Lewis Acid-promoted Vinyl Rearrangement and Halogen Exchange of Platinum-fluoro-olefin Complexes

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Treatment of the complexes $Pt[CF_2{:}CF(CF_3)]L_2$ [L = PPh_3, PPh_2Me, $(Ph_2PCH_2)_2$, or $AsPh_3$] with stannic chloride yields products dependent on the nature of L. With PPh_2Me or $AsPh_3$, perfluoropropene is displaced, but with PPh_3 or diphos the vinylplatinum compounds *trans*-$PtCl[CCl{:}CF(CF_3)](PPh_3)_2$ and $PtCl[CF{:}CF(CF_3)]$(diphos) are formed, respectively. Reaction of $SnCl_4$ with $Pt(C_2F_4)L_2$ (L = PPh_3, PPh_2Me, or $AsPh_3$) or with $Pt[$*trans*(CF_3)-$CF{:}CF(CF_3)](AsPh_3)_2$ leads to displacement of the fluoro-olefin and formation of $PtCl_2L_2$. In contrast, the tin halide reacts with $Pt[$*trans*$(CF_3)CF{:}CF(CF_3)]L_2$ [L = PPh_3, PPh_2Me, or $(Ph_2PCH_2)_2$] to yield vinylplatinum compounds *cis*-$PtCl[$*trans*$C(CF_3){:}CF(CF_3)]L_2$. A mechanism for the C–F bond cleavage and stereospecific nature of the reactions is proposed.

ALTHOUGH numerous transition-metal fluoro-olefin complexes[1,2] have been prepared little work has been reported on the reactivity of the co-ordinated fluoro-olefin moiety. Aside from simple displacement reactions, only three types of reaction involving co-ordinated fluoro-olefins have been reported.

Certain platinum(0)[3,4] and rhodium(I)[5] fluoro-olefin complexes undergo electrophilic addition by trifluoroacetic acid or hydrogen chloride respectively, to yield the corresponding platinum(II) or rhodium(III) fluoroethyl complexes.

Platinum(0) species[6] containing co-ordinated halogenofluoro-olefins (*e.g.* $CF_2{:}CFCl$) undergo readily a molecular rearrangement affording σ-bonded vinylmetal complexes [*e.g.* $PtCl(CF{:}CF_2)(PPh_3)_2$]. Similarly, the formation of nickel(II)[7,8] and palladium(II)[9] fluorovinyl compounds is thought to involve rapid molecular rearrangement of an initially co-ordinated halogen-substituted fluoro-olefin.

A number of low-valent iron,[10,11] cobalt,[12] rhodium,[13] nickel,[14] and platinum[15] complexes are known to react with an excess of fluoro-olefin to form complexes containing the $\overline{M{\cdot}CF_2(CF_2)_2C}F_2$ ring system. In at least one instance[14] the intermediary of a metallocyclopropane complex $\overline{M{\cdot}CF_2{\cdot}C}F_2$ has been demonstrated. Such ring-expansion processes represent the most thoroughly studied reaction of co-ordinated fluoro-olefins.[2]

In all the above cases, carbon–fluorine bond integrity is maintained with the final product containing either the original number, or an exact multiple of the original number, of fluorine atoms present in the starting complex. In contrast, we now report a new class of reaction of co-ordinated fluoro-olefins in which carbon–fluorine bond cleavage occurs under mild conditions. During the course of our work Kemmitt *et al.*[16] described a reaction in which treatment of $\overline{Pt{\cdot}CF_2{\cdot}C}F_2(PPh_3)_2$ with lithium iodide at 95° afforded $PtI(CF{:}CF_2)(PPh_3)_2$.

The identity of the new compounds described herein was established by elemental analysis, and i.r. and ^1H and ^{19}F n.m.r. spectroscopy (see Table).

Treatment of perfluoropropene complexes $\overline{Pt{\cdot}CF_2{\cdot}C}F(CF_3)L_2$ (L = PPh_3, PPh_2Me, $Ph_2PCH_2CH_2$-PPh_2, or $AsPh_3$) with stannic chloride gave several products which were dependent upon the nature of L but were independent of Sn : Pt ratios greater than one (Scheme 1).

With PPh_2Me or $AsPh_3$ as ligands, perfluoropropene was recovered quantitatively. Similar displacement of the fluoro-olefin by stannic chloride was observed for the three tetrafluoroethylene complexes $\overline{Pt{\cdot}CF_2{\cdot}C}F_2L_2$ (L = PPh_3, PPh_2Me, and $AsPh_3$), C_2F_4 being recovered quantitatively.

In contrast, the reaction of $\overline{Pt{\cdot}CF_2{\cdot}C}F(CF_3)(PPh_3)_2$ with stannic chloride gave a white crystalline, non-tin-containing platinum species (I), containing four fluorine and two chlorine atoms. The i.r. spectrum of (I) exhibited a weak absorbance at 1638 cm^{-1} ($\nu_{C=C}$), and absorbances in the 800—1400 cm^{-1} region characteristic of fluorovinyl metal complexes.[17,18] The replacement

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[1] M. I. Bruce and F. G. A. Stone, *Preparative Inorganic Reactions*, 1968, **4**, 177.

[2] F. G. A. Stone, *Pure and Applied Chem.*, 1972, **30**, 551.

[3] D. M. Barlex, R. D. W. Kemmitt, and G. W. Littlecott, *Chem. Comm.*, 1969, 613.

[4] R. D. W. Kemmitt, B. Y. Kimura, G. W. Littlecott, and R. D. Moore, *J. Organometallic Chem.*, 1972, **44**, 403.

[5] R. D. W. Kemmitt and D. I. Nichols, *J. Chem. Soc.* (*A*), 1969, 1577.

[6] M. Green, R. B. L. Osborn, A. J. Rest, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1968, 2525.

