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Synthesis and coordination chemistry of perfluoroalkyl-derivatised triarylphosphites

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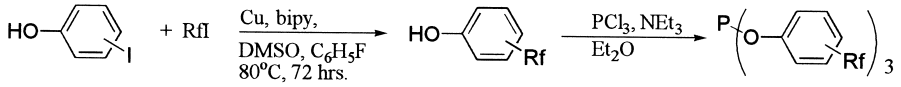
Abstract—A series of *ortho*-, *meta*- and *para*-perfluoroalkyl-substituted triaryl phosphites have been prepared and their coordination chemistry investigated. Spectroscopic and structural data for the metal complexes indicate that, even with the additional oxygen spacer unit, complete electronic insulation of the phosphorus(III) centres is not achieved.

One of the major foci in the development of catalysis under fluorous biphase conditions has been the electronic insulation of the ligand donor/metal centre from the powerful electron withdrawing influence of the perfluoroalkyl substituents. In Horváth and Rábai's seminal paper[1] this was attempted using C_2H_4 units but, subsequently, theoretical calculations[2] and experimental studies on perfluoroalkyl-phosphines[3] and amines[4] have shown that complete electronic insulation is not achieved even with a pentyl, C_5H_{10}, spacer group. We[5–11] and others[12–17] have focussed our attentions on aryl electronic insulating units. The direct attachment of one, two or three perfluoroalkyl groups in the *ortho*-, *meta*- or *para*-positions of triarylphosphine ligands causes stepwise reductions in the σ-donor strength of these ligands indicating that the aryl groups are also not perfect electronic insulators. Indeed, although $C_6H_4OCH_2$ and $C_6H_4C_2H_4$ spacer units in $P(C_6H_4\text{–}4\text{-}OCH_2C_7F_{15})_3$[10] and $P(C_6H_4\text{–}4\text{-}C_2H_4C_6F_{13})_3$[14,15] further reduce the electron withdrawing effect of the fluorous ponytails, they do not eliminate the electronic effects completely. In an attempt to establish whether it is possible, or even desirable, to completely insulate the donor phosphorus atoms without recourse to extremely sophisticated spacer units, here we describe the synthesis and coordination chemistry of a range of perfluoroalkyl-derivatised triaryl phosphite ligands. In a sister paper[35] we outline the application of some of these ligands for the rhodium-catalysed hydroformylation of long chain alkenes under FBS conditions. We note that the synthesis of $P(OC_6H_4\text{–}4\text{-}C_6F_{13})_3$ has been briefly described previously by us[5] and Mathivet et al. have also prepared similar ligands.[16]

1. Ligand synthesis

The triaryl phosphite ligands (**4**–**6**) were prepared (Scheme 1), in 36–42% overall yields, following our previous[5] synthetic rationale involving the copper-mediated coupling reaction of perfluoroalkyl iodides with iodophenols followed by reaction of the derivatised phenol products (**1**–**3**) with PCl_3 in the presence of triethylamine. Although two of the phenols (**1** and **3**) were obtained analytically pure following vacuum distillation, the product from the coupling of $C_6F_{13}I$ with 3-iodophenol was always contaminated with large quantities of DMSO, as shown by ^1H NMR spectroscopy. Previously,[18] it has been shown that 1,3-bis(2-hydroxyhexafluoro-2-propyl)-5-(perfluoro-*n*-alkyl)-benzenes can form extremely stable 1:1 molecular complexes with DMSO which can be sublimed under reduced pressure without dissociation. Consequently, 3-tridecafluorohexylphenol (**2**) was obtained free from



Rf = 2-C_6F_{13}, **1**
Rf = 3-C_6F_{13}, **2**
Rf = 4-C_6F_{13}, **3**

Rf = 2-C_6F_{13}, **4**
Rf = 3-C_6F_{13}, **5**
Rf = 4-C_6F_{13}, **6**

Scheme 1. Synthesis of perfluoroalkyl-substituted triarylphosphites

Keywords: fluorous biphase; triaryl phosphite; platinum group metals; X-ray analysis.
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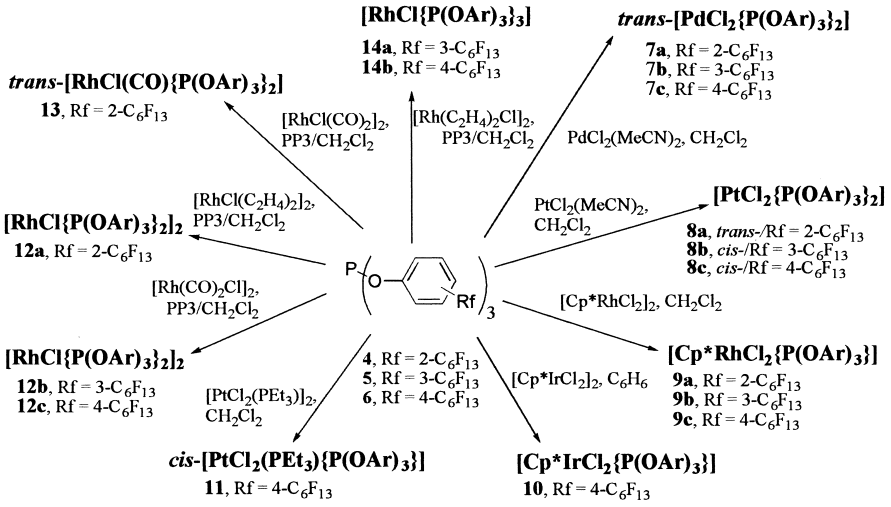

Scheme 2. Coordination chemistry of perfluoroalkyl-substituted triarylphosphites.

DMSO by heating at 80°C with a 5% sodium hydroxide solution followed by precipitation with hydrochloric acid. The perfluoroalkyl-derivatised phenols were characterised by standard procedures, the only unusual observation is the ^{1}H NMR resonance for the hydroxy proton in 2-tridecafluorohexylphenol which appears as a triplet due to through-space coupling with the α-CF_2 group; J=8.3 Hz.

All the phosphites were obtained as air-stable clear viscous oils. The electron withdrawing influence of the perfluoroalkyl chains is manifest in an increased susceptibility to hydrolysis.

2. Coordination chemistry and spectroscopic studies

We have previously used the spectroscopic and structural properties of transition metal complexes as a clear guide to the electronic and steric impact of perfluoroalkyl substituents on the donor properties of ligands.[6–8,11] The derivatised phosphites (**4**–**6**) react with platinum metal starting materials in, for the most part, exactly the same way as triphenylphosphite or perfluoroalkyl derivatised triaryl phosphines (Scheme 2); i.e. substitution of weakly coordinated ligands and cleavage of halide bridged dimers. The only exception to this rule arises in the reactions of two of the phosphites with [Rh(μ-Cl)(CO)$_2$]$_2$ (see below). As expected, the large steric influence of the perfluoroalkyl groups in the *ortho*-positions in tris(2-tridecafluorohexylphenyl)phosphite (**4**) is evidenced in the formation of the, usually, less-thermodynamically favourable *trans*-[$PtCl_2$(ligand)$_2$] (**8a**), for which $^1J_{PtP}$ is comparable to that for *trans*-[$PtCl_2${(P(OC$_6$H$_4$–2-CH$_3$)$_3$}$_2$][19] (Table 1) which contains the bulky tris-*ortho*-tolyl phosphite ligand, and the failure to prepare the analogue of Wilkinson's complex [RhCl(ligand)$_3$].

