

The synthesis and reactivity of perfluorinated undecafluorobicyclo[2,2,1]-heptan-1-yl platinum(II), palladium(II) and rhenium(V) complexes and the X-ray crystal structure of *cis*-PtCl(C₇F₁₁)(PPh₃)₂

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Abstract

1-Lithio-undecafluorobicyclo[2,2,1]-heptane (C₇F₁₁Li) reacts with *cis*-PtCl₂(PPh₃)₂, *trans*-PdCl₂(PPh₃)₂, *trans*-PdCl₂(MeCN)₂ and ReOCl₃(PPh₃)₂ to give *cis*-PtCl(C₇F₁₁)(PPh₃)₂, *trans*-Pd(C₇F₁₁)₂(PPh₃)₂, *trans*-Pd(C₇F₁₁)₂(MeCN)₂ and Re(=O)(C₇F₁₁)₃(PPh₃)₂, respectively. The reactions of these complexes with dilute HCl, NaOH, gaseous hydrogen, oxygen and air have been examined in order to assess the stability of the M–C bond. The X-ray crystal structure of *cis*-PtCl(C₇F₁₁)(PPh₃)₂ reveals bond distances to platinum of Pt–C = 2.167(28), Pt–P = 2.278(7), 2.405(10) and Pt–Cl = 2.333(7) Å. There are significant distortions from the ideal square-planar geometry, with *cis*-angles of C–Pt–P = 103.4(7), Cl–Pt–P = 80.8(3), C–Pt–Cl = 84.3(7) and P–Pt–P = 92.3(3)°.

Introduction

The noble metals, particularly gold, platinum and palladium, have applications in the construction of semiconductor devices and in the preparation of catalytic surface coatings. They are typically deposited by sputtering or electron beam evaporation but there is now increasing interest in Metal Organic Chemical Vapour deposition (MOCVD). The success of this technique depends upon the availability of suitable organometallic precursors which are volatile and which can decompose to give the pure metal under mild thermal or photochemical conditions [1–5]. High volatility can be achieved by surrounding a metal ion with bulky non-polar hydrocarbon or fluorocarbon ligands which saturate the coordination sphere and reduce intermolecular bonding interactions. Fluorocarbon ligands

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would be expected to provide the highest volatility [6] and a number of complexes containing perfluoroalkyl or perfluoroaryl ligands have been described [7]. Examples of metal complexes containing perfluoroalkyl ligands include $[(CF_3)_3C]_2Hg$ [7], CF_3SiI [8], perfluoroalkyl derivatives of cadmium [9], $RfCu$ ($Rf = n-C_3F_7$ or $n-C_7F_{15}$), $Cu(CF_2)Cu$ [10], $RfAg$ ($Rf = (CF_3)_2CF$, $n-C_3F_7$, $C(CF_3)_3$, $(CF_3)_2CCl$) [11], and $[(Ph_3P)Au]_2C_2(CF_3)_2$ [12]. Examples of complexes containing perfluoroaryl ligands include the neutral and cationic pentafluorophenylpalladium(II) complexes $\{PdX(C_6F_5)(AsPh_3)_2\}$ ($X = Br, I, CN, SCN, CNO, MeCO_2, NO_3$ or ClO_4) and $\{Pd(C_6F_5)(AsPh_3)_2L\}$ (ClO_4) ($L = C_5H_5N, PET_3, PPh_3, SbPh_3$) [13]. Binuclear complexes are also known [14] including $(Bu_4N)_2\{Pt_2(\mu-C_6F_5)_2(C_6F_5)_4, H_2O$ and $(NBu_4)\{Pt_2Ag(\mu-C_6F_5)_2C_6F_5)_4OEt_2\}$ which contain bridging pentafluorophenyl groups [15].

