Electrophilic Addition to Hexafluorobut-2-yne Complexes of Platinum(0), Rhodium(I), and Iridium(I)

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The hexafluorobut-2-yne complexes, $Pt(CF_3C\equiv CCF_3)L_2$ ($L = PPh_3$, $PMePh_2$, PMe_2Ph, PEt_2Ph; $2L = Ph_2PCH_2CH_2PPh_2$) react with trifluoroacetic acid to give the square planar alkenyl complexes, $Pt(OCOCF_3)(CF_3C{=}CHCF_3)L_2$ in which the phosphine ligands have a relative *cis*-configuration. The complex, *cis*-$Pt(OCOCF_3)(CF_3C{=}CHCF_3)(PPh_3)_2$ can be thermally isomerised to its *trans*-isomer and *cis–trans* isomerisation also occurs in [$^2H_6$]acetone solution. The action of heat on *cis*-$PtCl(CF_3C{=}CHCF_3)(PMePh_2)_2$ also effects isomerisation to the *trans*-isomer. Mercury(II) chloride and bromide similarly react with $Pt(CF_3C\equiv CCF_3)(PPh_3)_2$ and $Pt(CF_3C\equiv CCF_3)(PMePh_2)_2$ to give the mercuriated products $[PtCl\{CCF_3{=}C(HgCl)CF_3\}(PPh_3)_2]$ and *cis*-$[PtX\{CF_3C{=}C(HgX)CF_3\}(PMePh_2)_2]$ (X = Cl or Br). Protonation of $RhCl(CF_3C\equiv CCF_3)(PPh_3)_2$ and $IrCl(CO)(CF_3C\equiv CCF_3)(PPh_3)_2$ gives the alkenyl complexes $RhCl_2(CF_3C{=}CHCF_3)(PPh_3)_2$ and $IrCl(OCOCF_3)(CF_3C{=}CHCF_3)(CO)(PPh_3)_2$ respectively but $W(MeCN)(CF_3C\equiv CCF_3)_3$ does not react with trifluoroacetic acid under normal conditions.

WE have briefly reported that the formally zerovalent acetylene complexes $Pt(acetylene)(PPh_3)_2$ (acetylene $=$ $CF_3C\equiv CCF_3$ or $PhC\equiv CPh$) readily add one molecule of trifluoroacetic acid to give the substituted alkenyl complexes $Pt(OCOCF_3)(CF_3C{=}CHCF_3)(PPh_3)_2$ and $Pt(OCOCF_3)(CPh{=}CHPh)(PPh_3)_2$ respectively.[1,2] These experiments indicated that the co-ordinated acetylene was susceptible to electrophilic attack and we now describe, in more detail, our studies on a series of complexes of the type $Pt(CF_3C\equiv CCF_3)(PR_3)_2$ together with some related work on hexafluorobut-2-yne complexes of rhodium(I), iridium(I), and tungsten(0). Recently reactions of protonic acids with a series of non-fluorine containing acetylene complexes of the type $Pt(acetylene)(PPh_3)_2$ have been investigated [3-6] and the structures of the products have been determined by n.m.r. spectroscopy.[3]

RESULTS AND DISCUSSION

Trifluoroacetic acid readily reacts with the hexafluorobut-2-yne complexes, $Pt(CF_3C\equiv CCF_3)L_2$ ($L = PPh_3$, $PMePh_2$, PMe_2Ph, or PEt_2Ph; ^{2} $L = Ph_2PCH_2CH_2PPh_2$) to give white crystalline solids of general formulae $Pt(OCOCF_3)(CF_3C{=}CHCF_3)L_2$. The i.r. spectra of the adducts show bands due to ν_{asym} (CO_2) and ν_{sym} (CO_2) *ca.* 1690 and 1410 cm^{-1} respectively, the values being similar to those found for other trifluoroacetate complexes.[7] All the complexes also show an i.r. absorption in the region 1609—1630 cm^{-1} due to $\nu(C{=}C)$. In the complex *trans*-$PtCl(CF_3C{=}CHCF_3)(PEt_3)_2$ $\nu(C{=}C)$ occurs at 1603 cm^{-1}.[8] The ^{19}F n.m.r. spectra of the complexes (I)—(V) exhibit two resonances which may be assigned to α- and β-CF_3 groups present in the alkenyl system $Pt(C^{\alpha}F_3C{=}CHC^{\beta}F_3)$. For example the spectrum of (I) showed a quartet of doublets at $-11·7$ p.p.m. (α-CF_3) relative to benzotrifluoride with ^{195}Pt satellites which on double irradiation of the broad quintet at $-4·7$ p.p.m. (β-CF_3) collapsed to a doublet with platinum satellites, the doublet arising from ^{31}P–^{19}F coupling with the *cis*-triphenylphosphine ligand. Irradiation of the low-field resonance removed the ^{19}F–^{19}F coupling to give a doublet at $-4·7$ p.p.m. (β-CF_3) with ^{195}Pt satellites, the doublet in this instance arising from ^1H–^{19}F coupling with the geminal hydrogen atom. The ^{19}F n.m.r. spectrum of the deuterium substituted complex, *cis*-$Pt(OCOCF_3)(CF_3C{=}CDCF_3)(PMePh_2)_2$ exhibited a quartet for the β-CF_3 group.

