η-Bonded Ketone Complexes of Platinum(0). The Preparation of Complexes of Chloropentafluoropropan-2-one and 1,3-Dichlorotetrafluoropropan-2-one and the Kinetics of Isomerisation of $[Pt(\eta\text{-}CF_3COCF_2Cl)(PPh_3)_2]$ to *cis*-$[PtCl(CF_2COCF_3)(PPh_3)_2]$

By **John Burgess,* John G. Chambers, David A. Clarke,** and **Raymond D. W. Kemmitt,*** Department of Chemistry, The University, Leicester LE1 7RH

The preparation and characterisation of the η-bonded ketone complexes $[Pt(\eta\text{-}CF_2ClCOCF_2X)(PPh_3)_2]$ (X = F or Cl) are reported. The complexes isomerise in solution to *cis*-$[PtCl(CF_2COCF_2X)(PPh_3)_2]$. The kinetics of isomerisation of $[Pt(\eta\text{-}CF_2ClCOCF_3)(PPh_3)_2]$ are described, and the isomerisation mechanism discussed.

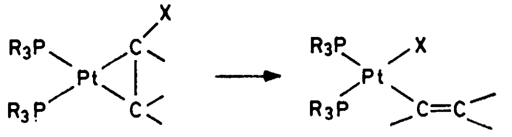
OUR interest in the mechanism of the 1,2-shift reaction which occurs when halogenoalkene complexes isomerise to alkenyl complexes (Scheme 1) [1,2] prompted us to investigate systems in which an analogous 1,3-shift re-

---

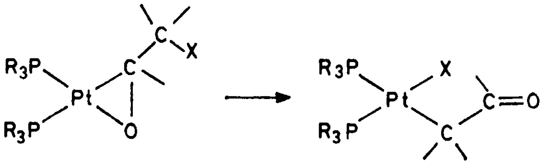
[1] W. J. Bland, J. Burgess, and R. D. W. Kemmitt, *J. Organometallic Chem.*, 1968, **14**, 201; **15**, 217.

[2] W. J. Bland, J. Burgess, and R. D. W. Kemmitt, *J. Organometallic Chem.*, 1969, **18**, 199.

action (Scheme 2) might occur. It had been reported that 1,3-dichlorotetrafluoropropan-2-one reacts with tetrakis(triphenylphosphine)platinum(0) to give $[Pt(\eta\text{-}CF_2ClCOCF_2Cl)(PPh_3)_2]$.[3] Since this system seemed to be a suitable model to study 1,3-shift reactions we decided to investigate the chemistry of this complex. It also became of interest to try and prepare related complexes of CF_3COCF_2Cl.



SCHEME 1



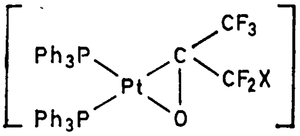
SCHEME 2

RESULTS AND DISCUSSION

Our initial studies on the reaction of $CF_2ClCOCF_2Cl$ with $[Pt(PPh_3)_4]$ in benzene solution at room temperature led only to the formation of *cis*-$[PtCl_2(PPh_3)_2]$ rather than the expected η-bonded ketone complex and we have found this to be an unreliable method for the preparation of $[Pt(\eta\text{-}CF_2ClCOCF_2Cl)(PPh_3)_2]$. However, further studies revealed that this complex could be isolated from the reaction of $CF_2ClCOCF_2Cl$ with $[Pt(\textit{trans}\text{-}PhCH{=}CHPh)(PPh_3)_2]$ suspended in light petroleum (b.p. 40—60 °C). In solution, $[Pt(\eta\text{-}CF_2ClCOCF_2Cl)(PPh_3)_2]$ is a very labile complex and when dissolved in benzene, chloroform, or methylene chloride it rapidly isomerises to *cis*-$[PtCl(CF_2COCF_2Cl)(PPh_3)_2]$. It is therefore not surprising to find that reactions of $CF_2ClCOCF_2Cl$ with various alkene or alkyne complexes of Pt^0 (Table 1) in these solvents result in the formation of the oxidative-addition product *cis*-$[PtCl(CF_2COCF_2Cl)(PPh_3)_2]$ rather than $[Pt(\eta\text{-}CF_2ClCOCF_2Cl)(PPh_3)_2]$. However, since the reaction of $CF_2ClCOCF_2Cl$ with $[Pt(\textit{trans}\text{-}PhCH{=}CHPh)(PPh_3)_2]$ suspended in diethyl ether gives the oxidative-addition product whereas the corresponding reaction with $[Pt(CH_2{=}CH_2)(PPh_3)_2]$ gives the η-bonded ketone complex, it appears that other factors can also operate in this isomerisation reaction.

