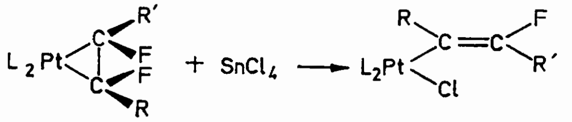
Tin(IV) Halide Promoted Vinyl Rearrangement of Hexafluorobuta-1,3-diene–Platinum Complexes

By **Peter K. Maples, Michael Green, F. Gordon A. Stone,*** and (in part) **John L. Spencer,** Department of Inorganic Chemistry, The University, Bristol BS8 1TS

The major products of reactions of stilbenebis(triphenylphosphine)platinum or tetrakis(triphenylarsine)platinum with hexafluorobuta-1,3-diene are complexes in which one double bond of the diene is co-ordinated to the metal, *viz.* $\overline{\mathrm{Pt\cdot CF_2\cdot C}}\mathrm{F\cdot CF{:}CF_2(L_2)}$ [L = PPh_3 or $AsPh_3$]. The arsenic compound reacts with diphenylmethylphosphine to give $\overline{\mathrm{Pt\cdot CF_2\cdot C}}\mathrm{F\cdot CF{:}CF_2(PPh_2Me)_2}$. Reactions of these hexafluorobutadiene complexes with stannic chloride or bromide in benzene afford the complexes *trans*-$\mathrm{Pt(X)(CF{:}CFCF{:}CF_2)L_2}$ (X = Cl; L = PPh_3, PPh_2Me, $AsPh_3$; X = Br; L = PPh_3, PPh_2Me). The ^{19}F n.m.r. spectra of the new compounds are described, and the mechanistic implication of the stereochemistry of the products discussed.

REACTIONS of several platinum–fluoro-olefin complexes with stannic chloride under mild conditions have been shown to result in stereoselective carbon–fluorine bond cleavage and concomitant vinyl group formation (Scheme 1).[1] The activating effect of co-ordination on the reactivity of the fluoro-olefin toward Lewis acid attack was demonstrated by the non-reactivity of the unco-ordinated fluoro-olefin under similar experimental conditions. In all the above cases, reaction occurred at one or more of the fluorine atoms α to the metal. Here we report on the reaction of stannic chloride and stannic bromide with platinum hexafluorobuta-1,3-diene compounds containing a potentially reactive centre not directly attached to the co-ordinated carbon atoms. The identity of the new compounds obtained was established by elemental analysis (Table 1), i.r., ^1H, and ^{19}F n.m.r. spectroscopy (Tables 2 and 3).



SCHEME 1

$R = F$; $R' = CF_3$; L = diphos
$R = CF_3$; $R' = CF_3$; L = PPh_3, PPh_2Me, diphos
$R = Cl$; $R' = F$; L = PPh_3

Hexafluorobuta-1,3-diene reacts with $Fe(CO)_5$,[2] $Ni(AsMe_2Ph)_4$,[3] $Ni(CNBu^t)_4$,[4] and $PtPr^i_2(C_8H_{12})$ [5] to give complexes, the ^{19}F n.m.r. spectra of which are interpretable only in terms of the compounds containing a five membered ring structure $\overline{\mathrm{M\cdot CF_2\cdot CF{:}CF\cdot C}}\mathrm{F_2}$ (M = Fe, Ni, or Pt) since two signals (relative intensity 2 : 1) are observed. An *X*-ray crystallographic study [6] of the iron compound has confirmed the presence of the ring in this complex. In contrast, hexafluorobuta-1,3-diene has been reported previously [7] to react with tetrakis(triphenylphosphine)platinum to yield a complex $\overline{\mathrm{Pt\cdot CF_2\cdot C}}\mathrm{F\cdot CF{:}CF_2(PPh_3)_2}$ formulated as containing both a co-ordinated and free olefinic function. The ^{19}F n.m.r. spectrum failed, however, to reveal a signal due to the CF group co-ordinated to platinum and this was attributed [7] to a low signal-to-noise ratio. In the present study repeated attempts to prepare this complex according to the published method, and by the reaction of hexafluorobuta-1,3-diene with (*trans*-stilbene)bis(triphenylphosphine)platinum, led instead to the isolation of a compound (I) with the same molecular composition but with different physical, chemical, and spectroscopic properties. The purity of the hexafluorobuta-1,3-diene used was established by its ^{19}F n.m.r. spectrum which was identical to the published spectrum.[8]