Despite the variety of known complexes of fluorocarbon ligands, examples of compounds containing perfluoroalkyl ligands that are particularly bulky in sterical terms are rare. Consequently we were interested in exploring the chemistry of the bulky perfluorobicyclo[2,2,1]-heptan-1-yl ligand (pfnb). The novel bridgehead mercurials $Hg(pfnb)_2$, **1**, and bis-4-H-octafluorobicyclo[2,2,1]heptanylmercury(II) can be obtained simply by adding the corresponding 1-H,4-X-perfluorobicyclo[2,2,1]heptanes [$X = H, F$] to a solution prepared from mercuric chloride, potassium hydroxide, water, Me_2SO and, in the case of the 4-H compound, sodium bromide [16]. Alternatively pfnbH can be lithiated with *n*-butyllithium in diethyl ether, and then treated directly with mercuric(II) chloride. In principle these mercury derivatives might offer a synthetic route to new *d*-block metal complexes through transmetallation reactions [17–19]. We have investigated this as well as the more direct route using Lipfnb as the reagent. In this paper we report the synthesis of platinum(II), palladium(II) and rhenium(V) complexes with pfnb, and an investigation of their reactivity towards dilute hydrochloric acid, dilute sodium hydroxide solution, gaseous H_2 , O_2 and air.

Experimental

Synthetic and spectroscopic studies

All reactions were performed under dinitrogen. Reaction solvents were dried by standard methods, and other reagents were used as supplied. Published methods were used to prepare $PdCl_2(PPh_3)_2$ [20], $PtCl_2(PPh_3)_2$ [21], $PdCl_2(MeCN)_2$ [22], $ReOCl_3(PPh_3)_2$ [23] and $C_7F_{11}H$ [24].

Infrared spectra were recorded with a Perkin–Elmer 297 spectrometer with samples prepared as KBr discs. 1H (90 MHz), ^{19}F (84 MHz), ^{31}P (36 MHz) and $^{13}C\{^1H\}$ (22.5 MHz) NMR spectra were recorded on a Jeol FX90Q instrument and mass spectra using Kratos MS80RF instruments at the University of Birmingham and the SERC Mass Spectroscopy Service, University of Swansea. Elemental analyses were performed by the Microanalytical Laboratory, School of Chemistry, University of Birmingham.

Cis-PtCl(C_7F_{11})(PPh_3)_2 (**3**). Undecafluorobicyclo[2,2,1]-heptane ($C_7F_{11}H$) (0.75 g; 3.44 mmol) was added to diethyl ether (10 cm³) at $-78^\circ C$ and the mixture stirred for 5 min. A solution of *n*-butyllithium (1.6 mol cm⁻³ in hexane, 5 cm³) was then added dropwise. The temperature was maintained at $-78^\circ C$ for a further 30 min; then *cis*- $PtCl_2(PPh_3)_2$ (0.99 g; 1.25 mmol) was added. The mixture was stirred

for a further 2 h at -78°C , the solution was then filtered, and the colourless filtrate reduced in volume under reduced pressure to afford a white solid. This was filtered off and washed with hexane ($3 \times 50 \text{ cm}^3$). Further purification was effected by recrystallisation from ethanol to give colourless crystals (0.59 g, 45%), m.p. $171\text{--}173^{\circ}\text{C}$. Anal. Found: C, 49.2; H, 3.0; Cl, 3.1. Calc. $\text{C}_{43}\text{H}_{30}\text{ClF}_{11}\text{P}_2\text{Pt}$: C, 49.3; H, 2.9; Cl, 3.4%. IR ν_{max} (cm^{-1}): 1290, 1222, C–F; 1490, 1440, C_6H_5 (KBr). NMR δ_{H} (CDCl_3) 7.0–7.8 [10H, nos *, C_6H_6]; δ_{F} (CDCl_3) -92 to -98 , -107 to -128 , -213 to -216 [2F, nos *, 8F, nos *, 1F, nos *, C_7F_{11}]; $\delta_{\text{C}}\{^1\text{H}\}$ (CDCl_3) 133–135, 127.5, 127.9, 129.9, [s, s, s, nos *, C_6H_5]; δ_{P} (CDCl_3) 16.83, 22.58, [1P, s: d, $^1J(\text{Pt-P})$ 1445 Hz; 1P, s: d, $^1J(\text{Pt-P})$ 1065 Hz, PPh_3]. m/z (EI) 993 ($M - \text{ClF}$), 749 [$M - (\text{Cl} + \text{PPh}_3)$], 718 ($M - \text{C}_7\text{F}_{11}\text{Cl}$), 456 [$M - (\text{C}_7\text{F}_{11}\text{Cl} + \text{PPh}_3)$]; m/z (FAB) 1012 ($M - \text{Cl}$), 719 ($M - \text{C}_7\text{F}_{11}\text{Cl}$), 456 [$M - (\text{C}_7\text{F}_{11}\text{Cl} + \text{PPh}_3)$], 378 [$M - (\text{C}_7\text{F}_{11}\text{Cl} + \text{PPh}_3 + \text{C}_6\text{H}_6)$].

