# Synthesis of a Novel Organoiridium(I) Fluoro Complex

**Michael Gorol,[a] Nadia C. Mösch-Zanetti,[a] Herbert W. Roesky,*[a] Mathias Noltemeyer,[a] and Hans-Georg Schmidt[a]**

*Dedicated to G.-V. Röschenthaler on the occasion of his 60th birthday*

**Keywords:** Syntheses / Crystal structures / Iridium(I) / Fluoro complexes / Pentafluorosilicates

Cyclooctadienefluorotriphenylphosphaneiridium(I) [IrF($C_8H_{12}$)($PPh_3$)] (**3**) was prepared and its structure determined by single crystal X-ray diffraction analysis. Complex **3** crystallises in the monoclinic space group $P2_1/n$. The lattice parameters are $a$ = 931.9(3) pm, $b$ = 1629.4(7) pm, $c$ = 1592.9(7) pm, $\alpha = \gamma = 90°$, $\beta$ = 92.85(3)°. Number of molecules per unit cell is 4. The square planar iridium complex **3** exhibits an Ir–F bond length of 201.3(5) pm. **3** was obtained in Teflon tubes, whereas the use of glass vessels led to cyclooctadienebis(triphenylphosphane)iridium(I)-pentafluorosilicate(IV) ([Ir($C_8H_{12}$)($PPh_3$)$_2$][$SiF_5$]) (**4**). The composition of **4** was confirmed by single crystal X-ray diffraction analysis. **4** crystallises in the monoclinic space group $P2_1/c$. The lattice parameters are $a$ = 1157.4(9) pm, $b$ = 1864.4(9) pm, $c$ = 1922.5(17) pm, $\alpha = \gamma = 90°$, $\beta$ = 96.16(7)°. The number of molecules per unit cell is 4. The square-planar coordinated iridium cation $[Ir(C_8H_{12})(PPh_3)_2]^+$ is separated from the trigonal bipyramidal $[SiF_5]^-$ anion by 461.1 pm (shortest Ir···F distance) and thus it is assumed that no interactions occur between the fluorine and iridium atoms.
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## Introduction

There is ongoing interest in low oxidation state transition metal compounds containing fluorine-metal and carbon-metal bonds as a result of their use in synthesis and catalysis.[1−3] In the presence of $\pi$ back-bonding ligands fluoro complexes of $d^8$ metals are stable although they object the predicted hard/soft acid/base (HSAB) rules. This has been shown for the iridium Vaska system $IrF(CO)(PPh_3)_2$, whose derivatives are the only known *organometallic fluorides* in the chemistry of iridium(I).[1,4] Compounds of this type are certainly the most extensively studied and readily prepared systems but structural characterisation has not been accomplished. Thus far, bond length parameters are available only for iridium $d^6$ centers e.g. Cp*IrF(Ph)($PMe_3$),[5] Ir(Cl)F($NSF_2$)(CO)($PPh_3$)$_2$,[6] [IrF($\eta^2$-NH=$NC_6H_3$-2-$CF_3$)(CO)($PPh_3$)$_2$][$BF_4$],[7] Ir($FBF_3$)$Me_2$($PMe_2Ph$)$_3$,[8] and [Ir{C(F)O}F(CO)$_2$($PEt_3$)$_2$][$BF_4$].[9] Iridium(I) complexes with cyclooctadiene or cyclooctene as the stabilising C-based ligands are well-known and widely used as starting materials in organometallic chemistry. However, appropriate fluorides are missing, although some are accessible, as in the case of homologous rhodium(I) olefin complexes.[10−12]