The i.r. spectrum of (I), recorded in Nujol, showed a sharp band at 1758 cm^{-1} characteristic of an unco-ordinated $CF{:}CF_2$ group.[9] The ^{19}F spectrum showed six separated resonance patterns of equal intensity (Table 2). The chemical shifts and coupling interactions of the multiplets at 99·5, 110·4, and 161·4 p.p.m. are typical for those of a vinyl group, $CF{:}CF_2$, not directly bonded to a transition metal.[9,10] Upon ^{31}P

---

[1] P. K. Maples, M. Green, and F. G. A. Stone, *J.C.S. Dalton*, 1973, 2069.
[2] R. L. Hunt, D. M. Roundhill, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1967, 982.
[3] J. Browning, M. Green, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1971, 453.
[4] M. Green, S. K. Shakshooki, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1971, 2828.
[5] J. Browning, H. D. Empsall, M. Green, and F. G. A. Stone, *J.C.S. Dalton*, 1973, 382.
[6] P. B. Hitchcock and R. Mason, *Chem. Comm.*, 1967, 242.
[7] M. Green, R. B. L. Osborn, A. J. Rest, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1968, 2525.
[8] M. G. Barlow and K. W. Cheung, *J. Chem. Soc.* (*B*), 1970, 525.
[9] M. Green, N. Mayne, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1968, 902.
[10] D. W. McBride, E. Dudek, and F. G. A. Stone, *J. Chem. Soc.*, 1964, 1752.

TABLE 1

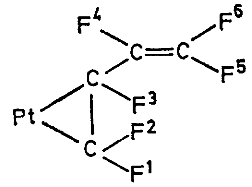
Analytical and physical data for the fluorocarbon complexes [a]

	Compound	M.p. (t/°C)	Yield (%)	C	H	F	Cl
(I)	$\overline{\mathrm{Pt{\cdot}CF_2{\cdot}C}}\mathrm{F{\cdot}CF{:}CF_2(PPh_3)_2}$ [b]	100—110 [c]	82	54·9 (54·5)	3·4 (3·4)	12·2 (12·9)	
(II)	$\overline{\mathrm{Pt{\cdot}CF_2{\cdot}C}}\mathrm{F{\cdot}CF{:}CF_2(AsPh_3)_2}$	160—161	47	49·5 (49·6)	3·0 (3·1)	11·6 (11·8)	
(III)	$\overline{\mathrm{Pt{\cdot}CF_2{\cdot}C}}\mathrm{F{\cdot}CF{:}CF_2(PPh_2Me)_2}$	155—157	73	47·4 (47·6)	3·3 (3·4)	15·5 (15·1)	
(IV)	$\mathrm{Pt(Cl)[CF{:}CFCF{:}CF_2](PPh_3)_2}$ [d]	230—231	68	53·4 (53·5)	3·4 (3·4)	10·0 (10·6)	3·8 (4·0)
(V)	$\mathrm{Pt(Cl)[CF{:}CFCF{:}CF_2](PPh_2Me)_2}$	174—175	53	46·1 (46·5)	3·4 (3·4)	11·9 (12·3)	4·0 (4·6)
(VI)	$\mathrm{Pt(Cl)[CF{:}CFCF{:}CF_2](AsPh_3)_2}$	177—178	39	48·5 (48·7)	3·1 (3·0)	9·8 (9·6)	3·1 (3·6)
(VII)	$\mathrm{Pt(Br)[CF{:}CFCF{:}CF_2](PPh_3)_2}$ [e]	237—240 [c]	51	50·8 (50·9)	3·2 (3·2)	9·8 (10·1)	7·8 (8·5) [f]
(VIII)	$\mathrm{Pt(Br)[CF{:}CFCF{:}CF_2](PPh_2Me)_2}$	182—183	24	44·1 (44·0)	3·5 (3·2)	11·2 (11·6)	9·5 (9·8) [f]

[a] Calculated values given in parentheses. [b] M, 917 (C_6H_6). Calc. 881. [c] With decomp. [d] M, 878 (C_6H_6). Calc. 897. [e] M, 950 (C_6H_6). Calc. 942. [f] Bromine analysis.