The presence of ^{31}P–^{19}F coupling with the α-CF_3 group in the complexes (I)—(V) indicates a *cis*-arrangement of phosphine ligands and further evidence for this geometry is provided by the ^1H n.m.r. spectrum of (II) which exhibits two resonances at τ 8·10 and 8·45, both signals occurring as doublets with ^{195}Pt satellites.[9] Previously [1,2] we have only isolated the *trans*-isomer of $Pt(OCOCF_3)(CF_3C{=}CHCF_3)(PPh_3)_2$ from the reaction of trifluoroacetic acid with $Pt(CF_3C\equiv CCF_3)(PPh_3)_2$. However, work-up of the reaction mixture at room temperature affords the *cis*-complex, *cis*-$Pt(OCOCF_3)(CF_3C{=}CHCF_3)(PPh_3)_2$. Examination of the ^1H n.m.r. spectrum of a freshly prepared solution of *cis*-$Pt(OCOCF_3)(CF_3C{=}CHCF_3)(PPh_3)_2$ in [$^2H_6$]acetone reveals that *cis-trans* isomerisation occurs in this solvent. Thus the broad quartet at τ 4·64 for hydrogen in the system $=CHCF_3$ (J_{HF} 10, $J_{PH} < 3$ Hz) is characteristic of the complex *trans*-$Pt(OCOCF_3)(CF_3C{=}CHCF_3)(PPh_3)_2$. The *cis*-complex in deuteriochloroform exhibits a broad quintet at τ 4·13 (J_{HF} 8·4, J_{PH} 9·5 Hz), the ^{31}P–^1H coupling resulting from the presence of a *trans*-phosphine ligand. *cis*-$Pt(OCOCF_3)(CF_3C{=}CHCF_3)(PPh_3)_2$ is also converted to its *trans*-isomer at 150° *in vacuo*.

The magnitude of ^{19}F–^{19}F coupling between the inequivalent CF_3 groups in the complexes (I)—(V) implies

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TABLE 1

	Yield (%)	M.p. (°C)[a]	Analyses (%)[b]			I.r. spectra (Nujol mull, cm^{-1})			
			C	H	F	(ν C=C)	ν(CO_2) asym	ν(CO_2) sym	ν(M–Hal)
$Pt(CF_3C\equiv CCF_3)(PEt_2Ph)_2$	62	120—122	41·5 (41·8)	4·3 (4·4)	16·7 (16·5)	1769m			
$Pt(CF_3C\equiv CCF_3)(Ph_2PCH_2CH_2PPh_2)$	92	224—226	47·9 (47·7)	3·2 (3·2)	16·0 (15·9)	1768m			
cis-$Pt(OCOCF_3)(CF_3C{=}CHCF_3)(PPh_3)_2$	87	154—165 [c]	50·3 (50·6)	3·3 (3·1)	18·3 (17·2)	1624w	1711s 1699s	1406m	
trans-$Pt(OCOCF_3)(CF_3C{=}CHCF_3)(PPh_3)_2$	92	236—239	50·6 (50·7)	3·1 (3·1)	17·1 (17·2)	1614m	1700s	4114m	
$PtCl(CF_3C{=}CHCF_3)(PPh_3)_2$	88	242—245	51·8 (52·3)	3·3 (3·4)	12·4 (12·4)	1623w			302s
$PtBr(CF_3C{=}CHCF_3)(PPh_3)_2$	70	259—261	49·0 (48·9)	3·2 (3·2)	12·5 (11·8)	1623w			
trans-$Pt(OSO_3H)(CF_3C{=}CHCF_3)(PPh_3)_2$	52	201—204	48·6 (48·9)	3·6 (3·2)	12·1 (11·9)	1620w			
$Pt(OCOCF_3)(CF_3C{=}CHCF_3)(AsPh_3)_2$	95	208—210	46·4 (46·5)	3·0 (2·9)	16·5 (15·8)	1609w	1688ms	1412m	
cis-$Pt(OCOCF_3)(CF_3C{=}CHCF_3)(PMePh_2)_2$	85	150—155	43·7 (44·1)	3·0 (3·1)	19·0 (19·6)	1627w	1696s	1413ms	
cis-$PtCl(CF_3C{=}CHCF_3)(PMePh_2)_2$	85	90—93	45·3 (45·4)	3·5 (3·4)	14·2 (14·4)	1626w			
cis-$Pt(OCOCF_3)(CF_3C{=}CHCF_3)(PMe_2Ph)_2$	90	100—103	35·1 (35·3)	3·0 (3·1)	23·1 (22·9)	1626w	1698s	1410m	
cis-$Pt(OCOCF_3)(CF_3C{=}CHCF_3)(PEt_2Ph)_2$	83	136—138	39·1 (38·9)	3·9 (3·8)	21·1 (21·3)	1625m	1700s 1715s	1408ms	
cis-$Pt(OCOCF_3)(CF_3C{=}CHCF_3)(Ph_2PCH_2CH_2PPh_2)$	85	234—237	44·4 (44·2)	2·5 (2·9)	19·1 (19·6)	1625w	1712s 1699s	1406ms	
trans-$PtCl(CF_3C{=}CHCF_3)(PMePh_2)_2$	91	158—160	45·5 (45·4)	3·5 (3·4)	14·5 (14·4)	1617w			
$IrCl(OCOCF_3)(CF_3C{=}CHCF_3)(CO)(PPh_3)_2$ [d]	86	175—178	49·1 (48·9)	3·1 (3·0)	16·4 (16·2)	1616w	1720s	1400m	
$RhCl_2(CF_3C{=}CHCF_3)(PPh_3)_2$	70	168—170	51·0 (50·4)	3·1 (3·3)		1610ms			
$PtCl\{CF_3C{=}C(HgCl)CF_3\}(PPh_3)_2$ [e]	83	230—234	41·6 (41·7)	2·7 (2·6)	9·8 (9·9)	1598w			341s, 306s
cis-$PtCl\{CF_3C{=}C(HgCl)CF_3\}(PMePh_2)_2$ [f]	80	118—122	34·5 (34·8)	2·3 (2·5)	10·9 (11·0)	1598w			310s, 348s
cis-$PtBr\{CF_3C{=}C(HgBr)CF_3\}(PMePh_2)_2$ [g]	77	122—125	32·4 (32·2)	2·2 (2·3)		1598w			

