Iridium derivatives of fluorinated aromatics by C–H activation: isolation of classical and non-classical hydrides[†]‡

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A reaction of *trans*-[Ir(H)₅(PiPr₃)₂] (1) with 2,3,5,6-tetrafluoropyridine, pentafluorobenzene or 1,3-difluorobenzene in the presence of neohexene affords the square-pyramidal C–H activation products *cis–trans*-[Ir(4-C₅NF₄)(H)₂(PiPr₃)₂] (2), *cis–trans*-[Ir(C₆F₅)(H)₂(PiPr₃)₂] (4) and *cis–trans*-[Ir(2-C₆H₃F₂)(H)₂(PiPr₃)₂] (6). Irradiation of complex 1 with 2,3,5,6-tetrafluoropyridine or pentafluorobenzene gave the hydrides *cis–trans*-[Ir(4-C₅NF₄)(H)₂(H₂)(PiPr₃)₂] (3) or *cis–trans*-[Ir(C₆F₅)(H)₂(H₂)(PiPr₃)₂] (5). The presence of non-classical bound H₂ moieties has been demonstrated by the measurement of T_1 times at different temperatures. For 3 the H–H distance in the H₂ ligand can be estimated to be 0.82 Å. The dihydride compounds 2, 4 and 6 react with CO to yield the complexes *cis–trans*-[Ir(Ar)(H)₂(CO)(PiPr₃)₂] (7: Ar = 4-C₅NF₄, 8: Ar = C₆F₅, 9: Ar = 2-C₆H₃F₂). A reaction of 2 or 3 with an excess of ethylene leads to the formation of ethane and the Ir(1) ethylene complex *trans*-[Ir(4-C₅NF₄)(CO)(PiPr₃)₂] (10). Treatment of 10 with CO furnishes the Ir(1) complex *trans*-[Ir(4-C₅NF₄)(CO)(PiPr₃)₂] (11).

Introduction

The C-F activation of fluoroaromatic compounds has proven to be a useful tool to access their metal derivatives.1 One critical issue of these reactions is their chemoselectivity. Very often the activation of a C-H bond is preferred to C-F bond activation.¹⁻³ Theoretical investigations on the oxidative addition of 1,2-difluorobenzene at a cyclopentadienyl rhodium system suggest that the activation of a C-F bond is energetically favourable, but a high kinetic barrier leads to a preference for C-H activation.⁴ In contrast $[Rh(\eta^5 C_5Me_5$)(H)₂(PMe₃)] reacts with C_6F_6 , C_6F_5H , in pyridine-benzene to give the C-F cleavage products.5 Kinetic studies reveal that the reactions have autocatalytic character, and fluoride anions are responsible for the catalysis. They act by deprotonating the rhodium dihydride, allowing nucleophilic attack of an anionic rhodium complex at the fluorinated substrate. The iridium or rhodium catalyzed borylation of pentafluorobenzene gave also products of C-H activation, whereas a borylation of tetrafluoropyridines at rhodium resulted in derivatives produced by C-H or C-F activation.⁶ Ozerov et al. reported that at iridium complexes bearing anionic pincer ligands, C-Hal (Hal = Cl, Br) oxidative addition of PhHal is thermodynamically preferred, but the C-H activation products are kinetically accessible.⁷ No products arising from the oxidative addition of the carbonfluorine bond in fluorobenzene were observed. C-H activation reactions of fluorobenzene and diffuorobenzenes at $\{IrCl(PiPr_3)_2\}$ are in accordance with that observation.8

provide new routes to fluorinated building blocks and fluorinated organics.9,10 On the other hand, the intrinsic strength and kinetic inertness of the metal-carbon bond to a fluorinated anionic ligand can be employed to stabilize organometallic compounds, and sometimes allows the identification and isolation of otherwise unstable complexes.¹¹ We were able to show that 2,3,5,6-tetrafluoropyridine can be activated at [RhH(PEt₃)₃] to give the Rh(I) pyridyl complex [Rh(4-C5NF4)(PEt3)3].¹² Further investigations on its reactivity revealed that the rhodium tetrafluoropyridyl ligand can be applied as building block for C-C coupling reactions in the coordination sphere of the metal.12 However, the tetrafluoropyridyl moiety also has a stabilizing influence on reaction intermediates. This led to the isolation of surprisingly stable rhodium(III) η^1 -hydroperoxo and η^1 -silylperoxo compounds, which are intermediates in the formation of hydrogen peroxide or silvl peroxides from an η^2 -peroxo complex and the corresponding electrophilic sources.13 In this paper we report on the synthesis of iridium tetrafluoropyridyl and fluoroaryl complexes by thermal or photochemical C-H activation of 2,3,5,6-tetrafluoropyridine, pentafluorobenzene

Oxidative addition reactions of fluorinated pyridines and pyrim-

idines at nickel exhibit a strong preference for C-F activation.9

Subsequent derivatization reactions at the metal center can

C-H activation of 2,3,5,6-tetrafluoropyridine, pentafluorobenzene or 1,3-difluorobenzene at *trans*- $[Ir(H)_5(PiPr_3)_2]$ (1). The investigations led to the isolation of classical and fairly stable non-classical hydrogen complexes. The isolation of a stable Ir(1) ethylene complex bearing a tetrafluoropyridyl ligand is also reported.

Results

C-H activation of fluorinated aromatics

A reaction of *trans*- $[Ir(H)_5(PiPr_3)_2]$ (1) with 2,3,5,6-tetrafluoropyridine at reflux conditions (*n*-hexane) affords the C–H activation products *cis*-*trans*- $[Ir(4-C_5NF_4)(H)_2(PiPr_3)_2]$ (2) and

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cis–trans-[Ir(4-C₅NF₄)(H)₂(H₂)(P*i*Pr₃)₂] (**3**) in a ratio of approximately 3:1 after 6 h. Prolonged heating of a hexane solution of **2** and **3** for further 12 h leads to the formation of a pure sample of **2**. Complex **2** can also be produced by a reaction of **1** with the fluorinated pyridine in the presence of neohexene (Scheme 1). However, irradiation of complex **1** with 2,3,5,6-tetrafluoropyridine in benzene or hexane generates the tetrahydride **3** (Scheme 1). Compound **3** is fairly stable in solution under argon. It can be converted into **2** by repeatedly bringing solutions of **3** to dryness. On treatment of **2** with dihydrogen the reverse reaction takes place.



Scheme 1 C-H activation reactions of fluorinated arenes at 1.

