DALTON
FULL PAPER

Syntheses and crystallographic studies of [Ir(η^5-C_5Me_5)(L)(R_F)I] (L = CO, PMe_3; R_F = CF_2CF_3, $CF_2CF_2CF_3$, $CF_2C_6F_5$, $CF(CF_3)_2$) complexes. Cone and solid angle steric parameters for perfluoroalkyl ligands

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Oxidative addition of R_FI ($R_F = CF_2CF_3$, $CF_2CF_2CF_3$, $CF_2C_6F_5$, $CF(CF_3)_2$) to [Ir(η^5-C_5Me_5)$(CO)_2$] gave the iridium(III) complexes, [Ir(η^5-C_5Me_5)(CO)(R_F)I] **2a**–**d** in good yield. Carbonyl substitution by PMe_3 to give [Ir(η^5-C_5Me_5)(PMe_3)(R_F)I] **3a**–**d** was achieved by heating in refluxing toluene. Complexes **2a**, **c**, **d** and **3a**, **b**, **d** were studied by X-ray crystallography. The perfluoroalkyl Ir–C bonds were found to be shorter than alkyl Ir–C bonds, while the α-C–F bonds were longer than the C–F bonds in non-coordinated perfluorocarbons. The steric sizes of the perfluoroalkyl ligands were determined as Tolman cone angles, θ, and solid angles, Ω. The sizes of the ligands followed the expected trend, $CF(CF_3)_2 > CF_2C_6F_5 > CF_2CF_2CF_3 \approx CF_2CF_3$, and were substantially larger than corresponding hydrocarbons.

Introduction

The activation and functionalisation of polyfluorocarbon C–F bonds by transition metal complexes has generated much research interest.[1,2] Fluoroalkenes can be produced from perfluoroalkanes in systems where the transition metal centre acts as a reductant[3–5] or a catalytic electron shuttle.[3,6] Other strongly reducing conditions,[7,8] using ammonia,[9] alkali metals,[10] or metal oxalate salts,[11] have also been reported. The reactions of coordinated perfluoroalkyl ligands, through hydrolysis[12] or hydrogenolysis,[13] offers another means of functionalising C–F bonds.

Generally, the incorporation of perfluoroalkyl ligands in transition metal complexes results in complexes which are more stable than the corresponding alkyl complexes. Calorimetric experiments[14] and DFT calculations[15] of CH_xF_{3-x} bound to metals suggest that greater fluorination of the alkyl ligand results in increased metal–carbon bond strength. Further evidence for stronger M–C bonds is exhibited in the shorter M–C bond lengths found in crystal structures,[16–19] and lower M–C reactivity than analogous metal alkyls. The stronger M–C bonds are usually accompanied by weaker α-C–F bonds, as indicated by their lower C–F stretching frequencies in IR spectra,[20,21] and longer C–F bond lengths in crystal structures.[16–19] These α-C–F bonds show increased reactivity and susceptibility to electrophilic attack, and thus are unusually reactive in the presence of Lewis acids like BX_3 and exogenous protic acids.[17,22,23]

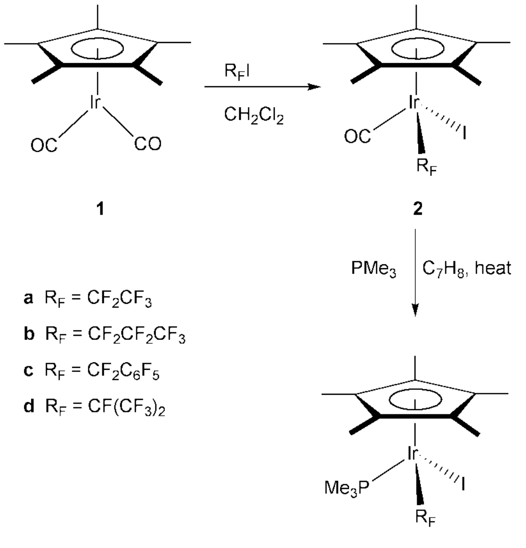
It is generally agreed that a number of steric parameters illustrate that fluorine is larger than hydrogen. The greater van der Waals' radius of fluorine (1.47 Å) as compared with hydrogen (1.20 Å)[24] is corroborated by X-ray crystal data and Taft steric parameters.[25] For instance, according to the Taft scale, the CF_3 group ($E_S = -2.40$) is larger than $CH(CH_3)_2$ ($E_S = -1.71$),[25] while kinetic activation barriers suggest that $CF(CF_3)_2$ is comparable in size to $C(CH_3)_3$.[26] Aside from these, however, there are very little data available on the steric parameters of perfluoroalkyl groups.

In this paper, we present a systematic crystallographic study of a series of perfluoroalkyl metal complexes. We have also examined the steric effects of perfluoroalkyl groups by two measures; Tolman cone angles[27–29] and solid angles.[30,31]

Results and discussion

Synthesis and spectroscopic characterisation

The complexes [Ir(η^5-C_5Me_5)(CO)(R_F)I] ($R_F = CF_2CF_3$, **2a**; $CF_2CF_2CF_3$, **2b**; $CF_2C_6F_5$, **2c**; $CF(CF_3)_2$, **2d**) were obtained in excellent yield by the oxidative addition of R_FI to [Ir(η^5-C_5Me_5)$(CO)_2$] **1** in CH_2Cl_2 (Scheme 1). The progress of the reaction was readily monitored by IR spectroscopy Complexes **2b**[32] and **2c**[33] had been previously reported. All complexes were characterised by IR and NMR spectroscopy, elemental analysis



