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Synthesis and coordination chemistry of fluorinated phosphonic acids

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ABSTRACT

Phosphonic acids $[(HO)_2P(O)C_2H_4C_nF_{2n+1}]$ ($n = 4, 6$) and $[(HO)_2P(O)C_6H_4\text{-}4\text{-}C_nF_{2n+1}]$ ($n = 0, 1, 6$) have been prepared in good yields. Deprotonation and reaction with *cis*-$[PtCl_2(PPh_3)_2]$ affords fluorinated platinum complexes which have been characterised by elemental analysis, mass spectrometry, IR and NMR spectroscopies. The structures of $[Pt\{O_2P(O)C_6H_4\text{-}4\text{-}F\}(PPh_3)_2]$, $[Pt\{O_2P(O)C_6H_4\text{-}4\text{-}CF_3\}(PPh_3)_2]$ and $[Pt\{O_2P(O)C_2H_4C_6F_{13}\}(PPh_3)_2]$ have been determined by single crystal X-ray diffraction.

1. Introduction

Since the introduction of *fluorous* chemistry by Horváth and Rábai in 1994 [1], there has been considerable interest in the synthesis and applications of species incorporating long perfluoroalkyl substituents [2–4]. We have been particularly interested in the electronic and steric implications of the perfluoroalkyl substituents on the donor properties of perfluoroalkylated ligands in coordination chemistry and the structural impact of the fluorous ponytails on the solid state structures of the coordination compounds [5–10]. We have also been investigating perfluoroalkylated α-zirconium phosphonates as alternative fluorous support materials that required the synthesis of fluorinated phosphonic acid intermediates. Here, we report the synthesis of these phosphonic acids, and some coordination chemistry, including the single crystal X-ray structures of three platinum(II) phosphonate coordination compounds.

2. Results and discussion

A number of fluorinated alkyl and aryl phosphonic acids have been prepared in moderate yields via a two-step sequence (Scheme 1) and fully characterised by elemental analysis, mass spectrometry and multinuclear NMR spectroscopies. For the alkyl series, the intermediate alkyldiethyl phosphonates were prepared from the reaction of fluorinated alkyl iodides with triethylphosphate, using the well established Michaelis-Arbuzov protocol [11,12], as reported recently by Gladysz as a step in the synthesis of some perfluoroalkylated primary phosphines [13]. For the aryl series, the Michaelis-Arbuzov protocol proved unsuccessful for the synthesis of the intermediate aryldiethyl phosphonates, but the palladium(0) mediated coupling of fluorinated aryl halides with diethylphosphonate [14] afforded the desired products in reasonable yields. The spectroscopic data for these new compounds are largely unremarkable, with ^{31}P NMR chemical shifts characteristic of the two classes of phosphorus(V) species and diastereotopic AB ^1H NMR multiplets for the methylene protons of the diethyl phosphonates. Both the fluorinated alkyl and aryl diethyl phosphonates were hydrolysed in high yields to the corresponding phosphonic acids with aqueous HCl.

The principle objective in the synthesis of these phosphonic acids was for the generation of perfluoroalkylated α-zirconium phosphonates as solid supports [15]. However the amorphous nature of these materials precluded conventional characterisation, and we sought an alternative approach to confirm the coordination properties and the influence of the fluorinated substituents in these phosphonic acids. Previously, Kemmitt et al. have structurally characterised the complex, $[Pt\{O_2P(O)Ph\}(PMePh_2)_2]$ as part of a wider series of platinum(II) species [16], and this offered a valuable range of coordination complexes for comparison purposes. Reaction of the fluorinated phosphonic acids with $[PtCl_2(PPh_3)_2]$ in the presence of silver oxide afforded the series

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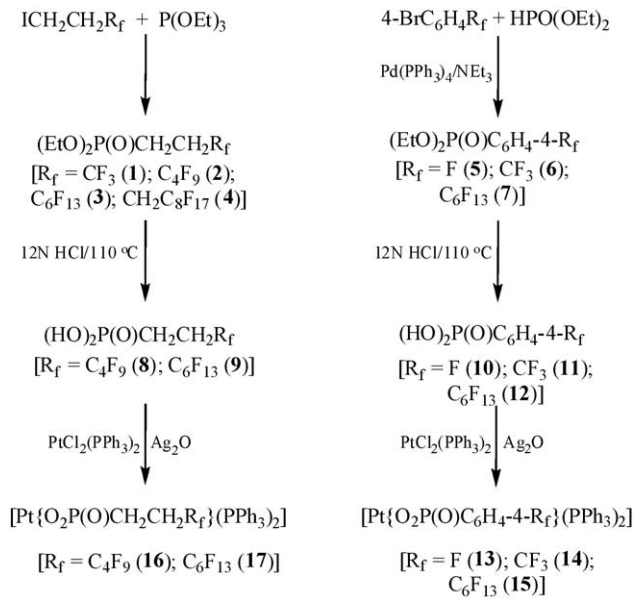

Scheme 1.

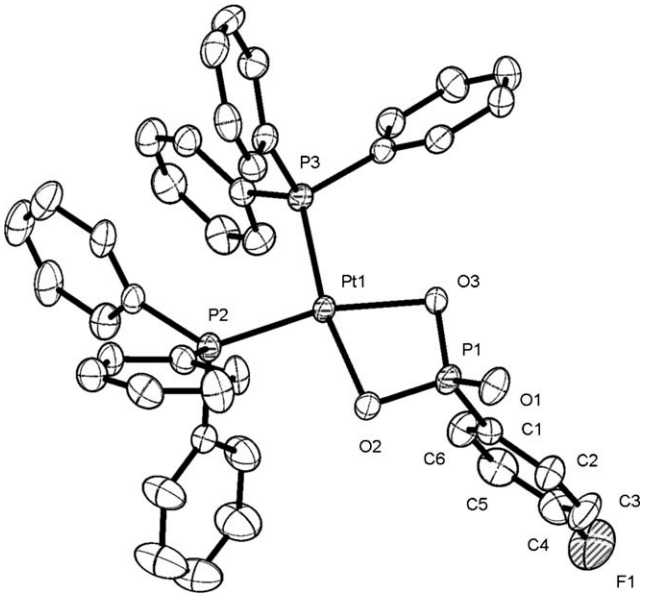

Fig. 1. Molecular structure of [Pt{$O_2P(O)(C_6H_4$-4-F)}$(PPh_3)_2$] (**13**) showing the atom labelling scheme with 50% probability ellipsoids. H-atoms are omitted for clarity.