In a comparable manner as described above the complexes *cis-trans*-[Ir(C₆F₅)(H)₂(PiPr₃)₂] (4) and *cis-trans*-[Ir(C₆F₅)-(H)₂(H₂)(PiPr₃)₂] (5) are accessible (Scheme 1). Compound 5 is less stable than 3 and can be detected in solution, only. Evaporation of a hexane solution of 5 leads to the formation of 4. Treatment of 4 with H₂ gives pentafluorobenzene, 1 and 5. A reaction of 1 with 1,3-difluorobenzene furnishes selectively the dihydride complex *cis-trans*-[Ir(2-C₆H₃F₂)(H)₂(PiPr₃)₂] (6) and no generation of a tetrahydride has been observed. As a matter of fact, 6 reacts with H₂ to yield 1 and 1,3-difluorobenzene. Note that the C–H activation reaction occurs at the 2-position of the aromatic ring, whereas {IrCl(PiPr₃)₂} leads to activation products with the metal at the 4-position.⁸ Photochemical activation of 1,3-difluorbenzene with [CpRh(PPh₃)(C₂H₄)] gives the C–H activation product with the metal at the 2-position.³

The ³¹P{¹H} NMR spectrum of **2** displays a singlet at δ 52.0 for the phosphines in the mutually trans position. The ¹⁹F NMR spectrum depicts two resonances for the tetrafluoropyridyl ligand. The integration of the signals for the isopropyl groups and a resonance at δ –28.09 in the ¹H NMR spectrum suggests the presence of two hydrido ligands, compatible with either equivalent hydrides or a fluxional structure. The fluorine decoupled spectrum of 2 reveals a proton-phosphorus coupling of 15 Hz (Fig. 1). Low temperature ¹H NMR spectra did not lead to decoalescence. The longitudinal T_1 spin lattice relaxation times for the hydrides in 2 were determined by ¹H NMR spectroscopy between 193 K and 263 K. All data indicate the presence of classical hydrido ligands.¹⁴ The T_1 at 233 K is 300 ms at 600 MHz. Comparable data have been obtained for the dihydrides 4 and 6. At 223 K values of 420 ms and 440 ms have been found, respectively. For 2, 4 and 6 we favor a square-pyramidal geometry with a *cis*-hydrido configuration. This assumption is reasonable, because such a configuration in



Fig. 1 Part of the ¹H NMR spectrum (top, 600.1 MHz), ¹H 31 PNMR spectrum (middle) and ¹H 19 FNMR spectrum (bottom) of **2**.

solution is consistent with the molecular structure in the solid state, the IR spectra and the DFT calculations (*vide infra*). The hydrides are characterized by a very rapid exchange on the NMR time scale. The IR spectrum of **2** exhibits an absorption band at 1935 cm⁻¹ in solution and in the solid state which can be assigned to a pure Ir–H vibration involving the hydride in the *trans* position to the pyridyl ligand. DFT calculations reveal two well separated absorption bands for Ir–H stretchings at 1939 cm⁻¹ and 2410 cm⁻¹ (very weak). Note that the trigonal-bipyramidal complex *trans*-[Ir(Cl)(H)₂(PiPr₃)₂] exhibits an M–H stretch at 2249 cm⁻¹.¹⁵ Our calculations of *trans*-[Ir(Cl)(H)₂(PiPr₃)₂] reveal bands at 2247 cm⁻¹ and 2285 cm⁻¹, which correspond to an asymmetric and symmetric vibration of the IrH₂ unit.

The molecular structure of 2 was also confirmed by X-ray diffraction analysis at 100 K (Fig. 2). Suitable crystals have been obtained from a hexane solution at 243 K. Selected bond lengths and angles are summarised in Table 1. The molecular structure reveals a square pyramidal configuration with the expected *trans* disposition of the phosphine ligands. The hydrides at iridium have been located and found to be in a *cis* position, one of them at the apical vertex of the square pyramid. The separation between H(19)



Fig. 2 An ORTEP diagram of 2. Ellipsoids are drawn at the 50% probability level.

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Ir(1)–C(19)	2.144(4)	C(19)–C(20)	1.404(5)
Ir(1)–H(19)	1.55(2)	C(20) - C(21)	1.382(5)
Ir(1)–H(20)	1.56(2)	C(22) - C(23)	1.390(5)
Ir(1)-P(1)	2.3209(9)	F(1) - C(20)	1.374(4)
Ir(1) - P(2)	2.3303(9)	F(2)–C(21)	1.352(4)
N(1)-C(21)	1.327(5)	F(3)–C(22)	1.357(4)
N(1)-C(22)	1.316(5)	F(4)–C(23)	1.378(4)
C(19)–C(23)	1.396(5)		
P(1)-Ir(1)-P(2)	167.37(4)	P(2)–Ir(1)–H(20)	83(2)
C(19) - Ir(1) - P(1)	96.21(9)	C(22) - N(1) - C(21)	115.1(3)
C(19)-Ir(1)-P(2)	96.41(9)	N(1)-C(21)-C(20)	124.0(4)
H(19)–Ir(1)–H(20)	87(2)	N(1)-C(22)-C(21)	124.0(4)
P(1)-Ir(1)-H(19)	85(1)	C(23)-C(19)-C(20)	110.7(3)
P(2)–Ir(1)–H(19)	93(1)	C(23)-C(19)-Ir(1)	122.4(3)
C(19)-Ir(1)-H(20)	176(2)	C(20)-C(19)-Ir(1)	126.8(3)
P(1)–Ir(1)–H(20)	85(2)	C(21)-C(20)-C(19)	123.0(4)
C(19)–Ir(1)–H(19)	97(2)	C(22)–C(23)–C(19)	123.2(4)

Table 1 Selected bond lengths (Å) and angles (°) in *cis–trans*-[Ir(4- C_5NF_4)(H)₂(PiPr₃)₂] (2) with estimated standard deviations in parentheses

and H(20) is 2.144 Å. The dihedral angle between the plane defined by the pyridyl ring and the coordination plane of the metal defined by Ir1, C19, P1 and P2 is 73.8°. The iridium–carbon distance is 2.144(4) Å. For comparison, the Ir–C separation of 2.010(5) Å in the complex *trans*-[Ir(Cl)(H)(Ph)(PiPr₃)₂], which exhibits a distorted trigonal-bipyramidal structure, is in a similar range.¹⁶

Complex 3 was characterized by its spectroscopic data. The ¹H NMR spectrum displays a broad signal at δ –9.36, which can be assigned to the metal bound hydrogen nuclei. The signal stays broad even at 193 K (600 MHz) indicating a very low barrier for hydrogen exchange. Comparable observations have been made for the hydrides cis-trans-[Ir(X)(H)₂(H₂)(PiPr₃)₂] (X = Cl, Br, I).¹⁵ Measurement of the T_1 times for **3** at different temperatures Θ reveal a minimum at 233 K with a $T_1 = 39$ ms (600 MHz). This demonstrates the presence of dihydrogen bound in a non-classical mode.¹⁴ However, the plot $\ln T_1$ vs. $1/\Theta$ does not follow the typical V-shaped curve as a result of exchange between classical and non-classical hydride sites (Fig. 3).¹⁴ Comparable data have been obtained for the tetrahydride 5 ($T_1 = 20 \text{ ms at } 233 \text{K} \text{ (600 MHz)}$). Another indication for the presence of classical and non-classical moieties in 3 is given by the downfield isotope shifts of the signals in the ¹H NMR spectrum of the d₁, d₂ and d₃ isotopologues of



Fig. 3 Plot of $\ln T_1$ vs. $1/\Theta$ for complex 3.

