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Coordination chemistry of perfluoroalkylated phosphorus(III) ligands

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ABSTRACT

Palladium(II), platinum(II), rhodium(I), rhodium(III) and iridium(III) complexes of the tridecafluorohexyl-derivatised diphenylethylphosphinite ($PPh_2OC_2H_4R_f$), phenyldiethylphosphonite $\{PPh(OC_2H_4R_f)_2\}$, triethylphosphite $\{P(OC_2H_4R_f)_3\}$, triphenylphosphinite ($PPh_2OC_6H_4$-4-R_f), triphenylphosphonite $\{PPh(OC_6H_4\text{-}4\text{-}R_f)_2\}$, ethyldiphenylphosphine ($PPh_2C_2H_4R_f$), diethylphenylphosphine $\{PPh(C_2H_4R_f)_2\}$ and triethylphosphine $\{P(C_2H_4R_f)_3\}$ ligands are synthesized by conventional ligand displacement and/or halide-bridge cleaved reactions, and their spectroscopic parameters are compared with those for the related ligands lacking the tridecafluorohexyl ponytails.

1. Introduction

Since the introduction of *fluorous* chemistry by Horváth and Rábai [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]. Phosphorus(III) ligands, primarily due to the widespread application in catalytic applications, have been the most extensively studied ligand class in fluorous chemistry, with considerable attention attached to electronically insulating the donor atom from the perfluoroalkyl substituents [5,6,11,12]. Theoretical calculations [13–15] and experimental studies, on alkyl- and aryl-phosphines, sometimes even with sophisticated spacer units [5,6,12,16–18], and triarylphosphites [19–22] have shown that complete electronic insulation is difficult, if not impossible. Recent work has inverted this rationale, by seeking to exploit this electronic influence to benefit the catalytic activity [23,24]. In order to be able to fully utilize such an electronic effect, it is necessary to have genuine insight into the influence of the perfluoroalkyl substituents and, here, we describe the coordination chemistry of a comprehensive series of perfluoroalkylated phosphorus(III) ligands with C_2H_4 and OC_2H_4 spacer units for comparison with our previously published C_6H_4 and OC_6H_4 systems.

2. Results and discussion

The preparation and characterization of the 1*H*,1*H*,2*H*,2*H*-tridecafluorooctyl-phosphine, phosphinite, phosphonite and phosphite ligands (**L1**–**L6**) and the related *para*-tridecafluorophenyl-phosphinite and phosphonite ligands (**L7**, **L8**) have been described previously [11]. We have shown that spectroscopic and structural properties of transition metal complexes [10] provide a clear guide to the electronic and steric impact of perfluoroalkyl substituents on the donor properties of ligands. For the most part, ligands (**L1**–**L8**) react with platinum metal starting materials in the same way as other phosphorus(III) ligands (Scheme 1); i.e. substitution of weakly coordinated ligands and cleavage of halide-bridged dimers. The new metal complexes (**1**–**52**) synthesized in this work have been characterized by a combination of elemental analysis, IR spectroscopy, mass spectrometry and multinuclear NMR spectroscopies (Table 1).

For the $[PtCl_2L_2]$ series (**1**–**8**), the thermodynamically favoured *cis*-isomers, clearly identified by the presence of two resonances assigned as ν(M-Cl) stretching vibrations in the IR spectra and large $^1J_{PtP}$ coupling constants (*ca.* L = phosphine, J = 3500–3600 Hz; L = phosphinite, J = 4100–4200 Hz; L = phosphonite, J = 4700–4900 Hz) are formed in all cases except when $L = P(C_2H_4C_6F_{13})_3$ (**L3**). Here, the single IR active M-Cl vibration together with

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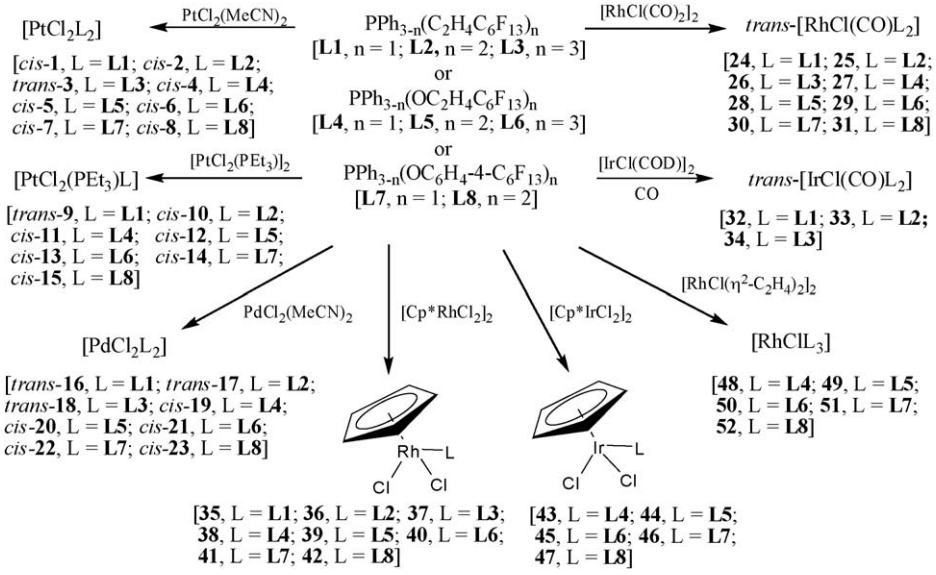

Scheme 1.

$^{1}J_{PtP}$ = 2941 Hz indicate formation of *trans*-[$PtCl_2L_2$] (**3**). Previously, we have reported the formation of *trans*-isomers in comparable reactions of the bulky phosphite ligand $P(OC_6H_4\text{-}2\text{-}C_6F_{13})_3$ [22] or phosphine ligands $P(C_6H_4\text{-}4\text{-}C_6F_{13})_3$ [5] and $P(C_6H_4\text{-}3\text{-}C_6F_{13})_3$ [12], and presume that formation of *trans*-[$PtCl_2\{P(C_2H_4C_6F_{13})_3\}_2$] (**3**) here is similarly related to the bulk of this tris-perfluoroalkylated ligand. We have previously highlighted the diastereotopic nature of the OCH_2 and CH_2CF_2 protons in the ^{1}H NMR spectrum of the free dialkylphosphonite ligand (**L5**) [11]. This effect is observed in the ^{1}H NMR spectrum of the platinum(II) dichloride complex of this ligand, (**5**), and all the other metal complexes of this ligand (**12**, **20**, **28**, **39**, **44**, **49**) prepared in this work. For illustration, the ^{1}H NMR spectrum of (**5**) reveals mutually coupled highly second order resonances for at 4.41 and 4.17 ppm associated with the OCH_2 protons and complicated overlapping multiplets for the CH_2CF_2 protons at 2.37 ppm. Here, for the first time, the diastereotopic inequivalence of the substituents along the carbon chain is also evident in the α-CF_2 resonances in the $^{19}F\{^{1}H\}$ NMR spectrum which appear as a highly asymmetric AB multiplet with $^{2}J_{FF}$ = 272 Hz.

Cleavage of the halide-bridges in $[PtCl_2(PEt_3)]_2$ with the phosphorus(III) ligands generates the related *cis*-[$PtCl_2(PEt_3)L$] complexes (**10**–**15**) with diagnostic $^{1}J_{PtP}$ and $^{2}J_{PP}$ coupling constants. Interestingly, $\Delta^{31}P$ for (**10**–**15**) ($\Delta^{31}P = \delta^{31}P_{complex} - \delta^{31}P_{ligand}$) are virtually identical to those for the related bis-complexes (**2**, **4**–**8**). In marked contrast, the NMR spectral data for the product (**9**) from the reaction of $[PtCl_2(PEt_3)]_2$ with $PPh_2C_2H_4C_6F_{13}$ (**L1**) are conspicuously different. The $^{31}P\{^{1}H\}$ NMR spectrum is a highly asymmetric AB pattern in which $^{1}J_{PtP}$ (2500 Hz, **L1**; 2455 Hz, PEt_3) and $^{2}J_{PP}$ (515 Hz) are assignable to the *trans*-[$PtCl_2(PEt_3)(PPh_2C_2H_4C_6F_{13})$] species (**9**). However, the formation of exclusively the *trans*-isomer in this particular reaction cannot be ascribed to the steric bulk of the incoming ligand, and must be a consequence of some highly specific electronic effect.

Turning now to the palladium(II) complexes, ^{31}P NMR chemical shifts and ν(Pd-Cl) absorptions in the infra-red spectra reveal *trans*-geometries for [$PdCl_2L_2$] (L = phosphine; **16**–**18**) and *cis*-geometries (L = phosphinite, phosphonite, phosphite; **19**–**23**), in line with the relative *trans*-effect for these ligands at palladium(II). Here, the reactions of [$PdCl_2(MeCN)_2$] with the ligands were unremarkable, except in the reaction of the triarylphosphinite (**L7**) where the crude ^{1}H NMR spectrum was complicated and the $^{31}P\{^{1}H\}$ NMR spectrum revealed two singlet resonances at δ 113.1 and 78.2 in an approximate 2:1 ratio. The desired product, (**22**), a pale yellow solid, and this impurity, pale yellow crystals, were readily separated by fractional crystallization from acetone. The ^{19}F NMR spectrum of the impurity had no resonances and a single crystal X-ray structural determination revealed the product to be the previously synthesized [25] and structurally characterized [26] chloride bridged dimer $[Pd_2Cl_2\{Ph_2PO\cdots H\cdots OPPh_2\}]$ containing two diphenylphosphinito groups from which the perfluoroalkyl-substituted aryl rings have, apparently, been hydrolysed. The providence of such a hydrolysis is unclear, since no related hydrolytic reactions were observed in any other reactions of **L7**, or indeed any of the, more hydrolytically unstable, phosphonite or phosphite ligands in this work.

Cleavage of the halide-bridges in $[RhCl(CO)_2]_2$ with the monodentate phosphorus(III) ligands readily generates the *trans*-[$RhCl(CO)L_2$] (**24**–**31**); the members of this series (**26**) [27,28], (**27**) and (**29**) [29] have been described previously. *trans*-[$IrCl(CO)L_2$] (L = **L1**, **L2**, **L3**; **32**, **33**, **34**) are prepared by carbonylation of the product from the cleavage of $[IrCl(COD)]_2$ with the respective phosphines; *trans*-[$IrCl(CO)(\mathbf{L3})_2$] (**34**) has been described previously [28]. For these complexes, the spectroscopic parameters ($^{1}J_{RhP}$, ν(CO)) are highly consistent with each of the aryl/alkyl-phosphine, -phosphinite and -phosphonite ligand classes; however, we note a significant difference for our perfluoroalkylated phosphite ligands where, whilst *trans*-[$RhCl(CO)(\mathbf{L6})_2$] (**29**) is generated in high yield, the analogous reaction with $L = P(OC_6H_4\text{-}4\text{-}C_6F_{13})_3$ yields exclusively the halide-bridged dimeric $[RhClL_2]_2$ [22].

The piano-stool [Cp^*MCl_2L] {M = Rh (**35**–**42**); M = Ir (**43**–**47**)}, similarly formed by halide-bridge cleavage reactions in high yields, display comparable spectroscopic data for each of the three ligand classes (Table 1). Finally, although the combined ligand displacement and halide-bridge cleavage reactions of $[Rh(\eta^2\text{-}C_2H_4)_2Cl]_2$ with an excess of each of the ligands (**L1**–**L8**) readily afforded the tris-ligand complexes [$RhClL_3$], only the phosphinite, phosphinite and phosphite ligands generated analytically pure and sufficiently solution stable products (**48**–**52**) to allow full characterization. Here, the complexes are readily identified from mutually coupled resonances in the $^{31}P\{^{1}H\}$ NMR spectra where $^{1}J_{RhP}$ vary systematically with both the donor ligand ($J_{phosphite} > J_{phosphonite} > J_{phosphinite}$) and *trans*-ligand ($J_{trans\text{-}Cl} > J_{trans\text{-}P}$) in line with the established ligand effects at rhodium(III).