The complexes have been characterised by a combination of elemental analysis, IR spectroscopy, mass spectrometry and multinuclear NMR spectroscopies. A comparison of the NMR data with those for related triarylphosphite metal complexes (Table 1), illustrates a small, but consistent, decrease in ΔP; $^1J_{MP}$ varies non-systematically. This suggests that the presence of the oxygen atom between the aryl ring and the phosphorus atom reduces, but does not completely eliminate, the electronic influence of the fluorous ponytails. Complexes **7a**, **8a**, **9a** and **12a**, which contain the *ortho*-perfluoroalkyl derivatised phosphite ligand, each show the largest differences in their ΔP and $^1J_{MP}$ values when compared to those for the underivatised triarylphosphite complexes, and this probably arises from a combination of the increased electronic influence of the *ortho*-substituent and the large steric bulk of this ligand. These effects are mirrored in the carbonyl stretching frequency of *trans*-[RhCl(CO){P(OC$_6$H$_4$–2-C$_6$F$_{13}$)$_3$}$_2$] (**13**) which is ca. 30 cm^{-1} higher than those for *trans*-[RhCl(CO)L$_2$] {L=P(OPh)$_3$—2016 cm^{-1};[20] P(OC$_6$H$_4$–2-CH$_3$)$_3$—2012 cm^{-1}}[21] indicating a significant reduction in electron density at the metal centre for the perfluoroalkylated metal complex.

However, it is very unlikely that the electronic influence of the perfluoroalkyl substituents can account for the most unusual reactions of these fluorous-derivatised phosphite ligands. In contrast to the reactions of phosphine, phosphinite, phosphonite and most phosphite ligands, including P(OC$_6$H$_4$–2-C$_6$F$_{13}$)$_3$ (**4**), with [Rh(μ-Cl)(CO)$_2$]$_2$, which result in the elimination of one equivalent of carbon monoxide and cleavage of the halide bridge to afford the ubiquitous *trans*-[RhCl(CO)L$_2$] complexes, the reactions of the *meta*- and *para*-perfluoroalkyl derivatised phosphites (**5** and **6**) with [Rh(μ-Cl)(CO)$_2$]$_2$ afford only [Rh(μ-Cl)L$_2$]$_2$ (**12**). Normally, this reaction[22,23] involves interaction of the incoming ligand with the metal centre followed by elimination of one equivalent of CO to give [Rh(μ-Cl)(CO)L]$_2$ followed by cleavage of the halide bridges with the second equivalent of ligand to give the mononuclear product. However, although tri-substituted complexes [RhL$_2$(μ-Cl)$_2$Rh(CO)L] (L=PPh_3, P(OMe)$_3$) have been observed in solution,[24,25] we can find no precedent for the isolation of the tetra-substituted [Rh(μ-Cl)L$_2$]$_2$ (**12**) as the exclusive product of this reaction. We can only surmise that the perfluoroalkyl substituents sufficiently alter the physical properties of the halide-bridged intermediates, which have been shown by X-ray crystallography to usually have folded (123°) $RhCl_2Rh$ bridges in the

Table 1. $^{31}P\{^{1}H\}$ NMR data for metal–phosphite complexes

Complex	δ*P* (free ligand) (ppm)	δ*P* (complex) (ppm)	Δ*P*[a] (ppm)	$^{1}J_{M-P}$ (Hz)
trans-[$PdCl_2\{P(OC_6H_4-2-CH_3)_3\}_2$][b]	129.8	86.8	43.0	–
trans-[$PdCl_2\{P(OC_6H_4-2-C_6F_{13})_3\}_2$] (**7a**)	124.9	85.5	39.4	–
trans-[$PdCl_2\{P(OC_6H_4-3-C_6F_{13})_3\}_2$] (**7b**)	126.1	82.3	43.8	–
trans-[$PdCl_2\{P(OC_6H_4-4-C_6F_{13})_3\}_2$] (**7c**)	125.0	83.6	41.4	–
trans-[$PtCl_2\{P(OC_6H_4-2-CH_3)_3\}_2$][b]	129.8	74.9	54.9	4405
trans-[$PtCl_2\{P(OC_6H_4-2-C_6F_{13})_3\}_2$] (**8a**)	124.9	77.2	47.7	4589
cis-[$PtCl_2\{P(OC_6H_5)_3\}_2$] [b]	127.8	59.1	68.7	5800
cis-[$PtCl_2\{P(OC_6H_4-3-C_6F_{13})_3\}_2$] (**8b**)	126.1	60.9	65.2	5777
cis-[$PtCl_2\{P(OC_6H_4-4-C_6F_{13})_3\}_2$] (**8c**)	125.0	65.4	59.6	5660
[$Cp^*RhCl_2\{P(OC_6H_5)_3\}$][c]	127.8	104.2	23.6	240
[$Cp^*RhCl_2\{P(OC_6H_4-2-C_6F_{13})_3\}$] (**9a**)	124.9	109.8	15.1	251
[$Cp^*RhCl_2\{P(OC_6H_4-3-C_6F_{13})_3\}$] (**9b**)	126.1	107.1	19.0	244
[$Cp^*RhCl_2\{P(OC_6H_4-4-C_6F_{13})_3\}$] (**9c**)	125.0	106.5	18.5	245
[$Cp^*IrCl_2\{P(OC_6H_4-4-C_6F_{13})_3\}$] (**10**)	125.0	67.7	57.3	–
cis-[$PtCl_2(PEt_3)\{P(OC_6H_5)_3\}$][c]	127.8	62.7[d]	65.1	6261
cis-[$PtCl_2(PEt_3)\{P(OC_6H_4-4-C_6F_{13})_3\}$] (**11**)	125.0	66.3[d]	58.7	6300
[$Rh(\mu\text{-}Cl)\{P(OC_6H_5)_3\}_2]_2$	127.8	114.9	12.9	311
[$Rh(\mu\text{-}Cl)\{P(OC_6H_4-2-C_6F_{13})_3\}_2]_2$ (**12a**)	124.9	108.2	16.7	318
[$Rh(\mu\text{-}Cl)\{P(OC_6H_4-3-C_6F_{13})_3\}_2]_2$ (**12b**)	126.1	113.6	12.5	309
[$Rh(\mu\text{-}Cl)\{P(OC_6H_4-4-C_6F_{13})_3\}_2]_2$ (**12c**)	125.0	113.2	11.8	313
[$RhCl(CO)\{P(OC_6H_5)_3\}_2$][e]	127.8	115.2	12.6	217
[$RhCl(CO)\{P(OC_6H_4-2-C_6F_{13})_3\}_2$] (**13**)	124.9	115.2	9.7	223
[$RhCl\{P(OC_6H_5)_3\}_3$][f]	127.8	118.9, 111.9	8.9, 15.9	285, 224
[$RhCl\{P(OC_6H_4-3-C_6F_{13})_3\}_3$] (**14a**)	126.1	119.0, 113.6	7.1, 12.5	276, 227
[$RhCl\{P(OC_6H_4-4-C_6F_{13})_3\}_3$] (**14b**)	125.0	121.2, 113.6	3.8, 11.4	286, 225

[a] $\Delta P = \delta P(\text{free ligand}) - \delta P(\text{complex})$.
[b] Data taken from Ref. 17.
[c] Data taken from Ref. 32.
[d] Phosphite ligand.
[e] Data taken from Ref. 33.
[f] Data taken from Ref. 34.

solid state,[26] to promote CO substitution over halide-bridge cleavage.