TABLE 2

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



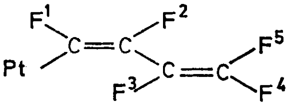
Compound	δ (1)	δ (2)	δ (3)	δ (4)	δ (5)	δ (6)
(I)	109·0	113·9	184·5	161·4	99·5	110·4
(II)	103·8	108·3	175·8	159·5	98·6	108·9

	$J(F^1F^2)$	$J(F^1F^3)$	$J(F^2F^3)$	$J(F^2F^4)$	$J(F^3F^4)$	$J(F^3F^5)$	$J(F^3F^6)$	$J(F^4F^6)$	$J(F^4F^5)$	$J(F^5F^6)$
(I) [b]	176·2	1·5	56·3	14·9	16·2	2·1	19·8	27·8	112·6	62·4
(II) [c]	171·0	—	56·1	17·1	15·9	4·4	20·1	30·1	110·3	56·1

[a] Measured in dichloromethane solution, relative to CCl_3F (0·0 p.p.m.) internal standard. [b] $J(PtF^4)$ 306 Hz. [c] $J(PtF^4)$ 401 Hz.

TABLE 3

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



Compound	δ (1)	δ (2)	δ (3)	δ (4)	δ (5)
(IV)	73·0	71·5	156·0	105·0	111·8
(V)	75·0	71·0	156·5	105·4	114·2
(VI)	73·2	69·1	155·8	105·0	113·2
(VIII)	75·2	70·8	156·1	105·1	113·9

	$J(F^1F^2)$	$J(F^1F^3)$	$J(F^1F^4)$	$J(F^1F^5)$	$J(F^1Pt)$	$J(F^2F^3)$	$J(F^2F^4)$	$J(F^2F^5)$	$J(F^3F^4)$	$J(F^3F^5)$	$J(F^3Pt)$	$J(F^4F^5)$
(IV)	42·1	1·9	7·0	8·0	232	23·2	13·9	29·6	27·8	108·2	269	68·0
(V) [b]	40·0	2·8	6·1	6·1	226	17·6	8·2	27·2	25·6	110·0	232	70·8
(VI)	38·8	1·3	6·0	7·4	220	20·8	12·3	27·6	27·2	109·8	240	67·7
(VIII) [c]	39·8	2·1	6·4	7·5	228	19·8	9·2	28·0	26·1	109·6	237	69·5

[a] Measured in dichloromethane solution, relative to CCl_3F (0·0 p.p.m.) internal standard. [b] $|J(PH) + J(P'H)|$ 4·2, $J(PtH)$ 17·0 Hz. [c] $|J(PH) + J(P'H)|$ 5·3, $J(PtH)$ 16·8 Hz.

decoupling, the AB pattern centred at 111·5 p.p.m. [J(AB) 176·2 Hz] was amenable to complete analysis and comparable to the spectral parameters determined for the CF_2 group of $\overline{\mathrm{Pt{\cdot}CF_2{\cdot}C}}\mathrm{F(CF_3)(PPh_3)_2}$ [δ(AB) 115·5 p.p.m., J(AB) 188 Hz].[7] The remaining high field multiplet at 184·5 p.p.m. occurred at a position characteristic of a fluorine nucleus *gem* to CF in a wide range of hexafluoropropene–metal complexes.[11-13] The reaction of (I) with iodine, or prolonged reaction with triphenylphosphine in benzene (reflux, 48 h), resulted in quantitative recovery of hexafluorobuta-1,3-diene.

These results are totally consistent with the structure $\overline{\mathrm{Pt{\cdot}CF_2{\cdot}C}}\mathrm{F{\cdot}CF{:}CF_2(PPh_3)_2}$ for (I), whereas the structure of the compound originally reported must have been incorrectly assigned. A determination of the correct structure of this species has been prevented by our inability to resynthesise it.

The reaction of hexafluorobuta-1,3-diene with tetrakis(triphenylarsine)platinum afforded (II). The ^{19}F n.m.r. spectrum of (II) was similar to (I). However, the solid state (Nujol) i.r. spectrum showed two bands in the $CF{:}CF_2$ spectral region at 1782 and 1761 cm^{-1}. In solution various samples of both (I) and (II) exhibited

---

[11] C. S. Cundy, M. Green, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1970, 1647.