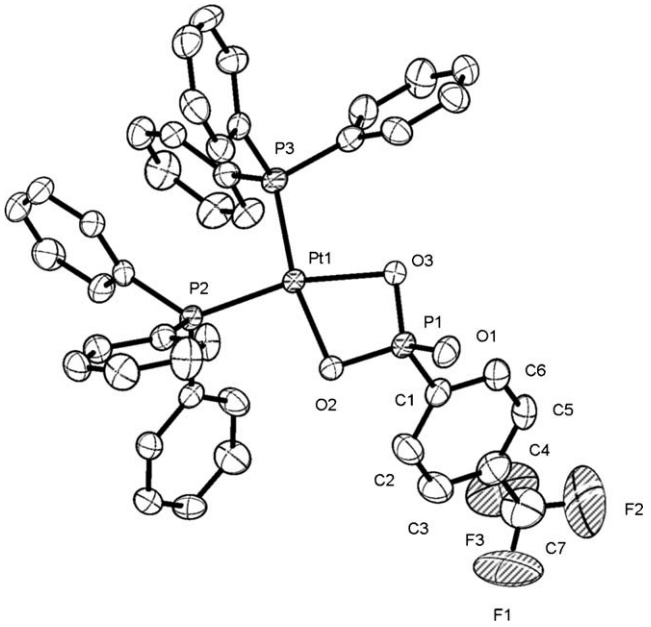

Fig. 2. Molecular structure of [Pt{$O_2P(O)(C_6H_4$-4-CF_3)}$(PPh_3)_2$] (**14**) showing the atom labelling scheme with 50% probability ellipsoids. H-atoms are omitted for clarity.

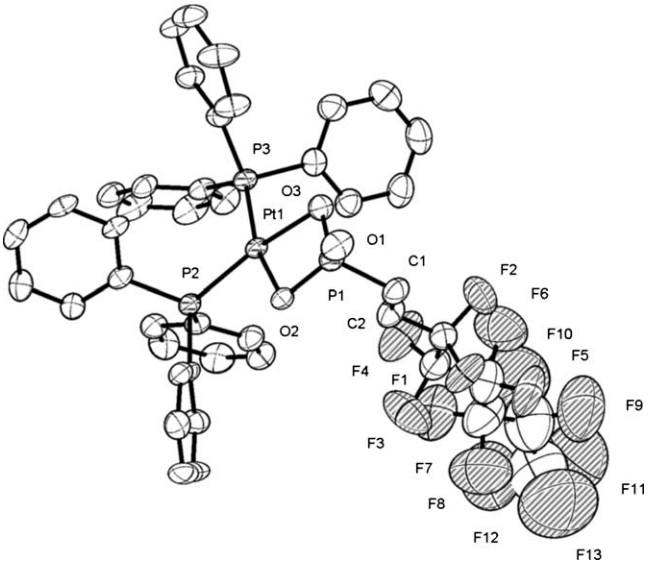

Fig. 3. Molecular structure of [Pt{$O_2P(O)(C_2H_4C_6F_{13}$)}$(PPh_3)_2$] (**17**) showing the atom labelling scheme with 50% probability ellipsoids. H-atoms are omitted for clarity.

of complexes [Pt{$O_2P(O)R$}$(PPh_3)_2$] in good yields (Scheme 1). ^{31}P NMR data demonstrate that the phosphonic acids readily coordinate to the metal centre and, although there are slight variations in the $^1J_{PtP}$ (PPh_3) and $^2J_{PtP}$ {$O_2P(O)R$} values (Table 1), the "O_2P" units effectively insulate the metal centre from the electronic influence of the fluorinated substituents.

Conclusive proof of the formation of these coordination complexes and the electronic insulation of the "O_2P" units arises

Table 1
A direct comparison between selected NMR data, bond distances (Å) and angles (°) for **13**, **14**, **17**, [Pt{$O_2P(O)Ph$}$(PPh_3)_2$] and [Pt{$O_2P(O)Ph$}$(PMePh_2)_2$].

Complex	$^1J_{PtP}$ (Hz)	$^2J_{PtP}$ (Hz)	Pt(1)–O(2) (Å)	Pt(1)–O(3) (Å)	Pt(1)–P(2) (Å)	Pt(1)–P(3) (Å)	O(2)–Pt(1)–O(3) (°)
[Pt{$O_2P(O)(Ph)$}$(PPh_3)_2$][a]	3872	127	2.061(6)	2.072(6)	2.223(3)	2.239(2)	71.4(2)
[Pt{$O_2P(O)(C_6H_4$-4-F)}$(PPh_3)_2$] (**13**)	3865	118	2.064(2)	2.075(3)	2.2191(10)	2.2385(11)	71.17(10)
[Pt{$O_2P(O)(C_6H_4$-4-CF_3)}$(PPh_3)_2$] (**14**)	3881	119	2.077(3)	2.085(3)	2.2230(11)	2.2373(11)	71.58(10)
[Pt{$O_2P(O)(C_2H_4C_6F_{13}$)}$(PPh_3)_2$] (**17**)	3867	118	2.077(5)	2.085(5)	2.217(2)	2.243(2)	71.8(2)
[Pt{$O_2P(O)(Ph)$}$(PMePh_2)_2$][b]	3755	122	2.070(4)	2.102(4)	2.222(1)	2.231(1)	71.2(2)

[a] J.A. Bennett and E.G. Hope, unpublished work.
[b] Data taken from Ref. [16].

Table 2
Crystal data.

