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Arene-polyfluoroarene π - π stacking between N-heterocyclic carbene ligands of pentamethylcyclopentadienyl group 9 metal complexes

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Graphical abstract

Highlights

- The crystal structures of the dichloromethane solvates of (η^5 -pentamethylcyclopentadienyl)rhodium(κ C-1-(4-trifluoromethyl-2,3,5,6-

tetrafluorophenylmethyl)-3-benzylimidazol-2-ylidene) dichloride and its iridium analogue contain intermolecular π – π stacking.

- The crystal structures of the dichloromethane solvates of (η^5 -pentamethylcyclopentadienyl)rhodium(κ C-1-(2,3,4,5,6-pentafluorophenylmethyl)-3-benzylimidazol-2-ylidene) dichloride and its iridium analogue contain intermolecular lone pair– π interactions.
- The crystals structures possess hydrogen-bonding between the complex and dichloromethane molecules.
- The strengths of the interactions have been probed by DFT calculations.
- The presence of π – π stacking or lone pair– π interactions, which are of approximately the same strength, is determined by the steric requirements of the para moiety: fluorine or trifluoromethyl.

Abstract -

(η^5 -Pentamethylcyclopentadienyl)rhodium(κ C-1-(2,3,4,5,6-pentafluorophenylmethyl)-3-benzylimidazol-2-ylidene) dichloride (**1a**) and its iridium analogue (**1b**) crystallize as dichloromethane solvates in the enantiomorphous space group $P2_12_12_1$. (η^5 -Pentamethylcyclopentadienyl)rhodium(κ C-1-(4-trifluoromethyl-2,3,5,6-tetrafluorophenylmethyl)-3-benzylimidazol-2-ylidene) dichloride (**2a**) and its iridium analogue (**2b**) crystallize as dichloromethane solvates in the polar space group $Pca2_1$. All the crystal structures possess columns of alternating complex and dichloromethane molecules which are linked by hydrogen bonding. Perpendicular to these is hydrogen bonding between the imidazol-2-ylidene hydrogen atoms and chloride ligands. The crystal structures of **2a** and **2b** also display intermolecular π – π stacking between

the phenyl and trifluoromethyltetrafluorophenyl rings of molecules in a direction perpendicular to the columns and hydrogen bonding between the complex molecules. In contrast those of **1a** and **1b** display intermolecular lone pair– π interactions in the same direction as the hydrogen bonding between the complex molecules. DFT calculations reveal that the π – π stacking and lone pair– π interactions are of approximately the same energy. The difference in the structures arises from the steric requirements of the trifluoromethyl group.

Keywords

N-Heterocyclic carbene, crystal structure, π – π stacking, lone pair– π interaction

1. Introduction

The attractive interaction between parallel arene and polyfluoroarene rings, commonly termed π – π stacking, has been known for five decades [1]. Until recently its use in crystal engineering had been restricted to relatively simple molecules [2], but more recently more elaborate systems that allowed the crystal engineering of crystal structures with particular properties, such as polarity, have been devised [3]. In particular, aryl- and polyfluoroaryl-substituted imidazolium salts have proved to be fruitful [4-7]. For example, 1-(2,3,4,5,6-pentafluorophenylmethyl)-3-benzylimidazolium bromide [4] and 1-(4-chloro-2,3,5,6-tetrafluorophenyl)-3-benzylimidazolium bromide [6] crystallize in the polar space groups *P1* and *Cc* respectively. Imidazolium salts are precursors to N-heterocycle carbenes, and so it is reasonable to expect that π – π stacking between the aryl and polyfluoroaryl substituents of NHCs coordinated to metals would also occur. The crystal structures of very few metal complexes of NHCs bearing both aryl- and polyfluoroaryl substituents have been reported [8-10], and none possess intermolecular π – π stacking between the complementary rings, although *trans*-[PdBr₂(κ C-C₆H₅CH₂NC₃(C₄H₄)NCH₂C₆F₅)₂] does display intramolecular π – π stacking [9].

Figure 1. Aryl and polyfluoroaryl-substituted NHC ligands

Complexes of 1-perfluoroarylmethyl-3-benzylimidazol-2-ylidene (**I**) (Figure 1) provide a rational area of study because the crystal structures of the precursor imidazolium salts possess $\pi-\pi$ stacking [4,6,11,12], and because complexes of 1-polyfluoroaryl-3-arylmethylimidazol-2-ylidene (**II**) undergo undesired reactions in their syntheses [13], and the sole example of an imidazolium salt that is a precursor to 1-polyfluoroarylmethyl-3-arylimidazol-2-ylidene (**III**) does not possess $\pi-\pi$ stacking [7]. Consequently a structural study of $(\eta^5\text{-pentamethylcyclopentadienyl})\text{rhodium}$ and iridium complexes of 1-(2,3,4,5,6-pentafluorophenylmethyl)-3-benzylimidazol-2-ylidene and its analogue 1-(4-trifluoromethyl-2,3,5,6-tetrafluorophenylmethyl)-3-benzylimidazol-2-ylidene, $[(\eta^5\text{-C}_5\text{Me}_5)\text{MCl}_2(\kappa\text{C-C}_6\text{H}_5\text{CH}_2\text{NC}_3\text{H}_2\text{NCH}_2\text{C}_6\text{F}_4\text{X})]$ (**1** X = F, **2** X = CF_3 ; **a** M = Rh, **b** M = Ir) was undertaken. Here are reported the results of the study, augmented by a DFT study.

