

Spontaneous Reductive Elimination at Iridium(III) Induced by the Strong π -Acceptor Ligand Trifluorophosphane

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Dedicated to Prof. Manfred Scheer on the Occasion of his 65th Birthday

Abstract. The reaction of the cyclometalated five-coordinate 16 VE iridium(III) compound $[\text{IrCl}(\text{H})(\text{P}(\text{tBu})_2\text{C}_6\text{H}_4-\kappa^2\text{P,C})(\text{P}(\text{tBu})_2\text{Ph})]$ (**1**) with the strong π -acceptor ligand trifluorophosphane resulted quickly in the quantitative formation of the new iridium(I) complex *trans*- $[\text{IrCl}(\text{PF}_3)(\text{P}(\text{tBu})_2\text{Ph})_2]$ (**2**). This unexpected spontaneous reductive elimination was already observed in reactions of **1** with the very strong

π -acceptor ligands CO and NO^+ . First indications during reactions of **1** with lesser strong π -acceptor ligands like alkyl or arylphosphanes did not show this inversion behavior of the cyclometalation. The title species **2** was characterized by spectroscopic methods and its molecular structure in the crystal was confirmed by X-ray crystallography.

Introduction

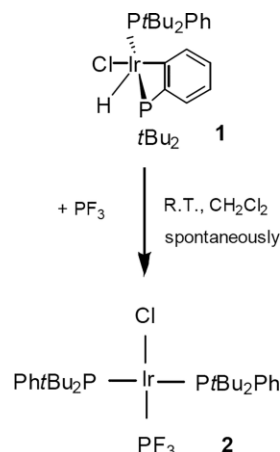
Recently we reported the X-ray crystal structure of the cyclometalated five-coordinate complex $[\text{IrCl}(\text{H})(\text{P}(\text{tBu})_2\text{C}_6\text{H}_4-\kappa^2\text{P,C})(\text{P}(\text{tBu})_2\text{Ph})]$ (**1**).^[1] Because that species exhibits 16 valence electrons, it showed a high reactivity towards small molecules. Thus we found that the coordinatively unsaturated complex **1** reacted spontaneously with the strong π -acceptor ligand CO and NO^+ , respectively, with an inversion of the cyclometalation affording the iridium(I) compound *trans*- $[\text{IrCl}(\text{CO})(\text{P}(\text{tBu})_2\text{Ph})_2]$ as well as the isoelectronic complex *trans*- $[\text{IrCl}(\text{NO})(\text{P}(\text{tBu})_2\text{Ph})_2]^+$ isolated as its tetrafluoridoborate salt in excellent yields.^[1] Preliminary investigations during reactions of **1** with lesser strong π -acceptor ligands like alkyl or arylphosphanes are currently under way in our laboratory, however these transformations are more complicated.

However, $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopic studies showed that in those cases no inversion of the cyclometalation seemed to occur, unambiguously indicated by the observed chemical shift values indicating the presence of the retained cyclometalated ligand in the corresponding reaction products. To complete the group of the strongest π -acceptor ligands within the spectrochemical row, we examined the reactivity of trifluorophosphane towards the species **1**. Now we were able to confirm the same reaction behavior as observed for the ligands CO and NO^+ . Thus we obtained the first structurally characterized

iridium(I) complex bearing PF_3 as the ligand, namely *trans*- $[\text{IrCl}(\text{PF}_3)(\text{P}(\text{tBu})_2\text{Ph})_2]$ (**2**), and on these findings we report in this communication. A review on transition metal complexes containing PF_3 as the ligand was, for example, given by Kruck.^[2]

Results and Discussion

The treatment of a dichloromethane solution of complex **1** with gaseous trifluorophosphane at room temperature resulted immediately in a color change from deep red to pale yellow. From the solution yellow crystals in high yield (96 %) suitable for X-ray diffraction were isolated, and the reaction product was unambiguously identified by the crystal structure analysis as *trans*- $[\text{IrCl}(\text{PF}_3)(\text{P}(\text{tBu})_2\text{Ph})_2]$ (**2**). Because the synthesis of complex **1** is accompanied by a cyclometallation of one phosphane ligand during the reaction of $[\{\text{Ir}(\mu\text{-Cl})(\text{coe})_2\}_2]$ with $\text{P}(\text{tBu})_2\text{Ph}$,^[1] the title reaction can be described as an inversion of the cyclometallation within the starting complex **1** (see Scheme 1). Moreover, we confirmed the identity of the new



Scheme 1. Synthesis of *trans*- $[\text{IrCl}(\text{PF}_3)(\text{P}(\text{tBu})_2\text{Ph})_2]$ (**2**).