[a] With decomposition. [b] Required values in parentheses. [c] Resolidification of the melt occurs *ca.* 180° and melts again at 218—222°. [d] ν(CO), 2083s, 2075s cm^{-1}. [e] Cl, 5·9 (6·2). [f] Cl, 7·8 (7·4). [g] Br, 14·0 (15·3)%.

TABLE 2

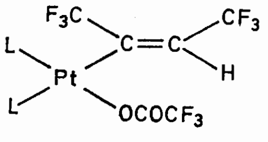
^1H and ^{19}F N.m.r. data for the alkenyl complexes

	^1H n.m.r.								
Compound	Solvent	τ =C(CF_3)H	J(P–H)	J(Pt–H)	τ Ph	τ MeP	J(P–H)	J(Pt–H)	Others
trans-$Pt(OCOCF_3)(CF_3C{=}CHCF_3)(PPh_3)_2$	[$^2H_6$]acetone	4·64q		nd [a]	2·1—2·6bm				
cis-$Pt(OCOCF_3)(CF_3C{=}CHCF_3)(PPh_3)_2$	$CDCl_3$	4·13quint	9·5	*ca.* 60	2·2—2·8bm				
trans-$Pt(OSO_3H)(CF_3C{=}CHCF_3)(PPh_3)_2$	$CDCl_3$	4·95q		nd	2·1—2·6bm				4·60bs(OSO_3H)
$Pt(OCOCF_3)(CF_3C{=}CHCF_3)(AsPh_3)_2$	$CDCl_3$	4·70m		nd	2·2—2·6bm				
cis-$Pt(OCOCF_3)(CF_3C{=}CHCF_3)(PMePh_2)_2$	$CDCl_3$	3·95quint	9·8	*ca.* 60	2·6—3·1bm	8·10d 8·45d	11 10	50 20	
cis-$PtCl(CF_3C{=}CHCF_3)(PMePh_2)_2$	$CDCl_3$	4·15quint	10	nd	2·2—2·9bm	8·12d 8·18d	10 9·0	28 38	
cis-$Pt(OCOCF_3)(CF_3C{=}CHCF_3)(PMe_2Ph)_2$	$CDCl_3$	3·8bm	nd	nd	2·3—2·7bm	8·43d 8·58d	11 9·0	48 14	
cis-$Pt(OCOCF_3)(CF_3C{=}CHCF_3)(PEt_2Ph)_2$	$CDCl_3$	3·77quint	9·5	*ca.* 60	2·3—2·6bm	8·9— 9·5bm	nd	nd	7·2bm CH_2
cis-$Pt(OCOCF_3)(CF_3C{=}CHCF_3)(Ph_2PCH_2CH_2PPh_2)$	[$^2H_6$]acetone	4·35quint	10	*ca.* 66	1·8—2·4bm				6·8—7·8bm CH_2
trans-$PtCl(CF_3C{=}CHCF_3)(PMePh_2)_2$	$CDCl_3$	4·42q		*ca.* 93	2·1—2·6bm	7·83t	7·4	31	
cis-$PtCl\{CF_3C{=}C(HgCl)CF_3\}(PMePh_2)_2$	$CDCl_4$				2·3—2·7bm	7·90d 8·21d	10 11	20 46	
cis-$PtBr\{CF_3C{=}C(HgBr)CF_3\}(PMePh_2)_2$	$CDCl_3$				2·3—2·7bm	7·78d 8·21d	9·6 10·5	20 46	