[7] J. Ashley-Smith, M. Green, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1969, 3019.

[8] Jane Browning, M. Green, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1971, 453.

[9] A. J. Mukhedkar, M. Green, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1969, 3023.

[10] R. Fields, M. M. Germain, R. N. Haszeldine, and P. W. Wiggans, *J. Chem. Soc.* (*A*), 1970, 1969.

[11] R. Burt, M. Cooke, and M. Green, *J. Chem. Soc.* (*A*), 1970, 2975 and references cited therein.

[12] T. D. Coyle, R. B. King, E. Pitcher, S. L. Stafford, P. M. Treichel, and F. G. A. Stone, *J. Inorg. Nuclear Chem.*, 1961, **20**, 172.

[13] A. J. Mukhedkar, V. A. Mukhedkar, M. Green, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1970, 3166.

[14] P. K. Maples, M. Green, and F. G. A. Stone, *J.C.S. Dalton*, 1973, 388 and references cited therein.

[15] J. Browning, H. D. Empsall, M. Green, and F. G. A. Stone, *J.C.S. Dalton*, 1973, 381.

[16] M. J. Hacker, G. W. Littlecott, and R. D. W. Kemmitt, *J. Organometallic Chem.*, 1973, **47**, 189.

[17] E. Pitcher and F. G. A. Stone, *Spectrochim. Acta*, 1961, **17**, 1244.

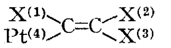
[18] H. C. Clark and W. S. Tsang, *J. Amer. Chem. Soc.*, 1967, **89**, 533.

of two fluorine atoms by chlorine with formation of a fluorovinyl group implies the presence of a Pt–Cl bond and incorporation of a chlorine atom in the vinyl moiety. Support for such a structure was obtained from the ^{19}F n.m.r. of (I) which showed only two multiplets (rel. CCl_3F, 0·0 p.p.m.) centred at 66·2 [3F, J_{PtF} 28·1 Hz] and 115·7 [1F, J_{PtF} 136·8 Hz] p.p.m. The ^{195}Pt–F coupling constants of both multiplets were much less than those commonly found in $Pt\cdot C(CF_3){:}C$ ($J_{Pt\alpha CF_3}$ 120—150 Hz) or $Pt\cdot CF{:}C$ ($J_{Pt\alpha CF}$ 450—500 Hz) substituted Pt^{II} fluorovinyl compounds.[18] Thus the vinyl function must contain both a fluorine atom and CF_3 group substituted on the β-carbon with a chlorine atom occupying the α-carbon site. In addition, the ^{195}Pt–F$_\beta$ coupling constant recorded is in the range (80—180 Hz) of those reported [18,19] for vinyl systems containing β-fluorine atoms *cis* to platinum. Each line of the basic β-CF_3 and β-CF resonance pattern was further split into a triplet by coupling with ^{31}P nuclei, suggesting the presence of stereochemically equivalent *trans*-PPh_3 groups. Confirmation of the presence of *trans* phosphine ligands was achieved by preparing the PPh_2Me analogue of (I) through a phosphine ligand-exchange reaction. It should be noted that $Pt(Cl)[C(Cl){:}CF(CF_3)](PPh_2Me)_2$ (II) was not formed in the direct reaction of $\overline{Pt\cdot CF_2\cdot C}F(CF_3)(PPh_2Me)_2$ with stannic chloride. The ^{19}F n.m.r. spectrum of (II) was virtually identical to that of (I), while the ^{1}H phosphine methyl resonance pattern showed a sharp 1 : 2 : 1 triplet at τ 7·90 characteristic of methyl groups coupled to two *trans* ^{31}P nuclei.[20] Further reaction of either (I) or (II) with stannic chloride did not occur even after a prolonged period under reflux (48 h) in benzene.

Analytical, spectral, and other physical data for the fluorocarbon complexes

	Compound	M.p.	Yield (%)	Analyses * C	H	F	Cl	P or As	M
(I)	$Pt(Cl)[CCl{:}CF(CF_3)](PPh_3)_2$	170—174 ‡	63	51·7(52·0)	3·4(3·6)	8·2(8·4)	7·8(7·9)	6·7(6·9)	882(902)
(II)	$Pt(Cl)[CCl{:}CF(CF_3)](PPh_2Me)_2$	173	57	43·6(43·3)	3·4(3·4)	9·9(10·2)	9·3(9·7)		
(III)	$Pt(Cl)[CF{:}CF(CF_3)](diphos)$	295—300 ‡	43	45·5(45·8)	3·3(3·8)	11·9(12·5)	5·1(4·7)		615(760)
(VIII)	$Pt(Cl)[C(CF_3){:}CF(CF_3)](PPh_3)_2$	290—291	76	50·9(51·3)	3·3(3·2)	14·4(14·2)	4·0(3·8)	6·7(6·6)	935(935)
(IX)	$Pt(Cl)[C(CF_3){:}CF(CF_3)](PPh_2Me)_2$	195—196	41	44·0(44·3)	3·3(3·2)	16·6(16·4)	4·4(4·4)	7·6(7·6)	776(812)
(X)	$Pt(Cl)[C(CF_3){:}CF(CF_3)](diphos)$	221—222	44	44·6(44·5)	3·1(3·0)	16·2(16·4)	4·5(4·4)		
(XI)	$Pt(Cl)[CCl{:}CF_2](PPh_3)_2$	257—259 ‡	67	53·5(53·2)	3·6(3·4)	4·5(4·0)	8·3(8·7)		