Scheme 1

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Table 1 Yields, IR, NMR and analytical for $[Ir(\eta^5\text{-}C_5Me_5)(CO)(R_F)I]$ **2a-d**

	R_F	Yield (%)	$\nu_{CO}{}^a$/cm^{-1}	^{1}H NMR^b	^{19}F NMR^b	Analysis^c (%)
2a	CF_2CF_3	92	2047	2.12 (s, C_5Me_5)	−64.4 [1F, d, *J*(AB) 263, $C_\alpha F_A$]; −76.0 [1F, d, *J*(AB) 263, $C_\alpha F_B$]; −82.2 (3F, s, CF_3)	C, 26.29 (25.96); H, 2.45 (2.51)
2b	$CF_2CF_2CF_3$	80	2045	2.10 (s, C_5Me_5)	−60.1 [1F, m, *J*(AB) 265, $C_\alpha F_A$]; −72.0 [1F, m, *J*(AB) 265, $C_\alpha F_B$]; −79.4 [3F, t, *J*(FF) 11, CF_3]; −113.8 [1F, m, *J*(AB) 264, $C_\beta F_A$); −117.4 (1F, m, *J*(AB) 264, $C_\beta F_B$]	C, 25.81 (25.81); H, 2.09 (2.32)
2c	$CF_2C_6F_5$	92	2033	2.13 (s, C_5Me_5)	−38.0 [1F, dt, *J*(AB) 241, *J*(FF) 24, $C_\alpha F_A$]; −59.9 [1F, dt, *J*(AB) 241, *J*(FF) 35, $C_\alpha F_B$]; −137.2 (2F, m, *o*-F); −156.0 [1F, t, *J*(FF) 22, *p*-F]; −163.2 (2F, m, *J*(FF) 22, *m*-F)	C, 30.97 (30.90); H, 2.13 (2.16)
2d	$CF(CF_3)_2$	85	2045	2.09 (s, C_5Me_5)	−66.9 [3F, dq, *J*(FF) 8, *J*(FF) 8, CF_3]; −70.2 [3F, dq, *J*(FF) 8, *J*(FF) 9, CF_3]; −159.5 (1F, br s, CF)	C, 25.94 (25.81); H, 2.35 (2.32)

[a] Recorded in CH_2Cl_2. [b] Recorded at 298 K in $CDCl_3$. Data given as: chemical shift (δ) [relative intensity, multiplicity (*J* Hz), assignment], s = singlet, d = doublet, t = triplet, br indicates a broad signal. [c] Required values are given in parentheses.

Table 2 Selected bond lengths (Å) and angles (°) for complexes **2**

	2a	**2c**	**2d**
Ir–CO	1.891(10)	1.881(15)	1.88(3)
Ir–I	2.7638(8)	2.675(5)	2.700(3)
Ir–R_F	2.135(12)	2.152(14)	2.11(3)
Ir–cen^a	1.914(9)	1.868(15)	1.85(3)
C_α–F_A	1.362(13)	1.375(16)	1.55(3)
C_α–F_A	1.400(13)	1.319(16)	
C_β–F_{ave}	1.387(9)	1.33(2)	1.34(4)
C–O	1.147(12)	1.056(19)	1.10(3)
R_F–Ir–CO	87.4(4)	93.6(6)	93.0(10)
R_F–Ir–I	91.2(3)	91.9(4)	89.1(10)
I–Ir–CO	87.7(4)	87.0(5)	93.0(10)
Ir–C–F_A	111.8(8)	106.5(8)	108.6(14)^b
Ir–C–F_B	112.1(8)	109.5(11)	118(2)^b
Ir–C–R_F	111.2(6)	116.2(12)	116(2)
F_A–C–F_B	105.9(9)	105.6(12)	116(3)^c

[a] cen = centroid of C_5Me_5 ring. [b] Ir–C–CF_3. [c] CF_3–C–CF_3.

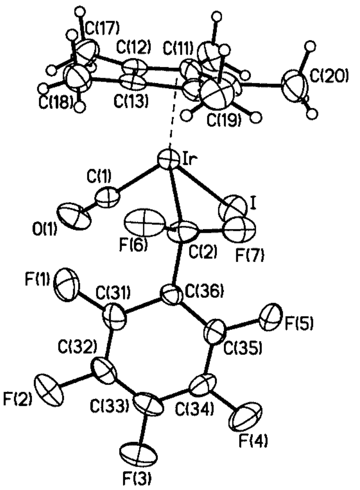

Fig. 2 ORTEP drawing of **2c** with thermal ellipsoids drawn at 30% probability level and hydrogen atoms omitted for clarity.

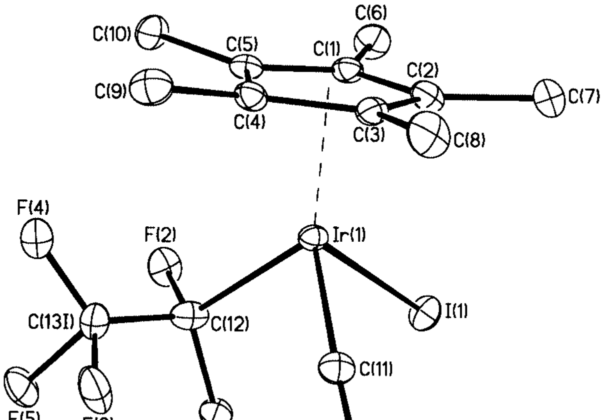

Fig. 1 ORTEP[48] drawing of **2a** with thermal ellipsoids drawn at 30% probability level and hydrogen atoms omitted for clarity. See Experimental section for an explanation of C(13)I.