	^{19}F n.m.r.									
Compound	Solvent	p.p.m. M–C(CF_3)	J(FF)	J(P–Fα)	J(Pt–Fα)	p.p.m. =C(CF_3)H	J(H–F–)	J(Pt–F–)	O_2CCF_3	J(H–F)
trans-$Pt(OCOCF_3)(CF_3C{=}CHCF_3)(PPh_3)_2$	[$^2H_6$]acetone [b]	−9·7q	11		84	−5·1bm	10		+12·1s	9·3
cis-$Pt(OCOCF_3)(CF_3C{=}CHCF_3)(PPh_3)_2$	CH_2Cl_2 [c]	−11·7q of d	11	7·8	90	−4·7b quint	8·4	*ca.* 14	+11·9s	11
trans-$Pt(OSO_3H)(CF_3C{=}CHCF_3)(PPh_3)_2$	CH_2Cl_2	−9·1q	11		nd	−50q of d	7·8			
$Pt(OCOCF_3)(CF_3C{=}CHCF_3)(AsPh_3)_2$	CH_2Cl_2	−8·7q	10		92	−3·5q of d	8·2		+12·4s	10
cis-$Pt(OCOCF_3)(CF_3C{=}CHCF_3)(PMePh_2)_3$	CH_2Cl_2 [c]	−11·7q of d	11	9·0	83	−4·5quint	9·0	*ca.* 13	+11·3s	12
cis-$PtCl(CF_3C{=}CHCF_3)(PMePh_2)_2$	CH_2Cl_2	−11·9quint	11	11	91	−4·1b quint	11			
cis-$Pt(OCOCF_3)(CF_3C{=}CHCF_3)(PMe_2Ph)_2$	CH_2Cl_2	−10·8quint	10	10	82	−4·0b quint	11		+12·0bs	nd
cis-$Pt(OCOCF_3)(CF_3C{=}CHCF_3)(PEt_2Ph)_2$	CH_2Cl_2 [c]	−12·2q of d	12	7·8	88	−4·6quint	9·4	*ca.* 14	+11·7s	11
cis-$Pt(OCOCF_3)(CF_3C{=}CHCF_3)(Ph_2PCH_2CH_2PPh_2)$	CH_2Cl_2	−10·2q of d	12	9·0	75	−3·8q of d	11		+12·0s	11
trans-$PtCl(CF_3C{=}CHCF_3)(PMePh_2)_2$	CH_2Cl [b]	−10·1q	12		127	−6·0b quint	9·2			
cis-$PtCl\{CF_3C{=}C(HgCl)CF_3\}(PMePh_2)_2$ [e]	CH_2Cl_2	−11·8quint	12	12	84	−8·6b quint				
cis-$PtBr\{CF_3C{=}C(HgBr)CF_3\}(PMePh_2)_2$ [f]	CH_2Cl_2	−10·9q of d	12	11	96	−8·6b quint				

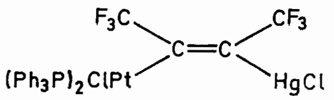
[a] nd = Not discernible. [b] Irradiation of high field multiplet collapses low field resonance into broad singlet plus ^{195}Pt satellites; irradiation of low field multiplet collapses high field resonance into broad doublet. [c] Irradiation of high field multiplet collapses low field resonance into doublet plus ^{195}Pt satellites; irradiation of low field multiplet collapses high field resonance into doublet plus ^{195}Pt satellites. [d] Signal disappears on addition of EtOD. [e] $J(^{199}Hg-^{19}F)$ *ca.* 270 Hz. [f] $J(^{199}Hg-^{19}F)$ *ca.* 290 Hz.

a *cis*-configuration of CF_3 groups in the co-ordinated alkenyl ligand[8] and hence these protonation reactions occur with retention of configuration about the platinum and carbon–carbon bonds of the acetylene. Further, it is apparent from our isomerisation experiments with the complex *cis*-$Pt(OCOCF_3)(CF_3C{=}CHCF_3)(PPh_3)_2$ that the formation of the *cis*-complex is kinetically controlled.

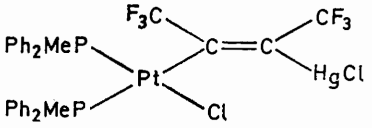


(I)–(V)

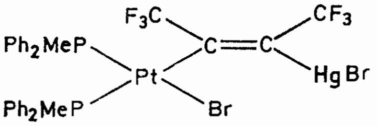
(I), L = PPh_3;
(II), L = $PMePh_2$;
(III), L = PMe_2Ph;
(IV), L = PEt_2Ph;
(V), L_2 = $Ph_2PCH_2CH_2PPh_2$



VI



(VII)



(VIII)