3. Structural characterisation

Crystals, suitable for single crystal X-ray structural analysis, of [$Cp^*RhCl_2\{P(OC_6H_4-4-C_6F_{13})_3\}$] (**9c**) were obtained by slow evaporation from acetone solution. Selected bond lengths and angles are shown in Table 2 and the molecular structure is shown in Fig. 1.

In previous structural determinations of metal complexes incorporating ligands with perfluoroalkyl substituents, we

Table 2. Selected bond distances (Å), angles (°), torsion angles (°) and non-bonded F···F distances (Å) for [$Cp^*RhCl_2\{P(OC_6H_4-4-C_6F_{13})_3\}$] (**9c**)

Rh(1)–C(4)	2.167(12)	Rh(1)–P(1)	2.237(3)
Rh(1)–C(5)	2.194(11)	Rh(1)–Cl(1)	2.386(3)
Rh(1)–C(1)	2.197(11)	Rh(1)–Cl(2)	2.405(3)
Rh(1)–C(3)	2.231(12)		
Rh(1)–C(2)	2.236(12)		
P(1)–O(1)	1.581(10)	O(1)–C(11)	1.399(16)
P(1)–O(2)	1.571(10)	O(2)–C(23)	1.360(15)
P(1)–O(3)	1.600(10)	O(3)–C(35)	1.421(17)
P(1)–Rh(1)–Cl(1)	89.96(11)	O(2)–P(1)–Rh(1)	121.6(4)
P(1)–Rh(1)–Cl(2)	87.78(11)	O(1)–P(1)–Rh(1)	115.5(4)
Cl(1)–Rh(1)–Cl(2)	89.70(11)	O(3)–P(1)–Rh(1)	120.4(4)
O(2)–P(1)–O(1)	96.9(7)	C(11)–O(1)–P(1)	121.7(10)
O(2)–P(1)–O(3)	95.6(7)	C(23)–O(2)–P(1)	136.9(10)
O(1)–P(1)–O(3)	102.5(6)	C(35)–O(3)–P(1)	129.8(9)
C(43)–C(44)–C(45)–C(46)	−175.25	C(42)–C(43)–C(44)–C(45)	−166.68
C(41)–C(42)–C(43)–C(44)	−165.14	C(38)–C(41)–C(42)–C(43)	−169.02
C(31)–C(32)–C(33)–C(34)	−175.25	C(30)–C(31)–C(32)–C(33)	−167.72
C(29)–C(30)–C(31)–C(32)	−50.16	C(26)–C(29)–C(30)–C(31)	−162.43
C(19)–C(20)–C(21)–C(22)	166.18	C(18)–C(19)–C(20)–C(21)	165.32
C(17)–C(18)–C(19)–C(20)	166.38	C(14)–C(17)–C(18)–C(19)	171.55
F(33B)···F(46A)	2.947	F(21A)···F(21B)	2.964
F(21B)···F(21B)	2.875	F(42A)···F(46B)	2.954
F(20B)···F(42B)	2.691	F(17A)···F(19A)	2.864
F(34A)···F(32A)	2.944	F(30B)···F(41A)	2.796
F(17B)···F(31A)	2.903	F(17B)···F(29A)	2.652

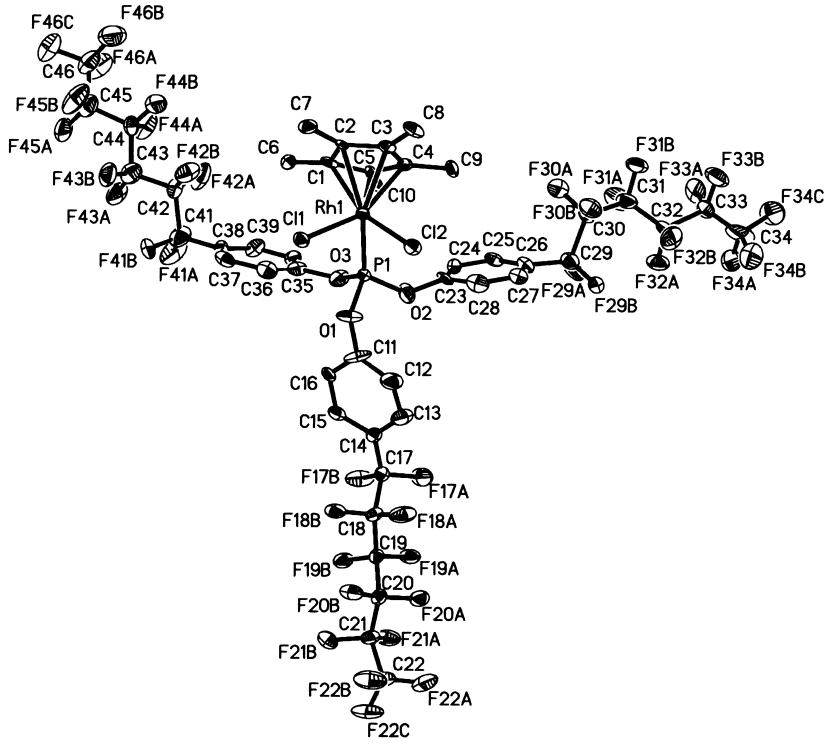

Figure 1. Molecular Structure of $[Cp^*RhCl_2\{P(OC_6H_4\text{–}4\text{-}C_6F_{13})_3\}]$ (**9c**). Displacement ellipsoids are shown at the 30% probability level. The H atoms are omitted for clarity.

have concluded that the fluorous ponytails have a negligible effect upon the geometry of the metal first coordination sphere but dominate the packing of these molecules in the solid state.[6,8,11] Similar conclusions can be drawn from the crystal structure of $[Cp^*RhCl_2\{P(OC_6H_4\text{–}4\text{-}C_6F_{13})_3\}]$ (**9c**) that displays the expected three-legged piano-stool geometry about the rhodium centre in which the bond lengths to rhodium and angles at rhodium and phosphorus are very similar to those for the related $[Cp^*IrCl_2\{P(OC_6H_3\text{-}2,6\text{-}F_2\}]$.[27] The average P–O bond distance, 1.583(6) Å, is slightly smaller than the average for coordinated triphenylphosphite ligands, 1.600(11) Å,[28] which could arise from the electronic influence of the perfluoroalkyl substituents. The three perfluoroalkyl tails radiate away from the metal centre, two in a regular linear fashion and the third with a single C–C–C–C torsion angle around 50°, and the extended view of the structure reveals fluorous domains in which the perfluoroalkyl chains line up affording a number of relatively short, non-bonded, intermolecular fluorine··· fluorine contacts.