Table 1
Spectroscopic data for selected metal complexes containing perfluoroalkylated ligands and some related perprotio congeners.

	Ligand	$PtCl_2L_2$[a]			*trans*-$[RhCl(CO)L_2]$				Cp^*RhCl_2L		
	δ(P)	δ(P)	Δ(P)[b]	$^1J_{PtP}$	δ(P)	Δ(P)[b]	$^1J_{RhP}$	ν(CO)	δ(P)	Δ(P)[b]	$^1J_{RhP}$
Phosphines											
PEt_3	−20.4	12.3[c]	32.7	2400	23.6[d]	44.0	117	1956[e]	28.0[f]	48.4	138
$P(CH_2CH_2C_6F_{13})_3$ (**L3**)	−25.0	11.8[g]	36.9	2491	22.8[h]	47.8	121	1990	19.4	44.4	147
$PPhEt_2$	−17.1	3.3[i]	20.4	3530	24.6[d]	40.6	121	1951[j]	11.4[k]	58.3	136
$PPh(CH_2CH_2C_6F_{13})_2$ (**L2**)	−23.0	−0.6	22.4	3518	22.8	45.8	125	1983	18.3	41.3	146
PPh_2Et	−12.5	9.8[i]	22.3	3640	27.1[d]	39.1	122	1960[l]	22.4[m]	50.5	146
$PPh_2(CH_2CH_2C_6F_{13})$ (**L1**)	−16.0	5.8	21.8	3630	24.5	40.5	125	1981	27.3	43.3	144
$P(C_6H_4\text{-}4\text{-}C_6F_{13})_2Et$	−10.8	11.7[n]	22.5	3617	27.0[n]	38.7	126	1984	34.3[n]	45.1	146
PPh_3	−5.0	13.9[o]	18.9	3676	28.9[d]	33.9	129	1962	30.2[p]	35.2	144
$P(C_6H_4\text{-}4\text{-}C_6F_{13})_3$	−6.0	15.5[p]	21.5	3631	30.0[p]	36.0	131	1993	29.6[p]	35.6	147
Phosphinites											
PPh_2OEt	109.8	81.1[q]	−28.7	4185	n.r.[r]				n.r.[r]		
$PPh_2(OCH_2CH_2C_6F_{13})$ (**L4**)	116.5	86.2	−30.3	4141	121.1	4.6	136	1990	117.1	0.6	157
$PPh_2(OPh)$	111.1	n.r.[r]			123.0[s]	11.9	143	1991	113.5[t]	2.4	171
$PPh_2(OC_6H_4\text{-}4\text{-}C_6F_{13})$ (**L7**)	112.6	87.6	−25.0	4189	125.0	12.4	141	1996	116.7	4.1	171
Phosphonites											
$PPh(OEt)_2$	153.5	92.2[u]	−61.3	4817	n.r.[r]				n.r.[r]		
$PPh(OCH_2CH_2C_6F_{13})_2$ (**L5**)	156.7	100.0	−56.7	4754	153.7	−3.0	167	2008	147.4	−9.3	181
$PPh(OPh)_2$	158.5	n.r.[r]			n.r.[r]				140.5[t]	−18.0	200
$PPh(OC_6H_4\text{-}4\text{-}C_6F_{13})_2$ (**L8**)	159.1	95.0	−64.1	4859	149.3	−9.8	176	2013	145.8	−13.3	203
Phosphites											
$P(OMe)_3$	141.1	73.8[v]	−67.3	5705	130.5[d]	−10.6	195	2006[e]	119.8[w]	−21.3	218
$P(OCH_2CH_2C_6F_{13})_3$ (**L6**)	139.4	n.r.[r]			128.7	−10.7	199	2036	120.3	−19.1	224
$P(OPh)_3$	127.8	59.4[v]	−68.4	5800	115.2[d]	−12.6	217	2016[e]	104.2[x]	−23.6	240
$P(OC_6H_4\text{-}4\text{-}C_6F_{13})_3$	125.0	65.4[y]	−59.6	5660	n.r.[r]				106.5[y]	−18.5	245

[a] *cis*-Isomer, unless otherwise stated.
[b] $\Delta(P) = \delta(P_{complex}) - \delta(P_{ligand})$.
[c] *trans*-isomer; data taken from Ref. [34].
[d] Data taken from Ref. [35].
[e] Data taken from Ref. [36].
[f] Data taken from Ref. [37].
[g] *trans*-Isomer.
[h] Data taken from Ref. [27].
[i] Data taken from Ref. [38].
[j] Data taken from Ref. [39].
[k] L = $PPhMe_2$; data taken from Ref. [40].
[l] Data taken from Ref. [41].
[m] L = PPh_2Me; data taken from Ref. [39].
[n] Data taken from Ref. [41].
[o] Data taken from Ref. [42].
[p] Data taken from Ref [5].
[q] Data taken from Ref. [43].
[r] Not reported in the literature.
[s] Data taken from Ref. [44].
[t] Data taken from Ref. [45].
[u] Data taken from Ref. [46].
[v] Data taken from Ref. [47].
[w] Data taken from Ref. [48].
[x] Data taken from Ref. [49].
[y] Data taken from Ref. [22].

In Table 1 we have brought together not only details of the spectroscopic data for three of the different classes of metal complex synthesized in this work, but also those for the related ligands without ponytails where available; for example, we list data for trimethylphosphite platinum and rhodium complexes since either the analogous triethylphosphite complexes have not been reported or key pieces of significant spectroscopic data are missing. Although the comparative data are less comprehensive for the PO-donor ligands than those for the phosphines, the analysis reveals that the incorporation of the perfluoroalkyl groups has, relatively, little impact upon the spectroscopic parameters. For example, Δ(P) for *cis*-$[PtCl_2L_2]$ {20 ± 2 ppm (phosphines); -27.5 ± 2.5 ppm (phosphinites); -60 ± 4 ppm (phosphonites); -64 ± 4 ppm (phosphites)} and $^1J_{RhP}$ for Cp^*RhCl_2L {142 ± 5 Hz (phosphines); 164 ± 7 Hz (phosphinites); 192 ± 11 Hz (phosphonites); 232 ± 14 Hz (phosphites)} occur within distinct regions. Within each series, as expected, the inclusion of perfluoroalkyl groups does cause the spectroscopic probe to shift (up or down) in line with the reduction in the σ-donor strength of the ligand, and this effect becomes more pronounced as the number of perfluoroalkyl groups increases; the ranges for the tris-derivatised phosphites are larger than those for the mono-derivatised phosphinites. However, these variations often amount to little more than 2–5% of the numerical magnitude of the particular experimentally observed parameter, some of which is within the inherent error in data acquisition. This observation is broadly in line with conclusions drawn from crystallographic studies of perfluoroalkylated and perprotio metal complexes [5–9,22,28], where variations in the bond lengths and bond angles in the first coordination spheres of the metal centres are minimal, suggesting that differences in catalytic activity between fluorous and non-fluorous metal complexes [30–32] may arise from other factors such as solubilities, clustering, catalyst/ligand mobility and solvent effects rather than the modest changes in electronic properties of the metal centres in such species.

3. Conclusions

Phosphine, phosphinite, phosphonite and phosphite ligands containing between one and three tridecafluorohexyl ponytails react readily with conventional platinum group metal starting materials to generate a range of perfluoroalkylated metal complexes either by ligand displacement, halide-bridge cleavage or a combination of these processes. The complexes have been characterized spectroscopically and their spectroscopic data compared with closely related metal complexes. This analysis reveals that the introduction of perfluoroalkyl substituents has a relatively minor impact upon the donor properties of these ligands with platinum group metals.

4. Experimental

4.1. General experimental procedures

Proton, ^{19}F and ^{31}P NMR spectroscopic studies were carried out on a Bruker DPX300 spectrometer at 300.14, 282.41 and 121.50 MHz. All chemical shifts are quoted in ppm using the high-frequency positive convention; ^{1}H 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 London Metropolitan University. Mass spectra were recorded on a Kratos Concept 1H mass spectrometer. IR spectra were recorded on a Digilab FTS40 spectrometer. Ligands **L1**–**L8** were prepared by the literature procedure [11]. Solvents were distilled under nitrogen from appropriate drying agents and degassed prior to use [33].

4.1.1. *cis*-[$PtCl_2(PPh_2C_2H_4C_6F_{13})_2$] (1)

cis-[$PtCl_2(MeCN)_2$] (0.105 g, 0.30 mmol) and $PPh_2(C_2H_4C_6F_{13})$ (0.346 g, 0.65 mmol) in dry dichloromethane (60 cm^3) were refluxed under nitrogen for 2 h. The solvent was removed *in vacuo* and the resulting off-white solid washed with light petroleum ether (bp 40–60 °C) (10 cm^3). Recrystallization from dichloromethane/hexane afforded the product as a fine white powder (0.311 g, 78%). Anal. Calc. for $C_{40}H_{28}Cl_2F_{26}P_2Pt$: C, 36.1; H, 2.1. Found: C, 35.9; H, 2.1. *m/z* (FAB) 1330 (M^+), 1295 ([M−Cl]$^+$). ^{1}H NMR (CD_2Cl_2) 7.59 (12H, m, 3-/4-C_6H_5), 7.30 (8H, m, 2-C_6H_5), 2.71 (4H, t, $^{3}J_{HH}$ = 10.2 Hz, PCH_2), 2.40 (4H, m, CH_2CF_2). $^{19}F\{^{1}H\}$ NMR (CD_2Cl_2) −81.13 (6F, t, $^{4}J_{FF}$ = 10.0 Hz, CF_3), −114.74 (4F, t, $^{4}J_{FF}$ = 14.1 Hz, α-CF_2), −122.13 (4F, m, CF_2), −123.07 (4F, m, CF_2), −123.33 (4F, m, CF_2), −126.35 (4F, m, CF_2). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2) 5.76 (s, $^{1}J_{PtP}$ = 3630 Hz). IR (Nujol) 317, 292 cm^{-1} [ν(M-Cl)].

4.1.2. *cis*-[$PtCl_2\{PPh(C_2H_4C_6F_{13})_2\}_2$] (2)

The title compound was prepared similarly as a fine white powder (0.365 g, 65%). Anal. Calc. for $C_{44}H_{26}Cl_2F_{52}P_2Pt$: C, 28.2; H, 1.4. Found: C, 27.4; H, 1.5. *m/z* (FAB) 1870 (M^+), 1835 ([M−Cl]$^+$). ^{1}H NMR (CD_2Cl_2) 7.46 (6H, m, 3-/4-C_6H_5), 7.31 (4H, m, 2-C_6H_5), 2.61 (8H, t, $^{3}J_{HH}$ = 8.2 Hz, PCH_2), 2.37 (8H, m, CH_2CF_2). $^{19}F\{^{1}H\}$ NMR (CD_2Cl_2) −80.92 (12F, t, $^{4}J_{FF}$ = 10.0 Hz, CF_3), −114.64 (8F, t, $^{4}J_{FF}$ = 14.0 Hz, α-CF_2), −121.75 (8F, m, CF_2), −122.71 (8F, m, CF_2), −123.12 (8F, m, CF_2), −126.12 (8F, m, CF_2). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2) −0.58 (s, $^{1}J_{PtP}$ = 3518 Hz). IR (Nujol) 317, 291 cm^{-1} [ν(M-Cl)].