An alkenyl complex, $Pt(OCOCF_3)(CF_3C{=}CHCF_3)(AsPh_3)_2$ is also readily obtained from trifluoroacetic acid and $Pt(CF_3C{\equiv}CCF_3)(AsPh_3)_2$. However, whilst the configuration of the arsine ligands could not be determined the ^{19}F–^{19}F coupling again establishes a *cis*-configuration of CF_3 groups. Alcoholic solutions of hydrogen chloride, hydrobromic acid, and sulphuric acid similarly react with $Pt(CF_3C{\equiv}CCF_3)(PPh_3)_2$ to give the complexes $PtX(CCF_3{=}CHCF_3)(PPh_3)_2$ ($X = Cl$, Br, or OSO_3H). The ^{19}F n.m.r. spectrum of the bisulphate complex establishes a *trans* configuration for this complex, but the chloride and bromide complexes were not sufficiently soluble for ^{19}F n.m.r. studies. The addition of nitric acid to $Pt(CF_3C{\equiv}CCF_3)(PPh_3)_2$ leads to the dinitrate complex, $Pt(ONO_2)_2(PPh_3)_2$. However, glacial acetic acid is not sufficiently acidic to effect protonation of the complex.

In addition to protonic acids, we have also found that the co-ordinated hexafluorobut-2-yne in the complexes $Pt(CF_3C{\equiv}CCF_3)L_2$ ($L = PPh_3$ or $PMePh_2$) can be mercuriated by mercury(II) halides to give the white crystalline adducts (VI), (VII), and (VIII). The i.r. spectrum of (VI) exhibited a C=C stretching frequency at 1598 cm^{-1} and metal–chlorine stretching frequencies at 341 and 306 cm^{-1} and this data is consistent with the proposed structure. However, the complex was not sufficiently soluble to obtain a ^{19}F n.m.r. spectrum. The more soluble complex (VII) exhibited two chemical shifts at $-11{\cdot}8$ and $-8{\cdot}6$ p.p.m. (relative to benzotrifluoride). The signal at $-11{\cdot}8$ p.p.m. occurred as a quintet with platinum satellites, the quintet arising since $J(^{19}F–^{19}F)$ and $J(^{31}P–^{19}F)$ are of very similar magnitude. The high field quartet at $-8{\cdot}6$ p.p.m. exhibited ^{199}Hg–^{19}F coupling. The appearance of the CH_3P protons in (VII) in slightly different environments as doublets confirms the geometry about the platinum.[9] A similar complex (IVb) may be obtained with mercury(II) bromide and as with the protonation studies it is apparent that these reactions proceed with retention of stereochemistry about both the platinum and acetylene. However, attempts to obtain similar adducts with triphenyltin chloride, mercury(II) nitrate, sulphate, and acetate were not successful.

Although the complexes (VII) and (VIII) were prepared in refluxing ethanol, no *cis–trans* isomerisation was observed to take place with these complexes. This may be a consequence of steric repulsion between a phosphine ligand and the HgX group in the *trans*-complexes. The complex *cis*-$PtCl(CF_3C{=}CHCF_3)(PMePh_2)_2$, however, may be converted to its *trans*-isomer in hot benzene solution.

Preliminary studies show that the hexafluorobut-2-yne complexes, $RhCl(CF_3C{\equiv}CCF_3)(PPh_3)_2$ and $IrCl(CO)(CF_3C{\equiv}CCF_3)(PPh_3)_2$ also add a molecule of acid to give $RhClX(CF_3C{=}CHCF_3)(PPh_3)_2$ and $IrClY(CO)(CF_3C{=}CHCF_3)(PPh_3)_2$ respectively ($X = Cl$, $Y = OCOCF_3$). None of these complexes was sufficiently soluble for ^{19}F n.m.r. studies but the i.r. spectra strongly support their formulation as alkenyl complexes. Recently it has also been shown[10] that the complex $Os(CF_3C{\equiv}CCF_3)(CO)_2\{P(OMe)_3\}_2$ similarly adds hydrogen chloride and it is clear that co-ordination of hexafluorobut-2-yne to certain d^{10} and d^8 transition metals can enhance electrophilic addition to the acetylene. However, the d^6 complex $W(MeCN)(CF_3C{\equiv}CCF_3)_3$ does not react with trifluoroacetic acid. It has been suggested that protonation of the complexes, $Pt(acetylene)(PPh_3)_2$ could proceed *via* a platinum hydride intermediate[3,4] but since the metal–acetylene bond is polarised in the sense $\overset{\delta+}{M}{-}\overset{\delta-}{C}$ then electrophilic attack of the co-ordinated acetylene seems equally likely[11] as has been proposed for the addition of hydrogen chloride to $Os(CF_3C{\equiv}CCF_3)(CO)_2\{P(OMe)_3\}_2$.[10] The reaction of pyridine bromide perbromide with $Pt(NCC{\equiv}CCN)(PPh_3)_2$ which appears to give the adduct $Pt\{C(Br)(CN){=}C(Br)(CN)\}(PPh_3)_2$ seems most likely to result from direct addition to the co-ordinated acetylene.[5]

All the metal hexafluorobut-2-yne complexes which have been protonated lead to complexes containing the

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

[11] E. O. Greaves, C. J. L. Lock, and P. M. Maitlis, *Canad. J. Chem.*, 1968, **46**, 3879.

cis-alkenyl system, *cis*-$CF_3C{=}CHCF_3$. However, the reactions of hexafluorobut-2-yne with metal hydride complexes can lead to both *cis*-[8,12] and *trans*-$CF_3C{=}CHCF_3$ [13-15] systems. While the formation of *cis*-alkenyls could imply a concerted addition this cannot be so when a *trans*-alkenyl system is isolated.

