

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. Rösenthaller on the occasion of his 60th birthday

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

Cyclooctadienefluorotriphenylphosphaneiridium(I) [IrF(C₈H₁₂)(PPh₃)] (**3**) was prepared and its structure determined by single crystal X-ray diffraction analysis. Complex **3** crystallises in the monoclinic space group *P*2₁/*n*. The lattice parameters are *a* = 931.9(3) pm, *b* = 1629.4(7) pm, *c* = 1592.9(7) pm, *α* = *γ* = 90°, *β* = 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(C₈H₁₂)(PPh₃)₂][SiF₅]) (**4**). The composition of **4** was con-

firmed by single crystal X-ray diffraction analysis. **4** crystallises in the monoclinic space group *P*2₁/*c*. The lattice parameters are *a* = 1157.4(9) pm, *b* = 1864.4(9) pm, *c* = 1922.5(17) pm, *α* = *γ* = 90°, *β* = 96.16(7)°. The number of molecules per unit cell is 4. The square-planar coordinated iridium cation [Ir(C₈H₁₂)(PPh₃)₂]⁺ is separated from the trigonal bipyramidal [SiF₅][−] anion by 461.1 pm (shortest Ir...F distance) and thus it is assumed that no interactions occur between the fluorine and iridium atoms.

© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2004)

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 *π* back-bonding ligands fluoro complexes of d⁸ 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)(PPh₃)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 d⁶ centers e.g. Cp* IrF(Ph)(PMe₃),^[5] Ir(Cl)F(NSF₂)(CO)(PPh₃)₂,^[6] [IrF(η²-NH=NC₆H₃-2-CF₃)(CO)(PPh₃)₂][BF₄],^[7] Ir(FBF₃)Me₂(PMe₂Ph)₃,^[8] and [Ir{C(F)O}F(CO)₂(PEt₃)₂][BF₄].^[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]

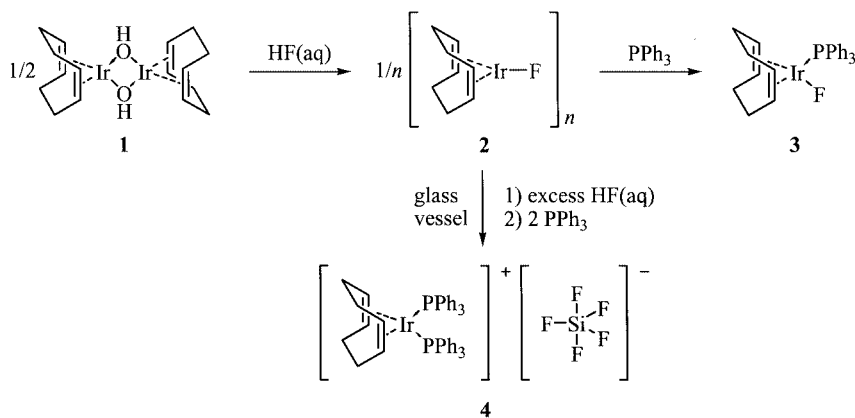
Moreover, complexes of weakly or non-coordinating fluorinated anions such as [BF₄][−], [PF₆][−], [AsF₆][−] and [SbF₆][−] are of special interest in organometallic fluorine chemistry. For instance, the iridium complex [Ir(C₈H₁₂)(PCy₃)(py)][PF₆] has been widely used as a catalyst for the reduction of hindered alkenes and [Ir(C₈H₁₂)(PPh₃)₂][PF₆] 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 [SiF₅][−] anion ([SiF₅][−] → SiF₄ + F[−]).^[15] In recent years a rising number of transition metal complexes containing [SiF₅][−], like in [PtCl(CO)(PEt₃)₂][SiF₅],^[16] [Ir(H)₂(CO)(PPh₃)₃][SiF₅],^[17] [Au(PPh₃)₃][SiF₅],^[18] [Ir(CO)₂(PrBu₂Ph)₂][SiF₅],^[19] [Ir(H)₂(CO)₂(PrBu₂Ph)₂][SiF₅]^[19] and [Co(NioxH)₂(PPh₃)₂][SiF₅] (NioxH₂ is 1,2-cyclohexanedione dioxime)^[20] have been reported.

