition of MeNC (0.015 ml, 0.18 mmol) to a stirred solution of $[Pt_2Cl_2(PEt_3)_4][BF_4]_2$ (0.21 g, 0.18 mmol) in methanol (20 cm^3) gave a yellow solution. Evaporation of solvent and addition of diethyl ether gave a yellow solid which, on addition of hexane to its solution in methanol–diethyl ether, gave colourless crystals of trans-*chloro-(methyl isocyanide)bis(triethylphosphine)platinum*(II) *tetrafluoroborate, trans*-$[Pt(CNMe)Cl(PEt_3)_2][BF_4]$ (0.19 g, 90%), m.p. 140—145 °C (Found: C, 28.0; H, 5.5; N, 2.5. $C_{14}H_{33}BClF_4NP_2Pt$ requires C, 28.3; H, 5.6; N, 2.4%), $\Lambda = 70$ S cm^2 mol^{-1}, $\nu(NC)$ at 2 260 cm^{-1}, $\nu_{asym}(BF_4)$ at 1 050vs,br cm^{-1}. ^1H N.m.r. spectrum: τ 6.1 (s, MeNC), 7.8 (m, PCH_2), and 9.10 (five lines, PCH_2CH_3).

(b) *With* MeCN. A solution of $[Pt_2Cl_2(PEt_3)_4][BF_4]_2$ (0.3 g, 0.27 mmol) in acetonitrile (8 cm^3) was kept for 3 d. Evaporation of solvent left a colourless oil which gave a white solid after stirring in hexane under reflux for 2 h. Recrystallisation from methanol–diethyl ether gave *cis*-$[PtCl(NCMe)(PEt_3)_2][BF_4]$ (0.29 g, 90%), m.p. 80—81 °C (Found: C, 28.4; H, 5.9; N, 2.3. $C_{14}H_{33}BClF_4NP_2Pt$ requires C, 28.3; H, 5.6; N, 2.4%), $\Lambda = 65$ S cm^2 mol^{-1}, $\nu(CN)$ at 2 305 cm^{-1}, $\nu_{asym}(BF_4)$ at 1 050vs,br cm^{-1}; τ 7.79 (s, MeCN), 7.9 (m, PCH_2), and 9.1 (m, PCH_2CH_3).

(c) *With hydrochloric acid.* Addition of concentrated HCl (1 cm^3) to $[Pt_2Cl_2(PEt_3)_4][BF_4]_2$ (0.31 g), after effervescence, gave a white solid, m.p. 191—192 °C, which was identified as *cis*-$[PtCl_2(PEt_3)_2]$ by comparison (m.p., i.r.) with an authentic sample.

Conversion of trans-$[PtCl_2(PEt_3)_2]$ *into the* cis-*Isomer*.—Methyl fluorosulphate (0.5 cm^3) was added to a solution of *trans*-$[PtCl_2(PEt_3)_2]$ (1.05 g) in dichloromethane (20 cm^3) and the mixture heated under reflux until colourless (30 min). Concentrated HCl (2 cm^3) was then added and after 5 min the organic layer was dried over calcium sulphate. Evaporation of the solution gave *cis*-$[PtCl_2(PEt_3)_2]$ (0.92 g, 90%), m.p. 191—192 °C, identical to an authentic sample.

Preparation of trans-*Bis(methyl isocyanide)bis(triethylphosphine)platinum*(II) *Tetrafluoroborate*.—Methyl isocyanide (0.1 cm^3, an excess) was added to a solution of *cis*-$[PtCl_2(PEt_3)_2]$ (0.5 g, 1 mmol) and $[Et_3O][BF_4]$ (0.4 g, 2.1 mmol) in dichloromethane (30 cm^3) and left for 30 min. Evaporation to dryness gave a yellow solid which was dissolved in a minimum of methanol and an equal volume of diethyl ether added. Addition of hexane gave *trans*-$[Pt(CNMe)_2(PEt_3)_2][BF_4]_2$ (0.55 g, 85%) as colourless crystals, m.p. 160—162 °C (Found: C, 28.2; H, 5.6; N, 4.1. $C_{16}H_{36}B_2F_8N_2P_2Pt$ requires C, 28.0; H, 5.3; N, 4.1%), $\Lambda = 146$ S cm^2 mol^{-1}, $\nu(NC)$ at 2 262 cm^{-1}, $\nu_{asym}(BF_4)$ at 1 050vs,br cm^{-1}; τ 6.17 (s, MeNC), 7.8 (m, PCH_2), and 9.0 (five lines, PCH_2CH_3).