3 on partial deuteration of the hydride sites (δ –9.23, –8.96 and –8.81). This could be explained by a non-statistical site-preference of the deuterium consistent with a perturbation of the equilibrium between the different hydride sites rather than a simple isotope effect.¹⁷ Solid state ATR IR spectra of **3** exhibit absorption bands at 2046 and 2192 cm⁻¹, which we assign to vibration modes of the iridium hydrides, which are bound in a classical mode. For the isotopologue *cis*–*trans*-[Ir(4-C₅NF₄)(D)₂(D₂)(PiPr₃)₂] (**3b**) these bands disappear. DFT calculations of **3** give bands at 1990 cm⁻¹ and 2275 cm⁻¹ which can be assigned to pure Ir–H stretchings. They correspond to the Ir–H bonds in the *trans* position to the pyridyl unit and in the *trans* position to the η^2 -H₂ ligand, respectively.

The geometries of **2** and **3** were further examined by density functional theory {RI-DFT, BP86, SV(P)}. The optimized structures are shown in Fig. 4. The calculations reproduce correctly the geometries and bonding modes which have been proposed for **2** and **3** on the basis of the analytical data. The calculated bond lengths and angles of **2** compare reasonable well with those determined by the X-Ray diffraction analysis. A trigonalbipyramidal geometry for **2** seems not to be a minimum structure. In contrast, the optimized structure of the chloro complex *trans*-[Ir(Cl)(H)₂(PiPr₃)₂] reveals a trigonal-bipyramidal geometry



Fig. 4 BP86/SV(P) optimized structure of cis-trans-[Ir(4-C₃NF₄)(H)₂(PiPr₃)₂] (2) and cis-trans-[Ir(4-C₃NF₄)(H)₂(PiPr₃)₂] (3).

(Fig. 5). This result is in good agreement to the calculations of *trans*-[Ir(Cl)(H)₂(PH₃)₂] and *trans*-[Ir(Cl)(H)₂(PMe₃)₂] as well as to results from neutron diffraction experiments for *trans*-[Ir(Cl)(H)₂(P*t*Bu₂Ph)₂], which also reveal trigonal-bipyramidal structures.¹⁸



Fig. 5 BP86/SV(P) optimized structure of cis-trans-[Ir(Cl)(H)₂(PiPr₃)₂].

Reactivity of the dihydride complexes 2, 4 and 6

The dihydride compounds **2**, **4** and **6** react with CO to afford the complexes *cis-trans*-[Ir(Ar)(H)₂(CO)(PiPr₃)₂] (7: Ar = 4-C₅NF₄, **8**: Ar = C₆F₅, **9**: Ar = 2-C₆H₃F₂) within seconds (Scheme 2). The ³¹P{¹H} NMR spectrum of 7 reveals a singlet at δ 30.6, which can be assigned to the *trans* phosphines. The presence of four signals in the ¹⁹F NMR spectrum indicates a hindered rotation of the tetrafluoropyridyl ligand about the Ir–C bond.¹³ The ¹H NMR spectrum shows two signals for the hydrides at the iridium center, confirming a *cis* configuration of the hydride nuclei. The



Scheme 2 Reactivity of dihydride complexes 2, 4 and 6 towards ethylene and CO.

IR spectrum of 7 exhibits two absorption bands at 2161 and 2079 cm⁻¹ for the hydride vibrations, as well as an absorption band at 1979 cm⁻¹ which can be assigned to the CO–ligand.^{8,19} We note that Werner *et al.* reported similar IR data for the complex *cis–trans-*[Ir(Cl)(H)₂(CO)(P*i*Pr₃)₂] (2205, 2100, 1965 cm⁻¹).⁸ The spectroscopic data for **8** and **9** are comparable to these found for **7**.

The structures of the octahedral complexes 7 and 9 were determined by X-ray diffraction at 100 K (Fig. 6 and 7). Selected bond lengths and angles are summarised in Table 2 (7) and Table 3 (9). The structure found for 9 confirms the configuration which has been suggested for 9 as well as for 6, with the iridium in the *ortho* position to the fluorines at the arene ligand. Neither the iridium–carbon distance in 7 to the C_5NF_4 unit of 2.143(5) Å nor the iridium–carbon distance to the arene in 9 of 2.161(2) Å show a significant difference to the Ir–C distance in 2 (2.137(3) Å).

A reaction of **2** with an excess of ethylene leads within hours to the formation of ethane and the Ir(I) ethylene complex *trans*-[Ir(4-C₅NF₄)(η^2 -C₂H₄)(P*i*Pr₃)₂] (**10**) (Scheme 2). The ¹⁹F NMR

Table 2 Selected bond lengths (Å) and angles (°) in *cis–trans*-[Ir(4- C_5NF_4)(H)₂(CO)(PiPr₃)₂] (7) with estimated standard deviations in parentheses

Ir-C(19)	1.923(5)	N(1)-C(23)	1.306(8)
Ir-C(20)	2.143(5)	N(1) - C(22)	1.309(8)
Ir-P(1)	2.338(1)	C(19)–O(1)	1.146(6)
Ir-P(2)	2.345(1)	F(1)-C(21)	1.367(7)
C(20)-C(24)	1.381(8)	F(2)-C(22)	1.368(6)
C(20) - C(21)	1.404(8)	F(3)-C(23)	1.357(6)
C(21) - C(22)	1.356(8)	F(4)-C(24)	1.368(6)
C(23)–C(24)	1.371(8)		
C(19)–Ir(1)–C(20)	98.4(2)	C(24)–C(20)–C(21)	109.9(5)
C(19)-Ir(1)-P(1)	95.3(2)	C(24)-C(20)-Ir(1)	125.6(4)
C(19)-Ir(1)-P(2)	95.6(2)	C(21)-C(20)-Ir(1)	124.5(4)
C(20)-Ir(1)-P(1)	95.2(1)	C(22)-C(21)-C(20)	122.8(5)
C(20)-Ir(1)-P(2)	94.9(1)	N(1)-C(22)-C(21)	125.4(5)
P(1)-Ir(1)-P(2)	163.89(5)	N(1)-C(23)-C(24)	124.7(5)
C(23)-C(24)-C(20)	123.5(5)	O(1)-C(19)-Ir(1)	174.3(4)
C(23)–N(1)–C(22)	113.7(5)		

Table 3 Selected bond lengths (Å) and angles (°) in *cis–trans*-[Ir(2- $C_6H_3F_2$)(H)₂(CO)(P*i*Pr₃)₂] (9) with estimated standard deviations in parentheses