4.1.3. *trans*-[$PtCl_2\{P(C_2H_4C_6F_{13})_3\}_2$] (3)

The title compound was prepared similarly as a fine white powder (0.423 g, 60%). Anal. Calc. for $C_{48}H_{24}Cl_2F_{78}P_2Pt$: C, 23.9; H, 1.0. Found: C, 23.7; H, 1.2. *m/z* (FAB) 2410 (M^+). ^{1}H NMR (CD_3COCD_3) 2.64 (12H, m, PCH_2), 2.30 (12H, m, CH_2CF_2). $^{19}F\{^{1}H\}$ NMR (CD_3COCD_3) −80.96 (18F, t, $^{4}J_{FF}$ = 8.4 Hz, CF_3), −114.38 (12F, t, $^{4}J_{FF}$ = 13.8 Hz, α-CF_2), −121.71 (12F, m, CF_2), −122.73 (12F, m, CF_2), −123.09 (12F, m, CF_2), −126.11 (12F, m, CF_2). $^{31}P\{^{1}H\}$ NMR (CD_3COCD_3) 11.79 (s, $^{1}J_{PtP}$ = 2491 Hz). IR (Nujol) 354 cm^{-1} [ν(M-Cl)].

4.1.4. *cis*-[$PtCl_2(PPh_2OC_2H_4C_6F_{13})_2$] (4)

The title compound was prepared similarly as a fine pale yellow solid (0.332 g, 77%). Anal. Calc. for $C_{40}H_{28}Cl_2F_{26}O_2P_2Pt$: C, 35.3; H, 2.1. Found: C, 34.7; H, 1.9. *m/z* (FAB) 1327 ([M−Cl]$^+$). ^{1}H NMR ($CDCl_3$) 7.84 (8H, m, 2-C_6H_5), 7.53 (12H, m, 3-/4-C_6H_5), 3.99 (4H, q, $^{3}J_{HH}$ = $^{3}J_{PH}$ = 6.3 Hz, OCH_2), 2.07 (4H, tt, $^{3}J_{FH}$ = 18.4 Hz, $^{3}J_{HH}$ = 6.3 Hz, CH_2CF_2). $^{19}F\{^{1}H\}$ NMR ($CDCl_3$) −81.39 (6F, tt, $^{4}J_{FF}$ = 10.0 Hz, $^{3}J_{FF}$ = 2.0 Hz, CF_3), −113.99 (4F, t, $^{4}J_{FF}$ = 12.6 Hz, α-CF_2), −122.44 (4F, m, CF_2), −123.44 (4F, m, CF_2), −124.21 (4F, m, CF_2), −126.71 (4F, m, CF_2). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$) 86.23 (s, $^{1}J_{PtP}$ = 4141 Hz). IR (Nujol) 317, 292 cm^{-1} [ν(M-Cl)].

4.1.5. *cis*-[$PtCl_2\{PPh(OC_2H_4C_6F_{13})_2\}_2$] (5)

The title compound was prepared similarly as a fine white solid (0.183 g, 63%). Anal. Calc. for $C_{44}H_{26}Cl_2F_{52}O_4P_2Pt$: C, 27.3; H, 1.3. Found: C, 27.4; H, 1.3. *m/z* (FAB) 1899 ([M−Cl]$^+$), 1863 ([M−2Cl]$^+$). ^{1}H NMR ($CDCl_3$) 7.71 (4H, m, 2-C_6H_5), 7.49 (6H, m, 3-/4-C_6H_5), 4.41 (4H, m, OC*H*), 4.17 (4H, m, OC*H*), 2.37 (8H, m, CH_2CF_2). $^{19}F\{^{1}H\}$ NMR ($CDCl_3$) −81.44 (12F, m, CF_3), −113.86 (4F, dt, $^{2}J_{FF}$ = 272 Hz, $^{4}J_{FF}$ = 14.1 Hz, α-CF), −114.11 (4F, dt, $^{2}J_{FF}$ = 272 Hz, $^{4}J_{FF}$ = 14.1 Hz, α-CF), −122.48 (8F, m, CF_2), −123.49 (8F, m, CF_2), −124.12 (8F, m, CF_2), −126.76 (8F, m, CF_2). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$) 100.03 (s, $^{1}J_{PtP}$ = 4754 Hz). IR (Nujol) 322, 301 cm^{-1} [ν(M-Cl)].

4.1.6. *cis*-[$PtCl_2\{P(OC_2H_4C_6F_{13})_3\}_2$] (6)

The title compound was prepared similarly as a clear colourless oil (0.246 g, 90%). *m/z* (FAB) 2471 ([M−Cl]$^+$), 2435 ([M−2Cl]$^+$). ^{1}H NMR (CD_3COCD_3) 4.63 (12H, m, OCH_2), 2.25 (12H, tt, $^{3}J_{FH}$ = 18.6 Hz, $^{3}J_{HH}$ = 6.1 Hz, CH_2CF_2). $^{19}F\{^{1}H\}$ NMR (CD_3COCD_3) −74.78 (18F, m, CF_3), −106.85 (12F, m, α-CF_2), −115.23 (12F, m, CF_2), −116.87 (12F, m, CF_2), −119.77 (12F, m, CF_2), −126.29 (12F, m, CF_2).

4.1.7. *cis*-[$PtCl_2(PPh_2OC_6H_4$-4-$C_6F_{13})_2$] (7)

The title compound was prepared similarly as a fine white solid (0.304 g, 72%). Anal. Calc. for $C_{48}H_{28}Cl_2F_{26}O_4P_2Pt$: C, 39.5; H, 1.9. Found: C, 39.8; H, 1.7. *m/z* (FAB) 1423 ([M−Cl]$^+$), 1387 ([M−2Cl]$^+$). ^{1}H NMR ($CDCl_3$) 7.54 (8H, m, 2-C_6H_5), 7.32 (4H, d, $^{3}J_{HH}$ = 8.7 Hz, 3-C_6H_4), 7.22 (12H, m, 3-/4-C_6H_5), 6.63 (4H, d, $^{3}J_{HH}$ = 8.7 Hz, 2-C_6H_4). $^{19}F\{^{1}H\}$ NMR ($CDCl_3$) −81.21 (6F, t, $^{4}J_{FF}$ = 10.6 Hz, CF_3), −110.55 (4F, t, $^{4}J_{FF}$ = 14.1 Hz, α-CF_2), −121.84 (4F, m, CF_2), −122.27 (4F, m, CF_2), −123.22 (4F, m, CF_2), −126.55 (4F, m, CF_2). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$) 87.60 (s, $^{1}J_{PtP}$ = 4189 Hz). IR (Nujol) 315, 290 cm^{-1} [ν(M-Cl)].

4.1.8. *cis*-[$PtCl_2\{PPh(OC_6H_4$-4-$C_6F_{13})_2\}_2$] (8)

The title compound was prepared similarly as a fine white solid (0.213 g, 61%). Anal. Calc. for $C_{60}H_{26}Cl_2F_{52}O_2P_2Pt$: C, 33.9; H, 1.2. Found: C, 33.9; H, 1.1. *m/z* (FAB) 2091 ([M−Cl]$^+$), 2055 ([M−2Cl]$^+$). ^{1}H NMR ($CDCl_3$) 7.49 (4H, m, 2-C_6H_5), 7.41 (8H, d, $^{3}J_{HH}$ = 8.8 Hz, 3-C_6H_4), 7.26 (6H, m, 3-/4-C_6H_5), 7.05 (8H, d, $^{3}J_{HH}$ = 8.8 Hz, 2-C_6H_4). $^{19}F\{^{1}H\}$ NMR ($CDCl_3$) −81.33 (12F, tt, $^{4}J_{FF}$ = 10.1 Hz, $^{3}J_{FF}$ = 2.2 Hz, CF_3), −110.78 (8F, t, $^{4}J_{FF}$ = 14.1 Hz, α-CF_2), −121.90 (8F, m, CF_2), −122.23 (8F, m, CF_2), −123.27 (8F, m, CF_2), −126.60 (8F, m, CF_2). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$) 94.99 (s, $^{1}J_{PtP}$ = 4859 Hz). IR (Nujol) 327, 305 cm^{-1} [ν(M-Cl)].

4.1.9. *trans*-[$PtCl_2(PEt_3)(PPh_2C_2H_4C_6F_{13})$] (9)

A slurry of [{PtCl(μ-Cl)(PEt_3)}$_2$] (0.150 g, 0.20 mmol) and the ligand (0.266 g, 0.50 mmol) in dry dichloromethane (30 cm^3) were refluxed under nitrogen for 10 min to give a clear solution. Concentration of the solution *in vacuo* and addition of light petroleum (bp 40–60 °C) (10 cm^3) afforded the product as a fine

white solid (0.245 g, 67%). Anal. Calc. for $C_{26}H_{29}Cl_2F_{13}P_2Pt$: C, 34.1; H, 3.2. Found: C, 34.1; H, 3.2. *m/z* (FAB) 881 ([M−Cl]$^+$). ^{1}H NMR ($CDCl_3$) 7.75 (4H, m, 2-C_6H_5), 7.42 (6H, m, 3-/4-C_6H_5), 2.70 (2H, m, PCH_2), 2.38 (2H, m, CH_2CF_2), 1.92 (6H, dq, $^2J_{PH}$ = 10.0 Hz, $^3J_{HH}$ = 7.7 Hz, PCH_2), 1.16 (9H, dt, $^3J_{PH}$ = 17.5 Hz, $^3J_{HH}$ = 7.7 Hz, CH_2CH_3). ^{19}F{^{1}H} NMR ($CDCl_3$) −81.25 (3F, tt, $^4J_{FF}$ = 9.4 Hz, $^3J_{FF}$ = 2.3 Hz, CF_3), −114.90 (2F, t, $^4J_{FF}$ = 14.1 Hz, α-CF_2), −122.36 (2F, m, CF_2), −123.31 (2F, m, CF_2), −123.59 (2F, m, CF_2), −126.59 (2F, m, CF_2). ^{31}P{^{1}H} NMR ($CDCl_3$) 13.61 (d, $^1J_{PtP}$ = 2500 Hz, $^2J_{PP}$ = 515 Hz, *P*Ph_2), 12.16 (d, $^1J_{PtP}$ = 2455 Hz, $^2J_{PP}$ = 515 Hz, *P*Et_3).

*4.1.10. cis-[$PtCl_2$(*P*Et_3){*P*Ph($C_2H_4C_6F_{13}$)$_2$}] (**10**)*

The title compound was prepared similarly as a fine white solid (0.132 g, 42%). *m/z* (EI) 1151 ([M−Cl]$^+$). ^{1}H NMR ($CDCl_3$) 7.74 (2H, m, 2-C_6H_5), 7.59 (3H, m, 3-/4-C_6H_5), 2.89 (4H, m, PCH_2), 2.42 (4H, m, CH_2CF_2), 1.80 (6H, dq, $^2J_{PH}$ = 10.1 Hz, $^3J_{HH}$ = 7.6 Hz, PCH_2), 1.15 (9H, dt, $^3J_{PH}$ = 17.4 Hz, $^3J_{HH}$ = 7.6 Hz, CH_2CH_3). ^{19}F{^{1}H} NMR ($CDCl_3$) −81.26 (6F, t, $^4J_{FF}$ = 9.4 Hz, CF_3), −114.67 (4F, t, $^4J_{FF}$ = 14.1 Hz, α-CF_2), −122.32 (4F, m, CF_2), −123.66 (8F, m, CF_2), −126.58 (4F, m, CF_2). ^{31}P{^{1}H} NMR ($CDCl_3$) 8.81 (d, $^1J_{PtP}$ = 3265 Hz, $^2J_{PP}$ = 16.0 Hz, *P*Ph_2), 2.37 (d, $^1J_{PtP}$ = 3743 Hz, $^2J_{PP}$ = 16.0 Hz, *P*Et_3).

