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REARRANGEMENTS OF SOME σ-BONDED POLYFLUOROALLYL TRANSITION METAL COMPLEXES

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Summary

The thermally induced rearrangements $CF_2{=}CClCF_2M(CO)_5 \rightarrow CF_3CCl{=}CFM(CO)_5$ (M = Mn, Re) have been studied by differential thermal analysis (DTA) and the enthalpies of reaction determined as -144 ± 20 kJ mol^{-1} (M = Mn) and -79 ± 20 kJ mol^{-1} (M = Re). Oxidative addition of $CF_2{=}CClCF_2Cl$ to $IrCl(CO)[P(C_6H_5)_3]_2$ gave an unrearranged allyl complex. The mechanism of the rearrangements is rationalised as an intermolecular process, sensitive to steric effects.

Introduction

In an earlier study [1], the spontaneous thermal rearrangement of a polyfluoroallyl manganese carbonyl to the propenyl isomer was reported and was compared with fluoride-ion induced rearrangements of polyfluoroallyl derivatives of some main group elements. In order to further our understanding of this 1,3-fluorine shift we have prepared an analogous rhenium complex, $CF_2{=}CClCF_2Re(CO)_5$ and studied the rearrangements of both the manganese and rhenium compounds by differential thermal analysis (DTA). We have also prepared some six-coordinate iridium complexes containing polyfluoroallyl groups by oxidative addition reactions, in order to examine the possibility of analogous rearrangements in these systems.

Experimental

IR spectra were determined on Beckman IR-5 and IR-12 spectrophotometers. ^{19}F NMR spectra were obtained on a Varian HA-100 spectrometer operating at 94.1 MHz.

2,3-Dichlorotetrafluoropropene [1], 2-chloro-3-iodotetrafluoropropene [2], and 2-chlorotetrafluoroallylmanganese pentacarbonyl [1] were prepared by published methods.

3-Bromo-2-chlorotetrafluoropropene [3]

A solution of 2-chloro-3-iodotetrafluoropropene (11.2 g, 0.041 mol) in acetone (25 ml) was added under N_2 to a vigorously stirred mixture of lithium bromide (10 g, 0.12 mol) in acetone (25 ml) at 0°C. The stirred mixture was heated to reflux for 2 h. The volatiles were then distilled off and washed with ice-water (2 × 25 ml), dried ($MgSO_4$) and distilled to give 3-bromo-2-chlorotetrafluoropropene (5.6 g, 0.025 mol, 60%), b.p. 61—2°C (reported [3], b.p. 64°C).

2-Chloro-1,1,3,3-tetrafluoropropene

A mixture of hydrogen iodide (1.07 g, 8.5 mmol) and 2-chloro-3-iodotetrafluoropropene (2.25 g, 8.2 mmol) was condensed, using standard vacuum line techniques, into a bulb containing mercury (4 ml). The bulb was sealed and shaken at room temperature for 1 h. The volatile contents were transferred to the vacuum line and fractionally condensed into traps at 0° and −78°C. The trap at —78°C contained 2-chloro-1,1,3,3-tetrafluoropropene (0.16 g, 0.8 mmol, 10%) characterised by its spectral properties (see Tables 1 and 2).

2-Chlorotetrafluoroallylrhenium pentacarbonyl and 2-chlorotetrafluoropropenylrhenium pentacarbonyl

A solution of sodium rhenium pentacarbonylate was prepared under N_2 from dirhenium decacarbonyl (2.0 g, 3.0 mmol) and sodium amalgam (0.5 g Na in 5 ml mercury) in tetrahydrofuran (50 ml) by a method analogous to that used for the corresponding manganese derivative [4]. Excess amalgam was removed and a solution of 2,3-dichlorotetrafluoropropene (5.0 g, 27 mmol) in tetrahydrofuran (25 ml) was added dropwise under N_2 to the vigorously stirred carbonyl solution which was held at —20°C throughout the addition. Solvent and excess alkene were removed in vacuo and the residue was sublimed (40°C, 0.1 torr) to give off-white crystals of a mixture of $CF_2{=}CCl{-}CF_2Re(CO)_5$ (70%) and $CF_3{=}CCl{=}CFRe(CO)_5$ (30%) (total yield 0.85 g, 1.8 mmol, 60%). (Found: C, 20.18; Cl, 7.68. $C_8ClF_4O_5Re$ calc.: C, 20.28; Cl. 7.48%). It was not possible to separate the isomers without rearrangement occurring. The composition of the mixture was determined by ^{19}F NMR spectroscopy (see text below).