[12] R. Burt, M. Cooke, and M. Green, *J. Chem. Soc.* (*A*), 1970, 2975.

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

an intense band in the i.r. *ca.* 1760 cm^{-1} but only a weak shoulder at 1782 cm^{-1}.

Since reactions of (I) and (II) with stannic chloride were to be examined, it was felt necessary to establish the molecular structure $\overline{\mathrm{Pt{\cdot}CF_2{\cdot}C}}\mathrm{FCF{:}CF_2(L_2)}$ by *X*-ray crystallography. Crystals of the arsenic compound (II) proved suitable for study but were observed to be of two forms by Penfold *et al.*[14]

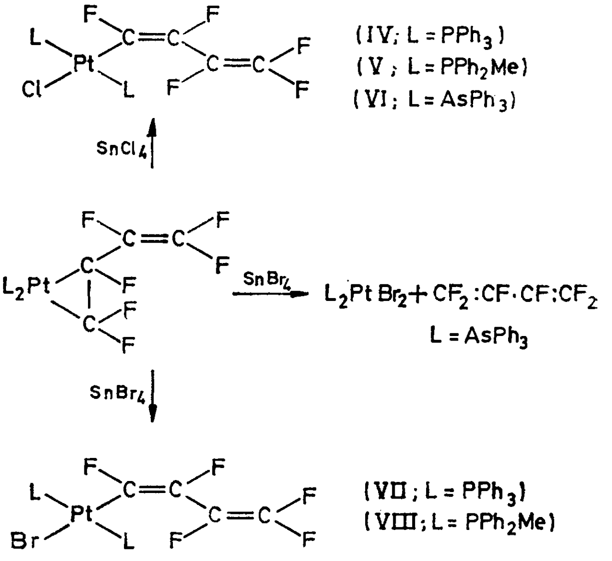
Single-crystal *X*-ray diffraction investigations were therefore undertaken on both, and it was thereby found that the two crystalline forms corresponded to the isomeric molecules $\overline{\mathrm{PtCF_2{\cdot}C}}\mathrm{FCF{:}CF_2(AsPh_3)_2}$ (IIa) and $\overline{\mathrm{PtCF_2{\cdot}CF{:}CF{\cdot}C}}\mathrm{F_2(AsPh_3)_2}$ (IIb) containing three- and five-membered rings, respectively. The ^{19}F n.m.r. spectrum of a hexafluoroplatina-cyclopent-3-ene complex if present in solution would be characterised by two resonances near 84 and 148 p.p.m. (int. 2 : 1).[5] However, careful searching of the ^{19}F spectra of the product from several reactions of $\mathrm{Pt(AsPh_3)_4}$ with $\mathrm{CF_2{:}CFCF{:}CF_2}$ revealed only the expected six peaks (Table 2) characteristic of the isomer $\overline{\mathrm{PtCF_2{\cdot}C}}\mathrm{FCF{:}CF_2(AsPh_3)_2}$ (IIa). We therefore conclude that the isomer $\overline{\mathrm{PtCF_2{\cdot}CF{:}CF{\cdot}C}}\mathrm{F_2}$-$\mathrm{(AsPh_3)_2}$ (IIb) is present in the mixture only in very small amount. Moreover, it was possible to convert (II) into (I) by reaction with two molecules of triphenylphosphine, and examination of the ^{19}F spectrum revealed an identical six band pattern to that (Table 2) shown by the product of reaction of $\mathrm{Pt(PPh_3)_4}$ with $\mathrm{CF_2{:}CFCF{:}CF_2}$. Therefore (I) also must very largely consist of the isomer $\overline{\mathrm{Pt{\cdot}CF_2{\cdot}C}}\mathrm{F{\cdot}CF{:}CF_2(PPh_3)_2}$.

A similar ligand exchange reaction of (II) with diphenylmethylphosphine gave $\overline{\mathrm{Pt{\cdot}CF_2{\cdot}C}}\mathrm{F{\cdot}CF{:}CF_2(PPh_2}$-$\mathrm{Me)_2}$ (III). The solution and solid state i.r. spectrum of (III) was virtually identical with that of (II). It was not possible, due to low solubility, to record the ^{19}F n.m.r. spectrum of (III). However, the ^{1}H phosphine methyl resonance pattern showed two doublets at τ 8·16 and 8·00; characteristic of environmentally non-equivalent *cis*-diphenylmethylphosphine ligands; a result consistent with an unsymmetrical co-ordinated fluorocarbon.