Similar studies with chloropentafluoropropan-2-one, CF_3COCF_2Cl, reveal that either the η-bonded complex, $[Pt(\eta\text{-}CF_3COCF_2Cl)(PPh_3)_2]$, or the oxidative-addition complex, *cis*-$[PtCl(CF_2COCF_3)(PPh_3)_2]$, are formed, the η-bonded complex again being isolated only in solvents in which it is sparingly soluble (Table 1). Both ketones react with either $[Pt(PPh_3)_4]$ or $[Pd(PPh_3)_4]$ to give only *cis*-$[PtCl_2(PPh_3)_2]$ or *trans*-$[PdCl_2(PPh_3)_2]$ respectively.

The i.r. spectra of Nujol mulls of the complexes $[Pt(\eta\text{-}CF_2ClCOCF_2X)(PPh_3)_2]$ ($X = F$ or Cl) exhibit strong bands in the 1 250—1 110 cm^{-1} region which can be associated with carbon–fluorine stretching frequencies but no bands in the ketonic region, data which are consistent with the formulation of these complexes as the η-bonded ketone complexes, (1).



(1)

The rapid isomerisation of these complexes in solution has precluded ^{19}F n.m.r. studies. The i.r. spectra of the oxidative-addition products, *cis*-$[PtCl(CF_2COCF_2X)(PPh_3)_2]$ ($X = F$ or Cl), exhibit strong bands in the ketonic region of their i.r. spectra and bands which can be assigned to $\nu(PtCl)$. The ^{19}F n.m.r. spectrum of *cis*-$[PtCl(CF_2COCF_3)(PPh_3)_2]$ exhibits two resonances at 11.8 and 28.6 p.p.m. on the high-field side of α,α,α-trifluorotoluene of relative intensity 3 : 2. The low-field resonance (intensity 3) consisted of a triplet with additional ^{195}Pt satellites, the triplet arising from

TABLE 1

Reactions of chlorofluoropropanones with platinum(0) complexes

Reactants	Solvent	Reaction time (t/h)	Product	Yield (%)
$[Pt(\textit{trans}\text{-}PhCH{=}CHPh)(PPh_3)_2] + CF_3COCF_2Cl$	Et_2O	3	*cis*-$[PtCl(CF_2COCF_3)(PPh_3)_2]$	99
	C_6H_6	3	*cis*-$[PtCl(CF_2COCF_3)(PPh_3)_2]$	68
	a	3 d	*cis*-$[PtCl(CF_2COCF_3)(PPh_3)_2]$	31
$[Pt(\textit{trans}\text{-}PhCH{=}CHPh)(PPh_3)_2] + CF_2ClCOCF_2Cl$	Et_2O	2	*cis*-$[PtCl(CF_2COCF_2Cl)(PPh_3)_2]$	80
	C_6H_6	2	*cis*-$[PtCl(CF_2COCF_2Cl)(PPh_3)_2]$	68
	a	2	$[Pt(\eta\text{-}CF_2ClCOCF_2Cl)(PPh_3)_2]$	80
$[Pt(PhC{\equiv}CPh)(PPh_3)_2] + CF_3COCF_2Cl$	Et_2O	4	$[Pt(\eta\text{-}CF_3COCF_2Cl)(PPh_3)_2]$	65
	C_6H_6	4	*cis*-$[PtCl(CF_2COCF_3)(PPh_3)_2]$	96
$[Pt(PhC{\equiv}CPh)(PPh_3)_2] + CF_2ClCOCF_2Cl$	Et_2O	4	$[Pt(\eta\text{-}CF_2ClCOCF_2Cl)(PPh_3)_2]$	96
	C_6H_6	4	*cis*-$[PtCl(CF_2COCF_2Cl)(PPh_3)_2]$	94
$[Pt(PhC{\equiv}CH)(PPh_3)_2] + CF_3COCF_2Cl$	Et_2O	3 d	*cis*-$[PtCl(CF_2COCF_3)(PPh_3)_2]$	52
$+ CF_2ClCOCF_2Cl$	$CHCl_3$ [b]	1	*cis*-$[PtCl(CF_2COCF_2Cl)(PPh_3)_2]$	67
$[Pt(CH_2{=}CH_2)(PPh_3)_2] + CF_2ClCOCF_2Cl$	Et_2O	4	$[Pt(\eta\text{-}CF_2ClCOCF_2Cl)(PPh_3)_2]$	57

[a] Light petroleum (b.p. 40—60 °C). [b] Under reflux.