*4.1.11. cis-[$PtCl_2$(*P*Et_3)(*P*$Ph_2OC_2H_4C_6F_{13}$)] (**11**)*

The title compound was prepared similarly as a fine white solid (0.261 g, 72%). Anal. Calc. for $C_{26}H_{29}Cl_2F_{13}OP_2Pt$: C, 33.5; H, 3.1. Found: C, 33.5; H, 2.8. *m/z* (FAB) 897 ([M−Cl]$^+$), 861 ([M−2Cl]$^+$). ^{1}H NMR ($CDCl_3$) 8.07 (4H, m, 2-C_6H_5), 7.75 (6H, m, 3-/4-C_6H_5), 4.27 (2H, q, $^3J_{HH}$ = $^3J_{PH}$ = 6.0 Hz, OCH_2), 2.48 (2H, tt, $^3J_{FH}$ = 18.4 Hz, $^3J_{HH}$ = 6.0 Hz, CH_2CF_2), 2.27 (6H, dq, $^2J_{PH}$ = 10.5 Hz, $^3J_{HH}$ = 7.6 Hz, PCH_2), 1.35 (9H, dt, $^3J_{PH}$ = 17.6 Hz, $^3J_{HH}$ = 7.6 Hz, CH_2CH_3). ^{19}F{^{1}H} NMR ($CDCl_3$) −81.21 (3F, tt, $^4J_{FF}$ = 10.0 Hz, $^3J_{FF}$ = 2.3 Hz, CF_3), −113.58 (2F, t, $^4J_{FF}$ = 13.9 Hz, α-CF_2), −122.25 (2F, m, CF_2), −123.27 (2F, m, CF_2), −124.06 (2F, m, CF_2), −126.58 (2F, m, CF_2). ^{31}P{^{1}H} NMR ($CDCl_3$) 86.61 (d, $^1J_{PtP}$ = 4342 Hz, $^2J_{PP}$ = 16.2 Hz, *P*O), 12.89 (d, $^1J_{PtP}$ = 3423 Hz, $^2J_{PP}$ = 16.2 Hz, *P*Et_3).

*4.1.12. cis-[$PtCl_2$(*P*Et_3){*P*Ph($OC_2H_4C_6F_{13}$)$_2$}] (**12**)*

The title compound was prepared similarly as a fine white solid (0.081 g, 26%). Anal. Calc. for $C_{28}H_{28}Cl_2F_{26}O_2P_2Pt$: C, 27.6; H, 2.3. Found: C, 28.0; H, 2.1. *m/z* (EI) 1183 ([M−Cl]$^+$), 1147 ([M−2Cl]$^+$). ^{1}H NMR ($CDCl_3$) 7.80 (2H, m, 2-C_6H_5), 7.59 (3H, m, 3-/4-C_6H_5), 4.67 (2H, m, OC*H*), 4.36 (2H, m, OC*H*), 2.57 (4H, m, CH_2CF_2), 2.25 (6H, dq, $^2J_{PH}$ = 10.5 Hz, $^3J_{HH}$ = 7.7 Hz, PCH_2), 1.29 (9H, dt, $^3J_{PH}$ = 17.6 Hz, $^3J_{HH}$ = 7.7 Hz, CH_2CH_3). ^{19}F{^{1}H} NMR ($CDCl_3$) −81.31 (6F, t, $^4J_{FF}$ = 10.0 Hz, CF_3), −113.84 (4F, t, $^4J_{FF}$ = 13.9 Hz, α-CF_2), −122.33 (4F, m, CF_2), −123.34 (4F, m, CF_2), −124.06 (4F, m, CF_2), −126.61 (4F, m, CF_2). ^{31}P{^{1}H} NMR ($CDCl_3$) 100.67 (d, $^1J_{PtP}$ = 4912 Hz, $^2J_{PP}$ = 16.6 Hz, *P*O$_2$), 15.60 (d, $^1J_{PtP}$ = 3383 Hz, $^2J_{PP}$ = 16.6 Hz, *P*Et_3).

*4.1.13. cis-[$PtCl_2$(*P*Et_3){*P*($OC_2H_4C_6F_{13}$)$_3$}] (**13**)*

The title compound was prepared similarly as a sticky white solid (0.187 g, 62%). Anal. Calc. for $C_{30}H_{27}Cl_2F_{39}O_3P_2Pt$: C, 23.9; H, 1.8. Found: C, 23.9; H, 1.8. *m/z* (FAB) 1469 ([M−Cl]$^+$). ^{1}H NMR ($CDCl_3$) 4.53 (6H, m, OCH_2), 2.49 (6H, tt, $^3J_{FH}$ = 18.3 Hz, $^3J_{HH}$ = 5.4 Hz, CH_2CF_2), 2.03 (6H, dq, $^2J_{PH}$ = 10.7 Hz, $^3J_{HH}$ = 7.6 Hz, PCH_2), 1.10 (9H, dt, $^3J_{PH}$ = 17.9 Hz, $^3J_{HH}$ = 7.6 Hz, CH_2CH_3). ^{19}F{^{1}H} NMR ($CDCl_3$) −81.48 (9F, tt, $^4J_{FF}$ = 10.0 Hz, $^3J_{FF}$ = 2.3 Hz, CF_3), −113.93 (6F, t, $^4J_{FF}$ = 14.0 Hz, α-CF_2), −122.46 (6F, m, CF_2), −123.48 (6F, m, CF_2), −124.14 (6F, m, CF_2), −126.78 (6F, m, CF_2). ^{31}P{^{1}H} NMR ($CDCl_3$) 75.28 (d, $^1J_{PtP}$ = 5875 Hz, $^2J_{PP}$ = 21.2 Hz, *P*O$_3$), 16.72 (d, $^1J_{PtP}$ = 3288 Hz, $^2J_{PP}$ = 21.2 Hz, *P*Et_3).

*4.1.14. cis-[$PtCl_2$(*P*Et_3)(*P*$Ph_2OC_6H_4$-4-C_6F_{13})] (**14**)*

The title compound was prepared similarly as a fine white solid (0.322 g, 83%). Anal. Calc. for $C_{30}H_{29}Cl_2F_{13}OP_2Pt$: C, 36.7; H, 3.0. Found: C, 37.2; H, 2.7. *m/z* (FAB) 945 ([M−Cl]$^+$), 909 ([M−2Cl]$^+$). ^{1}H NMR ($CDCl_3$) 7.62 (4H, m, 2-C_6H_5), 7.22 (8H, m, 3-C_6H_4, 3-/4-C_6H_5), 6.96 (2H, d, $^3J_{HH}$ = 8.2 Hz, 2-C_6H_4), 1.79 (6H, dq, $^2J_{PH}$ = 10.2 Hz, $^3J_{HH}$ = 7.6 Hz, PCH_2), 0.80 (9H, dt, $^3J_{PH}$ = 17.6 Hz, $^3J_{HH}$ = 7.6 Hz, CH_2CH_3). ^{19}F{^{1}H} NMR ($CDCl_3$) −81.28 (3F, tt, $^4J_{FF}$ = 10.6 Hz, $^3J_{FF}$ = 2.1 Hz, CF_3), −110.93 (2F, t, $^4J_{FF}$ = 14.6 Hz, α-CF_2), −121.84 (2F, m, CF_2), −122.44 (2F, m, CF_2), −123.25 (2F, m, CF_2), −126.58 (2F, m, CF_2). ^{31}P{^{1}H} NMR ($CDCl_3$) 88.68 (d, $^1J_{PtP}$ = 4189 Hz, $^2J_{PP}$ = 15.9 Hz, *P*O), 12.56 (d, $^1J_{PtP}$ = 3356 Hz, $^2J_{PP}$ = 15.9 Hz, *P*Et_3).

*4.1.15. cis-[$PtCl_2$(*P*Et_3){*P*Ph(OC_6H_4-4-C_6F_{13})$_2$}] (**15**)*

The title compound was prepared similarly as a fine white solid (0.233 g, 56%). Anal. Calc. for $C_{36}H_{28}Cl_2F_{26}O_2P_2Pt$: C, 32.9; H, 2.1. Found: C, 33.2; H, 2.1. *m/z* (EI) 1279 ([M−Cl]$^+$), 1243 ([M−2Cl]$^+$). ^{1}H NMR ($CDCl_3$) 7.77 (2H, m, 2-C_6H_5), 7.49 (4H, d, $^3J_{HH}$ = 8.8 Hz, 3-C_6H_4), 7.40 (3H, m, 3-/4-C_6H_5), 7.31 (4H, d, $^3J_{HH}$ = 8.8 Hz, 2-C_6H_4), 2.02 (6H, m, PCH_2), 0.93 (9H, m, CH_2CH_3). ^{19}F{^{1}H} NMR ($CDCl_3$) −81.25 (6F, tt, $^4J_{FF}$ = 10.0 Hz, $^3J_{FF}$ = 2.2 Hz, CF_3), −110.96 (4F, t, $^4J_{FF}$ = 14.6 Hz, α-CF_2), −121.85 (4F, m, CF_2), −122.35 (4F, m, CF_2), −123.24 (4F, m, CF_2), −126.58 (4F, m, CF_2). ^{31}P{^{1}H} NMR ($CDCl_3$) 97.92 (d, $^1J_{PtP}$ = 5195 Hz, $^2J_{PP}$ = 15.8 Hz, *P*O$_2$), 16.10 (d, $^1J_{PtP}$ = 3276 Hz, $^2J_{PP}$ = 15.8 Hz, *P*Et_3).

*4.1.16. trans-[$PdCl_2${*P*$Ph_2C_2H_4C_6F_{13}$}$_2$] (**16**)*

The title compound was prepared in a similar way to (**1**) from *trans*-[$PdCl_2$(MeCN)$_2$] (0.078 g, 0.30 mmol) and the ligand (0.346 g, 0.65 mmol) in dry dichloromethane, affording the product as a fine yellow powder (0.301 g, 81%). Anal. Calc. for $C_{40}H_{28}Cl_2F_{26}P_2Pd$: C, 38.7; H, 2.3. Found: C, 36.0; H, 2.1. *m/z* (FAB) 1171 ([M−2Cl]$^+$). ^{1}H NMR ($CDCl_3$) 7.71 (8H, m, 2-C_6H_5), 7.44 (12H, m, 3-/4-C_6H_5), 2.70 (4H, m, PCH_2), 2.42 (4H, m, CH_2CF_2). ^{19}F{^{1}H} NMR ($CDCl_3$) −81.29 (6F, t, $^4J_{FF}$ = 10.0 Hz, CF_3), −114.82 (4F, t, $^4J_{FF}$ = 14.0 Hz, α-CF_2), −122.38 (4F, m, CF_2), −123.40 (4F, m, CF_2), −123.57 (4F, m, CF_2), −126.58 (4F, m, CF_2). ^{31}P{^{1}H} NMR ($CDCl_3$) 15.61 (s). IR (Nujol) 361 cm^{-1} [ν(M-Cl)].

*4.1.17. trans-[$PdCl_2${*P*Ph($C_2H_4C_6F_{13}$)$_2$}$_2$] (**17**)*

The title compound was prepared similarly as a fine yellow powder (0.337 g, 63%). Anal. Calc. for $C_{44}H_{26}Cl_2F_{52}P_2Pd$: C, 29.7; H, 1.5. Found: C, 30.0; H, 1.3. ^{1}H NMR (CD_3COCD_3) 7.90 (4H, m, 2-C_6H_5), 7.40 (6H, m, 3-/4-C_6H_5), 2.64 (8H, m, PCH_2), 2.20 (8H, m, CH_2CF_2). ^{19}F{^{1}H} NMR (CD_3COCD_3) −80.94 (12F, tt, $^4J_{FF}$ = 10.0 Hz, $^3J_{FF}$ = 2.3 Hz, CF_3), −113.88 (8F, t, $^4J_{FF}$ = 14.0 Hz, α-CF_2), −121.62 (8F, m, CF_2), −122.62 (8F, m, CF_2), −123.20 (8F, m, CF_2), −125.99 (8F, m, CF_2). ^{31}P{^{1}H} NMR (CD_3COCD_3) 15.04 (s). IR (Nujol) 364 cm^{-1} [ν(M-Cl)].

