The coordination chemistry of perfluorovinyl substituted phosphine ligands, a crystallographic and spectroscopic study. Co-crystallisation of both *cis*- and *trans*-isomers of $[PtCl_2{P^iPr_2(CF=CF_2)}_2]$ within the same unit cell[†]

Nicholas A. Barnes, Alan K. Brisdon,* F. R. William Brown, Wendy I. Cross, Christopher J. Herbert, Robin G. Pritchard and Ghazala Sadiq

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The coordination chemistry of the perfluorovinyl phosphines $PEt_2(CF=CF_2)$, $PPr_2(CF=CF_2)$, $PCy_2(CF=CF_2)$ and $PPh(CF=CF_2)_2$ to rhodium(I), palladium(II), and platinum(II) centres has been investigated. The electronic properties of the ligands are estimated based on v(CO) and ${}^{1}J(Rh-P)$ values. X-Ray diffraction data for the square-planar Pd(II) and Pt(II) perfluorovinyl-phosphine containing complexes allow estimates of the steric demand for the series of ligands PPh₂(CF=CF₂), $PEt_2(CF=CF_2)$, $P^iPr_2(CF=CF_2)$, $PCy_2(CF=CF_2)$ and $PPh(CF=CF_2)_2$ to be determined. The $(CF=CF_2)$ fragment is found to be more electron withdrawing than (C_6F_5) yet sterically less demanding. These ligands therefore provide a range of electron-neutral to phosphite-like electronic properties combined with a range of steric demands. This study also reveals that short intramolecular interactions from the metal centre to the β -fluorine atom *cis* to phosphorus of the CF=CF₂ groups are observed in all-trans square planar complexes of the ligands. Unusually, the complex $[PtCl_2{P^iPr_2(CF=CF_2)}_2]$ crystallises with both *cis*- and *trans*-isomers present in the unit cell. It appears that co-crystallisation of both isomers occurs in order to maximise fluorous regions in the crystal packing, and the extended structure displays short fluorine-fluorine contacts. The generation of mixed geometries seems to be a phenomenon of crystallisation, as solution phase NMR studies reveal the presence of only the trans-isomer.

Introduction

Phosphorus(III) ligand systems are amongst the most widely studied and utilized in transition metal chemistry.¹ The majority of these ligands are tertiary phosphines, PR_3 , or phosphites, $P(OR)_3$, both of which offer the opportunity to vary the properties of the ligand by changing the nature of the organic substituents. In doing so it is possible to modify the physical and chemical properties of the ligand, and of their metal complexes, a number of which are important catalysts.

Two of the more important variables in these systems are steric, usually denoted by the Tolman cone angle² (or variants thereof) and electronic, which is most often characterised by the CO stretching frequency of an appropriate transition metal carbonyl complex, such as [Ni(CO)₃P], [Mo(CO)₅P] or [Rh(CO)ClP₂] (P = P(III) ligand). There have been many reports,³ both theoretical and experimental, measuring and rationalising the steric and electronic properties of P(III) systems, with much of our current understanding still being based on the original work of Chatt⁴ and Tolman.² Notable recent contributions in this area include work on generating a ligand knowledge base for P(III) systems⁵ and the mapping of the steric/electronic parameter-space for P(III) systems.⁶ The latter showed that the majority of known phosphine

ligands occupy about half of the available map and that there are still few readily-accessible, sterically-demanding, electron-poor P(III) ligand systems. This is unfortunate since in some cases these are exactly the types of ligand that have been shown to demonstrate enhanced reactivity and catalytic properties.⁷

Organofluorine-substituted phosphine ligands offer an opportunity to access this currently poorly represented area. Thus, by incorporating organofluorine groups onto a P(III) centre it is possible to generate ligands with σ -donation properties more akin to those of phosphites, but with a steric demand comparable to that found for phosphines, which results in fluorinated phosphines being distinct from both perprotio-phosphines and phosphites.⁸ The current range of organofluoro-phosphines is still quite small, with the majority containing fluoroaryl substituents9 (by virtue of the commercial availability of suitable precursors and the stability of their metal derivatives) or small fluoroalkyl groups such as CF3¹⁰ or C₂F₅.¹¹ Phosphines possessing long fluorinated chains, such as $CH_2CH_2(CF_2)_nCF_3$ (*n* = 5, 7) are also known, which are designed to render the phosphines, and their complexes, preferentially soluble in fluorous solvents and form the basis of fluorous-biphase systems.¹² However, these materials specifically include a nonfluorinated "spacer" group to insulate the phosphorus centre from the electron-withdrawing properties of the fluorocarbon chain and because of this usually have a steric demand similar to the parent phosphine.

We have previously reported the synthesis of the thermally and oxidatively stable, perfluorovinyl (pfv) containing phosphines

School of Chemistry, The University of Manchester, Manchester, UK M13 9PL. E-mail: alan.brisdon@manchester.ac.uk

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derived from the commercially available hydrofluorocarbon refrigerant HFC-134a (CF₃CH₂F).¹³⁻¹⁴ Although prior reports of perfluorovinyl-containing phosphines existed, dating back to 1960,¹⁵ there were no reports of their coordination chemistry until 1999.14 Subsequently we, and others, have reported on the coordination chemistry of these ligands,¹⁶⁻¹⁹ but even so the total number of reported complexes is far less than the many reported complexes of vinyl-containing phosphines, especially PPh₂(CH=CH₂), and PPh(CH=CH₂)²⁰ Despite the scarcity of fluorovinyl-phosphine complexes, the perfluorovinyl-containing ligands have been included in computational studies⁶ along with CF_3 , C_2F_5 and C_6F_5 -containing phosphines since these are essentially the only well established organo-fluorine containing phosphines. However, there is no experimental data with which to compare the perfluorovinyl-containing phosphines. Nor has there been any detailed comparison of the relative steric and electronic properties of the available organo-fluorine substituents. We have therefore undertaken a systematic study of the coordination chemistry of a series of perfluorovinyl-containing phosphine ligands with a range of ancillary substituents in order to assess their properties.

Results and discussion

The air-and moisture stable perfluorovinyl-containing phosphines PPh₂(CF=CF₂), PCy₂(CF=CF₂) (Cy = cyclohexyl), PⁱPr₂(CF=CF₂) and PEt₂(CF=CF₂) were successfully prepared using the previously reported method.^{14,17} Attempts to prepare pure samples of the bis-perfluorovinyl containing phosphines PCy(CF=CF₂)₂, PⁱPr(CF=CF₂)₂ and PEt(CF=CF₂)₂ were less successful, in each case a mixture of products being obtained, which were difficult to completely separate, however PPh(CF=CF₂)₂ was readily isolable. The resulting ligands were subsequently complexed to rhodium, palladium and platinum metal centres, as outlined in Scheme 1 below.



Synthesis and characterisation of trans-[RhCl(CO){PR_{3-n}(CF=CF₂)_n}₂] complexes

The reaction of four equivalents of the perfluorovinyl-containing ligands with $[Rh(\mu-Cl)(CO)_2]_2$ (Scheme 1) resulted in a series of yellow solids formulated as *trans*- $[RhCl(CO)\{PR_{3-n}(CF=CF_2)_n\}_2]$ (n = 1, R = Ph 1, Et 2, Pr 3, Cy 4; n = 2, R = Ph 5) on the basis of analytical and spectroscopic data, see Table 1.

The ${}^{31}P{}^{1}H$ NMR spectra for 1 to 5 each show a resonance which is shifted to higher frequencies (by 30–55 ppm) with respect to the free ligand, which is consistent with complex formation.

The signals of **2**, **3** and **4** showed a virtual doublet of triplets at room temperature, while those of **1** and **5** were broad and required cooling to 233 K before the additional coupling was resolved. A similar effect has been observed for other rhodium(1) phosphine complexes such as *trans*-[RhCl(CO){P(C₆H₃F₂-2,6)₃}₂] which is ascribed to hindered rotation about the P–C bonds.²¹ These complexes exhibit $|^{1}J(RhP)|$ couplings of between 128 and 142 Hz, which are greater than has been observed for the analogous vinyl-containing (124.5 Hz)²⁰ and triphenylphosphine complexes (126.9 Hz),²² but comparable to that found for other fluorine-containing phosphine ligands, *e.g.* for *trans*-[RhCl(CO){PPh₂(C₆F₅)₂], $^{1}J(RhP) = 133.0$ Hz,²³ and for the PPh(C₆F₅)₂ analogue $^{1}J(RhP) = 136$ Hz.

The presence of the perfluorovinyl group in complexes 1 to 5 is established unequivocally by ¹⁹F NMR spectroscopy—three mutually coupled doublet of doublet based signals for the AMX spin system are observed at *ca.* -80, -100, and -180 ppm, which are assigned to the *trans-*, *cis-* and *gem-*fluorine nuclei respectively.^{14,24} Additionally, PF coupling is observed (in all cases) on the resonance assigned to the *gem-*fluorine nucleus. In complexes 1–4 this coupling appears in both the ¹⁹F and ³¹P{¹H} NMR spectra as a virtual triplet, indicative of a system with mutually *trans-*phosphine ligands whilst for complex 5 a virtual quintet is observed as a result of the ligand being bis-CF=CF₂ substituted. All the complexes show an increase in magnitude of the ²*J*(PF) coupling constant compared to the free ligands,^{14,16,17} but no discernible *J*(RhF) coupling is resolved.

Vibrational spectroscopic features

The infra-red spectra of 1 to 5 all display four IR bands characteristic of a perfluorovinyl-containing compound: viz. v(C=C) at 1720-40 cm⁻¹ and three v(C-F) bands at 1304–14, 1146–57 and 1028– 51 cm⁻¹.²⁵ An evaluation of the electronic effects of the different combinations of alkyl, aryl and perfluorovinyl groups in the ligands $PR_2(CF=CF_2)$ (R = Ph, Cy, ⁱPr, Et), and $PPh(CF=CF_2)_2$ can be undertaken by comparison of the $v(C \equiv O)$ frequencies of complexes 1 to 5. For trans-[RhCl(CO){ $PPh_2(CF=CF_2)$ }], 1, this is observed at 1989 cm⁻¹. As anticipated, this is at higher frequency than the CO stretch for *trans*-[RhCl(CO)(PPh₃)₂] (1964 cm⁻¹)²² indicating a reduction in back bonding upon substitution of a phenyl group for an electron-withdrawing perfluorovinyl group in the phosphine ligand. This trend continues for the complex of PPh(CF=CF₂)₂, **5**, where $v(C\equiv O)$ is observed at 2002 cm⁻¹, which is only a little lower than that found for *trans*-[RhCl(CO){ $P(C_6F_5)_3$ }] (2008 cm⁻¹).²³ For the complexes of the remaining phosphines PEt₂(CF=CF₂), **2**, PⁱPr₂(CF=CF₂), **3**, and $PCy_2(CF=CF_2)$, 4, the absorptions are at 1981, 1981 and 1979 cm⁻¹ respectively. This suggests that they possess, essentially, the same electronic properties, lying mid-way between the PPh₃ and $P(C_6F_5)_3$ analogues.

