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Preparations of chloro(diene)polyfluorophenylplatinum(II) complexes and the structure of chloro(dicyclopentadiene)-pentafluorophenylplatinum(II)

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Abstract

The complexes, PtCl(diene)R (diene = hexa-1,5-diene (hex) or norbornadiene (nbd), R = C_6F_5, *p*-HC_6F_4, or *p*-$MeOC_6F_4$; diene = dicyclopentadiene (dcy), R = C_6F_5) have been prepared by reaction between equimolar amounts of $PtCl_2$(diene) and Me_3SnR in dichloromethane. Most reactions also gave some of the corresponding PtR_2(diene) complex, which was readily separated by chromatography, and Pt(*p*-$MeOC_6F_4$)$_2$(nbd) was obtained in high yield from $PtCl_2$(nbd) and Me_3Sn(*p*-$MeOC_6F_4$) when a 1/2 mole ratio was used. Attempts to prepare PtCl(dcy)R (R = *p*-HC_6F_4 or *p*-$MeOC_6F_4$) from Me_3SnR gave only PtR_2(dcy) in boiling CH_2Cl_2 despite the use of 1/1 reactant stoichiometry, and Pt(*p*-$MeOC_6F_4$)$_2$(dcy) or no reaction (R = *p*-HC_6F_4) at room temperature. Alternative reagents, R'_3 SnR (R′ = Bu or Et, R = C_6F_5 or *p*-$MeOC_6F_4$) had a variable effect on the selectivity of monoarylation. Thus, $Bu_3SnC_6F_5$ was more selective and $Et_3SnC_6F_5$ less selective in formation of PtCl(hex)C_6F_5 than $Me_3SnC_6F_5$. With Et_3SnR (R = C_6F_5 or *p*-$MeOC_6F_4$) and an equimolar amount of $PtCl_2$(dcy), PtCl(dcy)R was the major product. The crystal structure of PtCl(dcy)C_6F_5 shows near square planar stereochemistry for platinum and steric congestion. The double bond from the six-membered ring of dcy is unsymmetrically coordinated to platinum *trans* to C_6F_5 and is further from the metal than the other double bond, which is symmetrically bonded *trans* to chlorine. The pentafluorophenyl group is approximately normal to the coordination plane, and gives two *ortho*-fluorine resonances in the ^{19}F NMR spectrum.

Introduction

We have recently reported syntheses of PtR_2(diene) (R = C_6F_5 or *p*-HC_6F_4; diene = *cis,cis*-cycloocta-1,5-diene (cod), dicyclopentadiene (dcy), norbornadiene (nbd), hexa-1,5-diene (hex)) by the organolithium route and their ligand exchange reactions to give PtR_2L_2 complexes [1]. Attempts to obtain PtCl(diene)R derivatives from organolithium reagents were unsuccessful. Thus, equimolar amounts of $PtCl_2$(cod) and C_6F_5Li still gave $Pt(C_6F_5)_2$(cod) (and unreacted $PtCl_2$(cod)). The complexes PtCl(cod)R (R = C_6F_5 or *p*-HC_6F_4) were accessible by decarboxylation between $PtCl_2$(cod) and the thallous polyfluorobenzoate (mole ratio 1/1) in warm pyridine [1], but an attempt to prepare PtCl(hex)C_6F_5 by this method resulted in simultaneous ligand exchange, giving the previously unknown *cis*-PtCl(C_6F_5)(py)$_2$. In a search for a more general route to chloro(diene)polyfluorophenylplatinum(II) complexes, we have now investigated reactions of $PtCl_2$(diene) reactants with trialkylpolyfluorophenyltin compounds and some polyfluorophenylmercurials. Organotin reagents have been successfully used in the synthesis of PtCl(cod)R (R = non-fluorinated aryl) compounds [2] as well as other organoplatinum(II) complexes [3]. However, the reaction mechanism, electrophilic attack of platinum on the aryl group of the organotin reagent (electrophilic aromatic platinadestannylation) [2] suggests that polyfluorophenyl transfer should be less facile, since polyfluorophenyl groups are deactivated to electrophilic attack [4,5].

Results and discussion

(a) Syntheses

The trialkylpolyfluorophenyltin reagents Me_3SnR (R = C_6F_5, *p*-HC_6F_4, or *p*-$MeOC_6F_4$), $R'_3SnC_6F_5$ (R' = Et or Bu) and Et_3Sn(*p*-$MeOC_6F_4$) were prepared in satisfactory-good yield by the organolithium route. All except the last have previously been prepared, mainly by other, often less convenient routes [6–11]. Reactions of $PtCl_2$(diene) (diene = hex or nbd) with an equimolar amount of Me_3SnR (R = C_6F_5, *p*-HC_6F_4, or *p*-$MeOC_6F_4$) in boiling dichloromethane yielded the corresponding chloro(diene)polyfluorophenylplatinum(II) complexes (reaction 1, R' = Me).

$$PtCl_2(\text{diene}) + R'_3SnR \rightarrow R'_3SnCl + PtCl(\text{diene})R \qquad (1)$$

In all cases, there was competition from diarylation (reaction 2, R' = Me), and

$$PtCl_2(\text{diene}) + 2R'_3SnR \rightarrow 2R'_3SnCl + PtR_2(\text{diene}) \qquad (2)$$

reaction of $PtCl_2$(nbd) with Me_3Sn(*p*-$MeOC_6F_4$) on a mole ratio of 1/2 gave a good yield of norbornadienebis(2,3,5,6-tetrafluoro-4-methoxyphenyl)platinum(II). Thus, the organotin compounds also appear a convenient source of (diene)bis(polyfluorophenyl)platinum(II) complexes. Details of the syntheses are given in Table 1. Heating was needed to ensure a reasonable rate of reaction and was generally continued until the organotin reagent was consumed (TLC monitoring).

Reactions of Me_3SnR (R = C_6F_5, *p*-HC_6F_4, or *p*-$MeOC_6F_4$) with $PtCl_2$(dcy) were a less satisfactory source of PtCl(diene)R than those with $PtCl_2$(hex or nbd). In boiling CH_2Cl_2, only PtR_2(dcy) complexes were obtained (Table 1) (reaction 2, R' = Me, diene = dcy), despite the use of a 1/1 stoichiometry. Prolonged reaction of $PtCl_2$(dcy) with $Me_3SnC_6F_5$ at room temperature gave PtCl(dcy)C_6F_5 specifically and in good yield (reaction 1, R = C_6F_5, R' = Me, diene = dcy). However, similar treatment with Me_3Sn(*p*-HC_6F_4) and Me_3Sn(*p*-$MeOC_6F_4$) resulted in no reaction and formation of Pt(*p*-$MeOC_6F_4$)$_2$(dcy) as the major product, respectively.

Table 1

Reactions of $PtCl_2$(diene) complexes with R'_3SnR compounds

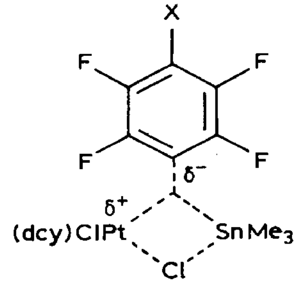
$PtCl_2$(diene) complex [a]	R'_3SnR reagent [a]	Reaction		Products	
		Temperature (°C)	Time (h)	PtCl(diene)R [b] % yield [c]	PtR_2(diene) [b] % yield [c]
$PtCl_2$(hex)	$Me_3SnC_6F_5$	41	72	39	6
$PtCl_2$(hex)	$Et_3SnC_6F_5$	41	48	19	13
$PtCl_2$(hex)	$Bu_3SnC_6F_5$	41	48	21	trace
$PtCl_2$(hex)	Me_3Sn(*p*-HC_6F_4)	41	96	33	5
$PtCl_2$(hex)	Me_3Sn(*p*-$MeOC_6F_4$)	41	13	28	11
$PtCl_2$(nbd)	$Me_3SnC_6F_5$	41	72	33	23
$PtCl_2$(nbd)	Me_3Sn(*p*-HC_6F_4)	41	96	51	17
$PtCl_2$(nbd)	Me_3Sn(*p*-$MeOC_6F_4$)	41	13	50	12
$PtCl_2$(nbd)	Me_3Sn(*p*-$MeOC_6F_4$) [d]	41	48	–	75
$PtCl_2$(dcy)	$Me_3SnC_6F_5$	41	48	trace	42
$PtCl_2$(dcy)	$Me_3SnC_6F_5$	25	168	60	–
$PtCl_2$(dcy)	$Et_3SnC_6F_5$	41	24 [e]	15	5
$PtCl_2$(dcy)	$Bu_3SnC_6F_5$	41	24	dec. > 2 h	
$PtCl_2$(dcy)	Me_3Sn(*p*-HC_6F_4)	(25) [f] 41	(72) [f] 48 [e]	–	32
$PtCl_2$(dcy)	Me_3Sn(*p*-$MeOC_6F_4$)	41	48	–	47
$PtCl_2$(dcy) [g]	Me_3Sn(*p*-$MeOC_6F_4$) [h]	25	264	trace	60 [i]
$PtCl_2$(dcy)	Et_3Sn(*p*-$MeOC_6F_4$)	41	48 [e]	24 [j]	5
$PtCl_2$(cod) [k]	$Me_3SnC_6F_5$ [k]	41	48	no reaction	

