

PREPARATIONS AND LIGAND DISPLACEMENT REACTIONS OF DIENE(POLYFLUOROPHENYL)PLATINUM(II) COMPLEXES

G.B. DEACON and K.T. NELSON-REED

Chemistry Department, Monash University, Clayton, Victoria, 3168 (Australia)

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Summary

The complexes $\text{PtR}_2(\text{diene})$ ($\text{R} = \text{C}_6\text{F}_5$ or $p\text{-HC}_6\text{F}_4$; diene = *cis,cis*-cycloocta-1,5-diene (cod), dicyclopentadiene (dcy), norbornadiene (nbd) or hexa-1,5-diene (hex)) have been prepared by the organolithium route. Reaction of $\text{PtCl}_2(\text{cod})$ with an equimolar amount of TiO_2CR ($\text{R} = \text{C}_6\text{F}_5$ or $p\text{-HC}_6\text{F}_4$) in pyridine yields $\text{Pt}(\text{R})\text{Cl}(\text{cod})$, which have been converted into $\text{Pt}(\text{R})\text{X}(\text{cod})$ ($\text{X} = \text{Br}$ or I) by halogen exchange reactions. Other decarboxylations result in diene displacement giving *cis*- $\text{Pt}(\text{C}_6\text{F}_5)\text{Cl}(\text{py})_2$ and *cis*- and *trans*- $\text{Pt}(\text{C}_6\text{F}_5)_2(\text{py})_2$. The complexes, *cis*- $\text{Pt}(\text{C}_6\text{F}_5)_2\text{L}_2$ ($\text{L} = \text{py}$ or Ph_3P) and *cis*- $\text{Pt}(p\text{-HC}_6\text{F}_4)_2(\text{PPh}_3)_2$ are formed by ligand replacement reactions of $\text{PtR}_2(\text{cod})$, but $\text{Pt}(\text{C}_6\text{F}_5)_2(\text{cod})$ does not react with *N,N,N',N'*-tetramethylethylenediamine (tmed) nor $\text{Pt}(\text{C}_6\text{F}_5)_2(\text{nbd}$ or $\text{dcy})$ with ethylenediamine (en). Diene displacement occurs more readily from $\text{PtR}_2(\text{hex})$ giving $\text{Pt}(\text{C}_6\text{F}_5)_2\text{L}_2$ ($\text{L}_2 = \text{cis}(\text{NH}_3)_2$, en, tmed or 1,10-phenanthroline) and *cis*- $\text{Pt}(p\text{-HC}_6\text{F}_4)_2(\text{PPh}_3)_2$.

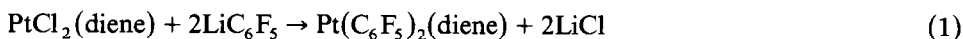
Introduction

Preparation of a range of PtR_2L_2 complexes is often more conveniently achieved by substitution reactions of a labile complex PtR_2L^1_2 rather than by a series of organolithium/Grignard syntheses, especially if these reagents can react with the ligand L or induce isomerization of the complexes. For the synthesis of $\text{Pt}(\text{C}_6\text{F}_5)_2\text{L}_2$ derivatives, the labile *cis*- $\text{Pt}(\text{C}_6\text{F}_5)_2\text{L}^1_2$ ($\text{L}^1 = \text{tetrahydrofuran (thf)}$ [1,2] or tetrahydrothiophen (tht) [3]) and *trans*- $\text{Pt}(\text{C}_6\text{F}_5)_2\text{L}^1_2$ ($\text{L}^1 = \text{tht}$ [3] or 1,4-dioxane (diox) [4–6]) have been used. However, the preferred route to the thf complex requires a three step synthesis from PtCl_2 [1,7], the *cis* tht complex has only been obtained in unspecified yield after separation from the *trans*-isomer [8], whilst the preparation of the diox complex [4] gave low yields of ill-defined pentafluorophenylplatinum(II) species in our hands. Diene displacement reactions of $\text{PtR}_2(\text{cod})$ ($\text{cod} = \text{cis,cis}$ -cycloocta-1,5-diene; $\text{R} = \text{Me}$, aryl or CF_3) have been used in the synthesis of

PtR₂L₂ complexes [9,10], and recently it has been shown that PtR₂(nbd) (nbd = norbornadiene) is even more reactive than PtR₂(cod) when R = Me or CF₃ [11]. We have now examined the possible conversion of PtR₂(diene) (R = C₆F₅ or *p*-HC₆F₄) derivatives into *cis*-PtR₂L₂ complexes. *Trans* influence data [9,12] suggest that diene replacement may be more difficult in Pt(C₆F₅)₂(diene) than in PtR₂(diene) (R = Me, CF₃ or aryl). Accordingly, we have investigated displacement of the flexible diene, hexa-1,5-diene (hex), as well as the more usual cod, nbd or dcy (dicyclopentadiene), since hex may be replaced more readily than the more rigid dienes.

Results and discussion

The complexes PtR₂(diene) (R = C₆F₅ or *p*-HC₆F₄; diene = cod, dcy, nbd or hex) have been prepared by reaction 1 in ether.

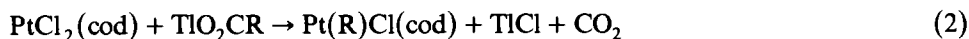


Only Pt(C₆F₅)₂(nbd) has previously been reported [13], the yield from a Grignard synthesis being significantly lower than that from reaction 1. Yields of purified products were high except in the case of Pt(*p*-HC₆F₄)₂(nbd), where the crude product decomposed substantially on recrystallization.

In the ¹H NMR spectrum of Pt(C₆F₅)₂(dcy), the four olefinic protons give three resonances (intensities 2/1/1). Two with a combined integration of 3H have similar *J*(PtH) coupling constants and are assigned to the three >CHCH= protons (similar protons of Pt(C₆F₅)₂(nbd) give similar *J*(PtH) coupling constants, see Experimental), whilst the resonance with a significantly different *J*(PtH) coupling is assigned to the unique CH₂CH= olefinic proton. With the C₆F₅ groups substantially twisted out of the coordination plane, the sterically favoured arrangement (see structures of *trans*-Ni(C₆F₅)₂(PPh₂Me)₂ [14], *cis*-Pt(C₆F₅)₂[S₂CP(*c*-C₆H₁₁)₃](CO) [15], and *cis*-PtPh₂(Me₂SO)₂ [16]), each *ortho*-fluorine is adjacent to a different olefinic proton, hence the fluorine (designated F(6'), Experimental section) near the unique olefinic proton has a chemical shift and ³*J*(PtF) coupling constant different from the other three. The ¹H and ¹⁹F NMR spectra of Pt(*p*-HC₆F₄)₂(dcy) show similar behaviour except that the ¹⁹⁵Pt-H satellites on one olefinic resonance are not clearly resolved. Assignment of the three different olefinic resonances of PtR₂(hex) complexes is based on the magnitude of the ³*J*(HH) coupling constants (see [17]). Because of the asymmetry of the coordinated diene, the two *ortho*-fluorines of the polyfluorophenyl ligands, presumably twisted from the coordination plane, are different, and give equal intensity, overlapping resonances in their ¹⁹F NMR spectra. The ³*J*(PtF) coupling constants (342–391 Hz) of PtR₂(diene) derivatives are of similar magnitude to that (354 Hz) of *cis*-Pt(C₆F₅)₂(PEt₃)₂ [18] and much lower than that (453 Hz) of Pt(C₆F₅)₂bpy (bpy = 2,2'-bipyridyl) [19]. All Pt(C₆F₅)₂(diene) complexes show two infrared absorption bands near 800 cm⁻¹ attributable [8,19] to 'X-sensitive' vibrations involving Pt–C stretching, as expected [8,19,20] for a *cis*-Pt(C₆F₅)₂ arrangement. A similar feature has not yet been identified in the spectra of 2,3,5,6-tetrafluorophenylorganometallics.