Cundari *et al.*⁶ reported semi-empirical electronic parameter (SEP) values derived from calculations of the CO stretching frequency of [RhCl(CO)P₂] complexes (P = P(III) ligand) for both PPh₂(CF=CF₂) and PPh(CF=CF₂)₂. Whilst the values obtained are *ca.* 7–10% higher than the experimental data they can still be used for comparison. The computed data suggest that the perfluorovinyl-containing phosphine PPh₂(CF=CF₂) [SEP = 2124 cm⁻¹] possesses similar electronic properties to

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Selected data for [Rh(CO)Cl{PR_{3-n}(CF=CF₂), }2], [PdX₂{PR_{3-n}(CF=CF₂), }2] and [PtX₂{PR_{3-n}(CF=CF₂), }2] complexes Table 1

						Elemental ar (calculated fi	ialysis C, H, gures) (%)	halide	
Complex	Geometry	δ $^{31}P\{^{1}H\}$ (CDCl ₃) (ppm), coupling constants/Hz	Colour	mp/°C	Yield (%)	С	Н	X	
$[Rh(CO)CI{PPh_2(CF=CF_2)}_2], 1$	trans	$+16.6$ [dvt, $1/2 ^2 J(PF) + ^4 J(PF) = 15, ^1 J(RhP) =$	Yellow	124-128	09	50.2 (49.8)	3.1 (2.9)	5.3 (5.1)	
$[Rh(CO)CI\{PEt_2(CF=CF_2)\}_2], 2$	trans	$^{1.2.2.1}_{1.2.4.1}$ (dvt, 1/2] $^{2}J(PF) + ^{4}J(PF) = 17, ^{1}J(RhP) = 1700$	Yellow	123-124	52	30.7 (30.8)	3.9 (3.9)	7.1 (7.0)	
$[Rh(CO)CI{PiPr_2(CF=CF_2)}_2], 3$	trans	$^{126.41}_{124.1}$ + $^{40.5}$ [dvt, 1/2] ^{2}J (PF) + ^{4}J (PF) = 12, ^{1}J (RhP) =	Yellow	99–102	67	36.7 (36.3)	4.3 (5.0)	6.9 (6.3)	
$[Rh(CO)CI{PCy_2(CF=CF_2)}_2], 4$	trans	$^{121.1}_{120.4}$ [dvt, 1/2] $^{2}J(PF) + ^{4}J(PF) = 12, ^{1}J(RhP) = ^{120.4}_{120.6}$	Yellow	131–134	54	48.4 (48.2)	6.2 (6.1)	4.7 (4.9)	
$[Rh(CO)CI{PPh(CF=CF_2)_2}, 5$	trans	1.2000] +3.3 [dvqt, $1/2 ^2 J(PF) + {}^4 J(PF) = 19, {}^1 J(RhP) =$ 1.42.3 [dvqt, $1/2 ^2 J(PF) + {}^4 J(PF) = 19, {}^1 J(RhP) =$	Yellow	62–65	78	35.9 (35.7)	1.1 (1.4)	4.7 (5.1)	
$[PdCl_{2}{PPh_{2}(CF=CF_{2})}, 6$	trans	$^{142.01}_{+12.3}$ [vt, 1/2 [² J(PF) + ⁴ J(PF)] = 17]	Apricot	85-87	38	48.3 (47.4)	3.0 (2.8)	9.4(10.0)	
$[PdBr_2 \{PPh_2(CF=CF_2)\}_2]$, 7	trans	$+9.4 [vt, 1/2]^2 J(PF) + {}^4 J(PF) = 17]$	Orange	134 - 136	51	42.2 (42.1)	2.5 (2.5)	20.4(20.1)	
$[PdI_2 \{PPh_2(CF=CF_2)\}_2], 8$	trans	-2.7 [vt, 1/2 ² J(PF) + ⁴ J(PF) = 16]	Brown	136 - 139	45	38.0 (37.7)	2.2 (2.2)	28.8 (28.5)	
$[PdCl_2 \{P^{i}Pr_2(CF=CF_2)\}_2]$, 9	trans	+34.3 [vt, 1/2 ² J(PF) + ⁴ J(PF) = 12]	Yellow	139–141	<i>LL</i>	33.5 (33.5)	4.9 (4.9)	11.9 (12.4)	
$[PdBr_{2} \{P^{i}Pr_{2}(CF=CF_{2})\}_{2}], 10$	trans	+34.1 [vt, $1/2$ ² J (PF) + ⁴ J (PF) = 13]	Orange	136-137	99	29.3 (29.0)	4.3 (4.2)	24.0 (24.2)	
$[PdI_{2}{PiPr_{2}(CF=CF_{2})}_{1}, 11$	trans	+32.2 [vt, 1/2 ² J(PF) + ⁴ J(PF) = 14]	Brown	129–130	81	25.9 (25.4)	3.7 (3.7)	33.4 (33.6)	
$[PdCl_{2}{PCy_{2}(CF=CF_{2})}_{2}, 12$	trans	$+24.1$ [vt, $1/2 ^2 J(PF) + ^4 J(PF) = 15$]	Yellow	166 - 167	77	46.0 (45.8)	5.9 (6.0)	9.3 (9.7)	
$[PdCl_2 \{PPh(CF=CF_2)_2\}_2], 13$	trans	$-2.1 [vqn, 1/2]^2 J(PF) + {}^4 J(PF) = 18]$	Yellow-orange	118 - 120	44	33.8 (33.5)	1.3(1.4)	10.0(9.9)	
$[PdBr_{2} \{PPh(CF=CF_{2})_{2}\}_{2}], 14$	trans	$-5.9 [vqn, 1/2]^{2} J(PF) + {}^{4} J(PF) = 17]$	Yellow	116-119	65	30.0 (29.8)	1.2 (1.2)	19.7 (19.9)	
$[PdI_{2} \{PPh(CF=CF_{2})_{2}\}, 15$	trans	$-20.6 [\mathrm{vqn}, 1/2]^2 J(\mathrm{PF}) + {}^4 J(\mathrm{PF}) = 17]$	Burgundy	100 - 102	72	27.1 (26.7)	0.7(1.1)	27.8 (28.2)	
$[PtCl_{2}{PiPr_{2}(CF=CF_{2})}], 16$	trans	+29.8 [vt, $1/2 ^2 J(PF) + {}^4 J(PF) = 16$, ${}^1 J(PtP) = 2673$]	Cream	143–144	68	29.6 (29.0)	4.3 (4.2)	10.3(10.7)	
$[PtBr_{2}{PiPr_{2}(CF=CF_{2})}_{1}, 17$	trans	+28.0 [vt, $1/2$] ² J (PF) $+$ ⁴ J (PF)] = 15, ¹ J (PtP) = 2598]	Yellow	144 - 146	61	25.8 (25.6)	3.5 (3.7)	21.2 (21.3)	
$[PtI_2{PiPr_2(CF=CF_2)}, 18$	trans	$+25.0 [vt, 1/2]^{2} J(PF) + {}^{4} J(PF) = 15, {}^{1} J(PtP) = 2533]$	Orange	140 - 141	74	22.8 (22.7)	3.1(3.3)	29.9 (30.1)	
$[PtCl_{2} \{PCy_{2}(CF=CF_{2})\}_{2}], 19$	trans	+19.8 [vt, 1/2] ² $J(PF)$ + ⁴ $J(PF)$] = 15, ¹ $J(PtP)$ = 2654]	Cream	179 - 181	50	41.3(40.9)	5.9 (5.4)	8.5(8.6)	
$[PtCl2 {PPh(CF=CF2)2}, 20$	cis	$-10.3 [t, {}^{2}J(PF) = 37, {}^{1}J(PtP) = 3711]$	White	67–71	27	30.2 (29.8)	1.2 (1.2)	9.3(8.8)	
	trans	$-0.6 [vqn, 1/2]^2 J(PF) + {}^4 J(PF) = 21, {}^1 J(PtP) = 3039]$							
$[PtBr_2{PPh(CF=CF_2)_2}], 21$	cis	-12.9 [t, ² J(PF) = 36, ¹ J(PtP) = 3645]	Lemon	109-112	61	27.5 (26.8)	0.7(1.1)	17.6 (17.9)	
	trans	-3.3 [vqn, 1/2 ² <i>J</i> (PF) + ⁴ <i>J</i> (PF) = 20, ¹ <i>J</i> (PtP) = 2929]							
$[PtI_{2}{Phh(CF=CF_{2})_{2}}, 22$	trans	-13.3 [vqn, $1/2$] ² $J(PF) + {}^{4}J(PF)$ = 19, ${}^{1}J(PtP) = 2858$]	Orange	122 - 124	74	24.4 (24.3)	0.9(1.0)	25.3 (25.7)	

 $PPh(C_6F_5)_2$ [SEP = 2123 cm⁻¹]. However, the experimental data for PPh_{3-n}(CF=CF₂)_n [$n = 1, 1989; n = 2, 2002 \text{ cm}^{-1}$] and $PPh_{3-n}(C_6F_5)_n$ [n = 1, 1982; n = 2, 1996 cm⁻¹]²³ suggests that the perfluorovinyl group is slightly more electron-withdrawing than C_6F_5 . This is supported by the ¹J(RhP) coupling constants, vide supra, where slightly larger values are observed for perfluorovinylcontaining phosphines compared with C₆F₅-containing analogues. Furthermore, the Tolman electronic parameter²⁶ χ_i derived from the v(CO) stretching data and the previously reported empirical relationship between CO-stretching frequencies of [Rh(CO)ClP₂] and [Ni(CO)₃P] complexes,²⁷ gives a value of 11.2 for the C_6F_5 group while for the C_2F_3 group the average value determined from complexes 1-5 is 12.3. This places the perfluorovinyl group between that of C_6F_5 and chlorine ($\chi_1 = 14.8$) on this scale. Unfortunately analogous data for the trifluoromethyl- and pentafluoroethyl-containing phosphines are not available, so it is not possible to make a similar comparison with those ligands.

Crystal structure of *trans*-[RhCl(CO){PPh₂(CF=CF₂)}₂], 1

Attempts were made to grow crystals for X-ray diffraction work for complexes 1–5, however, only for complex 1 were suitable crystals obtained. Analysis of the data (Table 2) confirm the complex to be *trans*-[RhCl(CO){PPh₂(CF=CF₂)}₂], the molecular structure of which is shown in Fig. 1.

The rhodium centre in **1** lies in a slightly distorted square planar environment, with Rh–P bond lengths of 2.304(2) and 2.297(2) Å, and d(Rh-Cl) = 2.349(2) Å. The Rh–P and Rh–Cl bonds are shorter than the average values for monomeric *trans*-[RhCl(CO)(PR₃)₂] complexes containing perprotio phosphines reported in the Cambridge Structural Database²⁸ [d(Rh-P):



Fig. 1 ORTEP representation of the structure of **1**. Thermal ellipsoids are shown at the 30% level. Selected bond lengths: Rh1–C1 1.827(9), Rh1–P1 2.304(2), Rh1–P2 2.297(2), Rh1–Cl1 2.349(2), P1–Cl4 1.790(9), P1–C8 1.812(8), P1–C2 1.815(8), C1–O1 1.101(9) Å. Selected bond angles: C1–Rh1–P1 90.9(3), C1–Rh1–P2 91.0(3), P1–Rh1–P2 77.5(3)°.

range 2.280–2.433 Å, mean 2.328(5) Å; d(Rh-Cl): range 2.341– 2.422, mean 2.375(3) Å, sample size: 38]. These shorter than average distances for 1 are anticipated for the presence of the electron-withdrawing group in the phosphine and are comparable with those found in other organofluoro-phosphine containing complexes *e.g. trans*-[RhCl(CO){PPh(C₆H₃F₂-2,6)₂}₂]; Rh–P = 2.3100(13) Å.²¹

Whilst the Rh–C distance of 1.827(9) Å in **1** is the same as that of the non-fluorinated analogue *trans*-[RhCl(CO)-{PPh₂(CH=CH₂)}₂] (1.827(1) Å),²⁰ the C=O distance in **1**

Table 2 Crystallographic data for *trans*-[Rh(CO)Cl{PPh₂(CF=CF)}₂], **1**, [PdX₂{PR₂(CF=CF₂)}₂] (X = Cl, R = ⁱPr **9**; X = Br, R = ⁱPr **10**; X = Cl, R = Cy, **12**) and [PdX₂{PPh(CF=CF₂)}₂] (X = Br, **14**; X = I, **15**)