Although the isomers $\overline{\mathrm{Pt{\cdot}CF_2{\cdot}CF{:}CF{\cdot}C}}\mathrm{F_2(L_2)}$ [L = PPh$_3$ or AsPh$_3$] cannot be detected in the reaction products by ^{19}F n.m.r. spectroscopy and, therefore cannot be present to an extent greater than about 5%, nevertheless, as mentioned above, i.r. spectroscopy showed under certain conditions two bands in the $\mathrm{CF{:}CF_2}$ spectral region, indicating the presence of another form. However, in solution the second band (1782 cm^{-1}) was very weak. We tentatively suggest the following explanation for this phenomenon. On the basis of u.v. and ^{19}F n.m.r. data[8,15] hexafluorobuta-1,3-diene exists largely in the skew conformational form, although the presence of some *s*-transoid conformer has not been totally eliminated. Evidence for the co-ordination of the fluoro-olefin predominantly in the skew form in solution is suggested by the large Pt–F^4 constants (300—400 Hz) observed in the ^{19}F spectra for both (I) and (II). The platinum–F^4 distance in a skew conformation should be much less than in the *s*-transoid form, thus leading to strong through space coupling. The higher frequency weak i.r. band measured in dichloromethane may be due to the presence of small amounts of the *s*-transoid conformer which in the solid state spectrum of (II) becomes more predominant, as revealed by the increase in intensity of this band.

Having established that the products (I)—(III) are predominantly of the form $\overline{\mathrm{Pt{\cdot}CF_2{\cdot}C}}\mathrm{FF{:}CF_2(L_2)}$ their reactions with stannic chloride in stoicheiometric quantity were investigated. Isostructural non-tin containing platinum compounds (IV—VI) containing five fluorine and one chlorine atom (Scheme 2) were obtained. The ^{19}F n.m.r., and the i.r. spectra were so similar that detailed discussion is limited to the diphenylmethylphosphine platinum complex (V).

Formation of a butadienyl species was evidenced by the presence in the i.r. spectra of two groups of bands in the range 1600—1800 cm^{-1}. A single sharp band was recorded at 1759 cm^{-1} characteristic of a C=C group not adjacent to the metal.[16,17] In addition, a set of two bands at 1678 and 1664 cm^{-1} was observed in the region associated with C=C groups adjacent to a transition metal.[18] The ^{19}F spectrum of (V) (Table 3) exhibited



Scheme 2

---

[14] B. R. Penfold, R. G. Holloway, and Theresa J. McLennan, personal communication.

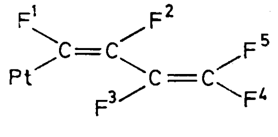
[15] A. A. Bothner-By and D. Jung, *J. Amer. Chem. Soc.*, 1968, **90**, 2342.

[16] S. L. Stafford and F. G. A. Stone, *Spectrochim. Acta*, 1961, **17**, 412.

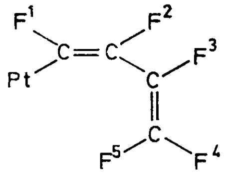
[17] E. Pitcher and F. G. A. Stone, *Spectrochim. Acta*, 1961, **17**, 1244.

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

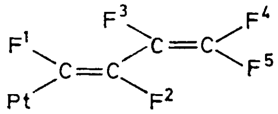
five multiplets of equal intensity, with splitting patterns expected for five spin-coupled non-equivalent fluorine nuclei. The six configurational possibilities for the perfluorobutadienyl group in (IV)—(VI) following attack at one of the co-ordinated olefinic fluorines are shown below:



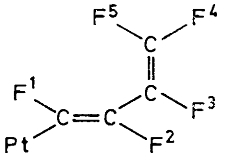
(a)



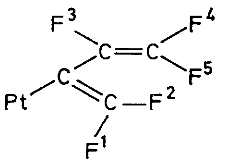
(b)