EXPERIMENTAL

Analytical data, yields, and melting points for all new complexes are given in Table 1. I.r. spectra (Table 1) were recorded in Nujol mulls on a Perkin-Elmer model 225 spectrophotometer. ^1H and ^{19}F N.m.r. spectra (Table 2) were obtained using Varian Associates T60 and DA60 spectrometers respectively. The ^{19}F n.m.r. spectra were measured relative to benzotrifluoride as internal standard and were recorded at 56·4 MHz.

The complexes $Pt(PPh_3)_4$,[16] $Pt(AsPh_3)_4$,[16] $Pt(CF_3C{\equiv}CCF_3)(PPh_3)_2$,[17] $RhCl(CF_3C{\equiv}CCF_3)(PPh_3)_2$,[18] $IrClCO(CF_3C{\equiv}CCF_3)(PPh_3)_2$,[19] and $W(MeCN)(CF_3C{\equiv}CCF_3)_3$ [20] were prepared as described in the literature.

Preparation of the Complexes $Pt(CF_3C{\equiv}CCF_3)(PR_3)_2$.—The complexes $Pt(CF_3C{\equiv}CCF_3)(L)_2$ ($L = PMePh_2$, PMe_2Ph, PEt_2Ph, $2L = Ph_2PCH_2CH_2PPh_2$) were prepared by treating the complex $Pt(CF_3C{\equiv}CCF_3)(AsPh_3)_2$ [17] with the appropriate phosphine using the procedure previously described for the tetrafluoroethylene complexes, $Pt(C_2F_4)(PR_3)_2$.[21] This method gave the complexes: $Pt(CF_3C{\equiv}CCF_3)(PMePh_2)_2$,[22] 83%; $Pt(CF_3C{\equiv}CCF_3)(PMe_2Ph)_2$,[11] 65%; $Pt(CF_3C{\equiv}CCF_3)(PEt_2Ph)_2$, 62%; $Pt(CF_3C{\equiv}CCF_3)(Ph_2PCH_2CH_2PPh_2)$, 92%. Although 2,2′-bipyridyl displaces triphenylarsine from $Pt(C_2F_4)(AsPh_3)_2$ [21] a similar reaction involving $Pt(CF_3C{\equiv}CCF_3)(AsPh_3)_2$ gave only the unchanged acetylene complex which was identified by its m.p. and i.r. spectrum. The ^{19}F n.m.r. spectrum of $Pt(CF_3C{\equiv}CCF_3)(PEt_2Ph)_2$ exhibited a doublet with platinum satellites at $-8{\cdot}5$ p.p.m. respectively (J_{PtF} 67, J_{PF} 9·9 Hz). The ^{19}F n.m.r. spectrum of $Pt(CF_3C{\equiv}CCF_3)(Ph_2PCH_2CH_2PPh_2)$ is typical of an $X_3AA'X'_3$ system [9,23,24] centred at $-8{\cdot}5$ p.p.m. with platinum satellites (J_{PtF} 71 Hz).

Preparation of cis-$Pt(OCOCF_3)(CCF_3{=}CHCF_3)(PPh_3)_2$.—Trifluoroacetic acid (0·03 ml) and $Pt(CF_3C{\equiv}CCF_3)(PPh_3)_2$ (0·2 g, 0·23 mmol) were dissolved in methylene chloride (3 ml) in a nitrogen atmosphere. After 1 h the solution was evaporated to dryness under reduced pressure at room temperature. The residue was dissolved in a mixture of methylene chloride–diethyl ether (15 ml) and filtered. Addition of ethanol (3 ml) to the filtrate and evaporation of the solution to a smaller volume gave white crystals of *cis*-$Pt(OCOCF_3)(CF_3C{=}CHCF_3)(PPh_3)_2$ which was recrystallised from ethanol–diethyl ether.

Preparation of trans-$Pt(OCOCF_3)(CCF_3{=}CHCF_3)(PPh_3)_2$.—Trifluoroacetic acid (0·3 ml) was added to a solution of $Pt(CF_3C{\equiv}CCF_3)(PPh_3)_2$ (0·4 g, 0·45 mmol) in methylene chloride (20 ml) at room temperature. After 5 min light petroleum (b.p. 100—120°) was added and the solvents were removed under reduced pressure on a hot water bath to give a yellow oil. Recrystallisation from methylene chloride–ethanol gave white crystals of *trans*-$Pt(OCOCF_3)(CCF_3{=}CHCF_3)(PPh_3)_2$.

