Synthesis of Platinum Complexes of 2-Methyl-2,4,6-tris(trifluoromethyl)-pyran. *X*-Ray Crystal Structure of (Cyclo-octa-1,5-diene)[2-methyl-2,4,6-tris(trifluoromethyl)pyran]platinum

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Bis(cyclo-octa-1,5-diene)platinum reacts with 2-methyl-2,4,6-tris(trifluoromethyl)pyran to afford the complex $[Pt\{\eta^2\text{-}CH{=}C(CF_3)CH{=}C(CF_3)OC(CF_3)Me\}(cod)]$. Fluorine-19, ^1H, and ^{13}C n.m.r. spectroscopy showed that the pyran ligand was η^2-co-ordinated to platinum. In order to define the structure rigorously an *X*-ray diffraction study was carried out at 218 K. Crystals are triclinic, space group $P\bar{1}$, $Z = 2$, in a unit cell with lattice parameters $a = 10.136(12)$, $b = 9.062(11)$, $c = 11.455(9)$ Å, $\alpha = 93.22(8)$, $\beta = 106.23(8)$, and $\gamma = 109.32(9)°$. The structure was refined to R 0.056 (R' 0.057) for 4 832 independent reflections with $2.9 \leqslant 2\theta \leqslant 50°$ (Mo-K_α *X*-radiation). The *X*-ray structure determination confirmed that the pyran ligand is η^2-co-ordinated to the platinum atom. Moreover, the linkage is such that the platinum atom is attached to the C=C double bond having the C(Me)-(CF$_3$) substituent. The pyran ring is essentially planar with the three CF$_3$ substituents bent away from this plane to the far side from the platinum, while the Me substituent projects from the plane on the near side to the metal atom. Reaction of $[Pt\{CH{=}C(CF_3)CH{=}C(CF_3)OC(CF_3)Me\}(cod)]$ with PPh$_3$ affords $[Pt\{CH{=}C(CF_3)CH{=}C(CF_3)OC(CF_3)Me\}(PPh_3)_2]$. Related complexes $[Pt\{CH{=}C(CF_3)CH{=}C(CF_3)OC(CF_3)Me\}L_2]$ (L = CNBu^t or CNC$_6$H$_3$-Me$_2$-2,6) are obtained by reacting 2-methyl-2,4,6-tris(trifluoromethyl)pyran with the triplatinum compounds $[Pt_3(CNR)_6]$. Reaction between the pyran and $[Pt(C_2H_4)_2(PPh_3)]$ yields $[Pt\{CH{=}C(CF_3)CH{=}C(CF_3)OC(CF_3)Me\}(C_2H_4)(PPh_3)]$. Fluorine-19 and ^{13}C n.m.r. studies reveal that the η^2 mode of attachment of the pyran to the platinum is similar to that established for the cyclo-octa-1,5-diene analogue. In contrast, 2-methyl-2,4,6-tris(trifluoromethyl)pyran reacts with $[Rh(acac)(C_2H_4)_2]$ (acac = acetylacetonate, pentane-2,4-dionate) to give $[Rh(acac)\{\eta^4\text{-}CH{=}C(CF_3)CH{=}C(CF_3)OC(CF_3)Me\}]$.

ALLENE and buta-1,3-diene react with $[Pt(cod)_2]$ (cod = cyclo-octa-1,5-diene) to give (η-cyclo-octa-1,5-diene)(2,3-dimethylenebutane-1,4-diyl)platinum and (η-cyclo-octa-1,5-diene)(1,4-*trans*-divinylbutane-1,4-diyl)platinum, respectively.[1] Dimerisation of allene and butadiene to form these complexes may proceed through intermediates in which two diene molecules are simultaneously η^2-bonded to vacant co-ordination sites on a Pt(cod) group. Electron transfer from platinum (d^{10}) to olefin π^* orbitals, with twisting and concomitant platinum–carbon and carbon–carbon σ-bond formation, could afford the platinacyclopentane rings found in the products. Some support for this idea comes from the observation that $[Pt(cod)_2]$ and methyl vinyl ketone (mvk) in a 1 : 2 mol ratio react initially to give an unstable complex $[Pt(\eta^2\text{-mvk})_2(cod)]$ which subsequently rearranges to (η-cyclo-octa-1,5-diene)(1,3-diacetyl-butane-1,4-diyl)platinum.[2]

In contrast to the behaviour of buta-1,3-diene, its 2,3-dimethyl and 2,3-diphenyl derivatives oxidatively add to $[Pt(cod)_2]$ to give (η-cyclo-octa-1,5-diene)(2,3-dimethyl- and 2,3-diphenyl-but-2-ene-1,4-diyl)platinum, respectively.[1] It has been suggested that these complexes form *via* transient tetrahedral species $[Pt\{\eta^4\text{-}CH_2{=}C(R)C(R){=}CH_2\}(cod)]$ (R = Me or Ph) which subsequently rearrange to give the platinacyclopentene structures observed. Thus a tetrahedral complex $[Pt(\eta^4\text{-}1,3\text{-diene})(cod)]$ has not as yet been firmly identified. However, the well established electron withdrawing properties of quinones has allowed synthesis of a stable compound $[Pt\{C(Me){=}C(Me)C(O)C(Me){=}C(Me)C(O)\}(cod)]$ from the reaction of 2,3,5,6-tetramethylbenzo-1,4-quinone with $[Pt(cod)_2]$.[3] Unfortunately *X*-ray studies on this quinone complex, although indicative of η^4 co-ordination, revealed a disordered crystal and complete refinement of the structure was precluded. Although studies are continuing on (cyclo-octa-1,5-diene)(quinone)platinum complexes it was decided to investigate a reaction of $[Pt(cod)_2]$ with either a 2- or a 4-pyran molecule in the expectation that the electronegative oxygen atoms in the rings would enhance bonding of the diene systems to platinum(0), as occurs with the quinones. However, the parent compound 2-pyran is unknown and 4-pyran is not readily accessible.[4] Fortunately the interesting potential ligand 2-methyl-2,4,6-tris(trifluoromethyl)pyran is commercially available. Containing a 1,3-diene system with electronegative CF$_3$ substituents, this compound seemed likely to be able to η^2- or η^4-bond to platinum. The reactions described below were investigated to test which mode of behaviour results.