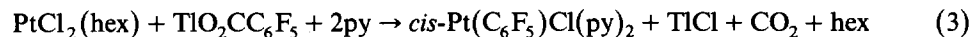
Reaction of PtCl₂(cod) and pentafluorophenyllithium on a 1:1 stoichiometry does not give Pt(C₆F₅)Cl(cod), but only Pt(C₆F₅)₂(cod) and the platinum reagent. The outcome can be attributed to lower reactivity for PtCl₂(cod), owing to its low

solubility in ether, than for the soluble $\text{Pt}(\text{C}_6\text{F}_5)\text{Cl}(\text{cod})$. However, $\text{Pt}(\text{R})\text{Cl}(\text{cod})$ ($\text{R} = \text{C}_6\text{F}_5$ or $p\text{-HC}_6\text{F}_4$) complexes are obtained by facile decarboxylation (reaction 2) in warm pyridine.



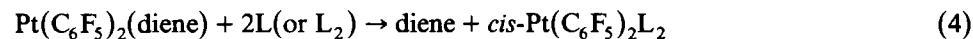
These compounds are converted into the corresponding bromo and iodo complexes by the appropriate sodium halides in aqueous acetone.

An attempt to prepare $\text{Pt}(\text{C}_6\text{F}_5)_2(\text{cod})$ by decarboxylation using a $\text{PtCl}_2(\text{cod})/\text{TlO}_2\text{CC}_6\text{F}_5$ mole ratio of 1/2 gave a mixture of *cis*- and *trans*- $\text{Pt}(\text{C}_6\text{F}_5)_2(\text{py})_2$. Formation of the *cis* isomer is attributable to the independently demonstrated (see below) diene displacement from $\text{Pt}(\text{C}_6\text{F}_5)_2(\text{cod})$. Since isomerically pure *cis*- $\text{Pt}(\text{C}_6\text{F}_5)_2(\text{py})_2$ is synthesized in pyridine at a higher temperature than used for decarboxylation, the *trans* isomer is not formed by isomerization of the *cis*. A more likely path to *trans*- $\text{Pt}(\text{C}_6\text{F}_5)_2(\text{py})_2$ is conversion of $\text{Pt}(\text{C}_6\text{F}_5)\text{Cl}(\text{cod})$ into $[\text{Pt}(\text{C}_6\text{F}_5)(\text{cod})\text{py}]\text{O}_2\text{CC}_6\text{F}_5$, diene displacement giving $[\text{Pt}(\text{C}_6\text{F}_5)(\text{py})_3]\text{O}_2\text{CC}_6\text{F}_5$, and then decarboxylation. The formation of the *trans* isomer in the final step is attributable to the greater *trans* effect of C_6F_5 than pyridine, as indicated by synthesis of *trans*- $\text{Pt}(\text{C}_6\text{F}_5)_2(\text{py})_2$ on decarboxylation of $[\text{Pt}(\text{py})_4](\text{O}_2\text{CC}_6\text{F}_5)_2$ [19]. Diene displacement is also observed in the decarboxylation reaction of $\text{PtCl}_2(\text{hex})$ with $\text{TlO}_2\text{CC}_6\text{F}_5$ (mole ratio 1/1) giving the previously unknown *cis*- $\text{Pt}(\text{C}_6\text{F}_5)\text{Cl}(\text{py})_2$.



In the ^1H NMR spectra of $\text{Pt}(\text{R})\text{X}(\text{cod})$ ($\text{R} = \text{C}_6\text{F}_5$ or $p\text{-HC}_6\text{F}_4$; $\text{X} = \text{Cl}$, Br or I) complexes, the olefinic protons *trans* to R are readily distinguishable from those *trans* to X by comparison of $J(\text{PtH})$ with those of $\text{Pt}(\text{Ph}$ or $\text{Me})\text{X}(\text{cod})$ complexes [9] and $\text{Pt}(\text{C}_6\text{F}_5)_2(\text{cod})$. The values of $J(\text{PtH})$ are smaller *trans* to R than *trans* to X , indicating [21] a higher *trans* influence for C_6F_5 (and $p\text{-HC}_6\text{F}_4$) than Cl , as is also evident from comparing $\nu(\text{Pt}-\text{Cl})$ of *trans*- $\text{Pt}(\text{C}_6\text{F}_5)\text{Cl}(\text{py})_2$ [19] with data for *trans*- $\text{PtCl}_2(\text{py})_2$ [22]. The metal-halogen stretching frequencies (Experimental section) are consistent with the *trans* influence of cod [12]. Platinum-fluorine coupling constants (266–289 Hz) are lower than those of $\text{PtR}_2(\text{cod})$, as also observed for *cis*- $\text{Pt}(\text{C}_6\text{F}_5)\text{X}(\text{PEt}_3)_2$ [18] and $\text{Pt}(\text{C}_6\text{F}_5)\text{X}(\text{bpy})$ ($\text{X} = \text{Cl}$ and C_6F_5) [19]. Assignment of *cis* stereochemistry for the product of reaction 3 is based on significantly different $^3J(\text{PtF})$ and $\nu(\text{PtCl})$ values (see Experimental) from those [19] of the *trans* isomer, and the similarity of $\nu(\text{PtCl})$ to that of $\text{Pt}(\text{C}_6\text{F}_5)\text{Clbpy}$ [19].

Details of ligand displacement reactions of the diene complexes are given in Table 1. Both $\text{Pt}(\text{C}_6\text{F}_5)_2(\text{cod})$ and $\text{Pt}(\text{C}_6\text{F}_5)_2(\text{dcy})$ are converted into *cis*- $\text{Pt}(\text{C}_6\text{F}_5)_2\text{L}_2$ ($\text{L} = \text{Ph}_3\text{P}$ or py) in high yield (reaction 4; diene = cod or dcy).