Reactions of $Pt(CF_3C{\equiv}CCF_3)(PPh_3)_2$.—*With (a) hydrogen chloride.* $Pt(CF_3C{\equiv}CCF_3)(PPh_3)_2$ (0·2 g, 0·23 mmol) in methylene chloride (20 ml) was treated with hydrogen chloride gas for 5 min. Evaporation of the solution to dryness gave, after recrystallisation of the residue from methylene chloride–methanol, white microcrystals of $PtCl(CCF_3{=}CHCF_3)(PPh_3)_2$.

(*b*) *Sulphuric Acid.* $Pt(CF_3C{\equiv}CCF_3)(PPh_3)_2$ (0·25 g, 0·28 mmol) in methylene chloride (20 ml) and sulphuric acid–methanol (1 : 1, 0·2 ml) were allowed to stand for 5 min at room temperature. Light petroleum (b.p. 100—120°) was added and the solvent was removed under reduced pressure. Recrystallisation of the oil from methylene chloride–hexane at −78° gave white crystals of *trans*-$Pt(OSO_3H)(CCF_3{=}CHCF_3)(PPh_3)_2$.

(*c*) *With hydrobromic acid.* As in (*b*) above but using hydrobromic acid–ethanol (1 : 1, 1 ml) gave $PtBr(CF_3C{=}CHCF_3)(PPh_3)_2$.

(*d*) *With nitric acid.* As in (*b*) above but using concentrated nitric acid–methanol (1 : 1, 0·5 ml) gave pale yellow crystals of $Pt(ONO_2)_2(PPh_3)_2$ [25] (0·2 g, 85%), m.p. 235—237° decomp. (Found: C, 51·7; H, 3·7; N, 3·3. Calc. for $C_{36}H_{30}N_2O_6P_2Pt$: C, 51·3; H, 3·6; N, 3·3%).

(*e*) *With acetic acid.* $Pt(CF_3C{\equiv}CCF_3)(PPh_3)_2$ (0·25 g) in benzene (20 ml) and glacial acetic acid (2 ml) were refluxed for 16 h. Evaporation to a small volume gave white crystals of the starting complex.

The same general procedure to that described in (*b*) above was used for all the other reactions of trifluoroacetic acid and hydrogen chloride with the complexes, $Pt(CF_3C{\equiv}CCF_3)L_2$ except that the reaction of $Pt(CF_3C{\equiv}CCF_3)(Ph_2PCH_2CH_2PPh_2)$ with trifluoroacetic acid was refluxed for 2 h.

Reaction of $Pt(CF_3C{\equiv}CCF_3)(PMePh_2)_2$ *with* CF_3CO_2D.—$Pt(CF_3C{\equiv}CCF_3)(PMePh_2)_2$ (0·1 g, 0·13 mmol) in $CDCl_3$ (1 ml) and CF_3CO_2D (0·3 ml) were mixed at room temperature. After 5 min the solvent was removed under reduced pressure on a hot water bath. Recrystallisation of the residue from methylene chloride–ethanol gave white crystals of *cis*-$Pt(OCOCF_3)(CF_3C{=}CDCF_3)(PMePh_2)_2$. The ^{19}F n.m.r. spectrum (CH_2Cl_2) showed bands at $-26{\cdot}2$ p.p.m. (3F, quintet, J_{FF} 11, J_{PF} 11, J_{PtF} 78 Hz) and $-18{\cdot}5$ p.p.m. (3F, quartet, J_{FF} 11 Hz) relative to trifluoroacetic acid as an external reference.

cis–trans-*Isomerisation of* cis-$Pt(OCOCF_3)(CCF_3{=}CHCF_3)(PPh_3)_2$.—(a) *cis*-$Pt(OCOCF_3)(CF_3C{=}CHCF_3)(PPh_3)_2$ (0·119 g, 0·120 mmol) was heated *in vacuo* at 150—170° for *ca.* 15 min. After cooling to room temperature, the material was recrystallised from ethanol–diethyl ether, washed with 1 : 1 ethanol–light petroleum (b.p. 40—60°) and light petroleum (b.p. 40—60°). The product (0·09 g, 75%) was

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identified as *trans*-$Pt(OCOCF_3)(CCF_3{=}CHCF_3)(PPh_3)_2$ by its m.p., i.r., ^1H, and ^{19}F n.m.r. spectra.