2. Results and discussion

The complexes $[(\eta^5\text{-C}_5\text{Me}_5)\text{MCl}_2(\kappa\text{C-C}_6\text{H}_5\text{CH}_2\text{NC}_3\text{H}_2\text{NCH}_2\text{C}_6\text{F}_4\text{X})]$ (**1** X = F; **2** X = CF_3 ; **a** M = Rh; **b** M = Ir) were prepared by transfer of the NHC ligand from the respective silver complexes. Recrystallization from dichloromethane yielded crystals of the monosolvates. The complexes, which are chiral by virtue of possessing different substituents on the NHC ligand, crystallized in non-centrosymmetric space groups in the orthorhombic crystal system; **1a** and **1b** as conglomerates in the enantiomorphous space group $P2_12_12_1$, and **2a** and **2b** as true racemates in the polar space group

*Pca*₂₁. Crystal data are given in Table 1 and selected distances and angles are given in Table 2. The bond distances and dihedral angles are virtually identical to those of the optimized structures of the rhodium complexes for gas phase molecules calculated using the ω B97X-D [14] method and the 6-311G++(2d,2p) basis set. The structures of **1a** (Figure 2) and **2a** (Figure 3) are similar, but show differences in the positions of the phenyl and polyfluoroaryl rings (Figure 4). The iridium complexes, **1b** and **2b**, are isostructural with their rhodium analogues.

Figure 2. The structure of complex **1a** showing the position of the closest molecule of dichloromethane. Thermal ellipsoids are at the 50% level. Hydrogen atoms are omitted for clarity.

Figure 3. The structure of **2a** showing the position of the closest molecule of dichloromethane.

Thermal ellipsoids are at the 50% level. Hydrogen atoms are omitted for clarity.

Figure 4. Overlay of the structures of complex **1a** (red) and complex **2a** (blue).

The crystal structures comprise columns of alternating complex and solvent molecules (parallel to the *a* axis for **1a** and **1b**, and parallel to the *b* axis for **2a** and **2b**) with the carbon atom of the closest dichloromethane molecule close to the chloride ligands of the complex (Figure 5). The geometric parameters suggest $\text{Cl}_2\text{CH}_2 \cdots \text{Cl}$ hydrogen bonding (Table 3). In particular the $\text{C} \cdots \text{Cl}$ distances are less than, or close to, 3.45 Å, the sum of the van der Waals' radii of carbon and chlorine [15]. The interactions were calculated to be attractive by 52 and 42 kJ mol^{-1} for **1a** and **2a** respectively. There are also short distances between one of the chlorine atoms of another molecule of dichloromethane and carbon atoms of the pentamethylcyclopentadienyl ligand (Figure 4). The

geometric parameters suggest $\text{CH}_3 \cdots \text{ClCH}_2\text{Cl}$ hydrogen bonding and the possibility of lone pair— π interactions. In support, theoretical studies on the interactions between anions, such as triflate and tetrafluoroborate, and the cyclopentadienyl ring of the neutral complex $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}\{\eta^6\text{-C}_6\text{H}_2(\text{O}_2\text{BF}_2)_2\}]$, which are attractive by *ca.* 100 kJ mol^{-1} , show that these comprise both hydrogen bonding and anion— π interactions [16]. The interactions in **1a** and **2a** were calculated to be attractive by 19 and 16 kJ mol^{-1} respectively.

Figure 5. The interactions between dichloromethane and (a) complex **1a** and (b) complex **2a** within a column of alternating complex and solvent molecules. Thermal ellipsoids are at the 50% level. Hydrogen atoms are omitted for clarity.

The chloride ligands are also close to the imidazol-2-ylidene carbon atoms C(12) and C(13) of a complex molecule of an adjacent antiparallel column, although ca. 0.2 Å further than from the carbon atom of the closest dichloromethane molecule (Table 4). These contacts link adjacent antiparallel columns parallel to the *b* axis for **1a** and **1b** (Figure 6) and parallel to the *a* axis for **2a** and **2b** (Figure 7). The number of atoms prevented calculations of the energies of these interactions for the complexes, but interactions between molecules of the 1,3-methyl substituted NHC complex $[(\eta^5\text{-C}_5\text{Me}_5)\text{RhCl}_2(\kappa\text{C-MeNC}_3\text{H}_2\text{NMe})]$ using the atomic positions of **1a** and **2a** were calculated to be attractive by 51 kJ mol⁻¹. For **1a** and **1b** the pentafluorophenyl ring of one molecule is also close to one of the chloride ligands of another, with distances that suggest a lone pair— π interaction [17] (Table 4). The energy of the interaction between a molecule of **1a** and pentafluorotoluene in the same relative position as the pentafluorobenzyl group of a second molecule of **1a** was calculated to be -38 kJ mol⁻¹. Similar interactions are not present in the crystal structures of **2a** and **2b**, with the chloride ligands being more distant and lying on normals to the rings' planes that are considerably outside the ring of carbon atoms.

Figure 6. The crystal structure of complex **1a** viewed parallel to the *a* axis showing interactions between the molecules. Thermal ellipsoids are at the 50% level. Dichloromethane molecules and hydrogen atoms are omitted for clarity.

Figure 7. The crystal structure of complex **2a** viewed parallel to the *b* axis showing interactions between the molecules. Thermal ellipsoids are at the 50% level. Dichloromethane molecules and hydrogen atoms are omitted for clarity.

In the crystal structures of **2a** and **2b** there is π – π stacking between the perfluorotolyl group of one molecule and the phenyl ring of an adjacent molecule of opposite configuration, thereby linking the complex molecules of parallel columns to form chains parallel to the *c* axis (Figure 7). The interactions between the molecules of **1a** and 4-trifluoromethyl-2,3,5,6-tetrafluorotoluene and between **1a** and toluene, with the positions of the atoms of the toluene molecules as for those of a second molecule of **2a**, were calculated to be attractive by 49 and 48 kJ mol^{–1} respectively, and that between 4-trifluoromethyl-2,3,5,6-tetrafluorotoluene and toluene was calculated to be attractive by 33

kJ mol^{-1} , which is consistent with those calculated for the interaction between toluene and hexafluorobenzene at a separation of $3.4 \text{ \AA}$ (-33.6 and $-36.0 \text{ kJ mol}^{-1}$) [18]. π – π stacking is not evident in the crystal structures of **1a** and **1b**.