RESULTS AND DISCUSSION

Bis(cyclo-octa-1,5-diene)platinum reacted with 2-methyl-2,4,6-tris(trifluoromethyl)pyran in hexane at room temperature to afford a yellow crystalline complex (1). Microanalysis indicated (Table 1) that the compound was a 1 : 1 adduct of the Pt(cod) group and the pyran. Examination of the ^{19}F, ^{1}H, and ^{13}C n.m.r. spectra confirmed the formulation, and also established that in (1) only one double bond of the pyran was co-ordinated to platinum.

In the ^{19}F spectrum of the free pyran resonances occur at 83.5, 73.9, and 70.3 p.p.m. (Table 2). In complex (1) these three signals are all shifted to low field, but the greatest change occurs with the signal at 70.3 p.p.m. which moves to 64.6 p.p.m. and shows substantial $^{195}Pt-^{19}F$ coupling (130 Hz). It is noteworthy that the resonance of the CF_3 group observed in the spectrum of perfluoropropene at 72.0 p.p.m. shifts to 67.9 p.p.m. [$J(^{195}Pt-^{19}F)$ 105 Hz] in the η^2 complex $[Pt(CF_2{=}CFCF_3)(PPh_3)_2]$.[5]

The ^{1}H spectrum of (1) also accords with a structure in which the pyran is η^2-co-ordinated to the platinum. In the spectrum of the free ligand there are the expected two resonances for the CH groups. Upon complex formation only one of the signals shifts to high field and has platinum satellites [$J(^{195}Pt-^{1}H)$ 70 Hz]. The other signal shifts slightly to low field with small $^{195}Pt-^{1}H$ coupling (14 Hz). The η^2 co-ordination of the pyran is further substantiated by the ^{13}C spectrum. Resonances due to the *C*H groups occur at 102 and 42 p.p.m. with only the latter showing $^{195}Pt-^{13}C$ coupling (474 Hz). In

TABLE 1

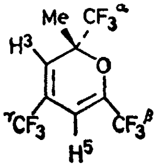
Physical and analytical data for complexes of 2-methyl-2,4,6-tris(trifluoromethyl)pyran

	Complex	M.p. (θ_c/°C)	Colour	Yield (%)	Analysis (%) [a]	
					C	H
(1)	$[Pt\{\eta^2\text{-}CH{=}C(CF_3)CH{=}C(CF_3)OC(CF_3)Me\}(cod)]$	94—97	Yellow	70	34.2 (33.8)	2.9 (2.8)
(2)	$[Pt\{\eta^2\text{-}CH{=}C(CF_3)CH{=}C(CF_3)OC(CF_3)Me\}(PPh_3)_2]$	136 (decomp.)	Yellow	75	52.0 (53.0)	3.3 (3.5)
(3)	$[Pt\{\eta^2\text{-}CH{=}C(CF_3)CH{=}C(CF_3)OC(CF_3)Me\}(CNBu^t)_2]$ [b]	100—102	White	73	34.2 (34.5)	3.7 (3.5)
(4)	$[Pt\{\eta^2\text{-}CH{=}C(CF_3)CH{=}C(CF_3)OC(CF_3)Me\}(CNC_6H_3Me_2\text{-}2,6)]$ [c]	158—160 (decomp.)	White	90	42.4 (42.8)	3.3 (3.1)
(5)	$[Pt\{\eta^2\text{-}CH{=}C(CF_3)CH{=}C(CF_3)OC(CF_3)Me\}(C_2H_4)(PPh_3)]$	92 (decomp.)	Yellow	50	43.6 (44.3)	3.4 (3.1)
(6)	$[Rh(acac)\{\eta^4\text{-}CH{=}C(CF_3)CH{=}C(CF_3)OC(CF_3)Me\}]$	171—172	Yellow	42	33.6 (33.5)	2.6 (2.4)

[a] Calculated values are given in parentheses. [b] N, 4.0 (4.2%). [c] N, 3.5 (3.7%).

TABLE 2

Fluorine-19 and hydrogen-1 n.m.r. data [a]



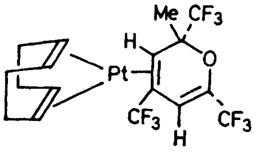
Compound	^{19}F [b]			^{1}H [c]			Other resonances
	$CF_3\alpha$	$CF_3\beta$	$CF_3\gamma$	H^3	H^5	Me	
Ligand [d,e]	83.5	73.9	70.3 *J*(HF) 2	4.50br [f]	4.28br	8.98	
(1) [g]	80.4	72.6 *J*(PtF) 40	64.6 *J*(FF) 2 *J*(PtF) 130	6.68 *J*(PtH) 70	3.88 *J*(PtH) 14	8.65	4.5—5.5 (m, 4 H, CH, cod) 8.0—8.8 (m, 8 H, CH_2, cod)
(2) [h]	79.2	72.0 *J*(PF) 5 *J*(PtF) 29	61.4 *J*(PF) 15 *J*(PtF) 106	7.04 *J*(PH) 7 *J*(PtH) 56	4.62br	9.25	2.4—3.0 (m, 30 H, Ph)
(3) [g]	80.0	72.2 *J*(PtF) 36	63.8 *J*(FF) 2 *J*(PtF) 123	6.35 *J*(PtH) 62	3.47 *J*(PtH) 10	8.24	9.18 (2, 18 H, Bu^t)
(4) [i,j]	79.6	72.2 *J*(PtF) 33	63.4 *J*(PtF) 118	6.52 *J*(PtH) 64	3.9 *J*(PtH) 10	8.43	7.54, 7.57 (s, 12 H, MeC_6) 2.7—2.8 (m, 6 H, HC_6)
(5) [k]	82.6	75.3 *J*(PF) 4 *J*(PtF) 24	66.1 *J*(PF) 12 *J*(PtF) 98	6.34 *J*(PH) 4 *J*(PtH) 70	3.46 *J*(PtH) 8	9.16	7.31, 6.98 (AA′BB′, C_2H_4) 2.4—3.2 (m, 15 H, Ph)
(6) [g]	79.4	69.4	64.0	6.12	5.26	8.68	8.23 (s, 6 H, Me, acac) 5.00 (s, 1 H, acac)