$CF_2{=}CClCF_2IrCl_2(CO)[P(C_6H_5)_3]_2$

A suspension of $IrCl(CO)[P(C_6H_5)_3]_2$[5] (0.25 g, 0.32 mmol) in 2,3-dichloro-

TABLE 1

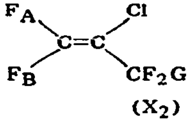
INFRARED SPECTRAL ASSIGNMENTS FOR $CF_2{=}CClCF_2G$ COMPOUNDS

G	$\nu(C{=}C)$ [a]	$\nu({=}CF)$	$\nu(CF)$	Other bands
Br [b]	1734	1339	1051, 1035	
H [b]	1750	1331	1039	$\nu(CH)$ 2900—3000
$Re(CO)_5$ [c]	1723	1297	992	$\nu(CO)$ 2122, 2050, 2004, 1955
$Mn(CO)_5$ [c,d]	1727	1308	980	$\nu(CO)$ 2082, 2043, 2015, 1967
$IrCl_2(CO)[P(C_6H_5)_3]_2$ [c]	1728	1332	[e]	$\nu(CO)$ 2044, 2020
$IrClI(CO)[P(C_6H_5)_3]_2$ [c] (?)	1720	1331	[e]	$\nu(CO)$ 2063

[a] Reported data are in units of cm^{-1}. [b] Gas phase. [c] $CHCl_3$ and CCl_4 solutions. [d] From ref. [1]. [e] Not clearly assignable; complex spectral region.

TABLE 2

^{19}F NMR SPECTRA [a] OF



G	δ(X$_2$) [b]	X$_2$		A		B	Other
		J(AX) [c]	J(BX)	δ(A)	J(AB)	δ(B)	
Br	46.2	7.0	33.8	77.7	13.0	75.7	
H	118.0	3.0	12.5	86.4	1.7	81.1	J(HX) 53.4; J(HA) 27.6; J(HB) 27.0
Re(CO)$_5$	51.0	6.5	35.5	87.7	39.1	84.5	

[a] Spectra determined on ca. 10% solutions in CDCl$_3$ containing 5% CCl$_3$F, at 94.1 MHz. [b] Chemical shifts in ppm upfield from CCl$_3$F (int.). [c] Coupling constants in Hz.

tetrafluoropropene (2.0 ml, 3.2 g, 17 mmol) was stirred under N$_2$ at room temperature for 70 h. The mixture was then added to petroleum ether (b.p. 40—60° C; 10 ml) and centrifuged to yield finely divided yellow crystals of CF$_2$=CClCF$_2$-IrCl$_2$(CO)[P(C$_6$H$_5$)$_3$]$_2$ which were washed twice in petroleum ether (2 ml) and dried in vacuo (yield: 0.21 g, 0.22 mmol, 70%). (Found: C, 51.1; H, 3.41; Cl, 10.91. C$_{40}$H$_{30}$Cl$_3$F$_4$IrOP$_2$ calc.: C, 49.9; H, 3.14; Cl, 11.04%).

An attempted preparation of the analogous CF$_2$=CClCF$_2$Ir(Cl)(I)(CO)[P-(C$_6$H$_5$)$_3$]$_2$ from CF$_2$=CClCF$_2$I gave a reddish tan crystalline compound which had the spectroscopic properties of the expected derivative, but for which correct analytical data could not be obtained.

Differential thermal analysis

Apparatus and calibration. The semi-micro apparatus was scaled down from a published description [6]. The two cells were borosilicate glass cylinders, 53 mm long × 8 mm diameter, each fitted with a copper-constantan thermocouple in a sealed quartz capillary tube. The cell holder was vibrated by an eccentric fitted to an electric motor to promote effective stirring and heat transfer. The cell assembly was mounted in an oil bath which could be heated in a controlled way. The output from the cell thermocouples, which were connected in opposition (zero potential difference when the cell temperatures were equal), was amplified by a Hewlett—Packard Model 425A DC μV meter and the meter output was recorded on a servorecorder. The enthalpy of dilution of standardised H$_2$SO$_4$ (aq.) was used to calibrate the instrument [7].