Reaction of cis-$[PtCl_2(SEt_2)_2]$ *with* $SFO_2(OMe)$.—An excess of $SFO_2(OMe)$ (0.1 cm^3) was added to a stirred solution of *cis*-$[PtCl_2(SEt_2)_2]$ (0.3 g, 0.67 mmol) in dichloromethane (10 cm^3). Bright yellow crystals formed after 30 min, and after 2 h these were filtered off, washed successively with dichloromethane and hexane, and dried *in vacuo*. Thus formed was bis-μ-diethylthio-bis[dichloroplatinum(II)] $[Pt_2Cl_4(SEt_2)_2]$ (0.39 g, 83%), m.p. 215—230 °C (lit.,[36] 213—230 °C) (Found: C, 13.4; H, 2.7. Calc. for $C_8H_{20}Cl_4Pt_2S_2$: C, 13.5; H, 2.8%). In a separate experiment in deuteriochloroform the supernatant liquor was shown to contain $[MeEt_2S][SFO_3]$ with an identical ^1H n.m.r. spectrum to the product of the reaction of SEt_2 with $SFO_2(OMe)$ [τ 6.5 (q), 7.0 (s), and 8.5 (t)].

Reaction of $SFO_2(OMe)$ *with* mer-$[RhCl_3(PMe_2Ph)_3]$.—An excess of $SFO_2(OMe)$ (0.25 cm^3) was added to a stirred solution of *mer*-$[RhCl_3(PMe_2Ph)_3]$ (1.0 g, prepared by the method of Brookes and Shaw [15]) in dichloromethane (35 cm^3). After 1 h the solution was concentrated and hexane added. On cooling this gave an orange solid which was recrystallised from dichloromethane–hexane to give orange prisms of *dichlorotris(dimethylphenylphosphine)(fluorosulphato)rhodium*(III) (0.825 g, 75%), m.p. 178—180 °C (Found: C, 41.8; H, 4.8; Cl, 10.8. $C_{24}H_{33}Cl_2FO_3PRhS$ requires C, 41.9; H, 4.8; Cl, 10.3%), $\Lambda = 87$ S cm^2 mol^{-1}, $\nu(Rh-Cl)$ at 342 and 323, $\nu_{asym}[FSO_2-O$(unco-ord.)] at 1 226s, $\nu[FSO_2-O$(co-ord.) at 1 059s, $\nu(S-F)$ at 765 (sh), $\delta_{asym}[FSO_2-O$(unco-ord.)] at 585m, $\delta_{sym}[FSO_2-O$(unco-ord.)] at 569m, and $\delta[FSO_2-O$(co-ord.)] at 562w cm^{-1}.

Reaction of $[Et_3O][BF_4]$ *with* mer-$[RhCl_3(PMe_2Ph)_2]$.—A solution of $[Et_3O][BF_4]$ (0.2 g, 1.05 mmol) and *mer*-$[RhCl_3(PMe_2Ph)_3]$ (0.30 g, 0.48 mmol) in dichloromethane

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[36] J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 1955, 2787.

(15 cm^3) was heated under reflux for 1 h, then reduced to half its volume. Addition of hexane and storage at 0 °C gave *di-μ-chloro-*bis[*chlorotris(dimethylphenylphosphine)rhodium*(III)] *tetrafluoroborate* (0.29 g, 89%) as deep red needles, m.p. 145 °C (decomp.) (Found: C, 42.7; H, 5.0. $C_{48}H_{66}B_2Cl_4F_8P_6Rh_2$ requires C, 42.7; H, 4.9%), $\Lambda = 209.7$ S cm^2 mol^{-1}.