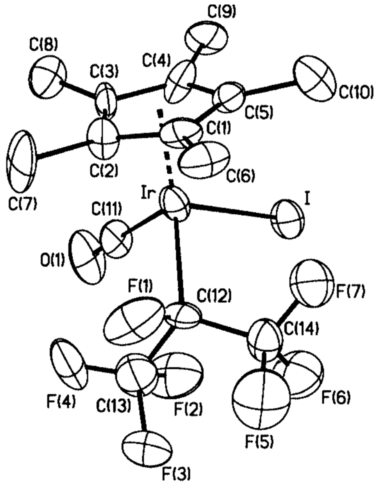

Fig. 3 ORTEP drawing of **2d** with thermal ellipsoids drawn at 30% probability level and hydrogen atoms omitted for clarity.

and X-ray crystallography, with the exception of **2b**, for which we were unable to obtain diffraction quality crystals. Yields, spectroscopic and elemental analysis data are presented in Table 1. Selected bond lengths and angles are presented in Table 2, and crystal structure diagrams are shown in Fig. 1–3.

The crystal structures confirmed oxidative addition of the perfluoroalkyl iodide to the metal. In all cases, the coordination geometry around the iridium atom is very close to octahedral, with the angles between I, CO, and R_F ligands being close to 90°, and with the pentamethylcyclopentadienyl ligand formally occupying three *fac* coordination sites. The crystal structure results are discussed in a later section.

The ^{19}F NMR spectra of the complexes were as expected, consistent with the solid state structures and similar to related rhodium and cobalt complexes.[33–35] The diastereotopic α-CF_2 fluorines of the perfluoroethyl complex **2a** resonate at δ −64.4 and −76.0, with a large geminal coupling (J_{AB} = 263 Hz), while the CF_3 group resonates as singlet at δ −82.2. The ^{19}F NMR spectrum of the perfluoro-n-propyl complex **2b** is similar, with an additional AB quartet due to the diastereotopic β-CF_2 fluorines at δ −113.8 and −117.4 (J_{AB} = 264 Hz). The spectrum of the perfluorobenzyl complex **2c** is very similar to those of previously reported cobalt and rhodium complexes.[34] The fluorines of the α-CF_2 group give rise to an AB quartet at δ −38.0 (dt) and −59.9 (dt, J_{AB} = 241 Hz), while the aromatic fluorine resonances of the perfluorobenzyl complex **2c** give rise to three resonances in a 2 : 1 : 2 ratio, indicative of free rotation around the CF_2–C_6F_5 bond on the NMR time scale, in line with previously observations for Co and Rh analogues.[34] The coupling constants between the individual fluorines of the CF_2 group and the *ortho*-fluorine atoms of the phenyl ring of this complex are inequivalent, suggesting that in the ground state conformation the phenyl ring does not bisect the CF_2 group, again similar to the analogous Co and Rh complexes.[34] The CF group of the perfluoroisopropyl complex **2d** resonates as a broad singlet at δ *ca.* −160.0, while the diastereotopic CF_3 groups give multiplets at δ −66.9 and −70.2.

The IR stretching frequencies for the CO ligands in these complexes are lower than analogous cobalt and rhodium complexes (Table 3), but still higher than that in an analogous hydrocarbon alkyl complex, $[Ir(\eta^5\text{-}C_5Me_5)(CO)(CH_3)I]$ which has a value of 2002 cm^{-1} (CH_2Cl_2).[32] With the exception of the perfluorobenzyl ligand, all R_F groups exert a remarkably similar electronic effect.

In contrast to the analogous cobalt and rhodium complexes,[34] carbonyl substitution by trimethylphosphine did not occur readily at room temperature. Heating the reagents in refluxing benzene also failed to give substitution, but heating in refluxing toluene gave carbonyl substitution within a couple of hours as determined by IR spectroscopy, to give the complexes $[Ir(\eta^5\text{-}C_5Me_5)(PMe_3)(R_F)I]$ (R_F = CF_2CF_3, **3a**; $CF_2CF_2CF_3$, **3b**; $CF_2C_6F_5$, **3c**; $CF(CF_3)_2$, **3d**) (Scheme 1). All complexes were characterised by NMR spectroscopy and elemental analysis. Compounds **3a–d** were also characterized by X-ray crystallography, although the structure of the perfluorobenzyl compound **3c** was of low quality due to an insufficiency of data. Yields, spectroscopic and elemental analysis data are presented in Table 4, while selected bond lengths and angles for the crystal structures are presented in Table 5. Crystal structure diagrams are shown in Fig. 4–6. No migration of the R_F ligand to CO was observed, nor was there any evidence for the C–C coupling of perfluoroaryl and pentamethylcyclopentadienyl ligands previously observed in analogous Co complexes.[34]

The crystal structures confirm that substitution of the carbonyl ligand by trimethylphosphine has occurred. Similarly to the carbonyl complexes **2**, the coordination environment around the metal is close to octahedral; the angles around the metal atom being close to 90°.

The ^1H NMR spectra of compounds **3** confirmed that substitution by PMe_3 had occurred, with the protons of the phosphine ligand giving rise to a doublet at δ 1.7–1.8 (J_{PH} = 10–10.5

Table 3 Infrared stretching frequencies of carbonyl ligands in $[M(\eta^5\text{-}C_5Me_5)(CO)(R_F)I]$ complexes

	ν_{CO}/cm^{-1} (CH_2Cl_2)		
R_F	M = Co[a]	M = Rh[b]	M = Ir
CF_2CF_3		2069	2047
$CF_2CF_2CF_3$		2065	2045
$CF_2C_6F_5$	2044[c]	2056	2033
$CF(CF_3)_2$	2062	2065	2045

[a] Ref. 38. [b] Ref. 33, 38. [c] Recorded in C_6H_6.