_	1	9	10	12	14	15
Formula Formula weight	C ₂₉ H ₂₀ ClF ₆ OP ₂ Rh 698.75	$C_{16}H_{28}Cl_2F_6P_2Pd$ 573.62	$C_{16}H_{28}Br_2F_6P_2Pd$ 662.54	$C_{28}H_{44}Cl_2F_6P_2Pd$ 733.87	$\begin{array}{c} C_{20}H_{10}Br_{2}F_{12}P_{2}Pd \\ 806.44 \\ \end{array}$	$\begin{array}{c} C_{20}H_{10}F_{12}I_2P_2Pd\\ 900.42\\ \end{array}$
Crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	$P2_1/n$	P1	$P2_1/n$	<i>P</i> 1	<i>P</i> 1	P1
a/A	11.688 (2)	8.090 (2)	9.7399 (2)	11.2691 (6)	9.105 (2)	9.9798 (10)
b/Å	23.638 (3)	8.3232 (14)	11.6112 (3)	11.6674 (6)	10.013 (1)	11.4305 (10)
c/Å	11.873 (2)	9.2824 (13)	10.7920 (3)	14.9514 (9)	7.870(1)	12.382 (2)
a/°	90	80.593 (12)	90	74.405 (2)	109.062 (10)	106.783 (10)
β/°	114.83 (2)	77.717 (16)	93.697 (1)	70.092 (3)	102.91 (2)	94.101 (10)
γ/°	90	70.897 (16)	90	63.955 (3)	99.26 (2)	102.413 (10)
$V/Å^3$	2977.1 (9)	574.08 (19)	1217.95 (5)	1644.00 (16)	639.4 (2)	1307.1 (3)
Ζ	4	2	2	2	1	2
T/K	293 (2)	203 (2)	293 (2)	150 (2)	293 (2)	293 (2)
$D_{\rm c}/{\rm g}~{\rm cm}^{-3}$	1.559	1.659	1.807	1.483	2.094	2.288
Crystal size/mm	$0.25 \times 0.25 \times 0.1$	$0.25 \times 0.15 \times 0.1$	$0.07 \times 0.15 \times 0.2$	$0.25\times0.04\times0.01$	$0.25\times0.15\times0.15$	$0.10\times0.15\times0.25$
μ/mm^{-1}	0.830	1.227	4.219	0.875	11.628	0.926
2θ range/°	$3.40 \rightarrow 50$	$4.52 \rightarrow 49.96$	$6.4 \rightarrow 50$	$4.52 \rightarrow 49.96$	$6.8 \rightarrow 65.0$	$3 \rightarrow 50.00$
Total reflections	5474	2152	19675	22106	2191	4874
Unique reflections (R_{int})	5211 (0.0360)	2152	2786 (0.052)	5820 (0.091)	2048 (0.056)	4383 (0.021)
Observed reflections	2974	1994	2083	4101	1474	3784
$[I > 2\sigma(I)]$						
Parameters	361	128	181	357	169	334
Final <i>R</i> indices $I > 2\sigma(I)$]	$R_1 0.0601, wR_2 0.1411$	$R_1 0.0485, wR_2 0.1612$	$R_1 0.0360, wR_2 0.0781$	$R_1 0.0792, wR_2 0.1758$	$R_1 0.0576, wR_2 0.1554$	$R_1 0.0336, wR_2 0.2747$
<i>R</i> indices (all data)	$R_1 0.1203, wR_2 0.1744$	$R_1 0.0567, wR_2 0.2090$	$R_1 0.0582, wR_2 0.0870$	$R_1 0.1155, wR_2 0.2006$	$R_1 0.0864, wR_2 0.1745$	$R_1 0.1205, wR_2 0.0908$
Max., min. $\Delta \rho / e \text{ Å}^{-3}$ Goodness of fit on F^2	0.499, -0.332 1.044	1.722, -2.198 1.229	0.89, -0.89 1.031	1.313, -1.011 1.069	0.77, -1.08 1.074	0.89, -0.76 1.05

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(1.101(9) Å) is shorter than the average for all crystallographically characterised *trans*-[RhCl(CO)(PR₃)₂] complexes (1.140(7) Å) which is consistent with the higher than typical v(CO) stretching frequency observed for **1**.

Examination of the data for **1** shows that there are two intramolecular interactions of 3.253(8) and 3.332(8) Å from the rhodium centre to the *cis* fluorine atoms of each of the perfluorovinyl groups (F3 and F6), which are significantly shorter than the sum of the van der Waals radii (3.72 Å). These interactions are orientated above and below the metal centre with F(3)–Rh–F(6) and F(3)–Rh–Cl(1) angles of 136.54(18)° and 67.82(14)° respectively, indicating considerable distortion from an arrangement where the two fluorine atoms could be said to distantly occupy the vacant octahedral sites. Additionally, two short Rh…H interactions to *ortho* protons are indicated [Rh…H(9) 3.007 Å, Rh…H(27) 3.068 Å]. In the extended structure of **1**, molecules align in infinite stacks perpendicular to the *a* direction, but with no particularly short contacts between adjacent molecules.

Synthesis and characterisation of Pd(II) and Pt(II) complexes

The reaction of K_2MX_4 (M = Pd, Pt; X = Cl, Br, I) in aqueous ethanolic solution with two equivalents of the perfluorovinylcontaining ligands in all cases resulted in the formation of complexes of the general formula $[MX_2{PR_n(CF=CF_2)_{3-n}}_2]$ (except for the bulky $PCy_2(CF=CF_2)$ ligand for which only the chlorides were prepared).

For all of the complexes NMR data was much as anticipated, and this is summarised in Table 1. In each case the ³¹P NMR resonance for the complex was shifted to higher frequency by 40–50 ppm compared with that observed for the free ligand. All of the

palladium complexes exhibit virtual coupling, and on this basis **6–15** are assumed to adopt *trans*-geometries. For the platinum complexes, in addition to the appearance of the spectrum, the magnitude of the ¹*J*(Pt–P) coupling constants (¹⁹⁵Pt, I = 1/2, 33.8%) were used to determine the geometry of the isomers formed. We note that the magnitude of this coupling constant increases in the order PCy₂(CF=CF₂) < P'Pr₂(CF=CF₂) < PPh(CF=CF₂)₂ for the series of *trans*-[PtCl₂P₂] complexes.

It is clear from the data in Table 1 that for the platinum(II) complexes the position of the *cis-trans* equilibrium in solution is finely balanced. Complexes of the larger phosphines *e.g.* $PCy_2(CF=CF_2)$ and/or larger halide ligands, such as iodide, result exclusively in platinum complexes of *trans*-geometries in solution, while for the sterically less demanding ligands the *cis*-isomer is more likely to be observed, *e.g. cis*-[PtCl₂{PEt₂(CF=CF₂)}₂].¹⁶ For ligands of intermediate size a mixture of *cis*- and *trans*-isomers is observed in solution. Because of these findings we were interested in quantifying the steric demand of these ligands as well as determining whether their solid state structures reflect the solution phase data.

Crystal structures of Pd(II) and Pt(II) complexes

Single crystals were successfully grown for the complexes $[PdCl_2{P^{P}r_2(CF=CF_2)}_2]$, 9, $[PdBr_2{P^{P}r_2(CF=CF_2)}_2]$, 10, $[PdCl_2{PCy_2(CF=CF_2)}_2]$, 12, $[PdBr_2{P^{P}r_2(CF=CF_2)}_2]$ 14, $[PdI_2{P^{P}r_2(CF=CF_2)}_2]$ 15, $[PtCl_2{P^{P}r_2(CF=CF_2)}_2]$, 16, $[PtBr_2{P^{P}r_2(CF=CF_2)}_2]$, 17, $[PtL_2{P^{P}r_2(CF=CF_2)}_2]$ 18, $[PtCl_2{PCy_2(CF=CF_2)}_2]$, 19 and $[PtBr_2{P^{P}r_2(CF=CF_2)}_2]$, 21. The crystallographic data for these complexes are presented in Tables 2 and 3 and ORTEP representations of their structures are shown in Fig. 2 and 3.

Table 3	Crystallographic data for	$[PtX_{2}]PR_{2}(CF=CF)$	$\{x_{i}\}_{i} = {}^{i}Pr. X =$	= Cl. 16; Br. 17; I. 18; R =	Cv, X = Cl, 19 and <i>cis</i> -[PtB	$r_{2}{PPh(CF=CF_{2})_{2}, 21}$
I HOIC C	Ci i stanographic data ioi		· · · · · · · · · · · · · · · · · · ·	-0.1, 10, 0.1, 17, 1, 10, 10 -	$C_{1,1} = C_{1,1} + C_{1$	
		L 21 21	2/121 /		<i>2/</i> /////	21 2/2/2/2/

	16	17	18	19	21
Formula Formula weight Crystal system	$C_{16}H_{28}Cl_2F_6P_2Pt$ 662.3 Monoclinic	$C_{16}H_{28}Br_2F_6P_2Pt$ 751.23 Monoclinic	$C_{16}H_{28}I_2F_6P_2Pt$ 845.20 Orthorhombic	$C_{28}H_{44}Cl_2F_6P_2Pt$ 822.20 Triclinic	$C_{20}H_{10}Br_2F_{12}P_2Pt$ 895.13 Monoclinic
Space group	$P2_1/c$	$P2_1/n$	Pbca	PĪ	$P2_1/c$
a/Å	8.1294 (9)	9.7227 (3)	12.6437 (16)	11.2760(2)	11.3236 (3)
b/Å	16.184 (7)	11.5780 (4)	12.9891 (18)	11.6583(2)	13.3972 (2)
$c/Å$ $a/^{\circ}$	25.965 (8) 90	10.7417 (4) 90	14.5673 (19) 90	14.9767(3) 74 5780(10)	16.7449 (2) 90
$\beta/^{\circ}$	93.315 (15) 90	93.241 (2) 90	90 90	70.0010(10) 63.9810(10)	106.182 (2) 90
$V/Å^3$	3410.4 (19)	1207.25(7)	2392.4 (5)	1646.86(5)	2439.63 (8)
Z	4	2	8	2	4
T/K	293 (2)	293 (2)	203 (2)	150(2)	293 (2)
$D_{\rm c}/{ m g~cm^{-3}}$	1.935	2.066	2.347	1.659	2.437
Crystal size/mm	$0.15\times0.15\times0.20$	$0.15\times0.15\times0.07$	$0.25 \times 0.20 \times 0.20$	$0.07 \times 01.8 \times 0.18$	$0.10 \times 0.10 \times 0.20$
$\mu/{ m mm^{-1}})$	6.595	9.299	8.626	4.570	9.259
2θ range/°	$2.96 \rightarrow 49.98$	$7.6 \rightarrow 50.00$	$5.4 \rightarrow 49.96$	$6.0 \rightarrow 55.0$	$4.0 \rightarrow 50.00$
Total reflections	6444	10256	2102	7530	4507
Unique reflections (R_{int})	5986 (0.019)	2117 (0.030)	2102	7530 (0.085)	4276 (0.030)
Observed reflections $[I > 2\sigma(I)]$	4824	1842	1713	5104	3115
Parameters	379	125	132	355	334
Final <i>R</i> indices $I > 2\sigma(I)$]	$R_1 \ 0.0627, \ wR_2 \ 0.1670$	$R_1 0.0314, wR_2 0.0842$	$R_1 0.0434, wR_2 0.1078$	$R_1 0.0531 \text{ w} R_2$ 0.1407	$R_1 0.0382, wR_2 0.0622$
R indices (all data)	$R_1 0.0806, wR_2 0.1842$	$R_1 0.0373, wR_2 0.0887$	$R_1 0.0549, wR_2 0.1129$	$R_1 0.0815 \text{ w} R_2 0.1607$	$R_1 0.0712, wR_2 0.0705$
Max., min. $\Delta \rho / e \text{ Å}^{-3}$	3.40, -4.30	1.287, -1.460	1.139, -1.313	-3.02, 3.04	0.947, -0.763
Goodness of fit on F^2	1.039	1.067	1.101	1.09	1.022