The calculations strongly suggest that the absence or presence of π – π stacking is not a result of the strengths of the interactions between the molecules, and certainly not as a result of π – π stacking interactions being weaker than the other types of interaction. Rather it appears to be a consequence of the greater size of the trifluoromethyl group compared to the fluorine atom. The change of fluorine to trifluoromethyl (van der Waals' radii 1.47 [15] and $2.73 \text{ \AA}$ [19] respectively) results in an increase in the unit cell volume of *ca.* 5% , which arises predominantly from an increase in the unit cell length in only one direction; parallel to the hydrogen bonding interactions between complex molecules (*b* for **1a** and **1b** and *a* for **2a** and **2b**) (Table 1). The values of the other analogous unit cell lengths are very similar for the four crystal structures. The trifluoromethyl group shifts the perfluoroaryl ring from a position that allows the lone pair– π interaction to one where π – π stacking can occur, without significantly disrupting the other interactions or changing the packing efficiency, which is *ca.* 28% for all four crystal structures. Since the two interactions are of approximately the same strength the absence of one is compensated by the presence of the other.

3. Conclusion

Intermolecular π – π stacking occurs between the complementary rings of $(\eta^5\text{-pentamethylcyclopentadienyl})\text{rhodium}(\kappa\text{C-1-(4-trifluoromethyl-2,3,5,6-tetrafluorophenylmethyl)-3-benzylimidazol-2-ylidene})\text{dichloride}$ (**2a**), but not between those of $(\eta^5\text{-pentamethylcyclopentadienyl})\text{rhodium}(\kappa\text{C-1-(2,3,4,5,6-pentafluorophenylmethyl)-3-benzylimidazol-2-ylidene})\text{dichloride}$ (**1a**). Calculations reveal that hydrogen bonding interactions between complex molecules and between complex and dichloromethane molecules are stronger than the π – π stacking interaction, and give rise to similar non-centrosymmetric arrangements of molecules of **1a** and **2a**, although with different space groups. The lack of π – π stacking in **1a** is ascribed to the

presence of a lone pair— π interaction between a chloride ligand and the pentafluorophenyl ring, which is of similar strength to a π — π stacking interaction. The presence of a trifluoromethyl group in **2a** prevents this interaction for steric reasons and as a consequence the phenyl and polyfluorotolyl rings align to facilitate π — π stacking.

4. Experimental

4.1 Instrumentation

The ^1H , $^{13}\text{C}\{^1\text{H}\}$ and ^{19}F NMR spectra were recorded in deuteriochloroform, except where stated otherwise, using Bruker DRX300 or DPX400 spectrometers. ^1H (300.13 or 400.14 MHz) were referenced internally using the residual proto solvent resonance relative to SiMe_4 (δ 0), $^{13}\text{C}\{^1\text{H}\}$ (75.48 or 100.61 MHz) externally to SiMe_4 (δ 0), and ^{19}F (282.40 MHz) externally to CFCl_3 (δ 0). All chemical shifts are quoted in δ (ppm), using the high frequency positive convention, and coupling constants in Hz. Elemental analyses were carried out by the Campbell Microanalytical Laboratory, The University of Otago. Electrospray mass spectra were recorded on a Bruker Daltonics micrOTOF spectrometer.

4.2 Materials

The imidazolium salt $[\text{C}_6\text{H}_5\text{CH}_2\text{NC}_3\text{H}_3\text{NCH}_2\text{C}_6\text{F}_5]\text{Br}$ [4] and the complexes $[(\eta^5\text{-C}_5\text{Me}_5)\text{RhCl}(\mu\text{-Cl})_2]$ and $[(\eta^5\text{-C}_5\text{Me}_5)\text{IrCl}(\mu\text{-Cl})_2]$ [20] were prepared as previously described. 1-Benzylimidazole, and silver(I) oxide (Aldrich), and 4-trifluoromethyltetrafluorophenylmethyl bromide (Apollo Scientific) were used as supplied.

4.3 Preparation of 1-(4-trifluoromethyl-2,3,5,6-tetrafluorophenylmethyl)-3-methylimidazolium bromide

1-Benzylimidazole (0.52 g, 3.3 mmol) was added to 4-trifluoromethyltetrafluorophenylmethyl bromide (1.02 g, 3.3 mmol) in dichloromethane (50 cm^3). The mixture was left at ambient

temperature for 166 h. The solvent was removed by rotary evaporation yielding the product as a white solid. Yield 1.33 g (86%). $[M - Br]^+$: $[C_{18}H_{12}F_7N_2]^+$ requires 389.0889; found 389.0942. δ_H ($(CD_3)_2SO$): 9.51 (1H, s, N_2CH), 7.88 (1H, CH), 7.84 (1H, s, CH), 7.43 (5H, m, C_6H_5), 5.76 (2H, s, CH_2), 5.46 (2H, s, CH_2). δ_F ($(CD_3)_2SO$): -55.7 (3F, t, $J_{FF} = 22$ Hz, CF_3), -139.2 (2F, m, C_6F_4), -141.3 (2F, m, C_6F_4).

4.4 Preparation of (κC -1-perfluoroarylmethyl-3-benzylimidazol-2-ylidene)silver bromide

The silver complexes $[(\kappa C-C_6H_5CH_2NC_3H_2NCH_2C_6F_4X-4)AgBr]$ ($X = F, CF_3$) were prepared as described for $[(\kappa C-MeNC_3H_2NCH_2C_6F_5)AgBr]$ [21].