Table 5 Selected bond lengths (Å) and angles (°) for complexes **3**

	3a[a]	**3b**	**3d**
Ir–P	2.283(4)	2.307(2)	2.333(4)
Ir–I	2.7498(19)	2.7206(6)	2.7466(13)
Ir–R_F	2.12(3)	2.098(8)	2.19(2)
Ir–cen[b]	1.914(14)	1.904(8)	1.896(17)
C_α–F_A	1.23(3)	1.411(9)	1.46(2)
C_α–F_B	1.52(3)	1.395(9)	
C_β–F_{ave}	1.36(4)	1.31(2)	1.33(3)
R_F–Ir–P	93.9(6)	92.7(2)	93.8(4)
R_F–Ir–I	90.6(10)	88.0(2)	88.1(5)
I–Ir–P	88.73(15)	89.20(7)	86.97(13)
Ir–C–F_A	105(2)	108.1(5)	110.0(9)
Ir–C–F_B	111.6(19)	116.8(6)	115.2(13)
Ir–C–R_F	113.2(16)	120.2(5)	110.9(14)
F_A–C–F_B	108.0(19)	102.2(6)	115(2)[c]

[a] Data shown for one of the two independent molecules in the unit cell. [b] cen = centroid of the C_5Me_5 ring. [c] CF_3–C–CF_3.

Table 4 Yields, NMR and analytical for $[Ir[\eta^5\text{-}C_5Me_5)(PMe_3)(R_F)I]$ **3a–d**

	R_F	Yield (%)	^1H NMR[a]	^{19}F NMR[a]	$^{31}P\{^1H\}$ NMR[a]	Analysis[b] (%)
3a	CF_2CF_3	80	1.89 [15H, d, *J*(PH) 2.1, C_5Me_5]; 1.72 [9H, d, *J*(PH) 10.5, PMe_3]	−69.4 [1F, d, *J*(AB) 277, $C_\alpha F_A$]; −70.4 [1F, dd, *J*(AB) 277, *J*(PF) 4, $C_\alpha F_B$]; −81.9 [3F, s, *J*(FF) 12, CF_3]	−37.6 [dd, *J*(PF) 4, *J*(PF) 3, PMe_3]	C, 27.87 (27.74); H, 3.52 (3.73)
3b	$CF_2CF_2CF_3$	83	1.89 [15H, d, *J*(PH) 1.8, C_5Me_5]; 1.72 [9H, d, *J*(PH) 10.5, PMe_3]	−65.6 [1F, m, *J*(AB) 288, *J*(PF) 12, $C_\alpha F_A$]; −67.0 [1F, m, *J*(AB) 288, *J*(FF) 12, *J*(PF) 8, $C_\alpha F_B$]; −79.3 [3F, t, *J*(FF) 12, CF_3]; −113.6 [1F, dd, *J*(AB) 280, *J*(PF) 13, $C_\beta F_A$]; −116.7 [1F, d, *J*(AB) 280, $C_\beta F_B$]	−38.0 [dd, *J*(PF) 8, *J*(PF) 12, PMe_3]	C, 27.83 (27.47); H, 3.31 (3.46)
3c	$CF_2C_6F_5$	53	1.88 (15H, s, C_5Me_5); 1.79 [9H, d, *J*(PH) 10, PMe_3]	1.79 [9H, d, *J*(PH) 10, PMe_3]; δ_F ($CDCl_3$) −41.5 [1F, dt, *J*(AB) 261, *J*(FF) 11, $C_\alpha F_A$]; −48.6 [1F, ddt, *J*(AB) 261, *J*(PF) 67, *J*(FF) 33, $C_\alpha F_B$]; −140.3 (2F, m, *o*-F); −158.8 (1F, t, *J*(FF) 21, *p*-F); −156.0 [2F, dt, *J*(FF) 21, *J*(FF) 5, *m*-F]	−35.3 [d, *J*(PF) 67, PMe_3]	C, 32.75 (32.14); H, 3.29 (3.24)
3d	$CF(CF_3)_2$	88	1.81 (15H, s, C_5Me_5); 1.75 [9H, d, *J*(PH) 10.5, PMe_3]	−63.2 (3F, s, CF_3); −70.8 (3F, s, CF_3); −155.9 (1F, br s, CF)	−38.3 (br s, PMe_3)	C, 27.64 (27.47); H, 3.57 (3.46)

[a] Recorded at 298 K in $CDCl_3$. Data given as: chemical shift (δ) [relative intensity, multiplicity (*J* Hz), assignment], s = singlet, d = doublet, t = triplet, br indicates a broad signal. [b] Required values are given in parentheses.

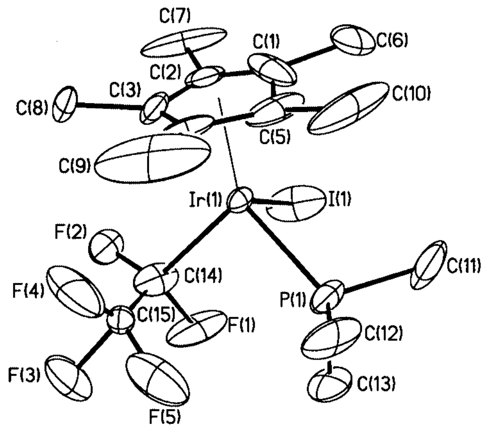

Fig. 4 ORTEP drawing of one of the independent molecules of **3a** with hydrogen atoms omitted for clarity.