*4.1.18. trans-[$PdCl_2${*P*($C_2H_4C_6F_{13}$)$_3$}$_2$] (**18**)*

The title compound was prepared similarly as a fine yellow powder (0.418 g, 60%). Anal. Calc. for $C_{48}H_{24}Cl_2F_{78}P_2Pd$: C, 24.9; H, 1.0. Found: C, 24.8; H, 1.0. *m/z* (FAB) 2286 ([M−Cl]$^+$), 2251 ([M−2Cl]$^+$). ^{1}H NMR (CD_3COCD_3) 2.73 (12H, m, PCH_2), 2.38 (12H, m, CH_2CF_2). ^{19}F{^{1}H} NMR (CD_3COCD_3) −80.98 (18F, t, $^4J_{FF}$ = 10.0 Hz, CF_3), −114.35 (12F, t, $^4J_{FF}$ = 14.2 Hz, α-CF_2), −121.65 (12F, m, CF_2), −122.67 (12F, m, CF_2), −122.98 (12F, m, CF_2), −126.06 (12F, m, CF_2). ^{31}P{^{1}H} NMR (CD_3COCD_3) 15.85 (s). IR (Nujol) 362 cm^{-1} [ν(M-Cl)].

*4.1.19. cis-[$PdCl_2${*P*$Ph_2OC_2H_4C_6F_{13}$}$_2$] (**19**)*

The title compound was prepared similarly as a fine yellow powder (0.350 g, 79%). Anal. Calc. for $C_{40}H_{28}Cl_2F_{26}O_2P_2Pd$: C, 37.7; H, 2.2. Found: C, 37.7; H, 2.0. *m/z* (EI) 1238 ([M−Cl]$^+$), 1203 ([M−2Cl]$^+$). ^{1}H NMR ($CDCl_3$) 7.73 (8H, m, 2-C_6H_5), 7.41 (12H, m, 3-/4-C_6H_5), 3.84 (4H, q, $^3J_{HH}$ = $^3J_{PH}$ = 6.3 Hz, OCH_2), 1.92 (4H, tt, $^3J_{FH}$ = 18.4 Hz, $^3J_{HH}$ = 6.3 Hz, CH_2CF_2). ^{19}F{^{1}H} NMR ($CDCl_3$) −81.36 (6F, t, $^4J_{FF}$ = 10.0 Hz, CF_3), −113.97 (4F, t, $^4J_{FF}$ = 13.6 Hz, α-CF_2),

−122.42 (4F, m, CF_2), −123.42 (4F, m, CF_2), −124.18 (4F, m, CF_2), −126.69 (4F, m, CF_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$) 112.92 (s). IR (Nujol) 315, 290 cm^{-1} [ν(M-Cl)].

4.1.20. cis-[$PdCl_2${$PPh(OC_2H_4C_6F_{13})_2$}$_2$] (20)

The title compound was prepared similarly as a pale yellow solid (0.608 g, 84%). *m/z* (EI) 1810 ([M−Cl]$^+$), 1775 ([M−2Cl]$^+$). ^1H NMR ($CDCl_3$) 7.77 (4H, m, 2-C_6H_5), 7.56 (6H, m, 3-/4-C_6H_5), 4.58 (4H, m, OC*H*), 4.36 (4H, m, OC*H*), 2.48 (8H, m, C*H*$_2CF_2$). $^{19}F\{^1H\}$ NMR ($CDCl_3$) −81.67 (12F, t, $^4J_{FF}$ = 10.0 Hz, CF_3), −114.17 (8F, t, $^4J_{FF}$ = 14.3 Hz, α-CF_2), −122.59 (8F, m, CF_2), −123.61 (8F, m, CF_2), −124.21 (8F, m, CF_2), −126.98 (8F, m, CF_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$) 126.38 (s). IR (Nujol) 325, 304 cm^{-1} [ν(M-Cl)].

4.1.21. cis-[$PdCl_2${$P(OC_2H_4C_6F_{13})_3$}$_2$] (21)

The title compound was prepared similarly as a viscous orange oil (0.173 g, 64%). *m/z* (FAB) 2382 ([M−Cl]$^+$), 2347 ([M−2Cl]$^+$). ^1H NMR (D_2O) 4.65 (12H, m, OC*H*$_2$), 2.60 (12H, m, C*H*$_2CF_2$). $^{19}F\{^1H\}$ NMR (CD_3COCD_3) −81.58 (18F, m, CF_3), −113.97 (12F, m, α-CF_2), −122.45 (12F, m, CF_2), −123.58 (12F, m, CF_2), −124.22 (12F, m, CF_2), −126.91 (12F, m, CF_2). $^{31}P\{^1H\}$ NMR (D_2O) 94.40 (s). IR (Nujol) 335, 303 cm^{-1} [ν(M-Cl)].

4.1.22. cis-[$PdCl_2$($PPh_2OC_6H_4$-4-$C_6F_{13})_2$] (22)

The title compound was prepared similarly as a fine pale yellow solid (0.192 g, 57%). ^1H NMR ($CDCl_3$) 7.49 (8H, m, 2-C_6H_5), 7.29 (4H, d, $^3J_{HH}$ = 8.8 Hz, 3-C_6H_4), 7.19 (12H, m, 3-/4-C_6H_5), 7.16 (4H, d, $^3J_{HH}$ = 8.8 Hz, 2-C_6H_4). $^{19}F\{^1H\}$ NMR ($CDCl_3$) −81.24 (6F, tt, $^4J_{FF}$ = 10.0 Hz, $^3J_{FF}$ = 2.2 Hz, CF_3), −110.69 (4F, t, $^4J_{FF}$ = 14.5 Hz, α-CF_2), −121.86 (4F, m, CF_2), −122.29 (4F, m, CF_2), −123.24 (4F, m, CF_2), −126.57 (4F, m, CF_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$) 113.11 (s). IR (Nujol) 316, 290 cm^{-1} [ν(M-Cl)].

4.1.23. cis-[$PdCl_2${$PPh(OC_6H_4$-4-$C_6F_{13})_2$}$_2$] (23)

The title compound was prepared similarly as a fine pale yellow solid (0.093 g, 34%). Anal. Calc. for $C_{60}H_{26}Cl_2F_{52}O_4P_2Pd$: C, 35.4; H, 1.3. Found: C, 35.3; H, 1.2. *m/z* (EI) 2002 ([M−Cl]$^+$), 1967 ([M−2Cl]$^+$). ^1H NMR ($CDCl_3$) 7.59 (4H, m, 2-C_6H_5), 7.54 (8H, d, $^3J_{HH}$ = 8.7 Hz, 3-C_6H_4), 7.38 (6H, m, 3-/4-C_6H_5), 7.19 (8H, d, $^3J_{HH}$ = 8.7 Hz, 2-C_6H_4). $^{19}F\{^1H\}$ NMR ($CDCl_3$) −81.27 (12F, t, $^4J_{FF}$ = 9.8 Hz, CF_3), −111.01 (8F, t, $^4J_{FF}$ = 13.8 Hz, α-CF_2), −121.88 (8F, m, CF_2), −122.22 (8F, m, CF_2), −123.27 (8F, m, CF_2), −126.59 (8F, m, CF_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$) 122.23 (s). IR (Nujol) 326, 294 cm^{-1} [ν(M-Cl)].

4.1.24. trans-[$RhCl(CO)${$PPh_2C_2H_4C_6F_{13}$}$_2$] (24)

[$RhCl(CO)_2]_2$ (0.044 g, 0.11 mmol) and $PPh_2(C_2H_4C_6F_{13})$ (0.250 g, 0.47 mmol) in dry dichloromethane (60 cm^3) were refluxed under nitrogen for 2 h. The solvent was removed *in vacuo* and the resulting off-white solid washed with light petroleum (bp 40–60 °C) (10 cm^3) to afford the product as a yellow powder (0.135 g, 50%). Anal. Calc. for $C_{41}H_{28}ClF_{26}OP_2Rh$: C, 40.0; H, 2.3. Found: C, 40.7; H, 2.4. *m/z* (FAB) 1202 ([M−CO]$^+$), 1167 ([M−CO-Cl]$^+$). ^1H NMR ($CDCl_3$) 7.69 (8H, m, 2-C_6H_5), 7.46 (12H, m, 3-/4-C_6H_5), 2.82 (4H, t, $^3J_{HH}$ = 10.0, PC*H*$_2$), 2.45 (4H, m, C*H*$_2CF_2$). $^{19}F\{^1H\}$ NMR ($CDCl_3$) −81.32 (6F, t, $^4J_{FF}$ = 10.0 Hz, CF_3), −114.90 (4F, t, $^4J_{FF}$ = 14.0 Hz, α-CF_2), −122.40 (4F, m, CF_2), −123.38 (4F, m, CF_2), −123.65 (4F, m, CF_2), −126.64 (4F, m, CF_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$) 24.54 (d, $^1J_{RhP}$ = 125 Hz). IR (Nujol) 1981 cm^{-1} [ν(CO)].

4.1.25. trans-[$RhCl(CO)${$PPh(C_2H_4C_6F_{13})_2$}$_2$] (25)

The title compound was prepared similarly as a sticky yellow powder (0.327 g, 84%). Anal. Calc. for $C_{45}H_{26}ClF_{52}OP_2Rh$: C, 30.5; H, 1.5. Found: C, 30.7; H, 1.5. *m/z* (FAB) 1770 (M$^+$), 1742 ([M−CO]$^+$). ^1H NMR ($CDCl_3$) 7.78 (4H, m, 2-C_6H_5), 7.56 (6H, m, 3-/4-C_6H_5), 2.68 (8H, m, PC*H*$_2$), 2.36 (8H, m, C*H*$_2CF_2$). $^{19}F\{^1H\}$ NMR ($CDCl_3$) −81.42 (12F, t, $^4J_{FF}$ = 10.0 Hz, CF_3), −114.90 (8F, t, $^4J_{FF}$ = 14.1 Hz, α-CF_2), −122.49 (8F, m, CF_2), −123.50 (8F, m, CF_2), −123.78 (8F, m, CF_2), −126.73 (8F, m, CF_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$) 22.78 (d, $^1J_{RhP}$ = 125 Hz). IR (Nujol) 1983 cm^{-1} [ν(CO)] [27,28].

4.1.26. trans-[$RhCl(CO)${$P(C_2H_4C_6F_{13})_3$}$_2$] (26)

The title compound was prepared similarly as a light brown powder (0.28 g, 55%). Anal. Calc. for $C_{49}H_{24}ClF_{78}OP_2Rh$: C, 25.5; H, 1.0. Found: C, 25.4; H, 1.0. *m/z* (FAB) 2310 (M$^+$). ^1H NMR (CD_3COCD_3) 3.22 (12H, t, $^3J_{HH}$ = 12.0 Hz, PC*H*$_2$), 2.62 (12H, m, C*H*$_2CF_2$). $^{19}F\{^1H\}$ NMR (CD_3COCD_3) −80.36 (18F, t, $^4J_{FF}$ = 11.5 Hz, CF_3), −114.39 (12F, t, $^4J_{FF}$ = 14.0 Hz, α-CF_2), −121.69 (12F, m, CF_2), −122.70 (12F, m, CF_2), −122.96 (12F, m, CF_2), −126.07 (12F, m, CF_2). $^{31}P\{^1H\}$ NMR (CD_3COCD_3) 22.87 (d, $^1J_{RhP}$ = 121 Hz). IR (Nujol) 1990 cm^{-1} [ν(CO)] [29].