Moreover, complexes of weakly or non-coordinating fluorinated anions such as $[BF_4]^-$, $[PF_6]^-$, $[AsF_6]^-$ and $[SbF_6]^-$ are of special interest in organometallic fluorine chemistry. For instance, the iridium complex [Ir($C_8H_{12}$)($PCy_3$)(py)][$PF_6$] has been widely used as a catalyst for the reduction of hindered alkenes and [Ir($C_8H_{12}$)($PPh_3$)$_2$][$PF_6$] has also proven to be useful as a hydrogenation catalyst.[13,14] However, the investigation of pentacoordinate fluorosilicon anions enjoys increasing interest. Large cations are required for the stabilisation of the rather unstable $[SiF_5]^-$ anion ($[SiF_5]^- \rightarrow SiF_4 + F^-$).[15] In recent years a rising number of transition metal complexes containing $[SiF_5]^-$, like in [PtCl(CO)($PEt_3$)$_2$][$SiF_5$],[16] [Ir(H)$_2$(CO)($PPh_3$)$_3$][$SiF_5$],[17] [Au($PPh_3$)$_3$][$SiF_5$],[18] [Ir(CO)$_2$(P$t$Bu$_2$Ph)$_2$][$SiF_5$],[19] [Ir(H)$_2$(CO)$_2$(P$t$Bu$_2$Ph)$_2$][$SiF_5$][19] and [Co(NioxH)$_2$($PPh_3$)$_2$][$SiF_5$] (NioxH$_2$ is 1,2-cyclohexanedione dioxime)[20] have been reported.

Herein, we describe the syntheses and characterisations of the novel organoiridium(I) fluoro complex IrF($C_8H_{12}$)($PPh_3$) (**3**) and of the complex salt [Ir($C_8H_{12}$)($PPh_3$)$_2$][$SiF_5$] (**4**). The crystal structure analysis of **3** lead to the first iridium(I) fluorine bond parameters, whereas that of **4** is probative for the formation of the $[SiF_5]^-$ anion.

## Results and Discussion

During our research with the aim of obtaining novel iridium fluorides, the use of most of the usual fluorination ag-

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[a] Institut für Anorganische Chemie der Universität Göttingen,
Tammannstr. 4, 37077 Göttingen, Germany
Fax: (internat.) +49-(0)551-393373
E-mail: hroesky@gwdg.de

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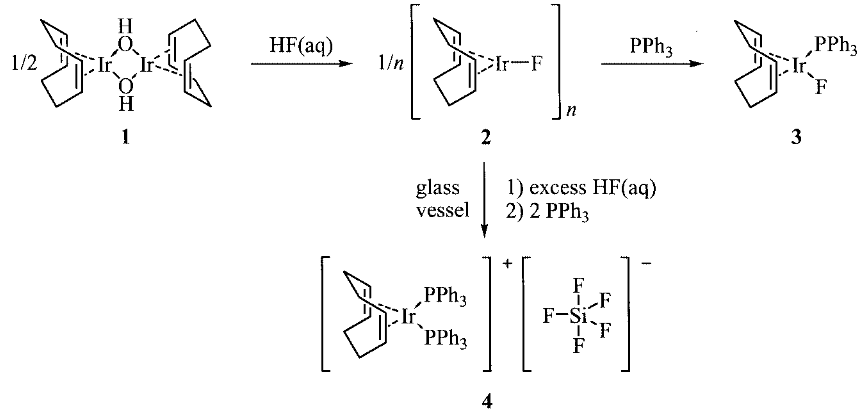

Scheme 1

ents including AgF, $Me_3SnF$, $(Me_2N)_3S^+(Me_3SiF_2)^-$ (TAS-F) or $XeF_2$ failed. The synthesis of $IrF(C_8H_{12})(PPh_3)$ (**3**) was finally successful using aqueous HF as the fluorinating agent, according to the procedure described for the rhodium(I) analogue.[10]

Treatment of a solution of $[Ir(\mu\text{-}OH)(C_8H_{12})]_2$ (**1**)[21] in THF with 73% aqueous HF in a Teflon tube gave compound **2** as a yellow precipitate in virtually quantitative yield (Scheme 1). Due to its insolubility in organic solvents NMR spectroscopic data are not available and, unfortunately, the mass spectrum only shows the fragmentation pattern of the coordinated cyclooctadiene ligand. The formation of an iridium fluoro complex can only be derived from the IR spectrum of compound **2**, which exhibits the $\tilde{\nu}_{IrF}$ stretching mode at 478 $cm^{-1}$ similar to that of $\tilde{\nu}_{IrF}$ = 451 $cm^{-1}$ in $IrF(CO)(PPh_3)_2$.[22] Therefore, a polymeric structure for compound **2** is proposed.