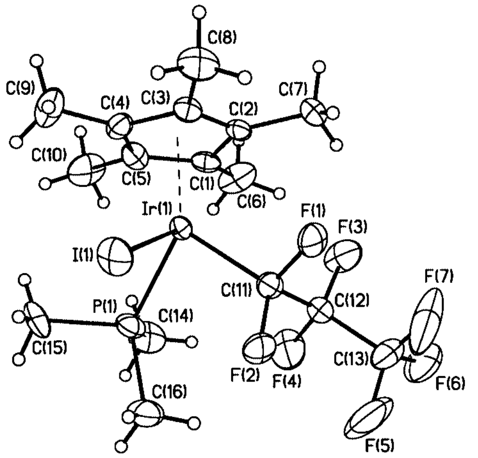

Fig. 5 ORTEP drawing of **3b** with thermal ellipsoids drawn at 30% probability level and hydrogen atoms omitted for clarity.

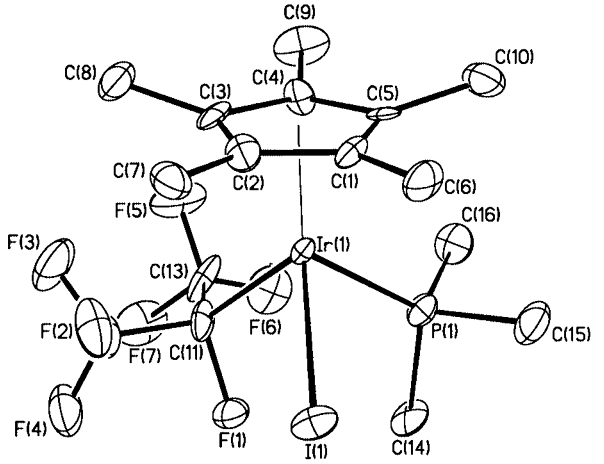

Fig. 6 ORTEP drawing of **3d** with thermal ellipsoids drawn at 30% probability level and hydrogen atoms omitted for clarity.

Hz). The ^{19}F NMR spectra of complexes **3a**–**c** are very similar to those of **2a**–**c**, and in accord with the crystal structures. The diastereotopic CF_2 groups give rise to AB quartets, with additional coupling between the fluorine atoms on the α-carbon and the phosphorus atom of the phosphine. The magnitude of phosphorus–fluorine coupling is inequivalent for each fluorine atom of the α-CF_2 group, consistent with a structure having one of the fluorine atoms closer to the phosphine than the other. The inequivalent C–F coupling resulted in the $^{31}P\{^1H\}$ resonances of complexes **3a** and **3b** being observed as doublets of doublets, and that of **3c** as a doublet. No P–F coupling was observed in the ^{19}F or $^{19}F\{^1H\}$ NMR spectra of **3d**.

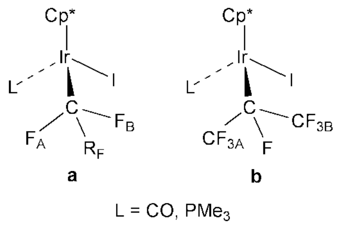

Fig. 7 (a) Labeling scheme used in discussing the crystal structures of **2a**, **c**, **3a**, **b**. (b) Labeling scheme used in discussing the crystal structures of **2d** and **3d**.

Crystallographic analysis of complexes

With the exception of **2b**, we were able to crystallise all complexes **2** and **3** and determine their crystal structures. The structure of **3c** was of low quality and the structural parameters are not included in the discussion. Complexes **2a** and **3a** both showed positional disorder of the iodine and perfluoroethyl groups, which resulted in slightly lower quality data for these two complexes. Thus, although qualitative descriptions of the conformations of these compounds will be mentioned, analysis of trends and differences in these two molecules will not be attempted. For ease of comparison, all the linear perfluoroalkyl structures will be discussed using the labeling scheme shown in Fig. 7a. For the perfluoroisopropyl complexes, a similar labeling scheme is used, shown in Fig. 7b.

CO complexes. Some changes in the geometry of the perfluoroalkyl ligand were observed on coordination to the metal. Generally, the Ir–R_F bond length in the crystal structure was found to be similar to, or slightly shorter than, analogous Ir–R bond lengths documented by Orpen *et al.*[36] Thus, for the perfluorobenzyl complex **2c**, the Ir–R_F bond is 2.152(14) Å, which is slightly shorter than other determined Ir–CH_2Ar bond lengths,[36] while for **2d**, the bond length of 2.11(3) Å is identical within experimental error to the average secondary alkyl Ir–CHR_2 bond length of 2.107(35) Å.[36] In addition the C–F bonds α to the metal were found to be similar to, or longer than typical C–F bond lengths. In the case of **2c**, both C–F bond lengths α to the metal compare well with the typical value of 1.36 Å for CF_2 groups, while the α-C–F bond length of 1.55(3) Å in **2d** is longer than average for tertiary C–F bonds (1.43 Å).[37] The rest of the perfluoroalkyl ligand did not show bond length changes upon coordination. For **2c**, the aromatic C–F bonds are very close to those determined for pentafluorobenzene (1.328 Å)[37] while in **2d** the average bond length of the CF_3 groups (1.34(4) Å) was about the same as the average C–F bond lengths for CF_3 groups (1.34 Å).[37]

The bond angles around the α-carbon of the perfluoroalkyl ligand are consistent with greater p-character in the M–C bond than expected for hydrocarbon analogues. In the case of **2c**, the F_A–C–F_B angle is 105.6(12)°, while the Ir–C–R_F angle is 116.2(12)°. For **2d**, with only one fluorine atom on the α-carbon, only the Ir–C–F bond angle is relatively small at 108.6(14)°. We assume that the bulky CF_3 groups of **2d** cause the other angles around the α-carbon to open up, resulting in the Ir–C–CF_3 angles being 116(2)° and 118(2)°, and the CF_3–C_α–CF_3 angle to be 116(3)°.