$[(\kappa C-C_6H_5CH_2NC_3H_2NCH_2C_6F_5)AgBr]$ from $[C_6H_5CH_2NC_3H_3NCH_2C_6F_5]Br$ (0.54 g, 1.2 mmol) and silver(I) oxide (0.16 g, 0.7 mmol). Yield 0.43 g (71%). $[M - Br]^+$: $[C_{34}H_{22}^{107}AgF_{10}N_4]^+$ requires 783.0736; found 783.0679. δ_H : 7.30 (5H, m, C_6H_5), 7.01 (1H, d, $^3J_{HH} = 1.8$ Hz, CH), 6.94 (1H, d, $^3J_{HH} = 1.8$ Hz, CH), 5.56 (2H, s, CH_2), 5.35 (2H, s, CH_2). δ_F : -140.5 (2F, m, F_{ortho}), -151.0 (1F, t, $^3J_{FF} = 21$ Hz, F_{para}), -159.7 (2F, m, F_{meta}).

$[(\kappa C-C_6H_5CH_2NC_3H_2NCH_2C_6F_4CF_3-4)AgBr]$ from $[C_6H_5CH_2NC_3H_3NCH_2C_6F_4CF_3-4]Br$ (0.47 g, 1.0 mmol) and silver(I) oxide (0.12 g, 0.5 mmol). Yield 0.50 g (87%). $[M - Br]^+$: $[C_{36}H_{22}^{107}AgF_{14}N_4]^+$ requires 883.0672; found 883.0547. δ_H : 7.34 (5H, m, C_6H_5), 7.04 (1H, d, $^3J_{HH} = 1.7$ Hz, CH), 6.97 (1H, d, $^3J_{HH} = 1.7$ Hz, CH), 5.62 (2H, s, CH_2), 5.34 (2H, s, CH_2). δ_F : -56.5 (3F, t, $^3J_{FF} = 21.5$ Hz, CF_3), -138.1 (2F, m, C_6F_4), -138.6 (2F, m, C_6F_4).

4.5 Preparation of (η^5 -pentamethylcyclopentadienyl)metal(κC -1-perfluoroarylmethyl-3-benzylimidazol-2-ylidene) dichloride complexes (**1a** - **2b**)

Complexes **1a**, **1b**, **2a** and **2b** were prepared as described for $[(\eta^5-C_5Me_5)RhCl_2(\kappa C-MeNC_3H_2NCH_2C_6F_5)]$ [21], and recrystallized from dichloromethane or dichloromethane and pentane. **1a** from $[(\eta^5-C_5Me_5)RhCl(\mu-Cl)]_2$ (0.097 g, 0.157 mmol) and $[(\kappa C-C_6H_5CH_2NC_3H_2NCH_2C_6F_5)AgBr]$ (0.165 g, 0.314 mmol). Yield: 0.191 g (94%). Anal. Calc. for $C_{27}H_{26}Cl_2F_5N_2Rh.(CH_2Cl_2)$: C, 45.9; H,

3.85; N, 3.8. Found: C, 45.7; H, 3.85; N, 3.8%. $[M - Cl]^+$: $[C_{27}H_{26}^{35}ClF_5N_2Rh]^+$ requires 611.0760; found: 611.0830. δ_H : 7.37 (5H, m, C_6H_5), 6.77 (1H, d, $^3J_{HH} = 2.0$ Hz, CH), 6.57 (1H, d, $^3J_{HH} = 2.0$ Hz, CH), 6.13 (2H, m, $NCHHC_6H_5$ and $NCHHC_6F_5$), 5.58 (1H, d, $^2J_{HH} = 15.8$ Hz, $NCHH$), 5.31 (1H, d, $^2J_{HH} = 14.8$ Hz, $NCHH$), 1.69 (15H, s, CH_3). δ_C : 172.3 (d, $^1J_{RhC} = 57$ Hz, $RhCN_2$), 145.8 (dm, $^1J_{CF} = 250$ Hz, C_6F_5), 141.8 (dm, $^1J_{CF} = 250$ Hz, C_6F_5), 137.8 (dm, $^1J_{CF} = 255$ Hz, C_6F_5), 136.3 (s, C_6H_5), 128.9 (s, C_6H_5), 128.5 (s, C_6H_5), 128.2 (s, C_6H_5), 123.0 (s, NCH), 120.7 (s, NCH), 109.5 (td, $^2J_{FC} = 16$ Hz, $^4J_{FC} = 4$ Hz, C_6F_5 ipso), 96.7 (d, $^1J_{RhC} = 7$ Hz, C_5), 55.3 (s, NCH_2), 44.2 (s, NCH_2), 9.5 (s, CH_3). δ_F : -140.7 (2F, m, F_{ortho}), -151.4 (1F, t, $^3J_{FF} = 21$ Hz, F_{para}), -159.9 (2F, m, F_{meta}).

1b: from $[(\eta^5-C_5Me_5)IrCl(\mu-Cl)]_2$ (0.108 g, 0.136 mmol) and $[(\kappa C-C_6H_5CH_2NC_3H_2NCH_2C_6F_5)AgBr]$ (0.143 g, 0.272 mmol). Yield: 0.172 g (86%). $[M - Cl]^+$: $[C_{27}H_{26}^{35}ClF_5^{193}IrN_2]^+$ requires 701.1407; found: 701.1355. δ_H : 7.35 (5H, m, C_6H_5), 6.70 (1H, d, $^3J_{HH} = 2.1$ Hz, CH), 6.50 (1H, d, $^3J_{HH} = 2.1$ Hz, CH), 6.08 (1H, d, $^2J_{HH} = 14.9$ Hz, $NCHH$), 6.04 (1H, d, $^2J_{HH} = 14.9$ Hz, $NCHH$), 5.55 (1H, d, $^2J_{HH} = 15.9$ Hz, $NCHH$), 5.25 (1H, d, $^2J_{HH} = 14.9$ Hz, $NCHH$), 1.69 (15H, s, CH_3). δ_C : 158.6 (s, $IrCN_2$), 145.8 (dm, $^1J_{CF} = 247$ Hz, C_6F_5), 141.7 (dm, $^1J_{CF} = 256$ Hz, C_6F_5), 137.8 (dm, $^1J_{CF} = 251$ Hz, C_6F_5), 136.4 (s, C_6H_5), 128.8 (s, C_6H_5), 128.4 (s, C_6H_5), 128.2 (s, C_6H_5), 122.1 (s, NCH), 119.9 (s, NCH), 110.0 (td, $^2J_{FC} = 17$ Hz, $^4J_{FC} = 4$ Hz, C_6F_5 ipso), 89.4 (s, C_5), 55.0 (s, NCH_2), 43.5 (s, NCH_2), 9.2 (s, CH_3). δ_F : -140.8 (2F, m, F_{ortho}), -151.5 (1F, t, $^3J_{FF} = 21$ Hz, F_{para}), -160.0 (2F, m, F_{meta}).