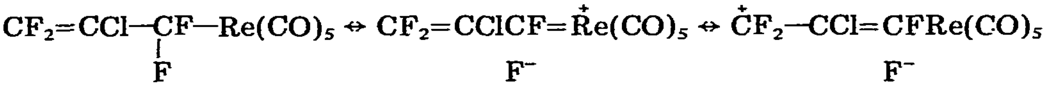
Rearrangement of CF$_2$=CClCF$_2$M(CO)$_5$ to CF$_3$CCl=CFM(CO)$_5$ (M = Mn, Re)

In a typical run a solution of 0.138 g of the compound (M = Mn) in 0.50 ml CHCl$_3$ was placed in the sample cell, and a solution of 0.14 g of CF$_3$CCl=CFMn-(CO)$_5$ in 0.50 ml CHCl$_3$ was used as the reference solution. The initial bath temperature was 20° C and the bath was heated at 4° min^{-1} to a final temperature of 60° C, by which time the exothermic reaction had been completed. Measurement of the area under the DTA curve, and comparison with the values obtained in the calibration experiments, indicated an average ΔH for the reaction over this temperature range of −144 ± 20 kJ mol^{-1} for $CF_2{=}CClCF_2Mn(CO)_5$ and −79 ± 20 kJ mol^{-1} for $CF_2{=}CClCF_2Re(CO)_5$. The products of thermal rearrangement were characterised by IR and ^{19}F NMR spectroscopy, and were found to be exclusively the rearranged $CF_3CCl{=}CFM(CO)_5$.

Results and discussion

Infrared spectra

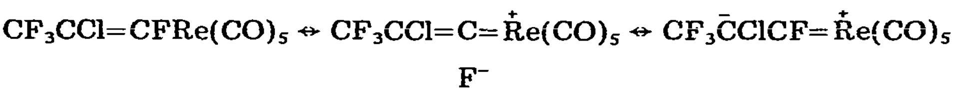
Table 2 presents the significant IR spectral data for the new allylic compounds of rhenium and iridium, together with newly reported data for $CF_2{=}CClCBrF_2$ and $CF_2{=}CClCF_2H$. The bands are assigned by analogy with assignments made previously for a variety of compounds of general type $CF_2{=}CClCF_2G$ [1]. Also included in Table 1 for comparison are previously reported data for $CF_2{=}CClCF_2$-$Mn(CO)_5$. In comparison with the compound $CF_2{=}CClCF_2H$, which can be regarded as a polyflyoroallyl derivative of the electropositive hydrogen substituent, the compounds $CF_2{=}CClCF_2M(CO)_5$, M = Mn, Re, which also carry relatively electropositive substituents, show a moderate lowering of frequency for the double bond stretch of the $CF_2{=}CCl$ group, and also a lowering of the characteristic frequencies of the C—F vibrations for both the vinylic CF_2 group and the allylic CF_2 group. These shifts are consistent with our earlier proposal [1] based on an analysis of the spectrum of $CF_3Mn(CO)_5$ [8], that there is a weakening of carbon—fluorine bonds α to a transition metal and that multiple bond character is present in the carbon—metal bond. In valence bond terms this can be shown as follows:



$$CF_2{=}CCl{-}\underset{F}{C}F{-}Re(CO)_5 \leftrightarrow \underset{F^-}{CF_2{=}CClCF{=}\overset{+}{R}e(CO)_5} \leftrightarrow \underset{F^-}{\overset{+}{C}F_2{-}CCl{=}CFRe(CO)_5}$$

Similar considerations would apply to the polyfluoroallyl iridium complexes prepared.

The spectrum of the rearranged $CF_3CCl{=}CFRe(CO)_5$ (a mixture of 18% *E* and 82% *Z*) shows the expected shift of $\nu(C{=}C)$ to low frequency. The observed band at 1572 cm^{-1} (in CCl_4 solution) is very close to that previously reported for $CF_3CCl{=}CFMn(CO)_5$ at 1570 cm^{-1} [1], and is significantly lower in frequency than absorptions for similar groups in main group compounds, e.g., $CF_3CCl{=}CFAs(CH_3)_2$, $\nu(C{=}C)$ = 1620 cm^{-1} [1]. This is interpreted as an indication of a modest degree of metal—carbon multiple bonding, and the participation of the electrons of the carbon—carbon double bond in this process as indicated:



$$CF_3CCl{=}CFRe(CO)_5 \leftrightarrow \underset{F^-}{CF_3CCl{=}C{=}\overset{+}{R}e(CO)_5} \leftrightarrow CF_3\overset{-}{C}ClCF{=}\overset{+}{R}e(CO)_5$$

^{19}F NMR spectra

Table 2 lists the ^{19}F NMR data for the newly prepared $CF_2{=}CClCF_2Re(CO)_5$, and for $CF_2{=}CClCF_2Br$, both of which were analysed as ABX_2 systems, and for $CF_2{=}CClCF_2H$, analysed as an ABX_2Y system. Assignments of the *A* and *B* resonances were made as previously reported [1]. The substantial downfield shift of the CF_2 group adjacent to a transition metal as compared with a CF_2 group adjacent to hydrogen or other electropositive groups (cf. [1]) is again seen. While there are other striking variations in several of the NMR parameters, a detailed explanation of them is not at all obvious.