Trans-Pd(C₇F₁₁)₂(PPh₃)₂ (4). This compound was prepared by a procedure similar to that described for **3** using *trans*-PdCl₂(PPh₃)₂ (0.88 g, 1.26 mmol) in place of the platinum complex. The product was obtained as a deep red-brown solid (0.86 g, 53%). Recrystallization from CH₂Cl₂/hexane or EtOH/hexane mixtures gave a red semi-crystalline product, dec. 100°C . Anal. Found: C, 51.6; H, 3.6. Calc. $\text{C}_{50}\text{H}_{30}\text{F}_{22}\text{P}_2\text{Pd}$. C_6H_{14} : C, 51.6; H, 3.4%. IR ν_{max} (cm^{-1}): 1280, 1220, C–F; 1480, 1435, C_6H_5 (KBr). NMR δ_{H} (CDCl_3) 7.0–7.8 [nos *, C_6H_5]; δ_{F} (CDCl_3) -90 to -97 , -109 to -130 , -210 to -222 [2F, nos *, 18F, nos *, 2F nos, C_7F_{11}]; $\delta_{\text{C}}\{^1\text{H}\}$ (CDCl_3) 133.9, 132.1, 131.7, 129.2, 128.7, 128.1 [s, s, s, s, s, C_6H_5]; δ_{P} (CDCl_3) 30.76 [s, PPh_3].

Trans-PdCl(C₇F₁₁)(MeCN)₂ (5). This compound was prepared by a procedure similar to that described for **3** using *trans*-PdCl₂(MeCN)₂ (0.32 g, 1.27 mmol) in place of the platinum complex. The product was obtained as a dark brown solid (0.41 g, 43%), m.p. $> 320^{\circ}\text{C}$. Anal. Found: C, 28.3; H, 1.7; N, 3.9. Calc. $\text{C}_{18}\text{H}_6\text{N}_2\text{F}_{22}\text{Pd}$: C, 27.9; H, 0.8; N, 3.6%. IR ν_{max} (cm^{-1}), 2950, CH₃, 2250, C≡N, 1290, 1220, C–F (KBr). NMR $\delta_{\text{H}}[(\text{CD}_3)_2\text{CO}]$ 3.01 [s, CH₃]; $\delta_{\text{F}}[(\text{CD}_3)_2\text{CO}]$ -90 to -94 , -109 to -128 , -211 to -214 [2F, nos *, 8F, nos *, 1F nos *, C_7F_{11}]; $\delta_{\text{C}}\{^1\text{H}\}[(\text{CD}_3)_2\text{CO}]$ [s, CH₃CN].

ReO(C₇F₁₁)₃(PPh₃)₂ (6). This compound was prepared by a procedure similar to that described for **3** using ReOCl₃(PPh₃)₂ (0.70 g, 0.84 mmol) in place of the platinum complex. The product was obtained as a dark brown solid (0.47 g, 35%), dec 130°C . Anal. Found: C, 42.8; H, 2.2. Calc. $\text{C}_{57}\text{H}_{30}\text{F}_{33}\text{OP}_2\text{Re}$: C, 42.6; H, 1.9%. IR ν_{max} (cm^{-1}), 1240, C–F; 1485, 1440, C_6H_5 (KBr). NMR δ_{H} (CDCl_3) 7.2–7.8 [nos *, C_6H_5]; δ_{F} (CDCl_3) -100 to -126 , -205 to -221 [30F, nos *, 3F nos, C_7F_{11}]; $\delta_{\text{C}}\{^1\text{H}\}$ (CDCl_3) 135, 132.2, 132.1, 131.9, 129.8, 128.8, 128.2 [s, s, s, s, s, s, C_6H_5]; δ_{P} (CDCl_3) 29.75 [s, PPh_3].

