Reactions of Co-ordinated Ligands. Part III.[1] Mechanism of the Rearrangement of Platinum Chlorofluoro-olefin Complexes

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Activation parameters have been measured for the rearrangement of $[\mathrm{PtCF_2{\cdot}CFXL_2}]$ to $[\mathrm{PtX(CF{=}CF_2)L_2}]$ ($\mathrm{L = PPh_3, X = Cl}$ or Br; $\mathrm{L = PMePh_2, X = Cl}$). The results are compared with those previously obtained for the rearrangement of the related chloro-olefin complexes. The stereochemistry of the rearrangement of *cis*- and *trans*-$[\mathrm{PtCFCl{\cdot}CFClL_2}]$ ($\mathrm{L = PPh_3}$ or $\mathrm{PMePh_2}$) to $[\mathrm{PtCl(}$*cis*$\mathrm{\text{-}CF{=}CFCl)L_2]}$ and $[\mathrm{PtCl(}$*trans*$\mathrm{\text{-}CF{=}CFCl)L_2]}$ have been studied, the stereochemistry of the fluoro-olefin being retained. A mechanism involving an intimate ion-pair is discussed.

ONE of the more interesting reactions which co-ordinated electronegatively substituted olefins have been shown to undergo is the so-called ' vinyl-rearrangement reaction ' as illustrated by the rearrangement of chlorotrifluoroethylenebis(triphenylphosphine)platinum,[2,3] $[\mathrm{PtCF_2{\cdot}CFCl(PPh_3)_2}] \longrightarrow [\mathrm{PtCl(CF{=}CF_2)(PPh_3)_2}]$, and of tetrachloroethylenebis(triphenylphosphine)platinum,[4] $[\mathrm{PtCCl_2{\cdot}CCl_2(PPh_3)_2}] \longrightarrow [\mathrm{PtCl(CCl{=}CCl_2)(PPh_3)_2}]$. It was shown in subsequent studies that similar rearrangements occurred in Ni,[5] Pd,[6] and Ru[7] chemistry. More recently the possibility has emerged of a reverse ' vinyl-rearrangement ' where the migrating group is hydrogen.

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[1] Part II, M. Green, Susan Heathcock, and D. C. Wood, *J.C.S. Dalton*, 1973, 1564.

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

[3] M. Green, A. J. Mukhedkar, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1970, 947.

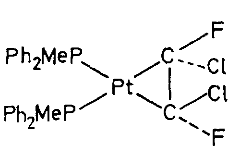
[4] W. J. Bland, J. Burgess, and R. D. W. Kemmitt, *J. Organometallic Chem.*, 1968, **15**, 217; W. J. Bland, J. Burgess, and R. D. W. Kemmitt, *ibid.*, 1969, **18**, 199.

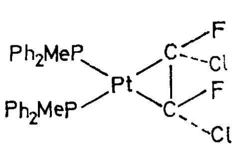
[5] J. Ashley-Smith, M. Green, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1969, 3109.

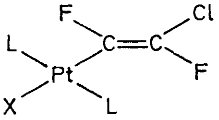
[6] M. Green, A. J. Mukhedkar, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1969, 3023; H. D. Empsall, M. Green, S. K. Shakshooki, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1971, 3472.

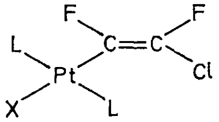
[7] R. Burt M. Cooke, and M. Green, *J. Chem. Soc.* (*A*), 1970, 2975.

This is indicated by work with Pt[8] and Mo[9] systems where the rearrangements $[\mathrm{PtH\{N{=}C(CF_3)_2\}(PPh_3)_2}] \longrightarrow [\overline{\mathrm{Pt\cdot NH\cdot C}}\mathrm{(CF_3)_2(PPh_3)_2}]$ and $[(\pi\text{-}\mathrm{C_5H_5})_2\mathrm{MoH\cdot C(CO_2R)}^{t}\mathrm{{=}CH(CO_2R)\}}] \longrightarrow [(\pi\text{-}\mathrm{C_5H_5})_2\overline{\mathrm{Mo\cdot CH(CO_2R)\cdot C}}\mathrm{H(CO_2R)}]$ have been established.