Fig. 2 ORTEP representation of the structures of (a) **9**, (b) **10**, (c) **12**, (d) **14** and (e) **15**. Thermal ellipsoids are shown at the 30% level. Selected bond lengths (Å) and angles (°) (other data are given in Table 4): (a) P–C1 1.810(6), P–C6 1.826(6), P–C3 1.837(6), F1–C1 1.363(7), F2–C2 1.324(7), F3–C2 1.303(9); Cl–Pd–P 91.23(6), C2–C1–F1 116.6(5), C2–C1–P 125.6(5), F1–C1–P 117.8(5), C1–C2–F3 125.4(6), C1–C2–F2 124.3(7), F3–C2–F2 110.3(6); (b) C1–C2 1.279(6), C1–F1 1.377(4), C1–P 1.822(4), C2–F3 1.291(6), C2–F2 1.331(5), C3–P 1.845(4), C6–P 1.846(4); C2–C1–F1 115.3(4), C2–C1–P 127.4(3), F1–C1–P 117.2(3), C1–C2–F3 123.6(4), C1–C2–F2 124.7(5), F3–C2–F2 111.7(4), P Pd Br 90.67(2); (c) C1–C2 1.292(15), C1–F1 1.390(11), C1–P 1.807(9), C2–F3 1.294(14), C2–F3 1.230(12), C3–P 1.830(9), C9–P 1.839(9); C2–C1–F1 115.9(9), C2–C1–P1 126.2(9), F1–C1–P1 117.9(7), C1–C2–F3 124.4(10), C1–C2–F2 125.3(12), F2–C2–F3 110.3(10), Cl–Pd–P 91.98(7); (d) P–C1 1.802(10), P–C5 1.810(10), P–C3 1.826(11), C1–C2 1.293(17), C1–F1 1.357(13), C2–F3 1.263(16), C2–F2 1.329(13); P–Pd–Br 88.56(7), C10–C5–P 121.5(9), C6–C5–P 118.6(7), C2–C1–F1 116.8(10), C2–C1–P1 125.7(10), F1–C1–P1 117.4(8), F3–C2–C1 126.3(11), F3–C2–F2 109.6(11), C1–C2–F2 124.1(14), C4–C3–F4 116.6(14), C4–C3–P 129.9(14), F4–C3–P1 113.4(8), C3–C4–F6 122.7(16), C3–C4–F5 120(2), F6–C4–F5 117.0(14); (e) C1–C2 1.282(9), C1–F1 1.349(7), C1–P 1.810(6), C2–F3 1.306(8), C2–F2 1.307(8), C3–C4–F6 122.7(16), C3–C4–F5 120(2), F6–C4–F5 117.0(14); (e) C1–C2 1.282(9), C1–F1 1.349(7), C1–P 1.810(6), C2–C1–P 126.9(5), F1–C1–P 116.3(4), C1–C2–F3 124.8(6), C1–C2–F2 124.9(7), F3–C2–F2 110.3(6), C4–C3–F4 115.9(6), C4–C3–P1 129.4(5), F4–C3–P1 114.7(4), C3–C4–F6 126.2(6), C3–C4–F5 124.0(7), F6–C4–F5 109.8(6).

Four of the palladium complexes, 9, 12, 14 and 15, crystallize in the triclinic $P\bar{1}$ space group, while 10 is monoclinic $(P2_1/n)$. Complexes 9, 10 and 15 are found to possess a single unique molecule, while 12 and 14 both contain two molecules. In the latter complex one of the molecules shows disorder of a single perfluorovinyl group, and this was modelled during the analysis using two sites of equal occupancy.

The X-ray crystallographic data confirms the interpretation of the ³¹P{¹H} NMR data, in that all of the palladium complexes adopt a *trans*-geometry. The Pd atoms are located on a centre of symmetry. The Pd–P distances range from *ca.* 2.306 Å for the PPhpfv₂-containing complexes to 2.3331(8) Å for the PⁱPr₂pfv complex, see Table 4. In each case these distances are slightly shorter than the average Pd–P distance for all *trans*-[PdX₂(PR₃)₂] complexes containing simple monodentate phosphine ligands in the CCDC database,²⁸ but are similar to Pd–P distances observed in other palladium complexes containing organofluorinesubstituted phosphines, for example, *trans*-[PdCl₂{P(C₆F₅)₃}₂], d(Pd-P) = 2.3051(12) Å and Pd–Cl = 2.2907(10) Å.²⁹

The C=C and C-F distances of the perfluorovinyl fragment in the palladium complexes are consistent with those found in the crystal structure of **1**, and are similar to those observed for other previously reported perfluorovinyl phosphine complexes.^{14,16,17} The longest of the three C–F bonds is that of the α -fluorine, whilst the bond to the *cis*-fluorine is slightly shorter than that to the *trans*-fluorine. The presence of intramolecular metal–fluorine interactions of *ca.* 3.4 Å, less than the sum of the van der Waals radii of palladium and fluorine (3.77 Å), are observed from the *cis*-fluorine atom to the palladium atom, similar to that found in the rhodium complex, **1**, (see Table 4). It is noteworthy that in **14** and **15** a M ··· F interaction is observed to only one of the two perfluorovinyl groups of each phosphine ligand. Also, for both complexes the Pd–P–C_{pfv} bond angle for the CF=CF₂ group involved in this interaction is smaller (114.4(4) *cf.* 116.3(5)° and 116.5(2) *cf.* 120.4(2)° respectively) than that observed for the second one not involved in such an interaction.

The extended structure of $[PdCl_2{PiPr_2(CF=CF_2)}_2]$, **9**, shows that molecules align in infinite stacks along the *c* direction, although no particularly short interactions are observed. $[PdBr_2{PiPr_2(CF=CF_2)}_2]$, **10**, packs in chains of infinite stacks along the *b* cell dimension (see Fig. 4) with both perfluorovinyl groups overlapping with those of adjacent molecules, albeit at a distance of *ca*. 6 Å. Intermolecular hydrogen bonds are also observed with $d(H(6) \cdots Br(1)) = 2.88(4)$ Å.



Fig. 3 ORTEP representation of the structures of (a) **17**, (b) **18**, (c) **19**, and (d) **20**. Thermal ellipsoids are shown at the 30% level. Selected bond lengths (Å) and angles (°) (other data are given in Table 4): (a) C1–C2 1.288(9), C1–F1 1.377(7), C1–P 1.820(6), C2–F3 1.298(9), C2–F2 1.334(8), C3–P 1.840(6), C6–P 1.847(7); C2–C1–F1 115.1(6), C2–C1–P 127.6(5), F1–C1–P 117.2(4), C1–C2–F3 123.8(7), C1–C2–F2 124.5(7), F3–C2–F2 111.7(6), P–Pt–Br 89.51(4); (b) P–C1 1.818(8), P–C6 1.841(9), P–C3 1.842(8), F1–C1 1.361(10), F2–C2 1.312(11), F3–C2 1.318(10), C1–C2 1.297(13); P–Pt–I 91.14(5), C2–C1–F1 114.9(7), C2–C1–P 128.0(7), F1–C1–P 117.0(6), C1–C2–F2 126.0(9), C1–C2–F3 124.1(8), F2–C2–F3 109.9(8), C5–C3–P 111.7(6), C4–C3–P 110.3(6), C7–C6–P 111.4(7), C8–C6–P 110.8(7); (c) C1–C2 1.307(12), C1–F1 1.363(10), C1–P 1.822(8), C2–F2 1.288(11), C2–F3 1.328(9), C3–P 1.845(7), C9–P 1.836(8); C2–C1–F1 116.4(8), C2–C1–P1 125.4(7), F1–C1–P 118.1(6), F2–C2–C1 125.1(8), F2–C2–F3 111.5(8), C1–C2–F3 123.4(10), C1 Pt P 91.74(6); (d) P1–C9 1.790(8), P1–C3 1.813(8), P1–C1 1.817(8), F1–C1 1.330(9), F2–C2 1.306(9), F3–C2 1.308(10), F4–C9 1.359(8), F5–C10 1.297(8), F6–C10 1.316(9), P2–C13 1.798(8), P2–C15 1.810(8), P2–C11 1.817(8), F1–C1 1.351(9) F8–C12 1.297(9), F9–C12 1.327(10), F10–C13 1.370(8), F11–C14 1.326(10), F12–C14 1.276(11), C1–C2 1.313(11), C9–C10 1.301(10), C11–C12 1.301(11), C13–C14 1.301(12); P1–Pt–P2 99.22(7), P1–Pt–Br1 90.28(6), P2–Pt–Br1 170.36(6), P1–Pt–Br2 176.04(6), P2–Pt–Br2 83.58(6), Br1–Pt–Br2 86.85(3), C2–C1–F1 117.4(7), C2–C1–P1 127.7(7), F1–C1–P1 114.7(6), F2–C2–F3 111.3(7), F2–C2–C1 123.9(9), F3–C2–C1 124.8(8), C4–C3–P1 114.7(6), C10–C9–F4 114.7(7), C10–C9–P1 128.9(6), F4–C9–P1 116.4(5), F5–C10–C9 124.8(8), F5–C10–F6 110.9(7), C9–C10–F6 124.4(7), C12–C11–F7 114.8(8), C12–C11–P2 133.0(7), F7–C11–P2 112.0(5), F8–C12–C11 125.4(9), F8–C12–F1 110.5(8), C14–C13–P2 130.6(7), F10–C13–P2 112.3(6), F12–C14–C13 126.4(9), F12–C14–F11 111.3(8), C13–C14–F11 112.3(9).



Fig. 4 Packing diagram for $[PdBr_2{PiP_2(CF=CF_2)}_2]$, 10 showing the stacking of perfluorovinyl groups from adjacent molecules.

Complex 12 also stacks along the crystallographic *b* direction with the perfluorovinyl groups overlapping similarly to that observed in 10. A number of intermolecular hydrogen bonding interactions are also observed between protons of the cyclohexyl fragment in one molecule and the chloride ligands (average distance 2.77 Å) and the *trans*-fluorine of the pfv group, $d(H \cdots F)_{av} = 2.50$ Å of another.

The extended structures of 14 and 15 both exhibit stacks of molecules in the *c* direction which show alignment between the phenyl groups of adjacent molecules. In 14 no particularly short arene–arene distances are apparent, but in 15 the arene rings are much closer with the centroid to centroid distance being 4.085 Å.

In addition to the X-ray data for the palladium complexes, solid state structures of five of the platinum(II) complexes 16–19 and 21 were also obtained (Table 3). Two of these are analogues of the palladium-containing complexes, viz. $[MCl_2{PCy_2(CF=CF_2)}_2]$ 19 (M = Pt) and 12 (M = Pd) and $[MBr_2{P^iPr_2(CF=CF_2)}_2]$ 17 (M = Pt) and 10 (M = Pd). In each case both complexes of the same ligand are isostructural. Complexes 17-19 all exhibit trans-geometries with Pt-P distances between 2.2985(19) Å [for $PCy_2(CF=CF_2)$] and 2.3143(14) Å for $P^iPr_2(CF=CF_2)$. These distances, and the platinum-halide distances, are comparable with those reported for other structurally characterised trans-[PtX₂(PR₃)₂] complexes in the Cambridge Crystallographic Database, where R contains electron-withdrawing substituents.²⁸ Intramolecular $M \cdots F$ interactions, similar to those observed for the rhodium and palladium systems, are observed in the trans square planar complexes and these distances are listed in Table 4. Interestingly, not all of the *cis*-complexes exhibit the same interaction.