Ir(1)–C(25)	1.912(2)	C(19)–C(20)	1.397(3)
Ir(1) - C(19)	2.161(2)	C(20) - C(21)	1.384(3)
Ir(1) - P(1)	2.3337(5)	C(21) - C(22)	1.383(3)
Ir(1) - P(2)	2.3339(5)	C(22) - C(23)	1.381(4)
Ir(1)-H(1A)	1.50(3)	C(23)-C(24)	1.389(3)
Ir(1)-H(1B)	1.58(3)	F(1)-C(20)	1.380(2)
O(1) - C(25)	1.146(2)	F(2) - C(24)	1.374(3)
C(19) - C(24)	1.397(3)		
H(1A)-Ir(1)-H(1B)	81(1)	P(1)-Ir(1)-P(2)	163.47(2)
C(25)-Ir(1)-H(1A)	172(1)	P(2)-Ir(1)-H(1A)	86(1)
C(25)-Ir(1)-H(1B)	91(1)	P(2)-Ir(1)-H(1B)	83(1)
C(25)-Ir(1)-C(19)	98.54(8)	C(24)-C(19)-Ir(1)	125.7(2)
C(25)-Ir(1)-P(1)	95.67(7)	C(20) - C(19) - Ir(1)	124.6(2)
C(25)-Ir(1)-P(2)	95.62(7)	C(24) - C(19) - C(20)	109.7(2)
C(19)-Ir(1)-H(1A)	90(1)	C(21)-C(20)-C(19)	127.5(2)
C(19)-Ir(1)-H(1B)	170(1)	C(22)-C(21)-C(20)	118.1(2)
C(19)-Ir(1)-P(1)	94.93(5)	C(23)-C(22)-C(21)	119.1(2)
C(19)-Ir(1)-P(2)	95.29(5)	C(22)-C(23)-C(24)	118.7(2)
P(1)-Ir(1)-H(1A)	82(1)	C(23)-C(24)-C(19)	126.8(2)
P(1)-Ir(1)-H(1B)	85(1)	O(1) - C(25) - Ir(1)	174.0(2)
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Fig. 6 An ORTEP diagram of 7. Ellipsoids are drawn at the 50% probability level.



Fig. 7 An ORTEP diagram of 9. Ellipsoids are drawn at the 50% probability level.

spectrum exhibits two multiplets in a ratio of 1 : 1 at δ –100.5 and -114.4 for the four fluorine atoms of the pyridyl ligand. The ¹H NMR spectrum shows a triplet at $\delta 2.34$ for the C₂H₄ ligand, with a H,P coupling constant of 4.2 Hz. The proposed structure of 10 was also confirmed by X-ray crystallography (Fig. 8). Suitable crystals were grown at 243 K from a hexane solution. Selected bond lengths and angles are summarised in Table 4. The molecular structure reveals a slightly distorted trigonal-bipyramidal geometry with the expected trans disposition of the phosphine ligands. The plane which is defined by the Ir and the ethylene ligand is almost perpendicular to the P-Ir-P axis. Thus, the carboniridium-phosphorus angles are 88.93(5)° and 90.49(5)°, indicating a nearly perfectly arranged plane of the three carbon atoms C19-C21 between the phosphorus atoms. The C-C separation in the ethylene ligand is with 1.390(3) Å identical with the analogous distance in *trans*-[Ir(Cl)(η^2 -C₂H₄)(PPh₃)₂] (1.375(10) Å).²⁰

Treatment of **10** with CO furnishes the Ir(I) complex *trans*-[Ir(4-C₅NF₄)(CO)(P*i*Pr₃)₂] (**11**) by replacement of the ethylene ligand

Table 4	Selected	bond	lengt	hs (Å) and	angle	s (°)	in tran	ns-[Ir(4
$C_5NF_4)($	$\eta^2 - C_2 H_4)(1$	$PiPr_3)_2$]	(10)	with	estima	ted sta	andard	deviat	ions in
parenthe	eses								

Ir(1)–C(21)	2.083(2)	C(21)–C(25)	1.392(3)
Ir(1) - C(19)	2.149(2)	C(21) - C(22)	1.394(3)
Ir(1)-C(20)	2.181(2)	C(22) - C(23)	1.375(3)
Ir(1) - P(2)	2.3679(5)	C(24)-C(25)	1.386(3)
Ir(1) - P(1)	2.3684(5)	F(1)-C(22)	1.367(3)
N(1)–C(24)	1.304(4)	F(2)-C(23)	1.350(3)
N(1)–C(23)	1.309(4)	F(3)-C(24)	1.348(3)
C(19)–C(20)	1.390(3)	F(4)-C(25)	1.351(3)
C(19)-Ir(1)-P(1)	90.18(5)	C(21)-Ir(1)-P(1)	88.93(5)
C(19)-Ir(1)-P(2)	90.22(5)	P(2)-Ir(1)-P(1)	179.35(2)
C(19)–Ir(1)–C(20)	37.45(8)	N(1)-C(23)-C(22)	124.7(3)
C(20)-Ir(1)-P(2)	90.92(5)	N(1)-C(24)-C(25)	124.9(3)
C(20)-Ir(1)-P(1)	89.71(5)	C(23)–C(22)–C(21)	122.8(2)
C(21)–Ir(1)–C(19)	155.38(8)	C(24)-C(25)-C(21)	122.3(2)
C(21)-Ir(1)-C(20)	167.08(8)	C(24)-N(1)-C(23)	114.4(2)
C(21)–Ir(1)–P(2)	90.49(5)	C(25)-C(21)-C(22)	110.8(2)



Fig. 8 An ORTEP diagram of 10. Ellipsoids are drawn at the 50% probability level.

(Scheme 2). The ¹⁹F NMR spectrum of **11** shows two multiplets in a ratio of 1:1 at δ –98.8 and –113.3 for the four fluorine atoms of the pyridyl ligand. The IR spectrum of **11** exhibits an absorption band at 1949 cm⁻¹ for the CO–ligand, consistent with the presence of an Ir(1) compound. Note, that this IR-band appears at higher energy in comparison to the corresponding bands in *trans*-[Ir(X)(CO)(PiPr₃)₂] (X = Cl, Br, I: 1935, 1935, 1938 cm⁻¹, respectively).²¹ This suggests less electron density at the iridium center for the tetrafluoropyridyl complex **11**.