Reaction of PMe_2Ph *with* $[RhCl_2(PMe_2Ph)_3(SFO_3)]$.—A solution of PMe_2Ph (0.25 g, an excess) and $[RhCl_2(PMe_2Ph)_3(SFO_3)]$ (0.25 g) in methanol was left for 15 min, then evaporated to a yellow oil. This was dissolved in the minimum of methanol, an equal volume of diethyl ether added, and addition of hexane gave dichlorotetrakis(dimethylphenylphosphine)rhodium(III) fluorosulphate (0.21 g, 70%) as yellow crystals, m.p. 145—150 °C (Found: C, 46.6; H, 5.5; P, 14.7. $C_{32}H_{44}Cl_2FOP_4RhS$ requires C, 46.6; H, 5.3; P, 15.0%), $\Lambda = 85$ S cm^2 mol^{-1}, ν(Rh–Cl) at 342 and 320, $\nu_{asym}(SO_3)$ at 1 290vs,br, $\nu_{sym}(SO_3)$ at 1 068s, ν(SF) at 768 (sh), $\delta_{asym}(SO_3)$ at 538m, and $\delta_{sym}(SO_3)$ at 560w cm^{-1}.

Miscellaneous Abstraction Reactions of $SFO_2(OMe)$.—Deuteriochloroform solutions of the following complexes reacted with $SFO_2(OMe)$ to give MeCl, identified by a ^1H resonance at τ 6.95: $[Mo(\eta\text{-}C_5H_5)(CO)_3Cl]$; *mer*-$[ReCl_3(PEt_2Ph)_3]$; $[RuCl_2(PPh_3)_3]$; *mer*-$[OsCl_3(PMe_2Ph)_3]$; $[Rh(C_8H_{12})Cl(PPh_3)_2]$; *fac*-$[RhCl_3(PMe_2Ph)_3]$; *mer*-$[IrCl_3(PBu_2Ph)_3]$; *trans*-$[PtCl(H)(PEt_3)_2]$; *trans*-$[PtCl(H)(PMe_2Ph)_2]$; *trans*-$[PtCl(PMe_2Ph)_2(SiPh_3)]$; *trans*-$[PtMe(Cl)(PMe_2Ph)_2]$; *trans*-$[PtPh(Cl)(PEt_3)_2]$; $[PtCl_4(PEt_3)_2]$; and $[AuCl(PPh_3)_3]$. For the platinum(II) complexes the ^1H n.m.r. spectra showed that the phosphines remained *trans*. In the presence of MeNC (0.2 cm^3), *trans*-$[PtCl(PMe_2Ph)_2(SiPh_3)]$ (0.32 g) in benzene (30 cm^3) reacted with $SFO_2(OMe)$ (0.15 cm^3) to give an orange solid during 1 h, ν(NC) at 2 280 cm^{-1}, $\nu_{asym}(SO_3)$ at 1 285 cm^{-1}, which decomposed with liberation of MeNC on attempted recrystallisation from acetone. In the reaction of $SFO_2(OMe)$ with *mer*-$[OsCl_3(PMe_2Ph)_3]$ the deep red oil obtained as product had an i.r. spectrum similar to that of $[RhCl_2(PMe_2Ph)_3(SFO_3)]$, and it was converted into a purple oil with ionic $[SFO_3]^-$ [$\nu_{asym}(SO)_3$ at 1 290 cm^{-1}] on reaction with PMe_2Ph.

Reactions with Nickel(II) *and Cobalt*(II) *Complexes*.—A solution of $SFO_2(OMe)$ (0.06 cm^3, 0.69 mmol) and $[NiCl_2(PPh_3)_2]$ (0.41 g, 0.61 mmol) in dichloromethane (30 cm^3) was put aside for 12 h. The deposited solid was shown to be $NiCl_2$ and evaporation of the solution gave methyltriphenylphosphonium fluorosulphate, recrystallised from methanol–diethyl ether, m.p. 105—115 °C (Found: C, 60.8; H, 5.0. $C_{19}H_{18}FO_3PS$ requires C, 60.8; H, 4.8%), τ 7.16 [^2J(PH) 14.0 Hz (PCH_3)]. In a similar manner, $[PhMeP][SFO_3]$ was obtained from the reaction between $[CoCl_2(PPh_3)_2]$ and $SFO_2(OMe)$, and $[Et_4P][BF_4]$, m.p. 285—295 °C (lit.,[37] 291 °C), from $[NiCl_2(PEt_3)_2]$ and $[Et_3O][BF_4]$.