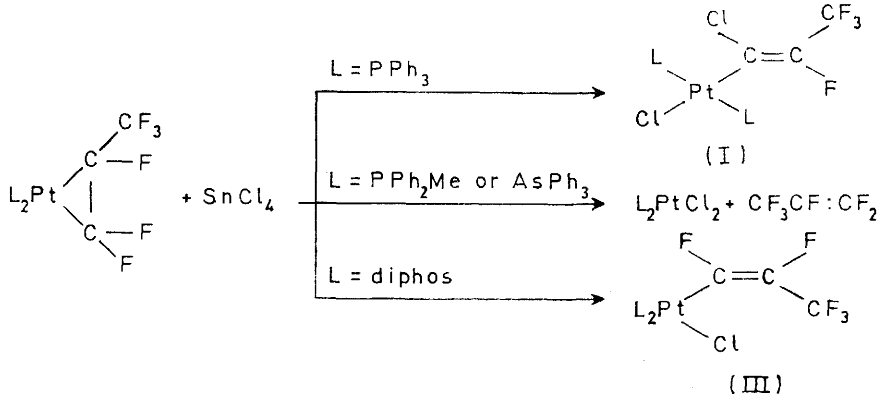
^{19}F Chemical shifts (p.p.m.) [a] and coupling constants (Hz)



	Compounds	$X^{(1)}$	$X^{(2)}$	$X^{(3)}$	$\delta X^{(1)}$	$\delta X^{(2)}$	$\delta X^{(3)}$	$J^{(1-2)}$	$J^{(1-3)}$	$J^{(2-3)}$	$J^{(4-1)}$	$J^{(4-2)}$	$J^{(4-3)}$	Comments
(I)	$Pt(Cl)[CCl{:}CF(CF_3)](PPh_3)_2$	Cl	CF_3	F		66·2	115·7			14·0		28·1	136·8	*b*
(II)	$Pt(Cl)[CCl{:}CF(CF_3)](PPh_2Me)_2$	Cl	CF_3	F		65·8	116·3			13·6		25·0	134·0	*c*
(III)	$Pt(Cl)[CF{:}CF(CF_3)](diphos)$	F	F	CF_3	99·0	153·2	66·4	38·2	9·1	16·0	352·3			
(VIII)	$Pt(Cl)[C(CF_3){:}CF(CF_3)](PPh_3)_2$	CF_3	F	CF_3	50·7	102·3	66·9	18·4	1·5	11·2	124·0	278	19·0	*d*
(IX)	$Pt(Cl)[C(CF_3){:}CF(CF_3)](PPh_2Me)_2$	CF_3	F	CF_3	49·6	102·2	66·9	15·0	2·0	12·1	87·0	200	17·8	*e*
(X)	$Pt(Cl)[C(CF_3){:}CF(CF_3)](diphos)$	CF_3	F	CF_3	50·4	100·1	68·0	18·0	2·1	12·2	80·1	208	18·1	*f*

* Calculated values given in parentheses. ‡ With decomposition.

[a] Measured in dichloromethane solution, relative to CCl_3F (0·0 p.p.m.) internal standard. [b] $J_{P,X(1)}$ 3·4, $J_{P,X(3)}$ 5·3. [c] $J_{P,X(1)}$ 3·0, $J_{P,X(3)}$ 5·3, $|J_{PH}+J_{P'H}|$ 7·4, J_{PtH} 15·0. [d] $J_{P,X(1)}$ 2·0. [e] $J_{P,X(1)}$ 6·4, J_{PH} 4·6, 5·0, J_{PtH} 10·4, 21·2. [f] $J_{P,X(1)}$ 6·2.



SCHEME 1

The reaction of $\overline{Pt\cdot CF_2\cdot C}F(CF_3)(diphos)$ with stannic chloride resulted in the loss of a single fluorine atom and the isolation of the platinum-perfluoropropenyl complex (III). The i.r. spectrum of (III) showed a band at 1650 cm^{-1} indicating the presence of a vinyl group.

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[19] A. J. Rest, D. T. Rosevear, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1967, 66.

[20] J. M. Jenkins and B. L. Shaw, *J. Chem. Soc.* (*A*), 1966, 770.

The ^{19}F n.m.r. spectrum consisted of three multiplets centred at 66·4 (3F), 99·0 [1F, J_{PtF} 353 Hz], and 153 [1F, J_{PtF} 72·0 Hz] p.p.m. The large ^{195}Pt–F coupling constant recorded for the 99·0 p.p.m. signal is good evidence for a fluorine atom attached to a carbon bonded to platinum, while the $J_{F\alpha F\beta}$ (Table, 38·2 Hz) coupling value is in the range of those reported for *cis* vinyl fluorine atoms and is much less than that expected for *trans* fluorine nuclei.[18,19] These facts together with the nearly identical chemical shift values of (III) compared with Pt(Cl)[*cis*-CF⁚CF(CF$_3$)](PEt$_3$)$_2$ [18] confirm the structure proposed (Scheme 1). Compound (III) was completely inert to further reaction with stannic chloride.

Reaction of stannic chloride with perfluoropropene in benzene under vigorous conditions (100 °C, two weeks) led to quantitative recovery of unchanged fluoro-olefin. No evidence of chlorination was observed.