4.1.27. trans-[$RhCl(CO)(PPh_2OC_2H_4C_6F_{13})_2$] (27)

The title compound was prepared similarly as a yellow solid (0.284 g, 49%). Anal. Calc. for $C_{41}H_{28}ClF_{26}O_3P_2Rh$: C, 39.0; H, 2.2. Found: C, 39.0; H, 1.7. *m/z* (FAB) 1234 ([M−CO]$^+$), 1227 ([M−Cl]$^+$). ^1H NMR ($CDCl_3$) 7.77 (8H, m, 2-C_6H_5), 7.43 (12H, m, 3-/4-C_6H_5), 4.47 (4H, m, OC*H*$_2$), 2.58 (4H, t, $^3J_{FH}$ = 18.6 Hz, C*H*$_2CF_2$). $^{19}F\{^1H\}$ NMR ($CDCl_3$) −81.30 (6F, t, $^4J_{FF}$ = 9.6 Hz, CF_3), −113.58 (4F, t, $^4J_{FF}$ = 12.3 Hz, α-CF_2), −122.30 (4F, m, CF_2), −123.34 (4F, m, CF_2), −124.04 (4F, m, CF_2), −126.59 (4F, m, CF_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$) 121.12 (d, $^1J_{RhP}$ = 136 Hz). IR (CH_2Cl_2) 1990 cm^{-1} [ν(CO)].

4.1.28. trans-[$RhCl(CO)${$PPh(OC_2H_4C_6F_{13})_2$}$_2$] (28)

The title compound was prepared similarly as a yellow oil (0.443 g, 89%). *m/z* (FAB) 1805 ([M−CO-H]$^+$). ^1H NMR ($CD_3C_6D_5$) 8.05 (4H, m, 2-C_6H_5), 7.39 (6H, m, 3-/4-C_6H_5), 4.54 (4H, m, OC*H*), 4.18 (4H, m, OC*H*), 2.30 (8H, m, C*H*$_2CF_2$). $^{19}F\{^1H\}$ NMR ($CD_3C_6D_5$) −81.48 (12F, tt, $^4J_{FF}$ = 10.0 Hz, $^3J_{FF}$ = 2.3 Hz, CF_3), −113.64 (8F, m, α-CF_2), −122.19 (8F, m, CF_2), −123.23 (8F, m, CF_2), −123.93 (8F, m, CF_2), −126.60 (8F, m, CF_2). $^{31}P\{^1H\}$ NMR ($CD_3C_6D_5$) 153.71 (d, $^1J_{RhP}$ = 167 Hz). IR (CH_2Cl_2) 2008 cm^{-1} [ν(CO)] [29].

4.1.29. trans-[$RhCl(CO)${$P(OC_2H_4C_6F_{13})_3$}$_2$] (29)

The title compound was prepared similarly as a yellow oil (0.534 g, 90%). Anal. Calc. for $C_{49}H_{24}ClF_{78}O_7P_2Rh$: C, 24.5; H, 1.0. Found: C, 24.1; H, 1.1. *m/z* (FAB) 2378 ([M−CO]$^+$). ^1H NMR (D_2O) 4.41 (12H, m, OC*H*$_2$), 2.47 (12H, m, C*H*$_2CF_2$). $^{31}P\{^1H\}$ NMR (D_2O) 128.69 (d, $^1J_{RhP}$ = 199 Hz). IR (PP3 solution) 2036 cm^{-1} [ν(CO)].

4.1.30. trans-[$RhCl(CO)(PPh_2OC_6H_4$-4-$C_6F_{13})_2$] (30)

The title compound was prepared similarly as a yellow powder (0.274 g, 77%). Anal. Calc. for $C_{49}H_{28}ClF_{26}O_3P_2Rh$: C, 43.3; H, 2.1. Found: C, 43.3; H, 1.9. *m/z* (FAB) 1295 ([M−Cl-CO]$^+$). ^1H NMR ($CDCl_3$) 7.92 (8H, m, 2-C_6H_5), 7.78 (20H, m, 2-/3-C_6H_4, 3-/4-C_6H_5). $^{19}F\{^1H\}$ NMR ($CDCl_3$) −81.26 (6F, t, $^4J_{FF}$ = 10.0 Hz, CF_3), −110.63 (4F, t, $^4J_{FF}$ = 14.4 Hz, α-CF_2), −121.91 (4F, m, CF_2), −122.25 (4F, m, CF_2), −123.25 (4F, m, CF_2), −126.59 (4F, m, CF_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$) 125.00 (d, $^1J_{RhP}$ = 141 Hz). IR (Nujol) 1996 cm^{-1} [ν(CO)].

4.1.31. trans-[$RhCl(CO)${$PPh(OC_6H_4$-4-$C_6F_{13})_2$}$_2$] (31)

The title compound was prepared similarly as a cream solid (0.093 g, 34%). Anal. Calc. for $C_{61}H_{26}ClF_{52}O_5P_2Rh$: C, 36.1; H, 1.3. Found: C, 36.3; H, 1.2. *m/z* (EI) 1963 ([M−Cl-CO]$^+$). ^1H NMR ($CDCl_3$) 7.60 (4H, m, 2-C_6H_5), 7.32 (8H, d, $^3J_{HH}$ = 8.8 Hz, 3-C_6H_4), 7.21 (6H, m, 3-/4-C_6H_5), 7.11 (8H, d, $^3J_{HH}$ = 8.8 Hz, 2-C_6H_4). $^{19}F\{^1H\}$ NMR ($CDCl_3$) −81.25 (12F, tt, $^4J_{FF}$ = 10.0 Hz, $^3J_{FF}$ = 2.2 Hz, CF_3), −110.76 (8F, t, $^4J_{FF}$ = 14.5 Hz, α-CF_2), −121.91 (8F, m, CF_2), −122.38 (8F, m, CF_2), −123.29 (8F, m, CF_2), −126.61 (8F, m, CF_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$) 149.33 (d, $^1J_{RhP}$ = 176 Hz). IR (Nujol) 2013 cm^{-1} [ν(CO)].

*4.1.32. trans-[IrCl(CO){PPh$_2$C$_2$H$_4$C$_6$F$_{13}$}$_2$] (**32**)*

[IrCl(COD)]$_2$ (0.074 g, 0.11 mmol) and PPh$_2$C$_2$H$_4$C$_6$F$_{13}$ (0.234 g, 0.44 mmol) were stirred in dry, degassed THF (20 cm^3) under CO gas (1 atm) for 30 min at room temperature. The solvent was removed *in vacuo* and the resulting solid was stirred with dry, degassed, hexane (5 cm^3) to afford the product as a fine yellow powder (0.183 g, 63%). Anal. Calc. for $C_{41}H_{28}ClF_{26}IrOP_2$: C, 37.3; H, 2.1. Found: C, 36.2; H, 1.9. *m/z* (FAB) 1320 (M^+), 1257 ([M−CO-Cl]$^+$). ^{1}H NMR ($CDCl_3$) 7.68 (8H, m, 2-C_6H_5), 7.48 (12H, m, 3-/4-C_6H_5), 2.88 (4H, t, $^3J_{HH}$ = 10.0, PCH_2), 2.50 (4H, m, CH_2CF$_2$). ^{19}F{^{1}H} NMR ($CDCl_3$) −81.32 (6F, t, $^4J_{FF}$ = 10.0 Hz, CF_3), −114.64 (4F, t, $^4J_{FF}$ = 14.0 Hz, α-CF_2), −122.30 (4F, m, CF_2), −123.48 (4F, m, CF_2), −123.86 (4F, m, CF_2), −126.75 (4F, m, CF_2). ^{31}P{^{1}H} NMR ($CDCl_3$) 19.40 (s). IR (Nujol) 1954 cm^{-1} [ν(CO)].

*4.1.33. trans-[IrCl(CO){PPh(C$_2$H$_4$C$_6$F$_{13}$)$_2$}$_2$] (**33**)*

The title compound was prepared similarly as a fine yellow powder (0.237 g, 58%). Anal. Calc. for $C_{45}H_{26}ClF_{52}IrOP_2$: C, 29.0; H, 1.4. Found: C, 28.3; H, 1.2. *m/z* (FAB) 1860 (M^+), 1832 ([M−CO]$^+$). ^{1}H NMR ($CDCl_3$) 7.81 (4H, m, 2-C_6H_5), 7.57 (6H, m, 3-/4-C_6H_5), 2.75 (8H, m, PCH_2), 2.60 (8H, m, CH_2CF$_2$). ^{19}F{^{1}H} NMR ($CDCl_3$) −81.34 (12F, t, $^4J_{FF}$ = 10.0 Hz, CF_3), −114.94 (8F, t, $^4J_{FF}$ = 14.0 Hz, α-CF_2), −122.49 (8F, m, CF_2), −123.49 (8F, m, CF_2), −123.77 (8F, m, CF_2), −126.76 (8F, m, CF_2). ^{31}P{^{1}H} NMR ($CDCl_3$) 18.32 (s). IR (Nujol) 1973 cm^{-1} [ν(CO)] [28].

*4.1.34. trans-[IrCl(CO){P(C$_2$H$_4$C$_6$F$_{13}$)$_3$}$_2$] (**34**)*

The title compound was prepared similarly as a fine yellow powder (0.348 g, 66%). Anal. Calc. for $C_{49}H_{24}ClF_{78}IrOP_2$: C, 24.5; H, 1.0. Found: C, 24.5; H, 0.9. *m/z* (FAB) 2400 (M^+). ^{1}H NMR (CD_3COCD_3) 2.69 (12H, m, PCH_2), 2.58 (12H, m, CH_2CF$_2$). ^{19}F{^{1}H} NMR (CD_3COCD_3) −81.01 (18F, t, $^4J_{FF}$ = 10 Hz, CF_3), −114.40 (12F, t, $^4J_{FF}$ = 14.1 Hz, α-CF_2), −121.67 (12F, m, CF_2), −122.69 (12F, m, CF_2), −123.00 (12F, m, CF_2), −126.06 (12F, m, CF_2). ^{31}P{^{1}H} NMR (CD_3COCD_3) 18.55 (s). IR (Nujol) 1977 cm^{-1} [ν(CO)].

*4.1.35. [Cp*RhCl$_2$(PPh$_2$C$_2$H$_4$C$_6$F$_{13}$)] (**35**)*

[Cp*RhCl$_2$]$_2$ (0.77 g, 0.12 mmol) and PPh$_2$C$_2$H$_4$C$_6$F$_{13}$ (0.133 g, 0.25 mmol) were refluxed in ethanol (60 cm^3) under nitrogen for 1 h. The solvent was removed *in vacuo*, and the resulting reddish solid was washed with hexane (10 cm^3) to afford the product as a fine, red/orange powder (0.151 g, 75%). Anal. Calc. for $C_{30}H_{29}Cl_2F_{13}PRh$: C, 42.8; H, 3.5. Found: C, 42.9; H, 3.6. *m/z* (FAB) 840 (M^+), 805 ([M−Cl]$^+$). ^{1}H NMR ($CDCl_3$) 7.83 (4H, m, 2-C_6H_5), 7.48 (6H, m, 3-/4-C_6H_5), 2.98 (2H, t, $^3J_{HH}$ = 11.6 Hz, PCH_2), 2.18 (2H, m, CH_2CF$_2$), 1.39 (15H, d, $^3J_{PH}$ = 3.8 Hz, Cp*). ^{19}F{^{1}H} NMR ($CDCl_3$) −81.29 (3F, t, $^4J_{FF}$ = 10.0 Hz, CF_3), −115.06 (2F, t, $^4J_{FF}$ = 13.6 Hz, α-CF_2), −122.52 (2F, m, CF_2), −123.44 (2F, m, CF_2), −123.99 (2F, m, CF_2), −126.68 (2F, m, CF_2). ^{31}P{^{1}H} NMR ($CDCl_3$) 27.28 (d, $^1J_{RhP}$ = 144 Hz).