[a] 1.00 mmol in CH_2Cl_2 (50 cm^3) unless indicated otherwise. [b] Analytically pure products or with properties identical with those of analysed compounds. [c] Based on $PtCl_2$(diene). [d] 2.00 mmol. [e] Some decomposition observed. [f] No reaction. [g] 1.05 mmol. [h] 0.74 mmol. [i] Based on the organotin reagent. [j] Impure. [k] 0.50 mmol.

In an attempt to achieve more selective monoarylation, reactions of the somewhat bulkier trialkylpolyfluorophenyltin compounds $R'_3SnC_6F_5$ (R' = Et or Bu) and Et_3Sn(*p*-$MeOC_6F_4$) were examined. Formation of PtCl(hex)C_6F_5 from $Bu_3SnC_6F_5$ and $PtCl_2$(hex) (reaction 1, R = C_6F_5, R' = Bu, diene = hex) was virtually specific (cf. $Me_3SnC_6F_5$). By contrast, reaction of $PtCl_2$(hex) with $Et_3SnC_6F_5$ was less selective than that with $Me_3SnC_6F_5$ (Table 1). The enhanced selectivity with $Bu_3SnC_6F_5$ (above) could not be utilised in reaction with $PtCl_2$(dcy) as substantial decomposition occurred. However, treatment of this complex with an equimolar amount of Et_3SnR (R = C_6F_5 or *p*-$MeOC_6F_4$) in boiling dichloromethane surprisingly (in view of the behaviour with $PtCl_2$(hex)) gave PtCl(dcy)R as the principal product (reaction 1, R' = Et, diene = dcy). This contrasts with formation of PtR_2(dcy) from Me_3SnR under similar conditions, and even at room temperature for R = *p*-$MeOC_6F_4$ (Table 1). Thus, longer chain alkyl groups (R') in R'_3SnR (R = polyfluorophenyl) can lead to more specific monoarylation, though not in a clearly systematic fashion.

The complexes $PtCl_2$(diene) (diene = hex or nbd) react significantly faster with Me_3Sn(*p*-$MeOC_6F_4$) than with Me_3SnR (R = C_6F_5 or *p*-HC_6F_4) (Table 1). Since the *p*-MeO substituent has a strong electron donating resonance effect, the substituent effects are indicative of an electrophilic aromatic platinadestannylation mechanism [2]. (There are two alternative transition states, both of which have substantial positive charge in the aromatic ring [2].) The activating effect of a *p*-MeO substituent on electrophilic substitution in polyfluoroaromatic compounds is well-established, e.g. [12]. Reactions of $PtCl_2$(nbd) with Me_3SnR are slower when $R = C_6F_5$, p-HC_6F_4, or p-$MeOC_6F_4$ (Table 1) than when R = 2-furyl [2], again suggesting electrophilic aromatic substitution. Failure of $PtCl_2$(cod) to react with Me_3SnR ($R = C_6F_5$) in boiling dichloromethane (Table 1) by contrast with ready arylation when R = non-fluorinated aryl [2] is also consistent with this mechanism.

Not all substituent effects are indicative of classical electrophilic aromatic substitution. In reactions of $PtCl_2$(dcy) with Me_3SnR at room temperature, the rate decreases in the order $R = C_6F_5 > p\text{-}MeOC_6F_4 > p\text{-}HC_6F_4$, * corresponding to a decrease in the inductive electron withdrawing character of the polyfluorophenyl group (F > MeO > H in inductive acceptor ability [13]). This is consistent with a transition state (I) (X = F, OMe, H) with significant aryl carbanion character.



(I)

Because the negative charge develops in an sp^2 orbital, the stability of I depends mainly on inductive not resonance substituent effects. Generation of carbanion character at the α-carbon requires that C–Sn bond breaking occurs slightly ahead of C–Pt bond formation. It is not clear why there should be a change of mechanism from diene = hex or nbd to diene = dcy. However, there is more steric crowding in bonding of dcy than hex or nbd to platinum, and it is possible that complex I with three centre, two electron bonding of the metals to the aromatic ring is more weakly bound and less sterically demanding than transition states [2] for electrophilic aromatic platinadestannylation.

The low selectivity of monopolyfluorophenylation (Table 1) contrasts with much higher selectivity in the monoarylation of $PtCl_2$(cod) [2]. This may be attributed to the combination of extended reaction times and a more electrophilic PtCl(diene)R complex when R = polyfluorophenyl than when R is a non-fluorinated aryl group. However, this explanation cannot account for the complete domination of bis(polyfluorophenylation) over mono(polyfluorophenylation) in the reaction of $PtCl_2$(dcy) with Me_3SnR ($R = p$-HC_6F_4 or p-$MeOC_6F_4$) (Table 1), especially if transition state I obtains. A similar domination of diarylation over monoarylation has been encountered in the reaction of $PtCl_2$(cod) with $Me_3Sn(\eta\text{-}p\text{-}MeC_6H_4\text{-}Cr(CO)_3)$ [2], and the $Cr(CO)_3$ group is also strongly electron withdrawing [14]. The possibility that PtR_2(dcy) ($R = p$-HC_6F_4 or p-$MeOC_6F_4$) arises from rearrangement of PtCl(dcy)R

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* Although a shorter reaction time was used for $R = p$-HC_6F_4 than for $R = C_6F_5$ or p-$MeOC_6F_4$, there was no evidence of reaction in the first case after 72 h by contrast with detection of products after 24 h for the others.

can be ruled out for the latter, since PtCl(dcy)(*p*-MeOC_6F_4) (prepared from Et_3Sn(*p*-MeOC_6F_4)) is stable towards decomposition into Pt(*p*-MeOC_6F_4)$_2$(dcy) and $PtCl_2$(dcy).

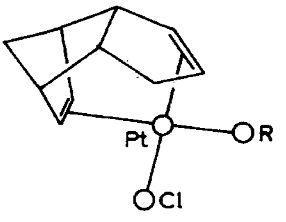
No reaction could be induced between $PtCl_2$(hex) and Pt(C_6F_5)$_2$(hex) in boiling dichloromethane, hence such rearrangements appear an unprofitable route to PtCl(diene)R when R = polyfluorophenyl, by contrast with R = non-fluorinated aryl and diene = cod [2]. Attempts to prepare PtCl(diene)R (diene = dcy, R = *p*-HC_6F_4 or *p*-MeOC_6F_4; diene = hex, R = C_6F_5) by cleavage of PtR_2(diene) with HCl failed under a variety of conditions (Experimental Section), reflecting deactivation of *p*-XC_6F_4Pt (X = F, H or MeO) bonds towards electrophilic cleavage. Some reactions of $PtCl_2$(diene) with polyfluorophenyl mercurials were also examined, but these reagents were far less satisfactory than trialkylpolyfluorophenyltin compounds. Prolonged reactions of $PtCl_2$(hex) with $(C_6F_5)_2Hg$ gave a low yield of the mono(pentafluorophenyl)platinum compound,

$$PtCl_2(hex) + (C_6F_5)_2Hg \rightarrow PtCl(hex)C_6F_5 + C_6F_5HgCl \qquad (3)$$

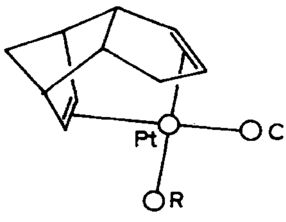
but reactions with $PhHgC_6F_5$ and (*p*-MeOC_6F_4)$_2$Hg gave metal mirrors and $PtCl_2$(dcy) did not react with $(C_6F_5)_2Hg$.