Lable .	Selected bond length and angle of the selected bond length angle of the selected bond	lata for [Rh(C	O)CI{PPh ₂ (CF=CF ₂	2)}2], [PdX2{PRn(CF=C	$(F_2)_{3-n}$ and $[PtX_2 \{PR_n(CF=CF_2)_{3-n}]$	"}] complexes		1
	Complex	Geometry	d(M-P)/Å	$d(M-X)/\text{\AA}$	M-P-C/o	C-P-C/°	$d(\mathbf{M}\cdots\mathbf{F}_{\mathrm{cis}})/\mathrm{\AA}$	
	$[Rh(CO)CI{PPh_2(CF=CF_2)}_2], 1$	trans	2.301(2) av.	2.349(2)	116.2(3), 116.4(3), 113.9(3)	103.2(4), 102.0(4), 103.3(5)	3.253(8), 3.332(8)	
	$[PdCl_{2}{Di}Pr_{2}(CF=CF_{2})]_{2}], 9$	trans	2.3158(15)	2.2856(16)	117.6(3), 114.8(3), 114.2(4) 114.5(2), 118.2(2), 110.8(2)	103.2(4), 101.7(4), 103.6(5) 102.6(3), 102.1(3), 107.1(3)	3.462(4)	
	$PdBr_2 PiPr_2 CF=CF_2 P_2 Dr_2 CF=CF_2 P_2 P_2 P_2 P_2 P_2 P_2 P_2 P_2 P_2 P$	trans	2.3331(8)	2.4226(4)	116.40(13), 111.54(14), 117.27(14)	101.1(2), 102.19(19), 106.6(2)	3.604(3)	
	$[PdCl_2[PCy_2(CF=CF_2)]_2], 12$	trans	2.317(2), 2.332(2)	2.2911(19), 2.300(2)	113.5(3), 111.0(3), 118.7(3)	102.5(4), 103.5(4), 106.2(4)	3.459(8), 3.493(8)	
					114.0(4), 110.1(3), 115.2(3)	102.6(6), 105.4(5), 108.7(4)		
	$[PdBr_2{PPh(CF=CF_2)_2}], 14$	trans	2.307(3)	2.4066(11)	114.4(4), 116.3(5), 114.9(4)	98.8(3), 105.9(4), 100.7(3)	3.352(5)	
	$[PdI_2{Phh(CF=CF_2)_2}], 15$	trans	2.3061(13)	2.5995(5)	116.5(2), 112.3(2), 120.4(2)	106.1(5), 103.0(5), 100.5(5)	3.281(9)	
	$[PtBr_2{PEt_2(CF=CF_2)}]^a$	cis	2.238(9), 2.228(7)	2.472(3), 2.463(4)	117.5(11), 107.6(12), 117.1(10)	102.2(17), 109.6(18), 100.3(17)		
					117.4(10), 114.4(13), 114.0(10)	102.3(16), 98.3(18), 108.7(16)		
	$[PtCl_2 \{PPh_2(CF=CF_2)\}_2]^b$	cis	2.234(3), 2.228(3)	2.315(3), 2.343(3)	122.5(4), 112.6(4), 110.4(4)	103.7(5), 102.7(5), 102.9(5)	3.254(8)	
	1 k				112.2(4), 114.1(4), 114.0(4)	112.7(4), 99.5(5), 103.1(6)		
	$[PtCl_2 \{P^i Pr_2 (CF=CF_2)\}_2], 16$	cis	2.243(3), 2.246(3)	2.326(3), 2.336(3)	117.5(4), 113.5(5), 113.9(4)	103.2(6) 99.9(6), 107.2(6)		
	1 k				118.1(4), 114.0(5), 113.0(5)	103.3(7), 99.1(6), 107.9(7)		
		trans	2.290(3)		114.5(4), 110.3(6), 117.9(5)	103.4(8), 102.2(6), 107.4(8)	3.486(10)	
	$[PtBr_2{PiPr_2(CF=CF_2)}_1, 17$	trans	2.3143(14)	2.4205(10)	116.0(2), 116.9(2), 112.1(2)	102.4(3), 101.1(3), 106.7(3)	3.590(5)	
	$[PtI_2 \{P^i Pr_2 (CF=CF_2)\}_2], 18$	trans	2.3131(19)	2.6060(6)	115.5(3), 111.8(3), 119.5(3)	101.1(4), 101.7(4), 105.2(4)	3.677(6)	
	$[PtCl_{2} \{PCy_{2}(CF=CF_{2})\}_{2}], 19$	trans	2.3092(16)	2.3020(17)	113.8(3), 118.8(2), 112.1(3)	103.4(4), 101.6(4), 105.3(4)	3.470(7)	
			2.2985(19)	2.310(2)	114.8(3), 111.1(2), 116.4(3)	101.8(5), 105.2(5), 106.2(4)	3.492(7)	
	$[PtBr_2{Pph(CF=CF_2)_2}, 21$	cis	2.236(2), 2.244(2)	2.4319(9), 2.4567(9)	116.3(3), 113.7(3), 116.6(3)	100.8(4), 100.3(4), 107.1(4)	3.243(4)	
					118.9(3), 109.7(3), 117.5(3)	100.5(4), 101.4(4), 107.0(4)		

Once again the extended structures of these complexes are largely dominated by interactions between protons and the metalbound halide ligands, as well as to the *cis*-fluorines of the perfluorovinyl group, to generate stacks of molecules.

Thus, for example, in **19**, Cl··· H distances of 2.754 and 2.772 Å are observed along with $F \cdots H$ interactions of 2.516 Å. However, in contrast to most of the other complexes studied here, the iodide complex of PⁱPr₂(CF=CF₂), **18**, displays no hydrogen interactions less than the sum of the van der Waals radii, with either the iodide or any perfluorovinyl fluorine atom. Instead, alignment of molecules occurs to generate alternate fluorinated and non-fluorinated layers, as is shown in Fig. 5.



Fig. 5 Packing diagram for $[PtI_2{P^iPr_2(CF=CF_2)}_2]$, **18**.

The solid-state structure of complex **21** (which in solution shows the presence of both *cis*- and *trans*-isomers) shows exclusively the *cis*-isomer. The molecule exhibits slight asymmetry in the Pt– P and Pt–Br bond lengths, with average values being 2.240(2) and 2.4493(9) Å respectively. Both the Pt–P and Pt–Br distances are somewhat shorter than typical values for *cis*-[PtX₂(PR₃)₂] systems, but are comparable with Pt–P bond lengths observed for complexes containing other perfluoro-organo substituted phosphines, such as *cis*-[PtCl₂{PEt(p-C₆F₁₃C₆H₄)₂}₂].³⁰ However, the Pt–P distances are still significantly longer than those observed in platinum(II) complexes of P–F containing phosphines, such as *cis*-[PtCl₂{PF₂(*o*-OMeC₆H₄}₂],³¹ (Pt–P = 2.180(5)/2.181(4) Å), or in tertiary phosphite complexes such as *cis*-[PtCl₂{P(OMe)₃}₂],³² (Pt–P = 2.192(3)/2.155(3) Å).

Unlike the *trans*-complexes a single intramolecular $Pt \cdots F$ interaction is observed (3.243(4) Å), but, in common with the other complexes, intermolecular $H \cdots F$ and $H \cdots Br$ interactions less than the sum of the van der Waals radii are apparent which result in stacks of molecules aligned along the *a* crystallographic direction. When viewed from this direction aggregation of the halogen-containing parts of the molecules is apparent, see Fig. 6.

Data reported previously.¹⁶ ^b Data reported previously.¹⁴

The most interesting of the structures determined was that for $[PtCl_2{P^iPr_2(CF=CF_2)}_2]$, **16**, which revealed a highly unusual mixture of *cis*- and *trans*-isomers co-crystallised in the same unit cell, see Fig. 7. The *trans*-isomers are located at the corners of

Table 4 Selected bond ler



Fig. 6 Packing diagram for $[PtBr_2{PPh(CF=CF_2)_2}_2]$, 21.



Fig. 7 ORTEP representation of $[PtCl_2{PiPr_2(CF=CF_2)}_2]$, **16**. Thermal ellipsoids are set to 50% and hydrogens have been removed for clarity.

the unit cell, and on the top and bottom face, whilst *cis*-isomers are located in-between, resulting in the unit cell containing 4 *cis* and 2 *trans* molecules, giving a *cis*: *trans* ratio of 2:1, as shown in Fig. 8.



Fig. 8 Representation of the unit cell of cis/trans- [PtCl₂{P'Pr₂-(CF=CF₂)}₂], **16**, showing the relative positions of the *cis* (black) and *trans* (red) isomers. Hydrogen atoms have been removed for clarity.

The *cis* isomer displays deviation from an ideal square planar geometry, with P–Pt–Cl angles of $170.86(13)^{\circ}$ and $171.18(12)^{\circ}$, and slight asymmetry in the Pt–P [2.243(3) and 2.246(3) Å] and Pt–Cl [2.326(3) and 2.336(3) Å] distances, as is typically observed

for cis-[PtX₂L₂] complexes. The Pt–P bonds in the cis isomer are shorter than the Pt-P bonds in the *trans* isomer [2.290(3) Å], whilst the reverse trend is seen for the Pt-Cl bonds, Table 3. These trends are anticipated based upon the relative trans influence of phosphine and chloride ligands, (P > Cl). The Pt–P bond in *cis*- $[PtCl_2{P^iPr_2(CF=CF_2)}_2]$ is comparable to that observed in **21** but slightly longer than that observed in the previously reported cis- $[PtCl_2{PPh_2(CF=CF_2)}_2]$ complex.¹⁴ The Pt-P and Pt-Cl bond lengths observed for the trans-isomer of 16 [Pt-P: 2.290(3) Å; Pt-Cl: 2.292(3) Å] are both shorter than the values reported for trans- $[PtCl_2(P^iPr_3)_2]$, where Pt-P = 2.339(1)Å, and Pt-Cl = 2.303(1)Å,³³ but once again are comparable to those distances observed for similar complexes containing perfluoro-organo substituted phosphines, such as 17, 18 and *trans*-[PtCl₂{ $P(C_6F_5)_3$ }₂].³⁴ Both isomers of 16 display the usual variations in C-F distances in that the α-C-F bond is the longest. Differences between the C-F bonds to the cis- and trans-fluorine atoms in both isomers are small, and not significant within the experimental error.

The *cis*-isomer displays no intramolecular metal-fluorine interactions, unlike the situation observed for nearly all the other structures reported here, but it does display $Pt \cdots H$ interactions to protons of the isopropyl fragment. In contrast a short $Pt \cdots F$ interaction of 3.486(10) Å is observed for the *trans*-isomer (*cf.* sum of the van der Waals radii of platinum and fluorine of 3.77 Å), along with three short $Pt \cdots H$ interactions. Once again a reduction in the M–P–C bond angle is observed to coincide with the presence of the M \cdots F interaction (Pt–P–C in the *trans*-isomer = 114.5(4)° *cf.* 117.5(4) and 118.1(4)° for the *cis*-analogue).

The *cis/trans*-arrangement of $[PtCl_2{P^iP_2(CF=CF_2)}_2]$, **16**, results in the fluorine-containing substituents congregating together to form a series of isolated fluorous domains, as shown in Fig. 9. Two short intermolecular $F \cdots F$ contacts are observed, $[F(5) \cdots F(8): 2.848(12) \text{ Å}; F(2) \cdots F(7): 2.866(14) \text{ Å}, which are less than double the van der Waals radius of fluorine, 2.94 Å]. The$ *cis* $-isomers also display a short intermolecular H(8A) <math>\cdots$ Cl(2) interaction of 2.763 Å, (*cf.* sum of the van der Waals radii of 2.95 Å)



Fig. 9 Space filling representation of co-crystallized *cis*- and *trans*- $[PtCl_2{P^iPr_2(CF=CF_2)}_2]$, **16**, showing the fluorous domains.

for $[PdBr_2{P^iPr_2(CF=CF_2)}_2]$, 10. The observation of co-crystallized cis- and trans-isomers within the same unit cell is highly unusual. Multi-metallic systems, particularly based on rings or clusters, are known in which different metal centres exhibit different coordination geometries. For example, the bidentate stibine³⁵ and arsine³⁶ ligands of the type $Ph_2ECH_2EPh_2$ (E = As, Sb) can form bridged bimetallic systems with platinum and palladium in which one metal adopts a cisgeometry and the other trans. But, to the best of our knowledge, there is only one other analogous example of the phenomenon we observe here. $[PtCl_2{P(C_6H_4C_6F_{13}-4)_3}_2]$ was found to adopt a similar packing arrangement to give a cis: trans ratio of 2:1.37 In that complex the long fluorous chains are believed to be responsible for the packing, and the solution phase also contained both cis- and trans-isomers. In 16 it appears unlikely that a C_2F_3 unit is sufficient to give rise to fluorophobic/fluorophilic interactions, although it is clear that in the extended structure, as shown in the space-filling representation in Fig. 9, that the fluorovinyl groups are found to aggregate.

from the metal bound chloride, akin to the interaction observed

The observation in the solid state of both isomers is in contrast with the solution phase where **16** exists as the *trans*-isomer alone, on the basis of the ³¹P{¹H} NMR data, *vide supra*. The cocrystallisation of both isomers appears to be a phenomenon arising from crystal growth, as re-dissolution of the crystals results in a ³¹P{¹H} NMR spectrum consistent with only the presence of the *trans*-isomer, as was obtained for the powder prior to crystallisation.