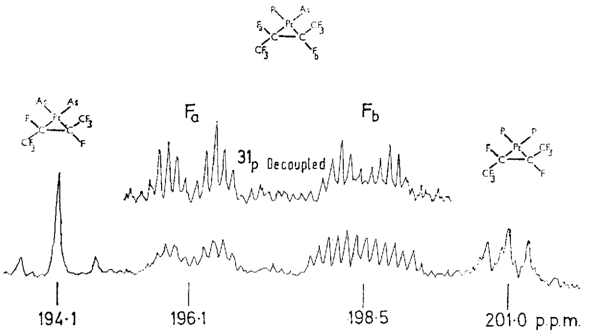
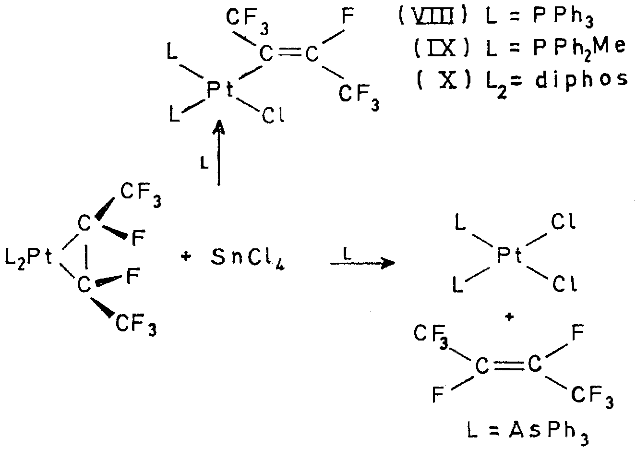


FIGURE ^{19}F N.m.r. spectrum (CF region) of an equimolar mixture of $\overline{\mathrm{Pt{\cdot}CF(CF_3){\cdot}C}}\mathrm{F(CF_3)(AsPh_3)_2}$ and PPh$_3$ in dichloromethane solution

To test the generality and stereochemical course of the above reactions, compounds of the type $\overline{\mathrm{Pt{\cdot}CF(CF_3){\cdot}C}}\mathrm{F(CF_3)L_2}$ (L = PPh$_3$, PPh$_2$Me, diphos, and AsPh$_3$) were prepared and treated with stannic chloride. Reaction of an excess of a *cis*/*trans* mixture (1 : 4) of perfluorobut-2-ene with *trans*-stilbene-bis(triphenylphosphine)platinum yielded a single isomer of $\overline{\mathrm{Pt{\cdot}CF(CF_3){\cdot}C}}\mathrm{F(CF_3)(PPh_3)_2}$ (IV). The ^{19}F n.m.r. showed a doublet at 68·2 [3F, J_{PF} 9·0, J_{PtF} 78 Hz] and a triplet at 201 [1F, J_{PtF} 68 Hz] p.p.m. The triplet pattern is typical of an X resonance of an AA′XX′ system ($|J_{PF} + J_{P'F}|$ 52·4 Hz), arising from strong J_{FF} coupling. Such a resonance pattern may result from either a *cis* or a *trans* arrangement of the substituents on the co-ordinated fluoro-olefin, and has been observed in the spectra of both isomers of $\overline{\mathrm{Pt{\cdot}CFCl{\cdot}C}}\mathrm{FCl(PPh_3)_2}$.[21]

The reaction of an excess of perfluorobut-2-ene with tetrakis(triphenylarsine)platinum also afforded a single isomer $\overline{\mathrm{Pt{\cdot}CF(CF_3){\cdot}C}}\mathrm{F(CF_3)(AsPh_3)_2}$ (V). The ^{19}F n.m.r. spectrum of (V) showed two singlets at 68·3 [3F, J_{PtF} 92 Hz] and 194·1 [1F, J_{PtF} 95 Hz] p.p.m. (see Figure). That (IV) and (V) have the same stereochemistry for the co-ordinated olefin was demonstrated by the direct conversion of (V) into (IV) by reaction with 2 mol. equiv. of triphenylphosphine, followed by examination of the i.r. spectrum. Similar ligand-exchange reactions of (V) with diphenylmethylphosphine and bisdiphenylphosphinoethane gave $\overline{\mathrm{Pt{\cdot}CF(CF_3){\cdot}C}}\mathrm{F(CF_3)(PPh_2Me)_2}$ (VI) and $\overline{\mathrm{Pt{\cdot}CF(CF_3){\cdot}C}}\mathrm{F(CF_3)(diphos)}$ (VIII) respectively. The ^{19}F spectrum of (VI) was similar to (IV) and exhibited an AA′XX′ pattern in the CF spectral region. Compound (VII) was too insoluble for n.m.r. measurement. Thus all perfluorobut-2-ene complexes prepared have an identical olefin stereochemistry but one which could not be established directly from their ^{19}F n.m.r. spectra.

In an effort to measure directly J_{FF}, and thus establish the stereochemistry of compounds (IV)—(VII) an attempt was made to prepare an unsymmetrical ligand-substituted perfluorobut-2-ene complex. Reaction of 1 mol. equiv. of triphenylphosphine with (V) yielded an equilibrium mixture in solution of (IV), (V), and $\overline{\mathrm{Pt{\cdot}CF(CF_3){\cdot}C}}\mathrm{F(CF_3)(PPh_3)(AsPh_3)}$ (1 : 1 : 4). An accumulated ^{19}F n.m.r. spectrum in the CF region is shown in the Figure. The resonance pattern of the environmentally different fluorine atoms F(*trans* to AsPh$_3$) and F(*trans* to PPh$_3$) are clearly resolved, and $J_{F_aF_b}$ can be measured directly from the F$_a$ pattern or from the ^{31}P decoupled F$_b$ pattern. The measured $J_{F_aF_b}$ coupling of 60 Hz is close to that reported for $J_{trans\text{-}FF}$ (39—44 Hz) in a number of fluoro-olefin Pt, Ru,[11] and Os [22] complexes, and is much larger than the corresponding $J_{cis\text{-}FF}$ (7—10 Hz) values reported. From the above data, compounds (IV)—(VII) must contain the ligand CF$_3$CF⁚CFCF$_3$ in the *trans*-configuration.