---

[3] B. Clarke, M. Green, R. B. L. Osborn, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1968, 167.

fluorine–fluorine coupling with the CF_2 group. The high-field resonance (relative intensity 2) consisted of four quartets since in addition to fluorine–fluorine coupling both the *cis*- and *trans*-phosphine ligands also couple to this signal. Again additional ^{195}Pt satellites are observed. The occurrence of both *cis*- and *trans*-phosphorus couplings indicates a *cis* configuration for this complex as has been established by *X*-ray methods for the analogous oxidative-addition product, *cis*-$[PtCl(CF_2COCF_2Cl)(PPh_3)_2]$.[4] Recent work has shown that the intensity of an i.r. band at 550 ± 5 cm^{-1} can be a guide to the *cis–trans* stereochemistry of bis(triphenylphosphine)platinum(II) complexes.[5] Both the complexes *cis*-$[PtCl(CF_2COCF_2X)(PPh_3)_2]$ exhibit a strong band at *ca.* 550 cm^{-1} in agreement with a *cis* stereochemistry. The ^{19}F n.m.r. spectrum of the complex *cis*-$[PtCl(CF_2COCF_2Cl)(PPh_3)_2]$ (see Experimental section) also establishes that this complex retains its *cis* stereochemistry in solution.

In the ^{19}F n.m.r. spectra of transition-metal perfluoroalkyl complexes a large downfield shift is usually observed for the CF_2 group bonded to the metal.[6] However, no downfield shift is observed for the α-CF_2 group in the complexes *cis*-$[PtCl(CF_2COCF_2X)(PPh_3)_2]$ ($X = F$ or Cl). In both complexes the α-CF_2 group resonates to high field of the CF_2X group. Studies on platinum trifluoromethyl complexes have shown that the position of the ^{19}F n.m.r. chemical shift is dependent on the nature of the *trans* ligand, ligands of high *trans* influence causing a shift to higher field.[7] In the present complexes the α-CF_2 is *trans* to a phosphine ligand which is known to possess an appreciable *trans* influence.

Kinetic Studies.—In solution the η-bonded complexes $[Pt(\eta\text{-}CF_2ClCOCF_2X)(PPh_3)_2]$ ($X = F$ or Cl) readily isomerise to *cis*-$[PtCl(CF_2COCF_2X)(PPh_3)_2]$. The complex with $X = Cl$ isomerises too rapidly for study by conventional spectrophotometric techniques, but when $X = F$ isomerisation rates are suitable for monitoring by conventional means. Unfortunately, the very low solubility of $[Pt(\eta\text{-}CF_2ClCOCF_3)(PPh_3)_2]$ in the majority of organic solvents has severely limited the extent of our investigation of its kinetics of isomerisation.

Kinetic runs were successfully carried out in the solvents chloroform, methylene chloride, and 1,2-dichloroethane. In each solvent the isomerisation followed first-order kinetics over at least three half-lives. There was an isosbestic point at 315 nm in each case. Computed first-order rate constants are reported in Table 2; activation parameters calculated from these rate constants are reported in Table 3. These rates are faster than for similar halogenoalkene complexes just as rates of substitution at an allyl carbon are greater than those at an alkenyl carbon. The kinetic pattern for reaction in dimethyl sulphoxide differed considerably; the product was not $[PtCl(CF_2COCF_3)(PPh_3)_2]$.