Discussion

The syntheses of the complexes cis-trans- $[Ir(Ar)(H)_2(PiPr_3)_2]$ (2: Ar = 4-C₅NF₄, 4: Ar = C₆F₅, 6: Ar = 2-C₆H₃F₂) by C–H activation of the fluorinated arenes ArH at trans- $[Ir(H)_5(PiPr_3)_2]$ (1) are shown in Scheme 1. In accordance to studies on the C–H activation of diffuorobenzenes at {IrCl(PiPr_3)_2}, we did not observe any C–F activation of the fluorinated substrates.⁸ As suggested by Goldman and Halpern, we assume that the formation of trans- $[Ir(H)_3(PiPr_3)_2]$ is the initial step for the C-H activation reactions.²² Nevertheless, a competition experiment with 1, neohexene and equimolar amounts of 2,3,5,6-tetrafluoropyridine, pentafluorobenzene and 1,3-difluorobenzene reveals a preference for the formation of 2 over 4 (ratio 4:1), whereas no formation of 6 was observed, indicating that the loss of dihydrogen is not the rate-determining step in the formation of the iridium dihydrides. A few examples of C-H activation reactions at 1 are known, among them is the C-H activation of indene yielding cis-cis- $[Ir(\eta^{3}-C_{9}H_{7})(H)_{2}(PiPr_{3})_{2}]$ and $[Ir(\eta^{5}-C_{9}H_{7})(H)_{2}(PiPr_{3})]^{23}$ The C-H activation of alkynes and olefins at 1 has also been observed.^{23,24} No C-H activation of fluorinated arenes have been known at 1, but Smith III et al. succeeded in derivatizing C-H bonds of pentafluoro- and 1,3,5-trifluorobenzene with 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (pinacolborane = HBpin) to give $C_6F_5(Bpin)$ and $C_6F_3H(Bpin)$ (pin = $O_2C_2Me_4$) using [Cp*Ir(PMe_3)(H)_2] as a catalyst.6

A photochemical approach allows the selective synthesis of the tetrahydrides cis-trans-[Ir(4-C₅NF₄)(H)₂(H₂)(PiPr₃)₂] (3) and *cis*-*trans*-[Ir(4-C₆F₅)(H)₂(H₂)(P*i*Pr₃)₂] (5). Whereas the complexes 3 and 5 are also accessible by reactions of cis-trans-[Ir(4- $C_5NF_4(H)_2(PiPr_3)_2$ (2) or *cis*-trans-[Ir($C_6F_5(H)_2(PiPr_3)_2$] (4) with dihydrogen, treatment of cis-trans-[Ir(2-C₆H₃F₂)(H)₂(PiPr₃)₂] (6) with dihydrogen leads to the generation of 1 and 1,3diffuorobenzene, only. A tetrahydride with the $C_6H_3F_2$ ligand could not be detected. The tetrahydrides 3 and 5 are stable at room temperature, and **3** is in contrast to *trans*- $[IrX(H)_2(H_2)(P_iP_3)_2]$ (X = Cl, Br, I) even stable without a hydrogen atmosphere.¹⁵ The higher stability of **3** in comparison to *trans*- $[IrX(H)_2(H_2)(PiPr_3)_2]$ can be attributed to the stabilizing properties of the C5NF4 ligand.¹¹⁻¹³ The π -acceptor properties of C₅NF₄, which would be conceivable for 2 and 3, are not supported by the shapes of the HOMO or HOMO-1 in 2 or 3. Although the C_5NF_4 ligand seems not to be a π -acceptor at iridium(III), it is also not a π -donor such as halogen ligands. Note that in contrast to the square-pyramidal geometry found for 2, the complexes cis-trans-[Ir(X)(H)₂(PiPr₃)₂] exhibit a trigonal-bipyramidal structure, which is favoured for $X = \pi$ -donor ligands.¹⁸ We believe that the stabilizing influence of the fluorinated ligands at our Ir(III) compounds are due to σ - rather than π -interactions.¹¹ Pyridyl ligands as well as a fluorinated organyl group are electron withdrawing and have higher group electronegativities which results in a stronger metalcarbon bond.11

The ¹H NMR spectra of 3 and 5 at 193 K at 600 MHz show only one signal for the four hydrides. This reflects a very low kinetic barrier for hydrogen exchange at the metal center. Decoalescence into separate resonances for the η^2 -H₂ and the classical hydrides could not be achieved at low temperature. The exchange process might involve an oxidative addition/reductive elimination pathway via an Ir(v) compound.²⁵ However, direct hydrogen-transfer steps from a non-classical bound H₂ to a metal hydride are also conceivable. This resembles a mechanism which has recently been discussed as σ -CAM (σ -CAM = σ -complexassisted-metathesis).²⁶ The reversible loss of H₂ from 3 or 5 to give the dihydrides 2 or 4, respectively, suggests an additional exchange process with free hydrogen. However, in contrast to *trans*- $[Ir(Cl)(H)_2(H_2)(PiPr_3)_2]$ this process is slow on the NMR time scale, because separate resonances for the tetrahydride 3 and the dihydride 2 as well as for 5 and 4 can be observed in the

NMR spectra at room temperature. A ¹H NMR EXSY spectrum (400 MHz) of a mixture of 2 and 3 shows cross-peaks for the hydrides confirming exchange of hydrogen between these two compounds.

NMR-relaxation experiments show a very short T_1 -relaxation time for **3** and **5** (Fig. 3). The data represent population-weighted average values for all four hydrogens, but nevertheless indicate the presence of a non-classical bound hydrogen molecule. The $T_{1,\text{non-classic}}$ time at 233 K for the non-classical hydrides in **3** can be calculated by eqn (1)¹⁴

$$(a+b)(T_{1,\min})^{-1} = a(T_{1,\text{classic}})^{-1} + b(T_{1,\text{non-classic}})^{-1}$$
(1)

where a is the number of classical bound H-atoms and b is the number of non-classical bound H-atoms.

As an estimation of $T_{1,classic}$ of complex **3** we used the T_1 of the hydrides in *cis–trans*-[Ir(4-C₅NF₄)(H)₂(P*i*Pr₃)₂] (**2**) at 233 K, which is 300 ms at 600 MHz. This assumption leads with $T_{1,min} = 39$ ms to a longitudinal relaxation time $T_{1,nonclassic}$ of 20 ms (600 MHz) for the non-classical hydrogens in **3**. If dipole–dipole interactions are the main contributors for the hydride relaxation, the H–H distance in the metal bound H₂ can be estimated to be 0.82 Å for the case of a rapid rotation of η^2 -H₂ at the metal centre (1.04 Å for a slow rotation).^{14,27} This value is nearly identical with the H–H distance in *trans*-[Ir(1)(H)₂(H₂)(P*i*Pr₃)₂] of 0.856(9) Å which has been determined by neutron diffraction analysis.²⁸ The DFT calculations for **3** reveal a H–H separation of 0.88 Å.

The hydride ligands in 2 or 3 can be removed on treatment with ethylene yielding *trans*-[Ir(4-C₅NF₄)(η^2 -C₂H₄)(PiPr₃)₂] (10) (Scheme 2). A reaction of 10 with H₂ refurnishes a mixture of 2 and 3. Note that Werner *et al.* reported the synthesis of the iridium(I) ethylene complex *trans*-[Ir(Me)(η^2 -C₂H₄)(PiPr₃)₂], which also features an anionic carbon ligand.²⁹ The dihydride complexes 2, 4 and 6 react readily with CO, yielding the octahedral complexes *cis*-*trans*-[Ir(Ar)(H)₂(CO)(PiPr₃)₂](7: Ar = 4-C₅NF₄, 8: Ar = C₆F₅, 9: Ar = 2-C₆H₃F₂). The compounds are fairly stable and do not lose hydrogen to give iridium(I) carbonyls. However, 11 can be synthesized on treatment of the ethylene complex 10 with CO.