(b) *cis*-$Pt(OCOCF_3)(CCF_3{=}CHCF_3)(PPh_3)_2$ was dissolved in [$^2H_6$]acetone. The ^1H n.m.r. spectrum exhibited a broad quartet at τ 4·64 ($=CHCF_3$) (J_{HF} 10, J_{PH} <3 Hz) characteristic of *trans*-$Pt(OCOCF_3)(CCF_3{=}CHCF_3)(PPh_3)_2$. Removal of the solvent under reduced pressure and recrystallisation of the product from diethyl ether–ethanol gave *trans*-$Pt(OCOCF_3)(CCF_3{=}CHCF_3)(PPh_3)_2$ which was identified by its m.p. and ^{19}F n.m.r. spectrum.

cis–trans-*Isomerisation of* cis-$PtCl(CCF_3{=}CHCF_3)(PMePh_2)_2$.—An n.m.r. sample tube containing a benzene solution of *cis*-$PtCl(CCF_3{=}CHCF_3)(PMePh_2)_2$ was heated at 60—70° for 7½ days. The ^1H n.m.r. spectrum of the methyl region gradually changed from one characteristic of a *cis*-phosphine configuration (τ 8·36, d, J_{PH} 8·6, J_{PtH} 18 Hz; τ 8·28, d, J_{PH} 9·6, J_{PtH} 46 Hz) to that of a *trans*-phosphine configuration (τ 7·93, apparent triplet, $|J_{PH}|$ 7·4, J_{PtH} 31 Hz). Removal of the solvent and recrystallisation of the residue from diethyl ether–ethanol gave *trans*-$PtCl(CCF_3{=}CHCF_3)(PMePh_2)_2$ which was identified by its m.p. and i.r. spectrum.

Reaction of Trifluoroacetic Acid with $IrCl(CO)(CF_3C{\equiv}CCF_3)(PPh_3)_2$.—*trans*-$IrCl(CO)(CF_3C{\equiv}CCF_3)(PPh_3)_2$ (0·3 g, 0·32 mmol) in methylene chloride (10 ml) and trifluoroacetic acid (0·2 ml) were shaken together for 30 min. Light petroleum (b.p. 100—120°) was added and the solvent was removed under reduced pressure. Recrystallisation of the residue from methylene chloride–hexane afforded white crystals of $IrCl(OCOCF_3)(CO)(CCF_3{=}CHCF_3)(PPh_3)_2$ (0·29 g).

Reaction of Hydrogen Chloride with $RhCl(CF_3C{\equiv}CCF_3)(PPh_3)_2$.—$RhCl(CF_3C{\equiv}CCF_3)(PPh_3)_2$ (0·2 g, 0·24 mmol) suspended in diethyl ether (10 ml) was treated with a slow stream of hydrogen chloride gas for 5 min. Addition of hexane afforded orange crystals of $RhCl_2(CCF_3{=}CHCF_3)(PPh_3)_2$ (0·16 g).

Reaction of Mercury(II) *Chloride with* $Pt(CF_3C{\equiv}CCF_3)(PPh_3)_2$.—$Pt(CF_3C{\equiv}CCF_3)(PPh_3)_2$ (0·5 g, 0·57 mmol) and mercury(II) chloride (0·5 g, 1·8 mmol) in ethanol (20 ml) were heated under reflux for 48 h. The resulting solution was evaporated to dryness, and the residue was shaken with water to remove the excess of mercury(II) chloride. The residue was recrystallised from methylene chloride–hexane to give white crystals of $PtCl\{CCF_3{=}C(HgCl)CF_3\}(PPh_3)_2$ (0·56 g).

Reaction of $Pt(CF_3C{\equiv}CCF_3)(PMePh_2)_2$ *with* (*a*) *Mercury*(II) *chloride*. The complex (0·5 g, 0·66 mmol) and mercury(II) chloride (0·3 g, 1·1 mmol) in ethanol (15 ml) were heated under reflux for 16 h. The solvent was removed under reduced pressure and the white residue was shaken with water to remove the excess of mercury(II) chloride. Recrystallisation of the product from methylene chloride–hexane gave white diamond shaped crystals of *cis*-$PtCl\{CCF_3{=}C(HgCl)CF_3\}(PMePh_2)_2$ (0·54 g).

(*b*) *Mercury*(II) *bromide*. As above the complex (0·5 g, 0·66 mmol) and mercury(II) bromide (0·4 g, 1·1 mmol) gave *cis*-$PtBr\{CF_3C{=}C(HgBr)CF_3\}(PMePh_2)_2$ (0·57 g).

Similar reactions with $Hg(NO_3)_2$ and $HgSO_4$ gave metallic mercury but no fluorine containing compounds could be isolated. $Pt(CF_3C{\equiv}CCF_3)(PMePh_2)_2$ and $Hg(OAc)_2$ gave the platinum complex unchanged as did a similar reaction with $SnClPh_3$.

Reaction of $W(MeCN)(CF_3C{\equiv}CCF_3)$ *with Trifluoroacetic Acid*.—Trifluoroacetic acid (1 drop) was added to a saturated solution of $W(MeCN)(CF_3C{\equiv}CCF_3)_3$ in methylene chloride. The ^{19}F n.m.r. spectrum of the solution after seven days at room temperature showed signals at $-5·7$ p.p.m. and $-3·1$ p.p.m. which were identical to that of $W(MeCN)(CF_3C{\equiv}CCF_3)_3$ in methylene chloride.

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