4. Experimental

4.1. General

Proton, ^{19}F and ^{31}P NMR spectroscopies were carried out on a Bruker ARX 250 spectrometer at 250.13, 235.34 and 101.26 MHz or on a Bruker DRX 400 spectrometer at 400.13, 376.50 and 161.98 MHz. All chemical shifts are quoted in ppm using the high-frequency positive convention; ^1H NMR spectra were referenced to external $SiMe_4$, ^{19}F NMR spectra to external $CFCl_3$ and ^{31}P NMR spectra to external 85% H_3PO_4. The IR spectra were recorded on a Digilab FTS40 Fourier-transform spectrometer at 4 cm^{-1} resolution for the complexes as Nujol mulls held between KBr discs. Elemental analyses were performed by Butterworth Laboratories Ltd. Mass spectra were recorded on a Kratos Concept 1H mass spectrometer.

The complexes *cis*-$[MCl_2(MeCN)_2]$ (M=Pd, Pt)[29] and $[PtCl_2(PEt_3)]_2$[30] were prepared as described previously and the complexes, $[RhCl(C_2H_4)_2]_2$, $[RhCl(CO)_2]_2$, $[Cp^*MCl_2]_2$ (M=Rh, Ir) (Aldrich) were used as supplied. Dichloromethane and perfluoro-1,3-dimethylcyclohexane (PP3) were each dried by refluxing over calcium hydride under nitrogen, distilled under nitrogen and stored in closed ampoules over molecular sieves. PP3 was also freezed/pumped/thawed three times to remove all dissolved gases. Hexane was dried by refluxing over potassium metal under nitrogen, distilled and was stored similarly. Diethyl ether was dried by refluxing over sodium metal under nitrogen, distilled and stored similarly.

2-Tridecafluorohexylphenol (**1**) and 3-tridecafluorohexylphenol (**2**) were prepared following our previously described procedure[5] for the preparation of 4-tridecafluorohexylphenol (**3**) in 69 and 89% yields, respectively. Tris(2-tridecafluorohexylphenyl)phosphite (**4**) and tris(3-trifluorohexylphenyl)phosphite (**5**), were similarly prepared following the procedure[5] for the preparation of tris(4-tridecafluorohexylphenyl)phosphite (**6**) in 52 and 45% yields, respectively.

4.1.1. 2-Tridecafluorohexylphenol (1). Bp 96–97°C (20 mmHg). ^1H NMR ($CDCl_3$) δ 7.31 (m, 2H), 6.89 (m, 2H), 6.32 (t, 1H, J_{HF}=8.3 Hz, OH). $^{19}F\{^1H\}$ NMR ($CDCl_3$) δ −81.30 (tm, 3F, $^4J_{FF}$=10.1 Hz, CF_3), −108.66

(tm, 2F, $^4J_{FF}$=14.8 Hz, α-CF_2), −122.09 (m, 2F, CF_2), −123.24 (m, 4F, CF_2), −126.65 (m, 2F, CF_2). MS (EI) *m/z* 412 (M^+), 393 ($M-F^+$); HRMS (EI) calcd for $C_{12}H_5F_{13}O$ 412.01328, found 412.01328.

4.1.2. 3-Tridecafluorohexylphenol (2). Following Kulgelrohr distillation, **2** was purified by heating at 80°C with a 5% sodium hydroxide solution, followed by precipitation with dilute hydrochloric acid. White solid. Bp 60–62°C (0.01 mmHg). ^{1}H NMR ($CDCl_3$) δ 7.30 (t, 1H, $^3J_{HH}$=7.9 Hz, 5-H), 7.09 (d, 1H, $^3J_{HH}$=7.6 Hz, 6-H), 6.96 (m, 2H), 5.21 (s, 1H, OH). ^{19}F{^{1}H} NMR ($CDCl_3$) δ −81.34 (tm, 3F, $^4J_{FF}$=11.3 Hz, CF_3), −111.03 (tm, 2F, $^4J_{FF}$=14.2 Hz, α-CF_2), −122.05 (m, 2F, CF_2), −122.46 (m, 2F, CF_2), −123.34 (m, 2F, CF_2), −126.67 (m, 2F, CF_2). MS (EI) *m/z* 412 (M^+), 393 ($M-F^+$); HRMS (EI) calcd for $C_{12}H_5F_{13}O$ 412.01328, found 412.01328.

4.1.3. 4-Tridecafluorohexylphenol (3). Bp 55°C (0.01 mmHg). ^{1}H NMR ($CDCl_3$) δ 7.31 (d, 2H, $^3J_{HH}$=7.1 Hz, 3,5-H's), 6.92 (d, 2H, $^3J_{HH}$=7.1 Hz, 2,6-H's), 5.23 (s, 1H, OH). ^{19}F{^{1}H} NMR ($CDCl_3$) δ −81.26 (tt, 3F, $^3J_{FF}$=2.5 Hz, $^4J_{FF}$=10.1 Hz, CF_3), −110.15 (tm, 2F, $^4J_{FF}$=14.6 Hz, α-CF_2), −121.92 (m, 2F, CF_2), −122.42 (m, 2F, CF_2), −123.24 (m, 2F, CF_2), −126.55 (m, 2F, CF_2). MS(EI) *m/z* 412 (M^+), 393 ($M-F^+$); HRMS (EI) calcd for $C_{12}H_5F_{13}O$ 412.01328, found 412.01327.

4.1.4. Tris(2-tridecafluorohexylphenyl)phosphite (4). Bp 180°C (0.01 mmHg). ^{1}H NMR (d^8-toluene) δ 7.50 (d, 1H, $^3J_{HH}$=8.1 Hz, 6-H), 7.41 (d, 1H, $^3J_{HH}$=8.1 Hz, 3-H), 7.10 (t, 1H, $^3J_{HH}$=8.1 Hz, 5-H), 6.79 (t, 1H, $^3J_{HH}$=8.1 Hz, 4-H). ^{19}F{^{1}H} NMR (d^8-toluene) δ −81.55 (tm, 3F, $^4J_{FF}$=10.1 Hz, CF_3), −107.97 (tm, 2F, $^4J_{FF}$=14.9 Hz, α-CF_2), −121.29 (m, 2F, CF_2), −122.08 (m, 2F, CF_2), −123.14 (m, 2F, CF_2), −126.64 (m, 2F, CF_2). ^{31}P{^{1}H} (d^8-toluene) δ 124.9 (s). MS (EI) *m/z* 1264 (M^+), 995 ($M-C_5F_{11}^+$), 853 ($M-OC_6H_4C_6F_{13}^+$). Anal. calcd for $C_{36}H_{12}F_{39}O_3P$: C, 34.17; H, 0.95; P, 2.45; found: C, 34.05; H, 1.02; P, 2.46%.

4.1.5. Tris(3-tridecafluorohexylphenyl)phosphite (5). Bp 185°C (0.01 mmHg). ^{1}H NMR (d^8-toluene) δ 7.31 (s, 1H, 2-H), 7.14 (d, 1H, $^3J_{HH}$=7.6 Hz, 6-H), 6.99 (d, 1H, $^3J_{HH}$=8.0 Hz, 4-H), 6.75 (t, 1H, $^3J_{HH}$=8.0 Hz, 5-H). ^{19}F{^{1}H} NMR (d^8-toluene) δ −81.86 (tt, 3F, $^3J_{FF}$=2.5 Hz, $^4J_{FF}$=9.3 Hz, CF_3), −111.38 (t, 2F, $^4J_{FF}$=15.9 Hz, α-CF_2), −121.99 (m, 2F, CF_2), −122.27 (m, 2F, CF_2), −123.40 (m, 2F, CF_2), −126.85 (m, 2F, CF_2). ^{31}P{^{1}H} (d^8-toluene) δ 126.1 (s). MS (EI) *m/z* 1264 (M^+), 995 ($M-C_5F_{11}^+$), 853 ($M-OC_6H_4C_6F_{13}^+$). Anal. calcd for $C_{36}H_{12}F_{39}O_3P$: C, 34.17; H, 0.95; P, 2.45; found: C, 34.20; H, 1.04; P, 2.25%.