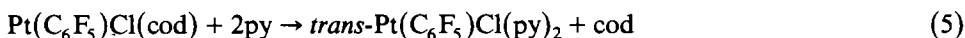
The failure of $\text{Pt}(\text{C}_6\text{F}_5)_2(\text{cod})$ to react with N,N,N',N' -tetramethylethane-1,2-diamine (tmed) by contrast with $\text{PtMe}_2(\text{cod})$ [9] can be attributed to lower *trans* effect for C_6F_5 than Me (paralleling the relative *trans* influences [12]) and/or to greater steric resistance to displacement for the pentafluorophenyl complex. Ethane-1,2-diamine (en) does not displace dcy and causes decomposition on reaction with $\text{Pt}(\text{C}_6\text{F}_5)_2(\text{nbd})$, by contrast with the facile ligand exchange between $\text{PtMe}_2(\text{nbd})$ and en [11]. However, both tmed and en react with $\text{Pt}(\text{C}_6\text{F}_5)_2(\text{hex})$ to give the corresponding $\text{Pt}(\text{C}_6\text{F}_5)_2\text{L}_2$ complexes (reaction 4, diene = hex , $\text{L}_2 = \text{en}$ or tmed),

TABLE I
LIGAND EXCHANGE REACTIONS OF DIENE(POLYFLUOROPHENYL)PLATINUM(II) COMPLEXES

Complex	mmol	Ligand	mmol	Solvent	ml	Temp. (°C)	Time (h)	Product	Yield (%)
Pt(C ₆ F ₅) ₂ (cod)	0.16	PPh ₃	2.00	CH ₂ Cl ₂	20	40	4	<i>cis</i> -Pt(C ₆ F ₅) ₂ (PPh ₃) ₂	85
Pt(C ₆ F ₅) ₂ (dcy)	0.08	PPh ₃	2.00	CH ₂ Cl ₂	20	40	4	<i>cis</i> -Pt(C ₆ F ₅) ₂ (PPh ₃) ₂	75
Pt(C ₆ F ₅) ₂ (cod)	0.24	py	^a	py	5	100	2	<i>cis</i> -Pt(C ₆ F ₅) ₂ (py) ₂	100
Pt(C ₆ F ₅) ₂ (dcy)	0.15	py	^a	py	5	100	2	<i>cis</i> -Pt(C ₆ F ₅) ₂ (py) ₂	87
Pt(C ₆ F ₅) ₂ (cod)	0.30	tmcd	^a	tmcd	5	100	4	Pt(C ₆ F ₅) ₂ (cod)	95
Pt(C ₆ F ₅) ₂ (dcy)	0.15	en	^a	en	5	100	3	Pt(C ₆ F ₅) ₂ (dcy)	90
Pt(C ₆ F ₅) ₂ (nbd)	0.08	en	^a	en	5	100	2(12) ^b	decomp.	
Pt(C ₆ F ₅) ₂ (hex)	0.08	en	^a	en	5	100	2	Pt(C ₆ F ₅) ₂ (en)	85
Pt(C ₆ F ₅) ₂ (hex)	0.09	phen	2.70	Et ₂ O	20	35	4	Pt(C ₆ F ₅) ₂ (phen)	88
Pt(C ₆ F ₅) ₂ (hex)	0.17	NH ₃	^a	Et ₂ O	15	25	0.33	<i>cis</i> -Pt(C ₆ F ₅) ₂ (NH ₃) ₂	57
Pt(C ₆ F ₅) ₂ (hex)	0.07	tmcd	3.30	Et ₂ O	15	35	72	Pt(C ₆ F ₅) ₂ (tmcd)	71
Pt(<i>p</i> -HC ₆ F ₄) ₂ (cod)	0.08	PPh ₃	2.00	CH ₂ Cl ₂	20	40	4	<i>cis</i> -Pt(<i>p</i> -HC ₆ F ₄) ₂ (PPh ₃) ₂	^c
Pt(<i>p</i> -HC ₆ F ₄) ₂ (cod)	0.28	PPh ₃	2.00	CHCl ₃	20	61	3	<i>cis</i> -Pt(<i>p</i> -HC ₆ F ₄) ₂ (PPh ₃) ₂	94
Pt(<i>p</i> -HC ₆ F ₄) ₂ (hex)	0.15	PPh ₃	2.00	CH ₂ Cl ₂	20	40	23	<i>cis</i> -Pt(<i>p</i> -HC ₆ F ₄) ₂ (PPh ₃) ₂	86
Pt(C ₆ F ₅)Cl(cod)	0.06	py	^a	py	5	100	3	<i>trans</i> -Pt(C ₆ F ₅)Cl(py) ₂	91

^a An excess of ligand used. ^b Two separate reactions. ^c Mixed with the reactant.

indicating easier displacement of the flexible diene. Similarly, $\text{Pt}(\text{C}_6\text{F}_5)_2(\text{hex})$ is converted into $\text{cis-Pt}(\text{C}_6\text{F}_5)_2(\text{NH}_3)_2$ and $\text{Pt}(\text{C}_6\text{F}_5)_2(\text{phen})$ under mild conditions (Table 1). Comparison of the reactions of $\text{Pt}(\text{C}_6\text{F}_5)_2(\text{cod})$ and $\text{Pt}(p\text{-HC}_6\text{F}_4)_2(\text{cod})$ with triphenylphosphine (Table 1) shows that displacement occurs more readily for the pentafluorophenyl complex. Since the steric effects of C_6F_5 and $p\text{-HC}_6\text{F}_4$ should be comparable in displacement reactions, the *trans* effect of C_6F_5 is greater than that of $p\text{-HC}_6\text{F}_4$. This may be attributed to the electron donating resonance effect of the *para* fluorine substituent of the C_6F_5 group. By contrast with (4), isomerization occurs in the substitution (5).



Loss of isomer selectivity in diene displacement from mono-organoplatinum(II) complexes is well established [23]. In the present case, initially formed $\text{cis-Pt}(\text{C}_6\text{F}_5)_2\text{Cl}(\text{py})_2$ can be converted by the excess of pyridine into $[\text{Pt}(\text{C}_6\text{F}_5)_2\text{py}_3]^+\text{Cl}^-$, which would give $\text{trans-Pt}(\text{C}_6\text{F}_5)_2\text{Cl}(\text{py})_2$ by preferential displacement of pyridine *trans* to C_6F_5 . Conversion of $\text{cis-Pt}(\text{C}_6\text{F}_5)_2\text{Cl}(\text{PEt}_3)_2$ into the *trans*-isomer by a trace of triethylphosphine has been demonstrated [24].

Identification of products of reactions 4 and 5 (Table 1) followed from spectroscopic data (Experimental Section). All complexes with a $\text{cis-Pt}(\text{C}_6\text{F}_5)_2$ arrangement gave the expected [8,19,20] two infrared bands near 800 cm^{-1} , attributable [8,19] to 'X-sensitive' vibrations involving Pt-C stretching. The melting point of $\text{cis-Pt}(\text{C}_6\text{F}_5)_2(\text{py})_2$ was higher by ca. 40°C than that reported [20] and this was not due to thermal isomerization into the *trans*-isomer (dec. temp. [20] 265°C). The *cis* stereochemistry was clearly confirmed by the difference in $^3J(\text{PtH})$ (30 Hz) and $^3J(\text{PtF})$ (473 Hz) from those (52 and 275 Hz, respectively) [19] of the *trans* isomer and the similarity to those (30 and 460 Hz, respectively) of $\text{Pt}(\text{C}_6\text{F}_5)_2(\text{phen})$. The $^3J(\text{PtF})$ coupling of $\text{cis-Pt}(\text{C}_6\text{F}_5)_2(\text{NH}_3)_2$ is similar to those of $\text{Pt}(\text{C}_6\text{F}_5)_2\text{L}_2$ ($\text{L}_2 = \text{en}$ or tmed) (Experimental section), confirming the *cis*-stereochemistry indicated by infrared spectroscopy. A complex of composition $\text{Pt}(\text{C}_6\text{F}_5)_2(\text{NH}_3)_2$ has previously been obtained from $\text{trans-Pt}(\text{C}_6\text{F}_5)_2(\text{diox})_2$ [6]. The possibility of *cis*-stereochemistry was raised on the basis of similarity to the spectrum of $\text{cis-PtCl}_2(\text{NH}_3)_2$ at $600\text{--}500\text{ cm}^{-1}$, but the number of stereochemically significant 'X-sensitive' absorptions was not discussed [6]. Moreover, $\text{trans-Pt}(\text{C}_6\text{F}_5)_2(\text{diox})_2$ gives $\text{trans-Pt}(\text{C}_6\text{F}_5)_2\text{L}_2$ complexes with other unidentate ligands [4,5]. The *cis*-stereochemistry of $\text{Pt}(p\text{-HC}_6\text{F}_4)_2(\text{PPh}_3)_2$ follows from the similarity of $^3J(\text{PtF})$ to that of $\text{cis-Pt}(\text{C}_6\text{F}_5)_2(\text{PPh}_3)_2$ (Experimental section) (cf. ca. 250 Hz for $^3J(\text{PtF})$ of $\text{trans-PtR}_2(\text{PPh}_3)_2$, $\text{R} = \text{C}_6\text{F}_5$ or $p\text{-HC}_6\text{F}_4$ [25]).