[a] Coupling constants in Hz. [b] In p.p.m. upfield from internal $CFCl_3$ (δ 0.0 p.p.m.). [c] Chemical shifts in τ. [d] 2-Me-2,4,6-$(CF_3)_3$-C_5H_2O. [e] Measured in CCl_4 (^{19}F) and [$^{2}H_6$]benzene (^{1}H). [f] Assignment for H^3 and H^5 may be reversed. [g] Measured in tetrahydrofuran (^{19}F) and [$^{2}H_6$]benzene (^{1}H). [h] Measured in toluene (^{19}F) and [$^{2}H_1$]chloroform (^{1}H). [i] Measured in tetrahydrofuran (^{19}F) and [$^{2}H_1$]chloroform (^{1}H). [j] Fourier-transform spectrum. [k] Measured in toluene (^{19}F) and [$^{2}H_6$]benzene (^{1}H).

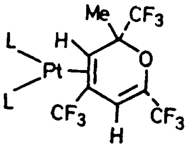
the maleic anhydride complex [Pt{CH=CHC(O)OC(O)}(cod)] the *C*H signals occur at 42 p.p.m. with $J(^{195}Pt-^{13}C) = 337$ Hz,[6] similar values to those observed for the platinum-bonded CH group in (1).

The i.r. spectrum of the free ligand shows two C=C stretching frequencies (1 685 and 1 644 cm^{-1}) whereas in the spectrum of (1) one such band is observed (1 670 cm^{-1}). If the ligand were bound to platinum *via* both double bonds no absorption near 1 650—1 700 cm^{-1} would be seen.

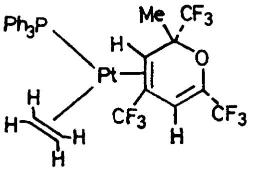
Although the spectroscopic studies on (1) established an η^2 mode of pyran-ligand bonding, they did not in themselves define with certainty which CH=C(CF_3) group is attached to platinum. Accordingly, a single crystal *X*-ray diffraction study was carried out on complex (1).



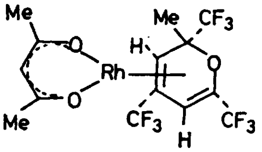
(1)



(2, L = PPh_3)
(3, L = $CNBu^t$)
(4, L = CNC_6H_3-2,6-Me_2)



(5)



(6)

The results of the study are given in Tables 3—5 and the molecular structure is shown in Figure 1, which also shows the crystallographic numbering system. The packing of the molecules in the unit cell is shown in Figure 2. From Figure 1 it is apparent that the platinum atom is η^2-co-ordinated to the carbon–carbon double bond of the (Me)(CF_3)CCH=C(CF_3) group. The bond distances and angles within the cod ligand are normal,[7] and interest centres on the pyran molecule. The plane defined by the atoms O(1) and C(2)—C(6) is at 76.3° to that defined by Pt, C(3), and C(4). Moreover, relative to the plane of the pyran ring the three CF_3 substituents are on the opposite side from the metal atom and point away from it while the methyl group is on the same side of the ring as the platinum and is inclined towards it. Not surprisingly the ring atom C(2) shows the maximum deviation from the O(1), C(2)—C(6) plane being displaced away from the metal (Table 5). The atoms C(3) and C(4) are separated by 1.46(1) Å and as expected, due to metal co-ordination, this distance is larger than that between the carbon atoms C(5)–C(6) of the non-co-ordinated double bond [1.32(1) Å]. The η^2 co-ordination of the pyran molecule is reminiscent of similar bonding in the arene complex

TABLE 3

Atomic positional (fractional co-ordinates) parameters with estimated standard deviations in parentheses for complex (1)