PMe_3 complexes. With the exception of **3a**, coordination of the more basic and weaker π-acceptor PMe_3 ligand appears to cause a slight elongation of the Ir–I bonds, but insignificant changes in the lengths of the Ir–R_F bonds. As in the carbonyl complexes, the C–F bond lengths in the α position are generally longer than is typical. The α-C–F bond length of **3d** of 1.46(2) Å is identical to the analogous bond in [Rh(η^5-C_5Me_5)(PMe_3)-

Table 6 Cone (°) and solid (sr) angle data for complexes **2** and **3**

		CF_2CF_3	$CF_2CF_2CF_3$	$CF_2C_6F_5$	$CF(CF_3)_2$
θ	CO	151		156	165
	PMe_3	154[a]	137		167
Ω	CO	2.64		4.11	4.53
	PMe_3	4.27[a]	3.37		4.54

[a] Data shown for one of the two independent molecules in the unit cell.

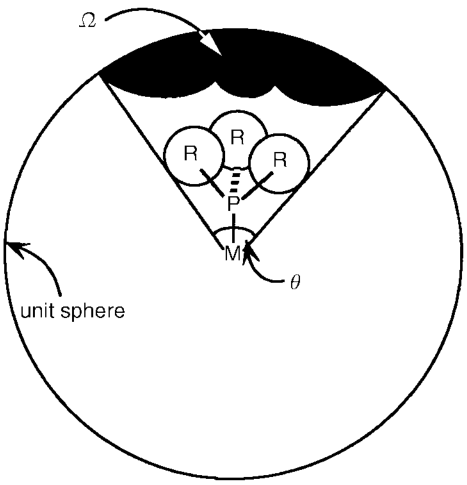

Fig. 8 Schematic explanation of the differences between cone (θ) and solid (Ω) angles.

$(CF(CF_3)_2)I]$ of 1.43(2) Å,[33] but shorter than that observed in **2d** (1.55(3) Å) and longer than the 1.377(9) Å observed in the cationic complex $[Rh(C_5H_5)(PMe_3)_2(CF(CF_3)_2)]^+[I]^-$.[35] The C_α–F bond lengths of **3b** are 1.411(9) Å and 1.395(9) Å, identical within experimental error to the analogous distances in $[Co(\eta^5\text{-}C_5Me_5)(PMe_3)_2(CF_2CF_2CF_3)]^+[I]^-$, which are 1.394(6) Å and 1.379(7) Å.[38]

Like the carbonyl complexes **2**, the bond angles around the α-carbon of complexes **3a**,**b** are consistent with greater p-character in the M–C bond, with relatively small F_A–C–F_B bond angles. The perfluoroisopropyl complex **3d** is once again the odd one out. The angles around the α-carbon are all greater than 109.3°, perhaps as a result of the bulky CF_3 groups.

Steric effects of perfluoroalkyl ligands

Ligand steric effects in organometallic chemistry are most often described by the Tolman cone angle, θ.[29] The cone angle was originally proposed for quantifying the sizes of phosphorus ligands, and the methodology has subsequently been applied to other ligands, such as isocyanides, amines, cyclopentadienyls, and alkyls.[30,39] Other methods have been proposed for quantifying ligand steric effects; the solid angle, Ω,[30,31,40,41] is the most similar in spirit to the cone angle. In essence, the solid angle is the surface area the ligand projects onto the surface of a sphere. The differences between the two methodologies are shown schematically in Fig. 8.

The cone and solid angles of the R_F groups have been determined from the crystal structure data, and are shown in Table 6. No previous data have been used to generate cone angles of perfluoroalkyl, except for CF_3, which was determined to be 133°.[39] The values follow the intuitively expected trend, with $CF_2CF_3 < CF_2C_6F_5 < CF(CF_3)_2$. Only the value of $CF_2CF_2CF_3$ appears anomalous, and deserves further comment. Comparison of the crystal structures of **3a** and **3b** reveals the reason why. The Ir–C–C bond angle in the perfluoroethyl group is 113°, while in the perfluoro-n-propyl group it is 120°. Thus, the larger angle at the metal causes the perfluoro-n-propyl group, which would be expected to be at least as bulky, if not bulkier than the perfluoroethyl group ($\theta = 152.5 \pm 1.5°$), to adopt a more svelte conformation in this particular crystal structure, which results in a smaller cone angle ($\theta = 137°$). To further examine the steric parameters of the perfluoroethyl and perfluoro-n-propyl ligands, complexes containing these ligands were retrieved from the Cambridge Structural Database.[42] Calculation of cone angles for the R_F ligands in these complexes gave a mean cone angle for CF_2CF_3 of $\theta = 149.3 \pm 1.5°$ (2 structures), and for $CF_2CF_2CF_3$ of $\theta = 149.5 \pm 2.1°$ (16 structures). Thus, the two straight chain perfluoroalkyl groups are about the same size, but unsurprisingly show some flexibility; our particular example gives an anomalously small value for $CF_2CF_2CF_3$, indicating the importance of looking at average cone angles for a number of structures.