Conclusions

In conclusion, we presented new carbon–hydrogen activation reactions of fluorinated compounds at Ir. In contrast to the trigonal-bipyramidal complexes *trans*-[Ir(X)(H)₂(PR₃)₂] (X = Cl, Br, I), the dihydride species feature a square-pyramidal geometry. This has been predicted for a {Ir(H)₂(PR₃)₂} fragment with an additional anionic ligand which is not a π -donor, but has never been observed before.¹⁸ In addition, the fluorinated ligands have a stabilizing influence. This allows the preparation of non-classical hydrido complexes which also feature two hydrides bound in a classical fashion. The compounds are highly dynamic involving exchange of all four hydrogen nuclei. For future investigations, the ethylene complex *trans*-[Ir(4-C₅NF₄)(η^2 -C₂H₄)(P*i*Pr₃)₂] (10) might be a valuable starting compound for various transformations such as C–H activation and C–C coupling reactions.^{29,30}

 $[D_6]$ Benzene and $[D_8]$ toluene were dried by stirring over potassium and then distilled under vacuum. 2,3,5,6-Tetrafluoropyridine, pentafluorobenzene and 1,3-difluorobenzene were obtained from Aldrich and distilled before use; *trans*- $[Ir(H)_5(PiPr_3)_2]$ (1) was prepared according to the literature.³¹

The NMR spectra were recorded on a Bruker DRX 500 or Bruker Avance 600 spectrometer at 300 K. The ¹H NMR chemical shifts were referenced to residual C₆D₅H at $\delta = 7.15$ or [D₇]toluene at $\delta = 2.09$ ppm. The ¹³C NMR chemical shifts were referenced to C₆D₆ at $\delta = 128.0$ ppm. The ¹⁹F NMR spectra were referenced to external C₆F₆ at $\delta = -162.9$ ppm. The ³¹P{¹H} NMR spectra were referenced externally to H₃PO₄ at δ 0.0 ppm. Infrared spectra were recorded on a Bruker Vector 22 spectrometer. Preparative irradiation experiments were carried out with a Hanau TQ 150 immersion mercury lamp with 25 W.

Synthesis of cis-trans-[Ir(H)₂(4-C₅NF₄)(PiPr₃)₂] (2)

A solution of 1 (520 mg, 1.0 mmol), neohexene (0.25 ml, 2.1 mmol) and 2,3,5,6-tetrafluoropyridine (0.2 mL, 2.0 mmol) in 20 mL *n*-hexane was heated to reflux for 6 h. The solution turned orange within one hour. The volatiles were removed *in vacuo* to give an orange powder, which was dissolved in 5 mL *n*-hexane. The solution was stored at -30 °C to obtain **2** as orange crystals. Yield 558 mg (84%). A comparable transformation without neohexene leads to a mixture of **2** and **3** in a ratio of 3:1 according to the NMR data of the reaction solution. Analytical data for **2**. Found: C, 41.31; H, 6.69; N, 2.11. C₂₃H₄₄F₄IrNP₂ requires C, 41.49; H, 6.67; N 2.10); $\tilde{\nu}$ (ATR)/cm⁻¹ 1935 (IrH₂); ¹H NMR (500 MHz, C₆D₆): δ 1.96 (m, 6 H, CH), 0.86 (m, 36 H, CH₃), -28.09 (tt, *J*_{HP} = 15.3 Hz, *J*_{HF} = 7.5 Hz, 2 H, IrH); ¹⁹F NMR (470.4 MHz, C₆D₆): δ -100.0 (m, 2 F), -119.3 (m, 2 F); ³¹P{¹H} NMR (202.4 MHz, C₆D₆): δ 52.0 (s).

Formation of cis-trans-[Ir(4-C₅NF₄)(H)₂(H₂)(PiPr₃)₂] (3)

Complex **1** (50 mg, 0.1 mmol), 2,3,5,6-tetrafluoropyridine (0.03 mL, 0.3 mmol) and 0.5 mL [D₆]benzene were transferred into a quartz-NMR-tube. The reaction mixture was irradiated for 4 h at room temperature. According to the NMR data, the solution contained **3** and **1** in a ratio of 95:5. $\tilde{\nu}$ (ATR)/cm⁻¹ 2192, 2046 (IrH₂); ¹H NMR (500 MHz, C₆D₆): δ 1.60 (m, 6 H, CH), 0.87 (m, 36 H, CH₃), -9.36 (s, br, 4 H, IrH); ¹⁹F NMR (470.4 MHz, C₆D₆): δ -98.7 (m, 2 F), -104.4 (m, 2 F); ³¹P{¹H} NMR (202.4 MHz, C₆D₆): δ 33.7 (s).

Synthesis of cis-trans-[Ir(H)₂(C₆F₅)(PiPr₃)₂] (4)

A solution of 1 (260 mg, 0.5 mmol), neohexene (0.12 ml, 1.0 mmol) and pentafluorobenzene (0.2 mL, 1.8 mmol) in 20 mL *n*-hexane was heated to reflux for 6 h. The solution turned orange within one hour. The volatiles were removed *in vacuo* to give an orange solid, which was dissolved in 5 mL *n*-hexane. The solution was stored at -30 °C and orange crystals were obtained. Yield 267 mg (78%). A comparable transformation without neohexene leads to a mixture of 4 and 5 in a ratio of 2.8 : 1 according to the NMR data of the reaction solution. Analytical data for 4. Found: C, 42.28; H, 6.62. C₂₄H₄₄F₅IrP₂ requires C, 42.21; H, 6.50; \tilde{v} (ATR)/cm⁻¹ 1937

(IrH₂); ¹H NMR (500 MHz, C₆D₆): δ 2.04 (m, 6 H, CH), 0.92 (m, 36 H, CH₃), -28.09 (tt, J_{HP} = 15.3 Hz, J_{HF} = 7.5 Hz, 2 H, IrH); ¹⁹F NMR (470.4 MHz, C₆D₆): δ -138.6 (m, 2 F), -153.6 (m, 1 F), -161.8 (m, 2 F); ³¹P{¹H} NMR (202.4 MHz, C₆D₆): δ 51.8 (s).