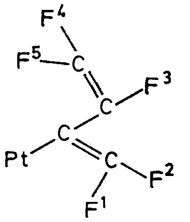
(c)



(d)



(e)



(f)

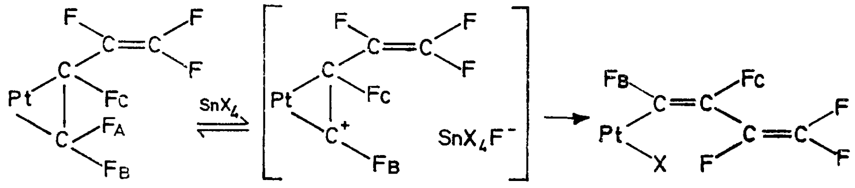
These include four geometric isomers which could arise through attack at either of the CF_2 fluorine atoms, and two isomers resulting from attack at the fluorine atom *gem* to the unco-ordinated olefin function. The chemical shifts and internal coupling value of the multiplets at 156·5 (F^3), 105·4 (F^4), and 114·2 (F^5) p.p.m. correspond to those expected for a $-CF{:}CF_2$ group not directly bonded to a metal.[9,10] The relatively large coupling of F^3 with platinum (*ca.* 230 Hz) is indicative of a small platinum–fluorine distance consistent with structure (a) or (e); thus making the other configurations unlikely. Of the remaining two patterns at 75·0 (F^1) and 71·0 (F^2) p.p.m. the higher field resonance also showed large Pt–F coupling [$J(PtF^1)$ 226 Hz] as expected for either structure (a) or (e). However, the coupling $J(F^1F^2)$ of *ca.* 40 Hz is in the range very characteristic for $J[FF(cis)]$ (35—60 Hz) and is much less than that commonly found for $J[FF(gem)]$ (90—110 Hz) in metal–$CF{:}CF_2$ systems.[7,18,19] From the above ^{19}F n.m.r. data, therefore, compounds (IV)—(VI) must contain the perfluorobutadienyl group bonded as in (a). In addition, the phosphine ligands are *trans* as evidenced by the ^1H-phosphine methyl resonance pattern showing a sharp 1 : 2 : 1 triplet at τ 7·71.[20] The presence of two i.r. bands of equal intensity in the region 1660—1680 cm^{-1} both in the solid state and in solution may result from the presence of isomers due to limited rotation about the C2–C3 bond, detectable on the i.r. time scale but unobservable by examination of the n.m.r. spectrum.

The rapid, high yield, reaction of (I)—(III) with stannic chloride led us to investigate the corresponding reaction with the much weaker Lewis acid stannic bromide (Scheme 2). In a similar manner, reaction of $\overline{\mathrm{Pt{\cdot}CF_2{\cdot}C}}\mathrm{F{\cdot}CF{:}CF_2(PPh_3)_2}$ or $\overline{\mathrm{Pt{\cdot}CF_2{\cdot}C}}\mathrm{F{\cdot}CF{:}CF_2(PPh_2Me)_2}$ with stannic bromide led to formation of perfluorobutadienyl complexes (VII) and (VIII) of configuration (a), containing a *trans* bromide ligand. In contrast, reaction of $\overline{\mathrm{Pt{\cdot}CF_2{\cdot}C}}\mathrm{F{\cdot}CF{:}CF_2(AsPh_3)_2}$ with $SnBr_4$ resulted in the isolation of $PtBr_2(AsPh_3)_2$ and displacement of hexafluorobuta-1,3-diene.

No evidence for any reaction of unco-ordinated hexafluorobuta-1,3-diene with stannic chloride or stannic bromide was observed under the reaction conditions which led to formation of perfluorobutadienyl complexes from (I)—(III). In addition, compounds (IV)—(VIII) were completely inert toward further reaction with the tin halides in benzene, even under vigorous conditions (90 °C, 1 week).