SCHEME 2

Stannic chloride reacted with the perfluorobut-2-ene platinum compounds according to Scheme 2. The formation of vinyl species from compounds (IV), (VI), and (VII) was evidenced by the presence of a weak $\nu_{C=C}$ absorbance at 1630—1640 cm^{-1} in the i.r. spectra of the

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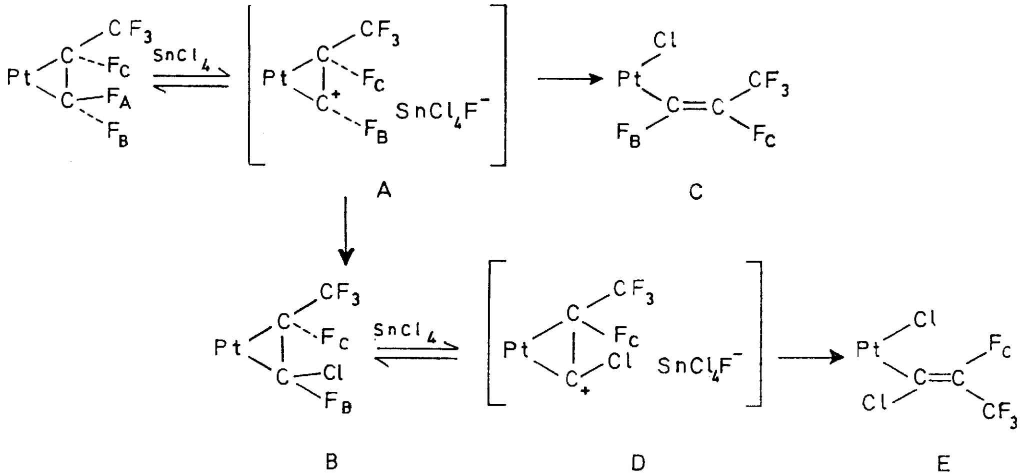
[21] J. Ashley-Smith, M. Green, and D. C. Wood, *J. Chem. Soc.* (*A*), 1970, 1847.

[22] M. Cooke, M. Green, and T. A. Kuc, *J. Chem. Soc.* (*A*), 1971, 1200.

products (VIII)—(X). The ^{19}F n.m.r. spectra of (VIII)—(X) were similar, so a detailed discussion is limited to the diphenylmethylphosphine species (IX). Data are presented in the Table for the three isostructural compounds.

Three widely separated resonance patterns (area ratio 3 : 3 : 1) were recorded in the ^{19}F spectrum of (IX). The multiplet at 49·6 p.p.m. (J_{PtF} 87 Hz) was assigned to a $Pt{\cdot}C(CF_3){:}CX_2$ group, based on the large ^{195}Pt–F coupling constant, while the equally intense multiplet at 66·9 p.p.m. (J_{PtF} 17 Hz) was assigned to a $Pt{\cdot}CX{\cdot}C(CF_3)X$ group. The remaining signal at 102·2 p.p.m. arises from a fluorine atom $Pt{\cdot}CX{:}CXF$. The stereochemistry of the perfluorobut-2-en-2-yl group $Pt{\cdot}C(CF_3){:}CF(CF_3)$ was determined on the basis of the $J_{CF_3\text{-}CF_3}$ coupling constants. In previous work on various $C(CF_3){:}CR(CF_3)$ [R = H or Me] [18,23-25] and $C(CF_3){:}CF(CF_3)$ [26] derivatives, compounds with *trans*-CF$_3$ groups showed coupling constants of 1—3 Hz in their ^{19}F spectra whereas the corresponding coupling between *cis*-CF$_3$ groups was 12—15 Hz. The $J_{CF_3\text{-}CF_3}$ values for complexes (VIII)—(X) ranged from 1·5 to 2·1 Hz, indicating a *trans*-stereochemistry for the CF$_3$ groups about the carbon–carbon bonds. The ^{1}H n.m.r. spectrum of (IX) confirmed a relative *cis*-configuration for the phosphine ligands. The methyl signal consisted of two doublets at τ 8·10 and 8·08, characteristic of environmentally non-equivalent *cis* diphenylmethylphosphine ligands.



SCHEME 3

Treatment of (V) with stannic chloride displaced the perfluorobut-2-ene, with no evidence for formation of any perfluorobutenyl platinum complex; a result similar to that described above for the bis(triphenylarsine)-platinum tetrafluoroethylene or perfluoropropene complexes.

DISCUSSION

Reaction of stannic chloride with the fluoro-olefin-platinum compounds either involved olefin displacement, or Lewis acid attack by the tin(IV) chloride on one or more of the fluorine atoms of the co-ordinated fluoro-olefin with subsequent formation of perfluoro- or chloro-fluoro-vinyl species. Both the initial site of attack and the subsequent formation of vinyl compounds appears to be highly stereospecific. A mechanistic pathway is proposed in Scheme 3, illustrated by the reactions of perfluoropropene complexes but consistent with the results found for the other fluoro-olefins.

Initial attack on co-ordinated perfluoropropene may occur at any of three sites F_A, F_B, or F_C. Attack and carbon–fluorine bond fission at F_C were eliminated by the fact that the CF$_3$ group in the vinyl product was always observed in the β-position. If the carbon atom of the cationic species A formed by attack at F_A or F_B effectively becomes sp^2 hybridized then a loss of stereospecificity would be expected in the vinyl products. On the other hand, retention of configuration about the carbon atom prior to rearrangement would result in either a *cis* or a *trans* arrangement of the fluorine atoms in the products dependent on whether attack occurred at either F_A or F_B. Non-selective attack at F_A and F_B under the same stereochemical constant would again lead to an isomeric mixture of vinyl compounds.

Stereochemical retention about the cationic carbon centre in the proposed intermediate A was strongly suggested by the observation that a single vinyl isomer containing two *trans* CF$_3$ groups was formed in every case from the reaction of stannic chloride with *trans*-perfluorobut-2-ene complexes. Retention may result from formation of a ' tight ' ion-pair as has been proposed [27] to account for the retention of stereochemistry in the thermal vinyl rearrangement of co-ordinated chlorofluoro-olefins.