(IIIa)

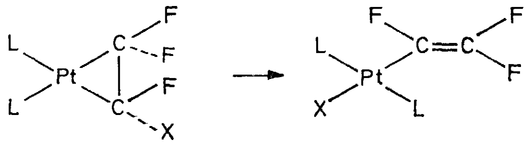

(IIIb)


(IVa) L = PMePh$_2$, X = Cl
(Va) L = PPh$_3$, X = OAc


(IVb) L = PMePh$_2$, X = Cl
(Vb) L = PPh$_3$, X = OAc

A study of the mechanism of the vinyl rearrangement of platinum chloro-olefin complexes has been reported;[4] however, aside from this investigation very little is known about the reaction paths followed. We now report experiments directed towards understanding more fully the rearrangement of platinum fluoro-olefin complexes, where the migrating group is a halogen.

As starting point it was important to compare activation parameters for the rearrangement of platinum fluoro- and chloro-olefin complexes. Synthetic experiments had shown[2,3] that chloro- and bromo-trifluoroethylene complexes rearrange smoothly in polar solvents (Scheme 1).


(L = PPh$_3$, X = Cl or Br; L = PMePh$_2$, X = Cl or Br)

Scheme 1

The kinetics of the rearrangement of the complexes $[\overline{\mathrm{PtCF_2\cdot C}}\mathrm{FXL_2}]$ (X = Cl, L = PPh$_3$ or PMePh$_2$; X = Br, L = PPh$_3$) were studied in ethanol as solvent. The reactions were conveniently followed spectrophotometrically by measurement of the decrease in the absorbance at 292 nm. The initial rates of reaction were, in each case, proportional to the concentration of the complex and plots of log $(A - A_\infty)$ against time gave linear plots for the first 50% of reaction. Average rate constants thus obtained are shown in Table 1, and from these values the activation parameters $\Delta H^\ddagger$ and $\Delta S^\ddagger$ were calculated.

These results indicate that the reactivity of the complexes is dependent on both the nature of the migrating halide and on the relative σ-donor and π-acceptor properties of the phosphine ligand. Examination of the activation parameters shows that a difference in the enthalpies of *ca.* 5 kcal mol^{-1} is the major factor in determining the relative rates of reaction; the difference between the entropy values obtained is smaller than the sum of the calculated standard deviation. Comparison of the activation parameters[4] in ethanol for $[\overline{\mathrm{PtCCl_2\cdot C}}\mathrm{Cl_2(PPh_3)_2}]$ ($\Delta H^\ddagger = 21\cdot4 \pm 1$, $\Delta S^\ddagger = -9 \pm 4$) and $[\overline{\mathrm{PtCCl_2\cdot C}}\mathrm{HCl(PPh_3)_2}]$ ($\Delta H^\ddagger = 17\cdot6 \pm 1$ kcal mol^{-1}, $\Delta S^\ddagger = -10 \pm 4$ cal K^{-1} mol^{-1}), shows that not only is the fluorine-substituted system less reactive, but that this arises from a higher activation enthalpy and a more positive activation entropy; the latter implying a dissociative process.

Table 1

Average first-order rate constants (k) and enthalpies ($\Delta H^\ddagger$) and entropies ($\Delta S^\ddagger$) of activation for rearrangement of $[\overline{\mathrm{PtCF_2\cdot C}}\mathrm{FX(L_2)}]$ in ethanol

	10^5k/s^{-1}					$\Delta H^\ddagger$	$\Delta S^\ddagger$
Complex	45·5 °C	48·9 °C	53·4 °C	57·5 °C	59·7 °C	kcal mol^{-1}	cal mol^{-1} K^{-1}
$\overline{\mathrm{PtCF_2C}}\mathrm{FCl(PPh_3)_2}$	4·8	8·5	14·5	21	45	29·3 ± 1·3	+9 ± 5
$\overline{\mathrm{PtCF_2C}}\mathrm{FCl(PMePh_2)_2}$	29·0	48·0	85·0	121·0	—	24·9 ± 0·6	+2 ± 3
$\overline{\mathrm{PtCF_2C}}\mathrm{FBr(PMePh_2)_2}$	30·0	54·0	86·0	127·0	—	24·6 ± 0·8	+2 ± 3