(b) *The crystal and molecular structures of PtCl(dcy)C_6F_5*

The crystal structure was investigated to establish which geometric isomer of PtCl(dcy)C_6F_5 (IIa or IIb, R = C_6F_5) was obtained and to provide a structural basis for interpretation of the ^{19}F NMR spectrum (see below).



(IIa)



(IIb)

Few structures of dicyclopentadiene complexes have been determined. Both $PtCl_2$(dcy) [15] and $PdCl_2$(dcy) [16] have been examined, but errors for the former were too large to justify reporting geometric parameters. Final positional parameters for PtCl(dcy)C_6F_5 are given in Table 2, selected bond lengths and angles in Table 3, equations of mean planes and some key interplanar angles in Table 4, and the structure is displayed in Fig. 1. The geometry is that of IIa (R = C_6F_5) with an approximately square planar arrangement of Cl, C(1), CT1 (mid point of C(7)=C(8)), and CT2 (mid point of C(12)=C(13)) about platinum (Table 3), and all are significantly displaced (0.08–0.10 Å) from the mean coordination plane (Table 4). There is a marked difference in coordination of the two double bonds with CT1 closer to platinum than CT2 by 0.13 Å, and C(7)=C(8) is slightly longer than C(12)=C(13) (Table 3). The former, *trans* to chlorine, is symmetrically bound to platinum, but the PtC(7)C(8) plane is substantially inclined to the coordination plane (Table 4). By contrast, C(12)=C(13), *trans* to C_6F_5, is unsymmetrically bound (Table 3) and the PtC(12)C(13) plane is normal to the coordination plane (Table 4). Weaker binding of the double bond from the six-membered ring is also observed in

Table 2

Atomic parameters for $C_{16}H_{12}ClF_5Pt$ (Esd values in parentheses)

Atom	x	y	z	U_{iso} (Å^2)
Pt	0.0071(1)	0.2385(1)	0.1157(1)	0.0330(2) [a]
Cl	0.1163(3)	0.2590(3)	0.4661(5)	0.060(2) [a]
F(2)	0.1921(6)	0.1290(6)	−0.1682(13)	0.065(4) [a]
F(3)	0.4378(7)	0.2542(8)	−0.1005(15)	0.086(6) [a]
F(4)	0.5634(6)	0.5242(9)	0.2338(15)	0.090(6) [a]
F(5)	0.4387(8)	0.6707(7)	0.4967(14)	0.093(5) [a]
F(6)	0.1935(7)	0.5465(6)	0.4370(12)	0.070(4) [a]
C(1)	0.1840(8)	0.3316(8)	0.1372(16)	0.037(2)
C(2)	0.2509(9)	0.2637(9)	0.0011(18)	0.044(2)
C(3)	0.3778(10)	0.3273(11)	0.0342(21)	0.055(2)
C(4)	0.4421(11)	0.4633(11)	0.2019(22)	0.057(3)
C(5)	0.3776(11)	0.5348(11)	0.3319(22)	0.060(3)
C(6)	0.2536(10)	0.4715(10)	0.2994(19)	0.048(2)
C(7)	−0.1031(10)	0.1625(10)	−0.2640(19)	0.049(2)
C(8)	−0.0688(10)	0.3016(10)	−0.1050(19)	0.051(2)
C(9)	−0.1849(11)	0.3314(12)	−0.0458(23)	0.063(3)
C(10)	−0.2900(10)	0.1956(10)	−0.1581(20)	0.054(2)
C(11)	−0.2434(10)	0.0867(10)	−0.3246(21)	0.055(2)
C(12)	−0.1863(9)	0.1711(9)	0.1714(18)	0.044(2)
C(13)	−0.1643(10)	0.0624(10)	0.0083(19)	0.049(2)
C(14)	−0.2676(11)	−0.0093(11)	−0.2477(21)	0.058(3)
C(15)	−0.3852(12)	0.0087(12)	−0.1644(24)	0.066(3)
C(16)	−0.3118(10)	0.1637(10)	0.0235(20)	0.051(2)

[a] $U_{eqv} = 1/3\Sigma_i\Sigma_j(U_{ij}a_i^{\star}a_j^{\star}a_i \cdot a_j)$.

$PdCl_2$(dcy) [16], but the difference in M–CT1 and M–CT2 (M = Pt or Pd) distances is much more marked in PtCl(dcy)C_6F_5, probably owing to the greater *trans* influence of C_6F_5 than chlorine [1,17]. The pentafluorophenyl group is approximately normal to the mean coordination plane (Table 4 and Fig. 1b) and the Pt–C(1) distance is close to Pt–C (2.01(2) Å) of Pt[C_6F_4-*o*-C(O)O](PPh$_3$)(2,6-Me$_2$C$_5$H$_3$N) [18] and within the range (1.96–2.07 Å) [19,20] for compounds contain-

Table 3

Selected bond distances and angles for PtCl(dcy)C_6F_5

Bond length	(Å)	Bond angle	(°)
Pt–Cl	2.307(4)	Cl–Pt–C(1)	87.0(3)
Pt–C(1)	2.02(1)	Cl–Pt–CT2 [b]	88.7(4)
Pt–C(7)	2.17(2)	CT2 [b]–Pt–CT1 [a]	93.1(5)
Pt–C(8)	2.17(1)	CT1 [a]–Pt–C(1)	91.5(5)
Pt–CT1 [a]	2.06(1)		
Pt–C(12)	2.34(1)	Cl–Pt–CT1 [a]	176.7(3)
Pt–C(13)	2.25(1)	C(1)–Pt–CT2 [b]	172.1(5)
Pt–CT2 [b]	2.19(1)	C(7)–CT1 [a]–Pt	90.0(1.7)
C(7)–C(8)	1.41(2)	C(8)–CT1 [a]–Pt	90.0(1.6)
C(12)–C(13)	1.37(1)	C(12)–CT2 [b]–Pt	94.1(1.3)
		C(13)–CT2 [b]–Pt	85.9(1.4)

[a] Mid point between C(7) and C(8). [b] Mid point between C(12) and C(13).

Table 4

Equation for the mean plane and deviations (Å) of individual atoms from the planes (e.s.d.'s in parentheses)

X, Y, Z are orthogonal coordinates and are related to the fractional coordinates x, y, z by the matrix equations:

$$\begin{matrix} 11.380 & -3.007 & -1.297 \\ 0 & 12.392 & -3.957 \\ 0 & 0 & 5.346 \end{matrix} \quad \begin{matrix} x \\ y \\ z \end{matrix} \quad = \quad \begin{matrix} X \\ Y \\ Z \end{matrix}$$

Plane 1 C(1), C(2), C(3), C(4), C(5), C(6)

$(-0.2552)X+(0.6430)Y+(-0.7221)Z-(1.5523)=0$

C(1)	−0.02(1)	C(4)	−0.02(1)
C(2)	0.02(1)	C(5)	0.01(1)
C(3)	0.00(1)	C(6)	0.01(1)

Plane 2 Pt, Cl, C(1), CT1, CT2 (CT1 and CT2 are the centre points of the double bonds between C(7) and C(8), and C(12) and C(13) respectively).