TABLE 2

First-order rate constants, *k*, for the isomerisation of $[Pt(CF_3COCF_2Cl)(PPh_3)_2]$ to $[PtCl(CF_2COCF_3)(PPh_3)_2]$

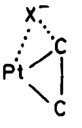
	$10^4k/s^{-1}$		
Solvent:	$CHCl_3$	CH_2Cl_2	CH_2ClCH_2Cl
T/K			
293.5		2.1	
294.2			0.95
297.4		2.7	
298.6			1.53
300.1	4.7	3.8	
302.9	5.7		2.1
303.5		4.9	
306.6			2.8
307.2	7.9		
310.5			3.5
313.2	13.8		

TABLE 3

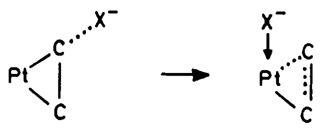
Activation parameters for the isomerisation of $[Pt(CF_3COCF_2Cl)(PPh_3)_2]$ (1 cal = 4.184 J)

Solvent:	$CHCl_3$	CH_2Cl_2	CH_2ClCH_2Cl
$\Delta H^\ddagger$/kcal mol^{-1}	14.8 ± 0.8	14.8 ± 1.4	13.8 ± 0.8
$\Delta S^\ddagger$/cal K^{-1} mol^{-1}	-24 ± 3	-25 ± 6	-30 ± 3

Isomerisation Mechanism.—The mechanism of isomerisation of halogenoalkene complexes can be intramolecular (Scheme 3) or intermolecular (Scheme 4), or even some intermediate path in which there is considerable C–Cl bond extension but not C–Cl bond breaking. We have previously suggested that the mechanism of isomerisation of halogenoalkene complexes of this type can be diagnosed from the sensitivity of the isomerisation rate to variation in solvent. Thus the isomerisation $[Pt(C_2Cl_4)(PPh_3)_2] \longrightarrow [PtCl(CCl{=}CCl_2)(PPh_3)_2]$ has been assigned an intermolecular mechanism on the basis of the marked sensitivity of its rate to solvent nature. In particular, the Grunwald–Winstein *mY* plot[8] for this isomerisation has a gradient, *m*, of 0.9, indicating a strong resemblance of the transition state here to that for solvolysis of t-butyl chloride (typical organic S_N1).[1] The isomerisations of $[Pt(C_2HCl_3)(PPh_3)_2]$[2] and of $[Pt(C_2F_3Br)(AsPh_3)_2]$[9] to the corresponding alkenyl complexes are less sensitive to solvent (*i.e.* $m < 1$) and consequently mechanisms of more intramolecular nature are suggested to operate in these cases. Green's description of the mechanism of isomerisation of analogous chloroalkene complexes in terms of the formation of tight ion pairs[10] is very similar to our S_N1 interpretation.



SCHEME 3



SCHEME 4

---

[4] D. R. Russell and P. A. Tucker, *J.C.S. Dalton*, 1975, 2222.

[5] S. H. Mastin, *Inorg. Chem.*, 1974, **13**, 1003.

[6] E. Pitcher, A. D. Buckingham, and F. G. A. Stone, *J. Chem. Phys.*, 1962, **36**, 124.

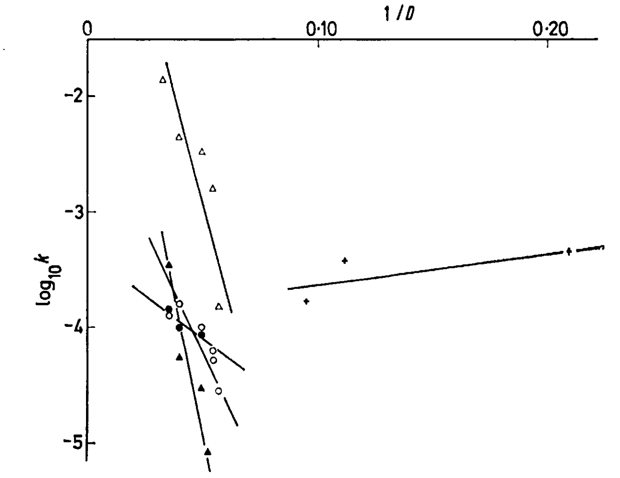
[7] T. G. Appelton, M. H. Chisholm, H. C. Clark, and L. E. Manzer, *Inorg. Chem.*, 1972, **11**, 1786.

[8] E. Grunwald and S. Winstein, *J. Amer. Chem. Soc.*, 1948, **70**, 846; P. R. Wells, *Chem. Rev.*, 1963, **63**, 171.

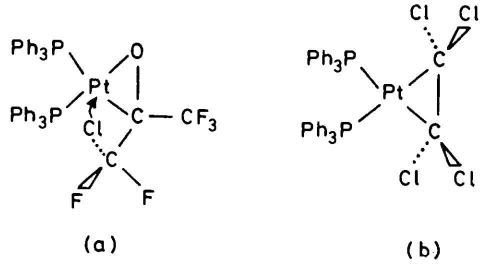
[9] J. Burgess, M. M. Hunt, and R. D. W. Kemmitt, *J. Organometallic Chem.*, 1977, **134**, 131.