Herein, we describe the syntheses and characterisations of the novel organoiridium(I) fluoro complex IrF(C₈H₁₂)(PPh₃) (**3**) and of the complex salt [Ir(C₈H₁₂)(PPh₃)₂][SiF₅] (**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 [SiF₅][−] anion.

Results and Discussion

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

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



Scheme 1

ents including AgF , Me_3SnF , $(\text{Me}_2\text{N})_3\text{S}^+(\text{Me}_3\text{SiF}_2)^-$ (TAS-F) or XeF_2 failed. The synthesis of $\text{IrF}(\text{C}_8\text{H}_{12})(\text{PPh}_3)$ (**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 $[\text{Ir}(\mu\text{-OH})(\text{C}_8\text{H}_{12})]_2$ (**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 $\tilde{\nu}_{\text{IrF}}$ stretching mode at 478 cm^{-1} similar to that of $\tilde{\nu}_{\text{IrF}} = 451\text{ cm}^{-1}$ in $\text{IrF}(\text{CO})(\text{PPh}_3)_2$.^[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, $\text{IrF}(\text{C}_8\text{H}_{12})(\text{PPh}_3)$ (**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 $\delta = 5.42\text{ ppm}$ (*m*, 2 H), whereas the other one is shifted upfield to $\delta = 2.59\text{ ppm}$ (*m*, 2 H). These values are similar to those ($\delta = 5.15$ and 2.73 ppm) reported for $\text{IrCl}(\text{C}_8\text{H}_{12})(\text{PPh}_3)$.^[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 $\delta = -219.3\text{ ppm}$, characteristic of an iridium(I)-bound fluorine atom and the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum displays a singlet at $\delta = 25.1\text{ ppm}$.

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 $\text{IrF}(\text{C}_8\text{H}_{12})(\text{PPh}_3)$ and half a solvent molecule of THF. Figure 1 shows the molecular structure of $\text{IrF}(\text{C}_8\text{H}_{12})(\text{PPh}_3)$ (**3**) along with selected bond lengths and angles. As expected from the larger *trans* influence of PPh_3 with respect to F^- , the $\text{Ir}(1)\text{--C}(5)$ and $\text{Ir}(1)\text{--C}(6)$ distances

are longer than the $\text{Ir}(1)\text{--C}(1)$ and $\text{Ir}(1)\text{--C}(2)$ ones (Figure 1). The $\text{Ir}(1)\text{--F}(1)$ bond length of $201.3(5)\text{ pm}$ in **3** is shorter than those in iridium d⁶ compounds, e.g. $\text{Cp}^*\text{IrF}(\text{Ph})(\text{PMe}_3)$ $206.9(4)\text{ pm}$,^[5] $\text{Ir}(\text{Cl})\text{F}(\text{NSF}_2)(\text{CO})(\text{PPh}_3)_2$ $208.9(4)\text{ pm}$,^[6] $[\text{IrF}(\eta^2\text{-NH}=\text{NC}_6\text{H}_3\text{-2-CF}_3)(\text{CO})(\text{PPh}_3)_2][\text{BF}_4]$ $221(4)\text{ pm}$,^[7] and $\text{Ir}(\text{FBF}_3)\text{Me}_2(\text{PMe}_2\text{Ph})_3$ $238.9(7)\text{ pm}$.^[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 $[\text{Ir}\{\text{C}(\text{F})\text{O}\}\text{F}(\text{CO})_2(\text{PEt}_3)_2][\text{BF}_4]$ with an $\text{Ir}\text{--F}$ separation of $199.8(3)\text{ pm}$.^[9] Complex **3** represents the first crystal structure to be determined for an organoiridium(I) fluoro complex.