$(0.5034)X+(-0.6222)Y+(-0.5996)Z-(-2.2944)=0$

Pt	−0.0262(4)	C(1)	0.10(1)	CT2	0.09(1)
Cl	−0.079(4)	CT1	−0.08(1)		
C(7)	0.57(1)	C(12)	−0.59(1)		
C(8)	−0.74(1)	C(13)	0.77(1)		

Plane 3 C(12), C(13), C(14), C(16)

$(0.4950)X+(0.8503)Y+(-0.1790)Z-(-0.3766)=0$

C(12)	0.03(1)	C(14)	0.02(2)
C(13)	−0.03(1)	C(16)	−0.02(1)

Plane 4 C(7), C(8), C(9), C(10), C(11)

$(-0.1724)X+(0.5789)Y+(-0.7970)Z-(3.1430)=0$

C(7)	−0.02(1)	C(10)	−0.07(1)
C(8)	−0.02(1)	C(11)	0.06(1)
C(9)	0.06(1)		

Plane 5 Pt, C(7), C(8)

$(0.9430)X+(0.3211)Y+(-0.1567)Z-(-0.0293)=0$

Plane 6 Pt, C(12), C(13)

$(-0.3773)X+(0.5247)Y+(-0.7631)Z-(1.1351)=0$

Dihedral angles:

Plane 1 to Plane 2	95.5°
Plane 2 to Plane 3	99.9°
Plane 2 to Plane 4	88.2°
Plane 2 to Plane 5	68.6°
Plane 2 to Plane 6	93.4°

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ing the *cis*-$Pt(C_6F_5)_2$ group. The Pt–Cl distance is similar to those (2.302(7) and 2.310(7) Å) of dichloro(1,3,5,7-tetramethyl-2,6,9-trioxabicyclo[3,3,1]nona-3,7-diene-platinum(II) [21], which has unsymmetrical diene coordination, and those (2.314(5) and 2.316(8) Å) of *cis*-$PtCl_2[(CH_2{=}CHCHMe)_2O]$ [22] with symmetrical diene coordination.

(c) Spectroscopic properties

For PtCl(hex)R (R = C_6F_5, *p*-HC_6F_4, or *p*-$MeOC_6F_4$) and PtCl(dcy)C_6F_5, two

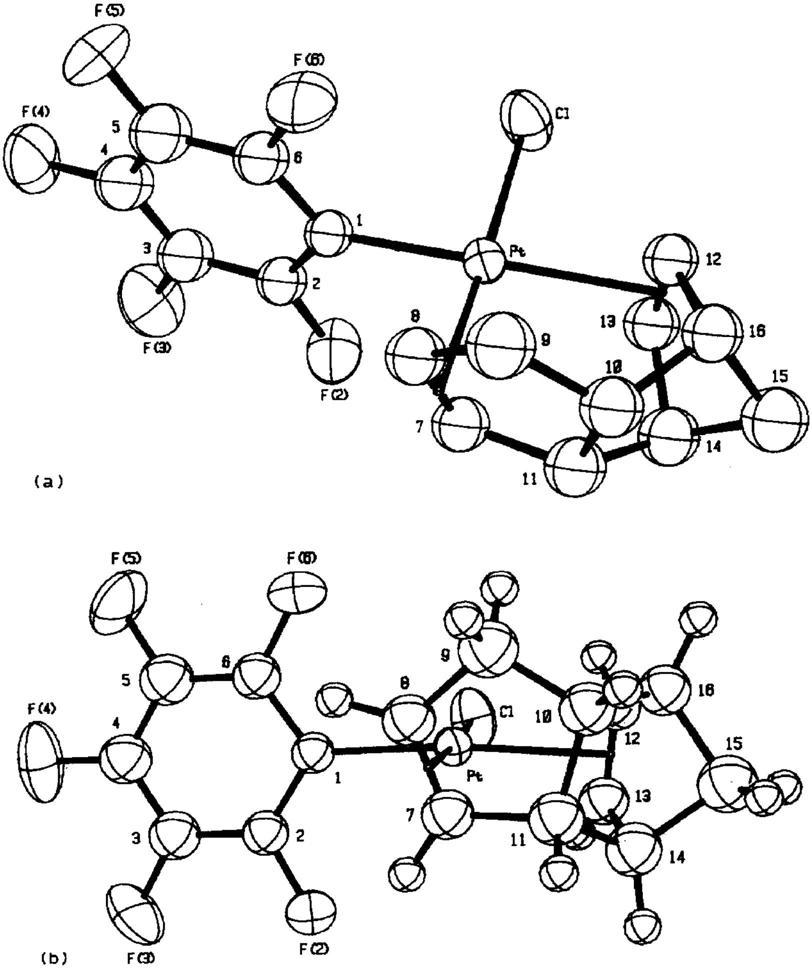

Fig. 1. The structure of PtCl(dcy)C_6F_5 (a), the coordination environment (b), the relationship of the C_6F_5 group to the coordination plane and H...F contacts. Hydrogen atoms are in their calculated positions.

ortho-fluorine resonances and usually two *meta*-fluorine resonances are observed (Experimental Section), the former having different ^3J(PtF) values (Table 5). If the polyfluorophenyl groups are approximately normal to the coordination plane, as established by X-ray crystallography for PtCl(dcy)C_6F_5 (Fig. 1b) and other Group 10 square planar polyfluorophenyls, e.g. *trans*-Ni$(C_6F_5)_2(PPh_2Me)_2$ [23] and *cis*-Pt$(C_6F_5)_2(S_2CP(\text{cyclo-}C_6H_{11})_3)$CO [24], and if rotation of the polyfluorophenyl group about Pt–C is restricted, the *ortho*- and the *meta*-fluorines are inequivalent, as observed. In the case of PtCl(dcy)C_6F_5, the structure is sterically crowded, as shown by Fig. 1b in which the hydrogen atoms are included in their calculated positions, with F(6)...H(8) and F(2)...H(7) contacts of 2.64(1) and 2.57(3) Å respectively (cf. 2.55 Å for the sum of the Van der Waals radii of fluorine * and hydrogen (mean value) [25]), hence free rotation of C_6F_5 which would involve closer H...F approaches, is unlikely. Moreover, a potential energy calculation (Experimental sec-

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* The value 1.35 Å may be an underestimate in the present system [26].

Table 5

Platinum–fluorine coupling constants and platinum–chlorine stretching frequencies of PtCl(diene)R complexes

Complex	^3J(Pt–F)	ν(Pt–Cl)
PtCl(hex)C_6F_5	276, 278	322s
PtCl(hex)(p-HC_6F_4)	263, 267	319s
PtCl(hex)(p-$MeOC_6F_4$)	267, 275	325vs
PtCl(nbd)C_6F_5	303	318vs [a]
PtCl(nbd)(p-HC_6F_4)	295	314vs
PtCl(nbd)(p-$MeOC_6F_4$)	323	321vs
PtCl(dcy)C_6F_5	264, 288	325m
PtCl(dcy)(p-$MeOC_6F_4$)	260, 283 [b] 257, 258 [c]	322s(br) [b,c]
Pt(p-$MeOC_6F_4$)$_2$(hex)	373	
Pt(p-$MeOC_6F_4$)$_2$(nbd)	379	
Pt(p-$MeOC_6F_4$)$_2$(dcy)	332, 349 355, 360	

[a] or 333 vs. [b] Isomer IIa (R = p-$MeOC_6F_4$). [c] Isomer IIb (R = p-$MeOC_6F_4$).

tion) shows that the configuration in Fig. 1 has the minimum energy for possible rotations of the C_6F_5 group. At the energy maximum F(6)...H(8) < 1 Å totally excluding C_6F_5 free rotation.

Unexpectedly, PtCl(dcy)(p-$MeOC_6F_4$) was obtained as an oil, and was identified by mass spectrometry (Experimental section), the similarity of the infrared spectrum to that of Pt(p-$MeOC_6F_4$)$_2$(dcy), and observation of a distinct ν(PtCl) absorption (Table 5). The ^{19}F NMR spectrum surprisingly showed two pairs of *ortho*-fluorine resonances (ratio 2/3). Comparison of the ^3J(PtF) values and chemical shifts with those of PtCl(dcy)C_6F_5 (Table 5 and Experimental section) suggests that the lower intensity pair is attributable to isomer IIa (R = p-$MeOC_6F_4$). Thus, the more intense pair may be assigned to isomer IIb (R = p-$MeOC_6F_4$). Calculations suggest there is little difference in potential energy between isomers IIa and IIb for R = C_6F_5. All four *ortho*-fluorines of PtR_2(dcy) (R = C_6F_5, p-HC_6F_4, or p-$MeOC_6F_4$) are different if R is normal to the coordination plane, and four resonances (Experimental Section) with different ^3J(PtF) values (Table 5) have been resolved for R = p-$MeOC_6F_4$. Lower resolution spectra for R = C_6F_5 or p-HC_6F_4 [1] revealed two resonances (intensities 3 (broadened)/1). The lower intensity, upfield, signal was attributed to the fluorine adjacent to the unique olefinic proton (=C*H*CH_2), and in Pt(p-$MeOC_6F_4$)$_2$(dcy), one resonance is significantly upfield from the other three. Lower ^3J(PtF) coupling constants are observed for PtCl(diene)R complexes than for the corresponding PtR_2(diene) complexes (Table 5, see also [1]), as generally found for *cis*-PtX(R)L_2 and *cis*-PtR_2L_2 complexes [27,28] and in contrast to *trans*-polyfluorophenylplatinum(II) complexes [27].