Reaction of triphenylphosphane with a suspension of **2** in THF results in the formation of a reddish solution. After addition of pentane, $IrF(C_8H_{12})(PPh_3)$ (**3**) crystallised as an orange solid. The $^1H$ NMR spectrum of **3** shows two sets of resonances for the four olefinic protons of the cyclooctadiene ligand. Due to the asymmetric coordination at the iridium(I) centre, one resonance appears at $\delta = 5.42$ ppm (*m*, 2 H), whereas the other one is shifted upfield to $\delta = 2.59$ ppm (*m*, 2 H). These values are similar to those ($\delta = 5.15$ and 2.73 ppm) reported for $IrCl(C_8H_{12})(PPh_3)$.[23] The difference between the two signals is presumably due to the unequal *trans* influence of $PPh_3$ and $F^-$. In the $^{19}F$ NMR spectrum of **3**, a singlet was observed at $\delta = -219.3$ ppm, characteristic of an iridium(I)-bound fluorine atom and the $^{31}P\{^1H\}$ NMR spectrum displays a singlet at $\delta = 25.1$ ppm.

Single crystals suitable for X-ray diffraction analysis of **3** were obtained by slow diffusion of pentane into a concentrated THF solution. Compound **3** crystallises in the monoclinic space group $P2_1/n$. The asymmetric unit contains one molecule of $IrF(C_8H_{12})(PPh_3)$ and half a solvent molecule of THF. Figure 1 shows the molecular structure of $IrF(C_8H_{12})(PPh_3)$ (**3**) along with selected bond lengths and angles. As expected from the larger *trans* influence of $PPh_3$ with respect to $F^-$, the Ir(1)−C(5) and Ir(1)−C(6) distances are longer than the Ir(1)−C(1) and Ir(1)−C(2) ones (Figure 1). The Ir(1)−F(1) bond length of 201.3(5) pm in **3** is shorter than those in iridium $d^6$ compounds, e.g. Cp* $IrF(Ph)(PMe_3)$ 206.9(4) pm,[5] $Ir(Cl)F(NSF_2)(CO)(PPh_3)_2$ 208.9(4),[6] $[IrF(\eta^2\text{-}NH{=}NC_6H_3\text{-}2\text{-}CF_3)(CO)(PPh_3)_2][BF_4]$ 221(4) pm,[7] and $Ir(FBF_3)Me_2(PMe_2Ph)_3$ 238.9(7) pm.[8] This might be due to π back-donation of the olefin ligand in **3**, causing stabilisation of such complexes.[4] The only exception is the iridium(III) fluoro complex $[Ir\{C(F)O\}F(CO)_2(PEt_3)_2][BF_4]$ with an Ir−F separation of 199.8(3) pm.[9] Complex **3** represents the first crystal structure to be determined for an organoiridium(I) fluoro complex.