2a from $[(\eta^5-C_5Me_5)RhCl(\mu-Cl)]_2$ (0.086 g, 0.139 mmol) and $[(\kappa C-C_6H_5CH_2NC_3H_2NCH_2C_6F_4CF_3-4)AgBr]$ (0.161 g, 0.279 mmol). Yield: 0.183 g (94%). Anal. Calc. for $C_{28}H_{26}Cl_2F_7N_2Rh \cdot (CH_2Cl_2)$: C, 44.5; H, 3.6; N, 3.6. Found: C, 44.5; H, 3.6; N, 3.6%. $[M - Cl]^+$: $[C_{28}H_{26}^{35}ClF_7N_2Rh]^+$ requires 661.0728; found: 661.0843. δ_H : 7.37 (5H, m, C_6H_5), 6.81 (1H, d, $^3J_{HH} = 2.1$ Hz, CH), 6.63 (1H, d, $^3J_{HH} = 2.1$ Hz, CH), 6.16 (2H, m, $NCHHC_6H_5$ and $NCHHC_6F_5$), 5.73 (1H, m, $NCHH$), 5.33 (1H, m, $NCHH$), 1.68 (15H, s, CH_3). δ_C : 172.9 (d, $^1J_{RhC} = 57$ Hz, $RhCN_2$), 145.6 (dm, $^1J_{CF} = 241$ Hz, C_6F_4), 144.2 (dm, $^1J_{CF} = 267$ Hz, C_6F_4), 136.2 (s, C_6H_5), 128.9 (s, C_6H_5), 128.4 (s, C_6H_5), 128.3 (s, C_6H_5), 123.3 (s, NCH), 121.0 (s, NCH), 120.5 (q, $^1J_{CF} = 275$ Hz, CF_3), 119.2 (t, $^2J_{CF} = 16$ Hz, C_6F_4 ipso), 110.9 (m, CCF_3), 96.8 (d, $^1J_{RhC} = 7$ Hz, C_5), 55.3 (s, NCH_2), 44.9 (s, NCH_2), 9.5 (CH_3). δ_F : -56.4 (3F, t, $^4J_{FF} = 21$ Hz, CF_3), -138.7 (2F, m, C_6F_4), -139.1 (2F, m, C_6F_4).

2b from $[(\eta^5\text{-C}_5\text{Me}_5)\text{IrCl}(\mu\text{-Cl})]_2$ (0.108 g, 0.136 mmol) and $[(\kappa\text{-C}_6\text{H}_5\text{CH}_2\text{NC}_3\text{H}_2\text{NCH}_2\text{C}_6\text{F}_4\text{CF}_3\text{-4})\text{AgBr}]$ (0.143 g, 0.272 mmol). Yield: 0.172 g (86%). $[\text{M} - \text{Cl}]^+$: $[\text{C}_{28}\text{H}_{26}^{35}\text{ClF}_7^{193}\text{IrN}_2]^+$ requires 751.1375; found: 751.1323. δ_{H} 7.35 (5H, m, C_6H_5), 6.72 (1H, d, $^3J_{\text{HH}} = 2.1$ Hz, CH), 6.57 (1H, d, $^3J_{\text{HH}} = 2.1$ Hz, CH), 6.15 (1H, d, $^2J_{\text{HH}} = 15.8$ Hz, NCHH), 6.05 (1H, d, $^2J_{\text{HH}} = 14.9$ Hz, NCHH), 5.66 (1H, d, $^2J_{\text{HH}} = 15.8$ Hz, NCHH), 5.25 (1H, d, $^2J_{\text{HH}} = 14.9$ Hz, NCHH), 1.69 (15H, s, CH_3). δ_{C} : 159.2 (s, IrCN_2), 145.6 (dm, $^1J_{\text{CF}} = 239$ Hz, C_6F_4), 144.1 (dm, $^1J_{\text{CF}} = 267$ Hz, C_6F_4), 136.3 (s, C_6H_5), 128.9 (s, C_6H_5), 128.4 (s, C_6H_5), 128.2 (s, C_6H_5), 122.5 (s, NCH), 120.2 (s, NCH), 120.5 (q, $^1J_{\text{CF}} = 275$ Hz, CF_3), 119.3 (t, $^2J_{\text{CF}} = 16$ Hz, $\text{C}_6\text{F}_4_{\text{ipso}}$), 110.6 (m, CCF_3), 89.5 (s, C_5), 55.0 (s, NCH_2), 44.1 (s, NCH_2), 9.2 (CH_3). δ_{F} : -56.4 (3F, t, $^4J_{\text{FF}} = 21$ Hz, CF_3), -138.8 (2F, m, C_6F_4), -139.2 (2F, m, C_6F_4).