The ^{1}H NMR spectra of the PtCl(diene)R complexes are complicated and a full assignment has not been made. However, comparison of the PtH coupling constants with those of the corresponding PtR_2(diene) [1] and $PtCl_2$(diene) complexes, as well as with data for PtCl(cod)R derivatives [1,2,29] enabled olefinic protons *trans* to chlorine (J(PtH) 67–90 Hz) to be distinguished from those *trans* to polyfluorophenyl (J(PtH) 35–41 Hz for diene = hex or nbd; 47–59 Hz for diene = dcy).

Platinum–chlorine stretching frequencies (Table 5) are similar to those of PtCl(cod)R (R = C_6F_5, p-HC_6F_4 [1] or non-fluorinated aryl [2]). The PtCl(diene)C_6F_5 complexes have a single IR absorption attributable [27,30] to an 'X-sensitive' vibration involving Pt–C stretching, but an analogous absorption cannot be located in the spectra of Pt(p-HC_6F_4 or p-$MeOC_6F_4$) compounds.

Experimental

(a) General

Microanalyses were by the Australian Microanalytical Service, Melbourne. Instrumentation was mainly as given previously [27], except that a Bruker AM300 spectrometer was used for NMR measurements and a Jasco IRA1 instrument for some IR spectra. IR bands (4000–650 cm^{-1}) (for liquid films of organotin compounds and Nujol and hexachlorobutadiene or Fluorolube mulls of organoplatinum complexes) and mass spectral peaks listed below are restricted to features of structural or identification importance *. Platinum–chlorine stretching frequencies are in Table 5. Each listed m/z value is the most intense peak (containing ^{195}Pt, or ^{231}(PtCl)) of a cluster with the correct isotope pattern. Proton and fluorine chemical shifts are in ppm downfield from internal Me_4Si and upfield from internal $CFCl_3$ respectively. All compounds were dissolved in $CDCl_3$. ^3J(PtF) values are given in Table 5.

(b) Solvents and reagents

Purification methods for solvents have been given [27] or are standard procedures. Petroleum ether refers to the fraction b.p. 60–80 ° C. Polyfluoroaromatics were from Bristol Organics, butyllithium from Metallgesellschaft and Aldrich, and trimethyltin chloride from Aldrich. The preparations of the dichloro(diene)platinum(II) complexes have been given [1]. Triethyl- and tributyl-tin chloride were prepared by standard methods [31]. Samples of $(C_6F_5)_2Hg$ [32], $PhHgC_6F_5$ [33] and $(p\text{-}MeOC_6F_4)_2Hg$ [34] were available from previously reported syntheses.

(c) Trialkylpolyfluorophenyltin compounds

A solution of trialkyltin chloride in dry ether or tetrahydrofuran was added dropwise to a stoichiometric amount of the appropriate polyfluorophenyllithium reagent (prepared 'in situ' from C_6F_5Br, p-HC_6F_4Br, or p-$MeOC_6F_4H$ and butyllithium [35,36]) in dry ether or tetrahydrofuran containing a little hexane at − 78 ° C. The mixture was stirred at this temperature for 2–3 h, allowed to warm to room temperature, and hydrolysed with aqueous ammonium chloride (10%, w/v). Extraction with ether or dichloromethane, drying ($MgSO_4$), and evaporation gave the crude trialkylpolyfluorophenyltin compounds, which were purified by distillation under vacuum. Some spectroscopic data are provided for known compounds where this has not previously been reported.

Trimethylpentafluorophenyltin. Yield 82%, b.p. 37–38 ° C (0.4 mm Hg) lit. [6] 34–36 ° C (0.1 mm Hg). IR in agreement with that reported [6]. ^{1}H NMR spectrum:

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* More complete data are available from the authors.

0.48 (s, with ^{117,119}Sn satellites ^2J(SnH) 58 Hz). ^{19}F NMR spectrum: −122.0 (m, 2F, F(2,6)); −153.1 (m, 1F, F(4)); −161.0 (m, 2F, F(3,5)).

Trimethyl(2,3,5,6-tetrafluorophenyl)tin. Yield, 43%, b.p. 43–45 °C (0.5 mm Hg) (Found: C, 34.2; H, 2.8; F, 24.2. $C_9H_{10}F_4Sn$ calcd.: C, 34.5; H, 3.2; F, 24.3%). IR 1455vs, 1215s, 1180s, 1165s, 895s, 845s, 780s, 705s cm^{-1}. ^{1}H NMR spectrum: 0.47 (m, ^2J(SnH) 58 Hz, 9H, Me); 6.97 (m, 1H, *p*-H). ^{19}F NMR spectrum: −123.6 (m, 2F, F(2,6)); −139.1 (m, 2F, F(3,5)).

Trimethyl(2,3,5,6-tetrafluoro-4-methoxyphenyl)tin. Yield, 78%, b.p. 64–70 °C (0.5 mm Hg) (Found: C, 35.4; H, 3.2; F, 22.8. $C_{10}H_{12}F_4OSn$ calcd.: C, 35.0; H, 3.5; F, 22.2%). IR 1490s, 1450vs, 1365s, 1095vs, 960vs, 780vs cm^{-1}. ^{1}H NMR spectrum: 0.45 (m, ^2J(SnH) 58 Hz, 9H, Me); 4.05 (m, 3H, OMe). ^{19}F NMR spectrum: −123.8 (m, 2F, F(2,6)); −156.9 (m, 2F, F(3,5)).

Triethylpentafluorophenyltin. Yield, 82%, b.p. 67–69 °C (0.3 mm Hg), lit. [10], 52–53 °C (0.1 mm Hg) [11], 221 °C (13 mm Hg). IR 1500s, 1465vs, 1080vs, 1060s, 965vs cm^{-1}. ^{1}H NMR spectrum: 1.23 complex m. ^{19}F NMR spectrum: −121.0 (m, 2F, F(2,6)); −153.0 (t, ^3J(FF) 39 Hz, 1F, F(4)); −160.7, (m, 2F, F(3,5)).

Tributylpentafluorophenyltin. Yield, 45%, b.p. 120–122 °C (0.5 mm Hg), lit. [7] 112–115 °C (0.5 mm Hg). IR 1235m (cf. [7] 1275m), 1510s, 1465vs, 1445s, 1075vs, 965vs cm^{-1}.

Triethyl(2,3,5,6-tetrafluoro-4-methoxyphenyl)tin. Yield, 75%, b.p. 83–87 °C (0.05 mm Hg) (Found: C, 40.5; H, 4.6. $C_{13}H_{18}F_4OSn$ calcd.: C, 40.6; H, 4.7%). IR 1490s, 1440vs, 1090vs, 955s (br) cm^{-1}. ^{1}H NMR spectrum: 1.24 (m, 15H, CH_2 and Me); 4.06 (s, 3H, OMe). ^{19}F NMR spectrum: −122.8 (m, 2F, F(2,6)); −156.7 (m, 2F, F(3,5)).

(d) Syntheses of chloro(diene)polyfluorophenylplatinum(II) complexes using organotin reagents

The solid dichloro(diene)platinum complex was added to a stoichiometric amount of the trialkylpolyfluorophenyltin reagent in dry dichloromethane under nitrogen. Amounts of reagents and reaction conditions are given in Table 1. After completion of (or at least substantial) reaction (TLC monitoring of the disappearance of the organotin reactant), the solvent was removed under vacuum. The residue was washed with warm petroleum ether (100 cm^3) to remove the trialkyltin chloride, leaving the chloro(diene)polyfluorophenylplatinum(II) compound, generally mixed with the corresponding dienebis(polyfluorophenyl)platinum(II) derivative. Separation and purification were effected by column or spinning disc (Chromatatron) chromatography on silica (eluant: dichloromethane/petroleum ether 2/1, v/v) and crystallization from the eluant solvent. The complexes were obtained as colourless crystals or white powders (yields, Table 1) and PtR_2(diene) (R = C_6F_5 or *p*-HC_6F_4; diene = hex, nbd, or dcy) derivatives had spectroscopic properties in agreement with those reported [1], whilst properties of the new complexes (R = *p*-$MeOC_6F_4$, diene = hex, nbd, or dcy) are given in the next section.