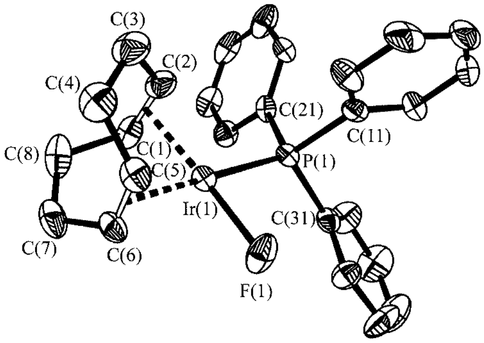

Figure 1. Molecular structure of $IrF(C_8H_{12})(PPh_3)$ (**3**) (without THF) with 50% probability ellipsoids and the labelling scheme; selected bond lengths (pm) and angles (°): Ir(1)−F(1) 201.3(5), Ir(1)−C(1) 209.3(9), Ir(1)−C(2) 208.7(8), Ir(1)−C(5) 218.9(8), Ir(1)−C(6) 217.2(7), C(1)−C(2) 140.0(13), C(5)−C(6) 139.3(12), Ir(1)−P(1) 231.93(19), P(1)−C(11) 181.9(7), P(1)−C(21) 181.7(7), P(1)−C(31) 181.8(8); F(1)−Ir(1)−C(1) 161.2(3), F(1)−Ir(1)−C(2) 157.9(3), F(1)−Ir(1)−C(5) 88.6(3), F(1)−Ir(1)−C(6) 86.6(3), F(1)−Ir(1)−P(1) 90.32(15), C(1)−Ir(1)−P(1) 97.8(2), C(2)−Ir(1)−P(1) 92.3(2), C(5)−Ir(1)−P(1) 159.0(2), C(6)−Ir(1)−P(1) 163.5(2)

However, treatment of **1** with aqueous HF carried out in glass vessels resulted in deep red crystals. This side product is insoluble in THF, but can be recrystallised from a dichloromethane/pentane mixture. This compound was unambiguously identified as the complex salt $[Ir(C_8H_{12})(PPh_3)_2][SiF_5]$ (**4**) by IR and NMR spectroscopy as well as single crystal structure analyses. The formation of the cationic iridium complex $[Ir(C_8H_{12})(PPh_3)_2]^+$ in the presence of weakly coordinating anions is well-known.[14] In addition, the appearance of the $[SiF_5]^-$ anion is not unexpected, if reactions involving HF are carried out in glass vessels.[20] Thus, the reaction of **1** in THF with an excess of aqueous HF in a glass vessel affords **4** in quantitative yield, after two equiv. of triphenylphosphane were added (Scheme 1). The $^1H$ NMR spectrum of **4** shows three resonances of equal intensity for the protons of the cyclooctadiene ligand [$\delta$ = 4.20 (br. s, 4 H), $\delta$ = 2.33 (m, 4 H) and $\delta$ = 1.97 ppm (m, 4 H)]. These values are similar to $\delta$ = 4.14 (s, 4 H) and $\delta$ = 2.12 ppm (m, 8 H) found in $[Ir(C_8H_{12})(PPh_3)_2][BF_4]$.[24] The formation of the cationic bisphosphane complex is best documented by its $^{13}C$ NMR spectrum. The resonance for the carbon atoms of the $=CH-$ groups of the cyclooctadiene ligand appears as a triplet [$\delta$ = 87.40 ppm (t, $J$ = 5.58 Hz)] indicative of coupling to two phosphorus nuclei, whereas the $-CH_2-$ groups show a singlet at $\delta$ = 31.37 ppm. In the $^{19}F$ NMR spectrum a broad resonance ($\delta$ = −139.1 ppm) is observed. This is in good agreement with that reported ($\delta$ = −139 ppm) for the $[SiF_5]^-$ anion in $[Au(PPh_3)_3][SiF_5]$.[18] The $^{31}P$ NMR resonance is shifted upfield in comparison to that of compound **3** and appears as a singlet at $\delta$ = 17.4 ppm. Compound **4** gives rise to bands in the infrared spectrum at ($\tilde{\nu}$ = 879, 790, 479 and 448 $cm^{-1}$ CsI plates), due to Si−F modes similar to those reported in the literature.[16]

Single crystals suitable for X-ray diffraction analyses of **4** were obtained by slow diffusion of pentane into a concentrated $CH_2Cl_2$ solution. Compound **4** crystallises in the monoclinic space group $P2_1/c$. A structure determination showed one $[Ir(C_8H_{12})(PPh_3)_2]^+$ cation, one non-coordinated $[SiF_5]^-$ anion and a solvent molecule $CH_2Cl_2$ in the asymmetric unit. The cation is depicted in Figure 2 together with selected bond lengths and angles. The iridium-phosphorus bond lengths [Ir(1)−P(1) 233.1(3) and Ir(1)−P(2) 235.3(3) pm] are similar to those of Ir−P(1) 236.7(2) and Ir−P(2) 232.6(3) pm found in $[Ir(C_8H_{12})(PPh_3)_2][PF_6]$.[14]