Based on the above, and on the fact that a single

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[23] J. B. Wilford and F. G. A. Stone, *Inorg. Chem.*, 1965, **4**, 93.

[24] W. R. Cullen, D. S. Dawson, and G. E. Styan, *Canad. J. Chem.*, 1965, **43**, 3392.

[25] H. C. Clark and R. J. Puddephatt, *Inorg. Chem.*, 1970, **9**, 2670.

[26] R. B. King and W. C. Zipperer, *Inorg. Chem.*, 1972, **11**, 2119.

[27] M. Green and G. Parker, *J.C.S. Dalton*, 1973, 2099.

cis-vinyl isomer *C* was isolated in the reaction of $\overline{\mathrm{Pt{\cdot}CF_2{\cdot}C}}\mathrm{F(CF_3)(diphos)}$, selective attack must occur at $\mathrm{F_A}$.

While participation of an intermediate of type A directly accounts for the stereospecific formation of perfluorovinyl compounds from $\overline{\mathrm{Pt{\cdot}CF_2{\cdot}C}}\mathrm{F(CF_3)(diphos)}$ and $\overline{\mathrm{Pt{\cdot}CF(CF_3){\cdot}C}}\mathrm{F(CF_3)L_2}$ it does not immediately account for the formation of a chlorofluorovinyl species from $\overline{\mathrm{Pt{\cdot}CF_2{\cdot}C}}\mathrm{F(CF_3)(PPh_3)_2}$. However, this result can be rationalised on the basis of an internal return reaction involving attack of one of the chlorine atoms of the intimately associated anionic tin species at the original site of carbon–fluorine fission. Subsequent fluorine abstraction could yield an intermediate D analogous to A which would undergo rearrangement to a chlorine-containing vinyl group. In order to test the ability of an intermediate such as B to undergo the necessary reaction with stannic chloride, the reaction of $\overline{\mathrm{Pt{\cdot}CFCl{\cdot}C}}\mathrm{F_2(PPh_3)_2}$ was studied. A single vinyl product was obtained in high yield and shown to be $\mathrm{Pt(Cl)(CCl{:}CF_2)(PPh_3)_2}$ by independent synthesis by thermal rearrangement of $\overline{\mathrm{PtCCl_2{\cdot}C}}\mathrm{F_2(PPh_3)_2}$. This result not only confirms the reactivity of species such as B toward attack by tin(IV) chloride but indicates that such attack occurs selectively at the fluorine atom bound to the chlorine substituted carbon. Thus attack at $\mathrm{F_B}$ in B is expected with subsequent formation of intermediate D which stereospecifically rearranges to the product E, observed. The possibility that E might be formed by secondary attack of $\mathrm{SnCl_4}$ on the α fluorine atom of any perfluorovinyl compound present was eliminated by the observation that both $\mathrm{Pt(Cl)[}$*trans*-$\mathrm{CF{:}CF(CF_3)](diphos)}$ and $\mathrm{PtCl(CF{:}CF_2)(PPh_3)_2}$ were inert toward reaction with stannic chloride even under the most stringent conditions (80 °C, 3 days).

The relative rate of tin(IV) chloride reaction at platinum leading to fluoro-olefin displacement, as compared with attack on the co-ordinated fluoro-olefin, is dependent on the nature of both the fluoro-olefin and the appended ligands. Quantitative fluoro-olefin displacement occurred with all tetrafluoroethylene complexes, and with the triphenylarsine perfluoropropene or perfluorobut-2-ene platinum compounds. In contrast only a small or often undetectable amount of displacement was observed with the $\mathrm{PPh_3}$ and diphos-substituted perfluoropropene, perfluorobut-2-ene, and chlorotrifluoroethylene compounds. These results parallel qualitatively the rate of displacement of co-ordinated fluoro-olefin by iodine, tetrafluoroethylene being rapidly liberated, perfluoropropene being slowly displaced, and the perfluorobut-2-ene platinum complexes being inert towards reaction with iodine.

The reactivity of $\mathrm{Pt{\cdot}CFX{\cdot}}$ toward Lewis acid attack is a function of the geminal substituent (X) and varies in the order $\mathrm{Cl > F > CF_3}$. The least electronegative germinal substituent would be expected, on the basis of simple inductive effects, to have the greater activating influence. However, steric factors may influence reactivity as suggested by the lower activating effect compared with chlorine of the equally electronegative [28] but more bulky $\mathrm{CF_3}$ group.

The broad scope and high stereoselectivity of these reactions offers a synthetic route to a wide range of vinyl platinum complexes unobtainable by conventional procedures. Results [29] on hexafluoro-butadiene systems indicate that a wide range of perfluorobutadienylmetal complexes may be generated by Lewis acid attack by both stannic chloride or bromide.

EXPERIMENTAL

^{1}H and ^{19}F N.m.r. spectra were recorded on a Varian Associates HA100 spectrometer at 100 and 94·1 MHz, respectively. I.r. spectra were recorded with a Perkin-Elmer 457 spectrophotometer using Nujol and hexachlorobutadiene mulls. Solvents were dried and distilled under nitrogen, and all operations were conducted in an atmosphere of dry oxygen-free nitrogen. Stannic chloride was distilled under nitrogen immediately prior to use. Tetrafluoroethylene, $\overline{\mathrm{Pt{\cdot}CF_2{\cdot}C}}\mathrm{F_2L_2}$ and perfluoropropene $\overline{\mathrm{Pt{\cdot}CF_2{\cdot}C}}\mathrm{F(CF_3)L_2}$ complexes were prepared by published procedures.[6,30]

Reaction between $\overline{\mathrm{Pt{\cdot}CF_2{\cdot}C}}\mathrm{F_2(PPh_3)_2}$ *and* $\mathrm{SnCl_4}$.—A stirred benzene (30 ml) solution of $\overline{\mathrm{Pt{\cdot}CF_2{\cdot}C}}\mathrm{F_2(PPh_3)_2}$ (0·90 g, 1·1 mmol) in a sealed evacuated flask was treated with stannic chloride (0·36 g, 1·4 mmol). Volatile products were fractionated in a vacuum system giving 0·92 mmol of tetrafluoroethylene (identified by its i.r. spectrum). The white precipitate remaining was filtered off, giving *cis*-$\mathrm{PtCl_2(PPh_3)_2}$ (0·78 g, 90%). Similar results were obtained for all $\overline{\mathrm{PtCF_2{\cdot}C}}\mathrm{F_2L_2}$ complexes ($\mathrm{L = PPh_2Me, AsPh_3}$, or diphos).