Atom	*x*	*y*	*z*
Pt	0.033 40(3)	0.217 65(3)	0.235 60(3)
C(11)	0.266 7(8)	0.236 0(9)	0.291 5(7)
H(11)	0.254(7)	0.127(7)	0.278(5)
C(12)	0.241 9(8)	0.284 0(9)	0.396 6(7)
H(12)	0.208(10)	0.189(10)	0.447(7)
C(13)	0.290 1(12)	0.455 2(13)	0.458 0(10)
H(131)	0.372(15)	0.500(15)	0.442(11)
H(132)	0.314(11)	0.460(11)	0.549(9)
C(14)	0.171 9(14)	0.526 5(13)	0 420 5(12)
H(141)	0.088(11)	0.466(11)	0.455(8)
H(142)	0.200(15)	0.629(16)	0.430(11)
C(15)	0.081 2(12)	0.478 6(11)	0.283 0(11)
H(15)	0.001(10)	0.473(10)	0.283(8)
C(16)	0.132 9(11)	0.458 7(10)	0.187 9(10)
H(16)	0.063(20)	0.438(19)	0.110(15)
C(17)	0.294 0(11)	0.493 1(11)	0.199 6(9)
H(171)	0.298(17)	0.519(18)	0.121(14)
H(172)	0.362(14)	0.610(15)	0.266(11)
C(18)	0.336 6(10)	0.346 5(11)	0.212 1(9)
H(181)	0.296(12)	0.272(12)	0.114(10)
H(182)	0.447(16)	0.354(16)	0.238(11)
O(1)	−0.220 6(6)	−0.082 1(6)	0.333 1(6)
C(2)	−0.149 1(8)	−0.132 4(8)	0.253 7(7)
C(21)	−0.019 4(10)	−0.163 7(10)	0.338 7(9)
H(211)	0.040(10)	−0.077(12)	0.397(8)
H(212)	0.030(12)	−0.199(12)	0.275(9)
H(213)	−0.053(13)	−0.253(14)	0.379(10)
C(22)	−0.264 3(10)	−0.290 4(9)	0.175 0(8)
F(221)	−0.381 6(6)	−0.272 4(7)	0.100 2(5)
F(222)	−0.204 5(7)	−0.355 4(6)	0.105 4(5)
F(223)	−0.311 5(8)	−0.397 8(6)	0.242 7(6)
C(3)	−0.103 8(8)	−0.015 1(8)	0.170 8(7)
H(3)	−0.078(12)	−0.054(13)	0.098(10)
C(4)	−0.184 5(8)	0.090 5(9)	0.133 5(7)
C(41)	−0.232 9(10)	0.111 6(11)	0.002 7(8)
F(411)	−0.361 0(6)	−0.002 9(8)	−0.064 5(5)
F(412)	−0.136 3(6)	0.109 8(8)	−0.057 3(5)
F(413)	−0.254 2(8)	0.247 7(8)	−0.007 9(6)
C(5)	−0.285 5(8)	0.098 1(9)	0.203 2(8)
H(5)	−0.334(7)	0.174(8)	0.187(6)
C(6)	−0.297 3(8)	0.014 7(9)	0.293 0(7)
C(61)	−0.394 6(9)	0.017 2(10)	0.369 6(8)
F(611)	−0.322 2(6)	0.048 4(7)	0.490 2(5)
F(612)	−0.457 0(6)	0.123 3(8)	0.344 7(5)
F(613)	−0.502 1(7)	−0.123 7(8)	0.348 9(7)

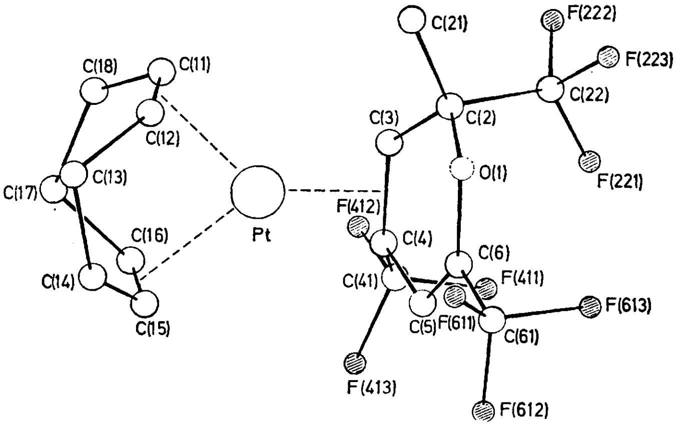


FIGURE 1 The molecule [Pt{η^2-CH=C(CF_3)CH=C(CF_3)OC(CF_3)(Me)}(cod)] showing the crystallographic numbering scheme

[Pt{η^2-$C_6(CF_3)_6$}$(PEt_3)_2$] in which the C–C distance of the two platinum-bonded carbon atoms is 1.51(3) Å and that between these carbon atoms and the platinum is 2.15(2) Å.[8] In complex (1), the distances Pt–C(3) and Pt–C(4) are shorter, averaging 2.065(7) Å.

TABLE 4

Bond lengths (Å) and angles (°) for the complex [Pt{η^2-$\overline{CH{=}C(CF_3)CH{=}C(CF_3)OC}(CF_3)Me$}(cod)] (1)

(*a*) Distances

Pt–C(3)	2.059(7)	Pt–C(4)	2.072(7)
C(3)–C(4)	1.46(1)	C(4)–C(5)	1.48(1)
C(5)–C(6)	1.32(1)	C(6)–O(1)	1.37(1)
O(1)–C(2)	1.45(1)	C(2)–C(3)	1.51(1)
C(4)–C(41)	1.49(1)	C(41)–F(411)	1.35(1)
C(41)–F(412)	1.35(1)	C(41)–F(413)	1.33(1)
C(6)–C(61)	1.50(1)	C(61)–F(611)	1.33(1)
C(61)–F(612)	1.32(1)	C(61)–F(613)	1.33(1)
C(2)–C(21)	1.52(1)	C(2)–C(22)	1.54(1)
C(22)–F(221)	1.32(1)	C(22)–F(222)	1.34(1)
C(22)–F(223)	1.33(1)		
Pt–C(11)	2.216(9)	Pt–C(12)	2.255(8)
Pt–C(15)	2.252(11)	Pt–C(16)	2.252(10)
C(11)–C(12)	1.37(1)	C(16)–C(15)	1.36(2)
C(12)–C(13)	1.52(1)	C(13)–C(14)	1.51(2)
C(14)–C(15)	1.54(1)	C(16)–C(17)	1.52(2)
C(17)–C(18)	1.53(2)	C(18)–C(11)	1.52(1)

(*b*) Angles *

C(11)–Pt–C(12)	35.7(3)	C(15)–Pt–C(16)	35.2(5)
C(3)–Pt–C(4)	41.4(3)	C(3,4)–Pt–C(15,16)	135.8
C(3,4)–Pt–C(11,12)	137.8	C(11,12)–Pt–C(15,16)	85.7

(*i*) Cyclo-octa-1,5-diene ligand

C(12)–C(11)–C(18)	125.1(8)	C(14)–C(15)–C(16)	126.3(11)
C(11)–C(12)–C(13)	125.6(8)	C(15)–C(16)–C(17)	125.2(9)
C(12)–C(13)–C(14)	113.7(7)	C(16)–C(17)–C(18)	113.0(7)
C(13)–C(14)–C(15)	113.6(11)	C(17)–C(18)–C(11)	114.8(9)