A comparison of steric and electronic properties

Many of the complexes reported here represent the first examples of structurally characterised coordination compounds of the specific perfluorovinyl phosphines. It is therefore appropriate to use these data to obtain estimates of the steric demand of these ligands, to compliment the electronic data derived from the rhodium complexes. For all of the reported complexes the Tolman cone angle has been derived using the STERIC program³⁸ and the S_4' value calculated based on the M–P–C and C–P–C bond angles $(S_4' = [\sigma(M-P-C) - \sigma(C-P-C)]$ listed in Table 4. The S_4' value determined is sensitive to the halide and the geometry of the complex. For example, the calculated S_4' values for $P^iPr_2(CF=CF_2)$ vary from 29.7° in trans-[PtCl₂{ $P^{i}Pr_{2}(CF=CF_{2})$ }], 16, to 38.8° in trans- $[PtI_2{P^iPr_2(CF=CF_2)}_2]$, 18, whilst the *cis*-isomer of 16 yields a value of 34.7° which lies between these two limits. Essentially, a lower S_4' is observed in complexes where the ligand participates in a less sterically congested coordination sphere, and can thus expand to fill the available space. This is further illustrated by the S_4' value obtained from the crystal structure of SPⁱPr₂(CF=CF₂) which is 26.4°.9 The Tolman cone angles also show some variation from complex to complex. In order to allow sensible comparison of the determined values, we have taken the average of data for monomeric square-planar complexes only, and ignored any ligand which exhibits disorder. These values, along with electronic data, for our ligands and some related systems are presented in Table 5.

Both the Tolman cone angle and the S_4' values give the same order for the size of the perfluorovinyl-containing phosphines, $PEt_2pfv < PPhpfv_2 < PPh_2pfv = P^iPr_2pfv < PCy_2pfv$. The ordering of the phenyl-containing ligands is consistent with that calculated by Cundari *et al.*, with theoretical S_4' values for PPh₂(CF=CF₂) and PPh(CF=CF₂)₂ of 39 and 49° respectively.⁶ The values that we obtain from the X-ray data are smaller, meaning that the ligands are larger than calculated, but of the same order. Thus, $PPh(CF=CF_2)_2$ is sterically less demanding than $PPh_2(CF=CF_2)$. It is noteworthy that the Tolman cone angle for $P^{i}Pr_{2}(CF=CF_{2})$ (165°) lies between those of $P^{i}Pr_{3}$ (160°) and PCy_{3} (170°), which suggests that the perfluorovinyl group possesses a considerable steric footprint. However its steric demand is not as great as that of the C₆F₅ substituent. It has been suggested recently that this is the reason why PPh(CF=CF₂)₂ successfully cleaves [Cp*RhCl(µ-Cl)]2 to form complexes yet PPh(C6F5)2 does not.40

It is clear from the data in Table 5 that from an electronic standpoint the phosphine ligands containing one perfluorovinylgroup and two donating fragments lie mid-way between traditional phosphines and phosphites in their electronic properties. Furthermore the exact donating power and steric demand of the ligand

 Table 5
 Electronic and steric parameters for selected phosphorus(III) ligands

P(III) ligand	$v(CO)^a/cm^{-1}$	Tolman cone angle ^{<i>b</i>} / $^{\circ}$	<i>S</i> ₄ ′ ^{<i>c</i>} / ^o
P ⁱ Pr ₃	1950 ^g	160 ^g	35 ^d
PPh ₃	1965 ^g	138 ^g	35 ^d
$PEt_2(CF=CF_2)^e$	1981	152	44
- (-)		[142, 157, 157, 154]	[45, 66, 30, 37]
$P^{i}Pr_{2}(CF=CF_{2})$	1981	165	34
- (-/		[168, 166, 160, 159, 169, 166, 165]	[32, 35, 35, 35, 30, 35, 39]
$PCy_2(CF=CF_2)$	1979	169	29
		[168, 170, 168, 170]	[31, 23, 34, 29]
$PPh_2(CF=CF_2)^f$	1989	163	$34, 39^d$
		[164, 162, 164, 160]	[38, 38, 36, 25]
$PPh(CF=CF_2)_2$	2002	161	$39, 49^d$
		[169, 163, 161, 150]	[44, 36, 38, 37]
$PPh_2(C_6F_5)$	1982 ^g	158 ^g	38 ^d
$PPh(C_6F_5)_2$	1996 ^g	171 ^g	38 ^d
$P(OMe)_3$	2006 ^g	107 ^g	63 ^d
P(OPh) ₃	2016 ^g	128 ^g	76 ^d

^{*a*} For the complex [Rh(CO)Cl(P)₂]. ^{*b*} Average and [observed] values, see text. ^{*c*} As for (b). ^{*d*} Calculated value taken from ref. 6. ^{*e*} Data also from ref. 16. ^{*f*} Data also from ref. 14. ^{*g*} Data from ref. 2, 27 or 39. can be tailored by altering its composition and the identity of the R-groups. In this respect these ligands are like other phosphines containing perfluorinated groups, but there are, however, subtle differences, in particular the perfluorovinyl group appears to have a smaller steric footprint than a pentafluorophenyl group yet has a greater electronic influence.

Conclusion

We report a systematic study of the coordination chemistry of a series of perfluorovinyl-containing phosphine ligands in squareplanar Rh(I), Pd(II) and Pt(II) systems. From these we have been able to quantify both the electronic and steric properties of these ligands. We find that electronically the ligands approximate to traditional phosphites, whilst their steric demand is significantly greater. As such they fill one of the previously identified voids in the stereoelectronic profile of P(III) ligands.6 The solid state structures of a number of the complexes have been obtained. For the smaller phosphines cis-geometries are observed, whilst trans-isomers are observed for the larger phosphines. Nearly all complexes exhibit intramolecular M ··· F interactions, as well as intermolecular hydrogen bonding. In some other complexes the formation of fluorous domains within the solid state structure occurs instead. The balance between these effects appears to be very fine, indeed it would appear that for the perfluorovinyl-containing phosphines of intermediate size there is little differentiation between the cisand trans-isomers. This is attributed to a small energy difference between the two isomers and is supported by the observation that secondary factors are able to tip the balance from one-isomer to the other to the point where $[PtCl_2{P^iPr_2(CF=CF_2)}_2]$ crystallises, unusually, as a *cis: trans* mixture which allows for the formation of localised fluorous domains within the crystal.

Experimental

All ligand synthesis reactions were carried out under an inert atmosphere of argon or dinitrogen in flame dried glassware as previously described.^{14,16,17} [RhCl(CO)₂]₂ (Aldrich), K₂PdCl₄ and K₂PtCl₄ (Johnson Matthey), were used as supplied after verification of their purity. ¹⁹F and ³¹P{¹H} NMR spectra were recorded on a Bruker DPX200 spectrometer operating at 188.310 and 81.014 MHz respectively. ¹H and ¹³C $\{^{1}H\}$ NMR spectra were recorded on a Bruker DPX300 spectrometer operating at 300.14 and 75.38 MHz. All samples were recorded as CDCl₃ solutions and peak positions are quoted relative to external CFCl₃, 85% H₃PO₄ and TMS using the high frequency positive convention. Infrared spectra were recorded as Nujol mulls of samples held between KBr discs, and Raman spectra in glass capillaries, on a Nicolet-Nexus combined FT-IR/FT-Raman spectrometer with OMNIC 5 software. Elemental analyses were performed by the UMIST Chemistry Department microanalytical service.

X-Ray crystallography

Details of the structure analyses carried out on compounds 1, 9, 10, 12, 14–19 and 21 are summarised in Tables 2 and 3. Measurements for the complexes were made on crystals prepared by slow solvent evaporation on a Rigaku AFC6S or Nonius MAC3 CAD4 diffractometer. X-Ray structural data solution was by direct methods and

refined against *F*² using SHELXTL⁴¹ or SHELX-97.⁴² All non-H atoms were modelled with anisotropic displacement parameters, H-atoms were placed in idealised positions and refined with isotropic thermal parameters. The computer packages PLUTON⁴³ and MERCURY⁴⁴ were used to investigate the extended structures and to produce graphical representations used in the figures.

General method of synthesis for rhodium(I) complexes 1-5

To a solution of one equivalent of $[RhCl(CO)_2]_2$ dissolved in degassed dichloromethane (20 cm³) four equivalents of the appropriate phosphine dissolved in dichloromethane (20 cm³) was added dropwise. Immediate effervescence was observed and the solution became yellow. The solution was stirred under an argon atmosphere at room temperature for 1 h, after which time the solvent was removed. The resulting residue was washed with 2 × 10 cm³ portions of hexane, filtered and dried *in vacuo* to yield the rhodium(I) complexes 1 to 5.

trans-[RhCl(CO){PPh₂(CF=CF₂)}₂], 1. ¹⁹F NMR: δ : -82.4 (*trans*) [dd, ²*J*(FF) = 34 Hz, ³*J*(FF) = 32 Hz], -96.0 (*cis*) [dd, ²*J*(FF) = 34 Hz, ³*J*(FF) = 119 Hz], -176.5 (*gem*) [ddvt, 1/2|²*J*(PF) + ⁴*J*(PF)| = 15 Hz, ³*J*(FF) = 32 Hz, ³*J*(FF) = 119 Hz]. Raman (cm⁻¹): 310 v(Rh–Cl). IR (Nujol, cm⁻¹): 1989 v(C=O), 1732 v(C=C), 1314, 1146, 1051 v(C–F).

trans-[RhCl(CO){PEt₂(CF=CF₂)}₂], 2. ¹⁹F NMR: δ : -84.1 (*trans*) [dd, ²*J*(FF) = 47 Hz, ³*J*(FF) = 32 Hz], -102.1 (*cis*) [dd, ²*J*(FF) = 47 Hz, ³*J*(FF) = 120 Hz], -182.1 (*gem*) [ddvt, 1/2|²*J*(PF) + ⁴*J*(PF)| = 17 Hz, ³*J*(FF) = 32 Hz, ³*J*(FF) = 120 Hz]. Raman (cm⁻¹): 306 v(Rh–Cl). IR (Nujol, cm⁻¹): 1981 v(C=O), 1736 v(C=C), 1314, 1146, 1030 v(C–F).

trans-[RhCl(CO){ $P^{i}Pr_{2}(CF=CF_{2})$ }], 3. ¹⁹F NMR: δ : -83.7 (*trans*) [dd, ²*J*(FF) = 45 Hz, ³*J*(FF) = 32 Hz], -100.2 (*cis*) [dd, ²*J*(FF) = 45 Hz, ³*J*(FF) = 119 Hz], -177.7 (*gem*) [ddvt, 1/2|²*J*(PF) + ⁴*J*(PF)| = 12 Hz, ³*J*(FF) = 32 Hz, ³*J*(FF) = 119 Hz]. Raman (cm⁻¹): 307 v(Rh-Cl). IR (Nujol, cm⁻¹): 1981 v(C=O), 1730 v(C=C), 1308, 1148, 1051 v(C-F).

trans-[RhCl(CO){PCy₂(CF=CF₂)}₂], 4. ¹⁹F NMR: δ : -84.3 (*trans*) [dd, ²*J*(FF) = 45 Hz, ³*J*(FF) = 33 Hz], -100.5 (*cis*) [dd, ²*J*(FF) = 45 Hz, ³*J*(FF) = 120 Hz], -177.0 (*gem*) [ddvt, 1/2|²*J*(PF) + ⁴*J*(PF)| = 12 Hz, ³*J*(FF) = 33 Hz, ³*J*(FF) = 120 Hz]. IR (Nujol, cm⁻¹): 1979 v(C=O), 1732 v(C=C), 1307, 1144, 1047 v(C-F).

trans-[RhCl(CO){PPh(CF=CF₂)₂}₂], **5.** ¹⁹F NMR: δ : -79.4 (*trans*) [dd, ²*J*(FF) = 32 Hz, ³*J*(FF) = 33 Hz], -96.1 (*cis*) [dd, ²*J*(FF) = 32 Hz, ³*J*(FF) = 120 Hz], -178.6 (*gem*) [ddvt, 1/2|²*J*(PF) + ⁴*J*(PF)| = 19 Hz, ³*J*(FF) = 33 Hz, ³*J*(FF) = 120 Hz]. Raman (cm⁻¹): 307 v(Rh-Cl). IR (Nujol, cm⁻¹): 2002 v(C=O), 1720 v(C=C), 1310, 1156, 1051 v(C-F).