4.1.6. Tris(4-tridecafluorohexylphenyl)phosphite (6). Bp 220°C (0.01 mmHg). ^{1}H NMR (d^8-toluene) δ 7.24 (d, 2H, $^3J_{HH}$=8.6 Hz, 3,5-H's), 6.88 (d, 2H, $^3J_{HH}$=8.6 Hz, 2,6-H's). ^{19}F{^{1}H} NMR (d^8-toluene) δ −81.45 (tt, 3F, $^3J_{FF}$=2.5 Hz, $^4J_{FF}$=10.1 Hz, CF_3), −110.50 (t, 2F, $^4J_{FF}$=14.6 Hz, α-CF_2), −121.68 (m, 2F, CF_2), −122.05 (m, 2F, CF_2), −123.09 (m, 2F, CF_2), −126.51 (m, 2F, CF_2). ^{31}P{^{1}H} (d^8-toluene) δ 125.1 (s). MS (EI) *m/z* 1264 (M^+), 995 ($M-C_5F_{11}^+$), 853 ($M-OC_6H_4C_6F_{13}^+$). Anal. calcd for $C_{36}H_{12}F_{39}O_3P$: C, 34.17; H, 0.95; found: C, 34.04; H, 1.00%.

4.2. General procedure for the preparation of [MCl_2L_2] (M=Pd, Pt)

A slurry of [$MCl_2(MeCN)_2$] (M=Pd, Pt) (0.29 mmol) and the ligand (0.80 mmol) in dichloromethane was heated under reflux under nitrogen for 2 h to give a clear colourless solution. After cooling, the solution was concentrated in vacuo and petroleum ether added to precipitate the product as a yellow (Pd) or white (Pt) solid, which was filtered, washed with petroleum ether and dried in vacuo.

4.2.1. *trans*-[$PdCl_2${$P(OC_6H_4$–2-$C_6F_{13})_3$}$_2$] (7a). Obtained in 43% yield. ^{1}H NMR (d^6-acetone) δ 7.50 (m, 4H). ^{19}F{^{1}H} NMR (d^6-acetone) δ −82.31 (tm, 3F, $^4J_{FF}$=11.0 Hz, CF_3), −108.91 (m, 2F, α-CF_2), −121.90 (m, 2F, CF_2), −122.67 (m, 2F, CF_2), −123.91 (m, 2F, CF_2), −127.41 (m, 2F, CF_2). ^{31}P{^{1}H} NMR (d^6-acetone) δ 85.5 (s). MS (FAB) *m/z* 2634 ($M-2Cl^+$). Anal. calcd for $C_{72}H_{24}Cl_2F_{78}O_6P_2Pd$: C, 31.94; H, 0.89; P, 2.29; found: C, 31.95; H, 0.91; P, 2.14%.

4.2.2. *trans*-[$PdCl_2${$P(OC_6H_4$–3-$C_6F_{13})_3$}$_2$] (7b). Obtained in 62% yield. ^{1}H NMR ($CDCl_3$) δ 7.42 (m, 3H), 7.11 (s, 1H, 2-H). ^{19}F{^{1}H} NMR ($CDCl_3$) δ −81.54 (tm, 3F, $^4J_{FF}$=11.3 Hz, CF_3), −111.72 (tm, 2F, $^4J_{FF}$=14.2 Hz, α-CF_2), −122.25 (m, 2F, CF_2), −122.39 (m, 2F, CF_2), −123.62 (m, 2F, CF_2), −126.89 (m, 2F, CF_2). ^{31}P{^{1}H} NMR ($CDCl_3$) δ 82.3 (s). MS (FAB) *m/z* 2671 ($M-Cl^+$). Anal. calcd for $C_{72}H_{24}Cl_2F_{78}O_6P_2Pd$: C, 31.94; H, 0.89; P, 2.29; found: C, 31.73; H, 0.98; P, 2.20%.

4.2.3. *trans*-[$PdCl_2${$P(OC_6H_4$–4-$C_6F_{13})_3$}$_2$] (7c). Obtained in 62% yield. ^{1}H NMR ($CDCl_3$) δ 8.10 (d, 2H, $^3J_{HH}$=8.7 Hz, 2,6-H's), 7.82 (d, 2H, $^3J_{HH}$=8.7 Hz, 3,5-H's). ^{19}F{^{1}H} NMR ($CDCl_3$) δ −80.86 (tt, 3F, $^3J_{FF}$=2.2, $^4J_{FF}$=11.3 Hz, CF_3), −109.75 (tm, 2F, $^4J_{FF}$=14.6 Hz, α-CF_2), −121.17 (m, 2F, CF_2), −121.63 (m, 2F, CF_2), −122.57 (m, 2F, CF_2), −125.98 (m, 2F, CF_2). ^{31}P{^{1}H} NMR ($CDCl_3$) δ 83.6 (s). IR (Nujol) ν(Pd–Cl) 332, 308 cm^{-1}. MS (FAB) *m/z* 2671 ($M-Cl^+$), 2634 ($M-2Cl^+$). Anal. calcd for $C_{72}H_{24}Cl_2F_{78}O_6P_2Pd$: C, 31.94; H, 0.89; Cl, 2.62; found: C, 30.68; H, 0.77; Cl, 2.24%.

4.2.4. *trans*-[$PtCl_2${$P(OC_6H_4$–2-$C_6F_{13})_3$}$_2$] (8a). Obtained in 25% yield. ^{1}H NMR (d^6-acetone) δ 7.76 (d, 1H, $^3J_{HH}$=8.5 Hz, 6-H), 7.69 (d, 1H, $^3J_{HH}$=8.5 Hz, 3-H), 7.58 (t, 1H, $^3J_{HH}$=7.3 Hz, 5-H), 7.48 (t, 1H, $^3J_{HH}$=7.6, 4-H). ^{19}F{^{1}H} NMR (d^6-acetone) δ −82.29 (tm, 3F, $^4J_{FF}$=8.5 Hz, CF_3), −108.87 (tm, 2F, $^4J_{FF}$=14.2 Hz, α-CF_2), −121.84 (m, 2F, CF_2), −122.65 (m, 2F, CF_2), −123.90 (m, 2F, CF_2), −127.39 (m, 2F, CF_2). ^{31}P{^{1}H} NMR (d^6-acetone) δ 77.2 (s, $^1J_{PtP}$=4589 Hz). MS (FAB) *m/z* 2759 ($M-Cl^+$), 2724 ($M-2Cl^+$). Anal. calcd for $C_{72}H_{24}Cl_2F_{78}O_6P_2Pt$: C, 30.92; H, 0.86; P, 2.22; found: C, 30.84; H, 0.85; P, 2.14%.