Formation of cis-trans-[Ir(C₆F₅)(H)₂(H₂)(PiPr₃)₂] (5)

A solution of 1 (50 mg, 0.1 mmol), pentafluorobenzene (0.03 mL, 0.2 mmol) in 0.5 mL [D₈]toluene was transferred into a quartz-NMR-tube. The reaction mixture was irradiated for 4 h at room temperature. According to the NMR data, the solution contained 5 and 1 in a ratio of 90 : 10. \tilde{v} (ATR)/cm⁻¹ 2176, 2104 (IrH₂); ¹H NMR (500 MHz, [D₈]toluene): δ 1.65 (m, 6 H, CH), 1.09 (m, 36 H, CH), -9.46 (s, br, 4 H, IrH); ¹⁹F NMR (470.4 MHz, [D₈]toluene): δ -98.5 (m, 2 F), -163.4 (m, 1 F), -163.9 (m, 2 F); ³¹P{¹H} NMR (202.4 MHz, [D₈]toluene): δ 33.0 (s).

Synthesis of cis-trans-[Ir(H)₂(2-C₆H₃F₂)(PiPr₃)₂] (6)

A solution of **1** (200 mg, 0.4 mmol) and neohexene (0.12 ml, 1.0 mmol) in 1,3-difluorobenzene (10 mL, 100 mmol) was heated to reflux for 10 h. The solution turned orange within the first hour. The volatiles were removed *in vacuo*. The residue was then extracted with *n*-hexane (10 mL) and the extract was brought to dryness to give an orange oil. Yield 150 mg (59%). A comparable preparation without neohexene leads to a mixture of **6** and **1** in a ratio of 4 : 1 according to the NMR data of the reaction solution. $\tilde{v}(\text{ATR})/\text{cm}^{-1}$ 1945 (IrH₂); ¹H NMR (500 MHz, C₆D₆): δ 6.91–6.87 (m, 3 H, C₆H₃F₂), 2.14 (m, 6 H, CH), 1.02 (m, 36 H, CH₃), -28.62 (tt, $J_{\text{HP}} = 16.3$ Hz, $J_{\text{HF}} = 7.9$ Hz, 2 H, IrH); ¹⁹F NMR (470.4 MHz, C₆D₆): δ -85.1 (m); ³¹P{¹H} NMR (202.4 MHz, C₆D₆): δ 51.9 (s).

Competition experiment of the reaction of 1 with 2,3,5,6tetrafluoropyridine, pentafluorobenzene and 1,3-difluorobenzene

A mixture of 1 (150 mg, 0.3 mmol), neohexene (0.2 ml, 1.7 mmol), 2,3,5,6-tetrafluoropyridine (0.10 mL, 1.0 mmol), pentafluorobenzene (0.12 mL, 1.0 mmol) and 1,3-difluorobenzene (0.10 mL, 1.0 mmol) in 10 mL *n*-hexane was heated to reflux for 6 h. The solution turned orange within one hour. The volatiles were removed *in vacuo* to give an orange powder which consists of **2** and **4** in a ratio of approximately 4:1 according to the NMR data. There is no indication for the formation of **6**.

Synthesis of cis-trans-[Ir(H)₂(4-C₅NF₄)(CO)(PiPr₃)₂] (7)

CO gas was bubbled for a few seconds into an orange solution of **2** (90 mg, 0.14 mmol) in 10 mL *n*-hexane until the solution turned colourless. After removing the volatiles *in vacuo*, the colourless residue was dissolved in 5 mL *n*-hexane and the solution was stored at -30 °C to obtain colourless crystals of **7**. Yield: 90 mg (95%). Found: C, 41.44; H, 6.16; N, 1.71. C₂₄H₄₄F₄IrNOP₂ requires C, 41.61; H, 6.40; N, 2.02; $\tilde{v}(ATR)/cm^{-1}$ 2161, 2079 (IrH₂), 1979 (CO); ¹H NMR (500 MHz, C₆D₆): δ 1.76 (m, 6 H, CH), 0.88 (m, two d at 0.89 and 0.88 in the ¹H{³¹P} NMR due to the prochirality, $J_{\rm HH} = 7.0$ Hz, 36 H, CH₃), -10.72 (m, 1 H, IrH), -14.55 (m, 1 H, IrH); ¹⁹F NMR (470.4 MHz, C₆D₆): δ -98.6 (m, 1 F), -99.0 (m, 1 F), -104.7 (m, 1 F) -104.8 (m, 1 F); ³¹P{¹H} NMR (202.4 MHz, C₆D₆): δ 30.6 (s).

Synthesis of cis-trans-[Ir(H)₂(C₆F₅)(CO)(PiPr₃)₂] (8)

A slow stream of CO was passed for 1 min through an orange solution of **4** (40 mg, 0.06 mmol) in 5 mL *n*-hexane. The solution turned immediately colourless. The volatiles were removed *in vacuo* to give a colourless solid, which was dissolved in 2 mL *n*-hexane and the solution was stored at -30 °C. A colourless powder was obtained. Yield: 37 mg (86%). Analytical data for **8**. Found: C, 42.13; H, 6.32. C₂₅H₄₄F₅IrOP₂ requires C, 42.24; H, 6.24; $\tilde{v}(ATR)/cm^{-1}$ 2139, 2077 (IrH₂), 1977 (CO); ¹H NMR (500 MHz, C₆D₆): δ 1.81 (m, 6 H, CH), 0.94 (m, two d at 0.93 and 0.94 in the ¹H{³¹P} NMR due to the prochirality, $J_{HH} = 7.1$ Hz, 36 H, CH₃), -10.72 (m, 1 H, IrH), -14.69 (m, 1 H, IrH); ¹⁹F NMR (470.4 MHz, C₆D₆): δ -96.1 (m, 1 F), -96.3 (m, 1 F), -162.5 (m, 1 F), -162.8 (m, 1 F), -162.9 (m, 1 F); ³¹P{¹H} NMR (202.4 MHz, C₆D₆): δ 29.8 (s).

Synthesis of cis-trans-[Ir(H)₂(2-C₆H₃F₂)(CO)(PiPr₃)₂] (9)

CO was bubbled into an orange solution of **6** (60 mg, 0.1 mmol) in 5 mL *n*-hexane until the colour of the solution disappeared (within seconds). After removing the volatiles *in vacuo* the colourless residue was dissolved in 5 mL *n*-hexane and stored at -30 °C to obtain colourless crystals. Yield: 60 mg (88%). Found: C, 45.98; H, 7.12. C₂₅H₄₇F₂IrOP₂ requires C, 45.79; H, 7.22; \tilde{v} (ATR)/cm⁻¹ 2165, 2059 (IrH₂), 1973 (CO); ¹H NMR (500 MHz, C₆D₆): δ 6.89–6.77 (m, 3 H, C₆H₃F₂), 1.95 (m, 6 H, CH), 1.04 (m, two doublets at 1.04 and 1.03 in ¹H{³¹P} due to the prochirality $J_{\rm HH} = 7.0$ Hz, 36 H, CH₃), -10.58 (m, 1 H, IrH), -14.30 (m, 1 H, IrH); ¹⁹F NMR (470.4 MHz, C₆D₆): δ -66.9 (m, 1 F), -67.2 (m, 1 F); ³¹P{¹H} NMR (202.4 MHz, C₆D₆): δ 30.5 (s).