Reaction of $\overline{\mathrm{Pt{\cdot}CF_2{\cdot}C}}\mathrm{F(CF_3)(PPh_3)_2}$ *with* $\mathrm{SnCl_4}$.—Stannic chloride (0·42 g, 1·6 mmol) was added dropwise to a stirred solution of $\overline{\mathrm{Pt{\cdot}CF_2{\cdot}C}}\mathrm{F(CF_3)(PPh_3)_2}$ (0·87 g, 1·0 mmol) in benzene (40 ml). A red oil was precipitated during the addition. The mixture was allowed to react for 8 h and solvent was removed *in vacuo*. The residue was washed with n-hexane and then extracted with benzene. Addition of n-hexane and cooling to 0° afforded white *crystals* of (I) (0·57 g, 63%) from dichloromethane–ethanol; ν(C=C) 1638 cm^{-1}. The red oil was dissolved in dichloromethane. Addition of ethanol gave *cis*-$\mathrm{PtCl_2(PPh_3)_2}$ (0·15 g) which was identified by its i.r. spectrum.

Synthesis of $\mathrm{Pt(Cl)[CCl{:}CF(CF_3)](PPh_2Me)_2}$.—A mixture of $\mathrm{PtCl[CCl{:}CF(CF_3)](PPh_3)_2}$ (0·45 g, 0·5 mmol) and diphenylmethylphosphine (0·20 g, 1 mmol) in benzene (20 ml) was refluxed for 12 h. The light yellow solution was filtered and solvent was removed *in vacuo*. Crystallisation

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[28] J. J. Lagowski, *Quart. Rev.*, 1959, **13**, 233.

[29] P. K. Maples, M. Green, and F. G. A. Stone, unpublished work.

[30] R. D. W. Kemmitt and R. D. Moore, *J. Chem. Soc.* (*A*), 1971, 2472.

from dichloromethane–n-hexane gave white *crystals* of (II) (0·22 g, 57%); ν(C=C) 1632 cm^{-1}.

Reaction of $\text{Pt}\cdot\text{CF}_2\cdot\text{CF(CF}_3\text{)}$(diphos) *with* SnCl_4.—Stannic chloride (0·26 g, 1·0 mmol) was added dropwise to a stirred suspension of $\text{Pt}\cdot\text{CF}_2\cdot\text{CF(CF}_3\text{)}$(diphos) (0·74 g, 1·0 mmol). The platinum compound rapidly dissolved to yield a red oily precipitate and a clear pale yellow solution. The mixture was allowed to react for 4 h and solvent was removed *in vacuo*. The residue was washed with n-hexane and extracted with benzene. Solvent was removed *in vacuo* and the residue crystallised from dichloromethane–n-hexane to give *crystals* of (III) (0·32 g, 43%) from dichloromethane–methanol; ν(C=C) 1650 cm^{-1}.

Synthesis of $\text{Pt}\cdot\text{CF(CF}_3\text{)}\cdot\text{CF(CF}_3\text{)(PPh}_3\text{)}_2$.—A solution of stilbenebis(triphenylphosphine)platinum (0·90 g, 1·0 mmol) in benzene (30 ml) in a Carius tube was treated with an excess of perfluorobut-2-ene (4 mmol) at −196° and the solution was allowed to react in the sealed tube at room temperature for 48 h. Solvent was removed *in vacuo* and the residue crystallised from dichloromethane–n-hexane to give white *crystals* (0·73 g, 79%) or (IV), m.p. 224—255° (Found: C, 52·0; H, 3·4; F, 16·6; P, 6·4%; *M*, 823 (C_6H_6). $\text{C}_{40}\text{H}_{30}\text{F}_8\text{P}_2\text{Pt}$ requires C, 52·2; H, 3·3; F, 16·6; P, 6·7%; *M*, 919). ^{19}F n.m.r.: 68·2 (d, 6F, CF_3, J_{PF} 9·0, J_{PtF} 78·1 Hz) and 201 (t, 2F, CF, $|J_{\text{PF}} + J_{\text{P'F}}|$ 52·4, J_{PtF} 68·0 Hz) p.p.m.; ^{1}H n.m.r.: τ 2·41 (m, 30H, C_6H_5).

Synthesis of $\text{Pt}\cdot\text{CF(CF}_3\text{)}\cdot\text{CF(CF}_3\text{)(AsPh}_3\text{)}_2$.—A suspension in benzene (50 ml) of tetrakistriphenylarsineplatinum (3·0 g, 2·1 mmol) was placed into a Carius tube, and treated with an excess of perfluorobut-2-ene (5 mmol). The solution was heated at 60° for 18 h. The yellow solution was filtered off and the solvent removed *in vacuo*. Crystallisation of the residue from dichloromethane–n-hexane gave white *crystals* of (V) (1·2 g, 57%), m.p. 199—201° (Found: C, 47·4; H, 3·1; F, 14·9. $\text{C}_{40}\text{H}_{30}\text{F}_8\text{As}_2\text{Pt}$ requires C, 47·6; H, 3·0; F, 15·1%); ^{19}F n.m.r.: 68·3 (s, 6F, CF_3, J_{PtF} 92·2 Hz) and 194·1 (s, 2F, CF, J_{PtF} 95·0 Hz) p.p.m.; ^{1}H n.m.r.: τ 2·36 (m, 30H, C_6H_5).