Structural studies

Crystal data for **3**, $\text{C}_{43}\text{H}_{30}\text{ClF}_{11}\text{P}_2\text{Pt}$ were as follows: $M = 1047.7$, monoclinic, $a = 20.20(1)$, $b = 19.30(1)$, $c = 12.48(1)$ Å, $\beta = 117.8(1)^{\circ}$, $U = 4308.9$ Å³, $F(000) = 2048$, $D_{\text{m}} = 1.63$ g cm⁻³, $D_{\text{c}} = 1.61$ g cm⁻³, $Z = 4$, Mo- K_{α} radiation ($\lambda = 0.7107$ Å), $\mu(\text{Mo-}K_{\alpha}) = 36.44$ cm⁻¹, space group $P2_1/a$.

* nos = number of overlapping signals.

Table 1

Atomic coordinates ($\times 10^{-4}$) with estimated standard deviations in parentheses

Atom	x	y	z
Pt(1)	2007(1)	1332(0)	116(1)
Cl(2)	1730(5)	2488(4)	-475(8)
P(11)	2187(4)	167(4)	388(7)
C(11)	1523(21)	-249(15)	-986(25)
C(12)	827(17)	46(12)	-1524(26)
C(13)	213(18)	-284(20)	-2568(35)
C(14)	324(18)	-863(20)	-3079(32)
C(15)	1130(21)	-1173(12)	-2444(28)
C(16)	1659(23)	-850(17)	-1485(25)
C(31)	1953(14)	-394(11)	1455(20)
C(32)	2614(17)	-581(15)	2458(24)
C(33)	2415(22)	-1038(16)	3282(29)
C(34)	1777(37)	-1352(34)	3028(67)
C(35)	1044(17)	-1017(13)	1803(28)
C(36)	1098(19)	-567(15)	1091(29)
C(21)	3148(15)	-6(13)	746(23)
C(22)	3731(14)	513(13)	962(20)
C(23)	4473(27)	310(19)	1197(38)
C(24)	4726(30)	-352(21)	1177(40)
C(25)	4188(24)	-881(22)	940(31)
C(26)	3391(25)	-751(20)	783(29)
P(41)	2182(5)	1313(4)	-1663(7)
C(41)	1427(15)	1823(12)	-2778(22)
C(42)	1554(16)	2329(13)	-3526(26)
C(43)	974(23)	2647(18)	-4390(32)
C(44)	196(24)	2398(17)	-4705(33)
C(45)	24(16)	1933(22)	-4012(34)
C(46)	585(24)	1668(20)	-3149(30)
C(51)	3082(16)	1734(15)	-1552(26)
C(52)	3390(19)	1690(15)	-2299(29)
C(53)	4075(23)	1975(18)	-2064(41)
C(54)	4511(14)	2270(14)	-963(30)
C(55)	4219(19)	2343(15)	-265(26)
C(56)	3441(11)	2096(11)	-208(24)
C(61)	2266(11)	551(9)	-2499(15)
C(62)	2946(19)	157(14)	-1954(33)
C(63)	3043(17)	-431(13)	-2560(31)
C(64)	2427(26)	-559(17)	-3726(36)
C(65)	1741(19)	-229(14)	-4165(27)
C(66)	1642(16)	372(13)	-3658(27)
C(71)	1988(14)	1673(15)	1756(20)
C(72)	1404(17)	1347(14)	2122(25)
F(721)	710(9)	1310(7)	1123(13)
F(722)	1453(10)	641(9)	2412(14)
C(73)	1316(14)	1767(12)	3179(21)
F(731)	1379(10)	1365(8)	4053(16)
F(732)	664(12)	2086(9)	2710(17)
C(74)	2007(16)	2255(14)	3362(29)
F(741)	1978(10)	2796(9)	3990(17)
C(75)	1921(20)	2354(16)	2072(27)
F(742)	1213(9)	2654(7)	1398(15)
F(743)	2439(9)	2831(8)	2067(15)
C(76)	2841(17)	1493(10)	2871(20)

Table 1 (continued)

Atom	x	y	z
F(761)	3359(10)	1748(11)	2609(17)
F(762)	2947(10)	829(10)	3193(16)
C(77)	2751(18)	1912(14)	3889(25)
F(771)	3263(11)	2381(12)	4376(20)
F(772)	2875(11)	1511(11)	4816(18)
O(100)	4953(24)	610(22)	5561(41)