As expected, the cone angles for perfluoroalkyl groups are larger than the analogous alkyl groups. Thus, the perfluoroethyl group has a cone angle more than 20° larger than an ethyl group ($\theta = 123°$),[39] and is closer in size to a *tert*-butyl group ($\theta = 146°$).[39] The perfluoroisopropyl group is more than 30° bigger than an isopropyl group, larger than a *tert*-butyl group ($\theta = 146°$),[39] and about the same size as CBr_3 ($\theta = 167°$).[39] The perfluoro-n-propyl ligand in our example (**3b**) does not show a major size difference, but as discussed above, our value appears to be anomalously low. Values extracted from other structures (see above) indicate that $CF_2CF_2CF_3$ is slightly larger ($\theta = 149.5 \pm 2.1°$) than n-propyl ($\theta = 143°$).[39] No value of θ has been reported for a benzyl group for comparison with our perfluorobenzyl complex **2c**.

The solid angle data of the perfluoroalkyl ligands follow the same trend as the cone angle data. Very little solid angle data have been published for alkyl groups, precluding a meaningful comparison with the perfluoroalkyl data. The solid angle of the perfluoroethyl group ($\Omega = 2.64$–4.27 sr) is greater than for the ethyl group ($\Omega = 1.638$ sr),[43] while the perfluoro-n-propyl ligand at 3.37 sr is larger than the n-propyl group ($\Omega = 2.017$ sr).[43] The perfluorobenzyl and perfluoroisopropyl groups are both larger than the *tert*-butyl group ($\Omega = 3.317$ sr),[43] and comparable to the CBr_3 group ($\Omega = 4.376$ sr).[43]

Conclusions

The perfluoroalkyl complexes $[Ir(\eta^5\text{-}C_5Me_5)(L)(R_F)I]$ (L = CO, PMe_3; $R_F = CF_2CF_3$, $CF_2CF_2CF_3$, $CF_2C_6F_5$, $CF(CF_3)_2$) were prepared from $[Ir(\eta^5\text{-}C_5Me_5)(CO)_2]$ by oxidative addition of R_FI followed by PMe_3 substitution in refluxing toluene. The structures of the fluoroalkyl groups were examined by X-ray crystallography, and confirm previous results. The Ir–C bond lengths are shorter than in alkyl complexes, while the α-C–F bond lengths are slightly longer than in non-coordinated fluoroalkyls. The bond angles around the α-carbon atom are consistent with greater p-character in the Ir–C bond. The steric sizes of the perfluoroalkyl ligands were determined, and were, not unexpectedly, larger than the corresponding alkyl ligands.

Experimental

General procedures

All reactions were performed in oven-dried glassware, using standard Schlenk techniques, under an atmosphere of nitrogen which had been deoxygenated over BASF catalyst and dried over molecular sieves, or in a Braun drybox. Diethyl ether, toluene and hexanes were distilled under nitrogen from K/benzophenone, and methylene chloride from CaH_2. ^1H (300 MHz), ^{19}F (282 MHz) and ^{31}P (121.4 MHz) NMR spectra were recorded on a Varian Unity Plus 300 Spectrometer at 25 °C. Chemical shifts are reported as ppm downfield of $SiMe_4$ (^1H, referenced to solvent) or internal $CFCl_3$ (^{19}F), or external 85% H_3PO_4 (^{31}P). Coupling constants are reported in Hz. IR spectra were recorded on a Perkin-Elmer FTIR spectrophotometer.

Table 7 Crystal data for **2a**, **2c**, **2d**, **3a**, **3b** and **3d**

Compound	**2a**	**2c**	**2d**	**3a**	**3b**	**3d**
Formula	$C_{13}H_{15}F_5IIrO$	$C_{18}H_{15}F_7IIrO$	$C_{14}H_{15}F_7IIrO$	$C_{15}H_{24}F_5IIrP$	$C_{16}H_{24}F_7IrIP$	$C_{16}H_{24}F_7IIrP$
M	601.35	699.40	651.36	649.41	699.42	699.42
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Tetragonal	Orthorhombic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P4_2/n$	$P2_12_12_1$
a/Å	7.5211(2)	13.373(4)	8.999(9)	16.7571(2)	23.0016(3)	8.68413(4)
b/Å	17.4802(5)	10.850(3)	14.477(5)	15.8571(3)	23.0016(3)	13.6408(2)
c/Å	12.5964(4)	15.330(6)	13.553(7)	16.8830(2)	8.1951(2)	18.0396(3)
β/°	96.4753(10)	114.02(2)	94.32(4)	118.0617(7)	90	90
U/Å^3	1645.47(13)	2031.7(10)	1761(2)	3958.75(15)	4335.8(2)	2136.94(3)
Z	4	4	4	8	8	4
μ/mm^{-1}	10.034	8.159	9.404	8.424	7.712	7.824
T/K	173(2)	296	249(2)	173(2)	298(2)	198(2)
Total data	7178	3921	3227	17159	18533	7477
Unique data, R_{int}	3608, 0.0531	3774, 0.0237	2300, 0.0459	8123	4151, 0.0319	7394, 0.0820
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0432, 0.1159	0.0554, 0.0625	0.0701, 0.1692	0.0776, 0.2210	0.0378, 0.1445	0.0651, 0.1490
(all data)	0.0501, 0.1244	0.0800, 0.0683	0.1081, 0.1988	0.0959, 0.2313	0.0458, 0.1571	0.0739, 0.1517

Elemental analyses were performed by Schwartzkopf (Woodside, NY).