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

For the isomerisation of $[Pt(CF_2ClCOCF_3)(PPh_3)_2]$ it is not possible to construct a Grunwald–Winstein plot and thence obtain an *m* value indicative of mechanism, since solvent *Y* values are unavailable (and indeed unobtainable) for chlorinated hydrocarbon solvents. Therefore we had to use some other solvent parameter, and chose dielectric constant ($1/D$ in fact). The dependence of rate constant on solvent dielectric constant has previously been of use in diagnosis of mechanisms of organometallic reactions, for example in oxidative addition to *trans*-$[IrCl(CO)(PPh_3)_2]$.[11] Plots of log *k* against $1/D$ are shown in the Figure for this and similar isomerisations. The gradient of such plots for halogenoalkene complexes parallel those of plots of log *k* against *Y*, with the largest gradient corresponding to the most intermolecular mechanism. Hence we tentatively assign an intramolecular mechanism to the isomerisation of $[Pt(CF_2ClCOCF_3))(PPh_3)_2]$. Steric and geometric considerations favour an intramolecular mechanism. Diagram (2a) shows the favourable disposition of atoms for an intramolecular transition state. The geometry of (halogenoalkene)platinum(0) complexes is less favourable to intramolecular reorganisation, (2b). It is unwise to place too much reliance on activation entropies in the diagnosis of mechanism of reactions in solution. Nevertheless, the negative values of $\Delta S^‡$ (Table 3) are consistent with an intramolecular mechanism in which transition-state formation involves loss of freedom.



Dependence of the rate of isomerisation (*k*) of halogenoalkene and halogenoketone complexes of platinum on solvent dielectric constant (*D*): (+) $[Pt(\eta\text{-}CF_2ClCOCF_3)(PPh_3)_2]$; (▲) $[Pt(C_2Cl_4)(PPh_3)_2]$; (△) $[Pt(C_2HCl_3)(PPh_3)_2]$; (●) $[Pt(CFCl{=}CF_2)(AsPh_3)_2]$; (○) $[Pt(CFBr{=}CF_2)(AsPh_3)_2]$



(a) (b)

(2)

EXPERIMENTAL

Infrared spectra were recorded using a Perkin-Elmer 225 spectrometer using Nujol and hexachlorobutadiene mulls between KBr or Polythene discs. Fluorine-19 n.m.r. spectra were obtained on a JEOL JNM PS 100 spectrometer at 94.1 MHz relative to $C_6H_5CF_3$ as internal standard. Melting points were determined on a Reichart hot-stage apparatus and are uncorrected. Microanalytical determinations (Table 4) were by the Butterworth Microanalytical Consultancy Limited.

The complexes $[Pt(PPh_3)_4]$,[12] $[Pt(\textit{trans}\text{-}PhCH{=}CHPh)(PPh_3)_2]$,[13] $[Pt(PhC{\equiv}CH)(PPh_3)_2]$,[14] $[Pt(C_2H_4)(PPh_3)_2]$,[15] and $[Pd(PPh_3)_4]$ [16] were prepared as described in the literature.

Reactions of Tetrakis(triphenylphosphine)platinum(0).—(*a*) *With chloropentafluoropropan*-2-*one*. An excess of chloropentafluoropropan-2-one was condensed (−196 °C) into a Carius tube (150 cm³) containing a suspension of $[Pt(PPh_3)_4]$ (0.7 g, 0.49 mmol) in diethyl ether (15 cm³). The tube was sealed and the reaction mixture was allowed to warm to room temperature and then shaken for 24 h. The tube was cooled, opened, and the volatile material was removed. The white suspension was filtered and the residue was washed with diethyl ether and dried *in vacuo* to afford cis-*dichlorobis(triphenylphosphine)platinum*(II) (0.4 g, 75%) identified by its m.p. and i.r. spectrum.[17]

TABLE 4

Microanalytical data and melting points of the complexes

	M.p.[a] (θ_c/°C)	Analysis (%) [b] C	H	Cl	F
$[Pt(\eta\text{-}CF_3COCF_2Cl)(PPh_3)_2]$	178—180	51.8 (51.9)	3.4 (3.4)		11.1 (10.5)
cis-$[PtCl(CF_2COCF_3)(PPh_3)_2]$	222—224	50.6 (51.9)	3.1 (3.4)	3.8 (3.9)	9.6 (10.5)
$[Pt(\eta\text{-}CF_2ClCOCF_2Cl)(PPh_3)_2]$	233—235	50.4 (51.0)	3.4 (3.3)	8.1 (7.7)	7.8 (8.3)
cis-$[PtCl(CF_2COCF_2Cl)(PPh_3)_2]$	230—234	50.9 (51.0)	3.4 (3.3)	7.8 (7.7)	8.3 (8.3)

[a] With decomposition. [b] Calculated values are given in parentheses.