DISCUSSION

Study of the reaction of compounds (I)—(III) with the tin halides offered an opportunity to investigate the relative reactivity of co-ordinated and unco-ordinated fluoro-olefin moieties present within a single molecular species. Although six potentially reactive centres exist, the structures of the products (IV)—(VIII) indicate that attack of the Lewis acids occurs only at the co-ordinated olefinic function. Subsequent stereospecific molecular rearrangement yielded a single perfluorobutadienyl species. The stereochemistry of the products is entirely consistent with the mechanism shown below, and is similar to that suggested to account for the related reactions of other fluoro-olefin platinum complexes.[1] No evidence was observed for chlorine or bromine substitution in the butadienyl moiety resulting from an internal-return reaction involving the intimately associated anionic tin species.[1]



X = Cl or Br

---

[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 highly reactive nature of these systems towards Lewis acid attack was shown by the ready reaction of (I) and (III) with stannic bromide, the latter being a thousand times weaker as a Lewis acid than stannic chloride on the basis of spectroscopic studies of 1 : 1 adducts of these halides with substituted anilines.[21] In contrast, the reaction of the other platinum–fluoro-olefin complexes previously studied (Scheme 1) with stannic bromide results only in fluoro-olefin displacement.

EXPERIMENTAL

^{1}H and ^{19}F N.m.r. spectra were recorded on a Varian Associates HA 100 spectrometer at 100 and 94·1 MHz, respectively. I.r. spectra were recorded with a Perkin-Elmer 457 spectrophotometer using Nujol mulls or dichloromethane solutions. 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.

Synthesis of $\overline{\mathrm{Pt{\cdot}CF_2{\cdot}C}}\mathrm{F{\cdot}CF{:}CF_2(PPh_3)_2}$.—A solution of stilbenebis(triphenylphosphine)platinum (1·35 g, 1·5 mmol) in benzene (40 ml) in a Carius tube was treated with an excess of hexafluorobutadiene (3 mmol) at −196°, and the solution was allowed to react in the sealed tube at room temperature for 24 h. Solvent was removed *in vacuo*, and the residue crystallised from dichloromethane–ethanol to give white *crystals* of (I) (1·08 g), $\nu(\mathrm{C{=}C})_{\mathrm{max.}}$ 1782sh, 1757s cm^{-1} ($\mathrm{CH_2Cl_2}$).

Synthesis of $\overline{\mathrm{Pt{\cdot}CF_2{\cdot}C}}\mathrm{F{\cdot}CF{:}CF_2(AsPh_3)_2}$.—A suspension of tetrakistriphenylarsineplatinum (3·6 g, 2·5 mmol) in benzene (60 ml) was placed in a Carius tube, and reacted with an excess of hexafluorobuta-1,3-diene (4 mmol). The solution was heated at 50° for 24 h. The yellow solution was filtered, and solvent removed *in vacuo*. Crystallisation of the yellow oily residue from dichloromethane–n-hexane gave white *crystals* of (II) (1·14 g), $\nu(\mathrm{C{=}C})_{\mathrm{max.}}$ 1782sh, 1760s cm^{-1} ($\mathrm{CH_2Cl_2}$).

Synthesis of $\overline{\mathrm{Pt{\cdot}CF_2{\cdot}C}}\mathrm{F{\cdot}CF{:}CF_2(PPh_2Me)_2}$.—A solution of $\overline{\mathrm{Pt{\cdot}CF_2{\cdot}C}}\mathrm{F{\cdot}CF{:}CF_2(AsPh_3)_2}$ (0·97 g, 1·0 mmol) and diphenylmethylphosphine (0·40 g, 2·0 mmol) was refluxed in ether (50 ml) for 18 h. The solvent was removed *in vacuo* and the yellow oil remaining was dissolved in dichloromethane. Slow addition of n-hexane caused precipitation of white solid. Recrystallisation from dichloromethane–methanol gave white *crystals* of (III) (0·55 g), $\nu(\mathrm{C{=}C})_{\mathrm{max.}}$ 1779sh, 1759s cm^{-1} ($\mathrm{CH_2Cl_2}$).

Reaction of $\overline{\mathrm{Pt{\cdot}CF_2{\cdot}C}}\mathrm{F{\cdot}CF{:}CF_2(PPh_3)_2}$ *with* $\mathrm{SnCl_4}$.—A stirred benzene solution (30 ml) of $\overline{\mathrm{Pt{\cdot}CF_2{\cdot}C}}\mathrm{F{\cdot}CF{:}CF_2(PPh_3)_2}$ (1·4 g, 1·6 mmol) was slowly treated with stannic chloride (0·44 g, 1·7 mmol) and allowed to react for 1 h. Precipitation of a red oil immediately occurred with formation of a clear yellow solution. The solution was decanted, filtered, and solvent removed *in vacuo*. The residue was washed with n-hexane and crystallised from dichloromethane–n-hexane. Recrystallisation from dichloromethane–ethanol gave white *crystals* of (IV) (0·98 g), $\nu(\mathrm{C{=}C})_{\mathrm{max.}}$ 1753m, 1687s, 1663s cm^{-1} ($\mathrm{CH_2Cl_2}$). A similar procedure was followed for the synthesis of all of the perfluorobutadienylplatinum compounds.