The $[SiF_5]^-$ anion is not coordinated to an iridium atom (shortest Ir···F distance is 461.1 pm). The geometry of the silicon atom is regular bipyramidal. The $Si-F_{eq}$ bond lengths are Si(1)−F(1) 158.4(10), Si(1)−F(3) 159.8(10) and Si(1)−F(5) 158.3(10) pm. The $Si-F_{ax}$ distances are longer, with values of Si(1)−F(2) 162.3(10) and Si(1)−F(4) 162.5(11) pm. The bond lengths and angles for the $[SiF_5]^-$ anions in the compounds $[Au(PPh_3)_3][SiF_5]$, $[Ir(CO)_2(PtBu_2Ph)_2][SiF_5]$ and $[Ir(H)_2(CO)_2(PtBu_2Ph)_2][SiF_5]$, are in the same range as those for compound **4**.[18,19]

Once compound **3** has been isolated it does not interact with the glass surface. Evidence for that is derived from NMR and IR spectroscopic data obtained from the oily residue, formed in a glass vessel, as a result of the decomposition of **3** after some weeks. In the $^{19}F$ NMR spectrum a triplet ($\delta$ = −256.3 ppm, t, $J$ = 28.8 Hz) and in the $^{31}P\{H\}$ NMR spectrum a doublet ($\delta$ = 24.5 ppm, d, $J$ = 28.7 Hz) suggest the formation of a complex, which has one fluorine atom and two phosphane groups bonded to the iridium atom. The IR spectrum exhibits a band at 1945 $cm^{-1}$ attributable to a $\tilde{\nu}_{CO}$ mode. These data lead to the assumption that one of the products of the decomposition of **3** is the Vaska complex $IrF(CO)(PPh_3)_2$. The formation of a carbonyl complex is in agreement with reports of the ability of rhodium(I) systems to abstract carbon monoxide from oxygen-containing organic solvents.[25]

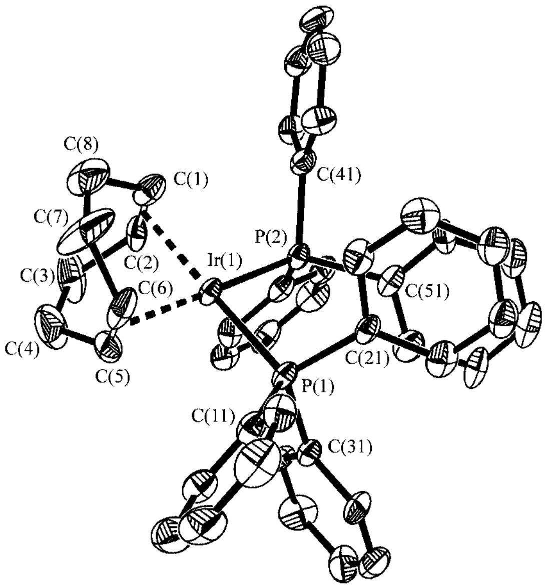

Figure 2. Molecular structure of the $[Ir(C_8H_{12})(PPh_3)_2]^+$ cation in **4** with 50% probability ellipsoids and the labelling scheme; selected bond lengths (pm) and angles (°): Ir(1)−C(1) 221.5(11), Ir(1)−C(2) 223.5(10), Ir(1)−C(5) 216.5(11), Ir(1)−C(6) 219.5(11), Ir(1)−P(1) 233.1(3), Ir(1)−P(2) 235.3(3), C(1)−C(2) 140.8(16), C(5)−C(6) 132.3(19), P(1)−C(11) 184.1(11), P(1)−C(21) 180.6(11), P(1)−C(31) 181.4(10), P(2)−C(41) 183.0(11), P(2)−C(51) 184.3(10), P(2)−C(61) 183.9(11); C(1)−Ir(1)−P(1) 153.7(3), C(2)−Ir(1)−P(1) 168.7(3), C(5)−Ir(1)−P(1) 95.6(3), C(6)−Ir(1)−P(1) 89.5(3), C(1)−Ir(1)−P(2) 93.9(3), C(2)−Ir(1)−P(2) 86.7(2), C(5)−Ir(1)−P(2) 152.0(4), C(6)−Ir(1)−P(2) 170.4(4), P(1)−Ir(1)−P(2) 94.43(9)