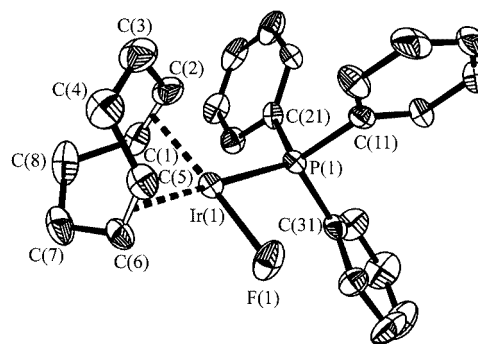


Figure 1. Molecular structure of $\text{IrF}(\text{C}_8\text{H}_{12})(\text{PPh}_3)$ (**3**) (without THF) with 50% probability ellipsoids and the labelling scheme; selected bond lengths (pm) and angles (°): $\text{Ir}(1)\text{--F}(1)$ $201.3(5)$, $\text{Ir}(1)\text{--C}(1)$ $209.3(9)$, $\text{Ir}(1)\text{--C}(2)$ $208.7(8)$, $\text{Ir}(1)\text{--C}(5)$ $218.9(8)$, $\text{Ir}(1)\text{--C}(6)$ $217.2(7)$, $\text{C}(1)\text{--C}(2)$ $140.0(13)$, $\text{C}(5)\text{--C}(6)$ $139.3(12)$, $\text{Ir}(1)\text{--P}(1)$ $231.93(19)$, $\text{P}(1)\text{--C}(11)$ $181.9(7)$, $\text{P}(1)\text{--C}(21)$ $181.7(7)$, $\text{P}(1)\text{--C}(31)$ $181.8(8)$; $\text{F}(1)\text{--Ir}(1)\text{--C}(1)$ $161.2(3)$, $\text{F}(1)\text{--Ir}(1)\text{--C}(2)$ $157.9(3)$, $\text{F}(1)\text{--Ir}(1)\text{--C}(5)$ $88.6(3)$, $\text{F}(1)\text{--Ir}(1)\text{--C}(6)$ $86.6(3)$, $\text{F}(1)\text{--Ir}(1)\text{--P}(1)$ $90.32(15)$, $\text{C}(1)\text{--Ir}(1)\text{--P}(1)$ $97.8(2)$, $\text{C}(2)\text{--Ir}(1)\text{--P}(1)$ $92.3(2)$, $\text{C}(5)\text{--Ir}(1)\text{--P}(1)$ $159.0(2)$, $\text{C}(6)\text{--Ir}(1)\text{--P}(1)$ $163.5(2)$.

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 $[\text{Ir}(\text{C}_8\text{H}_{12})(\text{PPh}_3)_2][\text{SiF}_5]$ (**4**) by IR and NMR spectroscopy as well as single crystal structure analyses. The formation

of the cationic iridium complex $[\text{Ir}(\text{C}_8\text{H}_{12})(\text{PPh}_3)_2]^+$ in the presence of weakly coordinating anions is well-known.^[14] In addition, the appearance of the $[\text{SiF}_5]^-$ 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 $[\text{Ir}(\text{C}_8\text{H}_{12})(\text{PPh}_3)_2][\text{BF}_4]$.^[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 $=\text{CH}-$ 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 $-\text{CH}_2-$ 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 $[\text{SiF}_5]^-$ anion in $[\text{Au}(\text{PPh}_3)_3][\text{SiF}_5]$.^[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 $[\text{Ir}(\text{C}_8\text{H}_{12})(\text{PPh}_3)_2]^+$ cation, one non-coordinated $[\text{SiF}_5]^-$ 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 [$\text{Ir}(1)–\text{P}(1)$ 233.1(3) and $\text{Ir}(1)–\text{P}(2)$ 235.3(3) pm] are similar to those of $\text{Ir}–\text{P}(1)$ 236.7(2) and $\text{Ir}–\text{P}(2)$ 232.6(3) pm found in $[\text{Ir}(\text{C}_8\text{H}_{12})(\text{PPh}_3)_2][\text{PF}_6]$.^[14]

The $[\text{SiF}_5]^-$ anion is not coordinated to an iridium atom (shortest $\text{Ir}\cdots\text{F}$ distance is 461.1 pm). The geometry of the silicon atom is regular bipyramidal. The Si–F_{eq} bond lengths are $\text{Si}(1)–\text{F}(1)$ 158.4(10), $\text{Si}(1)–\text{F}(3)$ 159.8(10) and $\text{Si}(1)–\text{F}(5)$ 158.3(10) pm. The Si–F_{ax} distances are longer, with values of $\text{Si}(1)–\text{F}(2)$ 162.3(10) and $\text{Si}(1)–\text{F}(4)$ 162.5(11) pm. The bond lengths and angles for the $[\text{SiF}_5]^-$ anions in the compounds $[\text{Au}(\text{PPh}_3)_3][\text{SiF}_5]$, $[\text{Ir}(\text{CO})_2(\text{P}t\text{Bu}_2\text{Ph})_2][\text{SiF}_5]$ and $[\text{Ir}(\text{H})_2(\text{CO})_2(\text{P}t\text{Bu}_2\text{Ph})_2][\text{SiF}_5]$, 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 $^{31}\text{P}\{\text{H}\}$ 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} at-