4.2.5. *cis*-[$PtCl_2${$P(OC_6H_4$–3-$C_6F_{13})_3$}$_2$] (8b). Obtained in 60% yield. ^{1}H NMR (d^6-acetone) δ 7.45 (m, 3H), 7.08 (s, 1H, 2-H). ^{19}F{^{1}H} NMR (d^6-acetone) δ −81.85 (m, 3F, CF_3), −111.79 (tm, 2F, $^4J_{FF}$=14.2 Hz, α-CF_2), −122.41 (m, 2F, CF_2), −122.65 (m, 2F, CF_2), −123.68 (m, 2F, CF_2), −127.01 (m, 2F, CF_2). ^{31}P{^{1}H} NMR (d^6-acetone) δ 60.9 (s, $^1J_{PtP}$=5777 Hz). MS (FAB) *m/z* 2759 ($M-Cl^+$),

2724 ($M-2Cl^+$). Anal. calcd for $C_{72}H_{24}Cl_2F_{78}O_6P_2Pt$: C, 30.92; H, 0.86; P, 2.22; found: C, 30.96; H, 0.84; P, 2.30%.

4.2.6. *cis*-[$PtCl_2${$P(OC_6H_4-4-C_6F_{13})_3$}$_2$] (8c). Obtained in 59% yield. ^1H NMR (d^6-acetone) δ 7.80 (d, 2H, $^3J_{HH}$=8.8 Hz, 2,6-H's), 7.64 (d, 2H, $^3J_{HH}$=8.8 Hz, 3,5-H's). $^{19}F\{^1H\}$ NMR (D_2O) δ −82.17 (t, 3F, $^4J_{FF}$=10.0 Hz, CF_3), −111.20 (tm, 2F, $^4J_{FF}$=13.9 Hz, α-CF_2), −122.36 (m, 4F, CF_2), −123.78 (m, 2F, CF_2), −127.24 (m, 2F, CF_2). $^{31}P\{^1H\}$ NMR (D_2O) δ 65.4 (s, $^1J_{PtP}$=5660 Hz). IR (Nujol) ν(Pt–Cl) 330, 308 cm^{-1}. MS (FAB) *m/z* 2759 ($M-Cl^+$), 2724 ($M-2Cl^+$). Anal. calcd for $C_{72}H_{24}Cl_2F_{78}O_6P_2Pt$: C, 30.92; H, 0.86; Cl, 2.54; found: C, 29.25; H, 0.82; Cl, 2.60%.

4.3. General procedure for the preparation of [Cp^*MCl_2L] (M=Rh, Ir)

A slurry of the [Cp^*MCl_2]$_2$ (M=Rh, Ir) (0.24 mmol) and the ligand (0.58 mmol) were refluxed in dichloromethane (Rh) or benzene (Ir) under dinitrogen for 1 h to give a clear red (Rh) or clear orange (Ir) solution. After cooling, the solution was concentrated in vacuo and petroleum ether added to precipitate the product as an orange solid, which was filtered, washed with petroleum ether and dried in vacuo.

4.3.1. Cp^*RhCl_2{$P(OC_6H_4-2-C_6F_{13})_3$}] (9a). Obtained in 41% yield. ^1H NMR ($CDCl_3$) δ 8.05 (d, 3H, $^3J_{HH}$=8.0 Hz, 6-H), 7.39 (m, 6H), 7.21 (m, 3H), 1.36 (d, 15H, J_{PH}=6.2 Hz, CH_3). $^{19}F\{^1H\}$ NMR ($CDCl_3$) δ −81.52 (tm, 3F, $^4J_{FF}$= 11.3 Hz, CF_3), −107.52 (m, 2F, α-CF_2), −121.55 (m, 2F, CF_2), −122.35 (m, 2F, CF_2), −123.53 (m, 2F, CF_2), −126.90 (m, 2F, CF_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 109.8 (d, $^1J_{RhP}$=251 Hz). MS (FAB) *m/z* 1572 (M^+), 1537 ($M-Cl^+$). Anal. calcd for $C_{46}H_{27}Cl_2F_{39}O_3PRh$: C, 35.09; H, 1.72; P, 1.97; found: C, 35.10; H, 1.68; P, 1.84%.

4.3.2. Cp^*RhCl_2{$P(OC_6H_4-3-C_6F_{13})_3$}] (9b). Obtained in 76% yield. ^1H NMR ($CDCl_3$) δ 7.71 (d, 3H, $^3J_{HH}$=7.6 Hz, 6-H), 7.45 (t, 3H, $^3J_{HH}$=7.9 Hz, 5-H), 7.38 (d, 3H, $^3J_{HH}$=7.9 Hz, 4-H), 7.21 (s, 3H, 2-H), 1.41 (d, 15H, J_{PH}=6.3 Hz, CH_3). $^{19}F\{^1H\}$ NMR ($CDCl_3$) δ −81.42 (tm, 3F, $^4J_{FF}$=8.5 Hz, CF_3), −111.34 (tm, 2F, $^4J_{FF}$=14.2 Hz, α-CF_2), −122.11 (m, 2F, CF_2), −122.34 (m, 2F, CF_2), −123.51 (m, 2F, CF_2), −126.78 (m, 2F, CF_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 107.1 (d, $^1J_{RhP}$=244 Hz). MS (FAB) *m/z* 1537 ($M-Cl^+$). Anal. calcd for $C_{46}H_{27}Cl_2F_{39}O_3PRh$: C, 35.09; H, 1.72; P, 1.97; found: C, 35.30; H, 1.71; P, 1.24%.

4.3.3. Cp^*RhCl_2{$P(OC_6H_4-4-C_6F_{13})_3$}] (9c). Obtained in 66% yield. ^1H NMR ($CDCl_3$) δ 7.32 (d, 6H, $^3J_{HH}$=8.8 Hz, 3,5-H's), 7.22 (d, 6H, $^3J_{HH}$=8.8 Hz, 2,6-H's), 1.41 (d, 15H, J_{PH}=6.3 Hz, CH_3). $^{19}F\{^1H\}$ NMR ($CDCl_3$) δ −81.41 (tt, 3F, $^3J_{FF}$=2.2 Hz, $^4J_{FF}$=10.0 Hz, CF_3), −110.99 (tm, 2F, $^4J_{FF}$=14.4 Hz, α-CF_2), −121.95 (m, 2F, CF_2), −122.43 (m, 2F, CF_2), −123.38 (m, 2F, CF_2), −126.71 (m, 2F, CF_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 106.5 (d, $^1J_{RhP}$=245 Hz). MS (FAB) *m/z* 1537 ($M-Cl^+$), 1502 ($M-2Cl^+$). Anal. calcd for $C_{46}H_{27}Cl_2F_{39}O_3PRh$: C, 35.09; H, 1.72; Cl, 4.51; found: C, 35.90; H, 1.45; Cl, 4.15%.