## Conclusion

The present study describes the synthesis and characterisation of $IrF(C_8H_{12})(PPh_3)$ and provides the first crystallographic data for an organoiridium(I) fluoro complex. The reaction of $[Ir(\mu\text{-}OH)(C_8H_{12})]_2$ with concentrated aqueous HF yields the fluoro complex, only in Teflon tubes, whereas the use of glass vessels led to $[Ir(C_8H_{12})(PPh_3)_2][SiF_5]$. The X-ray diffraction analysis of this iridium(I) complex salt shows that the rather unstable $[SiF_5]^-$ anion can be trapped.

## Experimental Section

**General Remarks:** Solvents were dried and distilled under nitrogen prior to use. All reactions were carried out under dry nitrogen, using standard Schlenk techniques. NMR spectra were recorded using a Bruker Avance 200, Bruker MSL 400 or a Bruker Avance 500 spectrometer and referenced to the resonances of the residual protons in deuterated benzene or $CD_2Cl_2$. $^1H$ NMR: external

Table 1. Crystallographic data for **3** and **4**

| | **3** (incl. THF) | **4** (incl. $CH_2Cl_2$) |
|---|---|---|
| Empirical formula | $C_{28}H_{31}FIrPO_{0.5}$ | $C_{45}H_{44}Cl_2F_5IrP_2Si$ |
| Molecular mass [$gmol^{-1}$] | 617.70 | 1032.93 |
| Temperature [K] | 200(2) | 200(2) |
| Wavelength $\lambda$ [pm] | 71.073 | 71.073 |
| Crystal system | monoclinic | monoclinic |
| Space group | $P2_1/n$ | $P2_1/c$ |
| $a$ [pm] | 931.9(3) | 1157.4(9) |
| $b$ [pm] | 1629.4(7) | 1864.4(9) |
| $c$ [pm] | 1592.9(7) | 1922.5(17) |
| $\alpha$ [°] | 90 | 90 |
| $\beta$ [°] | 92.85(3) | 96.16(7) |
| $\gamma$ [°] | 90 | 90 |
| $V$ [$nm^3$] | 2.4157(17) | 4.125(5) |
| $Z$ | 4 | 4 |
| Absorption coefficient [$mm^{-1}$] | 5.616 | 3.529 |
| $F$(000) | 1216 | 2056 |
| Reflections collected | 5803 | 7556 |
| Independent reflections | 4216 [$R_{int} = 0.0421$] | 7149 [$R_{int} = 0.1654$] |
| Data/restraints/parameters | 4216/0/292 | 7149/0/505 |
| Goodness-of-fit on $F^2$ | 1.111 | 1.050 |
| Final $R$ indices [$I > 2\sigma(I)$] | 0.0560, 0.1471 | 0.0671, 0.1620 |
| Largest diff. Peak/hole [$e\cdot Å^{-3}$] | 5.144/−3.777 | 3.414/−2.480 |

standard TMS. $^{13}C$ NMR: external standard TMS. $^{19}F$ NMR: external standard $CCl_3F$. $^{31}P$ NMR: external standard 85% $H_3PO_4$. Infrared spectra were recorded on a BIO-RAD Digilab FTS 7 spectrometer. $[Ir(\mu\text{-}OH)(C_8H_{12})]_2$ (**1**) was prepared by literature methods.[21] All other materials used in the syntheses were reagent grade chemicals and used without further purification.