Chloro(η^4-hexa-1,5-diene)pentafluorophenylplatinum(II). M.p. 163.5–164 °C (Found: C, 30.4; H, 2.4; F. 20.0. $C_{12}H_{10}F_5Pt$ calcd.: C, 30.0; H, 2.1; F, 19.8%). IR 1500s, 1460vs [ν(CC)], 1070vs, 965vs [ν(CF)], 805 ['X-sens'] cm^{-1}. ^{1}H NMR spectrum: 2.00–2.13 (m, 1H, CH_2); 2.53–2.96 (m, 3H, CH_2); 3.73 (d, ^3J(HH) 19 Hz, J(PtH) 67 Hz, 1H, =CH *cis* to CH_2, *trans* to Cl), 3.97 (d, ^3J(HH) 8 Hz, J(PtH) 66 Hz, 1H, =CH *trans* to CH_2, *trans* to Cl), 4.65 (m, ^3J(HH) 18 Hz, J(PtH) 35 Hz, 1H, =CH *cis* to CH$_2$, *trans* to C$_6$F$_5$); 5.10–5.30 (m, 1H, =CH *trans* to CH$_2$, *trans* to C$_6$F$_5$); 5.72–5.90 (m, 2H, =CH *gem* to CH$_2$). ^{19}F NMR spectrum: -123.5 (m, 1F, F(2 or 6)); -123.8 (m, 1F, F(2 or 6)); -158.6 (m, 1F, F4); -162.3 (m, 2F, F3). Mass spectrum: m/z 480 [6%, M^+]; 443 [2, $(M-\mathrm{HCl})^+$]; 381 [3, Pt(C$_6$F$_5$)F$^+$]; 362 [2, PtC$_6$F$_5$$^+$]; 312 [2, Pt(hex – H)Cl$^+$]; 277 [100, Pt(hex)$^+$]; 168 (90, C$_6F_5H^+$].

Chloro(η^4-hexa-1,5-diene)(2,3,5,6-tetrafluorophenyl)platinum(II). M.p. 177–179 °C (dec.) (Found: C, 31.4; H, 2.8; F, 16.7. C$_{12}$H$_{11}$ClF$_4$Pt calc.: C, 31.2; H, 2.4; F, 16.5%). IR 1470vs (br) [ν(CC)], 1200s, 1180s, 905vs [ν(CF)], 715s cm^{-1}. ^{1}H NMR spectrum: 1.99–2.18 (m, 1H, CH$_2$); 2.50–3.00 (m, 3H, CH$_2$); 3.73 (d, ^3J(HH) 14 Hz, J(PtH) 68 Hz, 1H, =CH *cis* to CH$_2$, *trans* to Cl); 3.98 (d, ^3J(HH) 8 Hz, J(PtH) 67 Hz, 1H, =CH *trans* to CH$_2$, *trans* to Cl); 4.65 (m, ^3J(HH) 18 Hz, J(PtH) 38 Hz, 1H, =CH *cis* to CH$_2$, *trans* to HC$_6$F$_4$); 5.05–5.30 (m, 1H, =CH *trans* to CH$_2$, *trans* to HC$_6$F$_4$); 5.68–5.97 (m, 2H, =CH gem to CH$_2$); 6.76 (m, 1H, HC$_6$F$_4$). ^{19}F NMR spectrum: -125.2 (m, 1F, F(2 or 6)); -125.5 (m, 1F, F(2 or 6)); -140.1 (m, 1F, F(3 or 5)); -140.4 (m, 1F, F(3 or 5)). Mass spectrum: m/z 462 [10%, M^+]; 425 [5, $(M-\mathrm{HCl})^+$]; 277 [100, Pt(hex)$^+$]; 150 [80, C$_6$H$_2$F$_4$$^+$].

Chloro(η^4-hexa-1,5-diene)(2,3,5,6-tetrafluoro-4-methoxyphenyl)platinum(II). M.p. 163–164 °C (Found: C, 32.0; H, 3.0; F, 15.2. C$_{13}$H$_{13}$ClF$_4$OPt calc.: C, 31.8; H, 2.7; F, 15.4%). IR 1460vs (br) [ν(CC)], 1080s, 1020s, 955s and 950s [ν(CF)] cm^{-1}. ^{1}H NMR spectrum: 2.05 (m(br), 1H, CH$_2$); 2.50–2.94 (m(br), 3H, CH$_2$); 3.71 (d, ^3J(HH) 15 Hz, J(PtH) 68 Hz, 1H, =CH *cis* to CH$_2$, *trans* to Cl); 3.97 (d, ^3J(HH) 8 Hz, J(PtH) 69 Hz, 1H, =CH *trans* to CH$_2$, *trans* to Cl); 3.98 (s, 3H, OMe), 4.64 (d, ^3J(HH) 18 Hz, J(PtH) 36 Hz, 1H, =CH *cis* to CH$_2$, *trans* to MeOC$_6$F$_4$); 5.17 (m, 1H, =CH *trans* to CH$_2$, *trans* to MeOC$_6$F$_4$); 5.76–5.85 (m, 2H, =CH *gem* to CH$_2$). ^{19}F NMR spectrum: -125.2 (m, 1F, F(2 or 6)); -125.6 (m, 1F, F(2 or 6)); -157.5 (m, 1F, F(3 or 5)); -157.7 (m, 1F, F(3 or 5)). Mass spectrum: m/z 492 [5%, M^+]; 455 [10, $M-\mathrm{HCl})^+$]; 276 [30, Pt(hex – H)$^+$]; 180 [60, MeOC$_6$F$_4$H$^+$].

Chloro(η^4-norbornadiene)pentafluorophenylplatinum(II). M.p. 179–181 °C (dec.) (Found: C, 32.2; H, 1.5; F, 19.6. C$_{13}$H$_8$ClF$_5$Pt calc.: C, 31.9; H, 1.7; F, 19.4%). IR 1460vs (br) [ν(CC)], 960vs [ν(CF)], 810s ['X-sens.'] cm^{-1}. ^{1}H NMR spectrum: 1.76–1.86 (m, 2H, CH$_2$); 4.37 (m, 2H, CH); 5.29 (m, J(PtH) 72 Hz, 2H, =CH *trans* to Cl); 5.92 (m, J(PtH) 41 Hz, 2H, =CH *trans* to C$_6$F$_5$). ^{19}F NMR spectrum: -122.3 (m, 2F, F(2,6)); -159.0 (m, 1F, F(4)); -162.7 (m, 2F, F(3,5)). Mass spectrum: m/z 490 [30%, M^+]; 471 [1, $(M-\mathrm{F})^+$]; 453 [2, $(M-\mathrm{HCl})^+$]; 286 [50, Pt(nbd – H)$^+$]; 168 [20, C$_6$F$_5$H$^+$]; 91 [100, (nbd – H)$^+$].

Chloro(η^4-norbornadiene)(2,3,5,6-tetrafluorophenyl)platinum(II). M.p. 222–223 °C (dec.) (Found: C, 33.1; H, 2.2; F, 16.4. C$_{13}$H$_9$ClF$_4$Pt calc.: C, 33.1; H, 1.9; F, 16.1%). IR 1460vs (br) [ν(CC)], 900 vs [ν(CF)], 715s cm^{-1}. ^{1}H NMR spectrum: 1.81 (m, J(PtH) 25 Hz, 2H, CH$_2$); 4.36 (m(br), 2H, CH); 5.30 (m, J(PtH) 72 Hz, 2H, =CH *trans* to Cl); 5.93 (m, J(PtH) 40 Hz, 2H, =CH *trans* to HC$_6$F$_4$); 6.71 (m, 1H, HC$_6$F$_4$). ^{19}F NMR spectrum: -124.2 (m, 2F, F(2,6)); -140.6 (m, 2F, F(3,5)). Mass spectrum: m/z 472 [20%, M^+]; 436 [2, $(M-\mathrm{Cl})^+$]; 286 [40, Pt(nbd – H)$^+$]; 150 [30, H$_2$C$_6$F$_4$$^+$]; 91 [100, (nbd – H)$^+$].