With $[NiCl_2(dppe)]$ (0.36 g) in dichloromethane (40 cm^3), $SFO_2(OMe)$ (0.3 cm^3) gave a yellow precipitate during 2 h. Recrystallisation from acetonitrile–diethyl ether gave $[Ni(dppe)_2][SFO_3]_2$ as yellow crystals, m.p. 245—250 °C (0.23 g, 30%) (Found: C, 60.5; H, 4.80. $C_{52}H_{48}F_2NiO_6P_4S_2$ requires C, 59.3; H, 4.6%), $\Lambda = 155$ S cm^2 mol^{-1}, identical with a sample prepared from $Ni[CO_3]$ and $HSFO_3$ in presence of dppe. Similarly obtained from $[Et_3O][BF_4]$ and $[NiCl_2(dppe)_2]$ was $[Ni(dppe)_2][BF_4]_2$ (Found: C, 61.2; H, 4.8. $C_{52}H_{48}B_2F_8NiP_4$ requires C, 60.7; H, 4.7%), $\Lambda = 172$ S cm^2 mol^{-1}.

Reaction of $SFO_2(OMe)$ *with Iridium*(I) *Complexes*.—A solution of $SFO_2(OMe)$ (0.25 cm^3, an excess) and *trans*-$[Ir(CO)Cl(PPh_3)_2]$ (0.22 g) in benzene (20 cm^3) was put aside for 5 min, then reduced to half its volume. Addition of hexane gave *carbonylchloro(fluorosulphato)methylbis(triphenylphosphine)iridium*(II), $[IrMe(CO)Cl(PPh_3)_2(SFO_3)]$, as a microcrystalline white solid (0.21 g, 84%), m.p. 165—170 °C (Found: C, 50.9; H, 3.9; Cl, 4.3. $C_{38}H_{33}ClFIrO_4P_3S$ requires C, 51.0; H, 3.7; Cl, 4.0%), ν(CO) at 2 062, ν(IrCl) at 312, ν_{asym}[FSO_2–O(unco-ord.)] at 1 350, ν_{sym}(FSO_2–O(unco-ord.)] at 1 225, ν[FSO_2–O(co-ord.)] at 1 053, δ_{asym}[FSO_2–O(unco-ord.)] at 582, and δ_{sym}[FSO_2–O(co-ord.)] at 569 cm^{-1}, $\Lambda = 62.5$ S cm^2 mol^{-1}. The same product was obtained from $[Ir(CO)ClL(PPh_3)_2]$ (L = O_2, SO_2, or C_2F_4).

Addition of *p*-MeC_6H_4NC (0.039 g, 0.3 mmol) to a solution of $[IrMe(CO)Cl(PPh_3)_2(SFO_3)]$ (0.27 g, 0.3 mmol) in benzene gave a white precipitate after 15 min. This was washed with benzene and recrystallised from methanol–diethyl ether to give *carbonylchloro(methyl)*(p-*tolyl isocyanide*)*bis(triphenylphosphine)iridium*(III) *fluorosulphate* (0.21 g, 70%), m.p. 182—186 °C (Found: C, 54.4; H, 4.2; N, 1.5. $C_{46}H_{40}ClFIrNO_4P_2S$ requires C, 54.6; H, 3.9; N, 1.4%), $\Lambda = 70$ S cm^2 mol^{-1}, ν(NC) at 2 219vs, ν(CO) at 2 091s, $\nu_{asym}(SO_3)$ at 1 285, and ν(IrCl) at 319 cm^{-1}.

A mixture of $[Et_4N]Cl$ (0.165 g, 1 mmol) and $[IrMe(CO)Cl(PPh_3)_2(SFO_3)]$ (0.29 g, 0.23 mmol) in chloroform (20 cm^3) was heated under reflux for 1 h. After washing with water, the chloroform was evaporated to dryness. Recrystallisation of the residue gave trans-*carbonyldichloro(methyl)bis(triphenylphosphine)iridium*(III) as a white solid (0.16 g, 83%), m.p. 221—223 °C (Found: C, 54.5; H, 4.1. $C_{38}H_{33}Cl_2IrOP_2$ requires C, 54.7; H, 3.9%), τ 9.36 (t) [^3J(PIrCH) 10 Hz], ν(CO) at 2 035 cm^{-1}.

Reaction of $SFO_2(OMe)$ *with* cis-$[PtMe_2(PMe_2Ph)_2]$.—(a) *Benzene solution*. The ^1H n.m.r. spectrum of a mixture of *cis*-$[PtMe_2(PMe_2Ph)_2]$ and an excess of $SFO_2(OMe)$ in deuteriobenzene comprised two sets of resonances in the Pt–Me region {τ 9.72 (t) [^3J(PPtCH) 7 Hz] (intensity 1); τ 8.73 (t) [^3J(PPtCH) 7 Hz] (intensity 2)}, and a triplet of triplets centred on τ 8.53 [|^4J(PPtPCH) + ^2J(PCH)| 7.5 Hz, ^3J(PtPCH) 15 Hz], indicative of a *trans* arrangement of phosphines and a meridional arrangement of methyl groups in $[PtMe_3(PMe_2Ph)_2(SFO_3)]$. This complex was not isolated.