(*b*) *With* 1,3-*dichlorotetrafluoropropan*-2-*one*. As above to give *cis*-$[PtCl_2(PPh_3)_2]$ (0.5 g, 78%).

Similarly, on repeating the above reactions in acetone,

---

[11] H. Kelm and H. Stieger, *J. Phys. Chem.*, 1973, **77**, 290.

[12] L. Malatesta and C. Cariello, *J. Chem. Soc.*, 1958, 2323.

[13] J. Chatt, B. L. Shaw, and A. A. Williams, *J. Chem. Soc.*, 1962, 3269.

[14] A. D. Allen and C. D. Cook, *Canad. J. Chem.*, 1964, **42**, 1063.

[15] D. M. Blake, S. Shields, and L. Wyman, *Inorg. Chem.*, 1974, **13**, 1595.

[16] D. R. Coulson, *Inorg. Synth.*, 1972, **13**, 121.

[17] W. J. Bland and R. D. W. Kemmitt, *J. Chem. Soc.* (*A*), 1968, 1278.

benzene, and light petroleum (b.p. 40—60 °C), only *cis*-$[\mathrm{PtCl_2(PPh_3)_2}]$ was isolated.

Reaction of Chlorofluoropropanones with Tetrakis(triphenylphosphine)palladium(0).—As above to give quantitative yields of *trans*-$[\mathrm{PdCl_2(PPh_3)_2}]$.[18,19]

Reaction of (*Diphenylacetylene*)*bis*(*triphenylphosphine*)-*platinum*(0) *with Chloropentafluoropropan*-2-*one in Diethyl Ether*.—An excess of chloropentafluoropropan-2-one (1.0 $\mathrm{cm^3}$) was condensed (−196 °C) on to a suspension of $[\mathrm{Pt(PhC{\equiv}CPh)(PPh_3)_2}]$ (0.05 g, 0.57 mmol) in diethyl ether (25 $\mathrm{cm^3}$) contained in a Carius tube (150 $\mathrm{cm^3}$). After shaking at room temperature for 4 h the tube was cooled, opened, and volatile material was removed. The white crystalline product was filtered off and washed with diethyl ether to give $[\mathrm{Pt(\eta\text{-}CF_3COCF_2Cl)(PPh_3)_2}]$ (0.33 g, 65%), m.p. 179—182 °C (decomp.).

Reaction of 1,3-*Dichlorotetrafluoropropan*-2-*one with* [Pt-(*trans*-PhCH=CHPh)$(\mathrm{PPh_3})_2$] *in Light Petroleum* (b.p. 40—60 °C).—An excess of 1,3-dichlorotetrafluoropropan-2-one (1.0 $\mathrm{cm^3}$) was added with stirring to a suspension of [Pt(*trans*-PhCH=CHPh)$(\mathrm{PPh_3})_2$] (0.05 g, 0.56 mmol) in light petroleum contained in a round-bottomed flask (150 $\mathrm{cm^3}$). After stirring for 2 h at room temperature the white suspension was filtered off and washed with diethyl ether to yield microcrystals of $[\mathrm{Pt(\eta\text{-}CF_2ClCOCF_2Cl)(PPh_3)_2}]$ (0.40 g, 80%).

The other reactions of the chlorofluoropropanones with platinum(0) complexes were similarly carried out and details of the reactions are summarised in Table 1.