	13	**14**	**17**
Formula	$C_{49}H_{50}Cl_2FO_3P_3Pt$	$C_{45.5}H_{38}Cl_6F_3O_3P_3Pt$	$C_{45}H_{36}Cl_2F_{13}O_3P_3Pt$
M	1064.79	1190.46	1230.64
Temperature	150(2) K	150(2) K	150(2) K
λ	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Triclinic	Triclinic
Space group	*P*(−)1	*P*(−)1	*P*(−)1
Unit cell dimensions	a = 10.750(3) Å b = 12.715(3) Å c = 18.134(4) Å α = 88.632(4)° β = 80.066(4)° γ = 69.989(3)°	a = 12.762(2) Å b = 13.973(3) Å c = 14.618(3) Å α = 75.523(3)° β = 89.498(3)° γ = 65.859(3)°	a = 10.742(2) Å b = 12.570(2) Å c = 19.076(4) Å α = 91.262(3)° β = 96.664(3)° γ = 111.477(3)°
U	2292.5(9) Å^3	2290.3(7) Å^3	2374.9(8) Å^3
Z	2	2	2
D_c	1.543 Mg m^{-3}	1.788 Mg m^{-3}	1.721 Mg m^{-3}
μ (Mo Kα)	3.327 mm^{-1}	3.571 mm^{-1}	3.258 mm^{-1}
F(0 0 0)	1068	1174	1208
Dimensions	0.23 × 0.16 × 0.09 mm^3	0.21 × 0.16 × 0.06 mm^3	0.21 × 0.17 × 0.07 mm^3
Data collection range	2.02–26.00°	1.76–25.00°	1.75–26.00°
Data collection range	$-13 \le h \le 13$ $-15 \le k \le 15$ $-22 \le l \le 22$	$-15 \le h \le 15$ $-17 \le k \le 16$ $-18 \le l \le 18$	$-13 \le h \le 13$ $-15 \le k \le 15$ $-23 \le l \le 23$
Reflections	17,788	16,683	18,537
Unique reflections	8864 [*R*(int) = 0.0349]	8882 [*R*(int) = 0.0345]	9192 [*R*(int) = 0.0388]
Completeness of data	98.3%	99.1%	98.3%
Absorption correction	Empirical	Empirical	Empirical
Max/min transmission factors	0.802/0.622	0.862/0.651	0.802/0.585
Data/restraints/parameters	8864/0/451	8882/0/478	9192/400/622
Goodness of fit on F^2	0.987	0.966	1.031
Final *R* indices	*R*1 = 0.0294	*R*1 = 0.0321	*R*1 = 0.0517
[$I > 2\sigma(I)$]	*wR*2 = 0.0659	*wR*2 = 0.0657	*wR*2 = 0.1319
R indices all data	*R*1 = 0.0351 *wR*2 = 0.0670	*R*1 = 0.0379 *wR*2 = 0.0668	*R*1 = 0.0645 *wR*2 = 0.1373
Largest diffraction peak and hole	1.573 eÅ^{-3}/−1.056 eÅ^{-3}	1.413 eÅ^{-3}/−0.886 eÅ^{-3}	2.259 eÅ^{-3}/−1.256 eÅ^{-3}

from the structural characterisation of three platinum(II) complexes (Tables 1 and 2; Figs. 1–3). For (**13**) and (**14**), disordered solvent molecules in the unit cells in these structural determinations have been removed using the squeeze option in Platon [17]. These structural characterisations confirm chelation of the phosphonic acids to the metal centre, and the Pt–O and Pt–P bond distances and the angles in the first coordination sphere are virtually identical for the fluoroalkyl, aryl and fluoroaryl complexes. The perfluorohexyl unit in (**17**) radiates linearly away from the phosphorus atom.

3. Conclusions

A series of fluorinated and fluoroalkylated diethylphosphonates and phosphonic acids have been readily prepared via literature procedures. The straightforward formation of a series of platinum(II) phosphonates demonstrates that the fluorine and fluoroalkylated substituents have no significant impact on the coordination chemistry of these species.

4. Experimental

4.1. General experimental procedures

Proton, ^{13}C, ^{19}F and ^{31}P NMR spectroscopic studies were carried out on a Bruker DPX300 spectrometer at 300.14, 75.47, 282.41 and 121.50 MHz. All chemical shifts are quoted in ppm using the high-frequency positive convention; ^1H and ^{13}C NMR spectra were referenced to external $SiMe_4$, ^{19}F NMR spectra to external $CFCl_3$ and ^{31}P NMR spectra to external H_3PO_4. Elemental analyses were performed by the Elemental Analysis Service at the London Metropolitan University. Mass spectra were recorded on a Kratos Concept 1H mass spectrometer.

4.1.1. 3,3,3-Trifluoropropyldiethylphosphonate (1) [18]

A mixture of 1,1,1-trifluoro-3-iodo-propane (5.00 g, 0.022 mol) and $P(OEt)_3$ (28 cm^3, 0.16 mol) was heated to 135 °C under nitrogen for 5 h. The crude reaction mixture was separated between Et_2O (50 cm^3) and H_2O (50 cm^3) and the aqueous layer was washed with Et_2O (2 × 50 cm^3) to ensure all product was extracted. The solvent was removed under vacuum and the resulting yellow liquid was Kugelröhr distilled (65 °C, 0.02 mmHg) to yield the product as a yellow oil (0.460 g, 9%). ^1H NMR ($CDCl_3$): δ 1.27 (6H, t, $^3J_{HH}$ = 7.3 Hz, CH_3), 1.88 (2H, m, CH_2), 2.29 (2H, m, CH_2), 4.04 (2H, ddq, $^2J_{HH}$ = 10.2 Hz, $^3J_{PH}$ = 8.2 Hz, $^3J_{HH}$ = 7.0 Hz, CH_A), 4.07 (2H, ddq, $^2J_{HH}$ = 10.2 Hz, $^3J_{PH}$ = 8.5 Hz, $^3J_{HH}$ = 7.0 Hz, CH_B). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 27.89 (s). $^{19}F\{^1H\}$ NMR ($CDCl_3$): δ −68.02 (s). ^{19}F NMR ($CDCl_3$): δ −68.02 (3F, t, $^3J_{FH}$ = 10.4 Hz). *m*/*z* (ES^+) 235 (MH^+, 100%).

4.1.2. 1H,1H,2H,2H-nonafluorohexyldiethylphosphonate (2)

1H,1H,2H,2H-nonafluorohexyldiethylphosphonate (**2**) was prepared similarly as a clear oil. Yield 57%. ^1H NMR ($CDCl_3$): δ 1.28 (6H, t, $^3J_{HH}$ = 7.0 Hz, CH_3), 1.91 (2H, m, CH_2), 2.31 (2H, m, CH_2), 4.04 (2H, ddq, $^2J_{HH}$ = 10.2 Hz, $^3J_{PH}$ = 8.2 Hz, $^3J_{HH}$ = 7.0 Hz, CH_A), 4.10 (2H, ddq, $^2J_{HH}$ = 10.2 Hz, $^3J_{PH}$ = 8.5 Hz, $^3J_{HH}$ = 7.0 Hz, CH_B). $^1H\{^{19}F\}$ NMR ($CDCl_3$): δ 1.28 (6H, t, $^3J_{HH}$ = 7.0 Hz, CH_3), 1.91 (2H, m, CH_2), 2.31 (2H, m, CH_2), 4.04 (2H, ddq, $^2J_{HH}$ = 10.2 Hz, $^3J_{PH}$ = 8.2 Hz, $^3J_{HH}$ = 7.0 Hz, CH_A), 4.10 (2H, ddq, $^2J_{HH}$ = 10.2 Hz, $^3J_{PH}$ = 8.5 Hz, $^3J_{HH}$ = 7.0 Hz, CH_B). $^1H\{^{31}P\}$ NMR ($CDCl_3$): δ 1.28 (6H, t,