(*ii*) Pyran ligand

C(6)–O(1)–C(2)	118.3(6)	O(1)–C(2)–C(3)	113.3(7)
O(1)–C(2)–C(21)	106.0(7)	O(1)–C(2)–C(22)	105.2(7)
C(3)–C(2)–C(21)	112.8(7)	C(3)–C(2)–C(22)	109.8(6)
C(2)–C(22)–F(221)	112.7(8)	C(21)–C(2)–C(22)	109.4(7)
C(2)–C(22)–F(222)	110.1(8)	F(221)–C(22)–F(222)	107.7(7)
C(2)–C(22)–F(223)	112.8(7)	F(222)–C(22)–F(223)	105.9(8)
C(2)–C(3)–C(4)	120.0(8)	F(221)–C(22)–F(223)	107.3(8)
C(3)–C(4)–C(5)	115.3(7)	O(1)–C(6)–C(5)	126.1(9)
C(5)–C(4)–C(41)	115.0(7)	O(1)–C(6)–C(61)	109.8(7)
C(3)–C(4)–C(41)	120.8(8)	C(5)–C(6)–C(61)	124.1(9)
C(4)–C(41)–F(411)	112.8(7)	C(6)–C(61)–F(611)	112.6(7)
C(4)–C(41)–F(412)	113.7(8)	C(6)–C(61)–F(612)	112.1(8)
C(4)–C(41)–F(413)	111.8(8)	C(6)–C(61)–F(613)	110.4(8)
F(411)–C(41)–F(412)	105.3(7)	F(611)–C(61)–F(612)	107.5(8)
F(412)–C(41)–F(413)	106.6(8)	F(612)–C(61)–F(613)	107.5(7)
F(411)–C(41)–F(413)	106.0(8)	F(611)–C(61)–F(613)	106.5(8)
C(4)–C(5)–C(6)	120.4(9)		

* C(*n*,*m*) refers to midpoint of bond joining atoms C(*n*) and C(*m*).

TABLE 5

Some least-squares planes in the form $Ax + By + Cz = D$, where x, y, and z are fractional crystal co-ordinates

Plane (i): Pt, C(11), C(12)
$0.242x + 8.346y - 3.751z = 0.941$
Plane (ii): Pt, C(15), C(16)
$7.682x - 2.253y + 4.647z = 0.861$
Plane (iii): Pt, C(11,12), C(15,16) [a]
$-5.612x + 1.653y + 10.809z = 2.719$
Plane (iv): Pt, C(3), C(4)
$-5.165x - 0.043y + 11.083z = 2.429$
Plane (v): O(1), C(2), C(3), C(4), C(5), C(6)
$4.225x + 4.010y + 4.817z = 0.223$
[C(21) 0.67, C(22) −1.66, C(41) −0.75, C(61) −0.04, C(2) −0.16] [b]
Plane (vi): Pt, C(3,4), C(11,12), C(15,16) [c]
$-5.922x + 1.391y + 10.240z = 2.569$

Angles (°) between the least-squares planes: (i)—(ii) 84.6, (iii)—(iv) 10.7, (iv)—(v) 76.3.

[a] C(*n*,*m*) define midpoints of lines joining atoms C(*n*) and C(*m*). [b] Distances (Å) of pertinent atoms from this plane are given in square brackets. Of the atoms defining the plane the maximum deviation is shown by C(2). [c] Maximum deviation from the plane is shown by the platinum atom and is 0.07 Å.

The distances between the platinum atom and C(11), C(12), C(15), or C(16) [2.244(10) Å average] are very similar to those found between platinum and the cod ligands in the complexes [Pt_2{μ-$(CF_3)_2CO$}$(cod)_2$] and [Pt_2{μ-$(CF_3C_2CF_3)_2$}$(cod)_2$].[7] The platinum atom and the midpoints of C(3,4), C(11,12), and C(15,16) define a least-squares plane from which the metal atom deviates by only 0.07 Å (Table 5). The dihedral angle between the two planes Pt–C(3)–C(4) and Pt–C(11,12)–C(15,16) is 10.7°, a value which is typical of platinum(0) olefin complexes.[9] Thus the ligands are essentially trigonally disposed around the platinum. The double bonds of the cod ligand, however, have a relatively small angle of ' bite ' on the platinum as measured by the dihedral angle of 84.6° between the planes defined by Pt–C(11)–

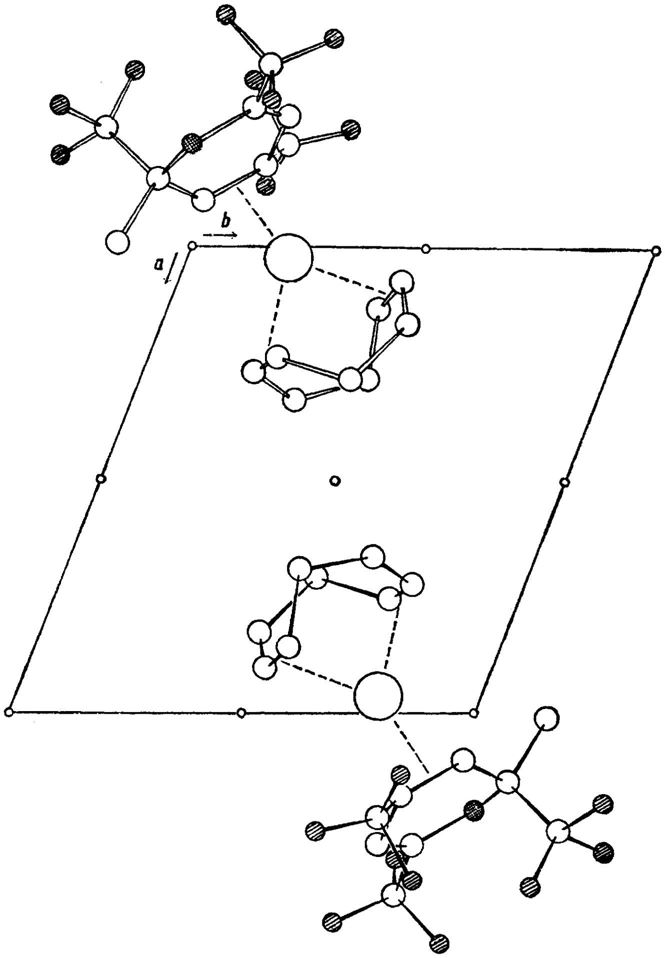


FIGURE 2 Contents of the unit cell of (1) viewed down c^* towards the origin

C(12) and by Pt–C(15)–C(16). This is characteristic for the Pt(cod) group and for $[\mathrm{Pt(cod)_2}]$ is 85°.[10]