A crystal of approximate size $0.3 \times 0.2 \times 0.2$ mm was mounted upon a STOE-2 diffractometer, rotating around the b axis. 7121 independent reflections were measured with a 2θ maximum of 50° . Background counts were for 20 s and a scan rate of $0.0333^\circ \text{ s}^{-1}$ was applied to a width of $(1.5 + \sin \mu / \tan \theta)$. No decay in intensity was observed for the standard reflections. 2642 reflections with $I > 2\sigma(I)$ were used in subsequent calculations. The position of the platinum atom was determined from the Patterson function and the remaining atoms in the molecule were located by successive cycles of difference Fourier syntheses and least-squares refinement. All non-hydrogen atoms in the molecule were given anisotropic thermal parameters, except for the carbon atoms in the phenyl rings which were refined isotropically. Hydrogen atoms were then included in calculated positions. A common refined thermal parameter was given to sets of hydrogen atoms in each ring. A water molecule was also found but its hydrogen atoms were not located. An empirical absorption correction was applied [25]. Parameters were refined using full-matrix least-squares methods with a weighting scheme $w = 1/[\sigma^2(F) + 0.003F^2]$. In the calculations we used SHELX76 [26] and some of our own programmes on the Amdahl 5870 computer at the University of Reading. The final R value was 0.083 ($R_w = 0.087$). In the final cycle of refinement, no shift was greater than 0.2σ . Maximum and minimum peaks in the final difference map were 1.6 and $-2.5 \text{ e } \text{\AA}^{-1}$ both close to the metal atom. Positional coordinates in the metal coordination sphere are given in Table 1. Tables of the remaining molecular dimensions, thermal parameters, hydrogen atom positions, and observed and calculated structure factors are available from the authors.

Discussion

Synthetic studies

Attempts to effect transmetallation reactions using $\text{Hg}(\text{pfnb})_2$ with PtCl_2 or PdCl_2 were unsuccessful. Similarly, reactions between Lipfnb and these salts only afforded black metallic deposits. The use of PPh_3 or MeCN co-ligands in *cis*- $\text{Pt}(\text{PPh}_3)_2\text{Cl}_2$, *trans*- $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ and *trans*- $\text{Pd}(\text{MeCN})_2\text{Cl}_2$ led to more promising results when Lipfnb was used, although intractable materials only were obtained when using $\text{Hg}(\text{pfnb})_2$. Lipfnb thus appears to be the reagent of choice in forming perfluoroalkyl complexes of this type, and this approach also proved successful with $\text{ReOCl}_3(\text{PPh}_3)_2$. All four metal complexes were reacted with Lipfnb in diethyl ether at -78°C to give the products **3**, **4**, **5** and **6**.

The reaction between *cis*- $\text{Pt}(\text{PPh}_3)_2\text{Cl}_2$ and Lipfnb affords the white compound **3**. The IR spectrum of this material contains bands consistent with the presence of

the PPh_3 and C_7F_{11} ligands, and the elemental analysis shows that chlorine is present. The ^1H NMR spectrum contains signals attributable to the phenyl protons of the PPh_3 ligands while the ^{31}P NMR spectrum shows that the phosphorus atoms occupy two different environments. These data are consistent with the formulation *cis*- $\text{PtCl}(\text{pfnb})(\text{PPh}_3)_2$ for **3** as confirmed by the X-ray crystal structure described below. The ^{19}F NMR spectrum of **3** is complex and contains a number of overlapping signals. In general terms the spectrum is similar to that of $\text{Hg}(\text{pfnb})_2$ which exhibits a number of signals in the regions -90 to -94 (2F) and -110 to -126 (8F) ppm along with a singlet at -211 (1F) ppm. The more complex nature of the spectrum of **3** may indicate the presence of isomers due to restricted rotation of the bulky pfnb ligand about the Pt–C bond in the presence of bulky PPh_3 ligands. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3** is also more complex than expected in that the signals attributable to the *ortho*-carbon atoms of the phenyl groups appear as a number of lines due to non-equivalent environments as well as to spin–spin coupling effects. The electron impact mass spectrum of **3** contained a number of ion envelopes attributable to fragment ions but no molecular ion was observed. The principal fragment ions at m/z 993, 749, 718 and 456 could be attributed to the loss of ClF , $(\text{Cl} + \text{PPh}_3)$, $\text{ClC}_7\text{F}_{11}$ and $(\text{ClC}_7\text{F}_{11} + \text{PPh}_3)$ respectively from the molecular ion. The positive ion FAB mass spectrum also contained ion envelopes based at 719 and 456, but in addition ions were present at m/z 1012 and 378 attributable to $(M - \text{Cl})^+$ and $(\text{PtPPh}_2)^+$ respectively.