Thus, $\text{Pt}(\text{C}_6\text{F}_5)_2(\text{diene})$ complexes are an attractive source of $\text{cis-Pt}(\text{C}_6\text{F}_5)_2\text{L}_2$ complexes. The yields for $\text{L} = \text{py}$ or Ph_3P are much higher than from the organolithium route, and the products are isomerically pure (cf. $\text{L} = \text{py}$ from $\text{C}_6\text{F}_5\text{Li}$ [20]). Of the $\text{Pt}(\text{C}_6\text{F}_5)_2(\text{diene})$ complexes examined, ligand displacement occurs most readily for $\text{Pt}(\text{C}_6\text{F}_5)_2(\text{hex})$.

Experimental

General

Microanalyses were by the Australian Microanalytical Service, Melbourne. Instrumentation was mainly as given previously [19], except that a Jasco IRA 1 and a

Bruker AM300 spectrometer were used for some infrared and NMR measurements respectively. Infrared bands (of Nujol and hexachlorobutadiene mulls) and mass spectral peaks given below are restricted to those of structural or identification importance. Each listed m/z value corresponds to the most intense peak (due to ^{195}Pt , $^{231}(\text{PtCl})$ or $^{275}(\text{PtBr})$) of a cluster with the appropriate isotope pattern. Proton chemical shifts are in ppm downfield from internal Me_4Si , and fluorine chemical shifts are in ppm upfield from internal CFCl_3 . The solvent was CDCl_3 or $(\text{CD}_3)_2\text{CO}$, and where both were used there was little solvent effect.

Solvents and reagents

Purification methods for solvents have either been reported [19] or were standard procedures. Petroleum ether refers to the fraction b.p. $60\text{--}80^\circ\text{C}$. Ethane-1,2-diamine and N,N,N',N' -tetramethylethane-1,2-diamine were dried over sodium, distilled under reduced pressure, and stored over sodium. Polyfluoroaromatics were from Bristol Organics and butyllithium from Aldrich. Preparations of thallos polyfluorobenzoates [26] and *trans*-bis(pentafluorophenyl)dipyridineplatinum(II) [19] have been given. Dichloro(diene)platinum(II) complexes were prepared by adaptation of the method [9] for $\text{PtCl}_2(\text{cod})$, and had melting points and/or spectroscopic data in agreement with those reported [27–30].

Preparation of dienebis(polyfluorophenyl)platinum(II) complexes

The solid dichloro(diene)platinum(II) complex (0.40–1.00 mmol) was added to the stoichiometric amount of the polyfluorophenyllithium reagent (synthesized 'in situ' from the appropriate bromopolyfluorobenzene and *n*-butyllithium [31]) in dry ether (20–30 cm^3) containing a little hexane under nitrogen at -78°C . The reaction mixture was stirred at this temperature for 2–3 h, warmed to 0°C , and hydrolysed with aqueous ammonium chloride (5%, w/v) at 0°C . Ether extraction and evaporation gave the crude complexes, which were purified by column chromatography on silica (eluant, dichloromethane/petroleum ether 1/1, v/v) and crystallization from the eluant solvent, except for $\text{Pt}(p\text{-HC}_6\text{F}_4)_2(\text{nbd})$ (see below). Complexes were obtained as colourless crystals or white powders.

η^4 -(*cis,cis*-Cycloocta-1,5-diene)bis(pentafluorophenyl)platinum(II)]. Yield 81%, m.p. $254\text{--}256^\circ\text{C}$ (dec.) (Found: C, 38.1; H, 1.7; F, 29.5. $\text{C}_{20}\text{H}_{12}\text{F}_{10}\text{Pt}$ calc: C, 37.7; H, 1.9; F, 29.8%). IR: 1500vs and 1465vs ($\nu(\text{CC})$); 1055vs and 955vs ($\nu(\text{CF})$); 795s and 790s ('X-sens') cm^{-1} . ^1H NMR spectrum: 2.40–2.80 (m, 8H, CH_2), 5.39 (m, $J(\text{PtH})$ 48 Hz, 4H, =CH). ^{19}F NMR spectrum: 120.7 (m, $^3J(\text{PtF})$ 360 Hz, 4F, F(2,6)), 160.0 (m, 2F, F(4)), 163.0 (m, 4F, F(3,5)). Mass spectrum: m/z 637[1%, M^+]; 470[1, $\text{Pt}(\text{C}_6\text{F}_5)(\text{cod})^+$]; 303[100, $\text{Pt}(\text{cod})^+$]. The compound was also prepared by a similar reaction between $\text{PtCl}_2(\text{cod})$ and $\text{C}_6\text{F}_5\text{Li}$ (mole ratio, 10/9) and between $\text{PtI}_2(\text{cod})$ and $\text{C}_6\text{F}_5\text{Li}$ (mole ratio, 3/4), yield, 94 and 51% respectively based on $\text{C}_6\text{F}_5\text{Li}$ (m.p. and spectroscopic identification).

η^4 -Dicyclopentadienebis(pentafluorophenyl)platinum(II). Yield 88%, m.p. $230\text{--}233^\circ\text{C}$ (dec.) (Found: C, 39.8; H, 1.6; F, 29.0. $\text{C}_{22}\text{H}_{12}\text{F}_{10}\text{Pt}$ calc: C, 40.0; H, 1.8; F, 28.7%). IR: 1500vs and 1470vs(br) ($\nu(\text{CC})$); 1060vs(br) and 955vs(br) ($\nu(\text{CF})$); 800s and 790s ('X-sens.') cm^{-1} . ^1H NMR spectrum: 2.16–4.08 (m, 8H, CH_2 , CH), 5.75 (m, $J(\text{PtH})$ 52 Hz, 2H, >CHCH=), 6.26 (m, $J(\text{PtH})$ 54 Hz, 1H, >CHCH=), 7.00 (m, $J(\text{PtH})$ 70 Hz, 1H, $\text{CH}_2\text{CH=}$). ^{19}F NMR spectrum: 120.0 (m, $^3J(\text{PtF})$ 345 Hz, 3F, F(2,2',6)) (see text); 122.6 (m, $^3J(\text{PtF})$ 354 Hz, 1F, F(6') (see

text); 159.7 (m, 2F, F(4,4')), 162.7 (m, 4F, F(3,3',5,5')). Mass spectrum: m/z 640[1%, ($M - H_2F$)⁺]; 529[1, Pt(C₆F₅)₂⁺]; 494[1, Pt(C₆F₅)(dcy)⁺]; 326[100, Pt(dcy - H)⁺].