Reaction of $\overline{\mathrm{Pt{\cdot}CF_2{\cdot}C}}\mathrm{F{\cdot}CF{:}CF_2(PPh_2Me)_2}$ *with* $\mathrm{SnCl_4}$.—As above, reaction of stannic chloride (0·23 g, 0·9 mmol) with $\overline{\mathrm{Pt{\cdot}CF_2{\cdot}C}}\mathrm{F{\cdot}CF{:}CF_2(PPh_2Me)_2}$ (0·60 g, 0·8 mmol) for 2 h gave white *crystals* of (V) (0·33 g) from dichloromethane, $\nu(\mathrm{C{=}C})_{\mathrm{max.}}$ 1759m, 1678s, 1664s cm^{-1} ($\mathrm{CH_2Cl_2}$).

Reaction of $\overline{\mathrm{Pt{\cdot}CF_2{\cdot}C}}\mathrm{F{\cdot}CF{:}CF_2(AsPh_3)_2}$ *with* $\mathrm{SnCl_4}$.—As above, reaction of stannic chloride (0·26 g, 1 mmol) with $\overline{\mathrm{Pt{\cdot}CF_2{\cdot}C}}\mathrm{F{\cdot}CF{:}CF_2(AsPh_3)_2}$ (0·97 g, 1 mmol) for 30 min gave white crystals of (VI) (0·38 g) from methylene chloride–hexane, $\nu(\mathrm{C{=}C})_{\mathrm{max.}}$ 1775m, 1690s, 1683s cm^{-1} ($\mathrm{CH_2Cl_2}$).

Reaction of $\overline{\mathrm{Pt{\cdot}CF_2{\cdot}C}}\mathrm{F{\cdot}CF{:}CF_2(PPh_3)_2}$ *with* $\mathrm{SnBr_4}$.—Stannic bromide (0·44 g, 1 mmol) was added slowly to a stirred solution of $\overline{\mathrm{Pt{\cdot}CF_2{\cdot}C}}\mathrm{F{\cdot}CF{:}CF_2(PPh_3)_2}$ (0·88 g, 1 mmol) in benzene (40 ml). After 2 h the yellow solution was filtered, and the solvent removed *in vacuo*. The yellow solid remaining was dissolved in dichloromethane. Addition of ethanol afforded white *crystals* of (VII) (0·46 g), $\nu(\mathrm{C{=}C})_{\mathrm{max.}}$ 1780m, 1683s, 1670s cm^{-1} ($\mathrm{CH_2Cl_2}$).

Reaction of $\overline{\mathrm{Pt{\cdot}CF_2{\cdot}C}}\mathrm{F{\cdot}CF{:}CF_2(PPh_2Me)_2}$ *with* $\mathrm{SnBr_4}$.—To a stirred solution of $\overline{\mathrm{Pt{\cdot}CF_2{\cdot}C}}\mathrm{F{\cdot}CF{:}CF_2(PPh_2Me)_2}$ (0·60 g, 0·79 mmol) in benzene (25 ml) was slowly added (0·35 g, 0·79 mmol) of stannic bromide. An immediate deep red colour developed with precipitation of a red oil; the mixture was allowed to react for 30 min. The solution was decanted and solvent removed *in vacuo*. Crystallisation of the yellow oily residue from dichloromethane–methanol gave white *crystals* of (VIII) (0·15 g), $\nu(\mathrm{C{=}C})_{\mathrm{max.}}$ 1767m, 1685s, 1687sh cm^{-1} ($\mathrm{CH_2Cl_2}$).

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

[3/2387 *Received, 21st November, 1973*]

---

[21] D. P. N. Satchell and J. W. Wardell, *J. Chem. Soc.*, 1964, 4134.