The reaction between *trans*- $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ and Lipfnb affords the red compound **4**. The IR spectrum of this material contains bands attributable to the presence of the PPh_3 and pfnb ligands and the elemental analysis shows that, in this case, chlorine is absent. The ^1H NMR spectrum contains signals attributable to the phenyl protons of the PPh_3 ligands in addition to signals attributable to the presence of some hydrocarbon solvent. The ^{31}P NMR spectrum consists of one singlet while the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum lacks the complexity found in **3** for the signals associated with the *ortho*-carbon atoms of the phenyl groups. The ^{19}F NMR spectrum of **4** is generally similar to that of **3** and again, as a consequence of signal overlap, too complex to allow detailed analysis. On the basis of the spectroscopic and analytical data we formulate **4** as *trans*- $\text{Pd}(\text{pfnb})_2(\text{PPh}_3)_2 \cdot \text{C}_6\text{H}_{14}$. Neither the electron impact or the FAB mass spectra of **4** contain a molecular ion or any identifiable fragment ions. In view of the poor thermal stability (see below) of this compound this finding may be the result of decomposition reactions.

The reaction between *trans*- $\text{Pd}(\text{MeCN})_2\text{Cl}_2$ and Lipfnb affords the dark brown compound **5**. The IR spectrum of **5** contains bands attributable to the presence of the MeCN and pfnb ligands and the elemental analysis shows that chlorine is absent. The ^1H NMR spectrum contains a singlet attributable to the methyl protons of the MeCN ligands, and the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum contains a singlet attributable to the methyl carbon atoms. The ^{19}F NMR spectrum of **5** is again generally similar to that of **3** but less complex and more similar to that of $\text{Hg}(\text{pfnb})_2$ in this respect. On the basis of the spectroscopic and analytical data we formulate **5** as *trans*- $\text{Pd}(\text{pfnb})_2(\text{MeCN})_2$. As with **4** no significant ions are apparent in the mass spectrum of **5**.

The reaction between $\text{ReOCl}_3(\text{PPh}_3)_2$ and Lipfnb affords a dark brown compound **6**. The IR spectrum of this material contains bands consistent with the

presence of the PPh_3 and pfnb ligands as well as the $\text{Re}=\text{O}$ moiety. Elemental analysis shows that chlorine is absent and the ^1H NMR spectrum contains signals attributable to the phenyl protons of the PPh_3 ligands. The ^{31}P NMR spectrum consists of one singlet while the $^{13}\text{C}(^1\text{H})$ NMR spectrum lacks the complexity found in **3** for the signals associated with the *ortho*-carbon atoms of the phenyl groups. This would be in accord with the presence of a plane of symmetry in the molecule. The ^{19}F NMR spectrum of **6** is again generally similar to that of **3** but more extensive signal overlap is apparent. On the basis of the spectroscopic and analytical data we formulate **6** as $\text{fac-Re}(\text{=O})(\text{pfnb})_3(\text{PPh}_3)_2$. Neither the electron impact or the FAB mass spectra of **6** contained a molecular ion or any identifiable fragment ions, possibly as a result of limited thermal stability.