η^4 -Norbornadienebis(pentafluorophenyl)platinum(II). Yield 53%, m.p. 236–237°C (dec.), lit. [13] 244–245°C (dec.) (Found: C, 36.0; H, 1.0; F, 31.0. C₁₉H₈F₁₀Pt calc: C, 36.7; H, 1.3; F, 30.6%). IR in agreement with limited reported data [13]. ¹H NMR spectrum: 1.79 (br s, 2H, CH₂), 4.47 (vbr s, 2H, CH), 5.96 (m, J (PtH) 48 Hz, 4H, =CH). ¹⁹F NMR spectrum: 120.9 (m, 3J (PtF) 378 Hz, 4F, F(2,6)), 159.6 (m, 2F, F(4)), 163.3 (m, 4F, F(3,5)). Mass spectrum: m/z 621 [1%, M^+]; 362[1, Pt(C₆F₅)⁺]; 286[60, Pt(nbd - H)]⁺; 91[100, nbd - H]⁺.

η^4 -Hexa-1,5-dienebis(pentafluorophenyl)platinum(II). Yield 77%, m.p. 204–205°C (dec.) (Found: C, 35.4; H, 1.5; F, 31.3. C₁₈H₁₀F₁₀Pt calc: C, 35.4; H, 1.7; F, 31.1%). IR: 1500vs and 1470vs(br) (ν (CC)); 1060vs(br) and 950vs(br) (ν (CF)); 800vs and 790vs ('X-sens.') cm⁻¹. ¹H NMR spectrum: 2.53–2.88 (m, 4H, CH₂), 4.33 (d, 3J (HH) 16, J (PtH) 42 Hz, 2H, =CH *cis* to CH₂), 4.82 (d, 3J (HH) 8, J (PtH) 46 Hz, 2H, =CH *trans* to CH₂), 5.41–5.74 (m, 2H, =CH *gem* to CH₂). ¹⁹F NMR spectrum: 121.0 (br m, 3J (PtF) 347 Hz, 4F, F(2,6)), 159.6 (m, 2F, F(4)), 162.6 (br m, 4F, F(3,5)). Mass spectrum: m/z 609[1%, [$M - 2H$]⁺]; 529[1, Pt(C₆F₅)₂⁻]; 362[1, Pt(C₆F₅)⁺]; 168[100, C₆F₅H⁺].

η^4 -(*cis-cis*-Cycloocta-1,5-diene)bis(2,3,5,6-tetrafluorophenyl)platinum(II). Yield 82%, m.p. 275–278°C (dec.) (Found: C, 40.0; H, 2.2; F, 25.4. C₂₀H₁₄F₈Pt calc: C, 39.9; H, 2.4; F, 25.3%). IR: 1470vs(br) (ν (CC)); 900s (ν (CF)) cm⁻¹. ¹H NMR spectrum: 2.51–2.67 (m, 8H, CH₂), 5.39 (m, J (PtH) 45 Hz, 4H, =CH), 6.66 (m, 2H, H(Ar)). ¹⁹F NMR spectrum: 120.4 (m, 3J (PtF) 343 Hz, 4F, F(2,6)), 140.5 (m, 4F, F(3,5)). Mass spectrum: m/z 601[1%, M^+]; 493[1, Pt(HC₆F₄)₂⁺]; 452[1, Pt(HC₆F₄)(cod)⁺]; 344[1, Pt(HC₆F₄)⁺]; 303[100, Pt(cod)⁺]. The complex was also prepared by a similar reaction between PtCl₂(cod) and *p*-HC₆F₄Li (mole ratio 1/1), yield, 73% (based on *p*-HC₆F₄Li) (m.p. and spectroscopic identification) and PtCl₂(cod), 31%, was recovered.

η^4 -Dicyclopentadienebis(2,3,5,6-tetrafluorophenyl)platinum(II). Yield 91%, m.p. 214–215°C (dec.) (Found: C, 42.6; H, 2.2; F, 24.5. C₂₂H₁₄F₈Pt calc: C, 42.3; H, 2.3; F, 24.3%). IR: 1470vs, 1460 and 1455vs(sh) (ν (CC)); 895vs (ν (CF)) cm⁻¹. ¹H NMR spectrum: 1.80–4.06 (m, 8H, CH₂, CH), 5.39–5.80 (m, 2H, >CHCH=) 6.25 (m, J (PtH) 55 Hz, 1H, >CHCH=), 6.65 (m, 2H, H(Ar)), 7.01 (m, J (PtH) 70 Hz, 1H, CH₂CH=). ¹⁹F NMR spectrum: 121.4 (m, 3J (PtF) 342 Hz, 3F, F(2,2',6) (see text)), 124.0 (m, 3J (PtF) 391 Hz, 1F, F(6') (see text)), 141.1 (m, 4F, F(3,5)). Mass spectrum: m/z 625[1%, M^+]; 493[1, Pt(HC₆F₄)₂⁺]; 326[100, Pt(dcy - H)⁺].

η^4 -Norbornadienebis(2,3,5,6-tetrafluorophenyl)platinum(II). Yield of crude product, 96%, which partly decomposed on crystallization from ether/petroleum ether giving a small amount of colourless needles, m.p. 135–137°C (dec.). IR 1460 vs(br) (ν (CC)); 895vs (ν (CF)) cm⁻¹. ¹H NMR spectrum: 1.76(m, 2H, CH₂), 4.45(m, 2H, CH), 5.97(m, J (PtH) 47 Hz, 4H, =CH), 6.64(m, 2H, H(Ar)). ¹⁹F NMR spectrum: 122.5 (m, 3J (PtF) 385 Hz, 4F, F(2,6)), 141.3(m, 4F, F(3,5)). Mass spectrum: m/z 585[5%, M^+]; 286 [60, Pt(nbd - H)]⁺; 91[100, (nbd - H)⁺].

η^4 -Hexa-1,5-dienebis(2,3,5,6-tetrafluorophenyl)platinum(II). Yield 36%, m.p. 212–214°C (dec.) (Found: C, 37.6; H, 1.9; F, 26.4; mol. wt. (osmometric in CH₂Cl₂ at 25°C), 583 (1.058%, w/v). C₁₈H₁₂F₈Pt calc: C, 37.6; H, 2.1; F, 26.4%; mol. wt., 575). IR: 1470vs(br) (ν (CC)), 905vs (ν (CF)) cm⁻¹. ¹H NMR spectrum: 2.55 (m, 2H,

CH₂), 2.79 (m, 2H, CH₂), 4.31 (d, ³J(HH) 16, J(PtH) 41 Hz, 2H, =CH *cis* to CH₂), 4.83 (d, ³J(HH) 8, J(PtH) 45 Hz, 2H, =CH *trans* to CH₂), 5.60 (m, 2H, =CH *gem* to CH₂), 6.66 (m, 2H, H(Ar)). ¹⁹F NMR spectrum: 122.7 (m, ³J(PtF) 351 Hz, 4F, F(2,6)), 140.8 (m, 4F, F(3,5)). Mass spectrum: *m/z* 573[1%(*M* - 2H)⁺]; 493 [1, Pt(HC₆F₄)₂⁺]; 344 [2, Pt(HC₆F₄)⁺]; 277[100, Pt(hex)⁺].