Infrared Spectra.—$[\mathrm{Pt(\eta\text{-}CF_3COCF_2Cl)(PPh_3)_2}]$ 1 587w, 1 575w, 1 295(sh),m, 1 279s, 1 243s, 1 225m, 1 191m, 1 171s, 1 159(sh),s, 1 119s, 1 095, 1 031m, 1 003m, 983s, 939w, 891m, 855s, 832(sh),m, 825m, 759s, 751s, 731m, 713(sh),s, 701s, 647m, 555s, 531s, 523s, 499s, 459m, and 427m; $[\mathrm{Pt(\eta\text{-}CF_2ClCOCF_2Cl)(PPh_3)_2}]$ 1 590w, 1 573w, 1 485s, 1 442s, 1 319m, 1 245s, 1 236s, 1 191m, 1 186m, 1 167w, 1 160s, 1 147s, 1 139s, 1 103s, 1 093s, 1 075w, 1 028m, 1 003m, 997m, 944s, 783s, 755s, 749s, 733s, 711s, 695s, 675m, 621m, 555s, 527s, 508s, 491w, 465w, 455w, 441w, and 430m; *cis*-$[\mathrm{PtCl(CF_2COCF_3)(PPh_3)_2}]$ 1 764s, 1 486s, 1 315w, 1 304m, 1 272w, 1 223s, 1 212s, 1 191m, 1 167m, 1 155m, 1 138s, 1 117(sh), 1 103s, 1 098s, 1 031w, 1 003s, 983m, 871m, 855m, 757s, 750s, 743s, 707(sh), 698s, 549s, 527s, 521s, 505m, 499m, 320m, and 268m; *cis*-$[\mathrm{PtCl(CF_2COCF_2Cl)(PPh_3)_2}]$ 1 759s, 1 590w, 1 571w, 1 483s, 1 438s, 1 335w, 1 317m, 1 243s, 1 215w, 1 191m, 1 171m, 1 159m, 1 139m, 1 103s, 1 096s, 1 039(sh), 1 025s, 989m, 977m, 947w, 880w, 863m, 849m, 784m, 760s, 751s, 747s, 723w, 711s, 695s, 664m, 647w, 642w, 554s, 531s, 515s, 503s, 477w, 457w, 443w, 427w, and 316m $\mathrm{cm^{-1}}$.

Fluorine-19 *N.M.R. Spectra* (*in* $\mathrm{CH_2Cl_2}$).—*cis*-$[\mathrm{PtCl(CF_2COCF_3)(PPh_3)_2}]$ +11.8 [t, 3 F, $\mathrm{CF_3}$, with $^{195}\mathrm{Pt}$ satellites, *J*(FF) 6, *J*(PtF) *ca.* 9] and +28.6 p.p.m. [m, 2F, $\mathrm{CF_2}$ with $^{195}\mathrm{Pt}$ satellites, *J*(FF) 6, *J*(PF)(*trans*) 36, *J*(PF)(*cis*) 26, *J*(PtF) 360 Hz]; *cis*-$[\mathrm{PtCl(CF_2COCF_2Cl)(PPh_3)_2}]$ −1.1 [t, 2F, $\mathrm{CF_2Cl}$, with $^{195}\mathrm{Pt}$ satellites, *J*(FF) 7.8, *J*(PtF) *ca.* 17] and +22.4 p.p.m. [m, 2F, $\mathrm{PtCF_2}$, with $^{195}\mathrm{Pt}$ satellites, *J*(FF) 7.8, *J*(PF)(*trans*) 37, *J*(PF)(*cis*) 27, *J*(PtF) 373 Hz].

Kinetic Studies.—Portions of $[\mathrm{Pt(\eta\text{-}CF_2ClCOCF_3)(PPh_3)_2}]$ were added to pre-thermostatted solvent and the resulting solutions were filtered into 10 mm silica cells. These cells were placed in the thermostatted cell compartment of a Unicam SP 800A recording spectrophotometer. When the cells had reached thermal equilibrium the optical densities of their contents were monitored as a function of time at 276 nm. This wavelength corresponded to a shoulder on the main absorption peak of the starting complex; at this wavelength the change in optical density with time was most marked and most easily followed. Rate constants were computed from plots of the optical density against time using a standard least-mean-squares program.

We thank Johnson, Matthey Limited for the generous loan of potassium tetrachloroplatinate(II), the Royal Society for a Grant-in-aid for the purchase of the spectrophotometer, the S.R.C. for their support, and Dr. M. M. Hunt for undertaking preliminary experiments.

[7/516 *Received*, 24*th March*, 1977]

---

[18] J. Chatt and F. G. Mann, *J. Chem. Soc.*, 1939, 1622.

[19] G. E. Coates and C. Parkin, *J. Chem. Soc.*, 1963, 421.