Synthesis of $\text{PtCF(CF}_3\text{)}\cdot\text{CF(CF}_3\text{)(PPh}_2\text{Me)}_2$.—A solution of $\text{Pt}\cdot\text{CF(CF}_3\text{)}\cdot\text{CF(CF}_3\text{)(AsPh}_3\text{)}_2$ (1·0 g, 1·0 mmol) and diphenylmethylphosphine (0·40 g, 2·0 mmol) was refluxed in benzene (20 ml) for 24 h. The solution was filtered and the solvent removed *in vacuo*. The yellow oil remaining was crystallised from dichloromethane–ethanol to give white *crystals* of (VI) (0·65 g, 82%), m.p. 161—162° (Found: C, 45·0; H, 3·3; F, 19·2; P, 7·7%; *M*, 718 (C_6H_6). $\text{C}_{30}\text{H}_{26}\text{F}_8\text{P}_2\text{Pt}$ requires C, 45·3; H, 3·5; F, 19·2; P, 7·8%; *M*, 795); ^{19}F n.m.r. 68·0 (d, 6F, CF_3, J_{PF} 9·8, J_{PtF} 80·0 Hz) and 200·9 (t, 2F, CF, $|J_{\text{PF}} + J_{\text{P'F}}|$ 54·8, J_{PtF} 66·2 Hz) p.p.m.; ^{1}H n.m.r.: τ 8·10 (d, 12H, CH_3, J_{PH} 3·8, J_{PtH} 14·0 Hz) and 2·43 (m, 20H, C_6H_5).

Synthesis of $\text{Pt}\cdot\text{CF(CF}_3\text{)}\cdot\text{CF(CF}_3\text{)}$(diphos).—A solution of $\text{Pt}\cdot\text{CF(CF}_3\text{)}\cdot\text{CF(CF}_3\text{)(AsPh}_3\text{)}_2$ (0·8 g, 0·8 mmol) and 1,2-bis(diphenylphosphino)ethane (0·32 g, 0·8 mmol) was refluxed in benzene (50 ml) for 6 h. Solvent was removed *in vacuo* and the residue was crystallised from dichloromethane–methanol to give white *crystals* of (VII) (0·55 g, 87%), m.p. 262—263° (Found: C, 45·3; H, 3·3; F, 19·0; P, 7·8. $\text{C}_{30}\text{H}_{29}\text{F}_8\text{P}_2\text{Pt}$ requires C, 45·4; H, 3·1; F, 19·7; P, 7·8%). The compound was too insoluble for ^{19}F n.m.r. measurements.

Reaction of $\text{Pt}\cdot\text{CF(CF}_3\text{)}\cdot\text{CF(CF}_3\text{)(PPh}_3\text{)}_2$ *with* SnCl_4.—Stannic chloride (0·39 g, 1·5 mmol) was added slowly to a benzene (50 ml) solution of $\text{Pt}\cdot\text{CF(CF}_3\text{)}\cdot\text{CF(CF}_3\text{)(PPh}_3\text{)}_2$ (0·91 g, 1·0 mmol). The mixture was stirred for 12 h during which time a light yellow oil was precipitated from the colourless solution. The solution was decanted, filtered, and the solvent removed *in vacuo*. The residue was washed with n-hexane and crystallised from dichloromethane–ethanol. Recrystallisation gave white *crystals* of (VIII) (0·71 g), ν(C=C) 1651 cm^{-1}.

Reaction of $\text{Pt}\cdot\text{CF(CF}_3\text{)}\cdot\text{CF(CF}_3\text{)(PPh}_2\text{Me)}_2$ *with* SnCl_4.—As above, reaction of stannic chloride (0·26 g, 1·0 mmol) and $\text{Pt}\cdot\text{CF(CF}_3\text{)}\cdot\text{CF(CF}_3\text{)(PPh}_2\text{Me)}_2$ (0·48 g, 0·6 mmol) afforded white *crystals* of (IX) (0·20 g) from dichloromethane–ethanol ν(C=C) 1659 cm^{-1}.

Reaction of $\text{Pt}\cdot\text{CF(CF}_3\text{)}\cdot\text{CF(CF}_3\text{)}$(diphos) *with* SnCl_4.—As above, reaction of stannic chloride (0·31 g, 1·2 mmol) and $\text{Pt}\cdot\text{CF(CF}_3\text{)}\cdot\text{CF(CF}_3\text{)}$(diphos) (0·80 g, 1·0 mmol) gave white *crystals* of (X) (0·36 g) from dichloromethane–ethanol ν(C=C) 1663 cm^{-1}.

Reaction of $\text{Pt}\cdot\text{CFCl}\cdot\text{CF}_2\text{(PPh}_3\text{)}_2$ *with* SnCl_4.—To a stirred solution of $\text{Pt}\cdot\text{CFCl}\cdot\text{CF}_2\text{(PPh}_3\text{)}_2$ (0·87 g, 1·0 mmol) in benzene (60 ml) was slowly added stannic chloride (0·52 g, 2·0 mmol). The mixture was allowed to react for 2 h. Solvent was removed *in vacuo* and the resulting solid was washed with n-hexane. Crystallisation from dichloromethane–ethanol gave white *crystals* of (XI) (0·57 g); $\nu_{\text{C=C}}$ 1689 cm^{-1}. The compound was too insoluble for ^{19}F n.m.r. measurements.

We thank the U.S.A.F. Office of Scientific Research for support.

[3/378 *Received*, 19*th February*, 1973]