4.6 X-ray crystallography

Crystals of **1a**, **1b**, **2a** and **2b** were obtained from dichloromethane. Diffraction data were collected on an Agilent SuperNova, single source at offset, Atlas diffractometer with graphite-monochromated Cu— K_{α} radiation. The structures were solved using Olex2 [22] with olex2.solve [23] structure solution programme using Charge Flipping and refined with the olex2.refine [23] refinement package using Gauss-Newton minimization. All non-hydrogen atoms were refined with anisotropic thermal parameters, except for C(1) - C(5), C(7) - C(10), C(13), C(15), C(16), C(18), C(21), C(23), C(24), N(1) and F(23) of **2b**. Hydrogen atom positions were added in idealized positions and a riding model with fixed thermal parameters ($U_{ij} = 1.2U_{eq}$ for the atom to which they are bonded (1.5 for CH_3)) was used for subsequent refinements. The function minimized was $\Sigma[w(|F_o|^2 - |F_c|^2)]$ with reflection weights $w^{-1} = [\sigma^2 |F_o|^2 + (g1P)^2 + (g2P)]$ where $P = [\max |F_o|^2 + 2|F_c|^2]/3$.

CCDC 1874162 (**1a**), 1874163 (**1b**), 1874164 (**2a**) and 1874165 (**2b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

4.6 Density functional theory calculations

DFT calculations were performed using Gaussian09 [24] with the long-range corrected functional ω B97X-D [14] method and the 6-311G++(2d,2p) basis set, except for the rhodium atom, for which LANL2DZ [25] was used. Harmonic vibrational frequencies were calculated to confirm that the optimized structures were indeed minima. The energies of interaction were calculated as the difference between the energy of the species and the sum of those of its components. All the C–H bond distances were adjusted to 1.083 Å [26] prior to single point energy calculations being undertaken.

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Table 1

Crystallographic data for (η^5 -pentamethylcyclopentadienyl)metal(κ C-1-perfluoroarylmethyl-3-benzylimidazol-2-ylidene) dichloride complexes **1a**, **1b**, **2a** and **2b**.^a

	1a	1b	2a	2b
Formula	C ₂₇ H ₂₆ Cl ₂ F ₅ N ₂ Rh.CH ₂ Cl ₂	C ₂₇ H ₂₆ Cl ₂ F ₅ N ₂ Ir.CH ₂ Cl ₂	C ₂₈ H ₂₆ Cl ₂ F ₇ N ₂ Rh.CH ₂ Cl ₂	C ₂₈ H ₂₆ Cl ₂ F ₇ N ₂ Ir.CH ₂ Cl ₂
Formula weight	732.26	821.57	782.26	871.57
Crystal system	orthorhombic	orthorhombic	orthorhombic	orthorhombic
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> ca2 ₁	<i>P</i> ca2 ₁
<i>a</i> , Å	10.60874(18)	10.6467(2)	16.3955(4)	16.3938(3)
<i>b</i> , Å	15.6614(2)	15.6791(3)	10.75786(16)	10.7913(3)
<i>c</i> , Å	17.5915(3)	17.5997(4)	17.3761(4)	17.3948(4)
<i>V</i> , Å ³	2922.78(8)	2937.94(10)	3064.8(1)	3077.31(12)
<i>Z</i>	4	4	4	4
<i>D</i> _c (g cm ⁻³)	1.664	1.8573	1.695	1.8811
Crystal size (mm ³)	0.142 × 0.088 × 0.060	0.189 × 0.082 × 0.029	0.109 × 0.052 × 0.031	0.317 × 0.063 × 0.044
μ (mm ⁻¹)	8.571	12.625	8.316	12.195

θ range (°)	3.78 – 73.88	3.78 – 74.02	4.11 – 74.00	4.10 – 73.81
Total reflections	15608	8718	15692	9352
Unique reflections (R_{int})	5775 (0.0394)	4916 (0.0299)	5580 (0.0483)	4933 (0.0318)
Observed reflections [$I > 2\sigma(I)$]	5264	4430	4845	4562
Parameters	366	361	393	303
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0334$, $wR_2 = 0.0746$	$R_1 = 0.0305$, $wR_2 = 0.0367$	$R_1 = 0.0466$, $wR_2 = 0.1196$	$R_1 = 0.0482$, $wR_2 = 0.1453$
R indices (all data)	$R_1 = 0.0464$, $wR_2 = 0.0792$	$R_1 = 0.0735$, $wR_2 = 0.0771$	$R_1 = 0.0564$, $wR_2 = 0.1268$	$R_1 = 0.0547$, $wR_2 = 0.1510$
Weighting scheme	$w = 1/[\sigma^2(F_o)^2 + \{0.0370(F_o^2 + 2F_c^2)/3\}^2 + 3.6990(F_o^2 + 2F_c^2)/3]$	$w = 1/[\sigma^2(F_o)^2 + \{0.0400(F_o^2 + 2F_c^2)/3\}^2]$	$w = 1/[\sigma^2(F_o)^2 + \{0.0860(F_o^2 + 2F_c^2)/3\}^2]$	$w = 1/[\sigma^2(F_o)^2 + 162.8190(F_o^2 + 2F_c^2)/3]$
Max., min. $\Delta\rho$ (eÅ ⁻³)	1.182, -1.201	1.079, -1.246	1.573, -0.640	2.739, -1.541
Goodness of fit on F^2	1.049	1.0326	1.025	1.038
Flack parameter	-0.022(8)	-0.005(11)	0.007(12)	-0.04(2)

^a Estimated standard deviations are given in parentheses.