$^3J_{HH}$ = 7.0 Hz, CH_3), 1.91 (2H, m, CH_2), 2.31 (2H, m, CH_2), 4.04 (2H, dq, $^2J_{HH}$ = 10.2 Hz, $^3J_{HH}$ = 7.0 Hz, CH_A), 4.10 (2H, dq, $^2J_{HH}$ = 10.2 Hz, $^3J_{HH}$ = 7.0 Hz, CH_B). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 16.26 (d, $^3J_{PC}$ = 6.0 Hz, CH_3), 17.05 (d, $^1J_{PC}$ = 147.2 Hz, CH_2), 25.03 (t, $^2J_{FC}$ = 22.7 Hz, CH_2), 62.11 (d, $^2J_{PC}$ = 6.0 Hz, CH_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 28.36 (s). $^{19}F\{^1H\}$ NMR ($CDCl_3$): δ −81.04 (3F, t, $^4J_{FF}$ = 9.5 Hz, CF_3), −115.53 (2F, m, α-CF_2), −124.28 (2F, m, CF_2), −126.04 (2F, m, CF_2). *m/z* (ES^+) 385 (MH^+, 100%).

4.1.3. 1H,1H,2H,2H-tridecafluorooctyldiethylphosphonate (3)

1H,1H,2H,2H-tridecafluorooctyldiethylphosphonate (**3**) was prepared similarly as a pale yellow oil. Yield 48%. Anal. Calcd. for $C_{12}H_{14}F_{13}O_3P$: C, 29.8; H, 2.9. Found: C, 29.8; H, 2.7. ^1H NMR ($CDCl_3$): δ 1.29 (6H, t, $^3J_{HH}$ = 7.0 Hz, CH_3), 1.92 (2H, m, CH_2), 2.30 (2H, m, CH_2), 4.07 (2H, ddq, $^2J_{HH}$ = 10.2 Hz, $^3J_{PH}$ = 7.9 Hz, $^3J_{HH}$ = 7.0 Hz, CH_A), 4.08 (2H, ddq, $^2J_{HH}$ = 10.2 Hz, $^3J_{PH}$ = 8.5 Hz, $^3J_{HH}$ = 7.0 Hz, CH_B). $^{13}C\{^1H\}$ ($CDCl_3$): δ 16.26 (d, $^3J_{PC}$ = 6.0 Hz, CH_3), 18.71 (d, $^1J_{PC}$ = 143.6 Hz, CH_2), 25.14 (m, CH_2), 62.19 (d, $^2J_{PC}$ = 6.0 Hz, CH_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 28.38 (s). $^{19}F\{^1H\}$ NMR ($CDCl_3$): δ −80.80 (3F, t, $^4J_{FF}$ = 9.5 Hz, CF_3), −115.31 (2F, m, α-CF_2), −121.90 (2F, m, CF_2), −122.86 (2F, m, CF_2), −123.33 (2F, m, CF_2), −126.12 (2F, m, CF_2). *m/z* (ES^+) 485 (MH^+, 40%).

4.1.4. 1H,1H,2H,2H,3H,3H-heptadecafluoroundecyldiethylphosphonate (4)

1H,1H,2H,2H,3H,3H-heptadecafluoroundecyldiethylphosphonate (**4**) was prepared similarly as a pale yellow oil. Yield 62%. Anal. Calcd. for $C_{15}H_{16}F_{17}O_3P$: C, 30.1; H, 2.7. Found: C, 30.0; H, 2.7. ^1H NMR ($CDCl_3$): δ 1.26 (6H, t, $^3J_{HH}$ = 7.0 Hz, CH_3), 1.75 (2H, m, CH_2), 1.88 (2H, m, CH_2), 2.15 (2H, m, CH_2), 3.96–4.14 (4H, m, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 14.04 (m, CH_2), 16.26 (d, $^3J_{CP}$ = 6.0 Hz, CH_3), 25.00 (d, $^1J_{PC}$ = 143.6 Hz, CH_2), 31.04 (m, CH_2), 62.00 (d, $^2J_{PC}$ = 7.2 Hz, CH_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 30.11 (s). $^{19}F\{^1H\}$ NMR ($CDCl_3$): δ −80.81 (3F, t, $^4J_{FF}$ = 10.0 Hz, CF_3), −114.50 (2F, m, α-CF_2), −121.71 (2F, m, CF_2), −121.92 (4F, m, CF_2), −122.70 (2F, s, CF_2), −123.55 (2F, m, CF_2), −126.11 (2F, m, CF_2). *m/z* (ES^+) 599 (MH^+, 100%).

4.1.5. 4-Fluorophenyldiethylphosphonate (5)

