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Preliminary communication

Reactions of methyl fluorosulphonate and triethyloxonium tetrafluoroborate with metal complexes

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SUMMARY

Methyl fluorosulphonate and triethyloxonium tetrafluoroborate (which is less reactive) have been found to give four distinct types of reaction with transition metal complexes, *viz.* (a) halogen abstraction, (b) oxidative-addition, (c) alkylation of the coordinated ligands, and (d) oxidation at the metal atom.

Methyl fluorosulphonate[1] and triethyloxonium tetrafluoroborate[2] are known to be effective alkylating agents in organic chemistry. We have undertaken a survey of their reactions with metal complexes, and present below a brief summary of the initial observations in a study which is still incomplete. During the course of our work Treichel and his colleagues[3] reported a study of some reactions of the trialkyloxonium tetrafluoroborates which overlapped to a small extent with our researches, as noted in Table 1. As in organic chemistry, methyl fluorosulphonate and triethyloxonium tetrafluoroborate bring about similar reactions, but the former seems always to be the more reactive; we have found, for example, that it can with advantage be used in place of the oxonium salt in the synthesis of $[Cr(CO)_5C(OMe)Ph]$[4].

The reactions with transition metal complexes so far examined appear to be of four types, as indicated in Table 1. Complexes in which the ligands, L, have no additional lone pairs and are more strongly bound than halide, tend to undergo halogen abstractions, represented by class (a) in Table 1, but when L has additional lone pairs available, alkylation of the ligand may occur, as in (c). Coordinatively unsaturated complexes can also undergo oxidative-addition, as in class (b), but when the halide is not labile and the other ligands are unreactive simple oxidation can occur, as in class (d).

In the one reaction examined with a main-group organometallic compound, *viz.* tetramethyltin, methyl fluorosulphonate caused cleavage of the Sn–Me bond, and trimethyltin fluorosulphonate was isolated.

TABLE I

REACTIONS OF $MeOSO_2F$ (A) AND $[Et_3O][BF_4]$ (B) WITH METAL COMPLEXES

Complex		*Reactant*	*Product(s)*
(a) Halogen abstraction			
$[L_2MX_2]$	(M = Pd or Pt; X = Cl, Br or I; L = tertiary phosphine, arsine, or pyridine; L_2 = norbornadiene or cyclooctadiene)	(A) or (B)	$[L_2MX_2ML_2]^{2+}$ (see also ref. 3)^a
$[L_2HgCl_2]$	(L = tertiary phosphine)	(A) or (B)	$[L_2Hg]^{2+}$
$[L_2Hg_2X_4]$	(L = tertiary phosphine; X = Cl or Br)	(A) or (B)	$[LHgX]^+$
$[L_2PtRCl]$	(L = tertiary phosphine; R = H, Me, MeCO or Ph_3Si)	(A)	MeCl evolved. In presence of PhC≡CH, $[(PEt_3)_2PtHCl]$ yielded product which may be $[(PEt_3)_2PtPhC{=}CH_2]SO_3F$
mer-$[L_3ReCl_3]$	(L = tertiary phosphine)	(A)	MeCl evolved; other products not identified
$[\pi C_5H_5Mo(CO)_2Cl]$		(A)	MeCl evolved; other products not identified
mer-$[L_3RhCl_3]$		(A)	MeCl evolved. For L = PMe_2Ph, initial product is $[L_3RhCl_2(OSO_2F)]$, which with L gives $[L_4RhCl_2](SO_3F)$
(b) Oxidative addition			
$[Ir(CO)Cl(PPh_3)_2]$		(A)	$[IrClMe(OSO_2F)(CO)(PPh_3)_2]$
$[Pt(PPh_3)_3]$ and $[(C_2H_4)Pt(PPh_3)_2]$		(A)	In presence of halide, $[PtMeX(PPh_3)_2]$ isolated
(c) Reactions of coordinated ligands			
$[L_2M(CN)_2]$	(M = Ni, L = tertiary phosphine; M = Pd or Pt, L = tertiary phosphine or tertiary arsine)	(A) or (B)	$[L_2M(CNR)_2]Y_2$ (R = Me, Y = SO_3F; R = Et, Y = BF_4) (see also ref. 3)
$[Fe(CN)_6]K_3$		(A)	$[Fe(CN)(CNMe)_5](SO_3F)_2$
$[Mn(CN)_5(NO)]K_3$		(A)	$[Mn(NO)(CNMe)_5](SO_3F)_2$
$[(Et_2S)_2PtCl_2]$		(A)	$[Pt_2Cl_4(Et_2S)_2]$ + $[Et_2MeS](SO_3F)$
$[(Ph_3P)_2NiCl_2]$		(A)	$(MePh_3P)(FSO_3)$ + $NiCl_2$
$[(n\text{-}Bu_3P)_2PtCl\{P(OPh)_2O\}]$		(A)	No product isolated; methylation of phosphonyl oxygen demonstrated by ^{1}H NMR

(continued)

TABLE I *(continued)*

REACTIONS OF $MeOSO_2F$ (A) AND $[Et_3O][BF_4]$ (B) WITH METAL COMPLEXES

Complex	*Reactant*	*Product(s)*
(d) Oxidation		
$[MoCl_2(Dpe)_2]$ (Dpe = 1,2-bis(diphenylphosphinoethane)	(A)	$[MoCl_2(Dpe)_2](SO_3F)$
$[(Ph_3P)_2Re(CO)_3Cl]$	(B)	$[(Ph_3P)_2Re(CO)_3Cl](BF_4)$

[a] In the cases in which L_2 = norbornadiene or cyclooctadiene, the cationic complexes react very readily even with neutral methanol to give the (uncharged) dienemethoxy dimers (*cf.* ref. 5).

Further studies are in progress, and full details will be published later.

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REFERENCES

1 M.G. Ahmed, R.W. Alder, G.H. James, M.L. Sinnott and M.G. Whiting, *Chem. Commun.*, (1968) 1533.

2 V.G. Gravik, B.M. Pyatin and R.G. Glushkav, *Russian Chem. Revs.*, 40 (1971) 747.

3 P.M. Treichel, K.P. Wagner and W.J. Knebel, *Inorg. Chim. Acta*, 6 (1972) 674; P.M. Treichel, W.J. Knebel and R.W. Hess, *J. Amer. Chem. Soc.*, 93 (1971) 5424.

4 R. Aumann and E.O. Fischer, *Chem. Ber.*, 101 (1968) 954.

5 J. Chatt, L.M. Vallarino and L.M. Venanzi, *J. Chem. Soc.*, (1957) 2496, 3413.