4.3.4. Cp^*IrCl_2{$P(OC_6H_4-4-C_6F_{13})_3$}] (10). Obtained in 52% yield. ^1H NMR ($CDCl_3$) δ 7.47 (d, 6H, $^3J_{HH}$=8.7 Hz, 3,5-H's), 7.38 (d, 6H, $^3J_{HH}$=8.7 Hz, 2,6-H's), 1.49 (d, 15H, J_{PH}=3.8 Hz, CH_3). $^{19}F\{^1H\}$ NMR ($CDCl_3$) δ −81.30 (tt, 3F, $^3J_{FF}$=2.3 Hz, $^4J_{FF}$=10.0 Hz, CF_3), −110.93 (tm, 2F, $^4J_{FF}$=14.4 Hz, α-CF_2), −121.88 (m, 2F, CF_2), −122.33 (m, 2F, CF_2), −123.29 (m, 2F, CF_2), −126.62 (m, 2F, CF_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 67.7 (s). Anal. calcd for $C_{46}H_{27}Cl_2F_{39}O_3PIr$: C, 33.21; H, 1.62; Cl, 4.27; found: C, 33.20; H, 1.45; Cl, 3.45%.

4.3.5. *cis*-[$PtCl_2(PEt_3)${$P(OC_6H_4-4-C_6F_{13})_3$}] (11). A slurry of [{$PtCl(\mu-Cl)(PEt_3)$}$_2$] (0.067 g, 0.09 mmol) and $P(OC_6H_4-4-C_6F_{13})_3$ (0.272 g, 0.22 mmol) in dichloromethane (30 cm^3) was heated under reflux under dinitrogen for 10 min. to give a clear colourless solution. After cooling, the solution was concentrated in vacuo, and petroleum ether added to precipitate the product as a fine white solid, which was filtered, washed with petroleum ether and dried in vacuo. Yield 0.209 g, 73%. ^1H NMR ($CDCl_3$) δ 7.73 (d, 6H, $^3J_{HH}$=8.7 Hz, 3,5-H's), 7.62 (d, 6H, $^3J_{HH}$=8.7 Hz, 2,6-H's), 2.21 (dq, 6H, $^2J_{PH}$=10.2 Hz, $^3J_{HH}$=7.6 Hz, CH_2), 1.04 (m, 9H, $^3J_{PH}$=18.2 Hz, $^3J_{HH}$=7.6 Hz, CH_3). $^{19}F\{^1H\}$ NMR ($CDCl_3$) δ −81.33 (tt, 3F, $^3J_{FF}$=2.3 Hz, $^4J_{FF}$= 10.1 Hz, CF_3), −111.03 (t, 2F, $^4J_{FF}$=14.3 Hz, α-CF_2), −121.90 (m, 2F, CF_2), −122.23 (m, 2F, CF_2), −123.28 (m, 2F, CF_2), −126.62 (m, 2F, CF_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 66.3 (d, 1P, $^1J_{PtP}$=6300 Hz, $^2J_{PP}$=19.9 Hz, P{OAr}$_3$), 17.6 (d, 1P, $^1J_{PtP}$=3105 Hz, $^2J_{PP}$=19.9 Hz, PEt_3). MS (FAB) *m/z* 1613 ($M-Cl^+$), 1577 ($M-2Cl^+$). Anal. calcd for $C_{42}H_{27}Cl_2F_{39}O_3P_2Pt$: C, 30.58; H, 1.64; Cl, 4.31; found: C, 30.60; H, 1.38; Cl, 4.15%.

4.4. General procedure for the preparation of [Rh(μ-Cl)L_2]$_2$

The addition of a colourless solution of the ligand (0.33 mmol) in dry PP3 (40 cm^3) to a deep red solution of [$Rh(CO)_2Cl$]$_2$ (0.08 mmol) in dry dichloromethane under dinitrogen resulted in an almost instantaneous decolourisation of the upper organic layer and the fluorous layer turned yellow. The lower fluorous layer was transferred, under nitrogen, to a Schlenk flask where the solvent was removed in vacuo, to leave a yellow solid, which was recrystallized from ethanol and dried in vacuo.

4.4.1. Rh(μ-Cl){$P(OC_6H_4-2-C_6F_{13})_3$}$_2$]$_2$ (12a). Was prepared similarly using [$Rh(\eta^2-C_2H_4)_2(\mu-Cl)$]$_2$ in 39% yield. ^1H NMR (D_2O) δ 7.65 (m, 4H). $^{19}F\{^1H\}$ NMR (D_2O) δ −82.22 (tm, 3F, $^4J_{FF}$=8.5 Hz, CF_3), −108.42 (m, 2F, α-CF_2), −121.65 (m, 2F, CF_2), −122.60 (m, 2F, CF_2), −123.77 (m, 2F, CF_2), −126.26 (m, 2F, CF_2) $^{31}P\{^1H\}$ NMR (D_2O) δ 108.2 (d, $^1J_{RhP}$=318 Hz). Anal. calcd for $C_{72}H_{24}ClF_{78}O_6P_2Rh$: C, 32.40; H, 0.90; P, 2.33; found: C, 32.22; H, 0.89; P, 3.20%.

4.4.2. Rh(μ-Cl){$P(OC_6H_4-3-C_6F_{13})_3$}$_2$]$_2$ (12b). Obtained in 39% yield. ^1H NMR (D_2O) δ 6.91 (m, 4H). $^{19}F\{^1H\}$ NMR (D_2O) δ −81.95 (m, 3F, CF_3), −111.85 (tm, 2F, $^4J_{FF}$=14.2 Hz, α-CF_2), −122.36 (m, 2F, CF_2), −122.60 (m, 2F, CF_2), −123.68 (m, 2F, CF_2), −126.91 (m, 2F, CF_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 113.6 (d, $^1J_{RhP}$=309 Hz). Anal. calcd for $C_{72}H_{24}ClF_{78}O_6P_2Rh$: C, 32.40; H, 0.90; P, 2.33; found: C, 32.45; H, 0.89; P, 2.64%.

4.4.3. Rh(μ-Cl){P(OC$_6$H$_4$–4-C$_6$F$_{13}$)$_3$}$_2$]$_2$ (12c). Obtained in 48% yield. ^{1}H NMR (D$_2$O) δ 7.21 (d, 2H, $^3J_{HH}$=8.3 Hz, 3,5-H's), 6.88 (d, 2H, $^3J_{HH}$=8.3 Hz, 2,6-H's). ^{19}F{^{1}H} NMR (D$_2$O) δ −82.08 (tm, 3F, $^4J_{FF}$=10.0 Hz, CF$_3$), −110.72 (tm, 2F, $^4J_{FF}$=14.2 Hz, α-CF$_2$), −122.05 (m, 2F, CF$_2$), −122.66 (m, 2F, CF$_2$), −123.56 (m, 2F, CF$_2$), −127.12 (m, 2F, CF$_2$). ^{31}P{^{1}H} NMR (CDCl$_3$) δ 113.2 (d, $^1J_{RhP}$=313 Hz). Anal. calcd for C$_{72}$H$_{24}$ClF$_{78}$O$_6$P$_2$Rh: C, 32.40; H, 0.90; Cl, 1.33; found: C, 32.81; H, 0.88; Cl, 1.30%.