Reaction of complex (1) with triphenylphosphine afforded compound (2), characterised by analysis and by n.m.r. spectroscopy. As in the ^{19}F n.m.r. spectrum of (1), one resonance in the spectrum of (2) was observed at distinctly lower field (61.4 p.p.m.) than that in the free ligand (Table 2). Moreover, this signal showed substantial ^{195}Pt–^{19}F coupling. In the ^{1}H spectrum of (2) one C*H* resonance was shifted to higher field with *J*(PtH) = 56 Hz and *J*(PH) = 7 Hz, again indicative of η^2-bonding of the pyran to platinum. In (2) the phosphine ligands are not equivalent, but the central portions of both ^{31}P n.m.r. patterns appear as a broad singlet because of their almost coincident chemical shifts {23.2 p.p.m. [m, *J*(PF) 3.5, *J*(PP) 22, *J*(PtP) 3 428 Hz] and 22.8 p.p.m. [m, *J*(PPt) 3 680 Hz]}. The i.r. spectrum of (2) has one band (1 660 cm^{-1}) in the C=C stretching region. These results indicate similar bonding of the pyran to platinum in (2) as in (1).

The triplatinum compounds $[\mathrm{Pt_3(CNR)_6}]$ (R = Bu^t or $\mathrm{C_6H_3Me_2}$-2,6) react with 2-methyl-2,4,6-tris(trifluoromethyl)pyran to give complexes (3) and (4), having ^{1}H and ^{19}F spectra (Table 2) similar to those of (1) and (2). It was not possible to observe a ^{13}C n.m.r. spectrum of (4) due to solubility problems, but the spectrum of (3) showed a signal for the co-ordinated *C*H group at 38.6 p.p.m. [*J*(PtC) 356 Hz]. The other *C*H group resonance occurs at 105.4 p.p.m. [*J*(PtC) 56 Hz]. Complex (3) could also be prepared by treating (1) with an excess of t-butyl isocyanide.

The complex $[\mathrm{Pt(C_2H_4)_2\{P(C_6H_{11})_3\}}]$ reacts with tetrafluoroethylene [11] and with 2,3,5,6-tetramethylbenzo-1,4-quinone [12] to afford trigonal 16-electron platinum compounds in which one ethylene group is replaced by an η^2-co-ordinated $\mathrm{C_2F_4}$ or duroquinone ligand. A similar complex (5) is formed by reacting $[\mathrm{Pt(C_2H_4)_2(PPh_3)}]$ with 2-methyl-2,4,6-tris(trifluoromethyl)pyran. The ^{31}P n.m.r. spectrum of (5) has a resonance at 19.00 p.p.m. [q of q, *J*(P$^\gamma$CF$_3$) 11, *J*(P$^\beta$CF$_3$) 4, and *J*(PtP) 3 522 Hz]. In the ^{13}C n.m.r. spectrum the platinum-co-ordinated *C*H group signal appears at 46.8 p.p.m. [*J*(PtC) 321 Hz] and that due to the ethylene ligand as a resonance at 59.7 p.p.m. [*J*(PtC) 58 Hz]. The appearance of only one signal for the $\mathrm{CH_2}$ groups indicates that olefin rotation occurs in solution, and this is confirmed by the AA′BB′ pattern observed in the ^{1}H spectrum (Table 2) albeit complicated by ^{19}F and ^{195}Pt coupling. As with complexes (1)—(4), the ^{19}F spectrum of (5) establishes that the pyran is η^2-bonded to the platinum.

In view of the results with the zerovalent platinum complexes it was of interest to ascertain whether the pyran ligand could form a complex employing both double bonds with any metal. It seemed likely that an η^4 complex might be formed by rhodium in view of the tendency of this metal to bond dienes in this manner.[13,14] Accordingly, the reaction between 2-methyl-2,4,6-tris(trifluoromethyl)pyran and $[\mathrm{Rh(acac)(C_2H_4)_2}]$ (acac = acetylacetonate, pentane-2,4-dionate) was investigated. Reaction occurred rapidly in hexane at room temperature to give a yellow crystalline compound (6). The ^{19}F n.m.r. spectrum (Table 2) contrasted from those of complexes (1)—(5) in that the signals of two of the $\mathrm{CF_3}$ groups are significantly shifted to low field implying that these groups are both linked to C=C bonds attached to a metal. Moreover, in the ^{1}H spectrum both C*H* resonances are shifted to higher field than in the free ligand.

EXPERIMENTAL

Nuclear magnetic resonance spectra (^{1}H, ^{19}F, hydrogen-1 decoupled ^{13}C and ^{31}P) were recorded on JEOL PFT and PS 100 spectrometers with ^{13}C shifts relative to $\mathrm{SiMe_4}$ (0.0 p.p.m.), ^{19}F shifts relative to $\mathrm{CCl_3F}$ (0.0 p.p.m.), and ^{31}P shifts relative to $\mathrm{H_3PO_4}$ (external). Infrared spectra were obtained as Nujol mulls on a Perkin-Elmer 457 spectrophotometer. Experiments were carried out using Schlenk-tube techniques under a dry oxygen-free nitrogen atmosphere, with solvents dried and distilled under nitrogen prior to use. Bis(cyclo-octa-1,5-diene)platinum,[15] $[\mathrm{Pt(C_2H_4)_2(PPh_3)}]$,[11] $[\mathrm{Pt_3(CNBu^t)_6}]$,[16] and $[\mathrm{Rh(acac)(C_2H_4)_2}]$ [17] were prepared by literature methods. Synthesis of the complex $[\mathrm{Pt_3(CNC_6H_3Me_2\text{-}2,6)_6}]$ is described below. 2-Methyl-2,4,6-tris(trifluoromethyl)pyran was purchased from PCR Incorporated, Gainesville, Florida, U.S.A. 32602. Analytical and other data for the pyran complexes are given in Table 1.