*4.1.36. [Cp*RhCl$_2${PPh(C$_2$H$_4$C$_6$F$_{13}$)$_2$}] (**36**)*

The title compound was prepared similarly as a red/orange powder (0.235 g, 88%). Anal. Calc. For $C_{32}H_{28}Cl_2F_{26}PRh$: C, 34.6; H, 2.5. Found: C, 35.2; H, 2.4. *m/z* (FAB) 1075 ([M−Cl]$^+$). ^{1}H NMR ($CDCl_3$) 7.91 (2H, m, 2-C_6H_5), 7.53 (3H, m, 3-/4-C_6H_5), 2.76 (4H, m, PCH_2), 2.10 (4H, m, CH_2CF$_2$), 1.41 (15H, d, J_{PH} = 4.0 Hz, Cp*). ^{19}F{^{1}H} NMR ($CDCl_3$) −81.35 (6F, t, $^4J_{FF}$ = 10.0 Hz, CF_3), −115.17 (4F, t, $^4J_{FF}$ = 13.6 Hz, α-CF_2), −122.38 (4F, m, CF_2), −123.37 (4F, m, CF_2), −123.67 (4F, m, CF_2), −126.64 (4F, m, CF_2). ^{31}P{^{1}H} NMR ($CDCl_3$) 18.30 (d, $^1J_{RhP}$ = 146 Hz).

*4.1.37. [Cp*RhCl$_2${P(C$_2$H$_4$C$_6$F$_{13}$)$_3$}] (**37**)*

The title compound was prepared similarly as a fine red/orange powder (0.249 g, 75%). Anal. Calc. For $C_{34}H_{27}Cl_2F_{39}PRh$: C, 29.6; H, 2.0. Found: C, 30.2; H, 2.0. *m/z* (FAB) 1345 ([M−Cl]$^+$). ^{1}H NMR ($CDCl_3$) 2.80 (6H, m, PCH_2), 2.40 (6H, m, CH_2CF$_2$), 1.56 (15H, d, J_{PH} = 3.6 Hz, Cp*). ^{19}F{^{1}H} NMR ($CDCl_3$) −81.27 (9F, t, $^4J_{FF}$ = 10.0 Hz, CF_3), −115.23 (6F, t, $^4J_{FF}$ = 14.0 Hz, α-CF_2), −122.28 (6F, m, CF_2), −123.28 (6F, m, CF_2), −123.60 (6F, m, CF_2), −126.62 (6F, m, CF_2). ^{31}P{^{1}H} NMR ($CDCl_3$) 19.38 (d, $^1J_{RhP}$ = 147 Hz).

*4.1.38. [Cp*RhCl$_2$(PPh$_2$OC$_2$H$_4$C$_6$F$_{13}$)] (**38**)*

The title compound was prepared similarly as a pale orange solid (0.400 g, 72%). Anal. Calc. for $C_{30}H_{29}Cl_2F_{13}OPRh$: C, 42.0; H, 3.4. Found: C, 42.1; H, 3.3. *m/z* (FAB) 821 ([M−Cl]$^+$), 786 ([M−2Cl]$^+$). ^{1}H NMR ($CDCl_3$) 7.93 (4H, m, 2-C_6H_5), 7.32 (6H, m, 3-/4-C_6H_5), 4.09 (2H, q, $^3J_{PH}$ = $^3J_{HH}$ = 6.1 Hz, OCH_2), 2.58 (2H, tt, $^3J_{FH}$ = 18.6 Hz, $^3J_{HH}$ = 5.8 Hz, CH_2CF$_2$), 1.36 (15H, d, J_{PH} = 3.8 Hz, Cp*). ^{19}F{^{1}H} NMR ($CDCl_3$) −81.22 (3F, t, $^4J_{FF}$ = 10.0 Hz, CF_3), −113.57 (2F, t, $^4J_{FF}$ = 14.1 Hz, α-CF_2), −122.18 (2F, m, CF_2), −123.28 (2F, m, CF_2), −124.01 (2F, m, CF_2), −126.54 (2F, m, CF_2). ^{31}P{^{1}H} NMR ($CDCl_3$) 117.12 (d, $^1J_{RhP}$ = 157 Hz).

*4.1.39. [Cp*RhCl$_2${PPh(OC$_2$H$_4$C$_6$F$_{13}$)$_2$}] (**39**)*

The title compound was prepared similarly as a red solid (0.261 g, 34%). Anal. Calc. for $C_{32}H_{28}Cl_2F_{26}O_2PRh$: C, 33.6; H, 2.5. Found: C, 34.0; H, 2.4. *m/z* (FAB) 1142 (M^+), 1107 ([M−Cl]$^+$). ^{1}H NMR ($CDCl_3$) 7.95 (2H, m, 2-C_6H_5), 7.44 (3H, m, 3-/4-C_6H_5), 4.68 (2H, m, OC*H*), 4.41 (2H, m, OC*H*), 2.45 (4H, m, CH_2CF$_2$), 1.39 (15H, d, J_{PH} = 4.1 Hz, Cp*). ^{19}F{^{1}H} NMR ($CDCl_3$) −81.34 (6F, t, $^4J_{FF}$ = 10.0 Hz, CF_3), −113.79 (4F, m, α-CF_2), −122.35 (4F, m, CF_2), −123.38 (4F, m, CF_2), −124.13 (4F, m, CF_2), −126.66 (4F, m, CF_2). ^{31}P{^{1}H} NMR ($CDCl_3$) 147.40 (d, $^1J_{RhP}$ = 181 Hz).

*4.1.40. [Cp*RhCl$_2${P(OC$_2$H$_4$C$_6$F$_{13}$)$_3$}] (**40**)*

The title compound was prepared similarly as a red oil (0.204 g, 42%). Anal. Calc. for $C_{34}H_{27}Cl_2F_{39}O_3PRh$: C, 28.6; H, 1.9. Found: C, 28.5; H, 2.0. *m/z* (FAB) 1393 ([M−Cl]$^+$), 1358 ([M−2Cl]$^+$). ^{1}H NMR ($CDCl_3$) 4.48 (6H, q, $^3J_{PH}$ = $^3J_{HH}$ = 6.0 Hz, OCH_2), 2.42 (6H, tt, $^3J_{FH}$ = 18.4 Hz, $^3J_{HH}$ = 6.0 Hz, CH_2CF$_2$), 1.62 (15H, d, J_{PH} = 5.7 Hz, Cp*). ^{19}F{^{1}H} NMR ($CDCl_3$) −81.47 (9F, tt, $^4J_{FF}$ = 10.0 Hz, $^3J_{FF}$ = 2.3 Hz, CF_3), −113.85 (6F, t, $^4J_{FF}$ = 13.9 Hz, α-CF_2), −122.46 (6F, m, CF_2), −123.49 (6F, m, CF_2), −124.18 (6F, m, CF_2), −126.78 (6F, m, CF_2). ^{31}P{^{1}H} NMR ($CDCl_3$) 120.25 (d, $^1J_{RhP}$ = 224 Hz).

*4.1.41. [Cp*RhCl$_2$(PPh$_2$OC$_6$H$_4$-4-C$_6$F$_{13}$)] (**41**)*

The title compound was prepared similarly as an orange powder (0.346 g, 79%). Anal. Calc. for $C_{34}H_{29}Cl_2F_{13}OPRh$: C, 45.1; H, 3.2. Found: C, 45.6; H, 3.3. *m/z* (FAB) 869 ([M−Cl]$^+$), 834 ([M−2Cl]$^+$). ^{1}H NMR ($CDCl_3$) 8.13 (4H, m, 2-C_6H_5), 7.55 (2H, d, $^3J_{HH}$ = 8.8 Hz, 3-C_6H_4), 7.39 (2H, d, $^3J_{HH}$ = 8.8 Hz, 2-C_6H_4), 7.31 (6H, m, 3-/4-C_6H_5), 1.26 (15H, d, J_{PH} = 4.1 Hz, Cp*). ^{19}F{^{1}H} NMR ($CDCl_3$) −81.28 (3F, tt, $^4J_{FF}$ = 10.0 Hz, $^3J_{FF}$ = 2.3 Hz, CF_3), −110.62 (2F, tt, $^4J_{FF}$ = 14.1 Hz, $^3J_{FF}$ = 3.3 Hz, α-CF_2), −121.89 (2F, m, CF_2), −122.51 (2F, m, CF_2), −123.25 (2F, m, CF_2), −126.58 (2F, m, CF_2). ^{31}P{^{1}H} NMR ($CDCl_3$) 116.65 (d, $^1J_{RhP}$ = 171 Hz).

*4.1.42. [Cp*RhCl$_2${PPh(OC$_6$H$_4$-4-C$_6$F$_{13}$)$_2$}] (**42**)*

The title compound was prepared similarly as a pale orange solid (0.264 g, 67%). Anal. Calc. for $C_{40}H_{28}Cl_2F_{26}O_2PRh$: C, 38.8; H, 2.3. Found: C, 39.2; H, 2.1. *m/z* (EI) 1203 ([M−Cl]$^+$), 1168 ([M−2Cl]$^+$). ^{1}H NMR ($CDCl_3$) 8.03 (2H, m, 2-C_6H_5), 7.32 (8H, m, 2-/3-C_6H_4), 7.22 (3H, m, 3-/4-C_6H_5), 1.33 (15H, d, J_{PH} = 4.7 Hz, Cp*). ^{19}F{^{1}H} NMR ($CDCl_3$) −81.25 (6F, t, $^4J_{FF}$ = 10.0 Hz, CF_3), −110.85 (4F, t, $^4J_{FF}$ = 14.0 Hz, α-CF_2), −121.85 (4F, m, CF_2), −122.60 (4F, m, CF_2), −123.26 (4F, m, CF_2), −126.60 (4F, m, CF_2). ^{31}P{^{1}H} NMR ($CDCl_3$) 145.83 (d, $^1J_{RhP}$ = 203 Hz).

*4.1.43. [Cp*IrCl$_2$(PPh$_2$OC$_2$H$_4$C$_6$F$_{13}$)] (**43**)*

The title compound was prepared in a similar way to (**33**) from [Cp*IrCl$_2$]$_2$ (0.100 g, 0.13 mmol) and the ligand (0.200 g,

0.34 mmol) in dry benzene, affording the product as a fine orange powder (0.278 g, 84%). Anal. Calc. for $C_{30}H_{29}Cl_2F_{13}IrOP$: C, 38.1; H, 3.1. Found: C, 38.0; H, 2.9. *m/z* (FAB) 946 (M^+), 911 ($[M-Cl]^+$). ^1H NMR ($CDCl_3$) 8.04 (4H, m, 2-C_6H_5), 7.47 (6H, m, 3-/4-C_6H_5), 4.20 (2H, q, $^3J_{PH} = {}^3J_{HH} = 5.9$ Hz, OCH_2), 2.39 (2H, tt, $^3J_{FH} = 18.7$ Hz, $^3J_{HH} = 5.9$ Hz, CH_2CF_2), 1.51 (15H, d, $J_{PH} = 2.2$ Hz, Cp*). $^{19}F\{^1H\}$ NMR ($CDCl_3$) −81.20 (3F, tt, $^4J_{FF} = 9.8$ Hz, $^3J_{FF} = 2.5$ Hz, CF_3), −113.59 (2F, t, $^4J_{FF} = 14.1$ Hz, α-CF_2), −122.19 (2F, m, CF_2), −123.27 (2F, m, CF_2), −124.01 (2F, m, CF_2), −126.52 (2F, m, CF_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$) 77.32 (s).