(b) *Chloroform solution*. Methyl fluorosulphate (0.2 cm^3, an excess) was added to a solution of *cis*-$[PtMe_2(PMe_2Ph)_2]$ (0.2 g, 0.4 mmol) in chloroform (10 cm^3). After 1 h, $[Et_4N]Cl$ (0.16 g, 1 mmol) in chloroform (10 cm^3) was added and the mixture put aside for 1 h. After washing with water, the chloroform layer was dried and evaporated to dryness and the residue recrystallised from chloroform–hexane to give *trans*-$[PtMe(Cl)(PMe_2Ph)_2]$ (0.16 g, 80%), m.p. 145—147 °C (lit.,[23] 146—148 °C) (Found: C, 39.3; H, 4.5. Calc. for $C_{17}H_{25}ClP_2Pt$: C, 39.1; H, 4.8%). ^1H N.m.r. spectra of reaction mixtures in deuteriochloroform indicated the production of ethane [τ 9.06 (s)].

Reactions of $SFO_2(OMe)$ *with Platinum*(0) *Complexes*.—Addition of $SFO_2(OMe)$ (0.5 cm^3, an excess) to a solution of $[Pt(PPh_3)_4]$ (1.24 g, 1.0 mmol) in benzene (25 cm^3) resulted in the immediate separation of a white solid {τ 7.16 (d) [^2J(PCH) 13 Hz]}, identical to an authentic sample of $[Ph_3MeP][SFO_3]$ and a yellow oil {τ 9.36 (t) [^3J(PPtCH) 7 Hz] (Pt–Me)} which could not be crystallised.

Addition of an excess of $SFO_2(OMe)$ to a benzene solution

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[37] L. Horner and B. Nippe, *Chem. Ber.*, **1958**, **91**, 209.

of $[Pt(PPh_3)_3]$ (0.98 g) gave a white precipitate which was recrystallised from acetone–benzene and dried *in vacuo* at 100 °C to give $[PtMe(PPh_3)_3][SFO_3]$, m.p. 155 °C (Found: C, 60.35; H, 4.55. Calc. for $C_{55}H_{48}FO_3P_3PtS$: C, 60.3; H, 4.40 %), ν_{asym} (SO_3) at 1 290 and $\delta_{asym}(SO_3)$ at 585 cm^{-1}, $\Lambda = 86$ S cm^2 mol^{-1}, ^1H parameters as reported by Peterson *et al.*[19] ^{31}P Parameters: $I = 2$, $^1J(Pt{-}P)$ 2 925 Hz, $\delta - 17.8$ p.p.m.; $I = 1$, $^1J(Pt{-}P)$ 1 919 Hz, $\delta - 9.6$ p.p.m.; $^2J(PPt{-}P)$ 20 Hz. Reaction with $[Et_4N]I$ in chloroform gave *trans*-$[PtMe(I)(PPh_3)_2]$ {τ 9.82 (t) [$^3J(PPt{-}CH)$ 7.0 Hz, $^2J(Pt{-}CH)$ 77 Hz]}.