Table 2 Selected distances (Å) and angles (°) for (η^5 -pentamethylcyclopentadienyl)metal(κ C-1-perfluoroarylmethyl-3-benzylimidazol-2-ylidene) dichloride complexes **1a**, **1b**, **2a** and **2b**.^a

	1a		1b	2a		2b
	Experimental	Calculated ^b	Experimental	Experimental	Calculated ^b	Experimental
Cp*—M	1.805(4)	1.822	1.802(7)	1.809(7)	1.821	1.82(2)
M—Cl(1)	2.4715(9)	2.444	2.4152(14)	2.4716(14)	2.446	2.474(3)
M—Cl(2)	2.4023(9)	2.423	2.4786(13)	2.4009(14)	2.421	2.410(3)
M—C(11)	2.069(4)	2.050	2.056(6)	2.061(5)	2.050	2.075(12)
C(11)—N(1)	1.361(5)	1.354	1.363(7)	1.355(9)	1.355	1.36(2)
N(1)—C(21)	1.464(5)	1.449	1.453(8)	1.483(10)	1.445	1.471(19)
C(21)—C(22)	1.513(5)	1.508	1.511(8)	1.515(9)	1.508	1.51(2)
C(11)—N(2)	1.354(5)	1.351	1.351(8)	1.359(9)	1.350	1.35(2)
N(2)—C(14)	1.464(5)	1.462	1.483(8)	1.484(9)	1.463	1.476(19)
C(14)—C(15)	1.507(6)	1.507	1.488(10)	1.529(9)	1.507	1.48(2)
Cl(1)···C(21)	3.232(5)	3.230	3.227(6)	3.373(7)	3.217	3.37(2)
Cl(2)···C(14)	3.283(5)	3.308	3.287(7)	3.310(7)	3.302	3.34(1)

Cp*—M—Cl(1)	119.6(1)	121.9	120.3(2)	120.7(2)	121.8	121.7(4)
Cp*—M—Cl(2)	124.5(1)	123.0	125.5(2)	124.4(2)	123.5	125.1(4)
Cp*—M—C(11)	128.5(2)	126.0	128.9(3)	124.7(2)	126.0	125.1(6)
Cl(1)—M—Cl(2)	88.77(3)	89.67	86.68(5)	88.85(5)	89.39	86.6 (1)
C(11)—M—Cl(1)	95.2(1)	93.8	94.4(2)	97.0(2)	93.7	96.6(5)
C(11)—M—Cl(2)	89.9(1)	93.0	89.6(2)	92.33(17)	92.9	91.8(5)
M—C(11)—N(1)	126.5(3)	126.9	127.3(5)	127.9(5)	126.5	127(1)
M—C(11)—N(2)	128.9(3)	128.4	128.6(4)	125.9(5)	128.8	126(1)
N(1)—C(11)—N(2)	104.5(3)	104.1	104.1(5)	103.2(5)	104.1	104(1)
C(11)—N(1)—C(21)	124.3(3)	126.4	124.1(5)	126.6(6)	126.3	127(1)
N(1)—C(21)—C(22)	112.6(3)	113.3	112.5(5)	108.5(5)	114.4	110(1)
C(11)—N(2)—C(14)	127.2(3)	127.3	127.9(5)	127.6(5)	127.3	129(1)
N(2)—C(14)—C(15)	112.3(3)	111.5	112.7(6)	109.4(5)	111.2	111(1)
Cp*—M—C(11)—N(1)	88.4(4)	84.8	88.9(8)	-82.1(7)	84.2	84(2)
Cp*—M—C(11)—N(2)	-89.3(4)	-84.5	-90.0(7)	74.8(6)	-85.3	-76(2)

M—C(11)—N(1)—C(21)	3.3(5)	10.0	-2.7(9)	-24.3(9)	10.8	23(2)
M—C(11)—N(2)—C(14)	5.0(5)	-8.0	5.4(9)	29.2(9)	-8.8	-28(2)
C(11)—N(1)—C(21)—C(22)	-166.8(3)	120.2	-163.8(6)	-128.5(7)	111.3	130(2)
C(11)—N(2)—C(14)—C(15)	-131.4(4)	-126.3	-132.0(7)	108.1(7)	-126.1	-109(2)
N(1)—C(21)—C(22)—C(23)	-90.3(4)	-38.5	-90.8(7)	63.4(8)	-29.0	-61(2)
N(1)—C(21)—C(22)—C(27)	90.4(5)	144.7	90.3(8)	-114.3(7)	155.1	114(2)
N(2)—C(14)—C(15)—C(16)	45.1(5)	60.5	43.6(9)	-60.2(8)	60.5	60(2)
N(2)—C(14)—C(15)—C(20)	-138.5(4)	-119.8	-139.8(6)	119.1(7)	-119.2	-119(2)
$\angle$ C ₃ N ₂ (plane) M—C(11)	0.2(2)	6.6	1.0(4)	15(1)	6.3	14(1)
$\angle$ C ₃ N ₂ (plane) C ₆ F ₄ (plane)	82.7(7)	79.0	82(3)	80(1)	81.8	79(2)
$\angle$ C ₃ N ₂ (plane) C ₆ H ₅ (plane)	81.9(8)	88.8	81(1)	86(1)	87.3	85(2)
$\angle$ C ₆ F ₄ (plane) C ₆ H ₅ (plane)	71.9(6)	56.3	71(1)	86.3(7)	46.8	87(1)

^a Estimated standard deviations are given in parentheses. Cp* indicates the centroid of the five carbon atoms of the cyclopentadienyl ring. ^b Calculated using the ω B97X-D [14] method with the 6-311G++(2d,2p) basis set, except for the rhodium atom, for which LANL2DZ [25] was used.