*4.1.44. [Cp*IrCl$_2${PPh(OC$_2$H$_4$C$_6$F$_{13}$)$_2$}] (44)*

The title compound was prepared similarly as an orange powder (0.289 g, 89%). Anal. Calc. for $C_{32}H_{28}Cl_2F_{26}IrO_2P$: C, 31.2; H, 2.3. Found: C, 31.2; H, 2.1. *m/z* (FAB) 1232 (M^+), 1197 ($[M-Cl]^+$). ^1H NMR ($CDCl_3$) 8.16 (2H, m, 2-C_6H_5), 7.72 (3H, m, 3-/4-C_6H_5), 4.82 (2H, m, OCH), 4.62 (2H, m, OCH), 2.72 (4H, m, CH_2CF_2), 1.69 (15H, d, $J_{PH} = 2.8$ Hz, Cp*). $^{19}F\{^1H\}$ NMR ($CDCl_3$) −81.34 (6F, tt, $^4J_{FF} = 10.0$ Hz, $^3J_{FF} = 2.3$ Hz, CF_3), −113.85 (4F, m, α-CF_2), −122.36 (4F, m, CF_2), −123.38 (4F, m, CF_2), −124.14 (4F, m, CF_2), −126.65 (4F, m, CF_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$) 105.48 (s).

*4.1.45. [Cp*IrCl$_2${P(OC$_2$H$_4$C$_6$F$_{13}$)$_3$}] (45)*

The title compound was prepared similarly as an orange powder (0.135 g, 63%). Anal. Calc. for $C_{34}H_{27}Cl_2F_{39}IrO_3P$: C, 26.9; H, 1.8. Found: C, 27.1; H, 1.7. *m/z* (FAB) 1518 (M^+), 1483 ($[M-Cl]^+$). ^1H NMR ($CDCl_3$) 4.44 (6H, dt, $^3J_{PH} = 7.6$ Hz, $^3J_{HH} = 6.0$ Hz, OCH_2), 2.43 (6H, tt, $^3J_{FH} = 18.4$ Hz, $^3J_{HH} = 6.0$ Hz, CH_2CF_2), 1.63 (15H, d, $J_{PH} = 3.5$ Hz, Cp*). $^{19}F\{^1H\}$ NMR ($CDCl_3$) −81.45 (9F, tt, $^4J_{FF} = 10.0$ Hz, $^3J_{FF} = 2.3$ Hz, CF_3), −113.86 (6F, t, $^4J_{FF} = 13.9$ Hz, α-CF_2), −122.45 (6F, m, CF_2), −123.47 (6F, m, CF_2), −124.16 (6F, m, CF_2), −126.79 (6F, m, CF_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$) 83.36 (s).

*4.1.46. [Cp*IrCl$_2$(PPh$_2$OC$_6$H$_4$-4-C$_6$F$_{13}$)] (46)*

The title compound was prepared similarly as a fine light orange powder (0.119 g, 48%). Anal. Calc. for $C_{34}H_{29}Cl_2F_{13}IrOP$: C, 41.1; H, 2.9. Found: C, 41.1; H, 2.9. *m/z* (FAB) 994 (M^+), 924 ($[M-2Cl]^+$). ^1H NMR ($CDCl_3$) 8.35 (4H, m, 2-C_6H_5), 7.72 (2H, d, $^3J_{HH} = 8.8$ Hz, 3-C_6H_4), 7.61 (2H, d, $^3J_{HH} = 8.8$ Hz, 2-C_6H_4), 7.51 (6H, m, 3-/4-C_6H_5), 1.46 (15H, d, $J_{PH} = 2.2$ Hz, Cp*). $^{19}F\{^1H\}$ NMR ($CDCl_3$) −81.23 (3F, t, $^4J_{FF} = 10.0$ Hz, CF_3), −110.64 (2F, t, $^4J_{FF} = 14.1$ Hz, α-CF_2), −121.85 (2F, m, CF_2), −122.45 (2F, m, CF_2), −123.23 (2F, m, CF_2), −126.55 (2F, m, CF_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$) 75.17 (s).

*4.1.47. [Cp*IrCl$_2${PPh(OC$_6$H$_4$-4-C$_6$F$_{13}$)$_2$}] (47)*

The title compound was prepared similarly as a pale orange solid (0.264 g, 67%). Anal. Calc. for $C_{40}H_{28}Cl_2F_{26}IrO_2P$: C, 36.2; H, 2.1. Found: C, 36.3; H, 2.0. *m/z* (EI) 1328 (M^+), 1293 ($[M-Cl]^+$). ^1H NMR ($CDCl_3$) 8.35 (2H, m, 2-C_6H_5), 7.63 (11H, m, 2-/3-C_6H_4, 3-/4-C_6H_5), 1.62 (15H, d, $J_{PH} = 3.1$ Hz, Cp*). $^{19}F\{^1H\}$ NMR ($CDCl_3$) −81.25 (6F, tt, $^4J_{FF} = 10.0$ Hz, $^3J_{FF} = 2.3$ Hz, CF_3), −110.85 (4F, t, $^4J_{FF} = 14.0$ Hz, α-CF_2), −121.85 (4F, m, CF_2), −122.58 (4F, m, CF_2), −123.27 (4F, m, CF_2), −126.59 (4F, m, CF_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$) 102.39 (s).

4.1.48. [RhCl{PPh$_2$OC$_2$H$_4$C$_6$F$_{13}$}$_3$] (48)

$[Rh(\eta^2\text{-}C_2H_4)_2Cl]_2$ (0.057 g, 0.15 mmol) and $PPh_2OC_2H_4C_6F_{13}$ (0.510 g, 0.93 mmol) were stirred in dry dichloromethane (80 cm^3) under nitrogen for 1 h. The solvent was removed *in vacuo*, and the resulting reddish solid was washed with hexane (10 cm^3) to afford the product as an orange solid (0.348 g, 67%). ^1H NMR ($CDCl_3$) 7.84 (4H, m, 2-C_6H_5), 7.71 (8H, m, 2-C_6H_5), 6.99 (12H, m, 3-/4-C_6H_5), 6.89 (6H, m, 3-/4-C_6H_5), 4.50 (6H, m, OCH_2), 2.27 (2H, tt, $^3J_{HF} = 19.0$ Hz, $^3J_{HH} = 6.5$ Hz, CH_2CF_2), 1.53 (4H, tt, $^3J_{HF} = 19.4$ Hz, $^3J_{HH} = 6.5$ Hz, CH_2CF_2). $^{19}F\{^1H\}$ NMR ($CDCl_3$) −81.42 (9F, m, CF_3), −113.54 (2F, t, $^4J_{FF} = 13.6$ Hz, α-CF_2), −113.76 (4F, t, $^4J_{FF} = 14.1$ Hz, α-CF_2), −121.15 (6F, m, CF_2), −123.21 (6F, m, CF_2), −123.96 (6F, m, CF_2), −126.54 (6F, m, CF_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$) 131.41 (1P, dt, $^1J_{RhP} = 207$ Hz, $^2J_{PP} = 41$ Hz, $P_{trans\text{-}Cl}$), 124.57 (2P, dd, $^1J_{RhP} = 160$ Hz, $^2J_{PP} = 41$ Hz, $P_{trans\text{-}P}$).

4.1.49. [RhCl{PPh(OC$_2$H$_4$C$_6$F$_{13}$)$_2$}$_3$] (49)

The title compound was prepared similarly as an orange solid (0.266 g, 42%). ^1H NMR ($CDCl_3$) 8.12–7.31 (15H, m, C_6H_5), 5.54 (6H, m, OCH), 4.18 (6H, m, OCH), 2.28 (12H, m, CH_2CF_2). $^{19}F\{^1H\}$ NMR ($CDCl_3$) −81.48 (18F, m, CF_3), −113.54 (12F, m, α-CF_2), −122.19 (12F, m, CF_2), −123.25 (12F, m, CF_2), −123.97 (12F, m, CF_2), −126.62 (12F, m, CF_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$) 159.32 (1P, dt, $^1J_{RhP} = 236$ Hz, $^2J_{PP} = 41$ Hz, $P_{trans\text{-}Cl}$), 156.69 (2P, dd, $^1J_{RhP} = 182$ Hz, $^2J_{PP} = 41$ Hz, $P_{trans\text{-}P}$).

4.1.50. [RhCl{P(OC$_2$H$_4$C$_6$F$_{13}$)$_3$}$_3$] (50)

The title compound was prepared similarly as an air- and moisture-sensitive yellow oil. Anal. Calc. for $C_{72}H_{36}ClF_{117}O_9P_3Rh$: C, 24.7; H, 1.0. Found: C, 24.6; H, 1.1. ^1H NMR (PP3/D_2O) 3.93 (18H, m, OCH_2), 1.98 (18H, t, $^3J_{HF} = 18.1$ Hz, CH_2CF_2). $^{31}P\{^1H\}$ NMR (PP3/D_2O) 140.28 (1P, dt, $^1J_{RhP} = 268$ Hz, $^2J_{PP} = 53$ Hz, $P_{trans\text{-}Cl}$), 131.74 (2P, dd, $^1J_{RhP} = 209$ Hz, $^2J_{PP} = 53$ Hz, $P_{trans\text{-}P}$).

4.1.51. [RhCl{PPh$_2$(OC$_6$H$_4$-4-C$_6$F$_{13}$)}$_3$] (51)

The title compound was prepared similarly as an orange/yellow solid (0.311 g, 54%). Anal. Calc. for $C_{72}H_{42}ClF_{39}O_3P_3Rh$: C, 44.9; H, 2.2. Found: C, 44.4; H, 2.1. *m/z* (FAB) 1891 ($[M-Cl]^+$). ^1H NMR ($CDCl_3$) 7.60–7.05 (42H, m, C_6H_5, C_6H_4). $^{19}F\{^1H\}$ NMR ($CDCl_3$) −81.26 (9F, tt, $^4J_{FF} = 10.0$ Hz, $^3J_{FF} = 2.3$ Hz, CF_3), −110.22 (4F, t, $^4J_{FF} = 14.6$ Hz, α-CF_2), −110.41 (2F, t, $^4J_{FF} = 14.4$ Hz, α-CF_2), −121.91 (6F, m, CF_2), −122.40 (6F, m, CF_2), −123.26 (6F, m, CF_2), −126.57 (6F, m, CF_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$) 142.68 (1P, dt, $^1J_{RhP} = 216$ Hz, $^2J_{PP} = 37$ Hz, $P_{trans\text{-}Cl}$), 129.82 (2P, dd, $^1J_{RhP} = 162$ Hz, $^2J_{PP} = 37$ Hz, $P_{trans\text{-}P}$).

4.1.52. [RhCl{PPh(OC$_6$H$_4$-4-C$_6$F$_{13}$)$_2$}$_3$] (52)

The title compound was prepared similarly as an orange/yellow solid (0.164 g, 54%). Anal. Calc. for $C_{90}H_{39}ClF_{78}O_6P_3Rh$: C, 36.9; H, 1.3. Found: C, 36.9; H, 1.3. *m/z* (FAB) 2928 (M^+), 2893 ($[M-Cl]^+$). ^1H NMR ($CDCl_3$) 7.40–7.05 (27H, m, 2-/3-/4-C_6H_5, 2-C_6H_4), 6.94 (8H, d, $^3J_{HH} = 8.6$ Hz, 3-C_6H_4) 6.71 (4H, d, $^3J_{HH} = 8.6$ Hz, 3-C_6H_4). $^{19}F\{^1H\}$ NMR ($CDCl_3$) −81.33 (18F, tt, $^4J_{FF} = 10.0$ Hz, $^3J_{FF} = 2.4$ Hz, CF_3), −110.56 (12F, t, $^4J_{FF} = 14.1$ Hz, α-CF_2), −121.98 (12F, m, CF_2), −122.28 (12F, m, CF_2), −123.33 (12F, m, CF_2), −126.66 (12F, m, CF_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$) 151.78 (1P, dt, $^1J_{RhP} = 245$ Hz, $^2J_{PP} = 44$ Hz, $P_{trans\text{-}Cl}$), 146.79 (2P, dd, $^1J_{RhP} = 187$ Hz, $^2J_{PP} = 44$ Hz, $P_{trans\text{-}P}$).

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