Preparation of $[MoCl_2(dppe)_2]X$ ($X = SFO_3$, BF_4, PF_6, *or* ClO_4).—A yellow solution of *trans*-$[MoCl_2(dppe)_2]$ [38] (0.48 g) in dichloromethane turned pink-red on addition of $SFO_2(OMe)$ (0.1 cm^3). After 1.5 h the solution was evaporated to dryness, the residue washed with benzene, and recrystallised from tetrahydrofuran–hexane to give trans-*bis*[1,2-*bis*(*diphenylphosphino*)*ethane*]*dichloromolybdenum*(III) *fluorosulphate* as a pink powder (0.39 g, 74%), m.p. 166—170 °C (Found: C, 58.8; H, 4.9. $C_{52}H_{48}Cl_2FMoO_3P_4S$ requires C, 58.7; H, 4.5%), $\Lambda = 78.6$ S cm^2 mol^{-1}, $\nu_{asym}(SO_3)$ at 1 285 and $\nu(Mo{-}Cl)$ at 345 cm^{-1}. The following salts were made by similar procedures: *trans*-$[MoCl_2(dppe)_2][BF_4]$ (from $[Et_3O][BF_4]$), m.p. 185—190 °C (Found: C, 59.0; H, 4.7; Cl, 7.1. $C_{52}H_{48}BCl_2F_4MoP_4$ requires C, 59.4; H, 4.6; Cl, 6.8%), $\Lambda = 87.5$ S cm^2 mol^{-1}, $\mu_{eff.}$ 3.35 B.M., $\nu(BF_4)$ at 1 048 and $\nu(Mo{-}Cl)$ at 342 cm^{-1}; *trans*-$[MoCl_2(dppe)_2][PF_6]$ (from $Ag[PF_6]$ in acetone), m.p. 166—170 °C (Found: C, 56.5; H, 4.5. $C_{52}H_{48}Cl_2F_6MoP_5$ requires C, 56.3; H, 4.3%), $\Lambda = 81$ S cm^2 mol^{-1}, $\mu_{eff.}$ 3.47 B.M., $\nu(PF_6)$ at 840 and $\nu(Mo{-}Cl)$ at 345 cm^{-1}; and *trans*-$[MoCl_2(dppe)_2][ClO_4]$ (from $Ag[ClO_4]$), m.p. 166—170 °C (Found: C, 59.1; H, 4.6; Cl, 9.1. $C_{52}H_{48}Cl_3MoO_4P_4$ requires C, 58.7; H, 4.5; Cl, 10.0%), $\Lambda = 87$ S cm^2 mol^{-1}, $\mu_{eff.}$ 2.63 B.M., $\nu(ClO_4)$ at 1 120 and $\nu(Mo{-}Cl)$ at 344 cm^{-1}.

Preparation of $[Re(CO)_3Cl(PPh_3)_2][BF_4]$.—A solution of $[Et_3O][BF_4]$ (0.25 g) and $[Re(CO)_3Cl(PPh_3)_2]$ [39] (0.22 g) in dichloromethane (35 cm^3) was heated under reflux for 4 h. On addition of hexane to the cooled solution, tricarbonylchlorobis(triphenylphosphine)rhenium(II) tetrafluoroborate was deposited as a white solid (0.12 g, 50%), m.p. 173—178 °C (Found: C, 46.8; H, 3.1. $C_{39}H_{30}BClF_4O_3P_2Re$ requires C, 47.1; H, 3.3%), $\Lambda = 63$ S cm^2 mol^{-1}, $\nu(CO)$ at 2 068, 1 990, and 1 921, $\nu_{asym}(BF_4)$ at 1 050 cm^{-1}.

Reaction of $SFO_2(OMe)$ *with* trans-$[PtCl\{PO(OPh)_2\}(PR_3)_2]$.—Addition of $SFO_2(OMe)$ (0.1 cm^3) to a solution of *trans*-$[PtCl\{PO(OPh)_2\}(PBu_3)_2]$ (0.32 g) in benzene (10 cm^3) gave two layers after 15 min. Hexane (10 cm^3) was added to the heavier layer and the mixture heated under reflux for 24 h during which time an oily white solid, which could not be further purified, separated out. This is formulated as *trans*-$[PtCl\{P(OMe)(OPh)_2\}(PBu_3)_2][SFO_3]$, $\nu_{asym}(SO_3)$ at 1 285 cm^{-1}, τ 6.1 (d) [$^3J(POCH)$ 12 Hz]; reaction with *trans*-$[PtCl\{PO(OPh)_2\}(PEt_3)_2]$ gave no MeCl and the phosphines remained *trans* (^1H n.m.r.).

Rates of Bromide Abstraction.—Solutions (0.25 cm^3, 0.12 mol dm^{-3}) of *trans*-$[PtBrR(PMe_2Ph)_2]$ (R = Ph or mesityl) in deuteriochloroform were placed in n.m.r. tubes and $SFO_2(OMe)$ (5 μl) added. The relative intensity of the MeBr peak (τ 7.32) and the $P{-}CH_3$ peaks was determined at intervals of *ca.* 10 min using the spectrometer integrator. The approximate half-lives (20 min, R = Ph; 18 min, R = mesityl) were obtained from graphs of the ratio of peak integrals against time.

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