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species by further spectroscopic methods (see below). Single-crystals suitable for an X-ray diffraction study were grown from dichloromethane/diethyl ether overnight at room temperature. The compound **2** crystallized as yellow crystals in the monoclinic non-centrosymmetric space group $P2_1$ with two molecules in the unit cell. A selected view of the molecule in the crystal is depicted in Figure 1, selected bond lengths and angles are given in the caption.

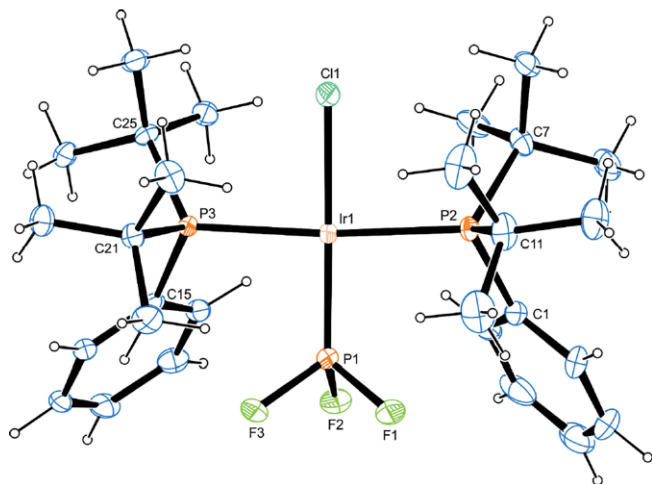


Figure 1. Molecular structure of **2** in the crystal (ORTEP drawing and atom labeling scheme with 50% probability level). Selected bond lengths /Å and angles /°: Ir1–C11, 2.3767(11); Ir1–P1, 2.1108(12); Ir1–P2, 2.3790(10); Ir1–P3, 2.3761(9); P1–F1, 1.563(3); P1–F2, 1.567(3); P1–F3, 1.566(3); P2–C1, 1.848(4); P2–C7, 1.921(4); P2–C11, 1.898(5); C11–Ir1–P1, 174.66(5); C11–Ir1–P2, 87.41(4); C11–Ir1–P3, 88.27(4); P1–Ir1–P2, 92.85(4); P1–Ir1–P3, 91.78(4); P2–Ir1–P3, 174.41(4).

The coordination sphere around the iridium atom in molecules of **2** can best be described as nearly square-planar with the bulky phosphane ligands in *trans* position to each other. The molecular structure is comparable to the cationic complex *trans*-[IrCl(NO)(P(*t*Bu)₂Ph)₂]⁺,^[1] for the latter the following selected bonding parameters were found: Ir1–C11, 2.2652(7); Ir1–P1, 2.429(6); Ir1–P2, 2.429(6) Å and P1–Ir1–P2, 178.31(2); P1–Ir1–N1, 89.71(6)° (for **2** compare the data in caption of Figure 1). Furthermore, the found data of **2** are comparable with the observed ones of *trans*-[IrCl(NO)(P(*t*Bu)₂H)₂]⁺ in its corresponding tetrafluoroborate salt.^[3]

In the literature, iridium complexes bearing the PF₃ ligand are structurally not explored to date. Only one example containing the unusual PF₄[−] ligand was described, and its molecular structure was confirmed by X-ray diffraction. In contrast to **2**, the species [Ir(CO)Cl₂(PEt₃)₂(PF₄)]^[4] exhibits an octahedral iridium(III) compound, therefore the bonding parameters are not directly comparable. For the latter species the following bond lengths were published: Ir–P(phosphane), 2.39(1); Ir–P(PF₄), 2.29(1); Ir–Cl, 2.36(1) and 2.42(1); P–F_a, 1.69(1) and 1.64(11); P–F_e, 1.56(2) and 1.52(2) Å. These data show however a good accordance with the found ones of **2**. Although the dinuclear complexes [{Ir(μ-Cl)(PF₃)₂}]₂^[5] and

[[Ir(PF₃)₄]]₂^[6] have been described in the literature, no crystal structure data of the latter species were reported till now.