4.4.4. RhCl(CO){P(OC$_6$H$_4$–2-C$_6$F$_{13}$)$_3$}$_2$] 13. The addition of a colourless solution of the P(OC$_6$H$_4$–2-C$_6$F$_{13}$)$_3$ (0.373 g, 0.30 mmol) in dry PP3 (40 cm^3) to a deep red solution of [Rh(CO)$_2$Cl]$_2$ (0.030 g, 0.08 mmol) in dry dichloromethane under dinitrogen resulted in an almost instantaneous decolourisation of the upper organic layer and the fluorous layer turned yellow. The lower fluorous layer was transferred, under nitrogen, to a Schlenk flask where the solvent was removed in vacuo, to leave a yellow solid, which was recrystallized from ethanol and dried in vacuo. Yield 0.251 g, 50%. ^{1}H NMR (d^6-benzene) δ 7.55 (d, 1H, $^3J_{HH}$=8.2 Hz, 6-H), 7.22 (d, 1H, $^3J_{HH}$=7.6 Hz, 3-H), 6.98 (t, 1H, $^3J_{HH}$=7.6 Hz, 5-H), 6.84 (t, 1H, $^3J_{HH}$=7.6 Hz, 4-H). ^{19}F{^{1}H} NMR (d^6-benzene) δ −82.25 (tm, 3F, $^4J_{FF}$=9.9 Hz, CF$_3$), −108.64 (tm, 2F, $^4J_{FF}$=14.2 Hz, α-CF$_2$), −121.49 (m, 2F, CF$_2$), −122.44 (m, 2F, CF$_2$), −123.65 (m, 2F, CF$_2$), −127.29 (m, 2F, CF$_2$). ^{31}P{^{1}H} NMR (d^6-benzene) δ 115.2 (d, $^1J_{RhP}$=223 Hz). Anal. calcd for C$_{73}$H$_{24}$ClF$_{78}$O$_7$P$_2$Rh: C, 32.51; H, 0.89; P, 2.30; found: C, 31.98; H, 0.84; P, 3.00%. IR (PP3 solution) ν(C≡O) 2045 cm^{-1}.

4.5. General procedure for the preparation of [RhClL$_3$]

The addition of a colourless solution of the ligand (0.32 mmol) in dry PP3 (40 cm^3) to a deep red solution of [Rh(η-C$_2$H$_4$)$_2$Cl]$_2$ (0.05 mmol) in dry dichloromethane (40 cm^3) under dinitrogen resulted in an almost instantaneous decolourisation of the upper organic layer and the fluorous layer turned yellow. The lower fluorous layer was transferred, under nitrogen, to a Schlenk flask where the solvent was removed in vacuo, to leave a yellow solid, which was recrystallized from ethanol and dried in vacuo.

4.5.1. RhCl{P(OC$_6$H$_4$–3-C$_6$F$_{13}$)$_3$}$_3$] (14a). Obtained in 39% yield. ^{1}H NMR (D$_2$O) δ 8.20 (m, 4H). ^{19}F{^{1}H} NMR (d^6-acetone) δ −81.89 (tm, 3F, $^4J_{FF}$=10.9 Hz, CF$_3$), −111.27 (tm, 2F, $^4J_{FF}$=14.0 Hz, α-CF$_2$), −122.09 (m, 2F, CF$_2$), −122.48 (m, 2F, CF$_2$), −123.67 (m, 2F, CF$_2$), −126.90 (m, 2F, CF$_2$). ^{31}P{^{1}H} NMR (CDCl$_3$) δ 119.0 (dt, 1P, $^1J_{RhP}$=276 Hz, $^2J_{PP}$=45 Hz, P *trans*-Cl), 113.6 (dd, 2P, $^1J_{RhP}$=227 Hz, $^2J_{PP}$=45 Hz, P *trans*-P). MS (FAB) *m/z* 3896 (M−Cl$^+$).

4.5.2. RhCl{P(OC$_6$H$_4$–4-C$_6$F$_{13}$)$_3$}$_3$] (14b). Obtained in 71% yield. ^{1}H NMR (CDCl$_3$) δ 7.68 (d, 4H, $^3J_{HH}$=8.7 Hz, 2,6-H's), 7.61 (d, 2H, $^3J_{HH}$=8.6 Hz, 2,6-H's), 7.42 (d, 4H, $^3J_{HH}$=8.6 Hz, 3,5-H's), 7.37 (d, 2H, $^3J_{HH}$=8.7 Hz, 3,5-H's). ^{19}F{^{1}H} NMR (CDCl$_3$) δ −82.13 (tm, 3F, $^4J_{FF}$=10.0 Hz, CF$_3$), −110.53 (tm, 2F, $^4J_{FF}$=14.0 Hz, α-CF$_2$), −122.03 (m, 2F, CF$_2$), −122.63 (m, 2F, CF$_2$), −123.59 (m, 2F, CF$_2$), −126.66 (m, 2F, CF$_2$). ^{31}P{^{1}H} NMR (CDCl$_3$) δ 121.2 (dt, 1P, $^1J_{RhP}$=286 Hz, $^2J_{PP}$=53 Hz, P *trans*-Cl), 113.6 (dd, 2P, $^1J_{RhP}$=225 Hz, $^2J_{PP}$=53 Hz, P *trans*-P). MS (FAB) *m/z* 3896 (M−Cl$^+$). Anal. calcd for C$_{108}$H$_{36}$ClF$_{117}$O$_9$P$_3$Rh: C, 32.97; H, 0.92; Cl, 0.90; found: C, 32.83; H, 0.83; Cl, 1.10%.

4.6. Crystal data for [Cp*RhCl$_2${P(OC$_6$H$_4$–4-C$_6$F$_{13}$)$_3$}].C$_3$H$_6$O (9c)

C$_{49}$H$_{33}$Cl$_2$F$_{39}$O$_4$PRh, M=1631.53, monoclinic, space group C2/c, a=38.221(4), b=15.676(2), c=22.579(2) Å, β=119.641(1)°, U=11758(3) Å^3 (by least squares refinement of the setting angles of 41 reflections in the 2θ range 5.24–12.49), T=190(2) K, graphite-monochromated Mo Kα radiation, λ=0.71073 Å, Z=8, D_c=1.843 g cm^{-3}, F(000)=6432, dimensions 0.39×0.31×0.27 mm, μ(Mo Kα)=0.577 mm^{-1}, semi-empirical absorption correction based on ψ scans, maximum and minimum transmission factors of 0.831 and 0.807 respectively, Siemens P4 diffractometer, ω scans, data collection range θ=2.6–25.0°, −1≤h≤45, −1≤k≤18, −26≤l≤23, no crystal decay was detected from periodically measured check reflections; 10247 reflections were measured and 9429 were unique (R_{int}=0.0336). The data were corrected for Lorentz and polarisation effects.

4.7. Structure solution and refinement for [Cp*RhCl$_2${P(OC$_6$H$_4$–4-C$_6$F$_{13}$)$_3$}].C$_3$H$_6$O (9c)

Structure solution by Patterson methods and structure refinement on F^2 employed SHELXTL/PC version 5.0.[31] All hydrogen atoms were included in calculated positions (C–H=0.96 Å) with isotropic displacement parameters set to 1.5 U_{eq}(C) for methyl H atoms and 1.2U_{eq}(C) for all other H atoms. All non-H atoms were refined with anisotropic displacement parameters. Final, R_1=0.102, wR_2=0.288 (0.163 and 0.363, respectively, for all data) for 829 variables. The final residual Fourier map showed peaks of 1.960 (1.60 Å from P1) and −1.708 eÅ^{-3}.

5. Conclusion

The coordination of a series of *ortho*-, *meta*- and *para*-perfluoroalkyl-substituted triaryl phosphites to platinum metal centres is readily achieved. Spectroscopic and structural data for the metal complexes indicate that complete electronic insulation of the phosphorus(III) centres is not achieved.

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