A more qualitative comparison indicates that the rate of rearrangement of the [Pt(olefin)(PPh$_3$)$_2$] complexes increases as the olefin varies in the sequence $\mathrm{CF_2{:}CFCl}$ > *trans*-CFCl:CFCl > *cis*-CFCl:CFCl. However, it is difficult to distinguish between possible electronic and steric effects, but the observation (see also below) that the *cis*-1,2-difluoro-1,2-dichloroethylene complex rearranges more rapidly than the corresponding *trans*-isomer suggests the importance of the release of steric compression as a driving force. The more positive activation entropies observed (Table 1) would suggest that a more dissociative reaction path is followed for the chlorotrifluoroethylene complex than the tetrachloroethylene complex.

A potential source of further information about the transition state or intermediates involved in these reactions was available from the previous observation[10] that

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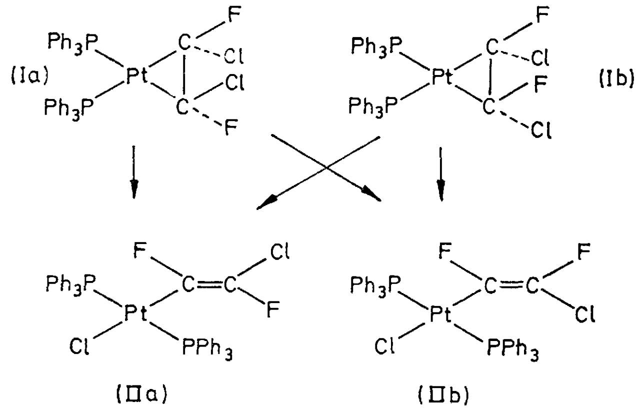
[8] B. Cetinkaya, M. F. Lappert, and J. McMeeking, *Chem. Comm.*, 1971, 215.

[9] A. Nakamura and S. Otsuka, *J. Amer. Chem. Soc.*, 1972, **94**, 1886.

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

mixtures other than 1 : 1 of the two isomers (Ia) and (Ib) can be obtained from the reaction of *cis*- and *trans*-CFCl=CFCl with $[\mathrm{Pt(stilbene)(PPh_3)_2}]$. As shown in Scheme 2 the rearrangement of these isomeric fluoro-olefin complexes can afford (IIa) and (IIb); the relative proportion of the two vinyl isomers obtained depending on the reaction path (mechanism) followed. Further work[11] showed that it was possible to utilise the solubility difference between (Ia) and (Ib) to effect a partial separation, and by careful crystallisation of large samples from methylene dichloride–hexane, samples containing up to 90% of the more soluble *trans*-isomer (Ia) and up to 70% of the less soluble *cis*-isomer (Ib) were obtained. The varying isomer mixtures thus obtained were converted (refluxing n-butanol) into a mixture of the vinyl complexes (IIa) and (IIb); the isomer distribution was determined by integration of the ^{19}F n.m.r. resonances of the respective complexes. The results are in Table 2.



SCHEME 2

TABLE 2

Stereochemical results of the rearrangement of $[\overline{\mathrm{PtCFCl{\cdot}C}}\mathrm{FCl(PPh_3)_2}]$

	Reaction conditions		Fraction[a] of *trans*-isomer in:	
Medium	t/°C	Time/h	Reactant	Product
Bu^{n}OH	118	10	0·3	0·2[b]
Bu^{n}OH	118	36	0·4	0·35
Bu^{n}OH	118	10	0·4	0·36
Bu^{n}OH	118	24	0·5	0·4
Bu^{n}OH	118	12	0·65	0·5
Bu^{n}OH	118	12	0·75	0·6
Bu^{n}OH	118	20	0·80	0·7[b]
Bu^{n}OH	118	20	0·90	0·75[b]
EtOH	78	24	0·70	0·60
Bu^{n}OH–LiOAc[c]	118	12	0·65	0·5
HOAc–LiOAc[c]	118	12	0·65	0·5