A solution of $Pd(PPh_3)_4$ (2.65 g, 2.3 mmol) and F-C_6H_4-Br (8.00 g, 0.046 mol) in toluene (20 cm^3) was added under N_2 to a mixture of $HPO(OEt)_2$ (6.4 cm^3, 0.050 mol) and NEt_3 (7.0 cm^3, 0.050 mol), and the mixture was stirred at 90 °C for 3.5 h. After cooling, Et_2O (50 cm^3) was added, the solution was filtered, the solvent was removed *in vacuo* and the crude product was distilled in a Kugelröhr to yield the product as a clear oil. Yield 69%. Anal. Calcd. for $C_{10}H_{14}FO_3P$: C, 51.7; H, 6.0. Found: C, 51.7; H, 6.2. ^1H NMR ($CDCl_3$): δ 1.25 (6H, t, $^3J_{HH}$ = 7.0 Hz, CH_3), 4.00 (2H, ddq, $^2J_{HH}$ = 10.0 Hz, $^3J_{PH}$ = 7.6 Hz, $^3J_{HH}$ = 7.0 Hz, CH_A), 4.06 (2H, ddq, $^2J_{HH}$ = 10.0 Hz, $^3J_{PH}$ = 7.9 Hz, $^3J_{HH}$ = 7.0 Hz, CH_B), 7.07 (2H, ddd, $^3J_{PH}$ = 12.8 Hz, $^4J_{FH}$ = 8.8 Hz, $^3J_{HH}$ = 8.8 Hz, 2-CH), 7.75 (2H, ddd, $^3J_{HH}$ = 8.8 Hz, $^3J_{FH}$ = 5.5 Hz, $^4J_{PH}$ = 3.2 Hz, 3-CH). $^1H\{^{31}P\}$ NMR ($CDCl_3$): δ 1.23 (6H, t, $^3J_{HH}$ = 7.0 Hz, CH_3), 4.00 (2H, dq, $^2J_{HH}$ = 10.0 Hz, $^3J_{HH}$ = 7.0 Hz, CH_A), 4.06 (2H, dq, $^2J_{HH}$ = 10.0 Hz, $^3J_{HH}$ = 7.0 Hz, CH_B), 7.07 (2H, dd, $^4J_{FH}$ = 8.8 Hz, $^3J_{HH}$ = 8.8 Hz, 2-CH), 7.75 (2H, dd, $^3J_{FH}$ = 5.5 Hz, $^3J_{HH}$ = 8.8 Hz, 3-CH). $^1H\{^{19}F\}$ NMR ($CDCl_3$): δ 1.25 (6H, t, $^3J_{HH}$ = 7.0 Hz, CH_3), 4.00 (2H, ddq, $^2J_{HH}$ = 10.0 Hz, $^3J_{PH}$ = 7.6 Hz, $^3J_{HH}$ = 7.0 Hz, CH_A), 4.06 (2H, ddq, $^2J_{HH}$ = 10.0 Hz, $^3J_{PH}$ = 7.9 Hz, $^3J_{HH}$ = 7.0 Hz, CH_B), 7.07 (2H, dd, $^3J_{PH}$ = 12.8 Hz, $^3J_{HH}$ = 8.8 Hz, 2-CH), 7.75 (2H, dd, $^3J_{HH}$ = 8.8 Hz, $^4J_{PH}$ = 3.5 Hz, 3-CH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 16.23 (d, $^3J_{PC}$ = 6.0 Hz, CH_3), 62.17 (d, $^2J_{PC}$ = 6.0 Hz, CH_2), 115.79 (dd, $^3J_{PC}$ = 15.6 Hz, $^2J_{FC}$ = 21.5 Hz, 3-CH), 124.4 (d, $^1J_{PC}$ = 193.2 Hz, 1-C), 134.33 (dd, $^2J_{PC}$ = 10.8 Hz, $^3J_{FC}$ = 8.4 Hz, 2-CH), 165.53 (d, $^1J_{FC}$ = 252.8 Hz, 4-C). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 18.36 (s). $^{19}F\{^1H\}$ NMR ($CDCl_3$): δ −106.04 (s). *m/z* (ES^+) 232 (M^+, 80%).

4.1.6. 4-Trifluoromethylphenyldiethylphosphonate (6)

4-Trifluoromethylphenyldiethylphosphonate (**6**) [19] was prepared similarly. Yield 69%. Anal. Calcd. for $C_{11}H_{14}F_3O_3P$: C, 46.8; H, 5.0. Found: C, 46.7; H, 5.0. ^1H NMR ($CDCl_3$): δ 1.33 (6H, t, $^3J_{HH}$ = 7.3 Hz, CH_3), 4.03 (2H, ddq, $^2J_{HH}$ = 10.2 Hz, $^3J_{PH}$ = 7.9 Hz, $^3J_{HH}$ = 7.0 Hz, CH_A), 4.12 (2H, ddq, $^2J_{HH}$ = 10.2 Hz, $^3J_{PH}$ = 8.2 Hz, $^3J_{HH}$ = 7.0 Hz, CH_B), 7.65 (2H, dd, $^3J_{HH}$ = 8.2 Hz, $^4J_{PH}$ = 3.5 Hz, 3-CH), 7.88 (2H, dd, $^3J_{PH}$ = 12.9 Hz, $^3J_{HH}$ = 8.5 Hz, 2-CH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 16.16 (d, $^3J_{PC}$ = 6.0 Hz, CH_3), 62.44 (d, $^2J_{CP}$ = 6.0 Hz, CH_2), 123.45 (q, $^1J_{FC}$ = 272.4 Hz, CF_3), 125.22 (dq, $^3J_{PC}$ = 14.4 Hz, $^3J_{FC}$ = 3.6 Hz, 3-CH), 132.15 (d, $^2J_{PC}$ = 10.8 Hz, 2-CH), 132.76 (d, $^1J_{PC}$ = 187.9 Hz, 1-C), 133.95 (qd, $^2J_{FC}$ = 32.3 Hz, $^4J_{PC}$ = 3.6 Hz, 4-C). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 16.34 (s). $^{19}F\{^1H\}$ NMR ($CDCl_3$): δ −63.31 (s). *m/z* (ES^+) 282 (M^+, 30%).

4.1.7. 4-Tridecafluorohexylphenyldiethylphosphonate (7)

4-Tridecafluorohexylphenyldiethylphosphonate (**7**) was prepared similarly. Yield 85%. Anal. Calcd. for $C_{16}H_{14}F_{13}O_3P$: C, 36.1; H, 2.6. Found: C, 35.9; H, 2.5. ^1H NMR ($CDCl_3$): δ 1.27 (6H, t, $^3J_{HH}$ = 7.0 Hz, CH_3), 4.04 (2H, ddq, $^2J_{HH}$ = 10.2 Hz, $^3J_{PH}$ = 7.9 Hz, $^3J_{HH}$ = 7.0 Hz, CH_A), 4.14 (2H, ddq, $^2J_{HH}$ = 10.2 Hz, $^3J_{PH}$ = 7.9 Hz, $^3J_{HH}$ = 7.0 Hz, CH_B), 7.62 (2H, dd, $^3J_{HH}$ = 8.2 Hz, $^4J_{PH}$ = 3.5 Hz, 3-CH), 7.89 (2H, dd, $^3J_{HH}$ = 8.2 Hz, $^3J_{PH}$ = 13.2 Hz, 2-CH). $^1H\{^{31}P\}$ NMR ($CDCl_3$): δ 1.27 (6H, t, $^3J_{HH}$ = 7.0 Hz, CH_3), 4.04 (2H, dq, $^2J_{HH}$ = 10.2 Hz, $^3J_{HH}$ = 7.0 Hz, CH_A), 4.14 (2H, dq, $^2J_{HH}$ = 10.2 Hz, $^3J_{HH}$ = 7.0 Hz, CH_B), 7.62 (2H, d, $^3J_{HH}$ = 8.2 Hz, 3-CH), 7.89 (2H, d, $^3J_{HH}$ = 8.2 Hz, 2-CH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 16.14 (d, $^3J_{PC}$ = 6.0 Hz, CH_3), 62.47 (d, $^2J_{PC}$ = 6.0 Hz, CH_2) 126.86 (dt, $^3J_{PC}$ = 14.4 Hz, $^3J_{FC}$ = 6.0 Hz, 3-CH), 131.93 (d, $^2J_{PC}$ = 10.8 Hz, 2-CH), 132.60 (td, $^2J_{FC}$ = 23.9 Hz, $^4J_{PC}$ = 3.6 Hz, 4-C), 133.23 (d, $^1J_{PC}$ = 167.6 Hz, 1-C). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 16.31 (s); $^{19}F\{^1H\}$ NMR ($CDCl_3$): δ −80.82 (3F, t, $^4J_{FF}$ = 9.5 Hz, CF_3), −111.29 (2F, t, $^4J_{FF}$ = 14.2 Hz, α-CF_2), −121.42 (2F, m, CF_2), −121.69 (2F, m, CF_2), −122.79 (2F, m, CF_2), −123.33 (2F, m, CF_2). *m/z* (ES^+) 533 (MH^+, 100%).