Chloro(η^4-norbornadiene)(2,3,5,6-tetrafluoro-4-methoxyphenyl)platinum(II). M.p. 151–153 °C (Found: C, 33.8; H, 2.6; F, 15.2. C$_{14}$H$_{11}$F$_4$ClOPt calc.: C, 33.5; H, 2.2; F, 15.2%). IR 1450vs, 1435s [ν(CC)], 1085vs, 980m, 965m and 950m [ν(CF)] cm^{-1}. ^{1}H NMR spectrum: 1.75–1.85 (m, 2H, CH$_2$); 3.96 (s, 3H, OMe); 4.33–4.38 (m, 2H, CH); 5.30 (m, J(PtH) 72 Hz, 2H, =CH *trans* to Cl); 5.91 (m, J(PtH) 40 Hz, 2H,

=CH *trans* to $\mathrm{MeOC_6F_4}$). ^{19}F NMR spectrum: −124.1 (m, 2F, F(2,6)); −158.0 (m, 2F, F(3,5)). Mass spectrum: *m/z* 502 [20%, M^+]; 286 [40, Pt(nbd − H)$^+$]; 180 [70, $\mathrm{MeOC_6F_4H^+}$]; 91 [100, (nbd − H)$^+$].

Chloro(η^4-dicyclopentadiene)pentafluorophenylplatinum(II). M.p. 166–168 °C (Found: C, 36.3; H, 2.6. $\mathrm{C_{16}H_{12}ClF_5Pt}$ calc.: C, 36.3; H, 2.3%). IR 1465vs [ν(CC)], 1070vs, 965vs [ν(CF)] cm^{-1}. ^{1}H NMR spectrum: 1.87–2.34 (m, 3H, CH$_2$ or CH); 2.53 (m, 1H, CH$_2$ or CH); 2.92 (m, 1H, CH$_2$ or CH); 3.07 (m, 1H, CH$_2$ or CH); 3.75 (m, 1H, CH$_2$ or CH); 4.77 (m, *J*(PtH) 50 Hz, 1H, CH$_2$ or CH); 5.26 (m, *J*(PtH) 74 Hz, 1H, =CH *trans* to Cl); 5.42 (m, *J*(PtH) 72 Hz, 1H, =CH *trans* to Cl); 6.66 (m, *J*(PtH) 47 Hz, 1H, =CH *trans* to $\mathrm{C_6F_5}$); 7.64 (m, *J*(PtH) 59 Hz, 1H, =CH *trans* to $\mathrm{C_6F_5}$). ^{19}F NMR spectrum: −121.3 (m, 1F, F(2 or 6)): −125.3 (m, 1F, F(2 or 6)); −159.4 (m, 1F, F(4)); −162.0 (m, 1F, F(3 or 5)); −162.6 (m, 1F, F(3 or 5)). Mass spectrum: *m/z* 530 [5%, M^+]; 491 [2, $\mathrm{Pt(C_6F_5)(C_{10}H_9)^+}$]; 326 [100, Pt(dcy − H)$^+$].

Chloro(η^4-dicyclopentadiene)(2,3,5,6-tetrafluoro-4-methoxyphenyl)platinum(II). Despite three purifications by chromatography, the complex was obtained as a light yellow oil. IR (neat oil): 1495vs, 1445vs(br) [ν(CC)], 1095vs(br), 1050s, 940vs(br) [ν(CF)], 795s cm^{-1}. ^{1}H NMR spectrum *: 2.00–2.40 (m, 11H, CH$_2$ or CH); 2.45–3.10 (m, 10H, CH$_2$ or CH); 3.20–3.40 (m, 1.5H, CH$_2$ or CH); 3.45–3.55 (m, 1H, CH$_2$ or CH); 3.70–3.90 (m, 5.3H, CH$_2$ or CH); 3.95 (m, 7H, OCH$_3$); 4.05–4.20 (m, 3.2H, ?); 5.26 (m, *J*(PtH) 78 Hz, 1H, =CH); 5.44 and 5.52 (each m, *J*(PtH) 76 and 83 Hz, 3.5H, =CH); 5.93 (m, *J*(PtH) 45Hz, 1.8H, =CH); 6.15 (m, *J*(PtH) 90 Hz, 1.8H, =CH); 6.58 (m, *J*(PtH) 41Hz, 1.6H, =CH); 6.63 (m, *J*(PtH) 47 Hz, 0.9H, =CH); 7.62 (m, *J*(PtH) 58Hz, 1.04H, =CH); 10.25 (s, 0.19H, ?). ^{19}F NMR spectrum: −123.1 (m, ^3J(PtF) 260 Hz, 1F, F(2 or 6) (isomer IIa, R = *p*-$\mathrm{MeOC_6F_4}$)); −123.8 (m, ^3J(PtF) 257 Hz, 1.5F, F(2′ or 6′) (isomer IIb)); −124.8 (m, ^3J(PtF) 258 Hz, 1.5F, F(2′ or F6′) (isomer IIb)); −126.8 (m, ^3J(PtF) 283 Hz, 1F, F(2 or 6) (isomer IIa)); −157.0 to −158.7 (m, 5F, F(3, 5 and 3′, 5′) (isomers IIa and IIb)). Impurities (integrations relative to each *ortho*-fluorine of isomer IIa); −141.0, 1.1F; −142.0, 0.7F; −146.6, 0.2F; −159.8, 1.3F; −160.2, 0.3F. Mass spectrum: *m/z* 542 [15%, M^+]; 363 [5, Pt(dcy)Cl$^+$]; 326 [80, Pt(dcy − H)$^+$]; 180 [10, $\mathrm{MeOC_6F_4H^+}$].

(e) Dienebis(2,3,5,6-tetrafluoro-4-methoxyphenyl)platinum(II) complexes

The separation and purification of the complexes is given in the previous section.

η^4-Hexa-1,5-dienebis(2,3,5,6-tetrafluoro-4-methoxyphenyl)platinum(II). M.p. 191–192 °C (dec.) (Found: C, 38.1; H, 2.8; F, 23.9. $\mathrm{C_{20}H_{16}F_8O_2Pt}$ calc.: C, 37.8; H, 2.6; F, 23.9%). IR 1485s, 1460s, and 1440s [ν(CC)], 1090s, 955vs [ν(CF)], 800s cm^{-1}. ^{1}H NMR spectrum: 2.56 (m, 2H, CH$_2$); 2.77 (m, 2H, CH$_2$); 3.94 (s, 6H, OMe); 4.30 (d, ^3J(HH) 16 Hz, *J*(PtH) 42 Hz, 2H, =CH *cis* to CH$_2$); 4.82 (d, ^3J(HH) 8 Hz, *J*(PtH) 45 Hz, 2H, =CH *trans* to CH$_2$); 5.41–5.64 (m, 2H, =CH *gem* to CH$_2$). ^{19}F NMR spectrum: −122.5 (m, 4F, F(2,6)); −158.1 (m, 4F, F(3,5)). Mass spectrum: *m/z* 635 [< 1%, M^+]; 277 [20, Pt(hex)$^+$]; 180 [100, $\mathrm{MeOC_6F_4H^+}$].

η^4-Norbornadienebis(2,3,5,6-tetrafluoro-4-methoxyphenyl)platinum(II). M.p. 218–220 °C (dec.) (Found: C, 39.3; H, 2.6; F, 23.3. $\mathrm{C_{21}H_{14}F_8O_2Pt}$ calc.: C, 39.1; H, 2.2; F, 23.5%). IR 1485s, 1460vs and 1455vs [ν(CC)], 1085vs, 960vs [ν(CF)], 805s

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* The total integration indicates the presence of considerable impurities.

cm^{-1}. ^1H NMR spectrum: 1.76 (s, 2H, CH_2); 3.93 (s, 6H, OMe); 4.43 (s(br), 2H, CH); 5.94 (m, *J*(PtH) 47 Hz, 4H, =CH). ^{19}F NMR spectrum: −122.3 (m, 4F, F(2,6)); −158.7 (m, 4F, F(3,5)). Mass spectrum: *m/z* 645 [10%, M^+]; 626 [1, $(M-F)^+$]; 286 [50, $Pt(nbd-H)^+$]; 180 [50, $MeOC_6F_4H^+$]; 91 [100, $(nbd-H)^+$].