[a] Expressed as [*trans*-$\overline{\mathrm{PtCFCl{\cdot}C}}\mathrm{FCl(PPh_3)_2}$]/*cis* + *trans* and [PtCl(*trans*-CF=CFCl)$\mathrm{(PPh_3)_2}$]/*cis* + *trans* vinyl complex. [b] Values estimated from peak heights, as minor isomer signal too weak for integration. [c] 0·5M-LiOAc.

Although the results become less accurate at low isomer concentration, it is clear that the stereochemistry of the olefinic substituents is essentially retained during the 'vinyl-rearrangement' in n-butanol, both in the presence and absence of added lithium acetate. A similar result was obtained in glacial acetic acid with LiOAc present.

It was clearly important to know whether the stereochemistry of the reaction was effected by the nature of the phosphine ligands. The synthesis of the more soluble methyldiphenylphosphine complexes (IIIa) and (IIIb) was therefore examined. Reaction of 1,2-dichloro-1,2-difluoroethylene (1 : 1 *cis*–*trans*-mixture) with tetrakis(methyldiphenylphosphine)platinum afforded a crystalline isomeric mixture of (IIIa) and (IIIb) characterised by elemental analysis and i.r. and n.m.r. spectroscopy. In refluxing ethanol the mixture rearranged to give chloro(2-chloro-1,2-difluorovinyl)bis(methyldiphenylphosphine)platinum isolated as a white crystalline mixture (1 : 1) of the isomers (IVa) and (IVb); the appearance of the *MeP* resonances as an apparent triplet confirms the relative *trans*-configuration of the phosphine ligands.

Unlike the bis(triphenylphosphine) system it proved more difficult to achieve a substantial separation of the fluoro-olefin complex isomers. However, some separation was achieved (crystallisation from methylene dichloride–hexane). Rearrangement of samples of (IIIa) and (IIIb) in ethanol, containing 60, 50, and 35% of (IIIa) afforded mixtures of the vinyl complexes containing respectively the vinyl complex (IVa) in 55, 50, and 30%. Thus, these observations suggest a similar high degree of retention of stereochemistry on rearrangement.

The question as to the relative reactivities of the *cis*- and *trans*-1,2-dichloro-1,2-difluoroethylene complexes was also examined. Rearrangement of a mixture (1 : 1) of (IIIa) and (IIIb) in ethanol followed by ^{19}F n.m.r. spectroscopy (Table 3) showed that the *cis*-isomer (IIIb) rearranged more rapidly than the *trans*-isomer (IIIa), thus supporting an earlier observation[10] with the (Ia) and (Ib) complexes.

We have shown previously[3] that the vinyl rearrangement of $[\overline{\mathrm{PtCF_2{\cdot}C}}\mathrm{FClL_2}]$ (L = $\mathrm{PPh_3}$ or $\mathrm{PMePh_2}$) is promoted by the presence of $\mathrm{Ag^+}$; the reaction with silver acetate affords $[\mathrm{PtOAc(CF{=}CF_2)L_2}]$. In refluxing acetone a mixture (1 : 1) of (Ia) and (Ib) reacted similarly with silver acetate to give white crystals of an acetato-complex, which was shown by elemental analysis and i.r. and n.m.r. spectroscopy to consist of a 1 : 1 mixture of (Va) and (Vb). A similar rearrangement of a mixture

TABLE 3

Rearrangement of *cis*–*trans*-$[\overline{\mathrm{PtCFCl{\cdot}C}}\mathrm{FCl(PMePh_2)_2}]$ in n-butanol (118 °C)

	Relative abundance			
Time/min	(IIIb)	(IIIa)	(IVb)	(IVa)
0	1	1	—	—
10	0·8	1	0·2[a]	—
20	0·4	1	0·9	0·3
30	0·3	0·8	1	0·4
45	0·1[a]	0·3	1	0·7
60	—	0·2[a]	1	0·8
180	—	—	1	0·9

[a] Estimated from signal height of ^{19}F n.m.r. resonance.