Table 3 Selected intermolecular distances (Å) and angles (°) between dichloromethane and (η^5 -pentamethylcyclopentadienyl)metal(κ C-1-perfluoroarylmethyl-3-benzylimidazol-2-ylidene) dichloride complexes **1a**, **1b**, **2a** and **2b**.^a

	1a	1b	2a	2b		1a	1b	2a	2b
Cl(1)···C(1S)	3.400(4)	3.422(7)	3.584(8)	3.56(2)	Cl(2)···C(1S)	3.582(4)	3.596(7)	3.472(8)	3.46(2)
Cl(1)···C(1S)—Cl(1S)	106.7(2)	106.6(3)	123.0(4)	121.4(9)	Cl(1)···C(1S)—Cl(2S)	133.4(2)	132.2(3)	107.1(4)	109.1(8)
Cl(2)···C(1S)—Cl(1S)	109.4(2)	108.9(3)	104.2(4)	102.9(8)	Cl(2)···C(1S)—Cl(2S)	84.4(2)	83.9(3)	144.4(4)	147(1)
$\angle$ MCl ₂ (plane) Cl(1)Cl(2)C1(1S)(plane)	42.3(2)	42.0(4)	18.5(7)	16.8(4)	$\angle$ Cl ₂ C(1S)(plane) Cl(1S) Cl(2S)C(1S)(plane)	71.0(7)	71.4(4)	62.1(6)	62.7(4)
x = 2 for 1 , 1 for 2									
C(1)···Cl(xS) (1S for 2)	3.603(4)	3.583(8)	3.927(7)	3.93(2)	C(2)···Cl(xS)	3.294(3)	3.280(7)	3.434(7)	3.44(2)
C(3)···Cl(xS)	3.564(4)	3.561(8)	3.391(7)	3.41(2)	Cp*···Cl(xS)	3.516(5)	3.499(8)	3.599(7)	3.61(1)
Cp(plane)···Cl(xS)	3.278(5)	3.270(8)	3.291(7)	3.32(1)	M—Cp*···Cl(xS)	157.7(2)	158.0(3)	156.0(3)	155.5(3)
Cp*···Cl(xS)—C(1S)	134.9(5)	134.0(3)	148.7(3)	148.3(3)	M—Cp*···Cl(xS)—C(1S)	24.4(4)	23.1(6)	79(1)	-80(1)

^a Estimated standard deviations are given in parentheses. Cp* indicates the centroid of the five carbon atoms of the cyclopentadienyl ring.

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Table 4 Selected intermolecular distances (Å) and angles (°) between molecules of (η^5 -pentamethylcyclopentadienyl)metal(κ C-1-perfluoroarylmethyl-3-benzylimidazol-2-ylidene) dichloride complexes **1a**, **1b**, **2a** and **2b**.^a

	1a	1b		2a	2b
Cl(1)···C(13)'	3.627(5)	3.643(6)	Cl(1)···C(12)'	3.786(7)	3.80(1)
M—Cl(1)···C(13)'	111.34(7)	112.5(1)	M—Cl(1)···C(12)'	90.8(1)	91.3(2)
Cl(1)···C(13)'—N(2)'	159.2(3)	160.3(4)	Cl(1)···C(12)'—N(1)'	132.8(4)	133(1)
Cl(1)···C(13)'—C(12)'	92.7(3)	92.3(4)	Cl(1)···C(12)'—C(13)'	121.7(5)	120(1)
Cl(2)···C(12)'	3.571(4)	3.590(7)	Cl(2)···C(13)'	3.317(7)	3.32(2)
M—Cl(2)···C(12)'	105.03(7)	105.6(1)	M—Cl(2)···C(13)'	110.2(1)	110.3(3)
Cl(2)···C(12)'—N(1)'	132.9(3)	132.4(4)	Cl(2)···C(13)'—N(2)'	154.3(4)	154(1)
Cl(2)···C(12)'—C(13)'	121.3(1)	120.7(4)	Cl(2)···C(13)'—C(12)'	88.5(4)	88(1)
Cl(2)···C(23)'	3.375(4)	3.374(7)	Cl(1)···C(26)'	3.785(8)	3.80(2)
Cl(2)···C(24)'	3.128(4)	3.122(7)	Cl(1)···C(27)'	3.699(7)	3.72(2)
Cl(2)···C ₆ F'*	3.375(5)	3.383(8)	Cl(1)···C ₆ F'*	4.211(8)	4.23(2)
M—Cl(2)···C ₆ F'*	163.5(3)	163(1)	M—Cl(1)···C ₆ F'*	121.4(1)	121.0(3)

$\angle \text{MCl}_2(\text{plane}) \text{Cl}_2\text{C}_2(\text{plane})$	41.0(1)	41.6(1)	$\angle \text{MCl}_2(\text{plane}) \text{Cl}_2\text{C}_2(\text{plane})$	53.7(1)	54.9(3)
$\angle \text{Cl}_2\text{C}_2(\text{plane}) \text{C}_3\text{N}_2'(\text{plane})$	3.9(3)	3.9(4)	$\angle \text{Cl}_2\text{C}_2(\text{plane}) \text{C}_3\text{N}_2'(\text{plane})$	22.0(4)	23(1)
			$\text{C}_6^* \cdots \text{C}_6\text{F}'^*$	3.95(1)	3.93(3)
			$\text{C}_6^* \cdots \text{C}_6\text{F}'(\text{plane})$	3.39(1)	3.38(3)
			$\text{C}_6(\text{plane}) \cdots \text{C}_6\text{F}'^*$	3.79(1)	3.76(3)
			$\angle \text{C}_6(\text{plane}) \text{C}_6\text{F}'(\text{plane})$	16.6(5)	16(1)
			$\text{Cl}(2) \cdots \text{C}_6\text{F}'^*$	4.024(7)	4.06(2)
			$\text{Cl}(2) \cdots \text{C}(26)'$	3.351(7)	3.37(2)
			$\text{Cl}(2) \cdots \text{C}(27)'$	3.510(7)	3.53(2)

^a Estimated standard deviations are given in parentheses. C_6 and $\text{C}_6\text{F}'$ represent the phenyl and polyfluorophenyl rings respectively. $\text{C}_6\text{F}'^*$ indicates the centroid of the six carbon atoms of the trifluoromethyltetrafluorophenyl ring.