**$IrF(C_8H_{12})(PPh_3)$ (3):** Aqueous HF (50.0 µL, 2.00 mmol, 73%) solution was added to a solution of **1** (0.63 g, 1.00 mmol) in THF (10 mL). The reaction mixture was allowed to stand overnight to form a yellow insoluble precipitate **2,** which was filtered off and dried in vacuo. The solid was treated with a solution of $PPh_3$ (0.52 g, 2.00 mmol) in THF (10 mL) and the mixture was stirred until all solids had dissolved. The resulting reddish solution was layered with pentane (40 mL). After standing overnight orange crystals had formed which were filtered off and dried under reduced pressure. The product was recrystallised from THF/pentane (0.83 g, 71%). M.p. 218 °C (decomp.). $C_{26}H_{27}FIrP$ (581.68): calcd. C 53.69, H 4.68; found C 53.47, H 4.81. $^1H$ NMR (300.13 MHz, $C_6D_6$): $\delta = 1.40$ (m, 4 H, $CH_2$), 2.05 (m, 4 H, $CH_2$), 2.59 (m, 2 H, CH), 5.42 (m, 2 H, *CH*), 7.08 (m, 9 H, $C_6H_5$), 7.93 (m, 6 H, $C_6H_5$) ppm. $^{19}F$ NMR (188.27 MHz, $CCl_3F$): $\delta = -219.3$ (s, IrF) ppm. $^{31}P$ NMR (121.50 MHz, $C_6D_6$): $\delta = 25.1$ (s, IrP). EIMS 70 eV, $m/z$ (rel. int.): 582 [M] (5), 262 [$M - Ir-C_8H_{12}-F$] (100), 108 [$M - Ir-P(C_6H_5)_3-F$] (20).

**$[Ir(C_8H_{12})(PPh_3)_2][SiF_5]$ (4):** Aqueous HF (0.50 mL, 20.0 mmol, 73%) solution was added to a solution of **1** (0.63 g, 1.00 mmol) in THF (10 mL) in a glass vessel . The reaction mixture was allowed to stand overnight to form a yellow insoluble precipitate, which was filtered off and dried in vacuo. The solid was treated with a solution of $PPh_3$ (1.05 g, 4.00 mmol) in THF (10 mL) and the mixture was stirred for 24 h. Deep red crystals formed which were filtered off and dried under reduced pressure. The product was recrystallised from $CH_2Cl_2$/pentane (1.80 g, 96%). $C_{44}H_{42}F_5IrP_2Si$ (948.05): calcd. C 55.74, H 4.47; found C 55.41, H 4.65. IR (CsI): $\tilde{\nu} = 879$, 790, 479 and 448 $cm^{-1}$ ($SiF_5^-$). $^1H$ NMR (300.13 MHz, $CD_2Cl_2$): $\delta = 1.97$ (m, 4 H, $CH_2$), 2.32 (m, 4 H, $CH_2$), 4.20 (s, 4 H, CH), 7.39 (m, 15 H, $C_6H_5$) ppm. $^{13}C$ NMR (125.77 MHz, $CD_2Cl_2$): $\delta = 31.4$ (s, C-3, C-4, C-7, C-8), 87.4 (t, $J = 5.6$ Hz, C-1, C-2, C-5, C-6), 128.9 (t, $J = 5.2$ Hz, $C_6H_5$), 131.7 (t, $J = 1.0$ Hz, $C_6H_5$), 134.6 (t, $J = 5.5$ Hz, $C_6H_5$) ppm. $^{19}F$ NMR (188.27 MHz, $CCl_3F$): $\delta = -139.1$ (s, $SiF_5$) ppm. $^{31}P$ NMR (121.50 MHz, $CD_2Cl_2$): $\delta = 17.8$ (s, $IrP_2$) ppm. $FAB^+MS$ 70 eV, $m/z$ (rel. int.): 825 [$Ir(C_8H_{12})(PPh_3)_2$] (100). $FAB^-MS$ 70 eV, $m/z$ (rel. int.): 123 [$SiF_5$] (100).

**X-ray Crystallographic Study:** The single crystals were mounted on a glass fibre in a frozen paraffin drop. Diffraction data were collected on a STOE AED2 four-circle diffractometer with graphite-monochromated Mo-$K_\alpha$ radiation ($\lambda = 71.073$ pm). The crystal structures were solved by direct methods using SHELXS-97[26] and refined with SHELXL-97[27] against $F^2$ for all data by full-matrix least-squares. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at fixed positions. A summary of the crystal data is given in Table 1.

CCDC-228254 (for **3**) and -228255 (for **4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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