Preparation of polyfluorophenylplatinum(II) complexes by decarboxylation

The dichloro(diene)platinum(II) complex and the thallose polyfluorobenzoate were mixed in dry pyridine (10 cm³) under nitrogen. Amounts of reagents and reaction conditions are given below. The nitrogen was passed through saturated aqueous barium hydroxide and evolved carbon dioxide was determined gravimetrically as barium carbonate. After reaction, the pyridine was removed under vacuum at room temperature, and the residue was washed with petroleum ether. Extraction of the residue (solvents below), filtration through a small silica pad and crystallization gave the polyfluorophenylplatinum(II) complex.

Chloro(η⁴-cis,cis-cycloocta-1,5-diene)pentafluorophenylplatinum(II). Reaction of PtCl₂(cod) (1.00 mmol) and TiO₂CC₆F₅ (1.00 mmol) at 40°C for 0.5 h and at room temperature for 2 h (CO₂, 93%), ether extraction and crystallization from ether/petroleum ether gave colourless needles, yield, 80%, m.p. 188–189°C (dec.) (Found: C, 32.7; H, 2.7; F, 18.6. C₁₄H₁₂ClF₅Pt calc: C, 33.2; H, 2.4; F, 18.8%). IR: 1495vs and 1460vs(br) (ν(CC)), 1050vs and 945 vs(br) (ν(CF)), 810vs ('X-sens'), 319vs, (ν(PtCl)) cm⁻¹. ¹H NMR spectrum: 2.30–2.76 (br, m, 8H, CH₂), 4.94 (m, J(PtH) 74 Hz, 2H, =CH *trans* to Cl), 5.91 (m, J(PtH) 43 Hz, 2H, =CH *trans* to C₆F₅). ¹⁹F NMR spectrum: 122.9 (m, ³J(PtF) 275 Hz, 2F, F(2,6)), 159.2 (m, 1F, F(4)), 162.6 (m, 2F, F(3,5)). Mass spectrum: *m/z* 505[10%, *M*⁺]; 469 [2, Pt(C₆F₅)(cod - H)⁺]; 362 [3, Pt(C₆F₅)⁺]; 303[100, Pt(cod)⁺].

Bis(pentafluorophenyl)dipyridineplatinum(II). Reaction between PtCl₂(cod) (1.00 mmol) and TiO₂CC₆F₅ (2.00 mmol) for 1 h at 30–35°C and 0.5 h at room temperature (CO₂, 53%), extraction with dichloromethane, and crystallization from dichloromethane/petroleum ether gave a mixture of *cis* and *trans* isomers of the title compound (65%), identified by comparison of TLC and IR with authentic samples, and a trace of Pt(C₆F₅)₂(cod).

Chloro(η⁴-cis,cis-cycloocta-1,5-diene)2,3,5,6-tetrafluorophenylplatinum(II). Reaction of PtCl₂(cod) (2.30 mmol) and *p*-HC₆F₄CO₂Tl (2.30 mmol) at 45–50°C for 4 h and at room temperature for 6 h (CO₂, 91%), extraction and column chromatography on silica with dichloromethane, and crystallization from dichloromethane/petroleum ether gave needles, yield 62%, m.p. 205–207°C (dec.) (Found: C, 33.8; H, 2.2, C₁₄H₁₃F₄ClPt calc: C, 34.5; H, 2.7%). IR 1460vs(br) (ν(CC)), 890vs, (ν(CF)), 321vs (ν(PtCl)) cm⁻¹. ¹H NMR spectrum: 2.05–2.73 (br m, 8H, CH₂), 4.96 (m, J(PtH) 70 Hz, 2H, =CH *trans* to Cl), 5.90 (m, J(PtH) 46 Hz, 2H, CH= *trans* to *p*-HC₆F₄), 6.75 (m, 1H, H(Ar)). ¹⁹F NMR spectrum: 124.7 (m, ³J(PtF) 266 Hz, 2F, F(2,6)), 140.7 (m, 2F, F(3,5)). Mass spectrum: *m/z* 488 [18%, *M*⁺]; 452[4, Pt(HC₆F₄)(cod)⁺]; 303[100, Pt(cod)⁺].

cis-Chloro(pentafluorophenyl)dipyridineplatinum(II). Reaction of PtCl₂(hex) (0.50 mmol) and TiO₂CC₆F₅ (0.50 mmol) in pyridine (5 cm³) for 3 h at room temperature and 5 min at 70°C, extraction with dichloromethane, and crystallization from dichloromethane/petroleum ether gave colourless crystals (83%), m.p. 184–185°C (dec.) (Found: C, 34.8; H, 1.9; F, 16.7; N, 5.2. C₁₆H₁₀ClF₅N₂Pt calc: C, 34.6; H,

1.8; F, 17.1; N, 5.0%). IR 1500s and 1450vs ($\nu(\text{CC})$); 1060s and 965, 960s ($\nu(\text{CF})$), 810s ('X-sens'), 341s ($\nu(\text{Pt}-\text{Cl})$) cm^{-1} . ^1H NMR spectrum: 7.34 (m, 4H, H(3,5)), 7.80 (m, 2H, H(4)), 8.70 (m, $J(\text{PtH})$ not determined, satellites poorly resolved, 4H, H(2,6)). ^{19}F NMR spectrum: 122.8 (m, $^3J(\text{PtF})$ 343 Hz, 2F, F(2,6)), 162.0 (m, 1F, F(4)), 164.7 (m, 2F, F(3,5)). Mass spectrum: m/z 556 [$<1\%$, M^+]; 520 [<1 , $\text{Pt}(\text{C}_6\text{F}_5)(\text{py})_2^+$]; 477 [<1 , $\text{Pt}(\text{C}_6\text{F}_5)\text{Cl}(\text{py})^+$]; 352 [$1, \text{Pt}(\text{py})_2^+$]; 273 [$2, \text{Pt}(\text{py})^+$]; 79 [$100, \text{py}^+$].

Halogen exchange reactions

A solution of $\text{Pt}(\text{R})\text{Cl}(\text{cod})$ ($\text{R} = \text{C}_6\text{F}_5$ or $p\text{-HC}_6\text{F}_4$) (0.05–0.10 g) in aqueous acetone (1/2, v/v; 30 cm^3) was stirred overnight with NaX ($\text{X} = \text{Br}$ or I) (0.5 g). Evaporation of acetone in vacuo, ether extraction of the resulting aqueous suspension, evaporation to dryness, and crystallization of the residue from ether/petroleum ether gave colourless ($\text{X} = \text{Br}$) or pale lemon ($\text{X} = \text{I}$) complexes.

Bromo(η^4 -*cis,cis*-cycloocta-1,5-diene)pentafluorophenylplatinum(II).