4.1.8. 1H,1H,2H,2H-nonafluorohexylphosphonic acid (8)

F_9C_4-C_2H_4-$PO(OEt)_2$ (**2**) (3.17 g, 8.2 mmol) was refluxed (110 °C) with vigorous stirring for 48 h in H_2O (20 cm^3) with 12 M HCl (20 cm^3). The solvent was removed *in vacuo*, the white solid was washed with chloroform and dried under vacuum to yield the product as white powder (1.80 g, 67%). Anal. Calcd. for $C_6H_6F_9O_3P$: C, 22.0; H, 1.8. Found: C, 22.1; H, 1.7. ^1H NMR (C_3D_6O): δ 2.05 (2H, m, CH_2), 2.51 (2H, m, CH_2), 10.45 (2H, s, OH). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 25.77 (s). $^{31}P\{^1H\}$ NMR (C_3D_6O): δ 27.56 (s). $^{19}F\{^1H\}$ NMR (C_3D_6O): δ −81.01 (3F, t, $^4J_{FF}$ = 9.5 Hz, CF_3), −115.90 (2F, m, α-CF_2), −124.91 (2F, m, CF_2), −126.84 (2F, m, CF_2); ^{13}C $\{^1H\}$ NMR (C_3D_6O): δ 18.85 (d, $^1J_{PC}$ = 146.0 Hz, CH_2), 25.93 (m, CH_2). *m/z* (ES^-) 327 ($[M-H]^-$, 100%).

4.1.9. 1H,1H,2H,2H-tridecafluorooctylphosphonic acid (9)

1H,1H,2H,2H-tridecafluorooctylphosphonic acid (**9**) was prepared similarly. Yield 91%. Anal. Calcd. for $C_8H_6F_{13}O_3P$: C, 22.4; H, 1.4. Found: C, 22.6; H, 1.4. ^1H NMR (C_3D_6O): δ 1.92 (2H, m, CH_2), 2.36 (2H, m, CH_2), 8.59 (2H, s, OH). $^{31}P\{^1H\}$ NMR (C_3D_6O): δ 27.81 (s). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 32.93 (s). $^{19}F\{^1H\}$ NMR (C_3D_6O): δ −81.82 (3F, t, $^4J_{FF}$ = 10.4 Hz, CF_3), −115.66 (2F, m, α-CF_2), −122.52 (2F, m, CF_2), −123.53 (2F, m, CF_2), −123.98 (2F, m, CF_2), −126.80 (2F, m, CF_2). $^{13}C\{^1H\}$ NMR (C_3D_6O): δ 18.91 (d, $^1J_{PC}$ = 149.6 Hz, CH_2), 25.95 (m, CH_2). *m/z* (ES^-) 427 ($[M-H]^-$, 100%).

4.1.10. 4-Fluorophenylphosphonic acid (10)

4-Fluorophenylphosphonic acid (**10**) [19] was prepared similarly. Yield 89%. Anal. Calcd. for $C_6H_6FO_3P$: C, 40.9; H, 3.4. Found: C, 40.8; H, 3.3. ^1H NMR (C_3D_6O): δ 7.25 (2H, ddd, $^3J_{FH}$ = 8.5 Hz, $^3J_{HH}$ = 8.5 Hz, $^4J_{PH}$ = 2.9 Hz, 3-CH), 7.85 (2H, ddd, $^3J_{PH}$ = 13.1 Hz, $^3J_{HH}$ = 8.7 Hz, $^4J_{FH}$ = 5.8 Hz, 2-CH), 10.17 (2H, s, OH). $^{13}C\{^1H\}$ NMR (C_3D_6O): δ

116.20 (dd, $^{2}J_{FC}$ = 21.4 Hz, $^{3}J_{PC}$ = 15.2 Hz, 3-CH), 134.45 (dd, $^{2}J_{PC}$ = 12.0 Hz, $^{3}J_{FC}$ = 8.2 Hz, 2-CH). $^{31}P\{^{1}H\}$ NMR (C_3D_6O): δ 17.08 (s). $^{31}P\{^{1}H\}$ NMR (D_2O): δ 15.14 (s). $^{19}F\{^{1}H\}$ NMR (C_3D_6O): δ −109.22 (s). *m/z* (ES^+) 177 (MH^+, 30%); *m/z* (ES^-) 175 ($[M-H]^-$, 100%).

4.1.11. 4-Trifluoromethylphenylphosphonic acid (11)

4-Trifluoromethylphenylphosphonic acid (**11**) [19] was prepared similarly. Yield 67%. Anal. Calcd. for $C_7H_6F_3O_3P$: C, 37.2; H, 2.7. Found: C, 37.0; H, 2.6. ^{1}H NMR (C_3D_6O): δ 7.13 (2H, s, OH), 7.75–7.91 (m, 2H), 8.01 (m, 2H); $^{31}P\{^{1}H\}$ NMR (C_3D_6O): δ 15.37 (s); $^{31}P\{^{1}H\}$ NMR (C_6D_6): δ 14.06 (s). $^{19}F\{^{1}H\}$ NMR (C_3D_6O): δ −63.73 (s, CF_3). $^{13}C\{^{1}H\}$ NMR (C_3D_6O): δ 123.92 (q, $^{1}J_{FC}$ = 272.3 Hz, CF_3), 126.05 (d, $^{3}J_{PC}$ = 10.8 Hz, 3-CH), 132.46 (d, $^{2}J_{PC}$ = 9.6 Hz, 2-CH), 132.80 (q, $^{2}J_{FC}$ = 32.3 Hz, 4-C), 137.23 (d, $^{1}J_{PC}$ = 184.1 Hz, 1-C). *m/z* (ES^-) 225 ($[M-H]^-$, 100%).