Synthesis of the Triplatinum Complex $[\mathrm{Pt_3(CNC_6H_3Me_2\text{-}2,6)_6}]$.—The compound $\mathrm{CNC_6H_3Me_2}$-2,6 (0.85 g, 6.5 mmol) in light petroleum (20 cm^3) was treated with $[\mathrm{Pt(cod)_2}]$ (1.23 g, 3 mmol), the latter being added as a finely powdered solid in portions (*ca.* 0.1 g) with stirring. A deep red precipitate formed which was allowed to settle. The supernatant liquid was decanted and the residue (1.21 g, 88%) recrystallised from toluene as red *crystals* of the toluene solvate $[\mathrm{Pt_3(CNC_6H_3Me_2\text{-}2,6)_6}]\cdot\mathrm{C_6H_5Me}$ (Found: C, 49.7; H, 4.4; N, 5.8. $\mathrm{C_{54}H_{54}N_6Pt_3\cdot C_6H_5Me}$ requires C, 50.0; H, 4.3; N, 5.7%), m.p. 122 °C, $\nu_{\mathrm{max.}}$ 2 130vs (br)(NC), 1 717m (br)(NC) cm^{-1}. ^{1}H n.m.r. spectrum ([^{2}H$_1$]chloroform), τ 2.7—3.6 (m, 3 H, $\mathrm{C_6H_3}$) and 7.52 (s, 6 H, Me).

Reactions of 2-*Methyl*-2,4,6-*tris*(*trifluoromethyl*)*pyran*.—(a) *With bis*(*cyclo-octa*-1,5-*diene*)*platinum*. The compound $[\mathrm{Pt(cod)_2}]$ (0.21 g, 0.5 mmol) was suspended in hexane (10 cm^3) at −50 °C, 2-methyl-2,4,6-tris(trifluoromethyl)pyran (0.3 g, 1 mmol) was added, and the mixture stirred for 1 h. After warming to room temperature and further stirring (4 h) the mixture was filtered and reduced in volume to *ca.* 5 cm^3. Cooling to −20 °C afforded greenish yellow *crystals* of $[\mathrm{Pt}\{\eta^2\text{-}\overline{\mathrm{CH{=}C(CF_3)CH{=}C(CF_3)OC}}\mathrm{(CF_3)Me}\}\mathrm{(cod)}]$ (1), dried *in vacuo*; $\nu_{\mathrm{max.}}$ at 1 670m (C=C) cm^{-1}. The ^{13}C n.m.r. spectrum in [^{2}H$_6$]benzene solution showed resonances at 102.3 [q, CH, *J*(CF) 3], 99.2 [CH(cod), *J*(PtC) 82], 99.0 [CH(cod), *J*(PtC) 89], 96.4 [CH(cod), *J*(PtC) 82], 93.3 [CH(cod), *J*(PtC) 107], 42.1 [*C*HPt, *J*(PtC) 474], 32 [2 × C,CH$_2$(cod)], 28.1 [CH$_2$(cod)], 27 [CH$_2$(cod)], and 24.4 p.p.m. [Me, *J*(PtC) 39 Hz].

(b) *With* $[\mathrm{Pt_3(CNR)_6}]$ (R = CNBu^t or $\mathrm{CNC_6H_3Me_2}$-2,6). The complex $[\mathrm{Pt_3(CNBu^t)_6}]$ (0.54 g, 0.5 mmol) was suspended in hexane (20 cm^3) at −50 °C and 2-methyl-2,4,6-tris(trifluoromethyl)pyran (0.45 g, 1.5 mmol) was added with stirring (1 h). The mixture was allowed to come to room temperature and filtered after 1 h. The cream residue was washed with hexane (2 × 3 cm^3) giving white *crystals* from diethyl ether–hexane of $[Pt\{\eta^2\text{-}CH{=}C(CF_3)CH{=}C(CF_3)OC(CF_3)Me\}(CNBu^t)_2]$ (3), dried *in vacuo*; $\nu_{max.}$ 2 199vs (NC), 2 160vs (NC), 1 671s (C=C) cm^{-1}. The ^{13}C n.m.r. spectrum in $[^2H_6]$benzene showed resonances at 105.4 [CH, J(PtC) 56], 57.3 (CMe_3), 38.6 [CHPt, J(PtC) 356], 29.6 [$Me(Bu^t)$], and 26.1 p.p.m. [Me, J(PtC) 49 Hz].

Compound (4), white *crystals*, was similarly prepared from $[Pt_3(CNC_6H_3Me_2\text{-}2,6)_6]$ (0.34 g, 0.25 mmol) and 2-methyl-2,4,6-tris(trifluoromethyl)pyran (0.23 g, 0.75 mmol); $\nu_{max.}$ 2 150vs (NC) and 2 120vs (NC) cm^{-1}.