The thermal stabilities of the new compounds were investigated and, when heated *in vacuo* (dynamic 10^{-2} to 10^{-2} Torr) at a temperature of 140°C , all of the compounds decomposed to black materials. No sublimate was observed, nor was any evolution of pfnbH or PPh_3 apparent during the decomposition. However, thermogravimetric analysis (TGA) of the PPh_3 complexes in air did reveal evidence for ligand dissociation. The trace obtained when heating **3** at $20^\circ\text{C min}^{-1}$ shows a loss in mass of 51.4% up to 400°C . This corresponds with a loss in relative molecular mass of 538 compared with expected values of 524 for 2PPh_3 or 555 for $(\text{PPh}_3 + \text{C}_7\text{F}_{11})$. At the lower heating rate of $10^\circ\text{C min}^{-1}$ two stages were resolved. The first involves a loss in mass of 16% at *ca.* 145°C followed by a further loss of 35% up to 300°C . On heating **4** at $10^\circ\text{C min}^{-1}$ a small initial loss in mass of 3% occurred at *ca.* 100°C which may be attributable to some loss of solvent from the lattice. This was followed by a loss of 18% at *ca.* 130°C and a further steady loss of 46% up to 300°C . These two figures correspond with losses in relative molecular mass of 238 and 595 respectively giving a total of 833 compared with a value of 817 expected for $(2\text{PPh}_3 + \text{C}_7\text{F}_{11})$ or 848 for $(\text{PPh}_3 + 2\text{C}_7\text{F}_{11})$. Heating **5** at $10^\circ\text{C min}^{-1}$ resulted in a 74% loss in mass starting at *ca.* 130°C but primarily occurring in the region $250\text{--}300^\circ\text{C}$. This corresponds with a loss in relative molecular mass of 573 compared to a value of 586 expected for $2\text{C}_7\text{F}_{11}$. Similarly, heating **6** at $10^\circ\text{C min}^{-1}$ resulted in 74% loss in mass starting at *ca.* 100°C but primarily occurring in the region $260\text{--}360^\circ\text{C}$. This figure corresponds with a loss in molecular mass of 1188 compared with values of 1110 and 1141 expected for $(2\text{PPh}_3 + 2\text{C}_7\text{F}_{11})$ and $(\text{PPh}_3 + 3\text{C}_7\text{F}_{11})$ respectively. The TGA results thus provide evidence for the thermal loss of the fluorocarbon ligand in the case of **5**. There is TGA evidence for the thermal loss of both PPh_3 and the fluorocarbon ligand from **4** and **6**. In the case of **3** the results are also consistent with the loss of both types of ligand but are more ambiguous since loss of 2PPh_3 would also be in accord with the observed loss of 530–538 in molecular mass. However, the mass spectral data for **3** contain no ions corresponding to $(M - 2\text{PPh}_3)^+$ although an ion attributable to $[M - (\text{PPh}_3 + \text{C}_7\text{F}_{11}\text{Cl})]^+$ is present. Thus, in the mass spectral measurement at least, loss of both phosphines does not appear to be a major decomposition process. The mass spectral data suggest that, only in the case of **3** can detectable gas phase concentrations of the complex be obtained.

The chemical reactivity of the new compounds was also investigated. Air was bubbled through solutions of the compounds **3**, **4** and **6** in diethyl ether and of **5** in ethanol for a period of 5 h after which time the compounds were recovered and their IR spectra recorded. In each case the spectral data indicated that the

Table 2

Molecular dimensions in the metal coordination sphere

	Distance (Å)		Angle (deg)
Pt(1)–Cl(2)	2.333(7)	Cl(2)–Pt(1)–P(11)	171.4(3)
Pt(1)–P(11)	2.278(7)	Cl(2)–Pt(1)–P(41)	80.8(3)
Pt(1)–P(41)	2.405(10)	P(11)–Pt(1)–P(41)	92.3(3)
Pt(1)–C(71)	2.167(28)	Cl(2)–Pt(1)–C(71)	84.3(7)
		P(11)–Pt(1)–C(71)	103.4(7)
		P(41)–Pt(1)–C(71)	162.0(8)

compound could be recovered unchanged. A similar procedure was carried out using oxygen in place of air, and again no evidence for reaction was obtained except in the case of **5** where some decomposition occurred. Complexes **3**, **4** and **6** did not react with dilute HCl in EtOH. The hydrogenolysis reactions of the new compounds were also studied. When hydrogen was bubbled through solutions of **3** and **4** in diethyl ether or **5** in ethanol, black intractable solids were deposited over a period of 6 h. On the basis of IR evidence hydrogenolysis occurs to form $C_7F_{11}H$ which remains in solution. In the case of **6** a similar reaction did not occur and the compound could be recovered unchanged.