4.1.12. 4-Tridecafluorohexylphenylphosphonic acid (12)

4-Tridecafluorohexylphenylphosphonic acid (**12**) was prepared similarly. Yield 97%. Anal. Calcd. for $C_{12}H_6F_{13}O_3P$: C, 30.3; H, 1.3. Found: C, 30.2; H, 1.2. ^{1}H NMR (C_3D_6O): δ 7.72 (2H, dd, $^{3}J_{HH}$ = 8.5 Hz, $^{4}J_{PH}$ = 2.9 Hz, 3-CH), 7.94 (2H, dd, $^{3}J_{PH}$ = 13.2, $^{3}J_{HH}$ = 8.5 Hz, 2-CH), 8.01 (2H, s, OH). $^{31}P\{^{1}H\}$ NMR (C_3D_6O): δ 15.20 (s). $^{31}P\{^{1}H\}$ NMR (C_6D_6): δ 19.59 (s). $^{19}F\{^{1}H\}$ NMR (C_3D_6O): δ −81.70 (3F, t, $^{4}J_{FF}$ = 10.4 Hz, CF_3), −111.41 (2F, t, $^{4}J_{FF}$ = 14.2 Hz, α-CF_2), −122.00 (2F, m, CF_2), −122.20 (2F, m, CF_2), −123.47 (2F, m, CF_2), −126.83 (2F, m, CF_2). $^{13}C\{^{1}H\}$ NMR (C_3D_6O): δ 127.71 (dt, $^{3}J_{PC}$ = 14.6 Hz, $^{3}J_{FC}$ = 6.1 Hz, 3-CH), 132 .33 (d, $^{2}J_{PC}$ = 10.8 Hz, 2-CH). *m/z* (ES^-) 475 (MH^-, 100%).

4.1.13. Platinum bis(triphenylphosphine)(4-fluorophenylphosphonate) [Pt{$O_2P(O)C_6H_4$-4-F}(PPh_3)$_2$] (13)

F-C_6H_4-$PO(OH)_2$ (0.074 g, 41.8 mmol) and silver(I) oxide (0.580 g, 251 mmol) were added in succession to a stirred solution of [$PtCl_2(PPh_3)_2$] (0.330 g, 41.8 mmol) in dichloromethane (40 cm^3) and the mixture was refluxed for 4 h. The cooled reaction mixture was filtered and the filtrate was evaporated to dryness under reduced pressure to yield the product as a white powder, which was recrystallised from dichloromethane-light petroleum and dried *in vacuo* (0.343 g, 92%). Anal. Calcd. for $C_{42}H_{34}FO_3P_3Pt$: C, 56.4; H, 3.8. Found: C, 55.3; H, 3.6. ^{1}H NMR (CD_2Cl_2): δ 6.93–7.02 (2H, m, 2-CH), 7.10–7.37 (30H, m, Ph), 7.66–7.76 (2H, m, 3-CH). $^{19}F\{^{1}H\}$ NMR (CD_2Cl_2): δ −112.9 (s). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2): δ 7.3 (d, $^{1}J_{PtP}$ = 3865, $^{3}J_{PP}$ = 7 Hz, PPh_3), 37.3 (t, $^{2}J_{PtP}$ = 118 Hz, $^{3}J_{PP}$ = 7 Hz, PO_3). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2): δ 114.71 (dd, $^{2}J_{FC}$ = 20.6 Hz, $^{3}J_{PC}$ = 14.4 Hz, 3-CH), 127.96 (m, C), 128.76 (m, CH), 131.84 (m, CH), 133.28 (dd, $^{2}J_{PC}$ = 10.5 Hz, $^{3}J_{FC}$ = 7.8 Hz, 2-CH), 134.68 (m, CH), 136.58 (dd, $^{1}J_{PC}$ = 165.2 Hz, $^{4}J_{FC}$ = 3.6 Hz, 1-C). *m/z* (FAB) 894 (MH^+, 100%).

4.1.14. Platinum bis(triphenylphosphine)(4-trifluoromethylphenylphosphonate) [Pt{$O_2P(O)C_6H_4$-4-CF_3}(PPh_3)$_2$] (14)

Platinum bis(triphenylphosphine)(4-trifluoromethylphenylphosphonate) [Pt{$O_2P(O)C_6H_4$-4-CF_3}(PPh_3)$_2$] (**14**) was prepared similarly as a white powder. Yield 91%. Anal. Calcd. for $C_{43}H_{34}F_3O_3P_3Pt$: C, 54.7; H, 3.6. Found: C, 54.6; H, 3.8. ^{1}H NMR (CD_2Cl_2): δ 7.09–7.36 (30H, m, Ph), 7.54–7.85 (4H, m, Ar). $^{19}F\{^{1}H\}$ NMR (CD_2Cl_2): δ −62.8 (s). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2): δ 7.2 (s, $^{1}J_{PtP}$ = 3881 Hz, PPh_3), 32.7 (s, $^{2}J_{PtP}$ = 119 Hz, PO_3). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2): δ 123.45 (q, $^{1}J_{FC}$ = 272.4 Hz, CF_3), 124.32 (dq, $^{3}J_{PC}$ = 13.2 Hz, $^{3}J_{FC}$ = 3.6 Hz, 3-CH), 127.44 (m, C), 128.41 (m, CH), 130.54 (qd, $^{2}J_{FC}$ = 31.6 Hz, $^{4}J_{PC}$ = 3.0 Hz, 4-C), 130.76 (d, $^{2}J_{PC}$ = 9.4 Hz, 2-CH), 131.48 (m, CH), 134.68 (m, CH), 144.90 (d, $^{1}J_{PC}$ = 159.3 Hz, 1-C). *m/z* (FAB) 944 (MH^+, 100%).