General method of synthesis for palladium(II) and platinum(II) complexes 6–22

One equivalent of K_2PdCl_4 or K_2PtCl_4 dissolved in water (10 cm³) was added to a stirred solution of two equivalents of the appropriate perfluorovinylphosphine dissolved in ethanol (10 cm³). The mixture was stirred for 15 min after which time the desired product precipitated out. This was filtered off, washed with a little water

and dried under vacuum for 1 h. The bromo and iodo-analogues were prepared by the reaction of the appropriate tetrachloropalladate or platinate salt with an excess of aqueous NaBr/HBr or KI solution respectively, followed by gentle warming for 10 min until the colour of the solution deepens. The tetrabromo/tetraiodo palladate/platinate salts were then reacted with two equivalents of phosphine as described above.

trans-[PdCl₂{PPh₂(CF=CF₂)}₂], 6. ¹⁹F NMR: δ : -82.1 (*trans*) [dd, ²*J*(FF) = 37, ³*J*(FF) = 33], -95.9 (*cis*) [dd, ³*J*(FF) = 119, ²*J*(FF) = 37], -177.7 (*gem*) [ddvt, ³*J*(FF) = 119, ³*J*(FF) = 33, 1/2|²*J*(PF) + ⁴*J*(PF)| = 17]. ¹H NMR (CDCl₃): δ : 7.45-7.59 [m, 12H, Ar], 7.72-7.84 [m, 8H, Ar]. ¹³C{¹H} NMR (CDCl₃): δ : 123.1 [*C*F=CF₂, dvtdd, ¹*J*(CF) = 265.6, 1/2|¹*J*(PC) + ³*J*(PC)| = 46.4, ²*J*(CF) = 31.9, 14.5], 125.1 [*C*₁, vt, 1/2|¹*J*(PC) + ³*J*(PC)| = 27.0], 129.0 [*C*_m, vt, 1/2|³*J*(PC) + ⁵*J*(PC)| = 5.8], 132.3 [*C*_P, s], 135.2 [*C*_o, vt, 1/2|²*J*(PC) + ⁴*J*(PC)| = 6.8], 159.6 [CF=*C*F₂, dddvt, ¹*J*(CF) = 306.1, 290.7, ²*J*(CF) = 40.6, 1/2|²*J*(PC) + ⁴*J*(PC)| = 13.5]. Raman (cm⁻¹): 307 v(Pd-Cl). IR (Nujol, cm⁻¹): 1732 v(C=C), 1314, 1150, 1051 v(C-F).

trans-[PdBr₂{PPh₂(CF=CF₂)₂], 7. ¹⁹F NMR: δ : -83.0 (*trans*) [dd, ²*J*(FF) = 37, ³*J*(FF) = 31], -95.0 (*cis*) [dd, ³*J*(FF) = 118, ²*J*(FF) = 37], -176.2 (*gem*) [ddvt, ³*J*(FF) = 118, ³*J*(FF) = 31, 1/2|²*J*(PF) + ⁴*J*(PF)| = 17]. ¹H NMR: δ : 7.43-7.58 [m, 12H, Ar], 7.77-7.90 [m, 8H, Ar]. ¹³C{¹H} NMR: δ : 124.7 [CF=CF₂, dvtdd, ¹*J*(CF) = 265.6, 1/2|¹*J*(PC) + ³*J*(PC)| = 45.4, ²*J*(CF) = 31.9, 15.5], 126.3 [*C_i*, vt, 1/2|¹*J*(PC) + ³*J*(PC)| = 28.0], 128.8 [*C_m*, vt, 1/2|³*J*(PC) + ⁵*J*(PC)| = 5.8], 132.2 [*C_P*, s], 135.4 [*C_o*, vt, 1/2|²*J*(PC) + ⁴*J*(PC)| = 6.8], 159.1 [CF=CF₂, dddvt, ¹*J*(CF) = 306.1, 289.7, ²*J*(CF) = 41.5, 1/2|²*J*(PC) + ⁴*J*(PC)| = 13.5]. Raman (cm⁻¹): 191 v(Pd–Br). IR (Nujol, cm⁻¹): 1732 v(C=C), 1309, 1167, 1051 v(C–F).

trans-[PdI₂{PPh₂(CF=CF₂)₂], 8. ¹⁹F NMR: δ : -83.9 (*trans*) [dd, ²*J*(FF) = 37, ³*J*(FF) = 31], -93.8 (*cis*) [dd, ³*J*(FF) = 119, ²*J*(FF) = 37], -173.3 (*gem*) [ddvt, ³*J*(FF) = 119, ³*J*(FF) = 31, 1/2|²*J*(PF) + ⁴*J*(PF)| = 16]. ¹H NMR: δ : 7.43-7.56 [m, 12H, Ar], 7.70-7.80 [m, 8H, Ar]. ¹³C{¹H} NMR: δ : 128.1 [*C*F≡CF₂, dvtdd, ¹*J*(CF) = 266.6, 1/2|¹*J*(PC) + ³*J*(PC)| = 46.4, ²*J*(CF) = 32.9, 13.5], 129.1 [*C_i*, vt, 1/2|¹*J*(PC) + ³*J*(PC)| = 29.0], 128.6 [*C_m*, vt, 1/2|³*J*(PC) + ⁵*J*(PC)| = 5.8], 132.0 [*C_P*, s], 135.3 [*C_o*, vt, 1/2|²*J*(PC) + ⁴*J*(PC)| = 5.8], 158.3 [CF=CF₂, ddvt, ¹*J*(CF) = 306.1, 289.7, ²*J*(CF) = 42.5, 1/2|²*J*(PC) + ⁴*J*(PC)| = 12.6]. Raman (cm⁻¹): 141 v(Pd–I). IR (Nujol, cm⁻¹): 1734 v(C=C), 1319, 1157, 1051 v(C–F).

trans-[PdCl₂{PⁱPr₂(CF=CF₂)}], **9**. ¹⁹F NMR: δ : -83.7 (*trans*) [dd, ²*J*(FF) = 45 Hz, ³*J*(FF) = 33 Hz], -97.7 (*cis*) [dd, ²*J*(FF) = 45 Hz, ³*J*(FF) = 117 Hz], -182.8 (*gem*) [ddvt, 1/2|²*J*(PF) + ⁴*J*(PF)| = 12 Hz, ³*J*(FF) = 33 Hz, ³*J*(FF) = 117 Hz]. Raman (cm⁻¹): 331 v(Pd-Cl). IR (Nujol, cm⁻¹): 1738 v(C=C), 1304, 1157, 1030 v(C-F).

trans-[PdBr₂{PⁱPr₂(CF=CF₂)₂], **10.** ¹⁹F NMR: δ : -84.6 (*trans*) [dd, ²*J*(FF) = 46 Hz, ³*J*(FF) = 32 Hz], -97.2 (*cis*) [dd, ²*J*(FF) = 46 Hz, ³*J*(FF) = 116 Hz], -180.0 (*gem*) [ddvt, 1/2|²*J*(PF) + ⁴*J*(PF)| = 13 Hz, ³*J*(FF) = 32 Hz, ³*J*(FF) = 116 Hz]. Raman (cm⁻¹): 191 v(Pd–Br). IR (Nujol, cm⁻¹): 1738 v(C=C), 1314, 1152, 1032 v(C–F).

trans-[PdI₂{PⁱPr₂(CF=CF₂)}₂], 11. ¹⁹F NMR: δ : -85.6 (*trans*) [dd, ²*J*(FF) = 49 Hz, ³*J*(FF) = 32 Hz], -97.1 (*cis*) [dd, ²*J*(FF) = 49 Hz, ³*J*(FF) = 116 Hz], -175.0 (*gem*) [ddvt, 1/2]²*J*(PF) + ⁴*J*(PF)| = 14 Hz, ³*J*(FF) = 32 Hz, ³*J*(FF) = 116 Hz]. Raman (cm⁻¹): 137 v(Pd–I). IR (Nujol, cm⁻¹): 1738 v(C=C), 1304, 1157, 1028 v(C–F).

trans-[PdCl₂{PCy₂(CF=CF₂)₂], 12. ¹⁹F NMR: δ : -83.9 (*trans*) [dd, ²*J*(FF) = 45 Hz, ³*J*(FF) = 32 Hz], -97.9 (*cis*) [dd, ²*J*(FF) = 45 Hz, ³*J*(FF) = 118 Hz], -181.7 (*gem*) [ddvt, 1/2|²*J*(PF) + ⁴*J*(PF)| = 12 Hz, ³*J*(FF) = 32 Hz, ³*J*(FF) = 118 Hz]. Raman (cm⁻¹): 302 v(Pd–Cl). IR (Nujol, cm⁻¹): 1738 v(C=C), 1308, 1152, 1047 v(C–F).

trans-[PdCl₂{PPh(CF=CF₂)₂}], 13. ¹⁹F NMR: δ : -78.1 (*trans*) [dd, ³*J*(FF) = 33, ²*J*(FF) = 31], -95.1 (*cis*) [dd, ³*J*(FF) = 118, ²*J*(FF) = 31], -180.1 (*gem*) [ddvt, ³*J*(FF) = 118, ³*J*(FF) = 33, 1/2|²*J*(PF) + ⁴*J*(PF)| = 18]. ¹H NMR: δ : 7.58 [m, 4H, Ar], 7.65 [m, 2H, Ar], 7.93 [m, 4H, Ar]. ¹³C{¹H} NMR: δ : 118.9 [C_i, vt, 1/2|¹*J*(PC) + ³*J*(PC)| = 29.9], 119.6 [CF=CF₂, dvtdd, ¹*J*(CF) = 265.6, 1/2|¹*J*(PC) + ³*J*(PC)| = 35.8, ²*J*(CF) = 31.9, 14.5], 129.6 [C_m, vt, 1/2|³*J*(PC) + ⁵*J*(PC)| = 6.8], 133.8 [C_P, s], 135.5 [C_o, vt, 1/2|²*J*(PC) + ⁴*J*(PC)| = 7.7], 159.6 [CF=CF₂, dddvt, ¹*J*(CF) = 302.6, 292.6, ²*J*(CF) = 39.6, 1/2|²*J*(PC) + ⁴*J*(PC)| = 15.5]. Raman (cm⁻¹): 318 v(Pd-Cl). IR (Nujol, cm⁻¹): 1732 v(C=C), 1312, 1159, 1055 v(C-F).

trans-[PdBr₂{PPh(CF=CF₂)₂}₂], 14. ¹⁹F NMR: δ : -78.8 (*trans*) [dd, ³*J*(FF) = 33, ²*J*(FF) = 33], -94.6 (*cis*) [dd, ³*J*(FF) = 118, ²*J*(FF) = 33], -178.6 (*gem*) [ddvt, ³*J*(FF) = 118, ³*J*(FF) = 33, 1/2|²*J*(PF) + ⁴*J*(PF)| = 17]. ¹H NMR: δ : 7.56 [m, 4H, Ar], 7.64 [m, 2H, Ar], 7.99 [m, 4H, Ar]. ¹³C{¹H} NMR: δ : 120.0 [*C_i*, vt, 1/2|¹*J*(PC) + ³*J*(PC)| = 30.9], 120.8 [*C*F≡CF₂, dvtdd, ¹*J*(CF) = 265.6, 1/2|¹*J*(PC) + ³*J*(PC)| = 49.2, ²*J*(CF) = 33.8, 13.5], 129.4 [*C_m*, vt, 1/2|³*J*(PC) + ⁵*J*(PC)| = 6.8], 133.7 [*C_P*, s], 135.9 [*C_o*, vt, 1/2|²*J*(PC) + ⁴*J*(PC)| = 7.8], 159.3 [*C*F=*C*F₂, ddvtt, ¹*J*(CF) = 308.1, 291.6, ²*J*(CF) = 38.6, 1/2|²*J*(PC) + ⁴*J*(PC)| = 14.5]. Raman (cm⁻¹): 199 v(Pd–Br). IR (Nujol, cm⁻¹): 1728 v(C=C), 1314, 1159, 1053 v(C–F).