Reaction of Complex (1) *with Triphenylphosphine*.—Compound (1) (0.17 g, 0.28 mmol) was suspended in hexane (5 cm^3) and triphenylphosphine (0.15 g, 0.56 mmol) was added portion-wise. The mixture was stirred (1 h) at room temperature, and then filtered. The residue was washed with hexane (2 × 3 cm^3) and crystallised from diethyl ether to give pale yellow *crystals* of $[Pt\{\eta^2\text{-}CH{=}C(CF_3)CH{=}C(CF_3)OC(CF_3)Me\}(PPh_3)_2]$ (2); $\nu_{max.}$ 1 660m (C=C) cm^{-1}. The ^{31}P n.m.r. spectrum in $[^2H_8]$toluene showed resonances at 23.22 [m, $J(P^{\gamma}CF_3)$ 3.5, J(PP) 22, J(PtP) 3 428] and 22.81 p.p.m. [m, J(PtP) 3 680 Hz]. The central portions of both ^{31}P patterns appear as a singlet because of their almost coincident chemical shifts. The ^{195}Pt satellites of the signal centred at 23.22 p.p.m. appear as two doublets of quartets so that it was possible to derive values of J(PF) and J(PP). The ^{195}Pt satellites of the other phosphorus nuclei appeared as an unresolved multiplet.

Synthesis of the Complex $[Pt\{\eta^2\text{-}CH{=}C(CF_3)CH{=}C(CF_3)OC(CF_3)Me\}(C_2H_4)(PPh_3)]$ (5).—A suspension of $[Pt(C_2H_4)_2(PPh_3)]$ (0.256 g, 0.5 mmol) in hexane (10 cm^3) was treated with 2-methyl-2,4,6-tris(trifluoromethyl)pyran (0.15 g, 0.5 mmol) at −50 °C. The mixture was warmed to room temperature and stirred (3 h), after which it was filtered, reduced in volume (*ca.* 3 cm^3) *in vacuo*, and cooled to −20 °C. The yellow *crystals* of (5) so obtained were recrystallised from hexane–diethyl ether; $\nu_{max.}$ 1 612m (C=C) cm^{-1}. The ^{13}C n.m.r. spectrum in $[^2H_6]$benzene showed resonances at 134.1 [C_{ortho}(Ph), J(PC) 12, J(PtC) 22], 130.8 [C_{para}(Ph)], 128.7 [C_{meta}(Ph), J(PC) 14], 104.6 (CH), 59.7 [C_2H_4, J(PtC) 88], 46.8 [CHPt, J(PtC) 321 Hz], and 22.9 p.p.m.(Me). The ^{31}P spectrum ($[^2H_6]$benzene) showed a resonance at 19.00 p.p.m. [q of q, $J(P^{\gamma}CF_3)$ 11, $J(P^{\beta}CF_3)$ 4, J(PtP) 3 522 Hz].

Reaction of (Acetylacetonato)bis(ethylene)rhodium with 2-Methyl-2,4,6-tris(trifluoromethyl)pyran.—The compound $[Rh(acac)(C_2H_4)_2]$ (0.26 g, 1 mmol) was suspended in hexane (10 cm^3) and treated with 2-methyl-2,4,6-tris(trifluoromethyl)pyran (0.3 g, 1 mmol) at room temperature for 1 h. The yellow solid produced was filtered off, washed with hexane (2 × 5 cm^3), and crystallised from toluene-hexane to give yellow *crystals* of $[Rh(acac)(\eta^2\text{-}CH{=}C(CF_3)CH{=}C(CF_3)OC(CF_3)Me\}]$ (6).

Crystal-structure Determination of the Complex $[Pt\{\eta^2\text{-}CH{=}C(CF_3)CH{=}C(CF_3)OC(CF_3)Me\}(cod)]$ (1).—Complex (1) crystallises as pale yellow prisms and that used for data collection was of dimensions 0.225 × 0.125 × 0.15 mm. Diffracted intensities were recorded on a Syntex $P2_1$ four-circle diffractometer for $2.9 \leqslant 2\theta \leqslant 50°$ at 218 K, according to methods described earlier.[18] Of the total of 5 577 reflections, 4 832 were 'observable' according to the criterion $I \geqslant 1\sigma(I)$, where $\sigma(I)$ is the estimated standard deviation of the measured intensity based on counting statistics and only these were used in the solution and refinement of the structure. Corrections were applied for Lorentz and polarisation effects and for the effects of X-ray absorption. All the computations were carried out with the 'X-Ray' system of programs available for the CDC 7600 at the London Computing Centre.

Crystal data. $C_{17}H_{17}F_9OPt$, $M = 603.4$, Triclinic, $a = 10.136(12)$, $b = 9.062(11)$, $c = 11.455(9)$ Å, $\alpha = 93.22(8)$, $\beta = 106.23(8)$, $\gamma = 109.32(9)°$, $U = 940.5$ Å^3, $D_m = 2.07$ (flotation), $Z = 2$, $D_c = 2.13$ cm^{-3}, $F(000) = 572$, Mo-K_α X-radiation (graphite monochromator), $\lambda = 0.710\ 69$ Å, μ(Mo-K_α) = 79.5 cm^{-1}, space group $P\bar{1}$ (no. 2).

Structure solution and refinement. The platinum atom was located from a Patterson synthesis, and all the remaining non-hydrogen atoms by successive electron-density difference syntheses. The structure was refined by blocked-matrix least squares with anisotropic thermal parameters for non-hydrogen atoms. All the hydrogen atoms were located and refined except for H(161), H(131), H(142), and H(172) which were incorporated into the refinement from calculated positions. Refinement converged at R 0.056 (R' 0.057) with a mean shift-to-error ratio in the final cycle of 0.03 : 1 with a maximum of 0.4 : 1. A weighting scheme of the form $w^{-1} = \sigma^2(F) + \alpha|F|^2$, where $\alpha = 0.002$, gave a satisfactory weight analysis. The final electron-density difference synthesis showed no peaks >0.8 or < −1.4 e Å^{-3} except in the vicinity of the metal atom. Scattering factors were from ref. 19 for C, O, and F and ref. 20 for Pt, including correction for the affects of anomalous dispersion ($\Delta f'$ −2.352, $\Delta f''$ 8.388) for the metal. Atomic positional parameters are in Table 3, interatomic distances in Table 4, and some least-squares planes in Table 5. Observed and calculated structure factors, C–H distances, and the thermal parameters are listed in Supplementary Publication No. SUP 22825 (26 pp.).*

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

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