4.1.15. Platinum bis(triphenylphosphine)(4-tridecafluorohexylphenylphosphonate) [Pt{$O_2P(O)C_6H_4$-4-C_6F_{13}}(PPh_3)$_2$] (15)

Platinum bis(triphenylphosphine)(4-tridecafluorohexylphenylphosphonate) [Pt{$O_2P(O)C_6H_4$-4-C_6F_{13}}(PPh_3)$_2$] (**15**) was prepared similarly as a white powder. Yield 85%. Anal. Calcd. for $C_{48}H_{34}F_{13}O_3P_3Pt$: C, 48.3; H, 2.8. Found: C, 48.2; H, 2.7. ^{1}H NMR (CD_2Cl_2): δ 7.09–7.36 (30H, m, Ph), 7.54–7.85 (4H, m, Ar). $^{19}F\{^{1}H\}$ NMR (CD_2Cl_2): δ −81.06 (3F, t, $^{4}J_{FF}$ = 10.4 Hz, CF_3), −110.77 (2F, t, $^{4}J_{FF}$ = 14.2 Hz, α-CF_2), −121.50 (2F, m, CF_2), −122.01 (2F, m, CF_2), −122.91 (2F, m, CF_2), −126.33 (2F, m, CF_2). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2): δ 7.3 (s, $^{1}J_{PtP}$ = 3886 Hz, PPh_3), 37.3 (t, $^{2}J_{PtP}$ = 117 Hz, PO_3). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2): δ 126.40 (m, CH), 127.78 (m, C), 128.81 (m, CH), 131.26 (d, $^{2}J_{PC}$ = 9.4 Hz, 2-CH), 131.89 (m, CH), 132.25 (m, C), 134.67 (m, CH), 144.90 (d, $^{1}J_{CP}$ = 160.1 Hz, 1-C). *m/z* (FAB) 1194 (MH^+, 100%).

4.1.16. Platinum bis(triphenylphosphine)(1H,1H,2H,2H-nonafluorohexylphosphonate) [Pt{$O_2P(O)C_2H_4C_4F_9$}(PPh_3)$_2$] (16)

Platinum bis(triphenylphosphine)(1H,1H,2H,2H-nonafluorohexylphosphonate) [Pt{$O_2P(O)C_2H_4C_4F_9$}(PPh_3)$_2$] (**16**) was prepared similarly as a white powder. Yield 75%. Anal. Calcd. for $C_{42}H_{34}F_9O_3P_3Pt$: C, 48.2; H, 3.3. Found: C, 48.2; H, 3.4. ^{1}H NMR (CD_2Cl_2): δ 1.67 (2H, m, CH_2), 2.26 (2H, m, CH_2), 7.13–7.37 (30H, m, Ph). $^{19}F\{^{1}H\}$ NMR ($CDCl_3$): δ −81.29 (3F, t, $^{4}J_{FF}$ = 9.5 Hz, CF_3), −115.52 (2F, m, α-CF_2), −124.42 (2F, m, CF_2), −126.11 (2F, m, CF_2). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2): δ 7.0 (s, $^{1}J_{PtP}$ = 3856 Hz, PPh_3), 45.12 (s, $^{2}J_{PtP}$ = 110 Hz, PO_3). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2): δ 22.14 (d, $^{1}J_{PC}$ = 199.3 Hz, CH_2), 27.29 (d, $^{2}J_{PC}$ = 22.1 Hz, CH_2), 127.50 (m, C), 128.41 (m, CH), 131.45 (m, CH), 134.20 (m, CH). *m/z* (FAB) 1046 (MH^+, 100%).

4.1.17. Platinum bis(triphenylphosphine)(1H,1H,2H,2H-tridecafluorooctylphosphonate) [Pt{$O_2P(O)C_2H_4C_6F_{13}$}(PPh_3)$_2$] (17)

Platinum bis(triphenylphosphine)(1H,1H,2H,2H-tridecafluorooctylphosphonate) [Pt{$O_2P(O)C_2H_4C_6F_{13}$}(PPh_3)$_2$] (**17**) was prepared similarly as a white powder. Yield 73%. ^{1}H NMR ($CDCl_3$): δ 1.76 (2H, m, CH_2), 2.30 (2H, m, CH_2), 7.07–7.45 (30H, m, Ph). $^{19}F\{^{1}H\}$ NMR ($CDCl_3$): δ −80.71 (3F, t, $^{4}J_{FF}$ = 9.5 Hz, CF_3), −115.11 (2F, m, α-CF_2), −121.77 (2F, m, CF_2), −122.78 (2F, m, CF_2), −123.40 (2F, m, CF_2), −126.04 (2F, m, CF_2). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 6.8 (s, $^{1}J_{PtP}$ = 3867 Hz, PPh_3), 47.3 (t, $^{2}J_{PtP}$ = 118 Hz, PO_3). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2): δ 21.59 (d, $^{1}J_{PC}$ = 121.5 Hz, CH_2), 27.21 (d, $^{2}J_{PC}$ = 23.6 Hz, CH_2), 127.85 (m, C), 128.78 (m, CH), 131.82 (m, CH), 134.58 (m, CH). *m/z* (FAB) 1145 [M^+] 70%.

4.2. Crystal structures of [Pt{$O_2P(O)C_6H_4$-4-F}(PPh_3)$_2$], [Pt{$O_2P(O)C_6H_4$-4-CF_3}(PPh_3)$_2$] and [Pt{$O_2P(O)C_2H_4C_6F_{13}$}(PPh_3)$_2$]

Crystals of **13**, **14** and **17** were grown by slow evaporation from DCM/petroleum ether solutions. Full details of the data collection and refinement are given in Table 2. Data were collected on a Bruker APEX 2000 CCD diffractometer using graphite-monochromated Mo Kα radiation.

4.3. Structure solution and refinement

Structure solution by Patterson methods and structure refinement on F2 employed SHELXTL Version 6.10 (SHELXTL, an integrated system for solving, refining and displaying crystal structures) [20]. The C–H hydrogen atoms were included in calculated positions (C–H = 0.96 Å) with isotropic displacement parameters set to 1.2 Ueq of the bonded atom. All non-hydrogen atoms were refined with anisotropic displacement parameters. The data were corrected for Lorentz and polarisation effects and empirical absorption corrections applied. For (**13**) and (**14**) the SQUEEZE option in PLATON [17] was used to remove disordered

solvent molecules. For (**17**) the H atoms of the disordered CH_2Cl_2 were not included in the model but were included in all formulae. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no.'s CCDC 680044-680046. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

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