In conclusion we have found that air-stable complexes of the bulky perfluoronorbonyl ligand can be prepared with Pd, Pt and Re. Although these are not suitable in themselves for MOCVD applications, displacement of the fluoroalkyl ligand is possible either thermally or by hydrogenolysis.

Structural studies

Complex **3** afforded crystals of sufficient quality to allow an X-ray crystal structure determination. The crystals selected contained H_2O in the lattice which was not present after drying *in vacuo* in the material submitted for elemental analysis. The structure consists of discrete molecules of $PtCl(PPh_3)_2(C_7F_{11})$, and fractional atomic coordinates are presented in Table 1 with dimensions in the metal coordination sphere being given in Table 2. The metal atom is in a distorted square-planar four-coordinate environment, being bonded to a chlorine atom {Pt–Cl(2) 2.333(7) Å}, two triphenyl phosphine ligands {Pt–P(11) 2.278(7) Å, Pt(1)–P(41) 2.405(10) Å} and a carbon atom Pt–C(71) {2.167(28) Å}, of the undecafluorobicycloheptane ligand (Fig. 1). The metal geometry is considerably distorted from the ideal by the bulky ligands, the *cis* angles being C(71)–Pt–P(11) 103.4(7), Cl(2)–Pt–P(11) 171.4(3), C(71)–Pt–Cl(2) 84.3(7), and P–Pt–P 92.3(3)°. The biggest distortion is thus found in the C(71)–Pt–P(11) angle where the bulky undecafluorobicycloheptane is *cis* to the triphenylphosphine ligand. Least-squares planes calculations on the equatorial plane P(11), P(41), C(71) and Cl(2) show deviations of –0.12, 0.14, 0.14 and –0.15 Å respectively. The metal atom is –0.04 Å from this plane.

There are no exact comparisons for the Pt–C(71) distance of 2.167(28) Å as there have been no other structure determinations of Pt with this ligand or indeed with the non-fluorosubstituted bicycloheptane. However, a search of the Cambridge Crystallographic Database for structures of the type $Pt-C(-C)_3$, containing

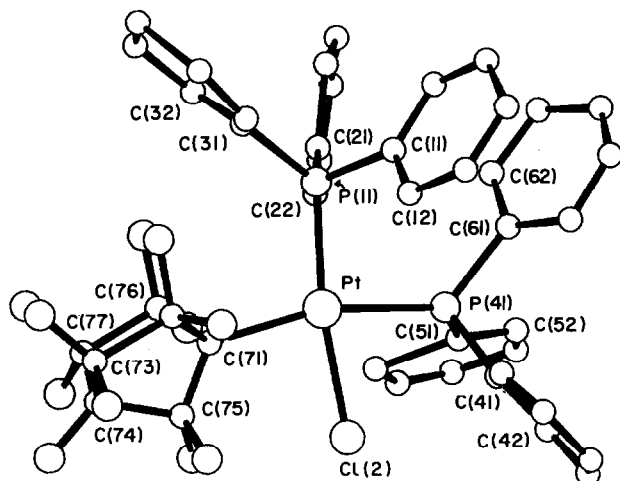


Fig. 1. A view of the structure of *cis*-PtCl(C₇F₁₁)(PPh₃)₂ showing the atom numbering. Hydrogen atoms have been omitted for clarity.

Pt bound to a tertiary carbon centre, gave five structures with Pt–C distances ranging between 2.09 and 2.17 Å.

The ligand maintains approximate C₅ symmetry either side of the equatorial plane. Thus the Cl(2)–Pt–C(71)–C(75) torsion angle is –7.7°. This relieves crowding in the equatorial plane as the two fluorine atoms on C(75) are thus above and below the plane and out of the way of Cl(2) (See Fig. 1). Because of this the C(71)–Pt–Cl(2) angle is reduced to 84.3(7)° so that there is more room in the equatorial plane for the bulky PPh₃ ligands. To compensate however the Pt–C(71)–C(75) angle is increased to 127.8(25)°, far larger than the other angles around C(71). The water molecule is hydrogen-bonded only to another symmetry-related water molecule across a centre of symmetry at a distance of 2.783 Å. There are no other intermolecular distances of note in the structure.

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