The new compound **2** was further characterized by NMR spectroscopic methods in solution. The ³¹P{¹H} NMR spectrum (CD₂Cl₂) of compound **2** showed at room temperature a quartet pattern centered at δ = 89.3 ppm assigned to the PF₃ ligand with a coupling $J_{PF} = 1335$ Hz. The coupling constant is comparable to the corresponding one reported for [Ir₂(PF₃)₈] (1230 Hz).^[5,6] (For comparative purposes: the non-coordinated PF₃ resonates at δ = 97.0 ppm as quartet with $J_{PF} = 1400$ Hz, CD₂Cl₂.) The signals of the P(*t*Bu)₂Ph ligands were found at δ = 40.4 ppm as multiplet. Interestingly, no noticeable coordination induced shift of the tertiary phosphane as well as for the PF₃ was found (compare for P(*t*Bu)₂Ph: 39.9 ppm, CD₂Cl₂). For closely related complexes *trans*-[MCl(CO)(P(*t*Bu)₂R)₂] (M = Rh, Ir; R = H, Me, Ph) a stereodynamic behavior due to decoalescence phenomena caused by a slowing the rotation about M–P and P–C(*t*Bu) was reported. These phenomena could be resolved and explained by DNMR measurements.^[7] We confirmed such observations e.g. also for *trans*-[IrCl(NO)(P(*t*Bu)₂H)₂]⁺ and related complexes.^[3]

In this light, we expected similar phenomena for compound **2**. To study the DNMR behavior at higher temperatures, the solvent was changed to [D₈]toluene exhibiting for **2** similar signals as observed in CD₂Cl₂ at room temperature. During heating to about 90 °C a fast decomposition was registered resulting in many signals over a broad range (from 115 to −42 ppm). Obviously, the complex is not stable in solution with increasing the temperature. On the other hand, during cooling to −60 °C (CD₂Cl₂) the found quartet pattern indicating the PF₃ ligand remained unchanged, that means a resolution in individual atoms could not be observed in the investigated temperature range. Furthermore the room temperature ¹⁹F NMR spectrum of **2** in CD₂Cl₂ showed a doublet at −22.4 ppm ($J_{PF} = 1338$ Hz) indicating the PF₃ ligand. These data are in good accordance with the reported ones for [[Ir(μ-Cl)(PF₃)₂]]₂ (δ = −24.1, $J_{PF} = 1270$ Hz).^[5] The ¹H and ¹³C{¹H} NMR spectra of **2** at room temperature showed the corresponding signals indicating the coordinated P(*t*Bu)₂Ph ligand (see Experimental Section).

Conclusions

The herein described investigations confirmed the already observed inversion of cyclometalation in the reaction of [IrCl(H)(P(*t*Bu)₂C₆H₄-κ²P,C)(P(*t*Bu)₂Ph)] (**1**) with strong π-acceptor ligands to yield, in a reductive elimination pathway, square-planar iridium(I) complexes. As already observed that phenomenon in reactions of **1** with CO or NO⁺, now we confirmed this also for the strong π-acceptor ligand PF₃. Thus we obtained in the reaction of **1** with trifluorophosphane the new compound *trans*-[IrCl(PF₃)(P(*t*Bu)₂Ph)₂] (**2**) in high yield and its molecular structure in the solid was confirmed by a single-crystal X-ray diffraction study.