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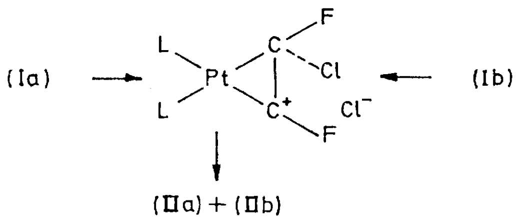
[11] G. Parker, Ph.D. Thesis, University of Bristol, 1972.

containing 80% of (Ia) gave a product containing 60% of (Va). Comparison with the results obtained in n-butanol (Table 2) shows that there is clearly a loss of stereospecificity in the presence of Ag^+.

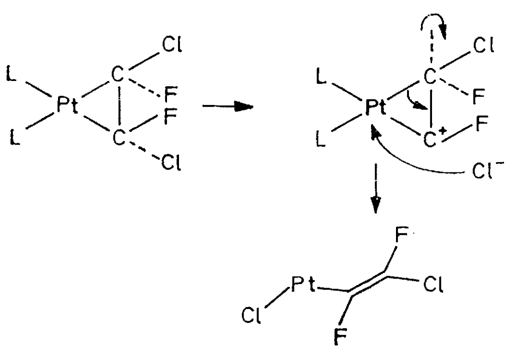
DISCUSSION

Although the activation parameters (Tables) and solvent dependency of the ' vinyl-rearrangement reaction ' are consistent with an S_N1 type of dissociative process, the stereochemical results clearly rule out a mechanism (Scheme 3) involving the intermediacy of a charge-separated species, in which the carbon atom from which the chlorine is migrating effectively becomes sp^2 hydridised; or if the intermediate is viewed as a co-ordinated vinyl cation, *sp* hybridised. If such a mechanism was operative then the common intermediate from either (Ia) or (Ib) would collapse to the same mixture of (IIa) and (IIb), whatever the starting relative proportions of (Ia) and (Ib). As shown in Table 2 this is not the case.



SCHEME 3

The stereochemical and kinetic data are compatible, however, with a mechanism (Scheme 4) in which carbon–chlorine bond fission occurs to give a tight ion-pair, the stereochemistry at the reacting carbon atom being retained. The absence of an effect on the stereochemistry on addition of lithium acetate is consistent with the formation of such a species. This is followed by collapse of the ion-pair, in which platinum–chlorine bond formation is synchronous with formation of the vinylic carbon–carbon double bond. Such a process would result in retention of stereochemistry. The effect of Ag^+ on the stereochemistry can also be explained within this framework, capture of Cl^- by Ag^+ destroying the intimate nature of the ion-pair.



SCHEME 4

There remains the important question as to what is the driving force which leads to carbon–halogen bond heterolysis. Our results suggest a steric contribution, but it is far less clear what electronic effects are important. In terms of the Chatt–Duncanson–Dewar model of π-bonding, co-ordination of a fluoro-olefin leads to extensive population of the π* antibonding orbital of the olefin, with a resultant change in geometry and bond lengths. It is possible that some population of the σ* orbitals of the C–F and C–Cl bonds also occurs, and in agreement with this the replacement of triphenylphosphine by the poorer π-acceptor methyldiphenylphosphine facilities the ' vinyl rearrangement.' It seems unlikely that a developing carbonium ion could in this system be stabilised by interaction with filled platinum *d*-orbitals.

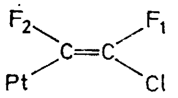
EXPERIMENTAL

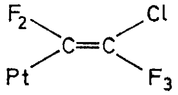
^{19}F N.m.r. spectra were recorded with a Varian Associates HA 100 spectrometer operating at 94·1 MHz; the internal reference was trichlorofluoromethane and the solvent methylene dichloride. I.r. spectra were recorded on a Perkin-Elmer 257 spectrophotometer, and the u.v. spectra were measured on a Beckman SP 800 spectrophotometer fitted with a thermostatted cell block and a time control unit.