trans-[PdI₂{PPh(CF=CF₂)₂], **15.** ¹⁹F NMR: δ : -79.6 (*trans*) [dd, ²*J*(FF) = 33, ³*J*(FF) = 32], -93.6 (*cis*) [dd, ³*J*(FF) = 118, ²*J*(FF) = 33], -176.1 (*gem*) [ddvt, ³*J*(FF) = 118, ³*J*(FF) = 32, 1/2|²*J*(PF) + ⁴*J*(PF)| = 17]. ¹H NMR: δ : 7.55 [m, 4H, Ar], 7.61 [m, 2H, Ar], 7.91 [m, 4H, Ar]. ¹³C{¹H} NMR: δ : 120.8 [CF=CF₂, dvtdd, ¹*J*(CF) = 266.6, 1/2|¹*J*(PC) + ³*J*(PC)| = 35.7, ²*J*(CF) = 31.9, 15.5], 122.7 [*C_i*, vt, 1/2|¹*J*(PC) + ³*J*(PC)| = 30.9], 129.1 [*C_m*, vt, 1/2|³*J*(PC) + ⁵*J*(PC)| = 5.8], 133.5 [*C_P*, s], 135.9 [*C_o*, vt, 1/2|²*J*(PC) + ⁴*J*(PC)| = 7.7], 158.6 [CF=CF₂, ddvt, ¹*J*(CF) = 307.1, 290.7, ²*J*(CF) = 39.6, 1/2|²*J*(PC) + ⁴*J*(PC)| = 14.5]. Raman (cm⁻¹): 143 v(Pd–I). IR (Nujol, cm⁻¹): 1728 v(C=C), 1316, 1159, 1049 v(C–F).

cis/trans-[PtCl₂{PⁱPr₂(CF=CF₂)}₂], 16. ¹⁹F NMR: δ : -83.7 (*trans*) [dd, ²*J*(FF) = 44 Hz, ³*J*(FF) = 32 Hz, ⁴*J*(PtF) = 5 Hz], -98.2 (*cis*) [dd, ²*J*(FF) = 44 Hz, ³*J*(FF) = 116 Hz, ⁴*J*(PtF) = 45 Hz], -183.2 (*gem*) [ddvt, 1/2|²*J*(PF) + ⁴*J*(PF)| = 16 Hz, ³*J*(FF) = 32 Hz, ³*J*(FF) = 116 Hz, ³*J*(PtF) = 91 Hz]. Raman (cm⁻¹): 300 v(Pt-Cl). IR (Nujol, cm⁻¹): 1740 v(C=C), 1306, 1156, 1032 v(C-F).

trans-[PtBr₂{PⁱPr₂(CF=CF₂)}₂], **17.** ¹⁹F NMR: δ : -84.7 (*trans*) [dd, ²*J*(FF) = 45 Hz, ³*J*(FF) = 32 Hz, ⁴*J*(PtF) = 10 Hz], -98.0 (*cis*) [dd, ²*J*(FF) = 45 Hz, ³*J*(FF) = 116 Hz, ⁴*J*(PtF) = 46 Hz], -180.5 (*gem*) [ddvt, 1/2|²*J*(PF) + ⁴*J*(PF)| = 15 Hz, ³*J*(FF) = 32 Hz, ³*J*(FF) = 116 Hz, ³*J*(PtF) = 81 Hz]. Raman (cm⁻¹): 206 v(Pt–Br). IR (Nujol, cm⁻¹): 1738 v(C=C), 1313, 1156, 1032 v(C–F).

trans-[PtI₂{PⁱPr₂(CF=CF₂)}₂], 18. ¹⁹F NMR: δ : -85.6 (*trans*) [dd, ²*J*(FF) = 48 Hz, ³*J*(FF) = 31 Hz, ⁴*J*(PtF) = 16 Hz], -97.3 (*cis*) [dd, ²*J*(FF) = 48 Hz, ³*J*(FF) = 115 Hz, ⁴*J*(PtF) = 47 Hz], -176.1 (*gem*) [ddvt, 1/2|²*J*(PF) + ⁴*J*(PF)| = 15 Hz, ³*J*(FF) = 31 Hz, ³*J*(FF) = 115 Hz, ³*J*(PtF) = 70 Hz]. Raman (cm⁻¹): 151 v(Pt-I). IR (Nujol, cm⁻¹): 1738 v(C=C), 1304, 1152, 1028 v(C-F).

trans-[PtCl₂{PCy₂(CF=CF₂)}₂], 19. ¹⁹F NMR: δ : -83.9 (*trans*) [dd, ²*J*(FF) = 43 Hz, ³*J*(FF) = 31 Hz, ⁴*J*(PtF) = 15 Hz], -98.3 (*cis*) [dd, ²*J*(FF) = 48 Hz, ³*J*(FF) = 116 Hz, ⁴*J*(PtF) = 43 Hz], -182.2 (*gem*) [ddvt, 1/2|²*J*(PF) + ⁴*J*(PF)| = 15 Hz, ³*J*(FF) = 31 Hz, ³*J*(FF) = 116 Hz, ³*J*(PtF) = 70 Hz]. Raman (cm⁻¹): 333 v(Pt-Cl). IR (Nujol, cm⁻¹): 1736 v(C=C), 1312, 1147, 1049 v(C-F).

 $cis/trans-[PtCl_2{PPh(CF=CF_2)_2}_2], 20.$ ¹⁹F NMR: cisisomer: δ : -76.5 (*trans*) [dd, ${}^{3}J(FF) = 33$, ${}^{2}J(FF) = 30$], -93.4 (cis) [dd, ${}^{3}J(FF) = 118$, ${}^{2}J(FF) = 30$], -178.4 (gem) [ddd, ${}^{3}J(FF) =$ 118, ${}^{3}J(FF) = 33$, ${}^{2}J(PF) = 37$], trans-isomer: δ : -78.3 (trans) $[dd, {}^{3}J(FF) = 31, {}^{2}J(FF) = 31], -95.3$ (*cis*) $[dd, {}^{3}J(FF) = 117,$ ${}^{2}J(FF) = 31$], -180.9 (gem) [ddvt, ${}^{3}J(FF) = 117$, ${}^{3}J(FF) = 31$, $1/2|^{2}J(PF) + {}^{4}J(PF)| = 21$]. ¹H NMR: δ : 7.54 [m, 4H, Ar], 7.67 [m, 2H, Ar], 7.95 [m, 4H, Ar].¹³C $\{^{1}H\}$ NMR: trans-isomer δ : 116.8 $[CF=CF_2, dvtdd, {}^{1}J(CF) = 263.7, 1/2 | {}^{1}J(PC) + {}^{3}J(PC) | = 43.8,$ ${}^{2}J(CF) = 40.6, 15.5], 117.0 [C_{i}, vt, 1/2]{}^{1}J(PC) + {}^{3}J(PC)] =$ 33.8, ${}^{2}J(PtC) = 9.7$], 128.1 [C_{m} , vt, 1/2 | ${}^{3}J(PC) + {}^{5}J(PC)$ | = 6.8], 132.5 [C_P , s], 134.6 [C_o , vt, $1/2|^2 J(PC) + {}^4 J(PC)| = 7.8$], 158.4 [CF= CF_2 , dddvt, ${}^{1}J(CF) = 308.1$, 293.6, ${}^{2}J(CF) = 39.6$, $1/2|^{2}J(PC) + {}^{4}J(PC)| = 15.5$]. Raman (cm⁻¹): trans-isomer 305 v(Pt-Cl). IR (Nujol, cm⁻¹): 1728 v(C=C), 1331, 1159, 1061 v(C-F).

cis/trans-[PtBr₂{PPh(CF=CF₂)₂}₂], 21. ¹⁹F NMR: cis-isomer δ : -76.9 (trans) [dd, ${}^{3}J(FF) = 33$, ${}^{2}J(FF) = 29$], -93.1 (cis) [dd, ${}^{3}J(FF) = 120, {}^{2}J(FF) = 29, {}^{4}J(PtF) = 44], -177.2 (gem) [ddd,$ ${}^{3}J(FF) = 120, {}^{3}J(FF) = 33, {}^{2}J(PF) = 36, {}^{3}J(PtF) = 68], trans$ isomer δ : -78.8 (*trans*) [dd, ${}^{3}J(FF) = 32$, ${}^{2}J(FF) = 29$], -94.5 (*cis*) $[dd, {}^{3}J(FF) = 117, {}^{2}J(FF) = 29, {}^{4}J(PtF) = 39], -179.3 (gem) [ddvt,$ ${}^{3}J(FF) = 117, {}^{3}J(FF) = 32, 1/2 |{}^{2}J(PF) + {}^{4}J(PF)| = 20, {}^{3}J(PtF) =$ 57]. ¹H NMR: δ: 7.56 [m, 4H, Ar], 7.69 [m, 2H, Ar], 7.94 [m, 4H, Ar]. ¹³C{¹H} NMR: cis-isomer δ : 117.9 [CF=CF₂, dddd, ¹J(CF)= 261.8, ${}^{1}J(PC) = 89.8$, ${}^{2}J(CF) = 44.4$, 15.5], 118.3 [C_i , vt, ${}^{1}J(PC) =$ $74.9, {}^{2}J(PtC) = 28.0], 129.4 [C_{m}, d, {}^{3}J(PC) = 13.0], 134.3 [C_{P}, d,$ ${}^{4}J(PC) = 2.9$], 135.4 [C_o , d, ${}^{2}J(PC) = 13.5$, ${}^{3}J(PtC) = 25.1$], 159.6 $[CF=CF_2, dddd, {}^{1}J(CF) = 309.0, 293.6, {}^{2}J(CF) = 39.6, {}^{2}J(PC) =$ 26.6], trans-isomer δ : 119.3 [C_i , vt, $1/2|^{-1}J(PC) + {}^{-3}J(PC)| = 34.3$], $120.4 [CF=CF_2, dvtdd, {}^{1}J(CF) = 265.6, 1/2 | {}^{1}J(PC) + {}^{3}J(PC) | =$ $43.8, {}^{2}J(CF) = 39.6, 15.5], 129.3 [C_{m}, vt, 1/2]{}^{3}J(PC) + {}^{5}J(PC)] =$ 6.8], 133.9 [C_P , s], 136.3 [C_o , vt, $1/2|^2 J(PC) + {}^4 J(PC)| = 7.7$], 159.6 [CF= CF_2 , dddvt, ${}^{1}J(CF) = 307.1$, 292.6, ${}^{2}J(CF) = 39.6$, $1/2|^2 J(PC) + {}^4 J(PC)| = 14.9$]. Raman (cm⁻¹): trans-isomer 216 v(Pt-Br). IR (Nujol, cm⁻¹): 1732 v(C=C), 1317, 1159, 1057 v(C-F).

trans-[PtI₂{PPh(CF=CF₂)₂}, 22. ¹⁹F NMR: δ : -79.7 (*trans*) [dd, ³*J*(FF) = 31, ²*J*(FF) = 29], -93.6 (*cis*) [dd, ³*J*(FF) = 119, ²*J*(FF) = 29, ⁴*J*(PtF) = 39], -176.8 (*gem*) [ddvt, ³*J*(FF) = 119, ³*J*(FF) = 31, 1/2 |²*J*(PF) + ⁴*J*(PF)| = 19, ³*J*(PtF) = 57]. ¹H NMR (CDCl₃): δ : 7.56 [m, 4H, Ar], 7.66 [m, 2H, Ar], 7.96 [m, 4H, Ar]. ¹³C{¹H} NMR: δ : 121.6 [*C_i*, vt, 1/2 |¹*J*(PC) + ³*J*(PC)| = 34.8], 121.9 [*C*F=CF₂, dvtdd, ¹*J*(CF) = 264.6, 1/2 |¹*J*(PC) + ³*J*(PC)| = 44.4, ²*J*(CF) = 43.5, 16.4], 129.1 [*C_m*, vt, 1/2 |³*J*(PC) + ⁵*J*(PC)| = 6.8], 133.5 [*C_P*, s], 136.4 [*C_o*, vt, 1/2 |²*J*(PC) + ⁴*J*(PC)| = 7.8], 158.9 [*C*F=CF₂, dddvt, ¹*J*(CF) = 307.1, 292.6, ²*J*(CF) = 40.6, 1/2 |²*J*(PC) + ⁴*J*(PC)| = 13.5]. Raman (cm⁻¹): 155 v(Pt-I). IR (Nujol, cm⁻¹): 1728 v(C=C), 1325, 1161, 1055 v(C-F).

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