$IrCl_3 \cdot 3H_2O$, (Pressure Chemical Company), ICF_2CF_3 (PCR) and PMe_3 (Aldrich) were obtained commercially and used as received. $I(CF_2)_2CF_3$, $ICF(CF_3)_2$ and $ICF_2C_6F_5$ (PCR) were purified by treatment with sodium thiosulfate to remove iodine, followed by vacuum distillation. The dicarbonyl complex, $[Ir(\eta^5\text{-}C_5Me_5)(CO)_2]$[44] was prepared by a literature procedure from $[Ir(\eta^5\text{-}C_5Me_5)Cl_2]_2$.

Synthesis

Preparation of $Ir(\eta^5\text{-}C_5Me_5)(CO)(R_F)I$ ($R_F = CF_2CF_3$, $CF_2CF_2CF_3$, $CF_2C_6F_5$, $CF(CF_3)_2$) 2a–d. All complexes **2a–d** were prepared in a similar manner. To a stirred yellow solution of $Ir(\eta^5\text{-}C_5Me_5)(CO)_2$ in CH_2Cl_2 (10 ml) was added the perfluoroalkyl iodide (1.1 equivalents). In most cases, there was noticeable evolution of gas from the solution as it was stirred at room temperature. The reaction was monitored by the disappearance of the 2009 cm^{-1} band in the IR. On completion (1–2 h), the volatiles were removed by vacuum pumping from the orange solution to give an orange-yellow powder. Crystallisation from CH_2Cl_2/hexanes gave analytically pure complexes.

Preparation of $Ir(\eta^5\text{-}C_5Me_5)(PMe_3)(R_F)I$ ($R_F = CF_2CF_3$, $CF_2CF_2CF_3$, $CF_2C_6F_5$, $CF(CF_3)_2$) 3a–d. To an orange slurry/solution of the iridium complex **2a–d** in toluene (20 ml) was added PMe_3 (1.5 equivalents). The reaction mixture was heated to reflux under N_2, by which time all the solid had dissolved. The course of the reaction was monitored by IR spectroscopy. On completion (*ca.* 2 h), the solution was cooled, and the volatiles removed by vacuum pumping. For complexes **3b** and **3d** an orange powder was obtained. For complexes **3a** and **3d** the residue was extracted with diethyl ether, and the solvent removed by rotary evaporation.

Attempts at purifying **3a–3c** by column chromatography resulted in hydrolysis of the α-CF_2 group to CO. Thus, for example, passing **3c** through a column (Florisil®, silica gel or alumina) results in formation of $[Ir(\eta^5\text{-}C_5Me_5)(PMe_3)(COC_6F_5)I]$ as an orange powder (Found: C, 33.42; H, 3.51%. $C_{20}H_{24}F_5IIrOP$ requires C, 33.11; H 3.33%); ν_{max}/cm^{-1} (CO) 1646 (CH_2Cl_2); $\delta_H(CDCl_3)$ 1.85 [15H, d, J(PH) 2 Hz, C_5Me_5]; 1.70 [d, 9H, J(PH) 11 Hz, PMe_3); $\delta_F(CDCl_3)$ −143.57 [d, 2F, J(FF) 22 Hz, *o*-F]; −157.46 [t, 1F, J(FF) 21 Hz, 1F, *p*-F]; −163.33 (m, 2F, *m*-F); $\delta_P(CDCl_3)$ −34.48 (s, PMe_3).

X-Ray crystallography

X-Ray quality crystals were grown by slow evaporation from CH_2Cl_2/hexanes (**2a**, **2d**, **3a**, **3b**, **3d**) or diethyl ether (**2c**). The single crystal X-ray diffraction experiment was conducted on a Siemens P4 diffractometer for complexes **2c** and **2d** or a Siemens P4 diffractometer equipped with a CCD detector for complexes **2a**, **2b**, **3a** and **3d**. Systematic absences and diffraction symmetry were consistent with the assigned space groups for **2a**, **c**, and **d** and **3a**, **b**, and **d**. The crystal data and experimental parameters for **2a**, **2c** and **2d**, and for **3a–d** are listed in Table 7. Complex **3a** exists as two crystallographically independent but chemically equivalent molecules per asymmetric unit. The structures were solved by direct methods, completed by subsequent difference Fourier synthesis and refined by full-matrix, least-squares procedures. An empirical absorption correction was applied to the data of all compounds using the program DIFABS.[45] For complexes **2a** and **3a**, the iodine and perfluoroethyl groups are positionally disordered. For complex **2a** the I–C_2F_5 disorder is approximately 82:18, while for **3a** the I-C_2F_5 disorder is approximately 82:18 for the first molecule, and approximately 72:28 for the second molecule. The minor portion of the perfluoroethyl group could not be located from the difference map of either **2a** or **3a** and was ignored in the refinement, but not in the global parameters. The minor portion of the perfluoroethyl group could not be located from the difference map and was ignored in the refinement, but not in the global parameters. The position of the β-carbon of the perfluoroethyl group in **2a** could not be discerned separately from the minor portion of the iodine atom on the difference map and was modeled as an undersized iodine atom [C(13)]. For all compounds except **3a**, the largest peak and hole lie about the Ir centre. For **3a** the peak and hole lie about the disordered I and F atom.

CCDC reference number 186/1812.

See http://www.rsc.org/suppdata/dt/a9/a907057e/ for crystallographic files in .cif format.

Steric parameter calculations

Cone and solid angles were calculated according to literature procedures,[29,31,46] using the program Steric[47] running on an SGI Indy R5000 running IRIX 6.2. The van der Waals' radius set used was that of Bondi,[24] while the M–C bond lengths were fixed at 1.54 Å, in accordance with previous work.[39]

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