All experiments, except those in Carius tubes, were carried out under an atmosphere of oxygen-free nitrogen. Where Carius tubes were used the reactants were sealed together at −196 °C *in vacuo*. The platinum fluoro-olefin complexes $[\overline{PtCF_2{\cdot}C}FX(PPh_3)_2]$ (X = Cl or Br), and the vinyl complexes *trans*-$[PtX(CF{=}CF_2)L_2]$ (X = Cl or Br; L = PPh_3 or $PMePh_2$) were prepared by published methods.

Preparation of 1,2-*Dichloro*-1,2-*difluoroethylenebis*(*methyldiphenylphosphine*)*platinum*.—An excess (2·0 mmol) of a 1 : 1 *cis–trans*-mixture of 1,2-dichloro-1,2-difluoroethylene was condensed into a tube containing tetrakis(methyldiphenylphosphine)platinum (0·65 g, 0·65 mmol) in benzene (30 ml). After 5 days at room temperature the solvent was removed *in vacuo* and the residue crystallised from methylene dichloride–hexane to afford white crystals of 1,2-*dichloro*-1,2-*difluoroethylenebis*(*methyldiphenylphosphine*)-*platinum* [mixture of isomers (IIIa) and (IIIb)] (0·45 g, 62%), m.p. 125—135 °C (Found: C, 45·9; H, 3·4. Calc. for $C_{28}H_{26}Cl_2F_2P_2Pt$: C, 46·2; H, 3·6%), $\nu_{max.}$ (Nujol) 3070m, 1589w, 1573w, 1482m, 1436s, 1415w, 1376s, 1366sh, 1340w, 1306m, 1287w, 1261w, 1178w, 1156w, 1100s, 1066w, 1022s, 1000m, 971w, 944s, 922w, 895m, 881s, 837w, 791m, 780w, 769m, 737s, 744s, 704sh, 693s, and 666s cm^{-1}. The ^1H n.m.r. spectrum showed resonances at τ 2·7 and 8·19 with $|J_{PMe} + J_{P'Me}|$ 8·1 and $J(PtMe)$ 27·5 Hz. The ^{19}F n.m.r. spectrum showed resonances of equal intensity at 121·8 p.p.m. [$|J_{PF} + J_{P'F}|$ 61·0 Hz, $J(PtF)$ 175·0 Hz] and 124·1 p.p.m. [$|J_{PF} + J_{P'F}|$ 49·0 Hz, $J(PtF)$ 218·0 Hz] assigned [10] to the *trans* (IIIa) and *cis* (IIIb) isomers respectively.

Vinyl Rearrangement of (IIIa) *and* (IIIb).—A solution of a 1 : 1 *cis–trans*-mixture of (IIIa) and (IIIb) (0·16 g, 0·21 mmol) in ethanol (10 ml) was heated under reflux for 10 h. On cooling white crystals were formed of (IVa) and (IVb) *chloro*(2-*chloro*-1,2-*difluorovinyl*)*bis*(*methyldiphenylphosphine*)*platinum* (0·12 g, 75%), m.p. 170—171 °C (Found: C, 46·4; H, 3·6. Calc. for $C_{28}H_{26}Cl_2F_2P_2Pt$: C, 46·2; H, 3·6%), $\nu_{max.}$ (Nujol) 1600w, 1584w, 1483sh, 1445sh, 1313m, 1297w, 1195m, 1164w, 1136m, 1114s, 1107s, 1088s, 1037m, 1030m, 1009w, 987m, 898s, 890s, 800m, 762s, 750s, 744sh, and 708s cm^{-1}. The ^{1}H n.m.r. spectrum showed resonances at τ 2·4—2·6 (m, 20H, C_6H_5) and 8·63 [apparent t, 6H, PMe, $|J_{\text{PMe}} + J_{\text{P'Me}}|$ 7·5 Hz, J(PtMe) 30·0 Hz] and 8·65 [apparent t, 6H, PMe, $|J_{\text{PMe}} + J_{\text{P'Me}}|$ 7·5 Hz J(PtMe) 30·0 Hz]. The ^{19}F n.m.r. spectrum showed resonances at 95·3 p.p.m. [F_2, J(PF) 1·8, J(PtF) 49·0] and 103·4 [F_1, $J(F_1F_2)$ 10·0, J(PF) 5·7, J(PtF) 49·0 Hz] owing to the *cis*-isomer (IVb), and at 111·9 p.p.m. [F_2, J(PF) 4·5, J(PtF) 49·9 Hz] and 123·9 p.p.m. [F_3, $J(F_3F_2)$ 122·0, J(Pt) 1·0, J(PtF) 99·0 Hz] owing to the *trans*-isomer (IVa).