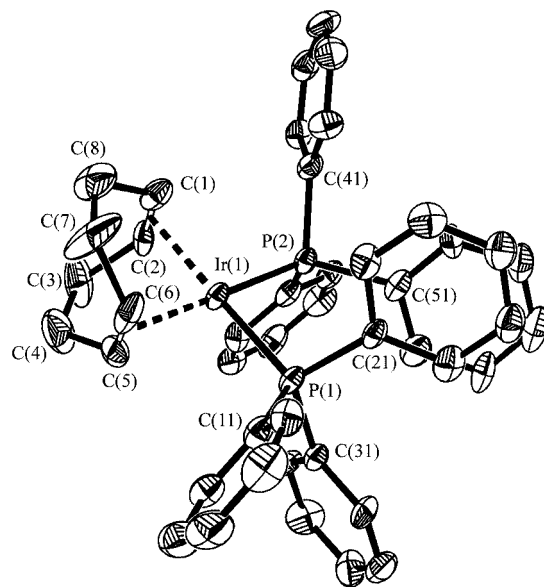


Figure 2. Molecular structure of the $[\text{Ir}(\text{C}_8\text{H}_{12})(\text{PPh}_3)_2]^+$ cation in **4** with 50% probability ellipsoids and the labelling scheme; selected bond lengths (pm) and angles ($^\circ$): $\text{Ir}(1)–\text{C}(1)$ 221.5(11), $\text{Ir}(1)–\text{C}(2)$ 223.5(10), $\text{Ir}(1)–\text{C}(5)$ 216.5(11), $\text{Ir}(1)–\text{C}(6)$ 219.5(11), $\text{Ir}(1)–\text{P}(1)$ 233.1(3), $\text{Ir}(1)–\text{P}(2)$ 235.3(3), $\text{C}(1)–\text{C}(2)$ 140.8(16), $\text{C}(5)–\text{C}(6)$ 132.3(19), $\text{P}(1)–\text{C}(11)$ 184.1(11), $\text{P}(1)–\text{C}(21)$ 180.6(11), $\text{P}(1)–\text{C}(31)$ 181.4(10), $\text{P}(2)–\text{C}(41)$ 183.0(11), $\text{P}(2)–\text{C}(51)$ 184.3(10), $\text{P}(2)–\text{C}(61)$ 183.9(11); $\text{C}(1)–\text{Ir}(1)–\text{P}(1)$ 153.7(3), $\text{C}(2)–\text{Ir}(1)–\text{P}(1)$ 168.7(3), $\text{C}(5)–\text{Ir}(1)–\text{P}(1)$ 95.6(3), $\text{C}(6)–\text{Ir}(1)–\text{P}(1)$ 89.5(3), $\text{C}(1)–\text{Ir}(1)–\text{P}(2)$ 93.9(3), $\text{C}(2)–\text{Ir}(1)–\text{P}(2)$ 86.7(2), $\text{C}(5)–\text{Ir}(1)–\text{P}(2)$ 152.0(4), $\text{C}(6)–\text{Ir}(1)–\text{P}(2)$ 170.4(4), $\text{P}(1)–\text{Ir}(1)–\text{P}(2)$ 94.43(9)

tributable to a $\tilde{\nu}_{\text{CO}}$ mode. These data lead to the assumption that one of the products of the decomposition of **3** is the Vaska complex $\text{IrF}(\text{CO})(\text{PPh}_3)_2$. 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]