Yield 90%, m.p. 179–180°C (dec.) (Found: C, 31.1; H, 2.4; F, 17.4. $\text{C}_{14}\text{H}_{12}\text{BrF}_5\text{Pt}$ calc: C, 30.6; H, 2.2; F, 17.3%). IR: 1500s, and 1460vs ($\nu(\text{CC})$); 1055s and 950vs ($\nu(\text{CF})$); 800s ('X-sens'); 218s ($\nu(\text{PtBr})$) cm^{-1} . ^1H NMR spectrum: 2.20–2.69 (br m, 8H, CH_2), 4.69 (m, $J(\text{PtH})$ 69 Hz, 2H, =CH *trans* to Br), 5.92 (m, $J(\text{PtH})$ 44 Hz, 2H, =CH *trans* to C_6F_5). ^{19}F NMR spectrum: 122.3 (m, $^3J(\text{PtF})$ 272 Hz, 2F, F(2,6)) 159.4 (m, 1F, F(4)), 162.8 (m, 2F, F(3,5)). Mass spectrum: m/z 550 [30%, M^+]; 469 [$5, \text{Pt}(\text{C}_6\text{F}_5)(\text{cod} - \text{H})^+$]; 362 [$5, \text{Pt}(\text{C}_6\text{F}_5)^+$]; 303 [100, $\text{Pt}(\text{cod})^+$].

(η^4 -*cis,cis*-Cycloocta-1,5-diene)iodo(pentafluorophenyl)platinum(II). Yield 76%, m.p. 177–179°C (dec.) (Found: C, 28.6; H, 2.0; F, 16.1. $\text{C}_{14}\text{H}_{12}\text{F}_5\text{IPt}$ calc: C, 28.2; H, 2.0; F, 15.9%). IR: 1500s and 1460vs ($\nu(\text{CC})$); 1055s and 950vs ($\nu(\text{CF})$); 800s ('X-sens'); 175 m ($\nu(\text{PtI})$) cm^{-1} . ^1H NMR spectrum: 2.03–2.56 (br m, 8H, CH_2), 5.04 (m, $J(\text{PtH})$ 67 Hz, 2H, =CH *trans* to I), 5.92 (m, $J(\text{PtH})$ 46 Hz, 2H, =CH *trans* to C_6F_5). ^{19}F NMR spectrum: 120.7 (m, $^3J(\text{PtF})$ 287 Hz, 2F, F(2,6)), 159.6 (m, 1F, F(4)), 163.0 (m, 2F, F(3,5)). Mass spectrum: m/z 596 [80%, M^+]; 470 [100, $\text{Pt}(\text{C}_6\text{F}_5)(\text{cod})^+$].

Bromo(η^4 -*cis,cis*-cycloocta-1,5-diene)(2,3,5,6-tetrafluorophenyl)platinum(II). Yield 80%, m.p. 223–225°C (dec.) (Found: C, 31.8; H, 2.4; F, 14.7. $\text{C}_{14}\text{H}_{13}\text{BrF}_4\text{Pt}$ calc: C, 31.6; H, 2.5; F, 14.3%). IR: 1460vs(br) ($\nu(\text{CC})$); 890vs and 885vs ($\nu(\text{CF})$); 219s ($\nu(\text{PtBr})$) cm^{-1} . ^1H NMR spectrum: 2.17–2.70 (br m, 8H, CH_2) 4.98 (m, $J(\text{PtH})$ 70 Hz, 2H, =CH *trans* to Br), 5.90 (m, $J(\text{PtH})$ 43 Hz, 2H, =CH *trans* to HC_6F_4) 6.75 (m, 1H, H(Ar)). ^{19}F NMR spectrum: 124.2 (m, $^3J(\text{PtF})$ 269 Hz, 2F, F(2,6)), 140.8 (m, 2F, F(3,5)). Mass spectrum: m/z 532 [40%, M^+]; 452 [8, $\text{Pt}(\text{HC}_6\text{F}_4)(\text{cod})^+$]; 344 [2, $\text{Pt}(\text{HC}_6\text{F}_4)^+$]; 302 [100, $\text{Pt}(\text{cod} - \text{H})^+$].

(η^4 -*cis,cis*-Cycloocta-1,5-diene)iodo(2,3,5,6-tetrafluorophenyl)platinum(II). Yield 83%, m.p. 219–220°C (dec.) (Found: C, 29.4; H, 2.1; F, 13.1. $\text{C}_{14}\text{H}_{13}\text{F}_4\text{IPt}$ calc: C, 29.0; H, 2.3; F, 13.1%). IR 1465vs(br) ($\nu(\text{CC})$); 890vs ($\nu(\text{CF})$); 185m ($\nu(\text{PtI})$) cm^{-1} . ^1H NMR spectrum: 2.02–2.62 (m, 8H, CH_2), 5.06 (m, $J(\text{PtH})$ 66 Hz, 2H, =CH *trans* to I), 5.91 (m, $J(\text{PtH})$ 45 Hz, 2H, =CH *trans* to HC_6F_4) 6.74 (m, 1H, H(Ar)). ^{19}F NMR spectrum: 122.4 (m, $^3J(\text{PtF})$ 271 Hz, 2F, F(2,6)), 140.9 (m, 2F, F(3,5)). Mass spectrum; m/z 579 [70%, M^+]; 452 [100, $\text{Pt}(\text{HC}_6\text{F}_4)(\text{cod})^+$].

Ligand displacement reactions

Platinum complexes and ligands were reacted together as indicated in Table 1.

Isolation methods are given below. Unless indicated otherwise, the product was recrystallized from CH_2Cl_2 /petroleum ether. Where the same complex was obtained from more than one reaction, the products had identical spectroscopic properties.

cis-Bis(pentafluorophenyl)bis(triphenylphosphine)platinum(II). The complex was isolated by removal of the solvent under vacuum, m.p. 259–263°C, lit. [24] 243–250°C (Found: C, 54.6; H, 2.6. $\text{C}_{48}\text{H}_{30}\text{F}_{10}\text{P}_2\text{Pt}$ calc: C, 54.7; H, 2.9%). IR in agreement with limited reported data [24,32]. ^{19}F NMR spectrum: 116.2 (m, $^3J(\text{PtF})$ 315 Hz, 4F, F(2,6)), 164.4 (m, 6F, F(3,4,5)). Mass spectrum: m/z 1053 [$< 1\%$, M^+]; 885 [< 1 , $\text{Pt}(\text{C}_6\text{F}_5)(\text{PPh}_3)_2^+$]; 719 [20, $\text{Pt}(\text{PPh}_3)_2^+$]; 262 [100, PPh_3^+]. Ether/petroleum ether was also a satisfactory recrystallization solvent.

cis-Bis(pentafluorophenyl)dipyridineplatinum(II). After removal of pyridine under vacuum, the residue was washed with petroleum ether and dissolved in CH_2Cl_2 , which was passed through a small silica gel pad. Evaporation to dryness gave the complex, m.p. 273–275°C (dec.), lit. [20] 230–235°C (dec.) (Found: C, 38.4; H, 1.4. $\text{C}_{22}\text{H}_{20}\text{F}_{10}\text{N}_2\text{Pt}$ calc: C, 38.4; H, 1.5%). IR in agreement with limited reported data [20]. ^1H NMR spectrum: 7.53 (m, 4H, H(3,5)), 8.01 (m, 2H, H(4)), 8.74 (m, $^3J(\text{PtH})$ 30 Hz, 4H, H(2,6)). ^{19}F NMR spectrum: 119.1 (m, $^3J(\text{PtF})$ 473 Hz, 4F, F(2,6)), 164.0 (m, 2F, F(4)), 166.1 (m, 4F, F(3,5)). Mass spectrum: m/z 687 [$< 1\%$, M^+]; 353 [1, $\text{Pt}(\text{py})_2^+$]; 274 (5, $\text{Pt}(\text{py})^+$); 168 [100, $\text{C}_6\text{F}_5\text{H}^+$].