η^4-Dicyclopentadienebis(2,3,5,6-tetrafluoro-4-methoxyphenyl)platinum(II). M.p. 154–155 °C (Found: C, 42.4; H, 2.6; F, 22.1. $C_{24}H_{18}F_8O_2Pt$ calc.: C, 42.1; H, 2.7; F, 22.2%). IR 1490s and 1460vs [ν(CC)]; 1090vs, 960vs(br) [ν(CF)] cm^{-1}. ^1H NMR spectrum: 2.07–2.32 (m, 3H, CH_2 or CH); 2.63–2.72 (m, 1H, CH_2 or CH); 2.89–2.92 (m, 2H, CH_2 or CH); 3.81 (m, 1H, CH_2 or CH); 3.93 (m, 6H, OMe); 4.02–4.17 (m, 1H, CH_2 or CH); 5.72 (m, *J*(PtH) 54 Hz, 1H, $=C\mathit{H}CH<$) *; 5.74 (m, *J*(PtH) 46 Hz, 1H, $=C\mathit{H}CH<$) *; 6.24 (m, J(PtH) 55 Hz, 1H, $=C\mathit{H}CH<$) *; 6.98 (m, *J*(PtH) 69 Hz, 1H, $=C\mathit{H}CH_2$) *. ^{19}F NMR spectrum: −121.0 (m, 1F, F(2, 6, or 2′)) **; −121.3 (m, 1F, F(2, 6, or 2′)) **; −122.0 (m, 1F, F(2, 6, or 2′) **; −124.2 (m, 1F, F 6′) **. Mass spectrum: *m/z* 439 [1%, $Pt(MeOC_6F_4)C_5H_5^+$]; 418 [1, $Pt(C_{12}H_6F_3O)^+$]; 326 [100, $Pt(dcy-H)^+$]; 180 [30, $MeOC_6F_4H^+$]; 66 [80, $C_5H_6^+$].

(f) Attempted syntheses of PtCl(diene)R using organomercurials

The solid dichloro(diene)platinum(II) complex (1.00 mmol) and the diorganomercurial (1.00 mmol) were heated under reflux in dichloromethane or 1,2-dichloroethane (50 cm^3) under nitrogen. The resulting solutions were examined by TLC for evidence of reaction. In the one case where an organoplatinum product was detected, it was separated by chromatography on a silica gel column with elution by dichloromethane/petroleum ether (3/1, v/v).

$PtCl_2$(hex) and $(C_6F_5)_2Hg$ in CH_2Cl_2 for 6 d gave PtCl(hex)C_6F_5 (6%) (m.p., IR, and mass spectral identification). $PtCl_2$(hex) and $PhHgC_6F_5$ in $(CH_2Cl)_2$ for 3 d gave only starting materials (TLC) though a metal mirror formed after only 10 min. $PtCl_2$(hex) and $(p\text{-}MeOC_6F_4)_2Hg$ in $(CH_2Cl)_2$ gave a metal mirror, and after 3 d, six products were detected by TLC but in insufficient amounts to warrant isolation. The same reagents in boiling CH_2Cl_2 for 2 d and at room temperature for 2 d were unchanged, as were $PtCl_2$(dcy) and $(C_6F_5)_2Hg$ in $(CH_2Cl)_2$ for 3 d.

(g) Attempted rearrangements

$Pt(C_6F_5)_2$(hex) was heated with an excess of $PtCl_2$(hex) in refluxing CH_2Cl_2 for 2 d, but no PtCl(hex)C_6F_5 could be detected by TLC. A similar reaction was attempted in the presence of a trace of trimethyltin chloride, but with the same result.

(h) Attempted cleavage of PtR_2(diene) with HCl

No reaction was observed (TLC analysis) in the following systems: $Pt(p\text{-}HC_6F_4)_2$(dcy) (0.128 mmol) with (i) HCl (1.84×10^{-3} mol dm^{-3}) in CH_2Cl_2 (70 cm^3) (3 h) (ii) aqueous HCl (2.0 mol dm^{-3}) in acetone (0.5 h) (iii) aqueous HCl (12 mol dm^{-3}) in acetone (2 h). $Pt(p\text{-}MeOC_6F_4)_2$(dcy) (0.014 mmol) in aqueous HCl (2.0 mol dm^{-3}, 10 cm^3) in acetone (10 cm^3) (0.5 h). $Pt(C_6F_5)_2$(hex) (0.070 mmol) in

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* Assignments based on those for PtR_2(dcy) ($R = C_6F_5$ or $p\text{-}HC_6F_4$) [1].

** F(6′) adjacent to the unique olefinic proton, $=C\mathit{H}CH_2$.

aqueous HCl (12 mol dm^{-3}, 10 cm^3) in acetone (10 cm^3) (2 h); gross decomposition after 16 h.

(i) Crystal and molecular structure determination

A representative tabular crystal (0.26 × 0.15 × 0.08 mm) obtained by crystallization from dichloromethane : petroleum ether (2/1, v/v) was selected and mounted on a silica capillary. All crystal data were collected using a Philips PW1100 diffractometer with Mo-K_α radiation (0.7107 Å).

Crystal data

$C_{16}H_{10}ClF_5Pt$, M 529.81, triclinic, a 11.380(2), b 12.751(3), c 6.777(2) Å, α 121.49(5), β 101.03(4), γ 103.64(4)°, U 753.90 Å^3, D_m 2.34(3), D_c ($Z = 2$) 2.34 g cm^{-3}, $F(000)$ 492, space group $P\bar{1}$ (by successful refinement) μ 95.9 cm^{-1} for Mo-K_α radiation.

Intensity measurements and structure solution

4386 unique reflections were collected by the ω-scan technique with a scan range of ±0.65° from the calculated Bragg scattering angle (with an allowance for dispersion) at a scan rate of 0.05° s^{-1}. Of the 4386 reflections, 3427 with $I \geq 3\sigma(I)$ were used in the structure solution and refinement, the data having been reduced in a manner previously described [37]. Three approximately axial reflections were monitored every 2 h and showed no systematic variation in intensity. An absorption correction was applied on the basis of indexed crystal faces ($12\bar{2}$, $\bar{1}22$, 710, $\bar{7}\bar{1}0$, $\bar{1}20$ and $1\bar{2}0$).

The atomic scattering factors [38] for neutral atoms were corrected for anomalous dispersion. All calculations were carried out on the Monash University DEC Vax 11/780 computers; the major program used was that of Sheldrick [39].

The structure was solved by conventional Patterson and Fourier methods for all non-hydrogen atoms. Geometrically idealized hydrogen atom coordinates were calculated for all hydrogen atoms and a riding model was employed for refinement. The C–H vectors were held constant in magnitude (1.08 Å) and direction, but the carbon atoms were free to move. The platinum, chlorine and fluorine atoms were refined anisotropically in the final refinement cycles in which 129 variables were refined. The hydrogen atoms were all given the same isotropic thermal parameter which was allowed to refine. With the data weighted as $1/\sigma^2(F)$ the refinement converged at $R_w = \Sigma\omega^{1/2}(\| F_0 | - | F_c \|)/\Sigma\omega^{1/2} | F_0 | = 0.047$ and a corresponding unweighted R of 0.049. Lists of anisotropic thermal parameters, hydrogen atom coordinates and observed and calculated structure factors may be obtained from the authors.

(j) Rotation barrier calculations

Calculations for $PtCl(dcy)C_6F_5$ were performed using programme EENY2 [40]. Potential energy parameters were taken from Giglio [41], with iodine and oxygen used as models for platinum and fluorine respectively. The intramolecular potential energies were calculated for 5° rotations of the C_6F_5 group about the Pt–C bond. An energy minimum was observed for a F(6)–C(1)–Pt–H(8) torsion angle of 66°, corresponding to the configuration of the crystal structure (Fig. 1). At the energy maximum, F(6)–C(1)–Pt–H(8) torsion angle 175°, F(6) and H(8) approach to within an impossible 1 Å with an energy barrier of ca. 4200 kJ/mole. In calculations of the potential energy difference between isomers IIa and IIb ($R = C_6F_5$), the geometric parameters for IIa (Fig. 1 and Table 3) were used as appropriate for the as yet unknown IIb ($R = C_6F_5$).

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