Synthesis of *trans*-[Ir(4-C₅NF₄)(η^2 -C₂H₄)(P*i*Pr₃)₂] (10)

Ethylene was bubbled into an orange solution of 2 (180 mg, 0.28 mmol) in *n*-hexane until the colour of the solution turned

Table 5 Crystallographic data

to deep-red (approx. 1 h). The reaction mixture was then stirred under an atmosphere of ethylene for 16 h. After removing the volatiles *in vacuo* the residue was dissolved in 5 mL *n*-hexane and the solution was stored at -30 °C to obtain deep-red crystals. Yield: 130 mg (67%). Found: C, 43.13, H, 6.56; N, 2.22 C₂₅H₄₆F₄IrNP₂ requires C, 43.47; H, 6.71; N, 2.03; ¹H NMR (500 MHz, C₆D₆): δ 2.34 (t, $J_{HP} = 4.2$ Hz, 4 H, C₂H₄), 1.89 (m, 6 H, CH), 0.99 (m, 36 H, CH₃); ¹³C{¹H} NMR (125.8 MHz, C₆D₆): δ 23.4 (t, $J_{CP} = 13$ Hz, C₂H₄); ¹⁹F NMR (470.4 MHz, C₆D₆): δ -100.5 (m, 2 F), -114.4 (m, 2 F); ³¹P{¹H} NMR (202.4 MHz, C₆D₆): δ 14.6 (s).

Synthesis of trans-[Ir(4-C₅NF₄)(CO)(PiPr₃)₂] (11)

A slow stream of CO was passed through a red solution of **10** (65 mg, 0.09 mmol) in 10 mL *n*-hexane. Within seconds the colour of the solution turned yellow. The volatiles were removed *in vacuo*. The residue was then extracted with *n*-hexane (10 mL) and the extract was brought to dryness to give **11** as a yellow powder. Yield: 60 mg (92%). Found: C, 42.02; H, 6.32; N, 1.88. $C_{22}H_{42}F_4IrNOP_2$ requires C, 41.73; H, 6.13; N, 2.03; $\tilde{\nu}(ATR)/cm^{-1}$ 1949 (CO); ¹H NMR (500 MHz, C_6D_6): δ 2.02 (m, 6 H, CH), 1.04 (m, 36 H, CH₃); ¹⁹F NMR (470.4 MHz, C_6D_6): δ –98.78 (m, 2 F), –113.3 (m, 2 F); ³¹P{¹H} NMR (202.4 MHz, C_6D_6): δ 35.8 (s).

Structure determinations for the complexes 2, 7, 9 and 10‡

Yellow crystals of **2**, colourless crystals of **7** and **9** and red crystals of **10** were obtained from a solution in hexane at 243 K. All diffraction data were collected on a Nonius Kappa CCD diffractometer at 100 K. Crystallographic data are depicted in Table 5. The structures were solved by direct methods (SHELXTL PLUS or SIR 97) and refined with the full matrix least square methods on F^2 (SHELX-97).^{32–34}

Hydrogen atoms were placed at calculated positions and refined using a riding model. For complex **2** H19 and H20 were located in the difference Fourier with a distance to Ir1 of 1.4 Å. They were

Compound	2	7	9	10		
Crystal dimensions/mm ³	$0.14 \times 0.13 \times 0.08$	$0.16 \times 0.06 \times 0.06$	$0.32 \times 0.25 \times 0.16$	$0.50 \times 0.38 \times 0.24$		
Empirical formula	$C_{23}H_{44}F_4IrNP_2$	$C_{24}H_{42}F_4IrNOP_2$	$C_{25}H_{47}F_2IrOP_2$	$C_{25}H_{46}F_4IrNP_2$		
Formula weight	664.73	690.73	655.77	690.77		
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic		
Space group	$P2_{1}/c$	$P2_{1}2_{1}2_{1}$	$P2_1/c$	$P2_1/n$		
a/Å	12.1550(12)	12.4740(3)	13.0680(6)	9.1850(1)		
b/Å	16.7400(11)	13.0700(2)	12.7220(9)	23.4600(2)		
c/Å	13.5350(13)	17.2910(4)	16.8010(13)	12.7920(1)		
$\beta/^{\circ}$	99.313(8)		92.181(6)	90.437(4)		
$V/Å^3$	2717.7(4)	2819.04(10)	2791.2(3)	2756.34(4)		
Ζ	4	4	4	4		
Density (calcd.)/Mg m ⁻³	1.625	1.627	1.561	1.665		
μ (Mo-K α)/mm ⁻¹	5.069	4.892	4.926	5.001		
θ Range/°	3.21 to 27.5	3.26 to 27.49	3.20 to 30.00	3.05 to 27.5		
Reflections collected	43911	33849	54355	101272		
Independent reflections	6233	6464	8070	6287		
R _{int}	0.0693	0.083	0.0316	0.047		
Goodness-of-fit on F^2	1.032	1.035	1.097	1.060		
R_1 , wR_2 on all data	0.0510, 0.0474	0.0404, 0.0618	0.0311, 0.0358	0.0167, 0.0349		
$R_1, wR_2 [I_0 > 2\sigma(I_0)]$	0.0275, 0.0420	0.0318, 0.0591	0.0181, 0.0316	0.0151, 0.0345		
Reflect. with $I_{o} > 2\sigma(I_{o})$	4780	5858	6748	5986		
Max diff peak, hole/e Å ⁻³	0.945 and -0.665	2.105 and -0.785	1.927 and -0.933	0.827 and -0.609		
CCDC	686375	686376	686377	686378		

then refined isotropically using a dfix "anti-bumping" restraint of -1.6 with an estimated standard deviation of 0.02 leading to the distances Ir(1)–H(19)= 1.548(18) Å and Ir(1)–H(20) = 1.558(19) Å. The hydrogen atoms bound at Ir in 7 were not located. However the largest diff. peaks are found near iridium. For compound 9 the hydrogens at iridium have been located and refined isotropically. The largest diff. peak is located near Ir (0.76 Å).

Computational details

The complexes were investigated with the BP86^{35,36} DFT method without introducing symmetry. (Analytical) vibrational frequencies were calculated at the BP86/SV(P)-level to verify the nature of the obtained minima and to determine the zero point vibrational energy.³⁷ All reported compounds are true minima with no imaginary frequencies. DFT calculations were performed with the TURBOMOLE program package (Version 5.7).^{38,39} The DFT calculations with the BP86 functional have been carried out with the resolution of identity (RI) approximation.⁴⁰ The def-SV(P)⁴¹ basis set was used for all atoms; for Ir the scalar relativistic effective core potential def-ECP was used together with def-SV(P) valence basis set.⁴² XYZ coordinates of the optimized compounds as well as the calculated frequencies and total energies are deposited. The assignment of the calculated vibrational frequencies and the calculated molecular orbitals was done by visualization of the modes/orbitals with the help of the program Molden.

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