Experimental Section

General: All synthetic work was carried out in a dry nitrogen atmosphere using standard Schlenk techniques. Chemicals were purchased from Sigma/Aldrich and used as received. PF_3 was prepared according to the literature procedure.^[8] NMR spectra were recorded using a Jeol Eclipse 400 instrument operating at 400 MHz (^1H), at 100 MHz (^{13}C), 376 MHz (^{19}F) and at 161 MHz (^{31}P). Chemical shifts are given in ppm relative to TMS (^1H , ^{13}C) and 85 % H_3PO_4 (^{31}P). Elemental analyses were performed by the Microanalytical Laboratory of the Department of Chemistry, LMU Munich, using a Heraeus Elementar Vario EL instrument.

Synthesis of 2: Compound **1** (336 mg, 0.50 mmol) was dissolved in dichloromethane (10 mL) with stirring and a slow stream of trifluorophosphane was bubbled through the solution at room temperature for ca. 2 min. The solution was stirred under the resulting PF_3 atmosphere for 30 min. Then the solvent was reduced to 3 mL and **2** precipitated as yellow crystals by addition of diethyl ether (10 mL). The resulting solid was filtered off and dried in vacuo. Yield: 365 mg (96 %). $\text{C}_{28}\text{H}_{46}\text{ClF}_3\text{IrP}_3$ (760.53): C 44.31 (calcd. 44.24); H 6.46 (6.10) %. ^1H NMR (CD_2Cl_2 , 400 MHz, 20 °C): δ = 7.43 (m, 10H, C_6H_5), 1.41 [d, 36H, $^3J_{\text{PH}}$ = 16.8 Hz, $\text{P}(\text{tBu})_2\text{Ph}$]. $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 100 MHz, 20 °C): δ = 137.5 (m, Ph), 134.8 (m, Ph), 131.4 (m, Ph), 130.6 (m, Ph), 129.9 (m, Ph), 128.2 (t, J = 14.3 Hz, Ph), 29.3 (t, J_{PC} = 13.4 Hz, CCH_3), 27.4 (s, CCH_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 161 MHz, 20 °C): δ = 89.3 (q, J_{PF} = 1335 Hz, PF_3), 40.4 [m, $\text{P}(\text{tBu})_2\text{Ph}$]. ^{19}F NMR (CD_2Cl_2 , 376 MHz, 20 °C): δ = -22.4 (d, J_{PF} = 1338 Hz, PF_3).

Crystal Structure Determination and Refinement: Crystals of **2** suitable for X-ray diffraction were obtained as described above. Crystals were selected by means of a polarization microscope, mounted on a MiTeGen MicroLoop, and investigated with a Bruker D8 Venture TXS diffractometer using $\text{Mo-}K_\alpha$ radiation (λ = 0.71073 Å). The structure was solved by direct methods (SHELXT)^[9] and refined by full-matrix least-squares calculations on F^2 (SHELXL-2014/7).^[10] Anisotropic displacement parameters were refined for all non-hydrogen atoms. Details of the crystal data, data collection, structure solution, and refinement parameters of compound **2** are summarized in Table 1.

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository number CCDC-1972752 (**2**) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, <http://www.ccdc.cam.ac.uk>).

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Table 1. Experimental details of the crystal structure determination of **2**.

	2
Formula	$\text{C}_{28}\text{H}_{46}\text{ClF}_3\text{IrP}_3$
M / $\text{g}\cdot\text{mol}^{-1}$	760.21
T / K	102(2)
Crystal system	monoclinic
Space group	$P2_1$
a / Å	8.3686(2)
b / Å	15.6855(4)
c / Å	12.0877(3)
α / °	90
β / °	105.5380(10)
γ / °	90
V / Å ³	1528.71(7)
Z	2
Density / $\text{g}\cdot\text{cm}^{-3}$	1.652
μ / mm^{-1}	4.646
θ range / °	3.13–30.50
Reflections, collected	17106
Reflections, independent	8197
R_{int}	0.0229
wR_2 (all data)	0.0452
R_1	0.0211
S	0.724
$\Delta\rho_{\text{fin}}$ (max/min) / $\text{e}\cdot\text{\AA}^{-3}$	0.896 / -0.661

Keywords: Cyclometalation; Iridium; Reductive elimination; Trifluorophosphane complexes; Structure elucidation

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