Ethane-1,2-diaminebis(pentafluorophenyl)platinum(II). After removal of the excess of ligand under vacuum, the resulting oil was dissolved in CH_2Cl_2 , from which the complex was precipitated by addition of petroleum ether, m.p. 284–286°C (dec.) (Found: C, 28.7; H, 1.5; F, 32.3; N, 5.0. $\text{C}_{14}\text{H}_8\text{F}_{10}\text{N}_2\text{Pt}$ calc: C, 28.5; H, 1.4; F, 32.3; N, 4.8%). IR 3385m and 3330m ($\nu(\text{NH})$), 1500vs and 1450vs(br) ($\nu(\text{CC})$), 1050vs(br) and 950vs(br) ($\nu(\text{CF})$), 800s and 790s ('X-sens') cm^{-1} . ^1H NMR spectrum: 3.01 (m, 4H, CH_2), 4.52 (br s, 4H, NH_2). ^{19}F NMR spectrum: 118.8 (m, $^3J(\text{PtF})$ 473 Hz, 4F, F(2,6)) 167.0 (br m, 6F, F(3,4,5)). Mass spectrum: m/z 589 [5%, M^+]; 254 [12, $\text{Pt}(\text{C}_2\text{H}_7\text{N}_2)^+$]; 168 [100, $\text{C}_6\text{F}_5\text{H}^+$].

Bis(pentafluorophenyl)(1,10-phenanthroline)platinum(II). The complex precipitated from the reaction mixture, was washed with ether and petroleum ether, and was not recrystallized, m.p. 353–354°C lit. [20] 335°C (dec.) IR in agreement with limited reported data [20]. ^1H NMR spectrum: 8.06 (dd, 2H, H(3,8)) 8.31 (s, 2H, H(5,6)), 8.82 (dd, $^3J(\text{PtH})$ 30 Hz, 2H, H(2,9)) 9.04 (dd, 2H, H(4,7)). ^{19}F NMR spectrum: 117.8 (m, $^3J(\text{PtF})$ 460 Hz, 4F, F(2,6)), 163.2 (m, 2F, F(4)) 165.0 (m, 4F, F(3,5)). Mass spectrum: m/z 709 [10%, M^+]; 541 [1, ($M - \text{C}_6\text{F}_5\text{H}$) $^+$]; 375 [100%, $\text{Pt}(\text{phen})^+$].

cis-Diamminebis(pentafluorophenyl)platinum(II). Dry ammonia gas was passed through an ether solution of the reactant complex, and the product was isolated by evaporation of the ether to dryness, m.p. $> 190^\circ\text{C}$ (dec.) (Found: C, 25.8; H, 1.5; F, 33.5; N, 4.5. $\text{C}_{12}\text{H}_6\text{F}_{10}\text{N}_2\text{Pt}$ calc: C, 25.6; H, 1.1; F, 33.7; N, 5.0%) IR: 3370m and 3340m ($\nu(\text{NH})$), 1505s and 1460vs ($\nu(\text{CC})$), 1065s and 960vs ($\nu(\text{CF})$), 810m and 805m ('X-sens'). ^{19}F NMR spectrum: 121.6 (m, $^3J(\text{PtF})$ 481 Hz, 4F, F(2,6)), 163.0 (m, 2F, F(4)), 165.2 (m, 4F, F(3,5)). Mass spectrum: m/z 563 [1%, M^+]; 546 [1, $\text{Pt}(\text{C}_6\text{F}_5)_2(\text{NH}_3)^+$]; 527 [$< 1\%$, $\text{Pt}(\text{C}_6\text{F}_5)_2^+$]; 395 [5, $\text{Pt}(\text{C}_6\text{F}_5)(\text{NH}_3)(\text{NH}_2)^+$]; 379 [6, $\text{Pt}(\text{C}_6\text{F}_5)(\text{NH}_3)^+$]; 168 [100, $\text{C}_6\text{F}_5\text{H}^+$].

Bis(pentafluorophenyl)(N,N,N',N'-tetramethylethane-1,2-diamine)platinum(II). The complex was isolated by evaporation of the solvent and excess ligand under

vacuum and was recrystallized from ether/petroleum ether, m.p. 300–302°C (dec.) (Found: C, 33.7; H, 2.9; N, 4.5. $C_{18}H_{16}F_{10}N_2Pt$ calc: C, 33.5; H, 2.5; N, 4.3%). IR: 1500s and 1460s(br) ($\nu(CC)$); 1060s and 960vs ($\nu(CF)$); 820s and 805s ('X-sens'). 1H NMR spectrum: 2.73 (m, $^3J(PtH)$ 28 Hz, 12H, Me), 2.82 (m, $^3J(PtH)$ unresolved, 4H, CH_2). ^{19}F NMR spectrum: 119.9 (m, $^3J(PtF)$ 464 Hz, 4F, F(2,6)), 162.8 (m, 2F, F(4)), 164.7 (m, 4F, F(3,5)). Mass spectrum: m/z 645 [10%, M^+]; 631 [1, ($M - CH_2$) $^+$]; 308 [20, ($M - [2C_6F_5 + 3H]$) $^+$]; 58 [100, (CH_3) $_2NCH_2^+$].

trans-Chloro(pentafluorophenyl)dipyridineplatinum(II). Evaporation of pyridine, and recrystallization of the residue from ether/petroleum ether gave needles, m.p. 178–180°C (dec.), lit. [19] 181–182.5°C (dec.), with IR, 1H and ^{19}F NMR and mass spectra in agreement with those reported [19].

Bis(2,3,5,6-tetrafluorophenyl)bis(triphenylphosphine)platinum(II). The residue on removal of ether was washed with boiling petroleum ether (100 ml) to remove triphenylphosphine, m.p. 270–274°C (Found: C, 56.7; H, 3.1; F, 14.7. $C_{48}H_{32}F_8P_2Pt$ calc: C, 56.6; H, 3.2; F, 14.9%). IR: 1460vs [$\nu(CC)$], 890vs [$\nu(CF)$], 760m, 750m and 740m (f , $\gamma(CH)$ of Ph_3P), 710s (τ , 'X-sens', Ph_3P), 695s ($\nu \Phi(CC)$, Ph_3P) cm^{-1} . 1H NMR spectrum: 6.27 (m, 2H, HC_6F_4), 7.0–7.5 (m, 30H, Ph_3P). ^{19}F NMR spectrum: 119.8 (m, $^3J(PtF)$ 305 Hz, 4F, F(2,6)) 142.6 (m, 4F, F(3,5)). Mass spectrum: m/z 868 [1%, $Pt(HC_6F_4)(PPh_3)_2^+$]; 719 [20, $Pt(PPh_3)_2^+$]; 262 [100, Ph_3P^+].

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