Table 3 lists the data for the mixture of rearranged products, *E* and *Z* CF_3-$CCl{=}CFRe(CO)_5$. Stereochemical assignments were made on the basis of the stereospecificity of the known trends in the ^4J (FCC=CF) [1] and thus the stereoselectivity of the rearrangement reaction could be estimated.

The polyfluoroallyl iridium complexes were not soluble enough to yield ^{19}F NMR spectra.

Enthalpies of rearrangement

Bond energy terms have been determined for a range of fluorinated and chlorinated hydrocarbons [9] and these justify quantitatively the well-known stability of CF_3 groups. From these bond energy terms the expected enthalpy change in the reaction:

$$CF_2{=}CClCF_2G \rightarrow CF_3CCl{=}CFG$$

(where G is, for example, Cl) can be calculated as approximately − 46 kJ mol^{-1}. For both the rhenium and manganese derivatives studied the observed negative enthalpy change in the rearrangement

$$CF_2{=}CClCF_2M(CO)_5 \rightarrow CF_3CCl{=}CFM(CO)_5$$

was substantially larger than this calculated amount; by −33 ± 20 kJ mol^{-1} for the rhenium complex and by −98 ± 20 kJ mol^{-1} for the manganese complex. These differences must reflect some combination of lower thermodynamic stability than expected for the starting allylic-metal compound, and higher stability for the rearranged product. This agrees with some of the spectral interpretation already presented. In particular, IR of the starting allyl-metal compounds, with the low frequency of the ν(CF) (see Table 1) were interpreted as indicating substantial C—F bond weakening in the CF_2 group adjacent to the metal. It may be significant that the frequency assigned to this vibration in the manganese compound (980 cm^{-1}) is lower than that for the rhenium compound (992 cm^{-1}) and that the rearrangement of the manganese compound is substantially the more exothermic of the two.

Mechanistic considerations

An initial aim of this study was to further clarify the mechanism of the fluorine shift. However, attempts to deduce kinetic data from the DTA curves obtained in the rearrangement studies were not fruitful. Plots of logarithms of

TABLE 3

^{19}F NMR SPECTRA [a] OF $CF_3CCl{=}CFRe(CO)_5$

Isomer	$\delta(CF_3)$ [b]	δ(CF)	J [c]	% in mixture [d]
E	58.1	15.8	8.8	18
Z	60.0	32.1	24.9	82

[a] Spectra determined on ca. 10% solutions in $CDCl_3$ containing 5% CCl_3F, at 94.1 MHz. [b] Chemical shifts in ppm upfield from CCl_3F (int.). [c] Coupling constants in Hz. [d] From integration of signals.

derived rate constants, assuming various orders of reaction [6], versus the reciprocal of the absolute temperature, exhibited discontinuities and were non-linear, probably because of imprecisions in the data. The only indication that could be drawn from this kinetic analysis was that the rearrangement reactions were possibly of an order larger than one.

The observation that the allylic manganese and rhenium compounds studied underwent facile rearrangement while the iridium complexes did not, supports the hypothesis [1] that the rearrangements are intermolecular processes in which a fluorine of a CF_2 group α to the metal, with a weakened C—F bond, acts as a nucleophile towards a terminal $CF_2=$ group in a second molecule. In the unhindered manganese and rhenium carbonyl derivatives intermolecular reaction is facile, whereas in the much bulkier iridium complexes, containing hindering triphenylphosphine ligands, intermolecular approach of the kind just postulated is severely retarded. An analogous set of observations of a similar kind was recently made on some cobalt complexes [10]. The compound $CF_2{=}CF{-}CF_2Co(CO)_4$ was found to undergo either rearrangement to $CF_3CF{=}CFCo(CO)_4$ or expulsion of CO to yield $(\pi\text{-}C_3F_5)Co(CO)_3$. However, *cis*-$CF_2{=}CFCF_2Co(CO)_3PPh_3$ did not undergo rearrangement, presumably because the bulky phosphine ligand impeded intermolecular attack [10].

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