Reaction of Silver Acetate with 1,2-*Dichloro*-1,2-*difluoroethylenebis(triphenylphosphine)platinum*.—Silver acetate (0·06 g, 0·4 mmol) was added to a solution of a 1 : 1 *cis–trans*-mixture of 1,2-dichloro-1,2-difluoroethylenebis(triphenylphosphine)platinum (0·16 g, 0·19 mmol) in acetone (20 ml), and the mixture refluxed (18 h). The solvent was removed *in vacuo* and the methylene dichloride extract of the residue filtered. Addition of hexane afforded white crystals *acetato*(2-*chloro*-1,2-*difluorovinyl*)*bis*(*triphenylphosphine*)-*platinum* (Va) and (Vb) (0·105 g, 70%), m.p. 170—172 °C (Found: C, 55·0; H, 4·0. Calc. for $C_{40}H_{33}ClF_2O_2P_2Pt$: C, 54·7; H, 3·8%), $\nu_{\text{max.}}$ (Nujol) 3046w, 1642s, 1599w, 1573w, 1482sh, 1437s, 1311s, 1183w, 1162w, 1135m, 1099s, 1058w, 1031m, 923w, 900m, 787m, 753sh, 748s, 711sh, 698s, and 681sh cm^{-1}. The ^{1}H n.m.r. spectrum showed resonances at τ 2·4 (m, 36H, C_6H_5) and 8·71 (s, 3H, $MeCO_2Pt$). The ^{19}F n.m.r. spectrum showed resonances at 94·6 p.p.m. [F_2, J(PF) 1·5, J(PtF) 49·2 Hz] and 100·5 [F_1, $J(F_1F_2)$ 10·0, J(PF) 6·0, J(PtF) 45·0 Hz] owing to the *cis*-isomer (Vb), and at 110·5 p.p.m. [F_2, J(PF) 4·5, J(PtF) 48·3 Hz] and 125·0 [F_3, $J(F_3F_2)$ 120·0, J(PF) 4·5, and J(PtF) 90·0 Hz] owing to the *trans*-isomer (Va).

Kinetic Measurements.—The rates of reactions were followed by u.v. spectrophotometry; the spectra were recorded on a Beckman SP 800 spectrophotometer fitted with a thermostatted cell block and a time control unit. Absorbance values at 292 nm were measured where the fluoro-olefin complexes absorb strongly while the absorption due to the vinyl complexes is negligible. The rate constants were calculated from the slopes of the linear part of the plots of log $(A_\infty - A_t)$ against time. The plots showed that the reaction is of the first order. The infinity spectrum, recorded after at least six half-lives was coincident with that of a solution of the particular vinyl complex of the correct concentration. The results are in Table 1. A concentration of $1{\cdot}5 \times 10^{-4}$M was used in all runs.

The Rearrangement of 1,2-*Dichloro*-1,2-*difluoroethylenebis*(*triphenylphosphine*)*platinum*.—The fluoro-olefin complex (IIIa + IIIb) (0·90 g, 0·125 mmol) in methylene dichloride (20 ml) was added to refluxing butanol (250 ml). At various intervals aliquot portions (30 ml) of the solutions were removed. The solvent was removed *in vacuo* and the residue dissolved in methylene dichloride (2 ml). The results obtained by measurement of the ^{19}F n.m.r. spectra of these standard solutions are in Table 2.

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