Conclusion

The present study describes the synthesis and characterisation of $\text{IrF}(\text{C}_8\text{H}_{12})(\text{PPh}_3)_2$ and provides the first crystallographic data for an organoiridium(i) fluoro complex. The reaction of $[\text{Ir}(\mu\text{-OH})(\text{C}_8\text{H}_{12})_2]$ with concentrated aqueous HF yields the fluoro complex, only in Teflon tubes, whereas the use of glass vessels led to $[\text{Ir}(\text{C}_8\text{H}_{12})(\text{PPh}_3)_2][\text{SiF}_5]$. The X-ray diffraction analysis of this iridium(i) complex salt shows that the rather unstable $[\text{SiF}_5]^-$ 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 ₂ Cl ₂)
Empirical formula	C ₂₈ H ₃₁ FIrPO _{0.5}	C ₄₅ H ₄₄ Cl ₂ F ₅ IrP ₂ Si
Molecular mass [g mol ⁻¹]	617.70	1032.93
Temperature [K]	200(2)	200(2)
Wavelength λ [pm]	71.073	71.073
Crystal system	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> [pm]	931.9(3)	1157.4(9)
<i>b</i> [pm]	1629.4(7)	1864.4(9)
<i>c</i> [pm]	1592.9(7)	1922.5(17)
α [°]	90	90
β [°]	92.85(3)	96.16(7)
γ [°]	90	90
<i>V</i> [nm ³]	2.4157(17)	4.125(5)
<i>Z</i>	4	4
Absorption coefficient [mm ⁻¹]	5.616	3.529
<i>F</i> (000)	1216	2056
Reflections collected	5803	7556
Independent reflections	4216 [<i>R</i> _{int} = 0.0421]	7149 [<i>R</i> _{int} = 0.1654]
Data/restraints/parameters	4216/0/292	7149/0/505
Goodness-of-fit on <i>F</i> ²	1.111	1.050
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	0.0560, 0.1471	0.0671, 0.1620
Largest diff. Peak/hole [e ⁻ Å ⁻³]	5.144/−3.777	3.414/−2.480

standard TMS. ¹³C NMR: external standard TMS. ¹⁹F NMR: external standard CCl₃F. ³¹P NMR: external standard 85% H₃PO₄. Infrared spectra were recorded on a BIO-RAD Digilab FTS 7 spectrometer. [Ir(μ-OH)(C₈H₁₂)₂] (**1**) was prepared by literature methods.^[21] All other materials used in the syntheses were reagent grade chemicals and used without further purification.

Ir(C₈H₁₂)(PPh₃) (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 PPh₃ (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.). C₂₆H₂₇FIrP (581.68): calcd. C 53.69, H 4.68; found C 53.47, H 4.81. ¹H NMR (300.13 MHz, C₆D₆): δ = 1.40 (m, 4 H, CH₂), 2.05 (m, 4 H, CH₂), 2.59 (m, 2 H, CH), 5.42 (m, 2 H, CH), 7.08 (m, 9 H, C₆H₅), 7.93 (m, 6 H, C₆H₅) ppm. ¹⁹F NMR (188.27 MHz, CCl₃F): δ = −219.3 (s, IrF) ppm. ³¹P NMR (121.50 MHz, C₆D₆): δ = 25.1 (s, IrP). EIMS 70 eV, *m/z* (rel. int.): 582 [M] (5), 262 [M − Ir−C₈H₁₂−F] (100), 108 [M − Ir−P(C₆H₅)₃−F] (20).

[Ir(C₈H₁₂)(PPh₃)₂][SiF₅] (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 PPh₃ (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 CH₂Cl₂/pentane (1.80 g, 96%). C₄₄H₄₂F₅IrP₂Si (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 (SiF₅⁻). ¹H NMR (300.13 MHz, CD₂Cl₂): δ = 1.97 (m, 4 H, CH₂), 2.32 (m, 4 H, CH₂), 4.20 (s, 4

H, CH), 7.39 (m, 15 H, C₆H₅) ppm. ¹³C NMR (125.77 MHz, CD₂Cl₂): δ = 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, C₆H₅), 131.7 (t, *J* = 1.0 Hz, C₆H₅), 134.6 (t, *J* = 5.5 Hz, C₆H₅) ppm. ¹⁹F NMR (188.27 MHz, CCl₃F): δ = −139.1 (s, SiF₅) ppm. ³¹P NMR (121.50 MHz, CD₂Cl₂): δ = 17.8 (s, IrP₂) ppm. FAB⁺MS 70 eV, *m/z* (rel. int.): 825 [Ir(C₈H₁₂)(PPh₃)₂] (100). FAB[−]MS 70 eV, *m/z* (rel. int.): 123 [SiF₅] (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*_α radiation (λ = 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].

Acknowledgments

This work was supported by the Deutsche Forschungsgemeinschaft, the Degussa-Hüls AG, the Fonds der Chemischen Industrie, and the Göttinger Akademie der Wissenschaften.

[1] N. M. Doherty, N. W. Hoffman, *Chem. Rev.* **1991**, *91*, 553–573.

[2] E. F. Murphy, R. Murugavel, H. W. Roesky, *Chem. Rev.* **1997**, *97*, 3425–3468.

[3] H. W. Roesky, *J. Fluorine Chem.* **1999**, *100*, 217–226.

- [4] K. Fagnou, M. Lautens, *Angew. Chem.* **2002**, *114*, 26–49; *Angew. Chem. Int. Ed.* **2002**, *41*, 26–47.
- [5] J. E. Veltheer, P. Burger, R. G. Bergman, *J. Am. Chem. Soc.* **1995**, *117*, 12478–12488.
- [6] P. G. Watson, E. Lork, R. Mews, *J. Chem. Soc., Chem. Commun.* **1994**, 1069–1070.
- [7] J. A. Carroll, R. E. Cobbleddick, F. W. B. Einstein, N. Farrell, D. Sutton, P. L. Vogel, *Inorg. Chem.* **1977**, *16*, 2462–2469.
- [8] E. G. Lundquist, K. Folting, J. C. Huffman, K. G. Caulton, *Organometallics* **1990**, *9*, 2254–2261.
- [9] A. J. Blake, R. W. Cockman, E. A. V. Ebsworth, J. H. Holmoway, *J. Chem. Soc., Chem. Commun.* **1988**, 529–530.
- [10] J. Vicente, J. Gil-Rubio, D. Bautista, *Inorg. Chem.* **2001**, *40*, 2636–2637.
- [11] H. L. M. van Gaal, F. L. A. van den Bekerom, J. P. J. Verlaan, *J. Organomet. Chem.* **1976**, *114*, C35–C37.
- [12] R. R. Burch, R. L. Harlow, S. D. Ittel, *Organometallics* **1987**, *6*, 982–987.
- [13] R. H. Crabtree, *Acc. Chem. Res.* **1979**, *12*, 331–338.
- [14] P. A. Chaloner, P. B. Hitchcock, M. Reisinger, *Acta Crystallogr., Sect. C* **1992**, *48*, 735–737.
- [15] F. Klanberg, E. L. Muetterties, *Inorg. Chem.* **1968**, *7*, 155–160.
- [16] H. C. Clark, P. W. R. Corfield, K. R. Dixon, J. A. Ibers, *J. Am. Chem. Soc.* **1967**, *89*, 3360–3361.
- [17] P. Bird, J. F. Harrod, K. A. Than, *J. Am. Chem. Soc.* **1974**, *96*, 1222–1224.
- [18] F. Olbrich, R. J. Lagow, *Z. Anorg. Allg. Chem.* **1995**, *621*, 1929–1932.
- [19] A. C. Cooper, J. C. Bollinger, J. C. Huffman, K. G. Caulton, *New J. Chem.* **1998**, *22*, 473–480.
- [20] Y. A. Simonov, N. V. Gerbeleu, M. Gdaniec, P. N. Bourosh, E. B. Koropchanu, O. A. Bologa, *Russ. J. Coord. Chem.* **2001**, *27*, 341–352.
- [21] L. M. Green, D. W. Meek, *Organometallics* **1989**, *8*, 659–666.
- [22] L. Vaska, J. Peone Jr., *Inorg. Synth.* **1974**, *15*, 64–68.
- [23] K. Vrieze, H. C. Volger, A. P. Praat, *J. Organomet. Chem.* **1968**, *14*, 185–200.
- [24] M. Green, T. A. Kuc, S. H. Taylor, *J. Chem. Soc., Sect. A* **1971**, 2334–2337.
- [25] J. A. Osborn, F. H. Jardine, J. F. Young, G. Wilkinson, *J. Chem. Soc., Sect. A* **1966**, 1711–1732.
- [26] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467–473.
- [27] G. M. Sheldrick, *SHELX-97, Program for Crystal Structure Analysis*, University of Göttingen, **1998**.

Received January 15, 2004

Early View Article

Published Online May 5, 2004